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Calibration of flame ionization detector for chlorinated hydrocarbons

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ABSTRACT

Title of Thesis: Calibration of Flame Ionization Detector
for Chlorinated Hydrocarbons

Nahid Jabalameli, Master of Engineering Science, 1982

Thesis directed by: Professor Joseph W. Bozzelli

ABSTRACT

Relative Responses and Calibration Factors were developed for several volatile organic (mostly chlorinated) priority pollutant species in order to use one single stable compound (e.g. Benzene) for daily instrument calibration. This would replace the procedure of using a standard mixture of target compounds (25-35). This is of particular advantage because the standard mixture may not have all species stable or may show loss of some components relative to others due to wall adsorption in the standard (compressed gas) stainless steel cylinder.

The use of a single standard species was made possible by developing "accurate" relative response and calibration factors of all target compounds relative to Benzene in this case. The response and calibration factors were obtained by injecting the targeted compounds for both vapor and liquid standards into the GC and then analysing and comparing the results for accuracy and precision.

Results from this analysis showed that this is a viable and even preferential way to standardize the GC for routine quantitative analysis of a number of organic species. Liquid injection is the most acceptable method for determining relative response factors and calibration factors of compounds with boiling temperature above 60 C. Results from gaseous mixture of species shows low accuracy for compounds with boiling temperature above 110 C. These results for high

boiling point vapors were all low and probably due to a combination of wall absorption, reaction with stainless steel tubing and cylinder and incomplete transfer of compounds into the vapor standard cylinder.

When developing calibration factors we obtained a linearity for the RRF's of these compounds with positive slope showing response enhancement for chlorine substituted compounds on FI detector at standard conditions. This is in contrast with previous investigators studies which employed older detector designs. Recent engineering improvement (1970 to present) in FI detector design and geometry with optimized combustion, flow velocities, improved electrodes (for ion collection) may account for the differences.

CALIBRATION OF FLAME IONIZATION DETECTOR FOR CHLORINATED
HYDROCARBONS

by
Nahid Jabalameli

Thesis submitted to the Faculty of the Graduate School of the
New Jersey Institute of Technology in partial fulfillment of
the requirements for the degree of Master of Science in
Engineering Science
1984

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Major: Engineering Science

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I-INTRODUCTION:

Two methods are used to perform the calibration of a Gas Chromatograph(GC) in air analysis for gaseous samples of volatile halocarbon pollutants at the parts per billion level and below. The first method uses a gas mixture standard, where a gravimetric mixture of liquid standards is prepared at room temperature and is injected by way of a syringe, into an evacuated stainless steel cylinder. Additional gaseous components, if required, are added by a gastight syringe, and the cylinder then pressurized with an inert gas. This vapor mixture (future vapor standard) can be standardized against a primary standard mixture containing a single reference vapor, when used for quantitative measurements. The relative concentrations of each species in the vapor mixture (in the cylinder) may be calculated by their known mole fractions through comparison of a single compound's peak area to that of a reference compound (both species the same). This leads to generation of relative response factors for each species in the standard with respect to the stable reference compound standard. The possible disadvantages of this method are 1- Adsorption on the cylinder walls which can be prevented to some extent by heating the tank. 2-Incomplete transfer of materials into cylinder. 3- Reaction and subsequent loss of the species on the walls of the cylinder.

The second method is injection of a liquid standard into

the GC and generation of relative response factors from these. Here, the compounds are dissolved in a high boiling solvent e.g. hexadecane, in order to allow the peaks of interest to elute before the solvent peak. The high boiling solvent is used in place of a low boiling one to reduce errors from overlap and co-elution for light species in the liquid analysis and solvent impurities. An internal standard is used to eliminate imprecise injection volumes and differing standards dilution by providing a known amount of a reference that can be used to compensate for changing chromatographic conditions.

A dynamic system, utilizing permeation tubes combined with gas blending may also be used to generate individual or mixes of a few standards of organic vapors. In these systems, each target compound is placed in a permeation tube and a standard gas mixture blended from the effluent of each tube purge gas stream. The major drawback to this system is that data on the permeation rates of each species must be obtained. This requires weighing the tubes at short intervals on a microbalance in addition to a rather complex apparatus for gas mixing, flow monitoring, and constant temperature maintenance and recording.

The goal in the development of the two calibration procedures investigated in this project is to use the response of a standard compound (e.g. Benzene), which is very stable,

and compare this response to peak areas of species eluting at known retention times where their response relative to this benzene standard is accurately known. This is in place of needing to inject a standard for each species as is often presently done. We also wish to provide a technique that is straightforward and readily adoptable by most laboratories. Therefore we have developed this methodology along with accurate relative response factors for halocarbons on the Flame Ionization Detector (FID). A mathematical formula to describe responses e.g. formula relating response to #C's and Cl's is also attempted.

The reasons for developing GC Calibration methods for halogenated organic species are:

- 1- These are common pollutants and the demand for their analysis is currently dramatically increasing in varied environmental media such as water, air, soil, and stack effluent.
- 2- Many are on list of U.S.EPA priority pollutants.
- 3- The present method for quantitative analysis requires GC/MS which is more complex and often very expensive compared to the cost of more straightforward and instrumentally reliable GC analysis.
- 4- Other calibration techniques are employed for these compounds which are often complex and not readily available to a typical analytical laboratory. These in addition, often require purchase of expensive equipment or processes such as

the use of permeation tubes or/and permeation systems and/or gas mixes . Analysis of halogenated species may still not give reliable or accurate vapor concentration data to the analyst when put into use.

5- Possible acceptance of a determination method using dual detection GC-Electron Capture Detector (ECD) and FID. Dual detection on two very differently responding detectors does allow positive qualitative identification because of the significant variation in responses. Thus accurate FID response factors would allow highly quantitative determinations for many compounds, with qualitative identification made possible using easily found reference retention times from the selective parallel ECD analysis.

6- Response factors published previously for chlorinated hydrocarbons show discrepancies and it is hoped this study will help to clarify responses and effects of halocompounds on the FID.

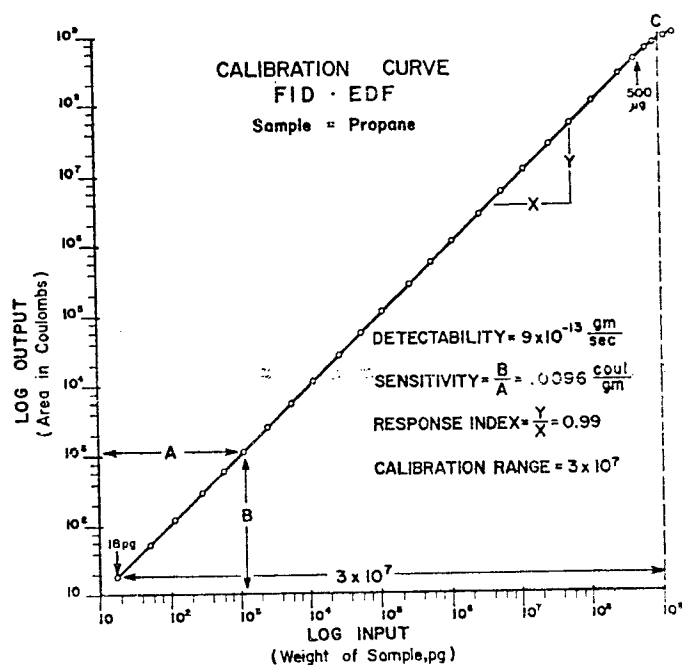
Previous studies:

Studies of response factors are reported by a number of authors. Sternberg et al. (1) in 1961 measured the response of number of compounds using a gaseous solution continuous flow procedure. Linearity was checked for oxygenated hydrocarbons like acetone and alcohols and also several aromatics like benzene and toluene in addition to methyl iodide and carbon tetrachloride. These results show a

LINEARITY TEST FOR HYDROGEN FLAME DETECTOR RESPONSE AS A FUNCTION
OF SAMPLE INTRODUCTION RATE

Sample introduction rate (gm atoms C/sec $\times 10^7$)	Sample signal (coulomb/sec $\times 10^3$)	Response (coulomb/gm atom C)
0.075	0.0181	0.242
0.752	0.184	0.244
1.96	0.475	0.243
7.28	1.798	0.247
680.5	168.6	0.248

TABLE-A (From ref.1)



Calibration Curve with Response Factors

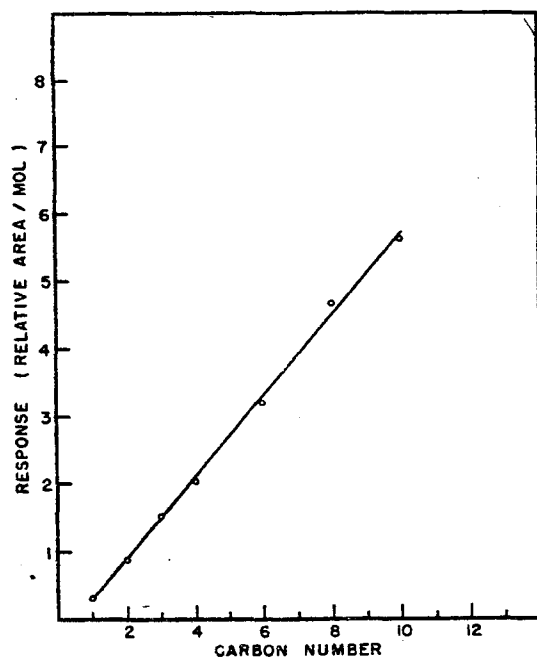
FIGURE-A (From ref.1)

6

linearity of FID response based on measurements at the indicated high and low sample introduction rates. The linear range of the hydrogen flame ionization detector was found to be in excess of 10^7 -fold, extending from beyond the highest sample introduction rate employed here to the detectable limit, taken as a signal equal to twice the noise level (2×10^{-14} amps). These results were shown in table-A and Figure-A.

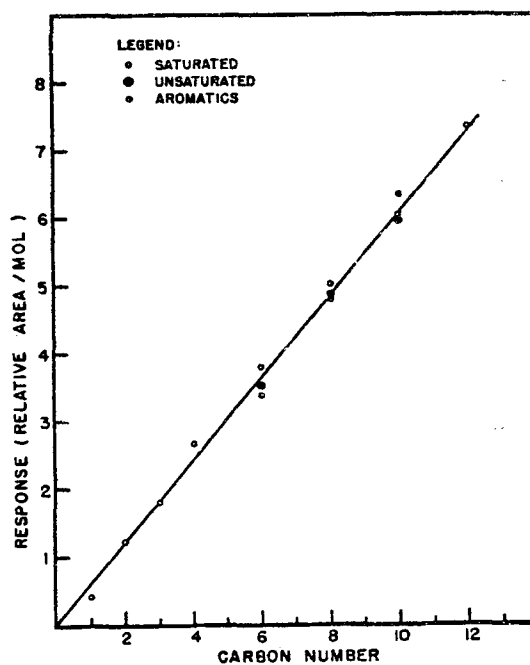
Perkins et al. (2) also found excellent linearity in 1962 with the FID for a variety of organic compound groups, including alkanes, alkenes, aromatics, alcohols, aldehydes, acids, esters, glycols and amines, when relative response per mole is plotted against carbon number. A graphical presentation of these data shown in Figure-B and Figure-C. It can be noted that the response (per carbon number), within experimental error, is linear, and that a single curve represents the data for alkanes, alkenes, and aromatics. Another conclusion was that the response of FID varies with class (type) of organic compounds; e.g., the response of the alcohols is equal to the response of the corresponding hydrocarbons of one-half less carbon. At the time this suggested that the FID should be generally applicable to quantitative analysis, if appropriate calibration factors are used.

Ackman (4,11) studied the FID response of oxygenated aliphatic hydrocarbons. His results in 1964 were not entirely



Relative response per mole of alcohols in the flame ionization detector. (Line represents predicted curve.)

FIGURE-B (From ref.2)



Relative response per mole of saturated, unsaturated, and aromatic hydrocarbons in the flame ionization detector.

FIGURE -C (from ref.2)

in agreement with those predicted by the conclusions of Perkins et al(2). The examination of the relative molar responses for a large number of oxygenated aliphatic hydrocarbons, he suggested that these responses can in many cases be correlated through the weight per cent carbon content of fundamental "groups". He also suggested that the formation of particular groups from classes of chemical compounds probably is due to the initial thermal breakdown or cracking of the molecule in the flame, influenced by the strength of the appropriate bonds and governed by neighbouring constituents.

W. A. Dietz (5), in 1967 found that for hydrocarbons, with two exceptions, the normalized values of FID response per carbon are all approximately 1.0. The two exceptions are benzene 1.12, and toluene 1.07. The relative values for other compounds such as oxygenated species can, however, vary appreciably. Alcohols, for example, vary from 0.23 to 0.85 per carbon; acids on the other hand from 0.01 to 0.65, etc.

The relative response of the FID has been the subject of considerable discussion. The response per unit weight of the individual compounds, for hydrocarbons (above C5) differ only slightly from each other and the relative molar responses seem directly proportional to the carbon number of the molecule. It was demonstrated by Etrre (1962) however that this rule is valid only in the first approximation; actually, some isomers with the same carbon number have different relative molar

responses, but the relative molar responses of a homologous series (e.g. normal paraffins, substituted cyclopentanes or substituted benzenes) do follow a linear relationship with the carbon number. It was also known that the relative molar responses of organic substances containing other elements besides carbon and hydrogen in the molecule differ from that of the corresponding normal paraffin with the same carbon number.

Relatively few studies have reported response data for such substituted organic compounds and even where such data are given, few conclusions have been offered regarding their relationships within the homologous series. The few previous data sets we have found for halogenated hydrocarbons show in addition, significant differences in responses. For example, the previously described Ackman results did not agree with the Perkins results with respect to the response of alcohols were Perkins found it to be equivalent the hydrocarbon with one-half carbon atom less but Ackman found it to be less than one-quarter carbon less.

Sternberg et al. (1,17) reported the responses of Carbon tetraChloride to be about one-half of the response of Methane. Perkins et al. (2) reported the value of methylene chloride, chloroform and carbon tetrachloride to be only $2/3$ of the response of methane. Etrre (3) reported the value of response of methylene chloride to be about 3% less than of methane, chloroform's response about 32% less than that of methane and carbon tetrachloride's response at 87% less than of methane.

Etrre also reported that perchloroethylene's response was 25% higher than of Ethane and trichloroethylene's response was about 18% higher than of Ethane. This was in agreement with our results. Ackman(4,11) reported the response of carbon tetrachloride to be 12% higher than of methane. Note that this is in contrast with the reduced response of Sternberg, Perkins and Etrre, but in agreement with our data for this compound (see results and discussion section). These investigators based their results on a value of 7.0 for the primary reference material, N-Heptane, and we take Methane and Ethane response to be 1/7 and 2/7 of the C7 value respectively.

Dietz(5) reported that the normalized value of ethylbenzene (Response ethylbenzene \times 6/8) was about 9% lower than of normalized value of benzene, in contrast to the results of Sternberg and Perkins and the concept of FID linearity response with number of carbons.

Karagozler(7,9) reported with an optimized flow (475 ml/min. air and 32 ml/min. hydrogen), for conventional FID, a response to chlorobenzene about 45% lower than of benzene and a response of 1,3-dichlorobenzene to be about 50% lower than of benzene and 37% lower than the response of chlorobenzene. Maggs(13) in a second study again with optimized FID gas flows (500 ml/min. Air and 30 ml/min. hydrogen) reported the response of chlorobenzene to be about 49% lower than of

benzene and the response of 1,3-dichlorobenzene to be about 52% lower than the response of benzene and 39% lower than of chlorobenzene. The finding that chlorine on an aromatic ring decreases the FID response is in agreement with our results (as will be discussed later), but by 33% magnitude.

Gough et al.(8) reported the response of chlorobenzene to be 3% lower than of benzene and ortho-dichlorobenzene's response was 16% lower than of benzene. This is about 13% lower than the response of chlorobenzene which is in agreement with our data and also in agreement with previous studies of Karagozler and Maggs. More variation can be clearly seen in the studies of Karagozler and Maggs than in Gough and this study.

Hainova et.al.(19) reported the response of CCl_4 to be about 10% lower than of methane (where methane response was assumed to 1/6 of benzene's response).

Guillemin et al.(15) have tried to calibrate FID for some chlorinated hydrocarbons, relative to Trichloroethylene. A comparison of his results with ours will be discussed in result and discussion section. Table-35 shows the list of all these discrepancies. The purpose of this study is to clarify and amplify these results.

TABLE-35

Compound Evaluated	(1)*	(2)*	(3)*	(4)*, (11)*	(5)
MeCl ₂		.66	87		
CHCl ₃		.66	68		
CCl ₄	.120	.66	48	100	
Perc			225		
TRIC			213		
CL-Ø					
Et-Ø					1.03
PDB					
ODB					
Benz	1.44			600	1.12
Hex.			596	598	1.03
Methane	.245	1	90	89	.97

*Results based on a value of 7.00 for the primary reference material, n-Heptane

TABLE-35 "Continued"

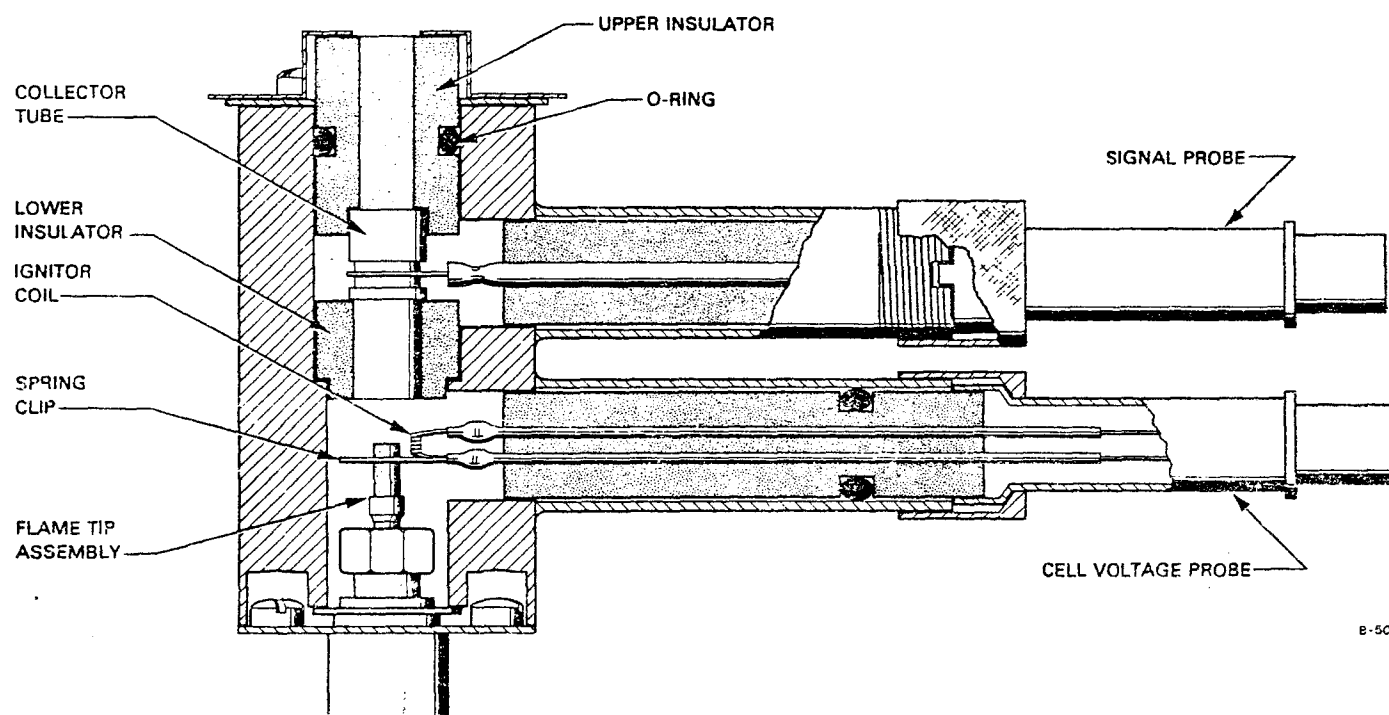
Compounds	(7) C/g	(13) C/g	(8) C/mole	(19)	THIS STUDY
MeCl ₂					18.3
CHCl ₃					22.0
CCl ₄				.10	23.6
PERC					39.9
TRIC					39.5
Cl-Ø	.69	.67	.96		135.1
Et-Ø					157.5
PDB	.50	.48			131.3
ODB	.50	.48	.85		132.1
Benz	1.0	1.0	.99	.66	100.0
Hex.			1.00		97.5
Methane			.18		

The FID Detector is highly sensitive to organic compounds and permits analysis of components in the nanogram (10^{-9}) range (22). This detector is insensitive to most inorganic compounds and relatively insensitive to temperature changes. As shown in Figure-III (FID Cross- Sectional View), the detector consists of a flame tip assembly attached to the detector base. Located above the flame tip is the collector (signal) tube. Attached to the flame tip assembly is the polarizer clip with ignitor coil. The flame is ignited by applying a current to the platinum ignitor coil. Heating it causes emission of electrons. Ionization voltage is applied via the cathode probe.

Three gas flows are required for operation of the detector: carrier gas, plus hydrogen, and air for the flame. The column effluent mixes with hydrogen and is burned in an oxidizer rich atmosphere of air. When organic matter is burned in the hydrogen flame, positive and negative ions are generated. Positive ions are collected on the collector producing an electrical current in proportion to the amount of material burned. This current is amplified by an electrometer which produces an output signal capable of driving a strip-chart recorder, integrator, or computer.

Detector Selectivity

The detector responds to most compounds with the exception of those listed in table-II. The lack of response



B-503

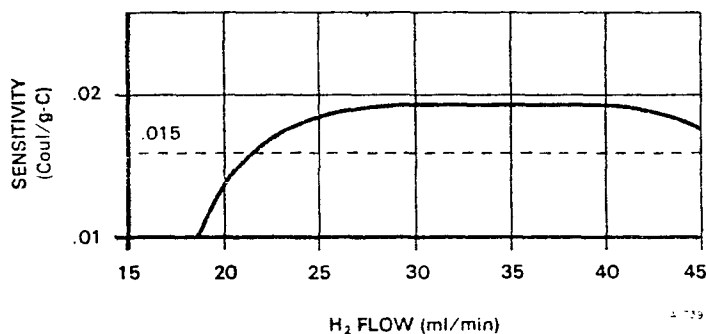
FID CROSS-SECTIONAL VIEWFIGURE-III (From ref.22)

**COMPOUNDS GIVING MINIMAL OR NO
RESPONSE WITH THE FID**

He	CS ₂	NH ₃
Ar	COS	CO
Kr	H ₂ S	CO ₂
Ne	SO ₂	H ₂ O
Xe	NO	SiCl ₄
O ₂	N ₂ O	SiHCL ₃
N ₂	NO ₂	SiF ₄
HCHO	HCOOH	

TABLE-II (From ref.22)

demonstrates the relationship between detector sensitivity and hydrogen flow rate. Using a 30 ml/min flow of carrier gas and 300 ml/min flow of air, the detector's response for propane reaches a maximum at 30 ml/min of hydrogen.



**FID SENSITIVITY VERSUS
HYDROGEN FLOW RATE**

FIGURE-IV (From ref.22)

to H₂O makes the detector especially suitable for analysis of aqueous samples of biological materials while the lack of response to air makes the detector suitable for analysis of air pollutants.

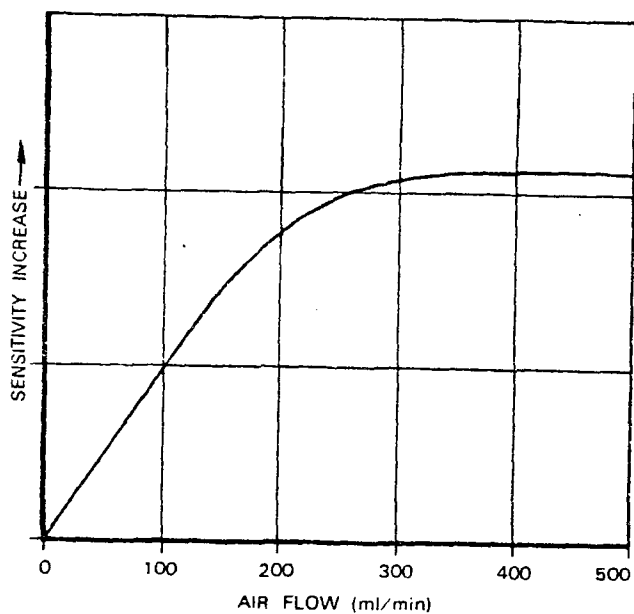
Detector Response vs. Flow Rate

Detector performance depends on the proper choice of gas flow rates (i.e. carrier gas, hydrogen, and air). In general, good sensitivity and stability can be obtained with a mixture ratio of 30 ml/min. carrier gas, 30 ml/min. hydrogen and 300 ml/min. air.

Figure- IV demonstrates the relationship between detector sensitivity and hydrogen flow rate using a 30 ml/min. flow of carrier gas and 300 ml/min. of air, the detector response for propane reaches a maximum at 30 ml/min. hydrogen. As shown in Figure- V, air flow rates also affect detector sensitivity. Generally, a flow rate of 300 ml/min. is satisfactory for sample concentrations up to several hundred micrograms.

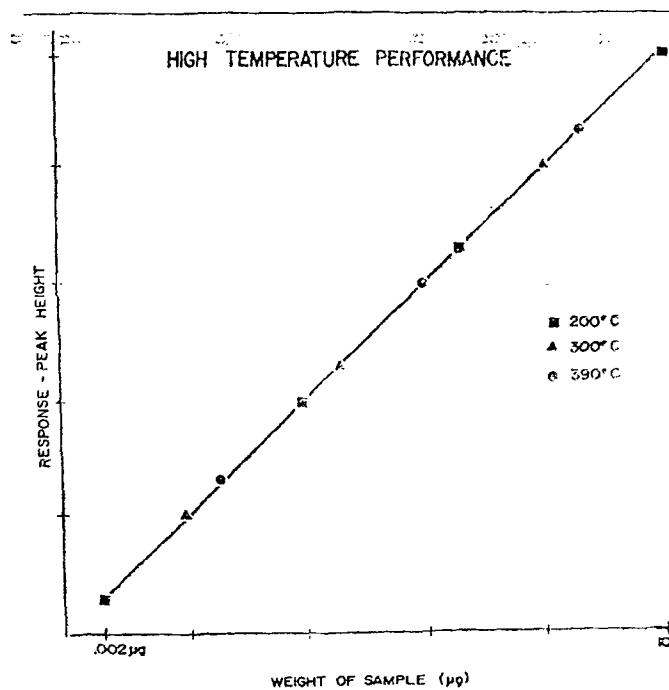
The flame ionization efficiency is generally a complex function of the flow rates of carrier gas, combustible gas, and the auxiliary air stream.

Subsequently, the sensitivity of this detector has been increased by designing efficient electron and collector



FID SENSITIVITY VERSUS AIR FLOW

FIGURE-V (From ref.22)



Effect of Detector Temperature on Response

FIGURE-VI (From ref.20)

electrodes, using high purity gases, stability and optimizing the gas flow rates, and by using low-noise electrometers (14) and very low bleed column packings.

Factors influencing the quantitative performance of the hydrogen flame detector have been studied. The role of each of the following variables must be considered in quantitative application of this instrument for analytical or theoretical purposes (17).

1) The ion collection system - It is essential that the electrode geometry and applied voltage gradient be such as to insure operation on the plateau portion of the current voltage curve; with either incomplete collection or ion multiplication, response becomes subject to space charge effects which produce nonlinearity.

2) The external atmosphere - The atmosphere flow rate must be such that the maximum diffusion-limited rate of transport of oxygen to the reaction zone occurs, and the flow pattern must not lead to turbulence even at higher air flows. The rate of oxygen transport and amount of diluent introduced into the reaction zone are then determined by the oxygen concentration and the diffusion properties of the atmosphere.

3) The fuel mixture - For a given carrier gas flow there is a hydrogen flow which results in maximum average molecular

energy in the reaction zone and in optimum response.

Diffusion, thermal conductivity, and heat capacity of the carrier gas influence the hydrogen requirement and the response level.

4) internal oxygen - Addition of oxygen to the fuel or sample increases the extent of cracking reactions occurring, but leads to pre-oxidation of sample molecules. The magnitude and direction of the effect depend upon the nature of both carrier gas and sample. Less uniform response per gram atom of carbon is obtained in premixed flames than in pure diffusion flames.

5) The jet diameter - The jet diameter determines the linear velocity of the jet gases and the mean diffusion distance for sample molecules to reach the reaction zone. Higher linear velocities place greater demands upon the ion collection system, and lower diffusion distances lead to enhanced responses. Flame-out occurs when the linear velocity exceeds the burning velocity; since high levels of hydrocarbon samples, and somewhat lower levels of halogenated compounds suppress the burning velocity of the hydrogen flame, the jet diameter must be so chosen that flame-out does not occur for standard sample sizes.

6) Jet temperature response - Response increases with jet temperature, which is influenced by fuel and atmosphere composition and flow rates, thermal mass and conductivity of

the jet, position of electrical contact on the jet, and thermostat temperature for the burner chamber.

7) The sample concentration - In a flame provided with an adequate supply of air, the ion formation processes are linear for sample induction rates ranging from zero to as great as three percent of the hydrogen flow. Proper design and operation of the ion collection system allows this entire linear range to be usable.

Figure-VII shows results from a study of the flame jet on FID performance(20). As shown in this figure a) the smaller jet diameter(.031 to .019 inches) gives better responses and the response drops sharply by increasing the internal diameter by 45 per cent to 0.031-in. The best response is when the jet diameter is 0.019 inch. This better response of the 0.019-in. is shown again in the calibration curves in Figure-VII b), where, the greater the slope, the better response. Another important result, however, is that the upper limit of linearity was found to be 200 microgram for 0.019-in. tip whereas the 0.031-in. tip gave linear results up to 540 micrograms.

The influence of the geometry of the Ion Collector on FID performance is shown in Figure-VIII using the 0.019 in. tip cylindrical collectors of various diameters and heights were

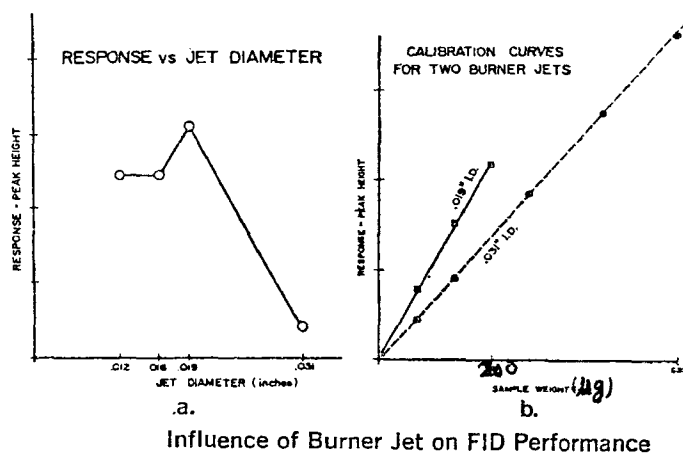


FIGURE-VII (From ref.20)

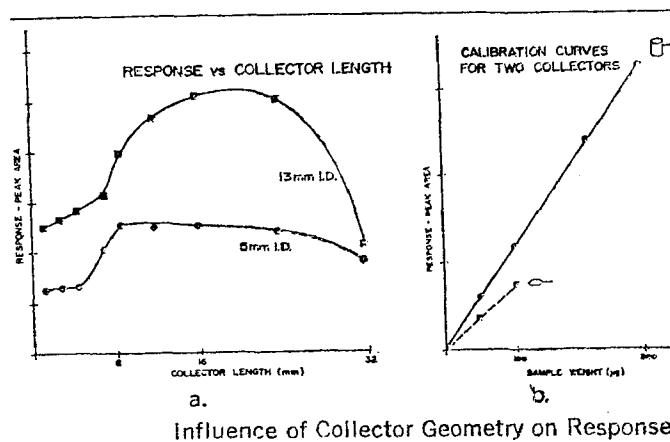


FIGURE-VIII (From ref.20)

compared. The smallest diameter electrode (5 mm) gave a 24 per cent greater response than the larger diameter electrode (13 mm) as shown in figure-a. Also illustrated here is the influence of cylinder height on response. For practical considerations, a 16 mm electrode was chosen, but there is little difference in response from 16 to 24 mm. The calibration curve in figure-b shows that not only is the longer electrode (16 mm) more sensitive but it is also linear to a larger sample weight. The detector was also operated at three elevated temperatures: 200, 300 and 390 C, with the resulting composite calibration curve as shown in Figure-VI. The points all fall on the same straight line illustrating the independence of response on temperature.

It was found from the results in this study that efficient ionization happens within the flame for chlorinated hydrocarbons contradicting literature published (prior to 1970) which reporting lower response due to chlorine. This may be due to changes (improvements) in combustion geometry and design of this FID detector. The relative increase in sensitivity of this detector is also due to: improved electron and ion collector electrodes, use of high purity gases, stabilizing and optimizing the gas-flow rates and by using stable low-noise electronics (14).

This data strongly indicates that vapor standards are unacceptable for most compounds with boiling point above 110°C.

II-EXPERIMENTAL:

Liquid Standards-

Standard mixtures of the compounds in table-I were made gravimetrically at room temperature. Each mix had 10 to 13 of the compounds in table-I. The specific group of compounds in each standard was selected on the basis of their known retention times so they would be clearly separated in the capillary column chromatogram. The compounds were chromatographed individually to determine their retention times and purity. These compounds were halogenated hydrocarbons which were included in the list of recent EPA Priority Pollutants for water. These liquids were purchased from J.T.Baker (ACS certified research grade) and Supelco (certified research grade). They were chosen and added to the sample vial such that no interferences between peak resulted (i.e. well separated on the chromatogram). This made the qualitative identification easier. These standards were made by adding gravimetrically the ones with higher boiling temperature first into a small bottle which was sealed with a teflon septum. They were added to the bottle using a 200 microliter syringe to minimize loss by evaporation respectively progressing toward lower Boiling Point. The volume of this bottle was 10 milliliter. Each compound was

Halo-Carbons of Interests

Table-I

Abbreviated Name

1-Methyl Chloride	MeCl	CH_3Cl
2-Dichloro Difluoro Methane	Freon-12	CCl_2F_2
3-Methylene Chloride	MeCl_2	CH_2Cl_2
4-1,1 Dichloroethylene	1,1-DCet	$\text{CH}_2=\text{CCl}_2$
5-Chloroform	CHCl_3	
6-1,2 Dichloroethane	1,2-DCE	$\text{CH}_2\text{ClCH}_2\text{Cl}$
7-1,1,1 Trichloroethane	1,1,1-Et	CCl_3CH_3
8-Benzene	Benz	C_6H_6
9-Carbon Tetrachloride	CCl_4	
10-1,2 Dichloro Propane	1,2-Prop	$\text{CH}_2\text{ClCHClCH}_3$
11-Trichloroethylene	TRIC	CHClCCl_2
12-1,1,2 Trichloroethane	1,1,2-Et	$\text{CCl}_2\text{HCClH}_2$
13-3,4 Dichlorobutene	3,4-But	$\text{CH}_3\text{CH}=\text{CClCH}_2\text{Cl}$
14-Tetrachloroethylene	Perc	CCl_2CCl_2
15-ChloroBenzene	Cl- ϕ	ClC_6H_5
16-EthylBenzene	Et- ϕ	$\text{C}_2\text{H}_5\text{C}_6\text{H}_5$
17-Bromoform	CHBr_3	
18-1,1,2,2-TetraChloroethane	TCE	$\text{CHCl}_2\text{CHCl}_2$
19-Bis(2-chloroethyl)ether	Bis-Ether	$\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$
20-ParaDichloroBenzene	PDB	ClC_6H_4
21-OrthoDichloroBenzene	ODB	ClC_6H_4
22-2-Chloroethylvinylether	Cl-Ether	$\text{ClCH}_2\text{CH}_2\text{OCHCH}_3$

weighed to 0.1 milligram accuracy with a Mettler 1000 balance when weighing standards-1 thru 4, and Mettler model-51 when weighing standards -5 thru 14. A 10% solution of each standard was then made by diluting it with hexadecane, a high boiling point solvent which eluted at the end of chromatogram. A 0.05 microliter aliquot of the standard solution was injected into the GC. This was repeated until at least 6 consistent sets of output data were obtained for each standard. Consistency was determined by qualitative analysis of the chromatogram and mathematical comparison with benzene ratios. The precision was about $\pm 3\%$ or better.

Vapor Standard-

In preparing the vapor standards, 200 microliter of each of the standard mixtures was injected by way of a syringe into an stainless steel cylinder which had previously been conditioned and evacuated under elevated temperature for about 12 hours. Additional gaseous materials, when required, were added by way of a gas-tight syringe. A 10 milliliter aliquot of the selected gas was injected into the cylinder. The two gaseous compounds present in the mixture were methyl chloride and Freon 12 and these were analysed first. The cylinder was then pressurized with an inert gas (helium) to 300-500 PSI. These standards were added into the GC through the sampling valve, a heated pressure regulator, and stainless steel line. The cylinder temperature was kept constant during the injection at 40 C by a Variac controlled heater. All the

lines from the cylinder through the sampling valve were heated and kept at 40 C. The vapor standards were then injected into the GC by way of a heated sampling valve (200 C) and loop (2 ml). First the area of benzene in the prepared standard was compared with the area of known concentration of standard benzene. This comparison was done to determine the quantity of benzene in the cylinder from the benzene in the absolute standard. It showed that the concentration of benzene in the prepared standard was about half that in the absolute standard and also that the standard vapor preparation technique was working well. About 5 PSI of the standard mix was repeatedly injected into the GC, until 6-8 reproducible results was obtained. This was decided by comparison between the ratios of compound areas to benzene area in the prepared standard in order to determine precision in injection. This ratio was found by dividing areas of the peak reported by the integrator (SP 4000) by the area under the peak for benzene in that particular standard. The precision was determined to be $\pm 5\%$.

A schematic diagram of the entire system is showed in figure-I. A schematic diagram of the injection process is shown in figure-II.

Gas Chromatograph Configuration-

The GC used was a Varian 3700 equipped with Flame Ionization Detector and Electron Capture Detector. The column

EXPERIMENTAL SET-UP

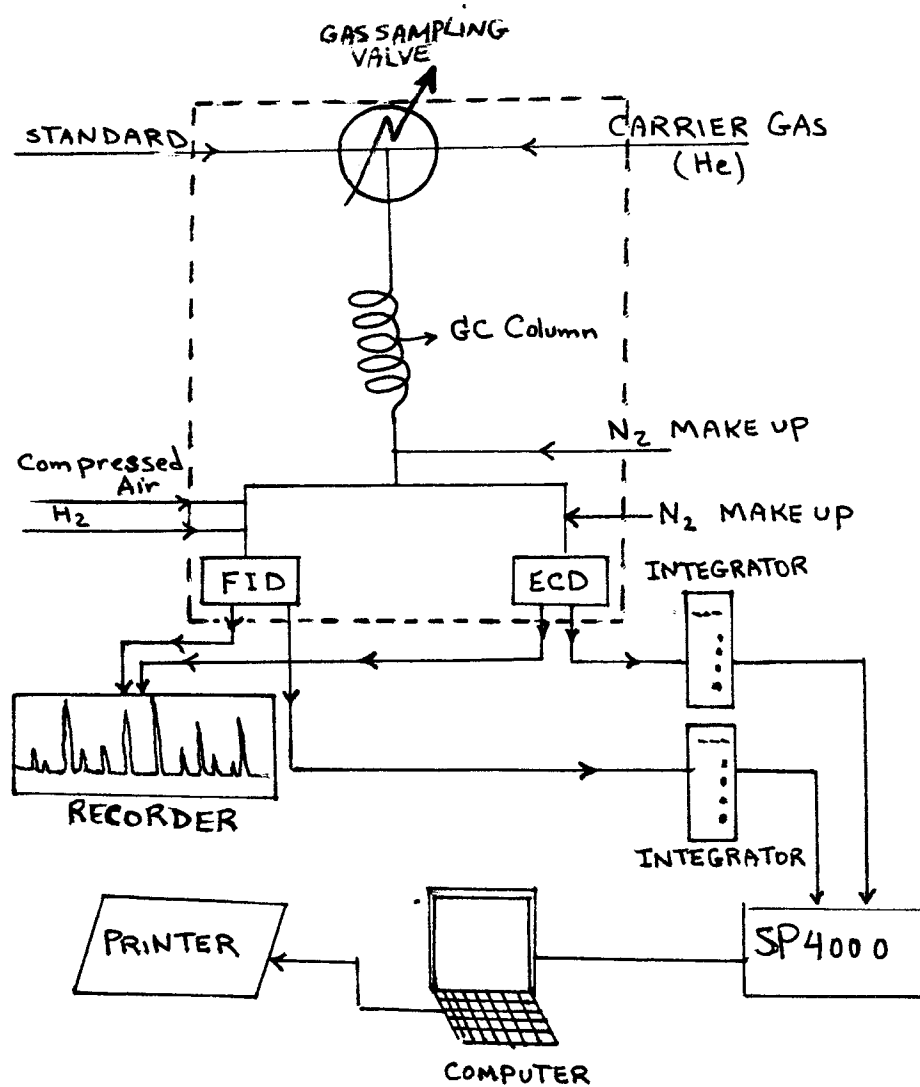
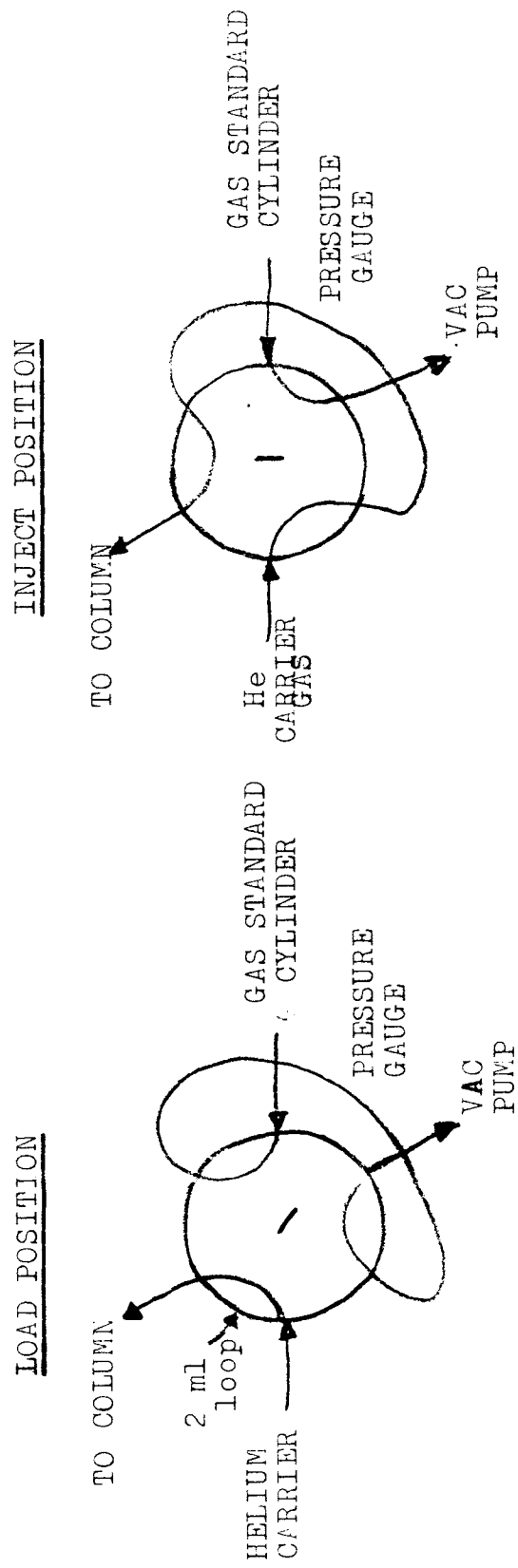


FIGURE-I

FIGURE - II



SAMPLING VALVE DIAGRAM

was a 60 meter SP 2100 Scientific Glass Engineering wall coated glass capillary. The column is rated at 150,000 effective plates. The helium carrier gas was kept at constant pressure (30 PSIG) on head of the column with a pressure controller. The purity of the carrier gas was zero grade MG-Scientific. This flow rate through the column was 5 ml/min as measured with a bubble flow meter, and each detector is supplied with make-up gas at the end of the column. The FID flow was 30 ml/min. nitrogen (make-up), 30 ml/min. hydrogen and 300ml/min. compressed air. The ratio of air to hydrogen flow was 10. ECD total flow was 30 ml/min. from nitrogen (make-up). The gas and liquid injector temperatures were kept at 200 C and the detector temperature was at 300 C for both liquid and vapor analyses. The temperature program was as follows during both analyses:

Isothermal at 40 C for 5min.

Program at 5 C/min. to 200 C

Isothermal at 200 C for 5min.

The chromatographic data would then be analysed with an Spectra Physics 4000 integrator system. The parameters to optimize the peak detection were 1- peak width (PW) = 3, which is related to peak detection sensitivity. Integration is optimized when PW value is width of peak at half height in seconds. 2- peak threshold (PT) = 35, the slope value above which peaks are detected, which is the value of the slope calculation at which SP-4000 identifies a peak. Because the value of a slope is determined by the frequency at which slope

calculations are made, and the frequency is determined by PW parameters, the threshold at which a peak is detected is determined by a combination PT and PW values.

Standard Analysis-

Calculation of Relative Response Factor)-

Knowing the weight of each compound in each of the standards and their respective molecular weight, allows calculation of the number of moles of each compound in the standard. The area of each peak from the GC-FID analysis of the standard divided by the number of moles of that species will yield the response of each compound (area/mole). The area under the peak was determined from the SP-4000 integrator output. Determination of a compound's relative molar response factor to Benzene is as follows:

$$\text{RRF (Relative Response Factor)} = \frac{(\text{area/mole})_{\text{cmpd}}}{(\text{area/mole})_{\text{benz.}}}$$

This is the relative response factor for both vapor and liquid standards.

$$\text{RRC\# (Relative Response by Carbon\#)} = \frac{\text{\#Carbons in Cmpd} \times 100}{6}$$

Assuming benzene response is 100 (e.g. RRC# Propane = 50).

This is the value used later in discussion for comparison of

RRF of our compounds.

Calibration Factor (CF) = $1/RRF$

A calibration procedure is performed twice each day within or during the analysis period: once at the beginning of the sample analysis period time, and once at the end of the period. It consists of measuring the area of the stable compound (e.g. benzene) which is in the "Absolute Standard" by injection of a known constant volume (volume of loop) and pressure into the GC. This Absolute Calibration Response is plotted to insure continued proper operation of FID.

Benzene Calibration Factor =

$(\text{Concentration Benz. in Absolute standard Benz. Cylinder} / \text{Area Benz. in Absolute std. Benz.}) \times (\text{Area Benz. from mix Std. Injection}) \times \text{Dilution Factor}$

$\text{Dilution Factor} = \text{\#moles in sampling Cylinder} / \text{\#moles in sampling loop}$

Define concentration of all the species in the sample by:

$\text{Conc. (I) Sample (PPB by volume)} =$

$(\text{Area (I) Sample} / \text{Calib. Factor (I)}) \times (\text{Benz. Daily Calib. Factor})$

In quantitative air analysis of organic substances the goal

was to develop two calibration procedures (vapor and liquid standard injection methods) to determine RRF's to Benzene and thus to use the response from this one standard compound, absolute standard (e.g. benzene) from its daily calibration analysis. That is only one primary standard (Absolute Standard), would need to be run for quantitation of the significant number of species in the air-sample. Compare this response to peak areas of species eluting at known retention times (identification also verified by Mass Spectrometer) and those compounds response relative to benzene (RRF'S). This is in place of needing to inject a standard for each species, daily.

III- RESULT AND DISCUSSION:

Tables-1 thru 8 show the results obtained from the vapor standards #1 thru 4. Seven to eight reproducible runs were obtained for each of these standards to insure reproducibility and good statistical averages. Standard-1 was made of 20 compounds with 12, 12 and 13 compounds in standards 2, 4 and 3 respectively. A listing of compounds in each respective standard is given in tables-1,3,5 and 7. Table-9A (derived from earlier tables) shows the overall results which were used in vapor discussion. Table-9B shows the average of these relative responses and the error-limits. Also listed in these tables are the weight of each compound in each liquid concentrate, the molecular weight, boiling point, the ratio of peak area of the compound to Benzene, Relative Response Factor (RRF), Normalized value of RRF = $RRF \times 6/\#C$, Relative Response by Carbon Number (RRC#) and number of carbons in each compound.

Tables-10 thru 29 show the results from liquid standards #5 thru 14. Standards 5-9 were made of 9 compounds each with 8, 10, 3, 2, 2, 5, 4 and 5 compounds in standards 6, 7, 8, 10, 11, 12, 13 and 14 respectively. A listing of compounds in each of these standards is given in each of the tables- 10, 12, 14, 16, 18, 20, 22, 24, 26 and 28. Table-30 shows the summary of the results of normalized relative responses in the liquid standards(Normalized with their number of their carbons in the compounds) and Table-31A shows the average values of

TABLE-1 "Standard-1" Vapor Data

Names of Compounds	Weight (gr)	M.W. (gr/mole)	$\frac{\text{Area Compd}}{\text{Area Benz}}$	B.P. (Deg C)
1,1-DCEt	0.2984	122.9	0.301	37
MeCl ₂	0.3214	84.9	0.507	40
CHCl ₃	0.3690	119.5	0.793	62
1,2-DCE	0.3243	98.9	0.549	83
1,1,1-Et	0.3157	133.3	0.499	74
CCl ₄	0.3968	153.8	0.170	76
Benz	0.2119	78.1	1.00	80
TRIC	0.3583	131.3	0.419	87
1,2-Prop	0.2957	112.9	0.638	96
1,1,2-Et	0.3696	133.4	0.362	114
Perc	0.4112	165.8	0.254	121
3,4-But	0.3094	124.9	0.078	130
Cl-Ø	0.2794	112.6	0.579	132
Et-Ø	0.2140	106.2	0.754	136
TCE	0.4035	167.8	0.133	146

TABLE-1 "Continued" Standard-1 Vapor

Names of Compounds ^a	Weight (gr)	M.W. (gr/mole)	Area Cmpd Area Benz	B.P. (°C)
CHBr ₃	.7373	252.7	0.0361	149.5
PDB	.0350	147.0	.0360	174.0
Bis-Ether	.3213	143.0	0.185	178.0
ODB	.3309	147.0	0.318	180.5
Hex.	.1824	84.0	—	68.9

Benz = Benzene

M.W. = Molecular Weight

gr = gram

B.P. = Boiling Point

^a- Abbreviations defined in Table-I

TABLE-2 "Standard-1" Vapor Data

Names of Cmpds.	No.of Carbons	RRC#	RRF*100	$\frac{RRF}{RRC\#} * 100$
1,1-DCEt	2	33.3	33.7	101.0
MeCl ₂	1	16.6	36.4	218.2
CHCl ₃	1	16.6	87.9*	527.4
Hex	6	100	—	—
1,1,1-Et	2	33.3	57.2	171.4
CCl ₄	1	16.6	18.0	108.3
Benz.	6	100	100	100
1,2-DCE	2	33.3	45.4	136.3
TRIC	2	33.3	41.6	124.9
1,2-Prop.	3	50.0	66.6	133.3
1,1,2-Et.	2	33.3	35.7	107.1
Perc.	2	33.3	27.7	83.3
3,4-But.	4	66.6	8.6	12.9
Cl-Ø	6	100	62.5	62.5
Et-Ø	8	133.3	102.0	76.5
TCE	2	33.3	15.1	45.4
CHBr ₃	1	16.6	3.35	20.1
PDB	6	100.0	40.8	40.8
Bis-Ether	4	66.6	22.2	33.3
ODB	6	100.0	38.5	38.5

*This value was dropped.

RRC# = Relative Response by carbon number

RRF = Relative Response Factor(Defined in standard analysis)

* = times

Cmpd = Compound

TABLE-3 "Standard-2" Vapor Data

Names of Cmpds.	Weight (gr)	M.W. (gr/mole)	Area Cmpd. Area Benz.	B.P. (°C)
1,1-Et	.0725	122.9	0.329	37.0
CHCl ₃	.0799	119.5	0.180	61.7
1,1,1-Et	.0727	133.3	0.144	74.1
Benz.	.0592	78.1	1.00	80.1
TRIC	.0916	131.3	0.408	87.0
1,1,2-Et	.1112	133.4	0.315	113.7
PERC	.1241	165.8	0.270	121.0
Cl-Ø	.0346	112.6	0.462	132.0
CHBr ₃	.1191	252.7	0.134	149.5
Bis-Ether	.1139	144.0	0.512	178.0
ODB	.1472	147.0	0.904	174.0
PDB	.0173	147.0	0.105	180.5

TABLE-4 "Standard-2" Vapor Data

Names of Cmpds.	% of Carbons	RRC#	RRF*100	RRF RRC#*100
1,1-Et	2	33.3	42.4	127.4
CHCl ₃	1	16.6	20.4	122.6
1,1,1-Et	2	33.3	20.1	60.3
Benz.	6	100.0	100.0	100.0
TRIC	2	33.3	44.4	133.1
1,1,2-Et	2	33.3	28.7	85.9
Perc	2	33.3	27.4	82.1
Cl-Ø	6	100.0	141.1	141.1
CHBr ₃	1	16.6	21.5	129.3
Bis-Ether	4	66.6	48.8	73.2
ODE	6	100.0	68.5	68.5
PDB	6	100.0	67.5	67.5

Table-5 "Standard-3" Vapor Data

Names of Cmpds.	Weight (gr)	M.W. (gr/moles)	$\frac{\text{Area Cmpd.}}{\text{Area Benz.}}$	B.P.
Freon(CCl_2F_2)	gas *	120.9	0.947	-29.8
CHCl_3	.07738	119.5	0.655	61.7
Ether	.03736	106.5	0.144	108.0
1,2-DCE	.03504	98.9	0.374	83.5
Benz.	.01613	78.1	1.00	80.1
CCl_4	.08194	153.8	0.498	76.5
1,2-Prop.	.09352	112.9	0.926	96.4
3,4-But.	.11003	124.9	0.335	130.5
Perc	.1045	165.8	0.506	121.0
CHBr_3	.26487	252.7	0.134	149.5
Et- ϕ	.09359	106.2	1.140	136.2
TCE	.16482	167.8	0.329	146.2
ODB	.18449	147.0	1.690	180.5

* $PV=nRT$

T=Room Temperature

P=1 atm.Pressure

V=24.19 lit/mole for n=1 mole

So 10ml Freon,

$$\frac{10 \text{ ml Freon}}{24.19 * 10^3 \text{ ml/moles}} = 4.13 * 10^{-3} \text{ moles}$$

TABLE-6 "Standard-3" Vapor Data

Names of Cmpds.	No. of Carbons	RRC#	RRF*100	$\frac{RRF}{RRC\#} * 100$
Freon 12	1	16.6	4.73	28.3
CHCl ₃	1	16.6	20.9	125.5
Cl-Ether	4	66.6	18.0	27.0
1,2-DCE	2	33.3	21.8	65.4
Benz	6	100.0	100.0	100.0
CCl ₄	1	16.6	19.3	115.7
1,2-Prop	3	50.0	23.1	46.2
3,4-But	4	66.6	7.85	11.8
Perc	2	33.3	16.6	49.7
CHBr ₃	1	16.6	2.63	15.8
Et-Ø	6	133.3	26.7	20.0
TCE	2	33.3	6.93	20.8
ODB	6	100.0	27.8	27.8

TABLE-7 "Standard-4" Vapor Data

Names of Cmpds.	Weight (gr)	M.W. (gr/moles)	Area Cmpd / Area Benz	B.P. (°C)
MeCl	gas*	50.4	0.552	-24.2
MeCl ₂	.11276	84.9	0.181	40.0
Hex.	.04560	84.0	1.259	68.9
1,2-DCE	.10390	98.9	0.687	83.5
1,1,1-Et	.13320	133.3	0.967	74.1
Benz.	.04570	78.1	1.0	80.1
1,2-Prop	.05826	112.9	.522	96.4
TRIC	.07080	131.3	.172	87.0
1,1,2-Et	.15020	133.4	0.192	113.7
Cl-Ø	.07880	112.6	0.192	132.0
CHBr ₃	.29232	252.7	0.131	149.5
TCE	.03252	167.8	0.109	146.2

*At room temperature and 1 atm. pressure, 1 mole of Methyl Chloride is 24.19 liter. Therefore, 10 ml of Methyl Chloride is 4.13×10^{-3} moles.

TABLE-8 "Standard-4" Vapor Data

Names of Cmpds.	#of Carbons	RRC#	RRF*100	$\frac{RRF}{RRC\#} * 100$
MeCl	1	16.6	7.83	46.9
MeCl ₂	1	16.6	7.98	47.9
Hex.	6	100.	99.6	99.6
1,2-DCE	2	33.3	38.3	115.0
1,1,1-Et	2	33.3	56.7	170.1
Benz.	6	100.	100.	100.0
1,2-Prop.	3	50.0	59.3	118.5
TRIC	2	33.3	18.7	56.1
1,1,2-Et	2	33.3	9.99	29.9
Cl-Ø	6	100.	16.1	16.1
CHBr ₃	1	16.6	6.63	39.8
TCE	2	33.3	33.2	99.6

TABLE-9A

"VAPOR DATA"

Compounds	Value of Relative*Response(RRF x 100)			
MeCl	—	—	—	7.83
MeCl ₂	36.4	—	—	7.98
Freon-12	—	—	4.73	—
CHCl ₃	—	20.4	20.9	—
CHBr ₃	3.35	21.5	2.63	6.63
CCl ₄	18.0	—	19.3	—
1,2-DCE	45.4	—	21.8	38.3
1,1-DCEt	33.7	42.4	—	—
1,1,1-Et	57.2	20.1	—	56.7
1,1,2-Et	35.7	28.7	—	9.99
TRIC	41.6	44.4	—	18.7
PERC	27.7	27.4	16.6	—
TCE	15.1	—	6.93	33.2
1,2-Prop.	66.6	—	23.1	59.3
3,4-But.	8.60	—	7.85	—
Bis-Ether	22.2	48.8	—	—
Cl-Ether	—	—	18.0	—
Cl-Ø	62.5	141.1	—	16.1
Et-Ø	102.0	—	26.7	—
PDB	40.8	67.5	—	—
ODB	38.5	68.5	27.8	—
Hex.	—	—	—	99.6

*Relative to Benzene = 100.

TABLE-9B

"VAPOR DATA"

Compounds	Average of Relative Response	Error
MeCl	7.83	—
MeCl ₂	22.2	<u>±14.21</u>
Freon-12	4.73	—
CHCl ₃	20.6	<u>±0.5</u>
CHBr ₃	8.50	<u>±9.4</u>
CCl ₄	18.6	<u>±1.3</u>
1,2-DCE	35.2	<u>±11.8</u>
1,1-DCEt	38.0	<u>±4.3</u>
1,1,1-Et	44.6	<u>±18.5</u>
1,1,2-Et	24.8	<u>±12.8</u>
TRIC	34.9	<u>±12.8</u>
PERC	23.9	<u>±5.5</u>
TCE	18.4	<u>±13.1</u>
1,2-Prop.	49.7	<u>±21.7</u>
3,4-But.	8.2	<u>±0.37</u>
Bis-Ether	35.5	<u>±13.3</u>
Cl-Ether	18.0	—
Cl-Ø	73.2	<u>±62.5</u>
Et-Ø	64.3	<u>±37.6</u>
PDB	54.1	<u>±13.3</u>
ODB	44.9	<u>±20.3</u>
Hex.	99.6	—

TABLE-9C

"VAPOR DATA"

Compounds	RRF x 6/#C
MeCl	46.8
MeCl ₂	133.2
Freon-12	28.2
CHCl ₃	123.6
CHBr ₃	51.0
CCl ₄	111.6
1,2-DCE	105.6
1,1-DCEt	114.0
1,1,1-Et	133.8
1,1,2-Et	74.8
TRIC	104.7
PERC	71.7
TCE	55.2
1,2-Prop.	98.4
3,4-But.	12.3
Bis-Ether	53.2
Cl-Ether	27.0
Cl-Ø	73.2
Et-Ø	48.2
PDB	54.1
ODB	44.9

TABLE-10 "Standard-5" Liquid Data

Names of Cmpds.	Weight (gr)	M.W. (gr/mole)	Area Cmpd	B.P. (°C)
			Area Benz	
MeCl ₂	0.0716	84.9	0.0929	40
CHCl ₃	0.1394	119.5	0.1986	61.7
1,1,1-Et	0.0932	133.3	0.1774	74.1
Benz	0.1007	78.1	1.0	80.1
1,2-Prop	0.0820	112.9	0.2924	96.4
1,1,2-Et	0.1042	133.4	0.2103	113.8
Perc	0.1138	165.8	0.1992	121.0
CHBr ₃	0.2011	252.7	0.1148	149.5
Bis-Ether	0.1289	143.0	0.4118	178.0

TABLE-11 "Standard-5" Liquid Data

Names of Cmpds.	#of Carbons	RRC#	RRF*100	RRF
				RRC#*100
MeCl ₂	1	16.6	14.2	85.3
CHCl ₃	1	16.6	21.9	131.6
1,1,1-Et	2	33.3	32.7	98.2
Benz.	6	100.	100.	100.0
1,2-Prop.	3	50.0	51.9	103.8
1,1,2-Et	2	33.3	34.7	104.1
Perc	2	33.3	37.4	112.2
CHBr ₃	1	16.6	18.6	111.5
Bis-Ether	4	66.6	58.9	88.4

* = times

RRC# = Relative Response by Carbon number

RRF = Relative Response Factor(Defined in standard analysis)

TABLE-12 "Standard-6" Liquid Data

Names of Cmpds.	Weight (gr)	M.W. (gr/mole)	Area Cmpd Area Benz	B.P. (°C)
Hex.	.0587	84.0	0.5656	68.9
1,2-DCE	.0895	98.9	0.5037	83.5
Benz	.0644	78.1	1.0	80.1
CCl ₄	.1124	153.8	0.2099	76.5
TRIC	.1035	131.3	0.3892	87.0
Cl-Ether	.1421	106.5	0.5636	108.0
3,4-But.	.0968	124.9	0.6868	130.5
TCE	.1296	167.8	0.4464	146.2

TABLE-13 "Standard-6" Liquid Data

Names of Cmpds.	#of Carbons	RRC#	RRF*100	RRF RRC# *100
Hex.	6	100.	66.7	66.7
1,2-DCE	2	33.3	46.3	138.6
Benz	6	100.	100.	100.0
CCl ₄	1	16.6	23.9	143.2
TRIC	2	33.3	41.1	123.2
Cl-Ether	4	66.6	34.8	52.2
3,4-But	4	66.6	73.7	110.5
TCE	2	33.3	48.1	144.2

TABLE-14 "Standard-7" Liquid Data

Names of Cmpds	Weight (gr)	M.W. (gr/mole)	$\frac{\text{Area Cmpd}}{\text{Area Benz}}$	B.P. (°C)
MeCl ₂	.1311	84.9	0.2462	40.0
1,2-DCE	.0874	98.9	0.3650	83.5
Benz	.0665	78.1	1.0	80.1
CCl ₄	.1073	153.8	0.1920	76.5
Cl-Ø	.0751	112.6	0.7947	132.0
Et-Ø	.0687	106.2	1.1647	136.2
CHBr ₃	.1877	252.7	0.1485	149.5
TCE	.1183	167.8	0.3173	146.2
PDB	.0710	147.0	0.7021	174.0
ODB	.0929	147.0	0.9178	180.5

TABLE-15 "Standard-7" Liquid Data

Names of Cmpds	#of Carbons	RRC#	RRF*100	$\frac{\text{RRF}}{\text{RRC\#}} * 100$
MeCl ₂	1	16.6	13.9	83.5
1,2-DCE	2	33.3	35.7	107.2
Benz	6	100.	100.	100.0
CCl ₄	1	16.6	23.2	139.1
Cl-Ø	6	100.	105.6	105.6
Et-Ø	8	133.3	162.3	121.7
CHBr ₃	1	16.6	17.7	106.3
TCE	2	33.3	39.6	118.9
PDB	6	100.	132.2	132.2
ODB	6	100.	136.7	136.7

TABLE-16 "Standard-8" Liquid Data

Names of Cmpds	Weight (gr)	M.W. (gr/mole)	$\frac{\text{Area Cmpd}}{\text{Area Benz}}$	B.P. (°C)
MeCl ₂	.12326	84.93	0.1615	40.0
CHCl ₃	.13109	119.5	0.1520	61.7
Benz	.12855	78.11	1.0	80.1

TABLE-17 "Standard-8" Liquid Data

Names of Cmpds	#Of Carbons	RRC#	RRF*100	$\frac{\text{RRF}}{\text{RRC\#*100}}$
MeCl ₂	1	16.6	18.3	109.9
CHCl ₃	1	16.6	22.8	136.8
Benz	6	100.	100.	100.0

TABLE-18 "Standard-9" Liquid Data

Names of Cmpds	Weight (gr)	M.W. (gr/mole)	Area Cmpd Area Benz	B.P. (°C)
Hex	.13638	84.0	.8732	68.9
1,2-DCE	.10645	98.9	.4793	83.5
1,1,1-Et	.12928	133.3	.3185	74.1
Benz	.08292	78.1	1.0	80.1
Perc	.17595	165.8	.4248	121.0
Et-Ø	.08156	106.2	1.1068	136.2
CHBr ₃	.27564	252.7	.2184	149.5
PDB	.12629	147.0	1.0565	174.0
ODB	.11895	147.0	.9719	180.5

TABLE-19 "Standard-9" Liquid Data

Names of Cmpds	#Of Carbons	RRC#	RRF*100	RRF RRC#*100
Hex	6	100.	57.0	57.0*
1,2-DCE	2	33.3	47.3	141.8*
1,1,1-Et	2	33.3	34.8	104.5
Benz	6	100.	100.	100.0
Perc	2	33.3	42.5	127.4
Et-Ø	8	133.3	152.7	114.5
CHBr ₃	1	16.6	21.2	127.4
PDB	6	100.	130.4	130.4
ODB	6	100.	127.5	127.5

*These values were dropped.

TABLE-20 "Standard-10" Liquid Data

Names of Cmpds	Weight (gr)	M.W. (gr/mole)	$\frac{\text{Area Cmpd}}{\text{Area Benz}}$	B.P. (°C)
Hex	.07706	84.0	0.4369	68.9
Benz	.16779	78.1	1.0	80.1

TABLE-21 "Standard-10" Liquid Data

Names of Cmpds	#of Carbons	RRC#	RRF^*100	$\frac{\text{RRF}}{\text{RRC\#}}^*100$
Hex	6	100.0	102.32	102.3
Benz.	6	100.0	100.	100.0

TABLE-22 "Standard-11" Liquid Data

Names of Cmpds.	Weight (gr)	M.W. (gr/mole)	$\frac{\text{Area Cmpd}}{\text{Area Benz}}$	B.P. (C)
CCl ₄	.19162	153.8	0.2196	76.5
Benz	.10599	78.1	1.0	80.1

TABLE-23 "Standard-11" Liquid Data

Names of Cmpds.	# of Carbons	RRC#	RRF*100	RRF RRC#*100
CCl ₄	1	16.6	23.9	143.5
Benz	6	100.	100.	100.0

TABLE-24 "Standard-12" Liquid Data

Names of Cmpds	Weight (gr)	M.W. (gr/mole)	Area Cmpd Area Benz	B.P. (°C)
CHCl ₃	.19273	119.5	.2324	61.7
Benz	.1161	78.1	1.0	80.1
1,1,2-Et	.14873	133.4	.3087	113.8
Cl-Ø	.1321	112.6	1.300	132.0
Bis-Ether	.14368	143.0	.6319	178.0

TABLE-25 "Standard-12" Liquid Data

Names of Cmpds	No. of Carbons	RRC#	RRF*100	RRF RRC#*100
CHCl ₃	1	16.6	21.4	128.6
Benz	2	100.	100.	100.0
1,1,2-Et	2	33.3	41.1	123.4
Cl-Ø	6	100.	164.7	164.7
Bis-Ether	4	66.6	93.5	140.3

TABLE-26 "Standard-13" Liquid Data

Names of Cmpds	Weight (gr)	M.W. (gr/mole)	$\frac{\text{Area Cmpd}}{\text{Area Benz}}$	B.P. (°C)
Hex	.09099	84.0	.7747	68.9
Benz	.10137	78.1	1.0	80.0
1,2-Prop	.1416	112.9	.5429	96.0
CHBr ₃	.23924	252.7	.13172	149.5

TABLE-27 "Standard-13" Liquid Data

Names of Cmpds	#of Carbons	RRC#	$\text{RRF} \times 100$	$\frac{\text{RRF}}{\text{RRC\#}} \times 100$
Hex	6	100.	92.8	92.8
Benz	6	100.	100.	100.0
1,2-Prop	3	50.	55.0	110.0
CHBr ₃	1	16.6	18.0	108.3

TABLE-28 "Standard-14" Liquid Data

Names of Cmpds	Weight (gr)	M.W. (gr/mole)	Area Cmpd Area Hex	B.P. (°C)
MeCl ₂	.16513	84.9	0.2748	61.7
Hex	.0847	84.0	0.0847	68.9
TRIC	.18899	131.3	0.5406	87.0
Cl-Ether	.10984	106.5	0.1450	108.0
3,4-But	.13194	124.9	.7072	130.5
TCE	.18839	167.8	0.6771	146.2

TABLE-29 "Standard-14" Liquid Data

Names of Cmpds	#of Carbons	RRC#	RRF*100	RRF*100 RRC#
MeCl ₂	1	16.6	14.2	85.5
Hex	6	100.	100.	100.0
TRIC	2	33.3	37.8	113.6
Cl-Ether	4	66.6	14.2	21.3
3,4-But	4	66.6	67.5	101.2
TCE	2	33.3	47.5	142.5

TABLE-30

"LIQUID DATA"

Names of Cmpds	VALUES OF $\frac{RRF}{RRC\#} * 100$ PLOTTED			
	1	2	3	4
MeCl ₂	—	—	109.9	—
CHCl ₃	131.6	136.8	128.6	—
CHBr ₃	111.5	106.3	127.4	108.3
CCl ₄	143.2	139.1	143.5	—
1,2-DCE	—	107.2	—	—
Perc	112.2	127.4	—	—
1,1,1-Et	98.2	104.5	—	—
1,1,2-Et	104.1	123.4	—	—
TRIC	123.2	113.6	—	—
TCE	144.2	118.9	142.5	—
1,2-Prop	103.8	110.0	—	—
3,4-But	110.5	101.2	—	—
Bis-Ether	88.4	140.3	—	—
Hex	—	92.8	102.3	—
Cl-Ø	105.6	164.7	—	—
Et-Ø	121.7	114.5	—	—
PDB	132.2	130.4	—	—
ODE	136.7	127.5	—	—
Cl-Ether	52.2	—	—	—

TABLE-31 A

"Liquid Data"

Names of Compounds	Average value of $\frac{RRF}{RRC\#} * 100$	Error
MeCl ₂	109.8	—
CHCl ₃	132.3	±4.1
CHBr ₃	113.4	±10.5
CCl ₄	141.9	±2.2
1,2-DCE	107.2	—
Perc	119.8	±7.6
1,1,1-Et	101.3	±3.1
1,1,2-Et	113.7	±9.6
TRIC	118.4	±4.8
TCE	135.2	±12.6
1,2-Prop	106.9	±3.1
3,4-But	105.8	±4.6
Bis-Ether	114.3	±25.9
Hex	97.5	±4.75
Cl-Ø	135.1	±29.5
Et-Ø	118.1	±3.6
PDB	131.3	±0.9
ODB	132.1	±4.6
Cl-Ether	52.2	—

TABLE-31B

Compounds	Calibration factors	±%Error
Methylene Chloride	5.46	—
Chloroform	4.54	3
Bromoform	5.32	9
Carbon Tetrachloride	4.24	1
1,2-Dichloroethane	2.80	—
Perchloroethylene	2.51	6
1,1,1-Trichloroethane	2.97	3
1,1,2-Trichloroethane	2.64	8
Trichloroethylene	2.53	4
Tetrachloroethylene	2.22	9
1,2-Dichloropropane	1.87	3
3,4-Dichlorobutene	1.42	4
Bis(2-Chloroethyl ether)	1.31	22
Chlorobenzene	0.74	21
Ethylbenzene	0.63	3
Paradichlorobenzene	0.76	.6
Orthodichlorobenzene	0.76	3

TABLE-32

Liquid Data

Names of Compounds	VALUES OF RRF*100 PLOTTED			
	#1	#2	#3	#4
MeCl ₂	—	—	18.3	—
CHCl ₃	21.9	22.8	21.4	—
CHBr ₃	18.6	17.7	21.2	18.0
CCl ₄	23.9	23.2	23.9	—
1,2-DCE	35.7	—	—	—
Perc	37.4	42.5	—	—
1,1,1-Et	32.7	34.8	—	—
1,1,2-Et	34.7	41.1	—	—
Tric	41.1	37.9	—	—
TCE	48.1	39.6	47.5	—
1,2-Prop.	51.9	55.0	—	—
3,4-But.	73.7	67.5	—	—
Cl-Ether	34.8	—	—	—
Bis-	58.9	93.5	—	—
Hex	102.3	92.8	—	—
Cl-Ø	105.6	164.7	—	—
Et-Ø	162.3	152.7	—	—
PDB	132.2	130.4	—	—
ODB	136.7	127.5	—	—

TABLE-33

"Liquid Data"

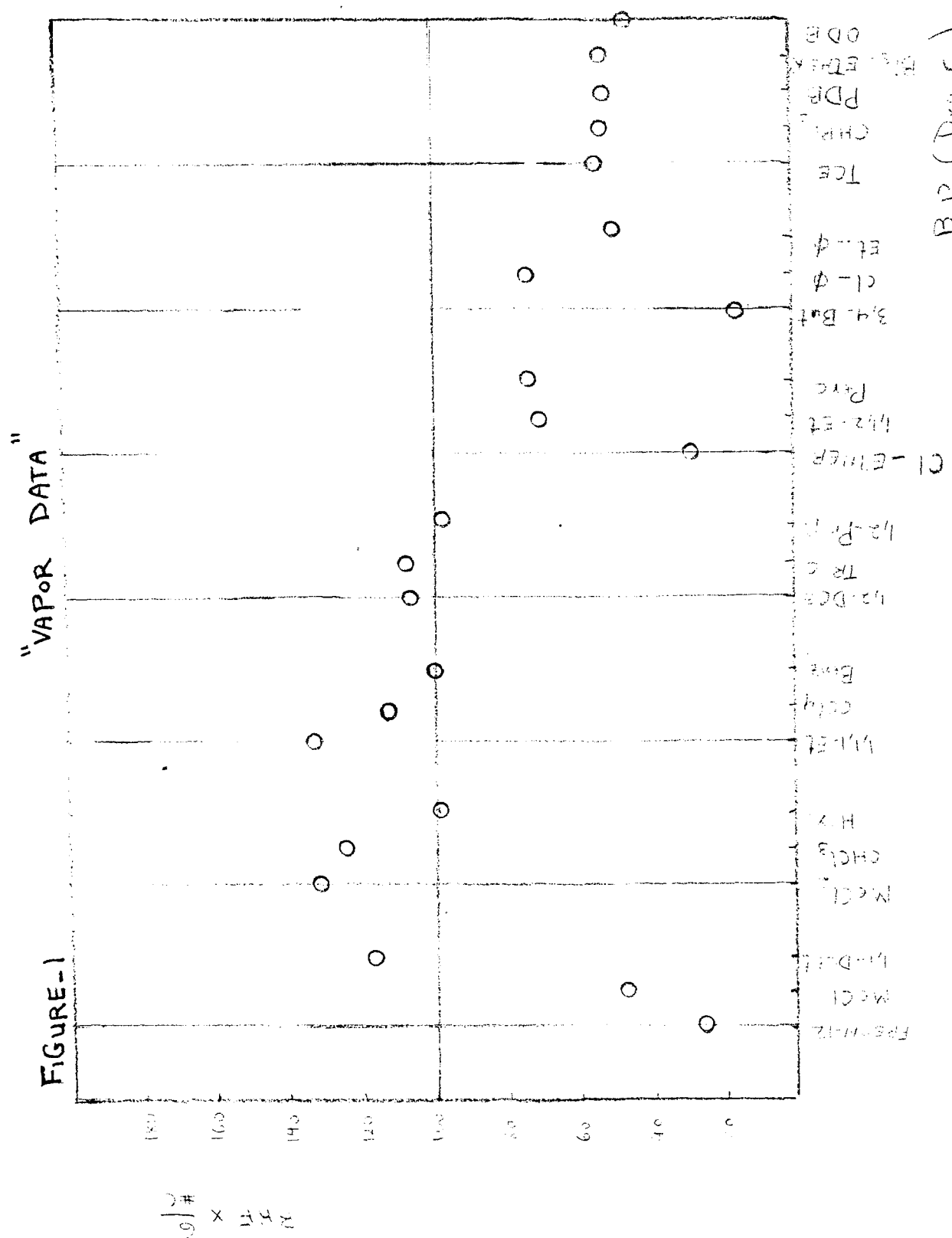
Names of Compounds	Average value of RRF _{*100}	Error
MeCl ₂	18.3	—
CHCl ₃	22.0	±0.45
CHPr ₃	18.8	±1.75
CCl ₄	23.6	±0.35
1,2-DCE	35.7	—
Perc	39.9	±2.5
1,1,1-Et	33.7	±1.0
1,1,2-Et	37.9	±3.2
TRIC	39.5	±1.6
TCE	45.0	±5.1
1,2-Prop.	53.4	±1.5
3,4-But	70.6	±3.1
Bis-Ether	76.2	±17.3
Hex	97.5	±4.7
Cl-Ø	135.1	±29.5
Et-Ø	157.5	±4.8
PDB	131.3	±0.9
ODB	132.1	±4.6
Cl-Ether	34.8	—

normalized relative responses (derived from earlier tables) and the error involved with these average values. Table-31B shows the Calibration Factors and error limits involved in these calibration factors values. Table-32 shows the results of relative responses of the liquid standards and Table-33 is the average of these relative responses in liquid standards and their precision.

Figure-1 shows the normalized relative response of the compounds to the number of their carbons versus their boiling points in vapor standards.

Figure-2 shows the normalized value of relative response of the compounds by their carbon number plotted against their boiling point for liquid standards and their averages.

Figure-3 shows the combined results from figure-1 and figure-2. It shows a comparison of the results of vapor and liquid standards.



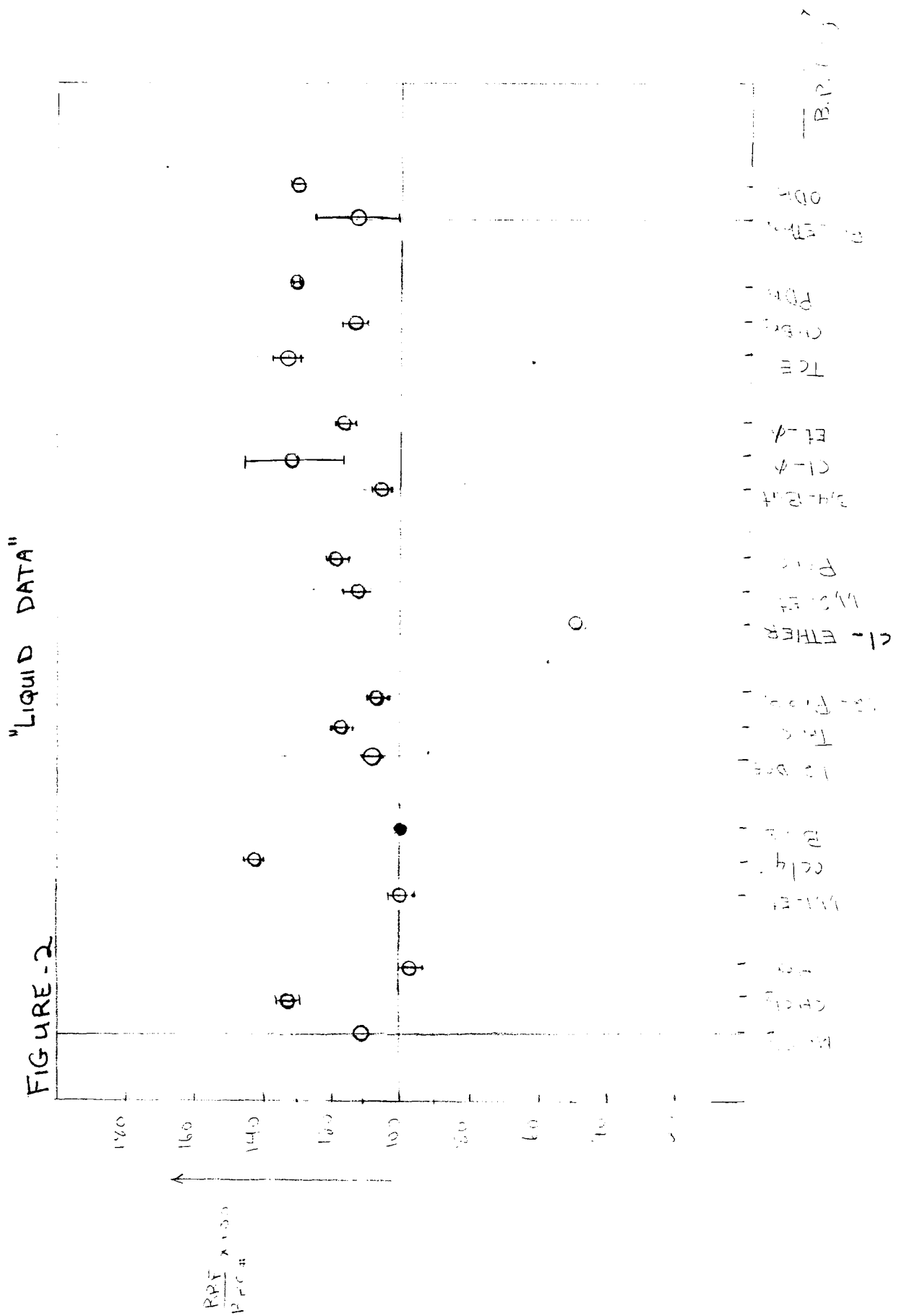
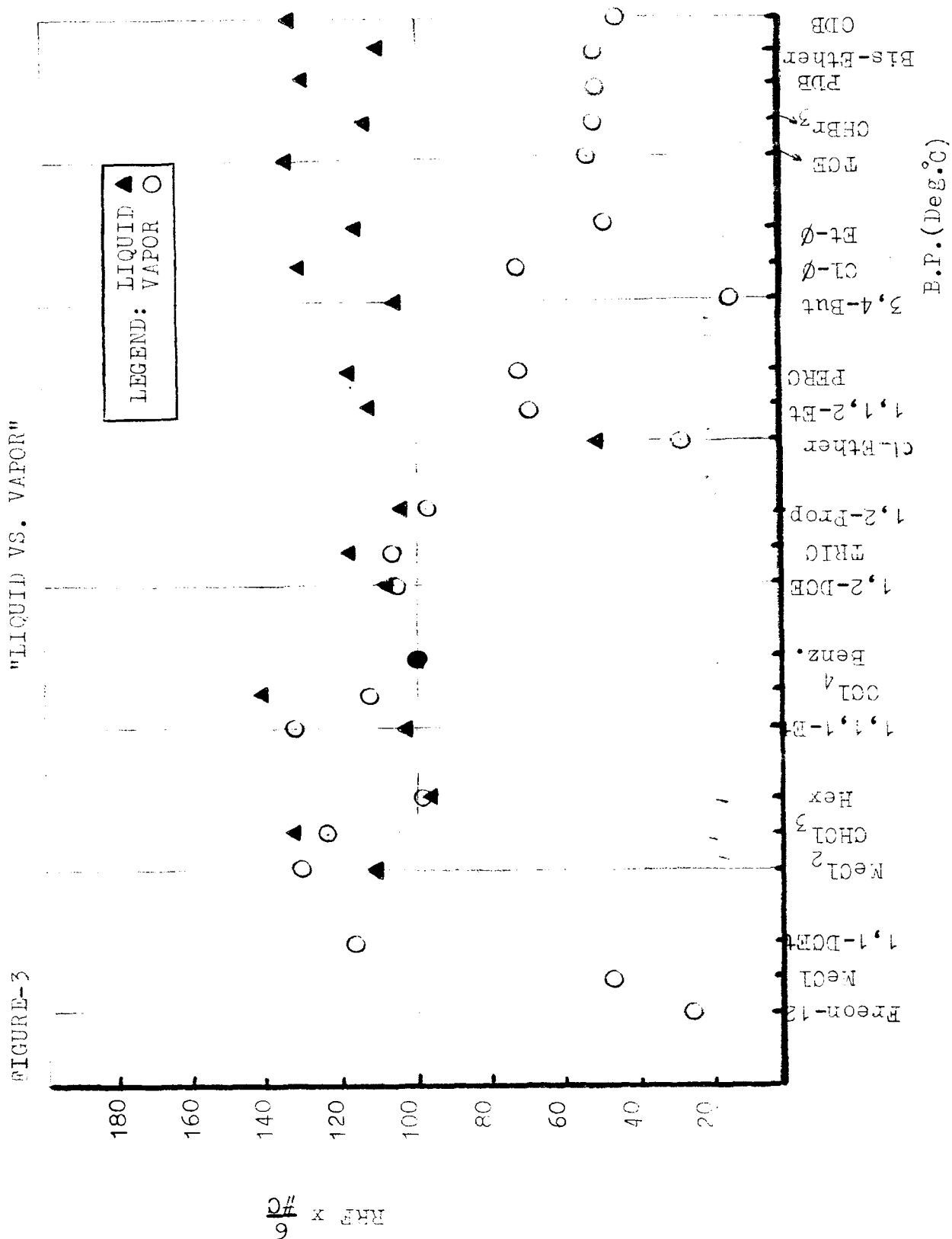


FIGURE-3



DISCUSSION AND ANALYSIS OF INDIVIDUAL COMPOUNDS (LIQUID AND VAPOR)

1- Chloro methane(CH_3Cl)

Chloro methane was included in vapor standard #4 with data listed in tables #7-8. The Relative Response Factor (RRF; Relative to Benzene = 100) for this compound was measured to be 7.8. This value was about one-half the Relative Response Factor of the hydrocarbon with one carbon (Methane = 16.6). The data was, however, determined to be low (see discussion of chloroform) and is not included in the statistical results. This is considered a low response for this compound and may be due to losses incurred from incomplete transfer of this compound into the gas standard cylinder. No conclusion can be derived based on this compound until future verification studies are complete.

2- Methylene Chloride(CH_2Cl_2)

Methylene Chloride was included in vapor standards #1 and 4, plus liquid standards #5,7,8 and 14 with data listed in tables #1,2,7,8,10,11 and 14-17. The RRF in the vapor was measured to be 22.2 and in the liquid was 18.3. Data from the vapor standard were about 21% higher than in liquid standards. The data in liquid standards #5,7,14 were about 30% lower than liquid standard #8. These data in liquid standards were

determined to be low (see discussion of chloroform) and they are not included in statistical results. This probable loss in liquid standards was due to rapid evaporation of this compound through the vial's septum (injection aperture) while mixing and storing at room temperature in the liquid standards. This partial evaporation occurred because of the high vapor pressure (low boiling point) of this compound. Therefore, both vapor and liquid data are recommended for use. The RRF in vapor in vapor and liquid were 34% and 10% higher than the RRF of methane respectively. Therefore chlorines do not appear to inhibit the response on the FID.

3- Dichlorodifluoromethane(CF_2Cl_2)-(Freon 12)

Freon-12 was included in the vapor standard #3 and the data are listed in tables #5 and 6. The RRF was measured to be only 4.9. This value is less than one-third of methane's RRF. The data is suspect because only one standard was used and it is felt that the vapor from the Freon concentrate may not have been inlet quantitatively to the gas standard cylinder. Thus no discussion for this Freon is included until a new supply of Freon is obtained and additional studies completed.

4- Chloroform(CHCl_3)

Chloroform was included in the vapor standards #2 and 3

with data listed in tables #3,4,5 and 6, plus liquid standards #5,8 and 12 with data listed in tables #10, 11, 16, 17, 24 and 25 respectively. The data in both vapor and liquid were in very good agreement. The average of measured RRF's in vapor standards was 20.6 with an error of ± 0.25 . The average RRF measured in liquid standards was 22.0 and error of ± 0.45 . Therefore it is recommended that both vapor and liquid standard are acceptable for this compound. RRF in liquid and vapor were about 24% and 32% higher than the RRF of methane respectively. These results strongly indicate that the chlorines on the carbon atom do not decrease the relative response of chlorocarbons on FID.

5- Bromoform(CHBr3)

Bromoform was included in the vapor standards #1-4 with data listed in tables #1-8, plus in liquid standards #5, 7 and 9 with data listed in tables #10, 11, 14, 15, 18 and 19 respectively. RRF in the vapor measured to be 8.5 with ± 0.4 error units. The average of RRF in liquid measured to be 18.8 with ± 1.75 error. The relatively high boiling point of this compound and the strong probability of adsorption to the cylinder's wall in several standards #1-3 when the cylinder was not hot enough, caused measurement of significantly lower response for this compound compared to the proper number. This was probably due to wall loss and/or possible "catalytic" decomposition of the CHBr3 on the stainless steel wall of the

gas cylinder. Therefore RRF from the liquid standard is recommended. The RRF of the liquid (18.8) was about 13% higher than the RRF of methane. These results indicate that bromine also enhanced the response of FID like CHCl_3 did and shows that combustion must be efficient for both chloroform and bromoform and probably follows the same mechanism.

6- Carbon Tetrachloride(CCl_4)

Carbon Tetrachloride was included in the vapor standard #1 and 3 with data listed in tables #1,2,5 and 6. Additionally, liquid standards #6, 7 and 11 were sampled and data are listed in tables #12-15 and 22-23 respectively. The RRF in vapor was calculated to be 18.6 with ± 1.3 error limits and liquid RRF was 23.6 with $\pm .35$ error limits. The lower response in the vapor was due to possible wall loss and/or possible "catalytic" decomposition of the CCl_4 on the heated stainless steel cylinder wall in the standard gas cylinder. The data in the vapor standard were therefore determined to be low and not included in the statistical result. the liquid RRF was determined to be 23.6 which was about 42% higher than RRF of methane. Again we can conclude that chlorine did not inhibit the response. Addition of one chlorine in CCl_4 increased the response of FID 10% over that of CHCl_3 .

7- 1,2- Dichloroethane($\text{ClH}_2\text{C:CH}_2\text{Cl}$)

1,2- Dichloroethane was included in the vapor standards #1,3 and 4 with the data are listed in tables #1,2 and 5-8. Additionally, the liquid standards #6-9 have determined with data listed in tables# 12-15 and 18,19. The average of RRF for this compound in vapor was 35.2 with ± 11.8 error units. Liquid RRF was 35.7. Liquid and vapor data were in good agreement with each other. Use of vapor standards is therefore recommended for this compound. The liquid and vapor RRF were 35.7 and 35.2, which is an increase in RRF over Ethane by 7% and 6% respectively.

8- Vinylidene Chloride($\text{Cl}_2\text{C}=\text{CH}_2$)

Vinylidene Chloride was included in vapor standard #1 and 2 and the data are listed in tables #1-4 respectively. The RRF was measured to be 38.0. This value was 14% higher than RRF of Ethane. No liquid data were obtained for this compound due to it's high evaporation rate at room temperature. The vapor data appear acceptable and vapor standards of this compound are recommended. The RRF was 14% higher than the RRF of Ethane. Therefore the two chlorines show enhanced response of FID again.

9- 1,1,1- TriChloroethane($\text{Cl}_3\text{C:CH}_3$)

1,1,1- TriChloroethane was included in vapor standards #1,2 and 4 and the data are listed in tables #1-4 and 7-8,

plus the liquid standards #5 and 9 with the data listed in tables #10,11,18 and 19 respectively. The RRF in vapor was measured to be 44.6 with ± 18.5 units error. The RRF in liquid was measured to be 33.7 ± 1.0 . Obviously from the high vapor values this compound is stable in the gas standard cylinder and it is recommended to have a vapor standard for this compound. The RRF of liquid and vapor were 33.7 and 44.6 which increased the RRF of Ethane about 1% and 34% respectively. This is also an example of enhancement of the response of hydrocarbon with addition of a chlorine.

10- 1,1,2- Trichloroethane($\text{Cl}_2\text{HC:CH}_2\text{Cl}$)

1,1,2- Trichloroethane was included in vapor standard #1,2 and 4 with data listed in tables #1-4 and 7-8, plus liquid standards #5 and 12 with data listed in tables #10,11,24 and 25 respectively. The average RRF in liquid standards were 37.9 with ± 3.2 error units. The value of RRF in vapor standards was 24.8 with ± 12.8 units error. The data in vapor were low and therefore were determined to be in error and not included in the statistical result and discussion. This loss was probably due to wall adsorption and therefore incomplete desorption of this compound in gas standard cylinder. This probably happened because the cylinder and/or regulator and connecting lines were not hot enough. The liquid RRF(37.9) was about 14% higher than of Ethane. This shows again chlorine enhanced the response of Ethane.

11- TriChloroethylene(ClHC:CCl2)

TriChloroethylene was included in vapor standards #1,2 and 4 with data listed in tables #1-4 and 7-8, plus liquid standards #6 and 14 with data listed in tables #12,13,28 and 29 respectively. The average RRF in vapor data yielded a value of 34.9 with ± 12.8 error units. The average RRF in liquid standards was 39.5 with ± 1.6 units error. Data in vapor was about 13% lower than data in liquid, therefore it was determined to be error and only the liquid data for this compound is included in further discussion and statistical result. Considering only liquid standard RRF (39.5), this value was about 17% higher than of Ethane. Therefore chlorine effect is enhancement of the response in this olefinic C2 halocarbon.

12- Tetrachloroethylene(Cl2C:CCl2)

Tetrachloroethylene was included in vapor standards #1-3 with data listed in tables #1-6, plus liquid standards #5 and 9 with data listed in tables #10,11,18 and 19 respectively. The average RRF of vapor standards was 23.9 ± 5.5 . The average RRF of liquid standards was 39.9 ± 2.5 . The data in vapor appears to be low, therefore data in vapor was not included in the statistical result or further discussion. The data in liquid standard(39.9) is used for further data analysis. This

value was about 20% higher than of Ethane. Therefore chlorine appears to enhance the response of this olefinic C2 hydrocarbon.

13 - 1,1,2,2- Tetrachloroethane($\text{C}_2\text{H}_2\text{Cl}_4$)

1,1,2,2- Tetrachloroethane was included in the vapor standards #1,3 and 4 with data listed in tables#1-2 and 5-8, plus liquid standards #6-7 and 14 with data listed in tables #12-15 and 28-29 respectively. The average RRF in liquid standards yielded values of 45.0 ± 5.1 . The average RRF in vapor standards was 18.4 ± 13.1 . The data in vapor was significantly lower than liquid data, and again the data in vapor is not included in the statistical results. These low data for vapor was probably due to adsorption of this compound on the gas standard cylinder. It should be pointed out that the vapor pressure is decreasing with these higher MW compounds and wall adsorption must also be increasing. The liquid RRF(45.0) was used for calibration purpose. This value was about 35% higher than of Ethane. Chlorine again in this compound enhanced the molar response of this corresponding hydrocarbon.

14- 1,2- Dichloropropane($\text{C}_3\text{H}_7\text{Cl}_2$)

1,2- Dichloropropane was included in vapor standards #1,3 and 4 with data listed in tables #1-2 and 5-8, plus

liquid standards #5,13 with data listed in tables #10,11,26 and 27 respectively. The average RRF in vapor standards was 49.7 ± 21.7 and the average RRF in liquid standards was 53.4 ± 1.5 . Data in vapor appears to be acceptable for this compound. RRF in liquid (53.4) was 7% higher than of Propane. This fact shows again small enhancement in molar response of Propane when two chlorines added to this compound.

15- 3,4- Dichlorobutene ($\text{H}_2\text{C}=\text{CH}=\text{CHCl}=\text{CH}_2\text{Cl}$)

3,4- Dichlorobutene was included in vapor standards #1 and 3 with data listed in tables #1,2,5 and 6, plus liquid standards #6 and 14 with data listed in tables #12,13,28 and 29 respectively. The average RRF in liquid was 70.6 with ± 3.1 units error. The average RRF in vapor was 8.2 with ± 3.37 units error. Data in vapor standards determined to be significantly lower than that of liquid, and it was unacceptable and not included in these statistical result or discussion. This wall loss was probably due to wall adsorption of this compound. The liquid RRF (70.6) was about 6% higher than of Butane. This value might be low, because this compound was not pure in original liquid form. We can again conclude that two chlorines caused small enhancement of molar response of Butane.

16- Bis(2-chloroethyl)ether ($\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$)

Bis(2-chloroethyl)Ether was included in vapor standards

#1 and 2 with data listed in tables #1-4, plus liquid standards #5 and 12 with data listed in tables #10,11,24 and 25 respectively. The average RRF in vapor standards was 35.5 ± 13.3 . The average RRF in liquid standards was 76.2 ± 17.3 . Data in vapor standards was significantly (50%) lower than of liquid standards and considered unacceptable. Therefore only liquid standard was recommended for this compound. The value of RRF for liquid (76.2) was about 14% higher than of Butane = 66.6, Relative to Benzene = 100. Therefore, oxygen in this compound did not reduce sensitivity, as oxygen is reported (1,2,11).

17- 2-Chloroethyl vinyl ether ($\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$)

2-Chloroethyl vinyl ether was included in vapor standard #3 with data listed in tables #5-6 plus liquid standards #6 and 14 with data listed in tables #12,13,28 and 29 respectively. RRF in vapor was 18.0 and RRF in liquid was 34.8. Data in both vapor and liquid were very low as they should be similar to the values of 60-76 of the above "Bis" Ether and are not included in the statistical result and further discussion. These values are low possibly because of some unidentified loss or decomposition of this toxic but relatively unstable compound. Assuming no loss and considering the liquid RRF (34.8), this value is about 91% lower than of Butane, and therefore chlorine has significantly reduced sensitivity. Even considering a response similar to

C3 (Propane) due to the oxygen these values are very low. Producing a standard of this compound will need to be further studied.

18- Chlorobenzene(ClC_6H_5)

Chlorobenzene was included in vapor standards #1,2 and 4 with data listed in tables #1-4 and 7-8, plus liquid standards #7 and 12 with data listed in tables #14,15,24 and 25 respectively. The average RRF in vapor standards 73.2 with ± 62.5 units of error. The average RRF in liquid standards was 135.1 with ± 29.5 units of error. Data in vapor was low and it was not included in the statistical results. The relative high boiling point temperature of this compound does not appear to make it an acceptable candidate for use in vapor standards and therefore only liquid standards are recommended. This loss was probably due to wall adsorption of this relative high boiling compound, even though the gas cylinder was heated. RRF in liquid (135.1) was about 35% higher than of Benzene. This value is suspected to be higher than it should be. May be because the actual weight of liquid concentrate is slightly less than that calculated from the summation of all individual component weights. This effect could result from partial evaporation of light (low boiling points) compounds from the liquid concentrate vial through the septum. The heavier compounds' responses will then be higher, because their relative concentrations are higher than that calculated.

We can approximate how much this effect contributes, by finding the ratio of EthylBenzene reported in this study (see next compound) to the RRF of $C_8H_{18} = 133.3$. Where it assumed EthylBenzene behaves ideally and gives linear unit (16.6) response for each carbon. This overconcentration effect was, thus, measured to be about 18%. Therefore one chlorine on aromatic ring enhanced the molar response of Benzene by a minimum of 17% and maximum of 35%.

19- Ethylbenzene($C_2H_5C_6H_5$)

Ethylbenzene was included in vapor standards #1 and 3 with data listed in tables #1,2,5 and 6, plus liquid standards #7 and 9 with data listed in tables #14,15,18 and 19 respectively. The average RRF in vapor standards was 64.3 with ± 37.6 units of error. The average RRF in liquid standards was 157.5 with ± 4.8 units of errors. Data in vapor standards were low and therefore not acceptable for use. This loss was probably due to wall adsorption. The liquid data (157.5) was about 18% higher than of his corresponding hydrocarbon with 8 carbons (Octane = 133.3). High RRF of this compound is due to the effect of evaporation of lighter compounds in liquid concentrate and consequently show our data has 18% higher response in the heavier compounds (high boiling point).

20- para-dichlorobenzene($C_{12}Cl_2H_4$)

para-dichlorobenzene was included in vapor standards #1 and 2 with data listed in tables #1-4, plus liquid standards #7 and 9 with data listed in tables #14,15,18 and 19 respectively. The average RRF in vapor was 54.1 with ± 13.3 units of error. The average RRF in liquid was 131.3 with ± 9 units of error. The data in vapor standards were low and therefore determined not to be included in the statistical results. This loss was probably due to wall adsorption and/or condensation. Data from liquid standard (131.3) was about 31% higher than of Benzene. If the enhancement due to loss of the low boiling point compounds in liquid concentrate is to be considered and the response reduced then there was 13% enhancement for this compound. Again, vapor data is not acceptable, and liquid standards are recommended.

21- ortho-Dichlorobenzene(C12C6H4)

Ortho-Dichlorobenzene was included in vapor standards #1,2 and 3 with data listed in tables #1-6, plus liquid standards #7 and 9 with data listed in tables #14,15,18 and 19 respectively. The average RRF in vapor was 44.9 with ± 20.3 units of error. The average RRF in liquid was 132.1 with ± 4.6 units of error. Data in vapor was low and therefore omitted and not included in the statistical results. The liquid data was recommended in further discussion and statistical results. Data from liquid standard (132.1) was about 32% higher than of

Benzene. Considering enhancement of the response of this compound due to evaporation of the light compounds in the liquid concentrate, there is still 14% enhancement for two chlorines substituted on the aromatic ring.

22- n-Hexane(C₆H₁₄)

Hexane was included in vapor standards #1 and 4 with data listed in tables #1,2,7 and 8, plus liquid standards #6,9,10 and 13 with data listed in tables #12-13, 18-21, 26 and 27 respectively. RRF in vapor was 99.6 and in liquid was 97.5 with ± 4.7 units of error. This compounds' RRF was measured in order to check the response of our FID. Data in vapor standard #1 was dropped because Hexane and Chloroform elute at the same time and they both were used in this standard. Data in liquid standard #6 and 9 were low and this was because one of the major impurity in our hexane eluted at the same time as 1,2-DiChloroEthane. Data in vapor was only 1% higher, than of Benzene and data in liquid was 2% lower than of Benzene. Comparing average results from vapor and liquid shows that both vapor and liquid data are reliable. We can conclude that Hexane is a stable compound in vapor and liquid standards. There was an absolute difference of 2.1 units between the vapor and liquid RRF of this compound.

Hydrocarbons:

Figure-3 shows a comparison of liquid and vapor data. This comparison shows that in general most of the heavier compounds with boiling point above 110 degrees centigrade (approximately) had lower response in vapor than in the liquids. This probably was due to adsorption on the cylinder walls by these compounds and appears to be a major drawback in calibration of GC using vapor standards for heavier and/or reactive light compounds with low Boiling Point. Obviously, this major problem was not resolved completely by heating the standard cylinder, regulator, and all the transfer lines. Therefore, these results were dropped from further discussion and will be focused upon future studies.

The liquid results on the other hand consistently gave more acceptable relative molar responses on FID. The average values of liquid data were, therefore, used in the statistical analysis and further discussion in this work.

Methylene Chloride's Relative Molar Response was 10% higher than of Methane (Relative to Benzene = 100). Chloroform had response about 32% higher than methane. Bromoform's response was 13% higher than Methane. Carbon Tetrachloride's response was about 42% higher than Methane.

Therefore, from CCl_4 and CCl_3H we can observe that each chlorine increased the response of the Methane about 10%.

Methylene Chloride showed a somewhat lower than this result probably due to partial evaporation of this compound from the liquid concentrate in the vial. This could be observed when weighing the vial with liquid Methylene Chloride in it. That is, the weight decreased gradually in time. This loss must have been through syringe hole in the sealing septum (the septum was used to eliminate or reduce just this problem).

1,2-Dichloroethane's response was about 7% higher than Ethane. 1,1,1-Trichloroethane's response was only 1% higher than of ethane and 1,1,2-Trichloroethane's response was about 14% higher than ethane, but Trichloroethylene (TRIC)'s response was about 19% higher than of Ethane. Tetrachloroethylene (PERC)'s response was about 20% higher than ethane and 1,1,2,2-Tetrachloroethane (TCE)'s response was about 35% higher than of ethane.

Therefore, it is observed that two chlorines gave increased response over the ethane by 7% and three chlorines increased this response over ethane by 1% (1,1,1-ET) and 14% (1,1,2-Et) and 19% (TRIC). Four chlorines increased this response over ethane by 20% (PERC) and 35% (TCE).

1,2-Dichloro Propane's response was about 7% higher than of Propane. 3,4-Dichloro Butene's response was about 6% higher than of Butane and Bis(2-Chloroethyl) Ether's response was about 14% higher than of butane. Note that for the Dichloro

Ethane, Propane and Butene compounds showed response increase over respective hydrocarbons to be consistency +7%. At this point we can not determine how much the first chlorine contributed to the response because we did not have a compound with only one chlorine in it to run. Clearly two chlorine increased the responses by 7% in each of the C2, C3 and C4 carbon compounds.

Three chlorines contributed different results to increase ethane responses. On the average this increase was +11% the response of ethane.

Four chlorines in CCl₄ contributed 42% increase to the response over Methane, and the fourth chlorine in this compound contributed about 10% increase to the response over CHCl₃. Four chlorines on the average increased response about 27.5% the response over ethane (From PERC and TCE).

Sternberg et al.(1) and Perkins et al.(2) found the Effective Carbon Number (ECN) of Isopropyl Ether with six carbons and Diethyl Ether with four carbons to be 5.01 and 2.9 respectively (i.e. one less than the 6 or 4 carbons of the parent species). They suggested that ether group (-O-CH₂-) or (-O-CH=) has no ECR value, in other words the Ether group caused the parent compound to show a loss in response equivalent to one carbon atom. Condon et al. (23) found the experimental value of response of Diethyl Ether (C₄) to be 299

(relative to heptane = 700). Sternberg et al.(1) found the value for response of Isopropyl Ether (C6) to be 501 (relative to Octane = 800). Results obtained in this study for C1-Ether are low, and more data on this compound needs to be obtained. The Bis-Ether response on the other hand, is reported at 76.2 which is 52% higher than RRF of C3 hydrocarbon (i.e. parent 4 carbon ether - 1 carbon). Therefore, the two chlorines apparantly show enhancement of relative response in this compound, because the hydrocarbon ether response should be 50.

Hexane's response was about 2% lower than of Benzene, which shows consistency of our FID and analytical procedures to those of C6 compounds, within our limits of error.

Aromatics:

Chloro Benzene's response was about 35% higher than that of Benzene. ParaDichloroBenzene's response was 31% higher than of Benzene and OrthoDichloroBenzene's response was about 32% higher than of Benzene.

Results on chlorine substituted aromatic compounds show a 35% increase in response of benzene for the first chlorine, and a slight decrease of 4% of ChloroBenzene for the second chlorine in the aromatic ring. These results on chlorine sustituted compounds therefore show a higher response than the corresponding stated saturated hydrocarbons, olefinic and aromatics, but the second chlorine does not "apparantly"

continue to enhance the response, like it does on hydrocarbons.

Comparing data reported in this study with the few sets of data reported from previous studies (table-35), shows, in general that we obtained higher responses in Flame Ionization Detector for these Chlorocarbon compounds. These results were probably due to development and introduction of better engineered FID detectors, i.e. more complete combustion of all species entering, higher temperature flames and more complete ion collection. It should be noted that the previous studies were done with detectors more than ten years old with respect to this study.

It can be determined from our data that the RRF obtained from liquid standards for compounds in boiling point range of 40-180 C were more accurate than those obtained from vapor standards for use in calibration of FID Gas Chromatograph analysis. The data from vapor standards show that RRF's obtained for compounds with boiling points of 110 C and higher have not reliable, because these RRF's were significantly lower than the corresponding liquid data. This loss in vapor standards was probably due to:

- 1- Possible reaction of some of these compounds (i.e. CHBr_3) with the stainless steel cylinder wall and therefore wall loss in the cylinder at the slightly elevated temperature of

cylinder and lines (40 C).

2- Wall adsorption yielding incomplete desorption of these compounds, because of their relative affinity for the materials. These compounds, therefore, did not go completely into the gas-phase, as ideal gases in the vapor standard should and these yielding lower partial pressure of the species than calculated from the quantity of liquid concentrate injected.

3- Incomplete transfer (inlet) of these lighter compounds (e.g. Freon-12, Methyl Chloride) into the gas cylinder.

The results obtained here showing increased response of the chlorinated compounds over previous reported values and probably resulted from better FID detectors' design and electronics. Within the flame formed by the combustion of hydrogen and air only, relatively few ions are formed. However, if an organic compound is introduced into the flame, a relatively large increase in ion production occurs (17). If two electrodes are present in proximity to the flame and are maintained at a potential difference, the ion current produced can then provide detection and quantitation of materials entering the flames. Factors which influence FID performance are 1) design of more efficient electron and ion collector electrodes (14). 2) Use of high purity gases 3) Stabilizing and optimizing the gas-flow rates 4) Using stable, low noise electrometers 5) Higher linear velocity place greater demands upon the ion collection system. 6) Optimizing combustion processes.

Table-36 shows calibration factors reported by Guillemin et al.(15) for a number of the compounds in this study. The ratio of calibration factors of these compounds to TRIC is compared in table-37A. Table 37-B shows a ratio comparison of calibration factors to Chloroform. As can be seen from table-37B Guillemin values are all significantly higher than ours. This is because of his extremely high value for CCl_4 . On the other hand the ratio comparison with TRIC shows that there is fairly a good agreement between our results and his results for the two carbon compounds. Reported responses are too high in his results for Methylene Chloride, Chloroform and Carbon tetrachloride, and this can be seen when his response ratios increase dramatically with increase in the number of chlorines. Table-38 is a comparison of the different experimental conditions of this work and Guillemin's work. He calibrated the FID using a Gas-Density Balance which is a detector that measures the response of compounds proportional to their weight. He then assembled the density detector in parallel with his FID and measured FID calibration factors. Ratios of flow rates were significantly different for his FID as can be seen from the table, while ours were more standard flows. The ratio of air/ H_2 flow rates in his work it was 7.5, while in this work was always greater or equal to 10. The ratio of Nitrogen/ H_2 flow in his work was 1.5, while it was 1.0 in this work. While Guillemin had helium as make-up gas, we used nitrogen, but the N_2/He difference should not have affected the results.

TABLE-36

CALIBRATION FACTORS

Compounds	This Work	Guillemin Work
Methylene Chloride	5.46	1.680
Chloroform	4.54	2.643
Carbon TetraChloride	4.24	3.476
1,2-DiChloroethane	2.80	0.777
Perchloroethylene	2.51	1.244
1,1,1-Trichloroethane	2.97	1.060
1,1,2-Trichloroethane	2.64	1.028
Trichloroethylene	2.53	1.00
Tetrachloroethylene	2.22	1.220
Benzene	1.0	—

TABLE-37A "Guillemin's data vs. this study"

Compounds	This work/TRIC	G. Work	Difference
MeCl_2	2.15	1.68	-28%
CHCl_3	1.79	2.64	+47%
CCl_4	1.67	3.48	+108%
1,2-DCE	1.11	.77	-43%
PERC	0.99	1.24	+25%
1,1,1-Et	1.17	1.06	-10%
1,1,2-Et	1.04	1.03	-1%
TCE	0.87	1.22	+39%
TRIC	1.0	1.0	0.0

TABLE-37B "A ratio comparison of Guillemin's work with this work"

This work/ CCl_4		Guillemin work/ CCl_4
Methylene Chloride	1.28	0.483
Chloroform	1.07	0.760
Carbon TetraChloride	1.0	1.0
1,2-DiChloroethane	0.66	0.223
PerChloroethylene	0.59	0.308
1,1,1-Trichloroethane	0.70	0.305
1,1,2-Trichloroethane	0.62	0.296
Trichloroethylene	0.59	0.288
Tetrachloroethylene	0.52	0.351
Benzene	0.23	—

TABLE-38 "Comparison of different conditions of this work
and G.'s work"

This Work	G.Work
Used Liquid and vapor for calibration of FID	Used Gas Density Balance for calibration of FID
Flow rate $\text{Air}/\text{H}_2 \gg 10$ $\text{N}_2/\text{H}_2 = 1$	$\text{Air}/\text{H}_2 = 7.5$ $\text{He}/\text{H}_2 = 1.5$
Used Nitrogen as make- up gas	Used He as make-up gas

Figure-4 shows a graph of normalized Relative Response Factors (Response per carbon normalized to Benzene) versus atomic ratio of Chlorine/Carbon in the compound. The graph shows linearity of these normalized values within the Cl/C ratio of 0.5 to 4.

Figure-5 shows a graph of ratio of our vapor to liquid data versus Boiling temperature of the compounds (derived from table-34). This graph shows relative good linearity with a negative slope over a range of .3 - 1.2 ratio vapor/liquid (V/L) and boiling temperature range of 40-180 C. This graph strongly indicates a loss in response from vapor standard that increases in magnitude, approximately, linearly with increase in boiling points, for gaseous standards from our heated (40 C) stainless-steel cylinder, and inlet assembly. Using this RRF ratio to cancel the differences in response due to molecules composition, the loss factor of slope can be calculated to be -1.12×10^{-2} /B.P.

The data strongly suggests that use of vapor standards for compounds with boiling points above 110 C (1,1,2-Trichloroethane) should be carefully checked against liquid standards for accuracy or not used.

Figure-6 shows a graph of a Relative Molar Responses of hydrocarbons and our chlorocarbons up to C4 vs. number of carbons and number of chlorines. This graph shows a linearity of relative response over a range of C1-C4 and CL1-CL4. It

FIGURE-4

"NORMALIZED RELATIVE MOLAR RESPONSES VS.
RATIO = #CL's/#C's"

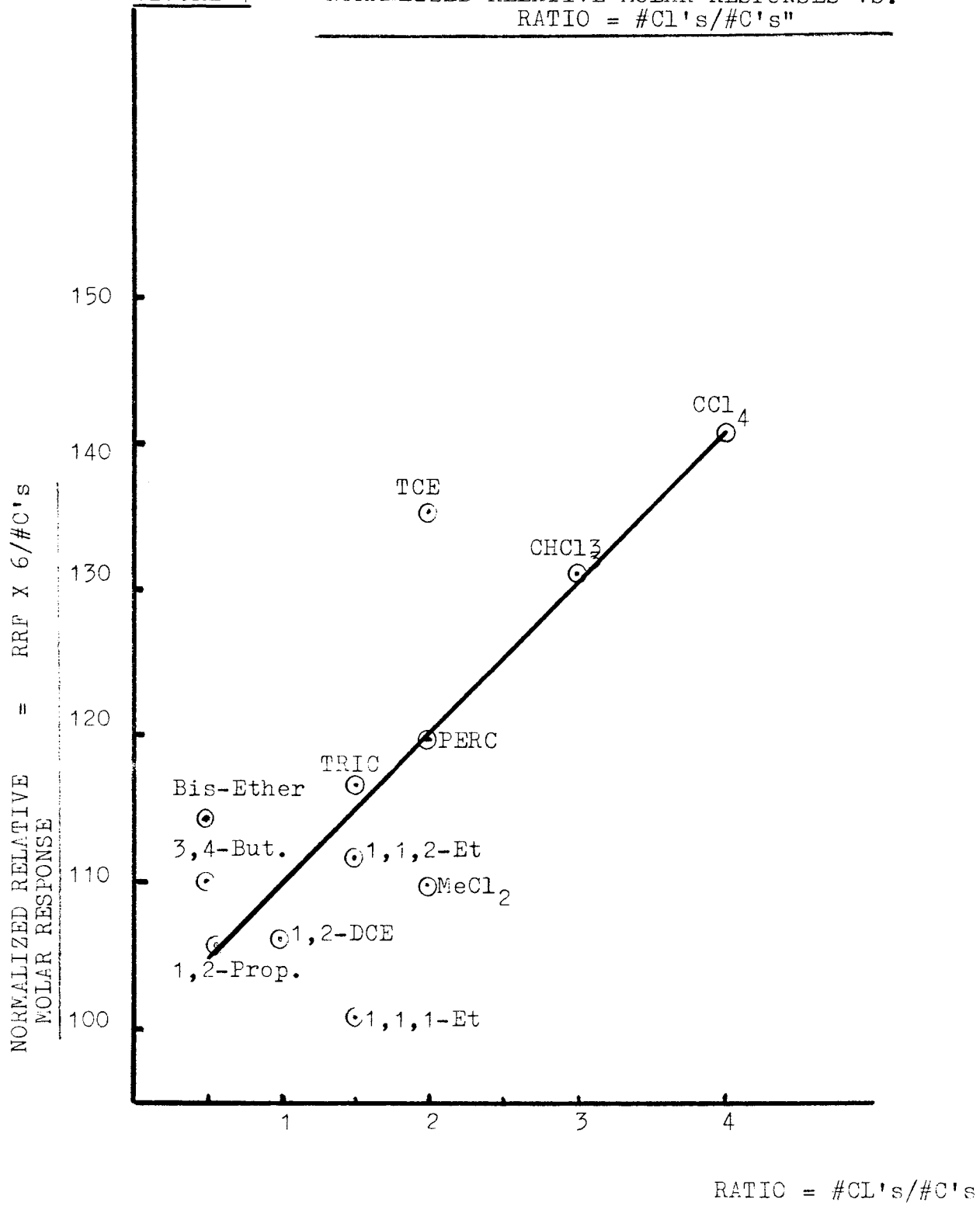


TABLE-34

VAPOR AND LIQUID DATA

Compounds	Values of Relative Responses		Ratio
	Vapor	Liquid	V/L
MeCl	7.8	—	—
MeCl ₂	22.2	18.3	1.2
Freon-12	4.73	—	—
CHCl ₃	20.6	22.0	.936
CHBr ₃	8.5	18.8	.452
CCl ₄	18.6	23.6	.788
1,2-DCE	35.2	35.7	.985
1,1-DCet	38.0	—	—
1,1,1-Et	44.6	33.7	1.32
1,1,2-Et	24.8	37.9	.657
TRIC	34.9	39.5	.883
PERC	23.9	39.9	.598
TCE	18.4	45.0	.408
1,2-Prop.	49.7	53.4	.930
3,4-But.	8.2	70.6	.123
Bis-Ether	35.5	76.2	.465
Cl-Ether	18.0	34.8	.517
Cl-Ø	73.2	135.1	.541
Et-Ø	64.3	157.5	.408
FDE	54.1	131.3	.412
ODB	44.9	132.1	.339
Hex.	99.6	97.5	1.02

FIGURE-5 "RATIO = VAPOR/LIQUID DATA VS. BOILING TEMPERATURE"

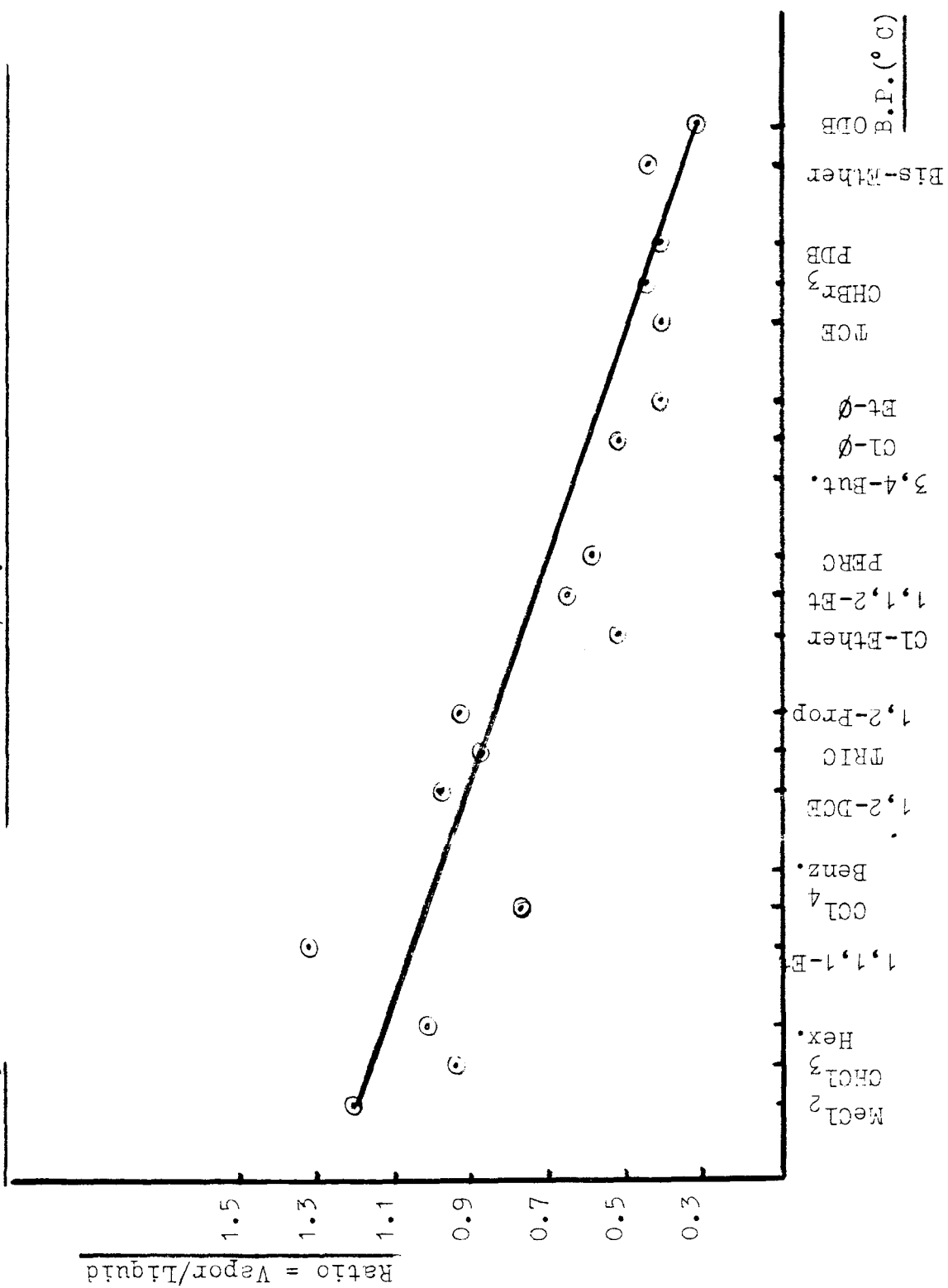
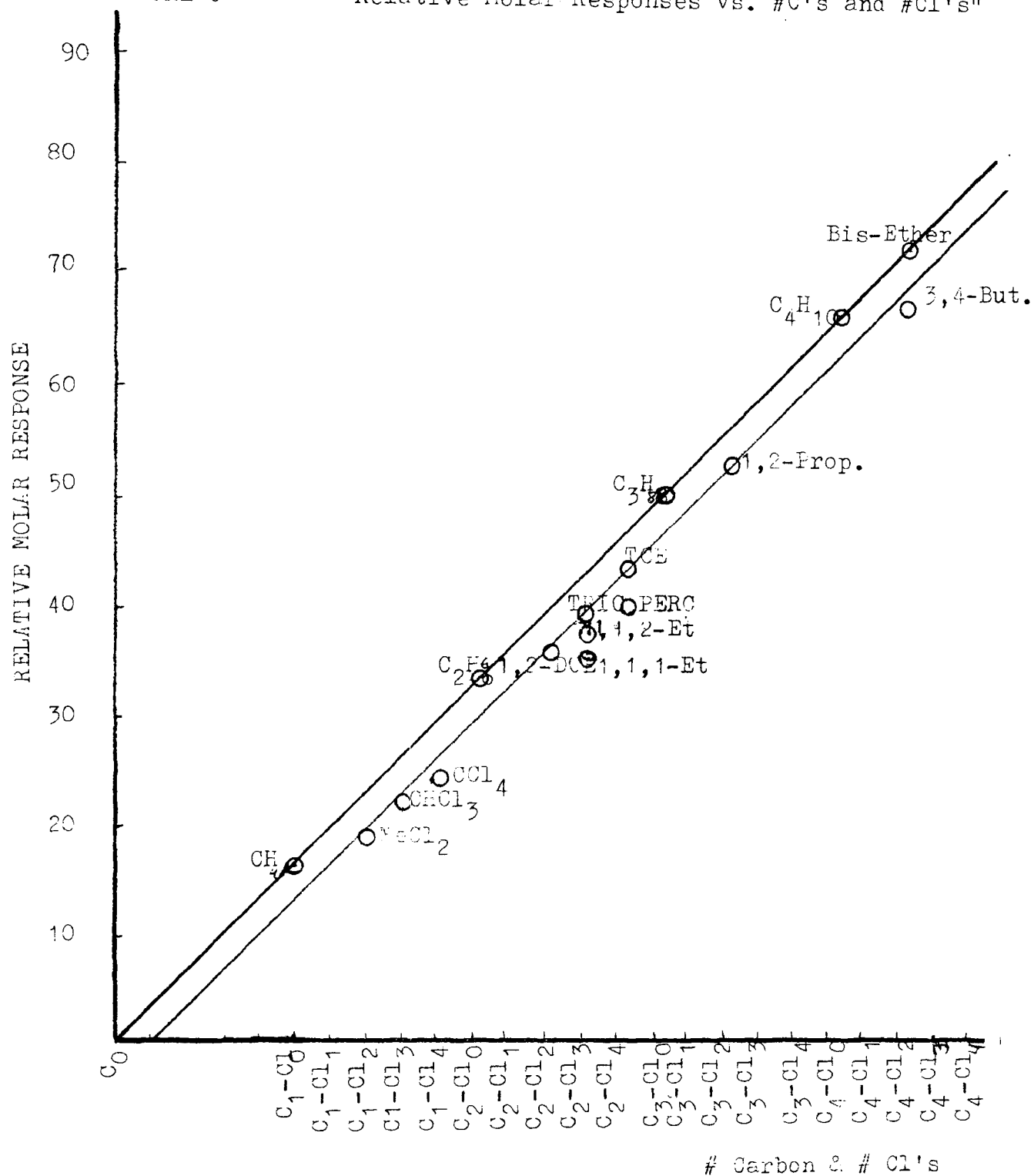


FIGURE-6

"Relative Molar Responses vs. #C's and #Cl's"



can be seen from this graph that most Chlorinated compounds lie in the vicinity of the graph line. Note that the slope of this line is the same as the slope of hydrocarbon line, but with different intercept. While the hydrocarbon line passes through CO, the chlorocarbon line has an intercept which lies below hydrocarbon line.

Figure-7 shows RRF vs. atomic ratio Cl/C for one carbon and for two carbons compounds in our work. The graph of one carbon data shows good linearity with a positive slope of .506 $\text{RRF}/(\text{Cl}/\text{C})$, and a correlation coefficient of .96, indicating for Cl compounds the FID response increases linearly. This data clearly demonstrates that chlorines enhances the FID response. Comparing this with a similiar plot of Fluorine, Figure-8, where the data is that of Blades (6), were a negative slope is clearly evident. This graph indicates that F decreases the FID response and the same argument is true for C2 compounds also. The positive slope of our line for two carbon compounds was .124.

The conclusion drawn from our results indicates that there is response enhancement due to chlorine substitution in hydrocarbons with standard operating parameters of FID-GC detector. This indicates that in current FID designs it is easier to break up the chlorinated molecules and ionize the chlorine than the corresponding hydrocarbon in the flame. Table-III shows a list of selected bond strengths. In order to breakup a $\text{CH}_3\text{-H}$ bond we need 104 KCal/Mole, but in order to

break up $\text{CH}_3\text{-Cl}$ we need only 84 KCal/Mole which is less energy. This implies that it is easier to break up $\text{CH}_3\text{-Cl}$ molecule than $\text{CH}_3\text{-H}$ molecule and produce Cl^- ions. Our data shows that this trend is carried out for chlorine substituted hydrocarbons (up to C_4). This concept continued to be true when there is chlorine substitution on the aromatic ring as can be seen from table-III bond strenght of $\text{C}_6\text{H}_5\text{-Cl}$ is less than of $\text{C}_6\text{H}_5\text{-H}$.

FIGURE-7 "Relative Response Factors vs. atomic ratio Chlorine/Carbon in one and two carbons compounds"

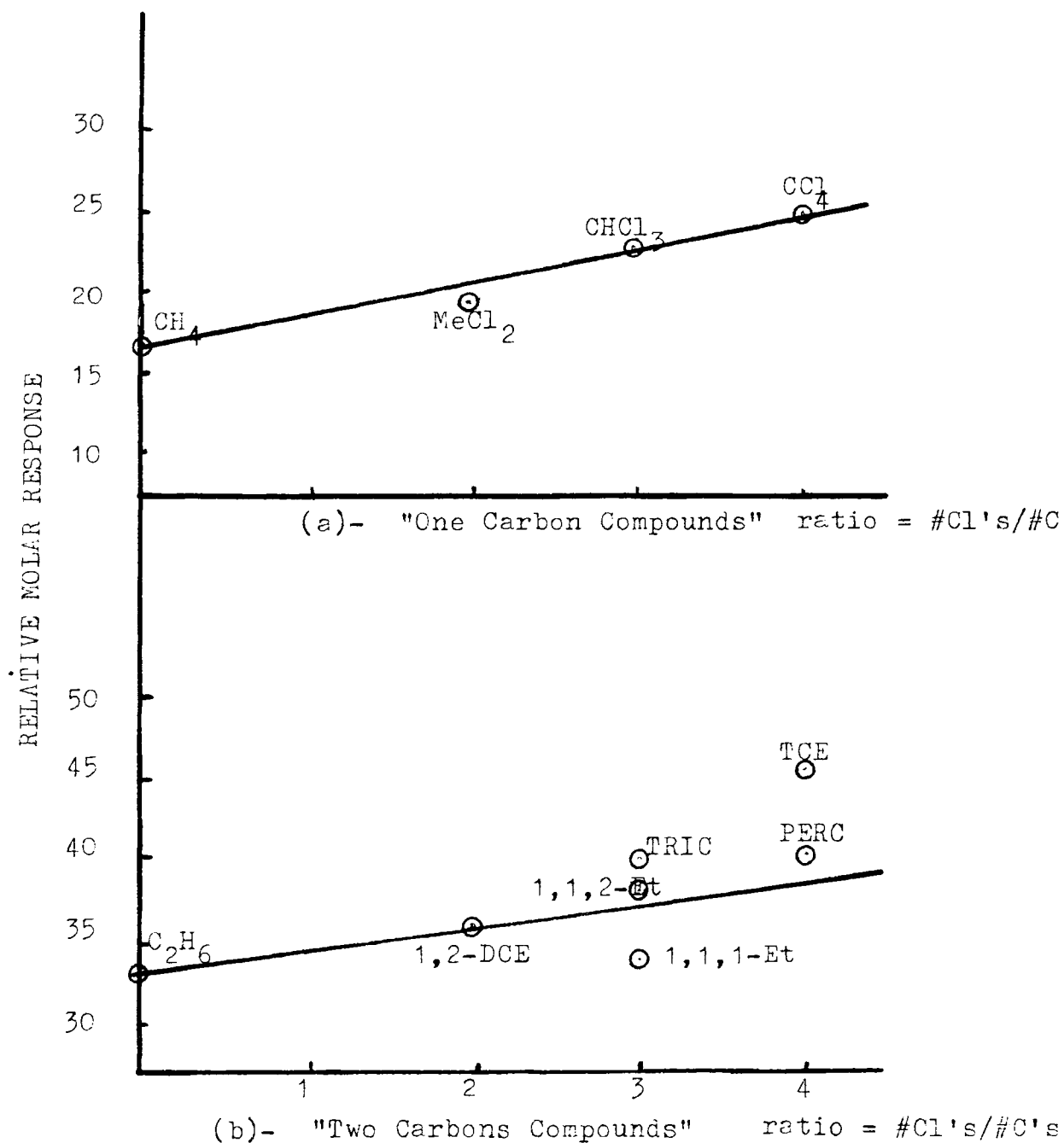


FIGURE-8 "Relative Response vs. atomic ratio of Fluorine/Carbon in one and two carbons compounds" (FROM REF. 6)

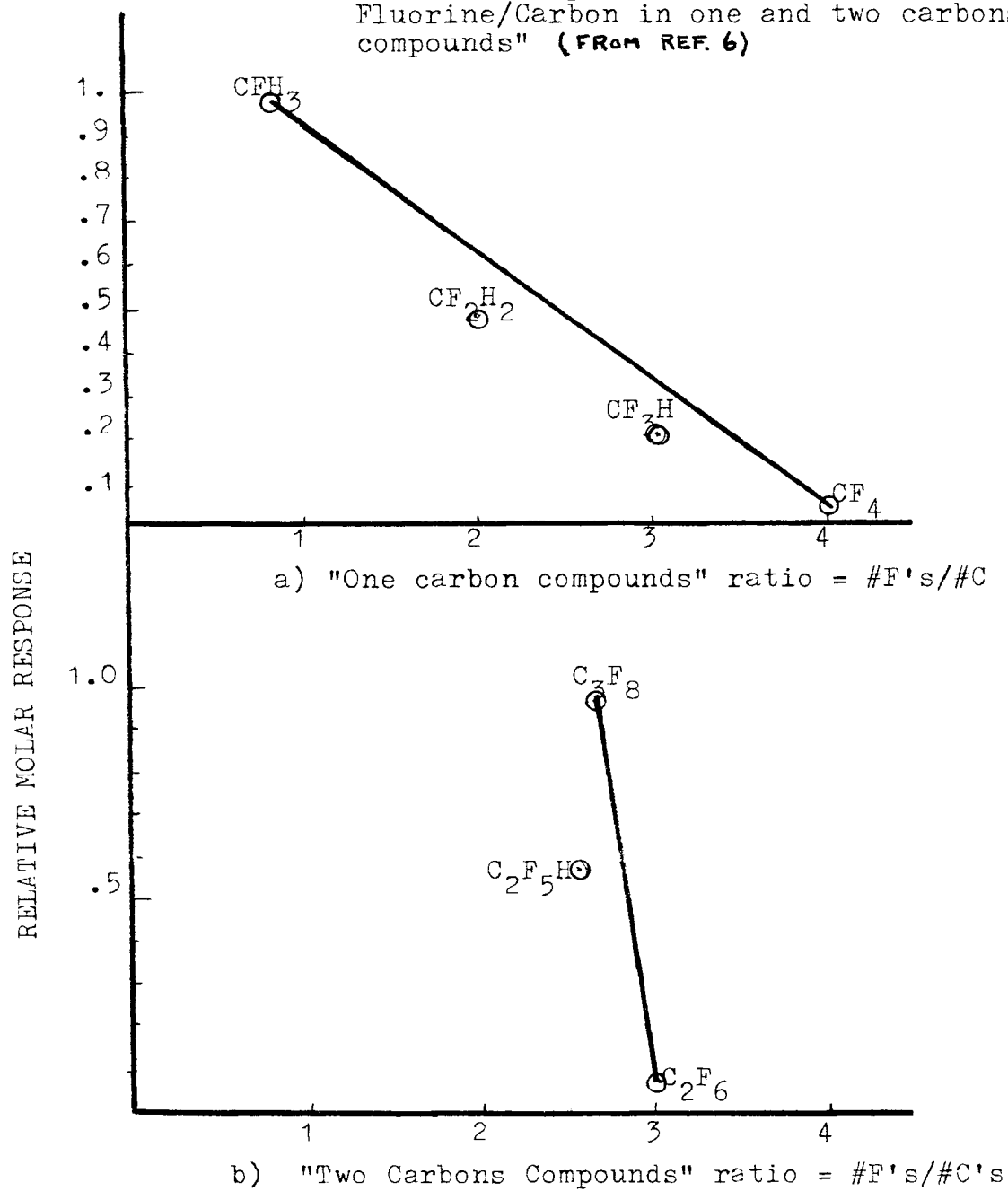


TABLE-III "Selected Bond Strengths*(R-X)Kcal/mole@298 K"

X	H	Cl
R		
CH ₃	104	84
C ₂ H ₅	98	81
i-C ₃ H ₇	95	81
t-C ₄ H ₉	92	81
C ₆ H ₅	110	95
CCl ₃	96	70

*R.C. Weast, Handbook of Physics and Chemistry, 63th ed.,
Chemical Rubber Company, F205

IV. CONCLUSION:

In order to use one single stable compound (e.g. benzene) for daily instrument calibration to replace the procedure of using a standard mixture of targeted compounds (25-35), Relative Response Factors (RRF's) and Calibration Factors (CF) developed. This was of particular advantages because the standard mixture may not have all species stable or may show loss of some components relative to others due to wall adsorption in the standard (compressed gas) stainless steel cylinder. We concluded from this work:

- 1- The use of a single standard species was made possible by developing "accurate" relative response and calibration factors of all target compounds relative to benzene in this case.
- 2- Results from liquid injection analysis showed that this is a viable and even preferential way to standardize the GC for routine quantitative analysis of a number of organic species with boiling points above 60 C.
- 3- Results from vapor injection analysis showed low accuracy for compounds with boiling points above 110 C. These results were probably due to a combination of wall adsorption, reaction with stainless steel cylinder and incomplete transfer of lighter compounds into the standard cylinder.
- 4- We obtained Relative Response Factors (Relative to Benzene), using liquid injection data. These data show that chlorines enhance the response of their corresponding hydrocarbons. This is in contrast with previous

investigators' studies which employed older detector designs. The recent engineering improvement (1970 to present) in FI detector design and geometry with optimized combustion, flow velocities, improved electrodes (for ion collection) may account for the differences.

5- We also observed a linearity of this Relative Response enhancement for chlorinated compounds when the number of chlorines increases. There was also a linearity between response versus atomic Cl/C with positive slope.

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