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Final Report
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Partial Combustion of Electrical Insulation Fluids

Prepared by
Westinghouse Electric Corporation
Sharon, Pennsylvania

REPORT SUMMARY

SUBJECTS: Hazardous/toxic substances / T&D: Substations

TOPICS: PCB; Transformers; Chemical analysis; Insulating oils; Fires

AUDIENCE: Environmental managers / Distribution engineers

Partial Combustion of Electrical Insulation Fluids

In partial-combustion tests, five dielectric fluids being used as insulating materials for power transformers left no evidence of the kinds of contaminants PCBs create. Although certain of the fluids decomposed into gases that could be toxic in confined spaces, procedures are available for the required short-term fire protection.

BACKGROUND: Until the late 1970s, askarels containing mixtures of polychlorinated biphenyls (PCBs) were the most common liquid coolants in transformers located in high fire hazard areas. After concluding that PCBs posed a significant environmental threat, EPA required the removal of a large number of PCB-containing transformers from service. Replacement insulating fluids needed evaluation to ensure that they met electrical, thermal, and physical requirements and that they did not decompose to produce residual toxic trace materials when combusted or pyrolyzed.

OBJECTIVE: To identify the chemical compounds—particularly the toxic compounds—formed during partial combustion of dielectric insulating fluids used in power transformers.

APPROACH: Investigators studied five fluids presently used as substitutes for PCBs in power transformers—tetrachloroethylene, trichlorotrifluoroethane, polydimethylsiloxane (silicone fluid), transformer mineral oil, and a high-temperature hydrocarbon fluid. The work included a literature search, a computer analysis of theoretical combustion equilibrium expressions to characterize the potential combustion products, and an experimental study. The testing included two sets of combustion reaction experiments—one employing a modified thermogravimetric analyzer and the other, a stainless steel reactor. The project team analyzed combustion products either by gas chromatography or by coupling gas chromatography with mass spectroscopy.

RESULTS: The experimental studies revealed no detectable production of such compounds as polychlorinated dibenzodioxins, polychlorinated dibenzofurans, or other polycyclic aromatic hydrocarbon compounds. Researchers concluded

that long-term contamination, such as that caused by fires involving askarels, would not result from fires involving these substitutes.

Under combustion, tetrachloroethylene produced chlorine and, in the presence of atmospheric humidity, hydrogen chloride. Trichlorotrifluoroethane produced hydrogen fluoride and various fluorocarbons during combustion. The production of these gases is a concern in the event of a fire. However, suitable fire protection is available to provide adequate safeguards for the firefighters.

EPRI PERSPECTIVE

To build a database on potential substitutes as extensive as that constructed for PCBs requires intensive analyses. By determining the trace combustion products of the five dielectric fluids examined, this study has added significantly to that database. The report indicates that there is little risk of long-term contamination from these substitutes and identifies the combustion products that could prove toxic in confined spaces in the short term. EPRI projects RP2028-15, RP2028-16, and RP2028-17, now under way, address a larger list of utility materials (liquids, solids, and gases) and examine trace by-products of critical materials. Related EPRI reports include EL-4407, *Maintenance and Handling of Perchloroethylene-Filled Electrical Equipment*; EL-4497, *Arc Products of Transformer Insulating Systems Containing Tetrachloroethylene*; EL-4503, *State-of-the-Art Review: Combustion and Pyrolysis of PCB Substitutes*; EL-4939, *Literature Review of Pyrolysis and Combustion Products of Selected Utility Materials*; and EL-5143-SR, *EPRI Workshop on Substitute Insulation for PCBs*.

PROJECT

RP2028-11
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Partial Combustion of Electrical Insulation Fluids

EL-5262
Research Project 2028-11

Final Report, July 1987

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ABSTRACT

Recurring fire incidents involving transformers have led to a desire to aquire information about the combustion products that may be generated not only in situations of complete combustion, but also in incidents when limited oxygen is present and combustion is incomplete or partial.

This report details some results from investigations designed to identify the products of incomplete combustion of five types of dielectric fluids commonly used in transformers, as alternatives to askarels. These fluids are tetrachloroethylene, trichlorotrifluoroethane, polydimethylsiloxane (silicone fluid), mineral oil, and a high temperature hydrocarbon.

The investigation of these fluids was begun with a theoretical study of the thermodynamic equilibrium over a range of temperatures and pressures. The experimental program was carried out in two separate studies, one which involved heating the fluid from room temperature to 1000° C and another which used injection into a furnace that was preheated to 1000° C. The air level in each chamber was chosen to provide 70% and 30% of the oxygen for stoichiometric total combustion.

None of the combustions produced detectable chlorinated or polycyclic aromatic hydrocarbon particulates. Detactable quantities of chlorine and hydrogen chloride were produced from tetrachloroethylene as well as a small amount of dichloroacetylene. Trichlorotrifluoroethane produced a number of fluorocarbon compounds as well as hydrogen fluoride. Silicone fluid produced substantial quantities of a solid material, believed to be silicon dioxide and like the two hydrocarbon fluids, produced several combustible hydrocarbon gases as well as carbon dioxide and carbon monoxide.

ACKNOWLEDGMENTS

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The technical guidance and support from EPRI in this work, through the offices of Dr. G. Addis, Project Manager, was also sincerely appreciated and is hereby acknowledged.

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SUMMARY

The object of this research was to provide information on the chemical compounds formed during partial or incomplete combustion of liquid dielectric insulating materials used in power transformers. This information was requested by the Environmental Protection Agency (EPA) as a first step in promulgating a rule concerning transformer fires.

Five fluids were investigated as a part of this project. All of these fluids have been considered or are being used as dielectric fluids in place of askarels or polychlorinated biphenyls (PCB's) in power transformers. These fluids are as follows: tetrachloroethylene, trichlorotrifluoroethane, polydimethylsiloxane (silicone fluid), transformer mineral oil and a high temperature hydrocarbon fluid.

The research was conducted in three separate phases: a literature search, a computer analysis of theoretical combustion equilibrium expressions and an experimental study. The experimental study involved two types of combustion devices in two laboratories and the combustion products were analyzed primarily by gas chromatography (GC) and by gas chromatography coupled with mass spectroscopy (GC/MS).

The results of the research revealed no evidence of the production of such compounds as polychlorinated dibenzodioxins, polychlorinated dibenzofurans or other polycyclic aromatic hydrocarbon compounds. Certain of the fluids generated gases that could be regarded as dangerous in confined areas, the importance of which should not be minimized in the event of a fire incident. However, suitable fire protection equipment should be available to provide adequate protection in the short term. No evidence was found that long term contamination such as can be caused in a fire incident with transformers which contain askarels will result from a fire involving these replacement dielectric fluids.

Section 1

INTRODUCTION

PERSPECTIVE AND BACKGROUND

Power distribution transformers are used to convert electrical power from a state of relatively low voltage and high current at the generating site, to a state of high voltage and low current for transmission to the user, where it is again converted to the lower voltages commonly used in buildings and homes. In each of the conversion processes, an energy loss is manifested as a heat loss. For reliable operation, safety considerations and damage prevention, a transformer must be kept cool. While smaller transformers, such as those found in electrical and electronic equipment may be air-cooled, power distribution transformers need a cooling system which can transfer the heat generated at the center of the transformer to the outside and to radiators where it may be removed from the transformer. At the same time, the material used in the cooling system must provide insulation between the transformer coils.

Two types of materials can provide the necessary cooling and insulating properties in large transformers: Dry or gaseous and liquid. Gas cooled transformers are nonflammable but often more expensive than liquid coolad ones, and they generally are noisier in use, which limits their use in indoor locations.

There are several liquid coolants currently in use. Until the late 1970's, the most commonly used liquid coolants in locations with relatively high fire hazard belonged to the class of compounds known as askarels which contained mixtures of polychlorinated biphenyls (PCB's). The determination that these compounds posed a significant environmental threat led to their prohibition in new transformers at that time.

Alternative dielectric fluids which may be used in place of askarels in electrical transformers are of relatively recent origin. In the final rule issued by the Environmental Protection Agency, published in the Federal Register of August 25, 1982 (1), that authorized the indefinite use of certain electrical transformers

containing PCB's, it was concluded "that adequate substitutes existed for PCB's in indoor transformer locations from the perspective of fire safety and electrical efficacy".

In 1982, although EPA was aware of the February 1981 fire incident in Binghamton, New York, involving a PCB-transformer, it believed that fires involving such transformers were rare, isolated events. However, the May 1983 incident in San Francisco and the September 1983 incident in Chicago brought this assumption into question. As a result of these incidents, EPA revised its planning and issued a request for information as a first step in promulgating a rule concerning transformer fires (Federal Register, March 23, 1984) (2).

Although that rule was directed at transformers which may contain PCB's, there have also been incidents such as the BART tunnel fire in San Francisco and an underground fire in New York City in which partial combustion products of mineral oil were suspected of harmful environmental interactions. These suspicions, coupled with the growing public concern over combustion products from plastic seat cushions and other commonly encountered items, apparently led to an expanded request by the EPA in the advance notice of proposed rulemaking, mentioned above.

In the advance notice, the EPA requested information on the partial and complete combustion products of several transformer insulating fluids. The fluids identified were chlorinated hydrocarbons, fluorocarbons, high temperature hydrocarbons, other synthetic insulating fluids, mineral oil and silicones. Although some information is available on the products of complete combustion (defined as occurring when there is an excess of oxygen present), information is lacking on the products of partial combustion (where insufficient oxygen is present for stoichiometric completion of the combustion) (3-5). The nature of many fires is such that partial or incomplete combustion is the predominant mode of combustion.

In many fires, the flow of air (oxygen) is limited by restricted air flow into a confined area such as a building, tunnel or vault. Also, the rate of burning can be so rapid as to consume the oxygen more rapidly than it can be replaced by convection flow. For many materials, partial combustion may result in the formation of toxic substances such as carbon monoxide and other substances not normally produced in complete combustion situations.

AIMS AND OBJECTIVES OF THE PROGRAM

This study was initiated to investigate the partial combustion products of several of the more common insulating liquids used in power distribution transformers. The program was restricted to combustion situations only, i.e. in the absence of decomposition products produced by an electric arc.

The primary objective of this program was to determine the chemical compounds formed during partial and complete combustion of liquid dielectric insulating materials used in power transformers. The secondary objectives of the program were to study the effect of reaction conditions (e.g., temperature or oxygen availability) on the combustion product mix, and to identify, in particular, toxic compounds produced under these conditions.

METHODS OUTLINE

To attain the project objectives, an experimental program, outlined in the following, was carried out after an extensive literature search. The literature search indicated that the information desired was generally unavailable. The references found in this search were transferred to SCS Engineers and are a part of a separate project (RP 2028-12) and report by that organization (9).

Thermodynamic Equilibrium Calculations

In order to establish some indication of the types and levels of potential combustion products from the liquid dielectric materials, theoretical thermodynamic equilibrium calculations were conducted for various oxygen levels over a range of reaction temperatures from room temperature to 1500 K. Data was assembled from various sources, including the "JANAF (Joint Army-Navy-Air Force) Thermochemical Tables", and input into a mainframe computer utilizing a program named "CHEMEQ", in the Westinghouse R & D laboratories. This proprietary program, similar to a computer program developed by NASA (6), but with a larger data base, has been used extensively to calculate:

1. Concentrations of chemical species in multicomponent polyphase mixtures at any specified pressure(s) and temperature(s).

2. Concentrations and adiabatic flame temperatures of chemical products formed in the combustion process.

3. Thermodynamic and transport properties of gas mixtures at equilibrium for specified pressure(s) and temperature(s).

Combustion Reaction Evaluations

Two separate sets of combustion experiments were conducted for each material. In one set, a thermogravimetric analyzer (TGA) was modified to conduct the combustion reaction. Reaction products were trapped in cold traps and fed to a gas chromatograph with an electron capture detector for subsequent analysis. This equipment and the techniques used in the analysis will be described in a subsequent section of this report.

In the other experiment set, a stainless steel reactor was employed for the combustion, and the reaction products were fed to a gas chromatograph/mass spectrometer for evaluation.

Section 2

LITERATURE SEARCH

A literature search was carried out to locate and examine any available published information on combustion products of the insulating liquids, with particular emphasis on partial combustion products.

This literature search was conducted through the use of the NERAC service of the University of Connecticut. Approximately 100 articles were identified which dealt with the combustion of the materials of interest. However, few of the abstracts of these articles indicated that they contained information of interest to this program. Several papers were identified which dealt with complete combustion and pyrolysis of the materials involved in this study, but only two (1,4) dealt with partial combustion situations and were, therefore, of use in conducting this program.

These articles considered combustion products of a high temperature hydrocarbon ($RTEmp^R$) and polydimethylsiloxane (PDMS) with limited oxygen present. In the first (1), simultaneous animal toxicity studies were carried out to evaluate the presence of trace amounts of toxic products. A comparison of the two materials showed that PDMS exhibited significantly less toxicity than the high temperature hydrocarbon. However, toxic products other than carbon monoxide were not identified. The second study (4) was a kinetic study of the oxidation of PDMS at temperatures ranging from 220-330°C and discussed the evolution of formaldehyde and formic acid as a consequence of a chain mechanism of oxidation.

One further study (5) discussed the evolution of phosgene ($COCl_2$) from tetrachloroethylene (C_2Cl_4) and concluded that $COCl_2$ was far less likely to be formed at dangerous levels than it was from carbon tetrachloride. Hydrogen chloride, which was assumed to be generated by reaction with water vapor in the air, was

predominant. The authors argued that the presence of HCl would cause exposure to any other toxic materials to be minimized because it would drive personnal from the area due to its pungent characteristics.

The information obtained from this search was released to SCS Engineers and is reviewed in their final report for RP 2028-12 (9).

Section 3

EXPERIMENTAL STUDIES

MATERIALS

One fluid of each of five types of insulating fluid was selected for this study:

1. Chlorinated hydrocarbon--tetrachloroethylene (C_2Cl_4), WECOSOL^R, Westinghouse Electric Corporation; original supplier: Diamond Shamrock Corporation.

2. Fluorocarbon--trifluorotrichloroethane ($C_2F_3Cl_3$), Freon 113^R, supplier: E.I. DuPont de Nemours.

3. Silicone fluid--polydimethylsiloxane, Dow Corning 551 Silicone Transformer Fluid; supplier: Dow Corning Company.

4. Mineral oil--WEMCO C^R, Westinghouse Electric Corporation; original supplier: Gulf Oil Corporation.

5. High temperature hydrocarbon--RTEmp^R; supplier: RTE Corporation.

In addition, the air used in the combustion experiments was Dry Grade air (< 3 ppm H_2O) supplied by Linde Division, Union Carbide.

EQUIPMENT AND PROCEDURES

The combustion apparatus used in the experiments conducted by the Materials and Manufacturing Technology laboratories of Westinghouse Electric Co., consisted of a Dupont 990 Thermogravimetric Analyzer with a 1090 Thermal Analysis Module for control and data interpretation. This instrument was slightly modified to conduct these experiments as is schematically illustrated in Figure 3-1. The liquid samples were placed in a small boat prepared from platinum foil. Air was continuously admitted to the chamber through a flowmeter which was adjusted to provide the desired amount for the combustion experiments. A trap at the exit port of the combustion chamber was filled with ice water to contain the reacting materials in the chamber. The cold traps consisted of a slurry of isopropanol and dry ice (-69°C) on the one hand, and a slurry of isopentane and liquid nitrogen (-160°C) on the other. Two replicate runs at each air level were carried out for each material. The samples collected in these traps were then analyzed in a Hewlett Packard Model 5730A gas chromatograph.

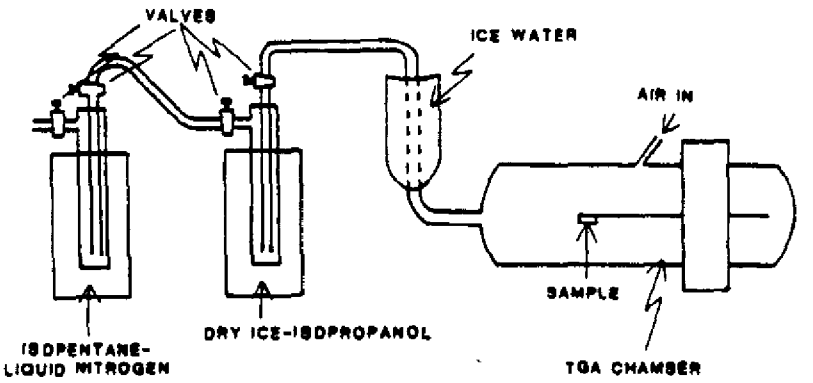

Fig. 3-1. Modified Thermal Analysis Combustion Apparatus (not to scale).

A Dupont 850 Liquid Chrometograph was used in an attempt to identify the constituents of the mineral oil and high temperature hydrocarbon. For mineral oil the best separations were achieved using 90% methanol and 10% water in isocretic* mode at a flow rate of 2 ml/min of solvent. For the high temperature hydrocarbon, a grsdient profile of tetrahydrofuran and methenol at a flow rate of 2 ml/min, achieved the best results.

The apparatus used in the combustion experiments at the Research and Development laboratories of Westinghouse Electric Corp., was constructed from a stainless steel cylinder, surrounded by an induction heater as is schematically illustrated in Figure 3-2. The reacting material was injected with a microliter syringe into the preheated combustion apparatus. The amount of reactant was varied to achieve the desired level of air for combustion. The products were collected in a sample loop, which was quickly attached to the Luer-Lok connector immediately to the left of the Luer-Lok valve in place of the syringe assembly. The loop was then used to transfer the products into a Hewlett Packard 5985A gas chromatograph/mass spectrometer for analysis.

During the course of the work, a modification to the R&D combustion apparatus was made, owing to the high viscosity of the high temperature hydrocarbon and the difficulty of transfer with a syringe. A piston assembly was constructed which allowed small aluminum ampules of the reacting materials to be transferred into the combustion chamber. The design of this modification is given in Figure 3-3 and in subsequent mention of this modification in this report, it will be referred to as the "piston/capsule" method.

The temperature of combustion was chosen after consultation with Dr. Richard Gann of the National Bureau of Standards (7). Although temperetures of combustion can often reach very high levels when sufficient oxygen is present, limiting the oxygen can reduce these temperatures signficently. It is generelly accepted that partial combustion temperatures are on the order of 1000° C or 1273 K. Consequently, the thermogravimetric analyzer was heated from ambient temperature to 1000°C at 30° per minute and the R & D apparatus was allowed to stebilize at 1000°C prior to the injection.

* isocratic - the mobile phase or mixture of solvents is unchanged in the proportion of each constituent during the separation.

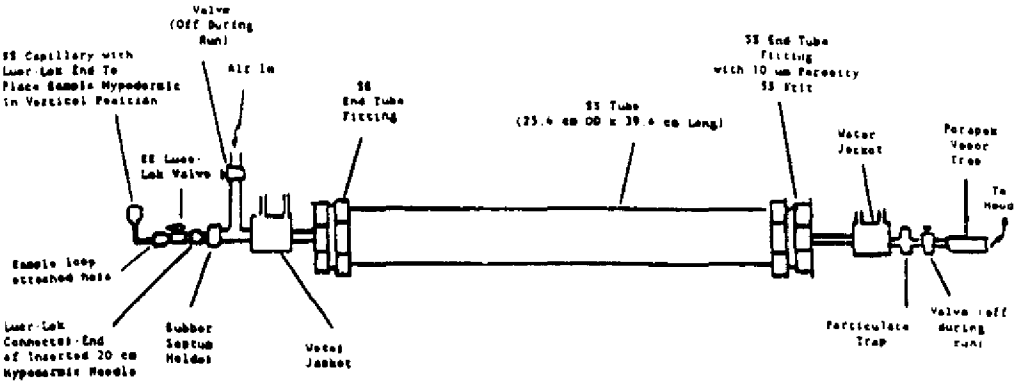

Fig. 3-2. Stainless Steel Combustion Chamber (not to scale).

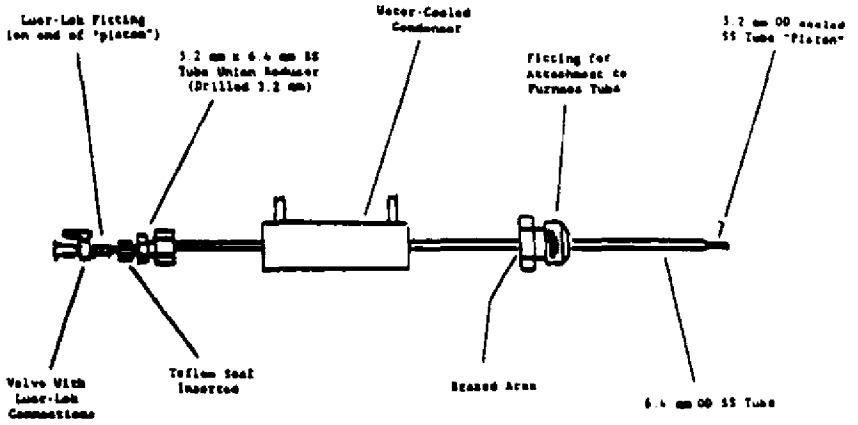

Fig. 3-3. Piston/Capsule Injection Mechanism. A device for inserting solids and viscous liquids into the stainless steel combustion chamber (not to scale).

Section 4

THERMODYNAMIC EQUILIBRIUM CALCULATIONS

The results of the thermodynamic calculations are given in Tables 4-1 through 4-5 for a combustion temperature of 1300 K. For tetrachloroethylene, a chemical combustion equation analogous to that of a hydrocarbon in pure oxygen was used to establish the levels of oxygen to be added for the partial combustion situation, although this combustion does not necessarily occur. The equation devised for this combustion reaction is:

$$C_2Cl_4 + 2\ O_2 \dashrightarrow 2\ Cl_2 + 2\ CO_2 \qquad (4\text{-}1)$$

Similarly, for the chlorofluorocarbon, the theoretical combustion can be proposed to follow the process:

$$2\ C_2Cl_3F_3 + 4\ O_2 \dashrightarrow 4\ CO_2 + 3\ Cl_2 + 3\ F_2 \qquad (4\text{-}2)$$

Polydimethylsiloxane must be treated in this situation as separate monomer units of the polymer chain for which the appropriate reaction can be considered to be:

$$-(CH_3)_2SiO- + 4\ O_2 \dashrightarrow 2\ CO_2 + 3\ H_2O + SiO_2 \qquad (4\text{-}3)$$

For the mineral oil and the high temperature hydrocarbon, the exact composition of the reacting materials was impossible to determine. Therefore, calculations were made for an aromatic hydrocarbon and for a saturated hydrocarbon, using the rationale that these materials had compositions lying somewhere between these two extremes. Indeed, carbon-hydrogen analysis of the high temperature hydrocarbon revealed that its hydrogen to carbon ratio was 1.92, and analysis of data provided by Gulf Oil Corporation, Pittsburgh, PA. (presented in Table 4-6), gives a hydrogen to carbon ratio of 1.71 for the mineral oil; i.e. both reacting materials consist primarily of saturated hydrocarbons whose hydrogen to carbon ratio would be near 2.0 (long aliphatic chain approximation).

Table 4-1

THERMODYNAMIC RESULTS FOR TETRACHLOROETHYLENE

Probable Products @ 1300 K	With 80% Air (Mole %)	With 20% Air (Mole %)
CO_2	1.121	-----
$COCl_2$	0.025	-----
CO	19.9	3.16
C (solid)	6.72	7.69
N_2	44.4	9.77

Table 4-2

THERMODYNAMIC RESULTS FOR TRICHLOROTRIFLUOROETHANE

Probable Products @ 1300 K	With 80% Air (Mole %)	With 20% Air (Mole %)
COClF	0.269	0.04
COF_2	5.25	0.157
CF_4	8.30	26.2
$CClF_3$	0.262	4.11
CCl_2F_2	0.007	0.531
CO_2	2.59	-----
CO	13.2	3.75
H_2O	0.007	-----
N_2	47.7	7.92
$COCl_2$	0.006	-----
ClF	0.001	-----
Cl_2	21.8	56.1
Cl	0.583	0.936
CCl_3F	-----	0.103

Table 4-3

THERMODYNAMIC RESULTS FOR POLYDIMETHYLSILOXANE

Probable Products @ 1300 K	With 80% Air (Mole %)	With 20% Air (Mole %)
CH_4	0.0415	0.0711
H_2O	0.211	0.0004
H_2	50.1	53.9
CO	10.5	0.0268
CO_2	0.0254	-----
SiC (solid)	1.24	-----
C (solid)	22.5	33.3
SiO_2 (solid)	16.5	9.91
Si (solid)	-----	0.013
Si_3N_4 (solid)	-----	1.00

Table 4-4

THERMODYNAMIC RESULTS FOR SATURATED HYDROCARBON

Probable Products @ 1300 K	With 80% Air (Mole %)	With 20% Air (Mole %)
N_2	65.0	17.0
H_2O	14.3	1.02
H_2	9.52	73.6
CH_4	-----	1.93
CO_2	11.2	6.5

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Table 4-5

THERMODYNAMIC RESULTS FOR AROMATIC HYDROCARBON

Probable Products @ 1300 K	With 80% Air (Mole %)	With 20% Air (Mole %)
N_2	65.4	33.4
H_2O	2.12	0.592
H_2	23.5	59.8
CH_4	0.04	0.315
CO_2	10.8	5.82

Although quantities of reaction products were calculated for other temperatures than 1300 K, it is unlikely that thermodynamic equilibrium will be present at lower temperatures due to kinetic considerations. Kinetic information on the combustion reactions represented by the materials of these experiments does not appear to be available. Thus any consideration of the data requires the assumption that thermodynamic equilibrium is valid at higher temperatures; an assumption that appears to be accepted at temperatures approaching 1500 K (8).

At the least, thermodynamic calculations can be used to provide an approximate answer in regard to the question of the presence or absence of a particular product species. The information can then be used to provide guidelines for the experimental evaluation of a combustion reaction. For example, these calculations were used to establish the probability of formation of chlorophenols and polychlorinated dibenzodioxins (PCDD's) in the combustion of tetrachloroethylene. It was found that the concentration of these species present in the product stream would be vanishingly small, on the order of 10^{-30}% at all temperatures in the range of consideration; in other words, these species were very strongly thermodynamically unfavored.

Table 4-6

HYDROCARBON ANALYSIS OF MINERAL OIL
(HPLC separation followed by mass spectrometry)

Component	Wt. %
Saturates	
Paraffins	11.4
Naphthenes	
1 Ring	16.3
2 Ring	16.8
3 Ring	12.2
4 Ring	10.0
5 Ring	3.9
Total Naphthenes	59.2
Total Saturates	70.6
Aromatics	
Mono	18.5
Di	8.8
Tri	0.6
Tetra	0.3
Aromatic Sulfur	1.2
Total Aromatics	29.4

Source: Gulf Oil Corporation, Pittsburgh, PA.

MONS 218073

Section 5

EXPERIMENTAL RESULTS

The experimental results will be treated in five separate sections, each considering one of the fluids involved in the experiment. Any difficulties encountered in the experimental arrangements due to particular fluid characteristics or products will also be addressed at this point.

TETRACHLOROETHYLENE

Tetrachloroethylene is a relatively low viscosity, high vapor pressure liquid at room temperature, which necessitated expeditious weighing and charging to the combustion chamber in the case of the thermogravimetric apparatus. On the other hand, the low viscosity, in particular, was effective in providing a ready means of transfer (via syringe injection) into the other combustion chamber.

In the MMT chamber considerable problems were encountered when the combustion was carried out at an air level corresponding to 70% of theoretical total combustion. Detectable amounts of chlorine were generated and in addition, since the chamber was heated from ambient temperature upward, the presence of water on the interior walls of the chamber caused the production of small amounts of HCl. This in turn caused corrosion of some of the metal parts in the TGA measurement system such as the sample reference thermocouple which broke down at approximately 600° C. Since this component is not essential to the operation of the instrument, it was omitted in the next run. However, the second run caused enough deterioration of the other components of the apparatus to require overhaul of the instrument. As a result, the runs at 30% air were postponed and indeed were not completed during the project.

The results of the analyses of the products contained in the traps are summarized in Table 5-1. In this and succeeding tables, run 1 and run 2 represent the replicate runs that were performed with each material. Other than the expected chlorine and the normal constituents of air, only HCl was noted in small amounts in the products. As was predicted in the thermodynamic equilibrium calculations,

Table 5-1

COMBUSTION PRODUCTS FROM TETRACHLOROETHYLENE

Run 1 Isopropanol-Dry-Ice Trap 70% Air	
Nitrogen	65.625 %
Oxygen & Argon	15.341
Carbon Dioxide	1.320
Chlorine	16.232
HCl	1.483
Sum	100.000 %

Run 2 Isopropanol-Dry-Ice Trap 70% Air	
Nitrogen	64.452 %
Oxygen & Argon	16.302
Carbon Dioxide	0.896
Chlorine	14.776
HCl	3.574
Sum	100.000 %

Run 1 Isobutane-Liq. N_2 70% Air	
Nitrogen	70.743 %
Oxygen & Argon	21.015
Carbon Dioxide	-----
Chlorine	8.242
HCl	-----
Sum	100.000 %

Run 2 Isobutane-Liq. N_2 70% Air	
Nitrogen	72.445 %
Oxygen & Argon	19.187
Carbon Dioxide	-----
Chlorine	7.206
HCl	1.163
Sum	100.001 %

phosgene was not detected in any of the traps. No enrichment of products generated at lower temperatures could be substantiated. However, unreacted starting material was recovered in significant quantities, both in the traps and in the combustion chamber. Table 5-2 lists the detection limits for various gases expected to be found in these and subsequent experiments.

The R & D combustion apparatus was used to conduct three analytical runs with tetrachloroethylene. The two direct injection runs gave chlorine as the primary product (see Figure 5-1). The instrumentation of the mass spectrometer causes a "tic" to be inserted at the normally unused m/z position 1 when any signal from the spectrum swamps the instrumentation capacity, such as is the case for $^{35}Cl^{+}$. It is believed that the other carbon-chlorine peaks are an artifact generated from an interaction between chlorine and carbon "dirt" which occurs in the mass spectrometer. However, it is also possible that sufficient carbon is generated from the combustion reaction to produce these small quantities.

A low level (approximately 0.1%) of dichloroacetylene was seen (Fig. 5-2) in one of the direct injection runs. Unreacted tetrachloroethylene was also recovered in both of these runs. An additional sample run with the piston/capsule method gave essentially the same results with dichloroacetylene again being found.

No particulates were detected on the glass fiber disk trap (Fig. 5-3). With the sample quantities used in the experiment, this indicates <3 ppm of halogenated or polycyclic particulates.

TRICHLOROTRIFLUOROETHANE

The physical characteristics of trichlorotrifluoroethane and tetrachloroethylene are quite similar. The same considerations apply to the handling and placement of trichlorotrifluoroethane in the combustion chamber as were outlined for tetrachloroethylene.

Few problems were encountered when this substance was examined in the MMT combustion chamber. However, the presence of water on the interior walls did cause production of HF which in turn caused a minor amount of etching of the chamber. Precautions were taken to remove as many metal parts from the apparatus as possible, similar to the previous experiments.

Table 5-3 summarizes the analysis results for this substance. In this particular case, however, not all peaks in the chromatograph from the electron capture

Table 5-2

GAS CHROMATOGRAPHIC DETECTION LIMITS

Gas Species	Detection Limit %
H_2	0.04
O_2	0.008
N_2	0.009
CH_4	0.003
CO	0.03
CO_2	0.006
C_2H_4	0.002
C_2H_6	0.003
C_2H_2	0.002
C_3's	0.001
$COCl_2$	0.0008
HCl	0.0008
H_2O (g)	0.001

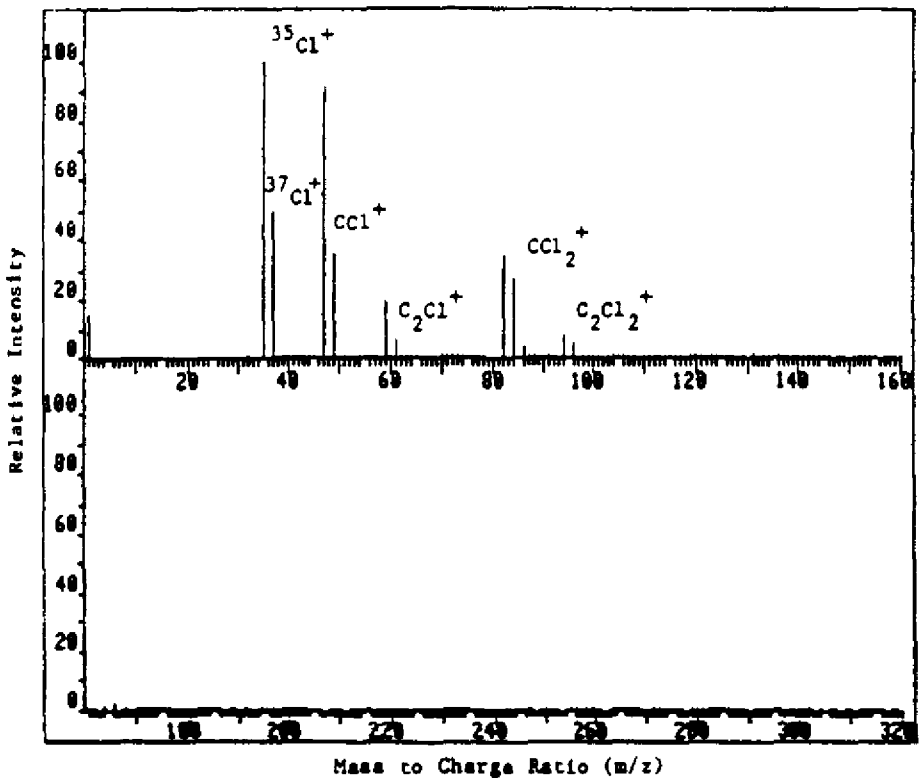

Fig. 5-1. Tetrachloroethylene Direct Injection With Chlorine. Mass spectrum of chlorine as obtained from combustion of tetrachloroethylene. Saturation of detector indicated by "tic" at m/z = 1.

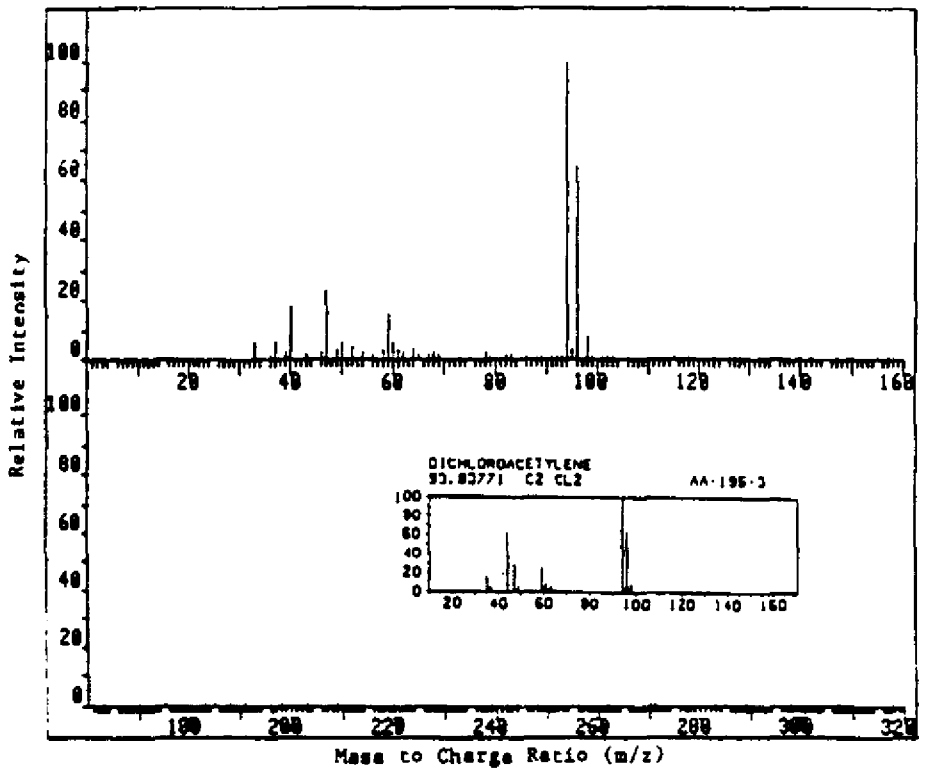

Fig. 5-2. Tetrachloroethylene Direct Injection With Dichloroacetylene. Mass spectrum of dichloroacetylene as recovered from one of the direct injection runs of tetrachloroethylene.

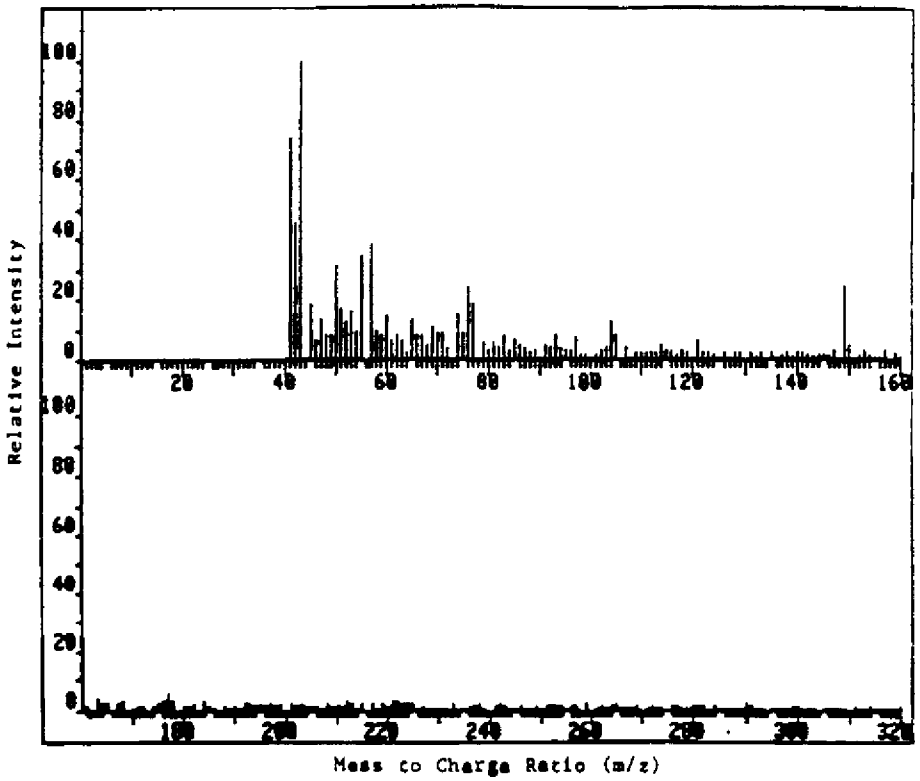

Fig. 5-3. Tetrachloroethylene Particulate Chromatogram. Mass spectrum of particulates from pyrolysis of tetrachloroethylene.

Table 5-3

COMBUSTION PRODUCTS OF TRICHLOROTRIFLUOROETHANE

Run 1 Isopropanol-Dry-Ice Trap 70% Air	
Nitrogen	68.406 %
Oxygen & Argon	29.464
Carbon Dioxide	-----
Peak 1	0.074
Peak 2	-----
Peak 3	0.034
Peak 4	-----
HF	2.022
Sum	100.000 %

Run 2 Isopropanol-Dry-Ice Trap 70% Air	
Nitrogen	66.023 %
Oxygen & Argon	31.032
Carbon Dioxide	-----
Peak 1	-----
Peak 2	-----
Peak 3	-----
Peak 4	-----
HF	2.945
Sum	100.000 %

Run 1 Isobutane-Liq. N_2 70% Air	
Nitrogen	66.741 %
Oxygen & Argon	32.871
Carbon Dioxide	-----
Peak 1	-----
Peak 2	-----
Peak 3	-----
Peak 4	-----
HF	0.388
Sum	100.000 %

Run 2 Isobutane-Liq. N_2 70% Air	
Nitrogen	64.234 %
Oxygen & Argon	33.452
Carbon Dioxide	1.528
Peak 1	-----
Peak 2	-----
Peak 3	-----
Peak 4	-----
HF	0.786
Sum	100.000 %

Table 5-3 (Cont.)

COMBUSTION PRODUCTS OF TRICHLOROTRIFLUOROETHANE (Cont.)

Run 3 Isopropanol-Dry-Ice Trap 30% Air	
Nitrogen	41.861 %
Oxygen & Argon	17.369
Carbon Dioxide	10.693
Peak 1	13.524
Peak 2	0.070
Peak 3	0.431
Peak 4	0.034
HF	16.018
Sum	100.000 %

Run 4 Isopropanol-Dry-Ice Trap 30% Air	
Nitrogen	45.250 %
Oxygen & Argon	19.461
Carbon Dioxide	9.652
Peak 1	11.236
Peak 2	0.050
Peak 3	0.232
Peak 4	0.068
HF	14.052
Sum	100.001 %

Run 3 Isobutane-Liq. N_2 30% Air	
Nitrogen	61.710 %
Oxygen & Argon	33.228
Carbon Dioxide	0.258
Peak 1	0.596
Peak 2	-----
Peak 3	-----
Peak 4	-----
HF	4.208
Sum	100.000 %

Run 4 Isobutane-Liq. N_2 30% Air	
Nitrogen	64.753 %
Oxygen & Argon	33.212
Carbon Dioxide	-----
Peak 1	-----
Peak 2	-----
Peak 3	-----
Peak 4	-----
HF	2.036
Sum	100.001 %

detector could be identified. Certain of these peaks undoubtedly could be associated with various fluorocarbon compounds that are not readily available for confirmation of the peak identities. It was decided that the results of the R&D combustion apparatus would be used to identify these other products.

The results from the R & D apparatus are somewhat inconsistent. Two runs were made in the stainless steel reactor using the direct injection procedure. The first run, in which the withdrawal of products was carried out after 10 seconds, showed chlorotrifluoroethylene and dichlorotetrafluoroethane (Figures 5-4 and 5-5). However, over 99% of recovered gaseous material was unreacted starting material (Figures 5-6 and 5-7). A second injection was made and the gas sample was withdrawn after 10 minutes. A little chlorine was detected (Figure 5-8) but unreacted material was predominant. Figure 5-8 shows CF_2^+ and $CFCl^+$ which may indicate a trace of active fluorine, although that seems unlikely. Fluorine would be outside of the scanning range. This run did not detect the other two materials seen in the first run.

Four runs were made on trichlorotrifluoroethane with the piston/capsule technique. In this technique, products detected included tetrafluoromethane (Figure 5-9), dichlorodifluoroethylene (Figure 5-10), chlorotrifluoroethylene (Figure 5-11), trichlorofluoroethylene (Figure 5-12), tetrafluoroethylene and fluorochloroethylene (Figure 5-13). Again, no particulates of interest were detected, even in the run with the greatest variety of products, with the same detection limit as with C_2Cl_4, 3 ppm.

Many of these products may well correspond to the results of the other combustion technique. Since it was not possible to acquire these materials, confirmation is limited to the observation that some of these materials were predicted by the thermodynamic calculations.

SILICONE (POLYDIMETHYLSILOXANE)

The results of the combustion product analyses for this material are given in Table 5-4. For the first time, a relatively large variety of products were detected. Again in this case, a large amount of unreacted material was present in the chamber and in the combustion boat at the completion of the experiment.

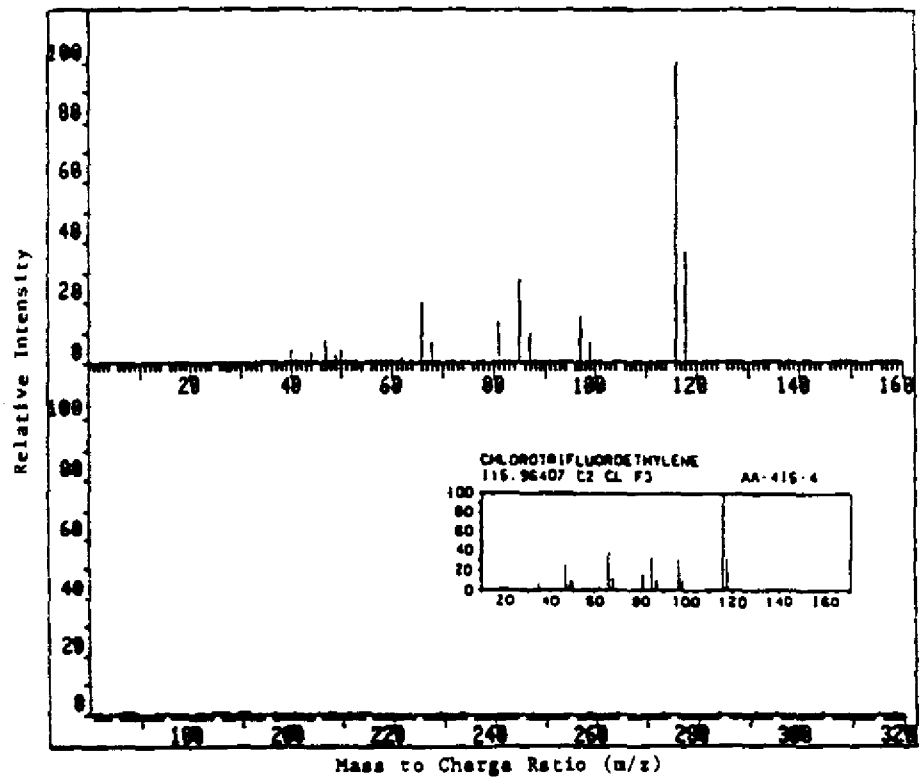

Fig. 5-4. Chlorotrifluoroethylene from Trichlorotrifluoroethane. Mass spectrum of chlorotrifluoroethylene as recovered from combustion of trichlorotrifluoroethane at 1000°C (ca. 10 sec).

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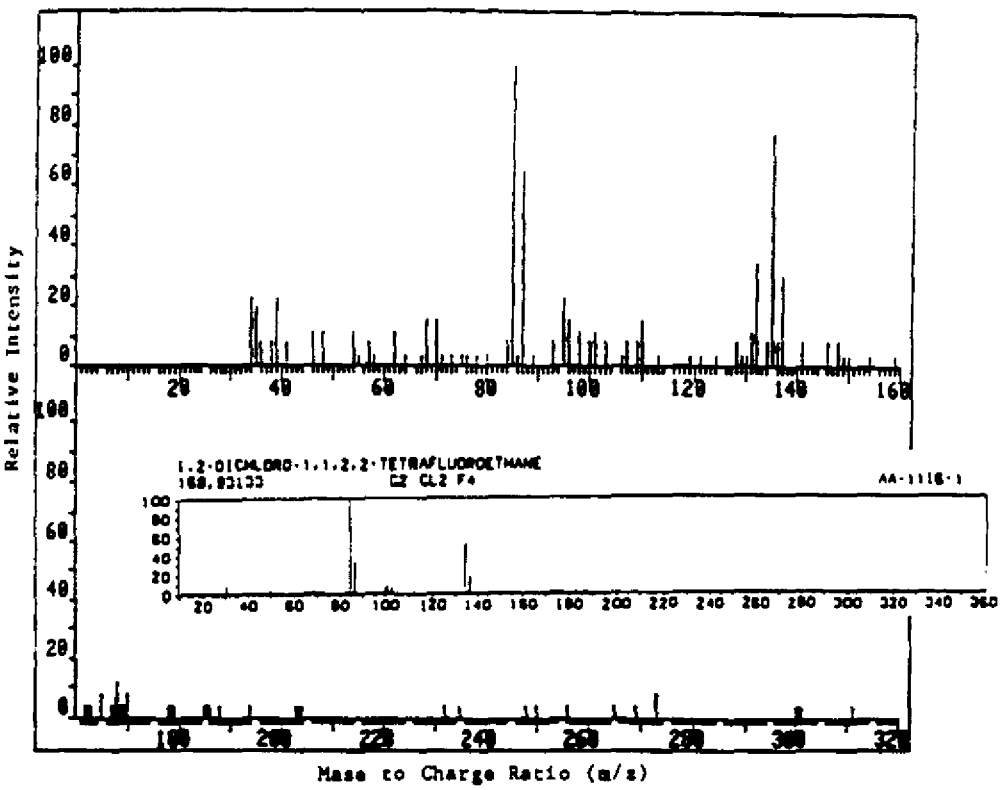

Fig. 5-5. Dichlorotetrafluoroethene from Trichlorotrifluoroethane. Mass spectra including that of dichlorotetrafluoroethane as recovered from combustion of trichlorotrifluoroethane at 1000°C (ca. 10 sec).

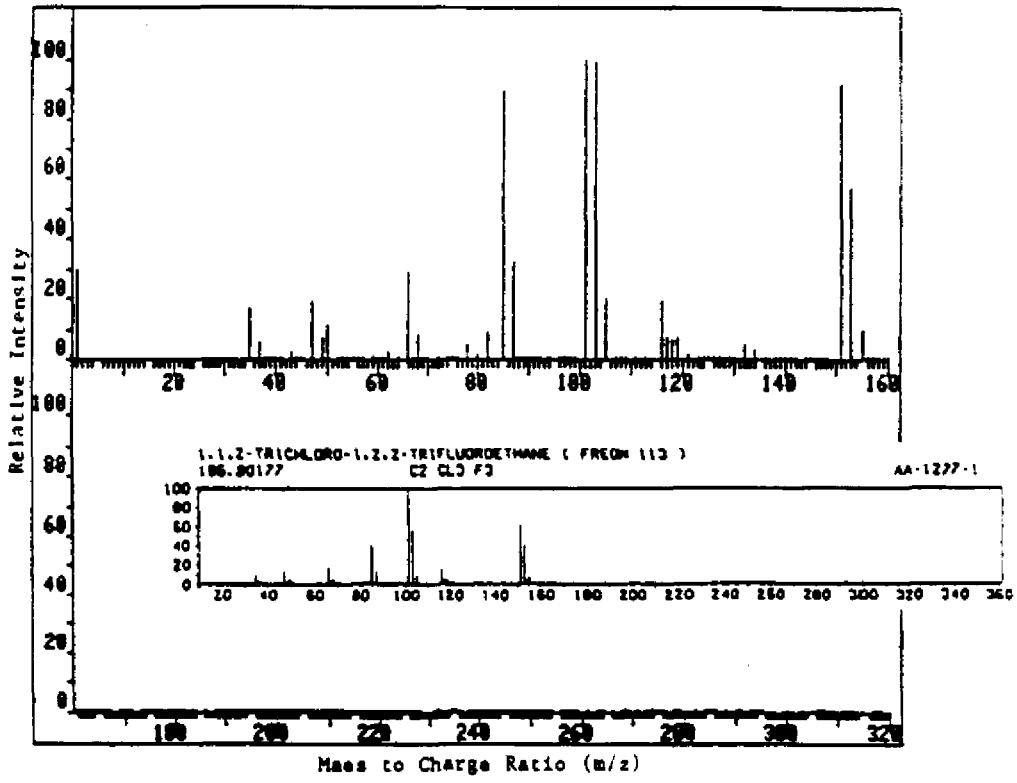

Fig. 5-6. Unreacted Starting Meterial from Trichlorotrifluoroethane. Mass spectrum of trichlorotrifluoroethane as recovered from combustion at 1000°C (ca. 10 sec).

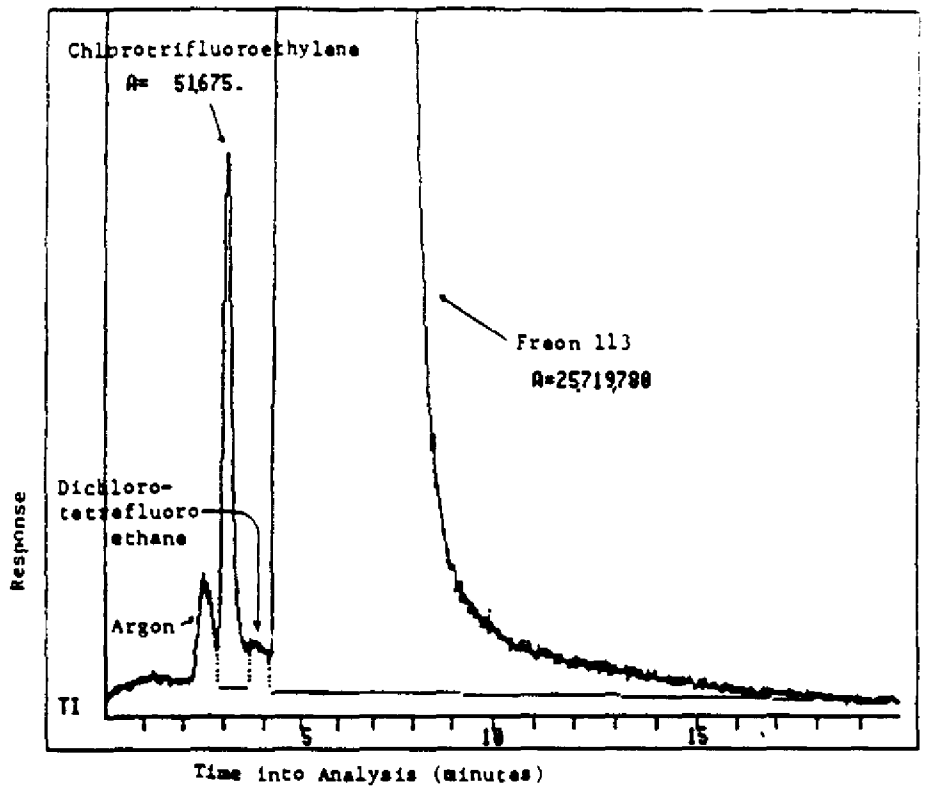

Fig. 5-7. Remnant Starting Materials from Trichlorotrifluoroethane. Analyticel area counts for trichlorotrifluoroethane and chlorotrifluoroethylene as recovered from combustion of trichlorotrifluoroethane at 1000 °C (ca. 10 sec).

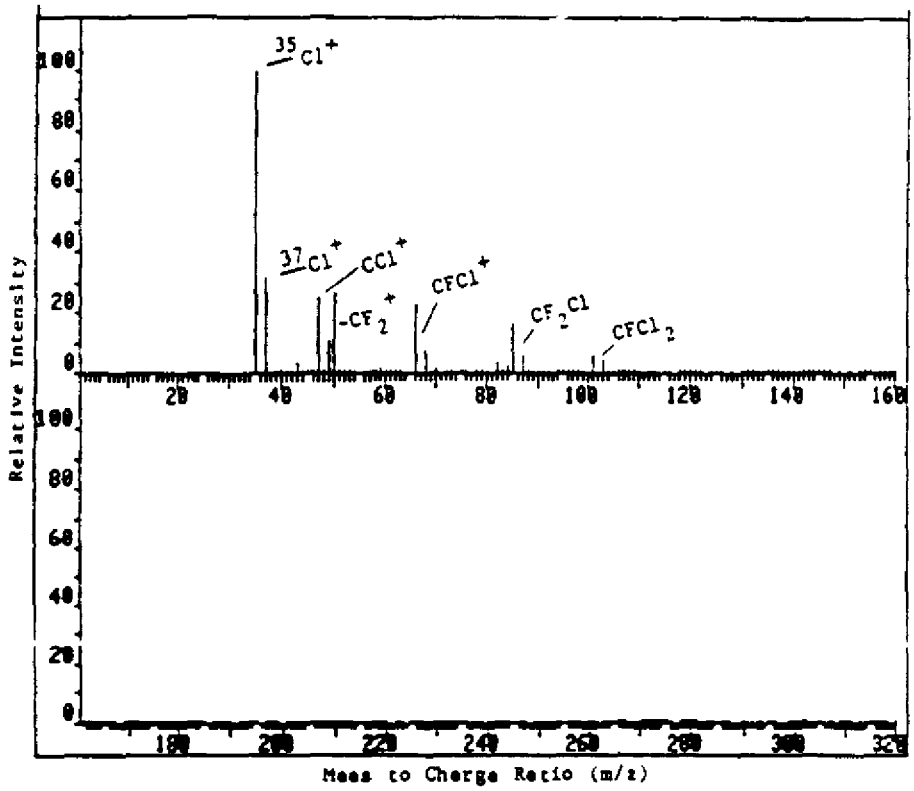

Fig. 5-8. Chlorine and Starting Material from Trichlorotrifluoroethane. Mass spectrum of (primarily) chlorine as recovered from combustion of trichlorotrifluoroethane, second run only (10 min at 1000°C).

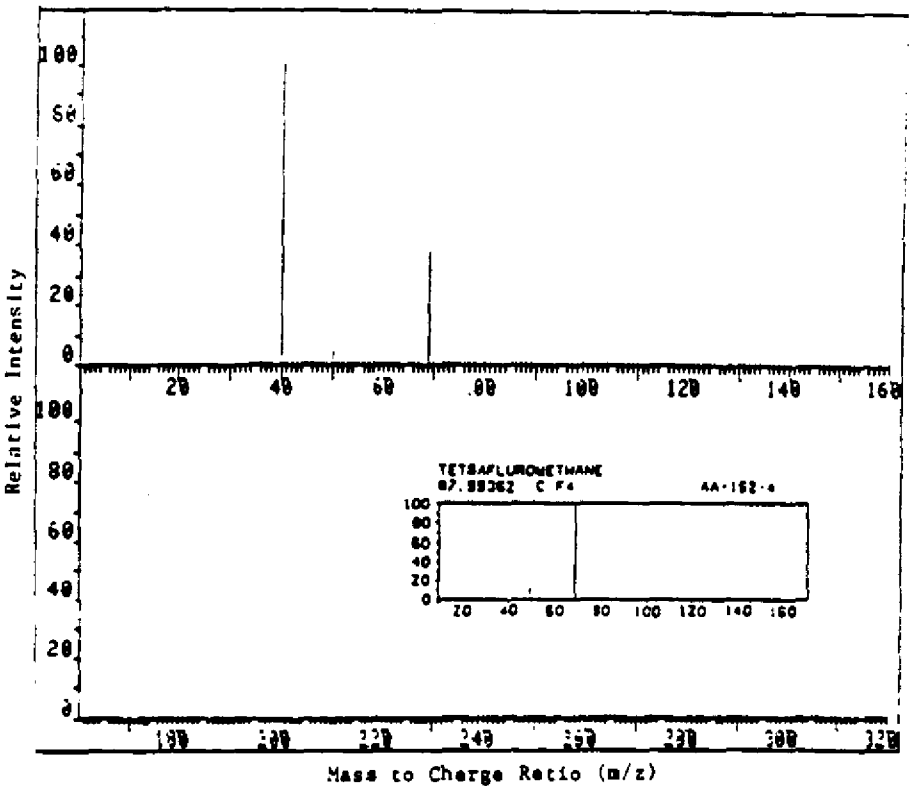

Fig. 5-9. Tetrafluoromethene from Trichlorotrifluoroethane. Mass spectrum of tetrafluoromethene as recovered from pyrolysis of trichlorotrifluoroethane (with argon at m/z 40).

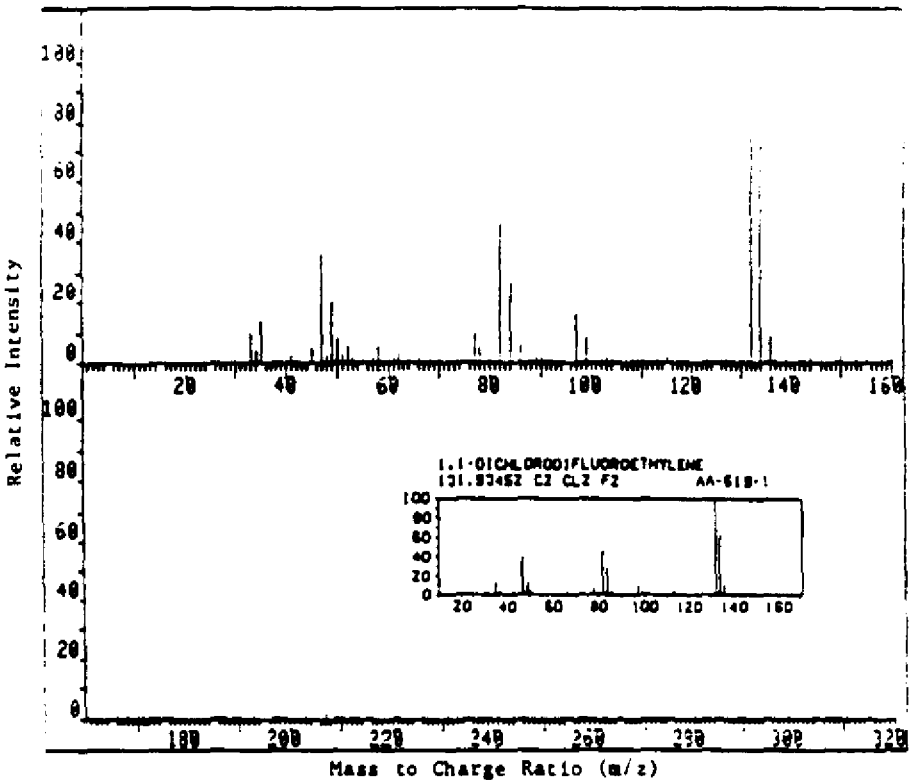

Fig. 5-10. Dichlorodifluoroethylene from Trichlorotrifluoroethane. Mass spectrum of dichlorodifluoroethylene as recovered from pyrolysis of trichlorotrifluoroethene.

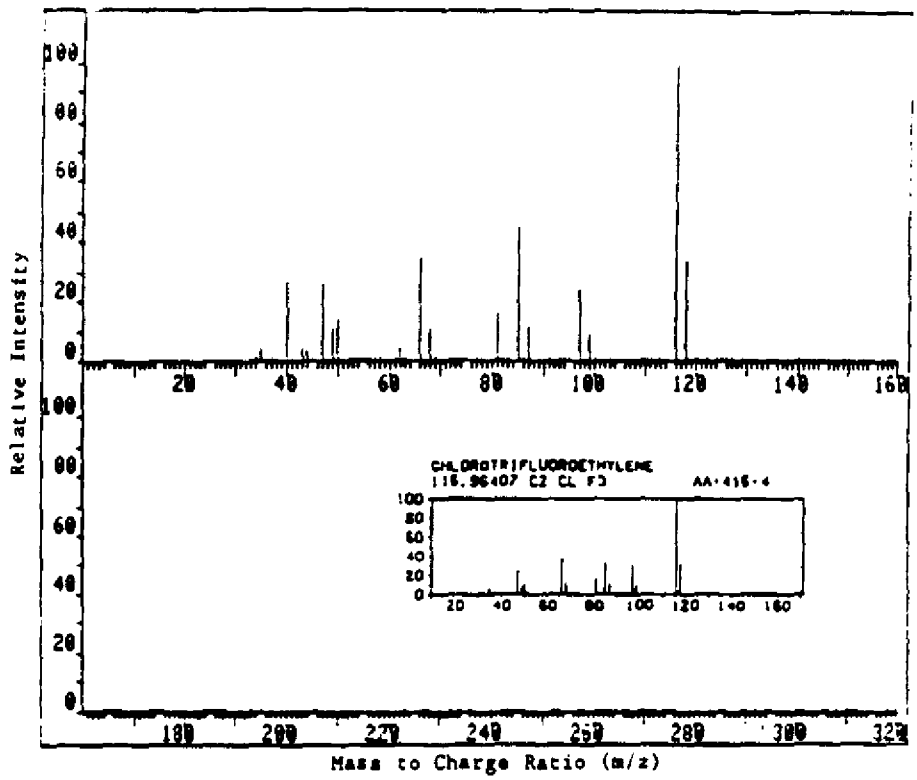

Fig. 5-11. Chlorotrifluoroethylene from Trichlorotrifluoroethane. Mass spectrum of chlorotrifluoroethylene as recovered from pyrolysis of trichlorotrifluoroethane.

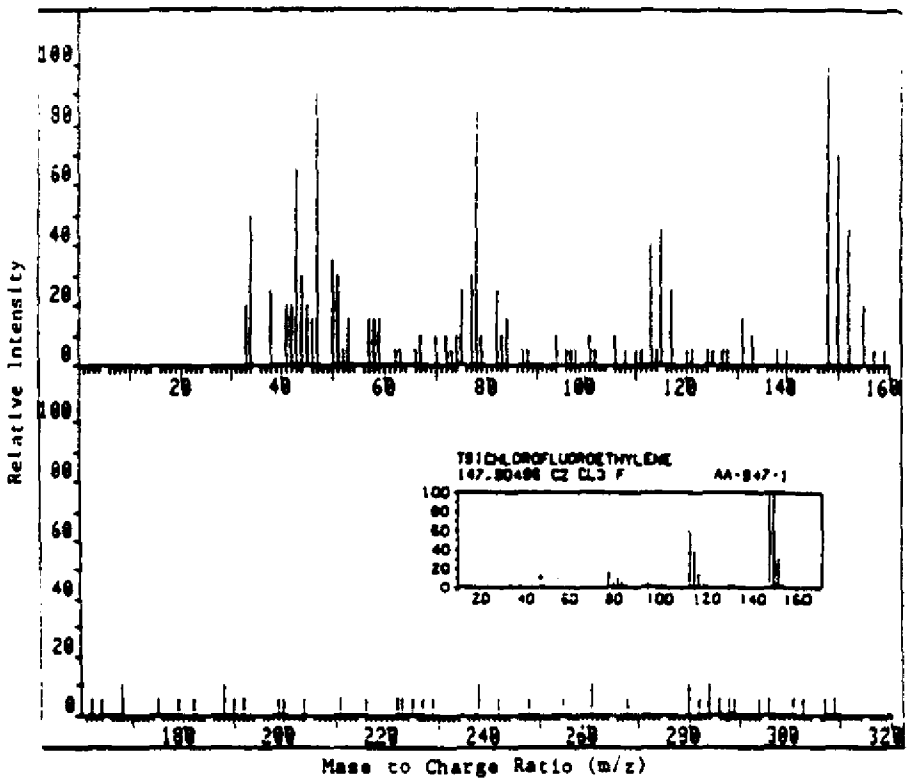

Fig. 5-12. Trichlorofluoroethylene from Trichlorotrifluoroethane. Mass spectrum of trichlorofluoroethylene as recovered from pyrolysis of trichlorotrifluoroethane.

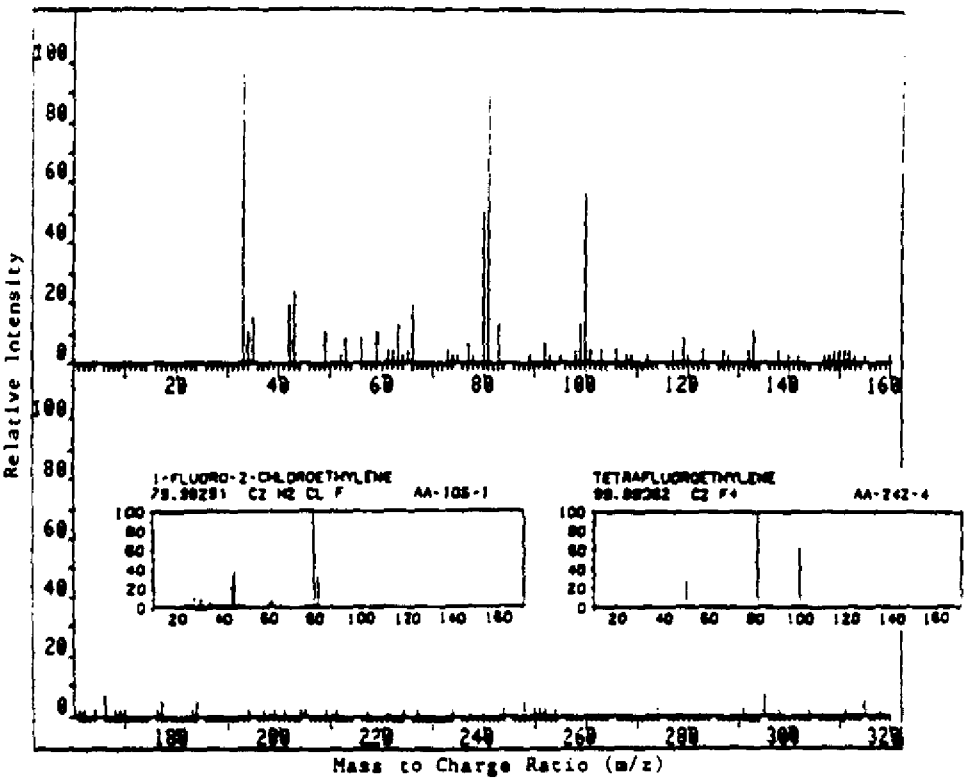

Fig. 5-13. Tetrafluoroethylene and Fluorochloroethylene. Mass spectra of tetrafluoroethylene and fluorochloroethylene as recovered from pyrolysis of Freon 113.

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Table 5-4

POLYDIMETHYLSILOXANE COMBUSTION PRODUCTS

Run 1 Isopropanol-Dry-Ice Trap 70% Air		Run 2 Isopropanol-Dry-Ice Trap 70% Air	
Nitrogen	78.83 %	Nitrogen	78.68 %
Oxygen & Argon	20.33	Oxygen & Argon	18.39
Carbon Dioxide	0.82	Carbon Dioxide	0.93
Hydrogen	0.02	Hydrogen	0.32
Carbon Monoxide	-----	Carbon Monoxide	0.49
Methane	-----	Methane	0.35
Ethane	-----	Ethane	0.01
Ethylene	-----	Ethylene	0.08
Acetylene	-----	Acetylene	0.05
C_3 Hydrocarbons	-----	C_3 Hydrocarbons	0.01
Water	-----	Water	0.70
Sum	100.00 %	Sum	100.01 %

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Table 5-4 (Cont.)

POLYDIMETHYLSILOXANE COMBUSTION PRODUCTS (Cont.)

Run 1 Isobutene-Liq. N_2 70% Air		Run 2 Isobutene-Liq. N_2 70% Air	
Nitrogen	76.07 %	Nitrogen	71.34 %
Oxygen & Argon	12.53	Oxygen & Argon	10.35
Carbon Dioxide	9.57	Carbon Dioxide	15.54
Hydrogen	0.04	Hydrogen	0.18
Carbon Monoxide	0.30	Carbon Monoxide	0.35
Methane	-----	Methane	0.86
Ethane	0.02	Ethane	0.01
Ethylene	0.04	Ethylene	0.07
Acetylene	-----	Acetylene	0.02
C_3 Hydrocarbons	0.04	C_3 Hydrocarbons	0.03
Water	1.39	Water	1.25
Sum	100.00 %	Sum	100.00 %

Table 5-4 (Cont.)

POLYDIMETHYLSILOXANE COMBUSTION PRODUCTS (Cont.)

Run 3 Isopropanol-Dry-Ice Trap 30% Air		Run 4 Isopropanol-Dry-Ice Trap 30% Air	
Nitrogen	82.446 %	Nitrogen	83.43 %
Oxygen & Argon	14.963	Oxygen & Argon	14.17
Carbon Dioxide	2.024	Carbon Dioxide	1.81
Hydrogen	-----	Hydrogen	-----
Carbon Monoxide	0.469	Carbon Monoxide	0.49
Methane	-----	Methane	-----
Ethane	-----	Ethane	-----
Ethylene	-----	Ethylene	-----
Acetylene	-----	Acetylene	-----
C_3 Hydrocarbons	-----	C_3 Hydrocarbons	-----
Water	0.099	Water	0.10
Sum	100.001 %	Sum	100.00 %

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Table 5-4 (Cont.)

POLYDIMETHYLSILOXANE COMBUSTION PRODUCTS (Cont.)

Run 3 Isobutane-Liq. N_2 30% Air		Run 4 Isobutane-Liq. N_2 30% Air	
Nitrogen	83.151 %	Nitrogen	82.163 %
Oxygen & Argon	3.200	Oxygen & Argon	3.953
Carbon Dioxide	6.940	Carbon Dioxide	7.062
Hydrogen	2.036	Hydrogen	1.913
Carbon Monoxide	2.696	Carbon Monoxide	3.152
Methane	1.659	Methane	1.423
Ethene	0.028	Ethene	0.024
Ethylene	0.159	Ethylene	0.173
Acetylene	0.066	Acetylene	0.052
C_3 Hydrocarbons	0.040	C_3 Hydrocarbons	0.035
Water	0.024	Water	0.030
Sum	99.999 %	Sum	99.980 %

Above all, a significant amount of solid material was found in all tubing leading from the quartz combustion chamber. This material was white and fluffy in appearance and was most likely silicon dioxide which is known to result from combustion of polydimethylsiloxane (1). The extent of this material may well have influenced the detection of certain gases such as carbon monoxide, which would normally be found in relatively small quantities in the traps, by essentially plugging the exit from the trap.

In the R & D effort, two runs with the direct injection method were completed. Since no volatiles were detected and because of the relative difficulty of transferring this rather viscous substance, the piston method was developed. However, again no volatiles were detected. The furnace tube contained a large amount of black, fluffy material. When the material was heated in a muffle furnace at 1000° C, the substance left a white ash. This led to the conclusion that the material was probably SiO_2 mixed with carbon.

No other particulates of interest were detected on the glass fiber collector. In this case, detectability would be on the order of <15 ppm, due to the different mass of starting material.

TRANSFORMER MINERAL OIL

The results from the combustion of the mineral oil are presented in Table 5-5. Significant quantities of combustible materials such as methane and ethene, possibly resulting from cracking of the starting material, were found in both traps when the amount of air was limited to 30%, indicating that the combustion was quite decidedly not complete in this case. A surprisingly low amount of carbon dioxide was found with both the 70% and 30% air levels.

Owing to the limited time and funding involved in the project, R & D was not able to complete the experiments with this material.

HIGH TEMPERATURE HYDROCARBON

Table 5-6 shows that the quantities of combustible materials present in the products are relatively less than for the transformer mineral oil. Again however, they are present, with significant quantities of ethylene being present. Once again a large amount of unreacted material, comparable to the quantity found with polydimethylsiloxane, was present in the combustion chamber of the thermogravimetric analyzer.

Table 5-5

TRANSFORMER MINERAL OIL COMBUSTION PRODUCTS

Run 1 Isopropenol-Dry-Ice Trap 70% Air		Run 2 Isopropenol-Dry-Ice Trap 70% Air	
Nitrogen	77.842 %	Nitrogen	75.444 %
Oxygen & Argon	21.444	Oxygen & Argon	22.821
Carbon Dioxide	0.139	Carbon Dioxide	0.142
Hydrogen	0.023	Hydrogen	0.038
Carbon Monoxide	0.311	Carbon Monoxide	0.351
Methane	-----	Methene	-----
Ethane	-----	Ethene	-----
Ethylene	-----	Ethylene	-----
Acetylene	-----	Acetylene	-----
C_3 Hydrocarbons	-----	C_3 Hydrocarbons	-----
Water	0.241	Water	1.204
Sum	100.000 %	Sum	100.000 %

Teble 5-5 (Cont.)

TRANSFORMER MINERAL OIL COMBUSTION PRODUCTS (Cont.)

Run 1 Isobutene-Liq. N_2 70% Air		Run 2 Isobutene-Liq. N_2 70% Air	
Nitrogen	77.917 %	Nitrogen	75.626 %
Oxygen & Argon	21.846	Oxygen & Argon	22.960
Carbon Dioxide	0.066	Carbon Dioxide	1.046
Hydrogen	-----	Hydrogen	-----
Carbon Monoxide	-----	Carbon Monoxide	-----
Methane	-----	Methane	-----
Ethane	-----	Ethane	-----
Ethylene	-----	Ethylene	-----
Acetylene	-----	Acetylene	-----
C_3 Hydrocarbons	-----	C_3 Hydrocarbons	-----
Water	0.171	Water	0.371
Sum	100.000 %	Sum	100.003 %

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Table 5-5 (Cont.)

TRANSFORMER MINERAL OIL COMBUSTION PRODUCTS (Cont.)

Run 3 Isopropanol-Dry-Ice Trap 30% Air		Run 4 Isopropanol-Dry-Ice Trap 30% Air	
Nitrogen	61.676 %	Nitrogen	59.667 %
Oxygen & Argon	12.370	Oxygen & Argon	13.240
Carbon Dioxide	0.793	Carbon Dioxide	0.929
Hydrogen	5.691	Hydrogen	4.989
Carbon Monoxide	4.527	Carbon Monoxide	7.352
Methane	11.856	Methane	10.452
Ethane	0.256	Ethane	0.275
Ethylene	2.444	Ethylene	2.684
Acetylene	0.130	Acetylene	0.096
C_3 Hydrocarbons	0.076	C_3 Hydrocarbons	0.096
Water	0.181	Water	0.172
Sum	100.000 %	Sum	99.999 %

Table 5-5 (Cont.)

TRANSFORMER MINERAL OIL COMBUSTION PRODUCTS (Cont.)

Run 3 Isobutene-Liq. N_2 30% Air		Run 4 Isobutene-Liq. N_2 30% Air	
Nitrogen	44.338 %	Nitrogen	43.433 %
Oxygen & Argon	4.900	Oxygen & Argon	5.420
Carbon Dioxide	3.745	Carbon Dioxide	3.343
Hydrogen	6.060	Hydrogen	8.050
Carbon Monoxide	6.512	Carbon Monoxide	6.456
Methane	25.477	Methane	23.567
Ethane	1.091	Ethane	1.350
Ethylene	6.691	Ethylene	6.869
Acetylene	0.426	Acetylene	0.492
C_3 Hydrocarbons	0.740	C_3 Hydrocarbons	0.980
Water	0.020	Water	0.040
Sum	100.000 %	Sum	100.000 %

Table 5-6

HIGH TEMPERATURE HYDROCARBON COMBUSTION PRODUCTS

Run 1 Isopropanol-Dry-Ice Trap 70% Air		Run 2 Isopropanol-Dry-Ice Trap 70% Air	
Nitrogen	74.136 %	Nitrogen	71.010 %
Oxygen & Argon	14.053	Oxygen & Argon	15.746
Carbon Dioxide	5.023	Carbon Dioxide	6.432
Hydrogen	1.340	Hydrogen	1.178
Carbon Monoxide	3.032	Carbon Monoxide	3.052
Methane	1.118	Methane	1.187
Ethane	0.012	Ethane	0.011
Ethylene	0.171	Ethylene	0.160
Acetylene	0.025	Acetylene	0.023
C_3 Hydrocarbons	0.069	C_3 Hydrocarbons	0.075
Water	1.025	Water	1.126
Sum	100.000 %	Sum	100.000 %

Table 5-6 (Cont.)

HIGH TEMPERATURE HYDROCARBON COMBUSTION PRODUCTS (Cont.)

Run 1 Isobutane-Liq. N_2 70% Air		Run 2 Isobutane-Liq. N_2 70% Air	
Nitrogen	65.135 %	Nitrogen	67.920 %
Oxygen & Argon	7.123	Oxygen & Argon	7.310
Carbon Dioxide	5.559	Carbon Dioxide	5.536
Hydrogen	3.753	Hydrogen	2.961
Carbon Monoxide	4.494	Carbon Monoxide	3.932
Methane	3.916	Methane	2.525
Ethane	1.674	Ethane	1.485
Ethylene	6.010	Ethylene	6.425
Acetylene	0.202	Acetylene	0.242
C_3 Hydrocarbons	0.715	C_3 Hydrocarbons	0.634
Water	1.419	Water	1.028
Sum	100.000 %	Sum	99.998 %

Table 5-6 (Cont.)

HIGH TEMPERATURE HYDROCARBON COMBUSTION PRODUCTS (Cont.)

Run 3 Isopropanol-Dry-Ice Trap 30% Air		Run 4 Isopropanol-Dry-Ice Trap 30% Air	
Nitrogen	74.164 %	Nitrogen	75.105 %
Oxygen & Argon	8.092	Oxygen & Argon	6.886
Carbon Dioxide	3.073	Carbon Dioxide	3.456
Hydrogen	1.660	Hydrogen	2.185
Carbon Monoxide	10.324	Carbon Monoxide	10.077
Methane	2.243	Methane	1.876
Ethane	0.018	Ethane	0.017
Ethylene	0.274	Ethylene	0.163
Acetylene	0.046	Acetylene	0.036
C_3 Hydrocarbons	0.019	C_3 Hydrocarbons	0.075
Water	0.085	Water	0.126
Sum	100.000 %	Sum	100.000 %

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Table 5-6 (Cont.)

HIGH TEMPERATURE HYDROCARBON COMBUSTION PRODUCTS (Cont.)

Run 3 Isobutane-Liq. N_2 30% Air	
Nitrogen	55.156 %
Oxygen & Argon	4.134
Carbon Dioxide	4.533
Hydrogen	4.731
Carbon Monoxide	10.985
Methane	7.926
Ethane	1.696
Ethylene	8.124
Acetylene	0.606
C_3 Hydrocarbons	1.917
Water	0.192
Sum	100.000 %

Run 4 Isobutane-Liq. N_2 30% Air	
Nitrogen	45.050 %
Oxygen & Argon	2.390
Carbon Dioxide	2.556
Hydrogen	5.981
Carbon Monoxide	10.322
Methane	12.515
Ethane	3.859
Ethylene	12.254
Acetylene	0.407
C_3 Hydrocarbons	4.643
Water	0.023
Sum	100.000 %

The high viscosity of the high temperature hydrocarbon was yet another reason for the development of the piston/capsule method for the R & D procedures of combustion. In a run made with this material, only two products were detected in the gaseous product analysis by mass spectroscopy, benzene (Figure 5-14) and toluene (Figure 5-15). Figure 5-16 illustrates the relative proportions of these substances. Nevertheless, in absolute terms only a small proportion of the starting sample, on the order of 1-2%, seems to be represanted by these products. No particulate material was detected with a detectability limit of approximately 10 ppm.

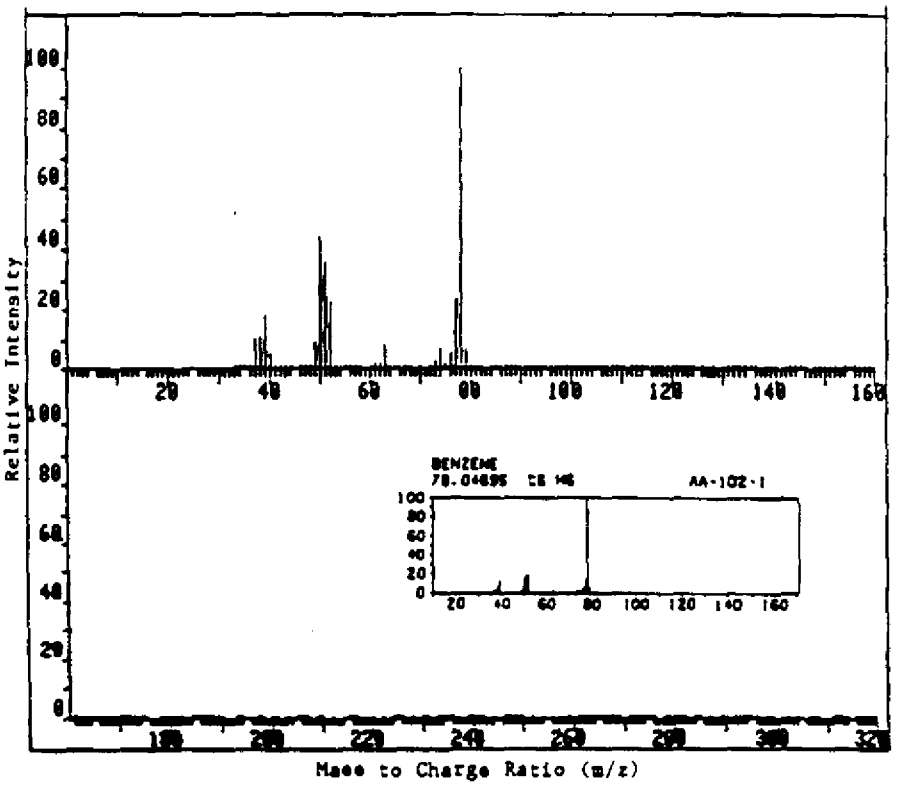

Fig. 5-14. Benzene in Combustion Products of High Temperature Hydrocarbon. Mass spectrum of benzene as recovered from pyrolysis of high temperature hydrocarbon.

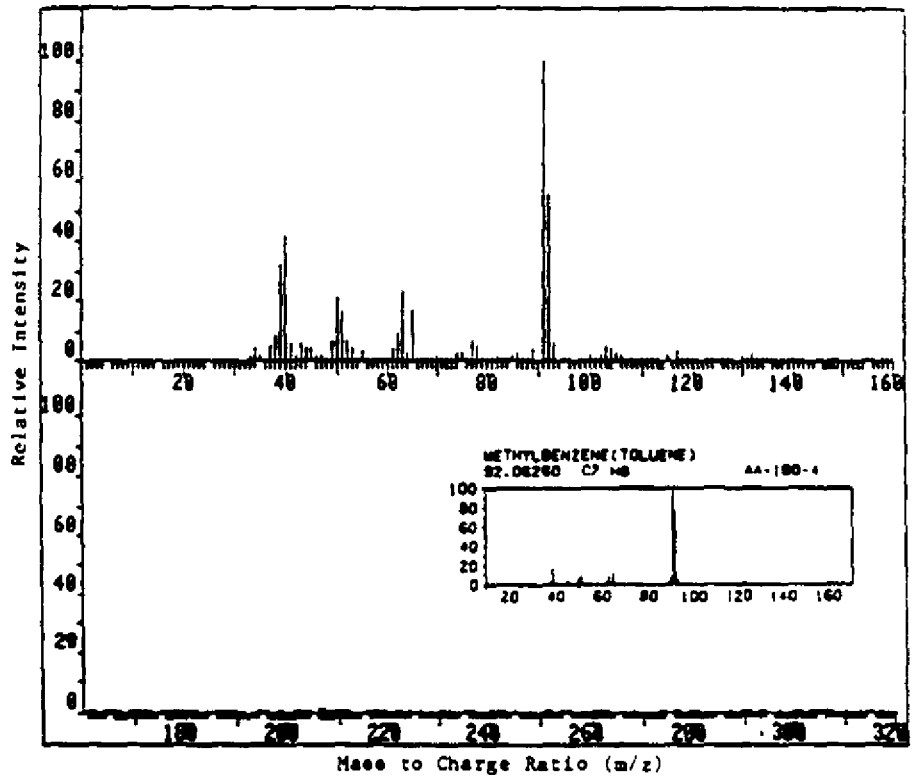

Fig. 5-15. Toluene in Combustion Products of High Temperature Hydrocarbon. Mass spectrum of toluene as recovered from pyrolysis of high temperature hydrocarbon.

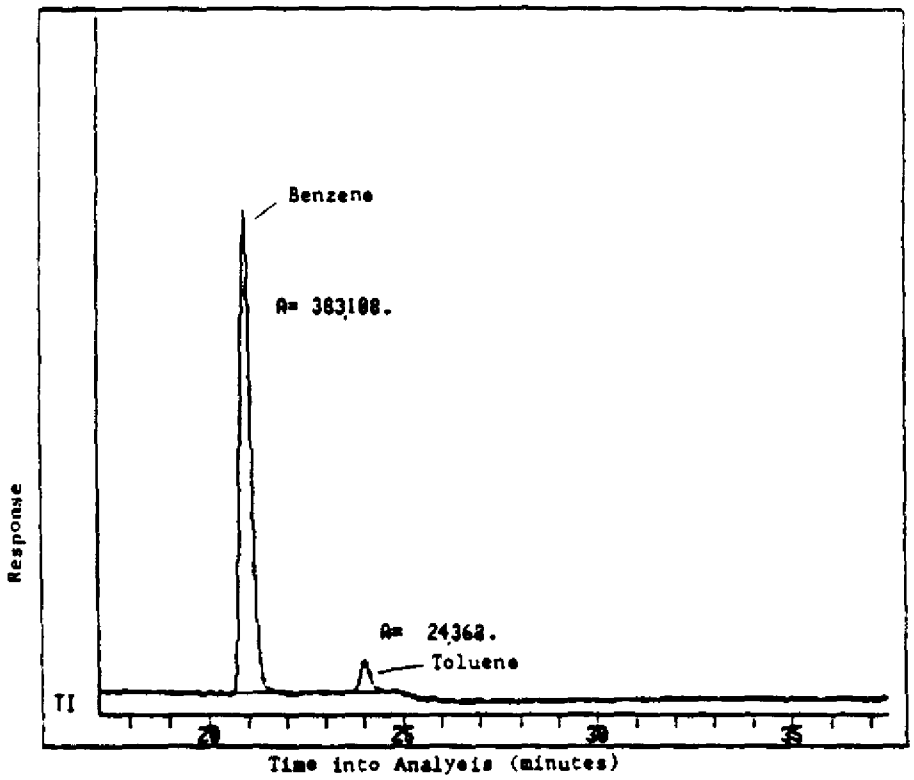

Fig. 5-16. Benzene to Toluene Relative Ratio. Gas chromatographic trace of gaseous products from pyrolysis of high temperature hydrocarbon.

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Section 6

DISCUSSION

In summation, none of the combustions produced detectable chlorinated or polycyclic aromatic hydrocarbon particulates. The production of chlorine (and hydrogen chloride in the presence of atmospheric humidity) from tecrachloroethylene must not be minimized, but rather should be balanced against the nonflammable nature of the material. Much the same statement may be made about trichlorotrifluoroethane and its production of hydrogen fluoride and the various fluorocarbon materials. The absence of phosgene in these experiments should also be noted.

For the other materials, the presence of combustible materials in the product stream indicates that even in events with only partial combustion, a potentially dangerous situation may remain even after the heat source is removed. Combustion could expand upon opening a vault or chamber with the consequent admission of oxygen if the site has not had sufficient time to cool.

The production of gases such as chlorine, hydrogen chloride and hydrogen fluoride from certain of the fluids does form a concern in the event of a fire incident. However, suitable fire protection equipment should be available to provide adequate protection in the short term. No evidence was found that long term contamination such as can be caused in a fire incident with transformers which contain askarels will result from a fire involving the replacement dielectric fluids investigated in this study.

Section 7

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