

IONIZATION DETECTION SYSTEMS FOR THE DETERMINATION OF
ELECTRON AFFINITIES OF ORGANIC MOLECULES

A Dissertation
Presented to
the Faculty of the Department of Chemistry
College of Arts and Sciences
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Gerald Ronald Shoemake

January 1966

363689

DEDICATION

This dissertation is dedicated to Anne for her sustained loyalty and support as well as her extraordinary patience during the past thirteen years.

ACKNOWLEDGMENT

The author wishes to express his sincere gratitude to Dr. Albert Zlatkis and Dr. James E. Lovelock under whose auspices this research was carried out. Their constant enthusiasm and constructive criticism is in large part responsible for the successful completion of this program. Acknowledgment is due to my colleagues in the Gas Chromatography Section for their many helpful suggestions and clarifying discussions. Thanks are also due to the members of the author's committee for their cooperation and helpful suggestions in the preparation of this manuscript. In particular I should like to thank Dr. W. E. Wentworth whose previous work provided the theoretical model of the electron capture phenomenon used in the latter stages of this investigation. Finally, special appreciation is extended to the National Aeronautics and Space Administration and the Public Health Service whose support provided the necessary funds and equipment to carry out this research.

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ABSTRACT

One of the most useful analytical tools for the study of organic compounds to become available in recent years is gas chromatography. Its high resolving power and extreme sensitivity for vaporizable components of a mixture make it an invaluable aid to the analyst.

A more recent advance in detection systems used in conjunction with gas chromatography is the electron capture ionization detector. This device shows a high sensitivity and a large degree of selectivity for certain organic molecules, depending upon their molecular structure. The extreme sensitivities and high degree of selectivity however can often lead to erroneous conclusions based on the data obtained. For this reason it is imperative that the information obtained from an electron capture system be correlated with other data from a non selective system in order to assign any meaning of an absolute nature to the observations.

The ionization cross section detector is the only cathodic ionization detector which is precise, reliable, robust and linear in its response. The only drawback to this otherwise ideal detector is poor sensitivity and a weak signal. A small volume ionization detector has been developed which retains all of the good qualities of the method and is potentially valuable in all applications of gas chromatography where reliability and precision at a moderate sensitivity are required. This device is used as a reference standard for the electron capture measurements.

The development of an improved ionization cross section detector and the union of this device with the electron capture detector to provide the basis for a dual gas chromatographic system, which yields simultaneous observations from both cells, forms the subject matter of this dissertation.

TABLE OF CONTENTS

PART	PAGE
DEDICATION.....	i
ACKNOWLEDGEMENT.....	ii
ABSTRACT.....	iii
I. RADIATION SOURCE SELECTION.....	1
Introduction.....	1
Experimental.....	2
Results and Discussion.....	4
II. TRITIUM EVALUATION.....	9
Introduction.....	9
Experimental.....	11
Results and Discussion.....	23
III. IONIZATION CROSS SECTION.....	30
Introduction.....	30
Physical Basis.....	32
Experimental.....	54
Results and Discussion.....	71
IV. IONIZATION CROSS SECTION - ELECTRON CAPTURE.....	104
Introduction.....	104
Physical Basis.....	106
Experimental.....	113

TABLE OF CONTENTS CONTINUED

PART	PAGE
Results and Discussion.....	117
Conclusions.....	150
V. BIBLIOGRAPHY.....	151

LIST OF FIGURES

FIGURE	PAGE
1 Experimental Arrangement for Radiation Source Selection.....	3
2 Experimental Arrangement for Temperature-Carrier Gas Study on Tritium Loss Rate.....	12
3 Ionization Chamber for Tritium Loss Rate.....	13
4 Experimental Furnace.....	15
5 Glass Envelope.....	16
6 Voltage versus Current for the Ionization Chamber.....	17
7 Experimental Arrangement for Reduced Pressure Study on Tritium Loss Rate.....	22
8 Ion Current versus Temperature for Various Carrier Gases: Before Correction for Changes in Source Strength.....	24
9 Illustration of Proper Volume Reduction in Detector Cell.....	33
10 Reference Diagram for Radiation Source Contribution to Current Flow Within Cell.....	37
11 Model of Eluted Gas Chromatographic Peak.....	39
12 Simplified Model of Eluted Gas Chromatographic Peak.....	50
13 Small Volume Plane Parallel Ionization Cross Section Detector.....	56
14 8 Microliter Volume Ionization Cross Section Detector....	58
15 Balanced Pair Ionization Cross Section Detector.....	60
16 Experimental Arrangement for the Measurement of Detector Performance for Plane Parallel Ionization Cross Section Detector.....	62
17 Exponential Dilution Chamber.....	63

LIST OF FIGURES CONTINUED

FIGURE		PAGE
18	Experimental Arrangement for Investigation of Operating Characteristics of the Balanced Pair Ionization Cross Section Detector.....	65
19	Experimental Arrangement for Investigation of Detector Performance under Reduced Pressure.....	66
20	Experimental Arrangement for Single Column Operation of the Balanced Pair Ionization Cross Section Detector...	68
21	Experimental Arrangement for Parallel Column Operation or Temperature Programmed Operation of the Balanced Pair Ionization Cross Section Detector.....	69
22	Experimental Arrangement for Series Column Operation of the Balanced Pair Ionization Cross Section Detector...	70
23	Relationship Between Ionization Current and Applied Potential for the Plane Parallel Ionization Cross Section Detector: 1 Millimeter Electrode Separation.....	72
24	Relationship Between Ionization Current and Electrode Separation for the Plane Parallel Ionization Cross Section Detector: Hydrogen and Nitrogen.....	73
25-26	Calibration of the Plane Parallel Ionization Cross Section Detector by the Exponential Decay Method.....	76-77
27	The Effect of Electrode Separation on the Linearity of Response for the Plane Parallel Ionization Cross Section Detector.....	79
28	Exponential Decay Curve of Nitrogen with Pure Helium as the Carrier Gas: Plane Parallel Ionization Cross Section Detector.....	85
29	Chromatogram Showing Separation of Low Boiling Organic Compounds.....	87
30	Series of Chromatograms for Various Quantities of Air Applied to a 5A Molecular Sieve Column.....	88
31	The Separation of Three Steroids and One Tetracyclic Aromatic Hydrocarbon.....	89

LIST OF FIGURES CONTINUED

FIGURE		PAGE
32	Chromatogram Obtained with 8 Microliter Volume Ionization Cross Section Detector.....	91
33	Two Possible Circuit Arrangements for Balanced Pair Ionization Detector.....	94
34	Chromatogram Illustrating Parallel Column Operation of the Balanced Pair Ionization Cross Section Detector...	97
35	Chromatogram Illustrating Series Column Operation of the Balanced Pair Ionization Cross Section Detector.....	98
36	Chromatogram of Temperature Programmed Operation of the Plane Parallel Ionization Cross Section Detector.....	99
37	Chromatogram Illustrating Temperature Programmed Operation of the Balanced Pair Ionization Cross Section Detector.....	100
38	Effect of Pressure on the Response of the Balanced Pair Ionization Cross Section Detector.....	101
39	Description of Terms Used in Theoretical Model.....	110
40	Experimental Arrangement for Dual System.....	114
41	Electron Concentration versus Pulse Interval.....	118
42	Saturation Current versus Pulse Interval.....	119
43	Pulse Voltage versus Current.....	123
44	Temperature Dependence of Saturation Current.....	124
45	Flow versus Pressure.....	129
46	Flow versus Pressure.....	130
47	Schematic of Flow System.....	131
48	Chromatogram of Mesityl Oxide.....	132
49	Chromatogram of Mesityl Oxide on Dual System.....	133

LIST OF FIGURES CONTINUED

FIGURE		PAGE
50	Chromatogram of Chlorocyclohexane.....	134
51	Chromatogram of Di-tertiarybutyl Ketone.....	135
52	Plots of $b - e^-/e^-$ versus Relative Sample Size - Benzaldehyde.....	138
53	Plots of $b - e^-/e^-$ versus Relative Sample Size - α -Chlorotoluene.....	139
54	Plots of $b - e^-/e^-$ versus Relative Sample Size - Cyclooctatetraene.....	140

LIST OF TABLES

TABLE		PAGE
I.	General Characteristics of Possible Radiation Sources.....	5
II.	Operating Characteristics of Radiation Sources.....	6
III.	Relative Source Strength for Experimental Radio-active Foil.....	20
IV.	Loss Rate of Tritium for Various Gases at Different Temperatures Based on a 50 Millicurie Source.....	25
V.	Estimated Half Life of Tritium Foil for Various Gases at the Temperatures Indicated.....	27
VI.	Current Measurements Indicating Tritium Loss at Reduced Pressure in a Hydrogen Atmosphere.....	29
VII.	Performance Characteristics of the Small Parallel Plate Ionization Cross Section Detector Compared with Those of a Typical Ionization Cross Section Detector.....	74
VIII.	Relative Atomic Ionization Cross Sections for Tritium Radiation: The Cross Section of the Hydrogen Atom Taken as Unity.....	80
IX.	Analysis of ASTM Test Mixture.....	82
X.	Performance Characteristics of the Balanced Pair Ionization Cross Section Detector and 8 Microliter Ionization Cross Section Detector Compared with the Plane Parallel Ionization Cross Section Detector....	92
XI.	Electron Concentration versus Pulse Interval.....	120
XII.	Saturation Current versus Pulse Width.....	121
XIII.	Temperature Dependence of Saturation Current.....	125
XIV.	Temperature Dependence of Saturation Current.....	127
XV.	Flow Relationships.....	136

LIST OF TABLES CONTINUED

TABLE		PAGE
XVI.	Summary of Data - Benzaldehyde.....	141
XVII.	Summary of Data - α -Chlorotoluene.....	145
XVIII.	Summary of Data - Cyclooctatetraene.....	147
XIX.	Relative K Values.....	149

RADIATION SOURCE SELECTION

I.

INTRODUCTION

INTRODUCTION

The introduction of ionization detectors in gas chromatography (1) has opened new areas for investigation. A cursory glance at the recent literature reveals the rapid acceptance and expansion of this analytical technique to include nearly all chemical disciplines. However, the full potential of the technique is still restricted by certain practical limitations. Foremost among these is the thermal stability of the cell proper and its associated radiation source.

In their present form the ionization detectors utilize a source of ionizing radiation with a metallic backing, for it is convenient to use the source as one of the chamber electrodes. The choice of the ionizing radiation used is determined as follows: The fluctuations in ion current will depend upon the number of primary particles generated per unit time. Therefore, an alpha radiation source which produces 10^5 ion pairs per centimeter of travel would for the same ion current be noisier than beta radiation which produces 10^2 to 10^3 ion pairs per centimeter of travel (2). Gamma radiation, which yields no more than one ion pair per centimeter is not considered as a primary radiation source since a potentially hazardous amount of radioactive material would be required to obtain a useful ion current.

The following radiation sources have been compared for their utility in gas chromatographic ionization detectors: Americium-241, Technetium-99, Tritium and Radium-226. The comparisons were made using a typical electron capture detector.

RADIATION SOURCE SELECTION

II.

EXPERIMENTAL

EXPERIMENTAL

Apparatus: The electron capture detector was that described by Lovelock (3).

The polarizing potential was provided by a Kepco Model 1500M regulated power supply for d.c. operation and an Ionics Research Model 1000 Pulser/Power Supply for pulsed operation.

The ionization current of the detector was measured using a Cary Model 31 vibrating reed electrometer, in terms of the potential developed across a known high resistance.

Chromatograms were obtained and noise measurements recorded using a Leeds and Northrup Model G potentiometric recorder.

Both the Tritium and Radiation sources were obtained from the U.S. Radium Corporation, Morristown, New Jersey. The Technetium foil was supplied by Oak Ridge National Laboratory, Oak Ridge, Tennessee. The Americium foil was prepared by the Hastings Radiochemical Works, Houston, Texas.

Procedure: Figure 1 shows a schematic representation of the experimental system used in this study. The radiation sources were installed in the detector and the necessary measurements made.

EXPERIMENTAL ARRANGEMENT FOR RADIATION SOURCE SELECTION

- A Carrier Gas Supply
- B Inlet
- C Column
- D Detector
- E Oven
- F Power Supply
- G Electrometer
- H Recorder

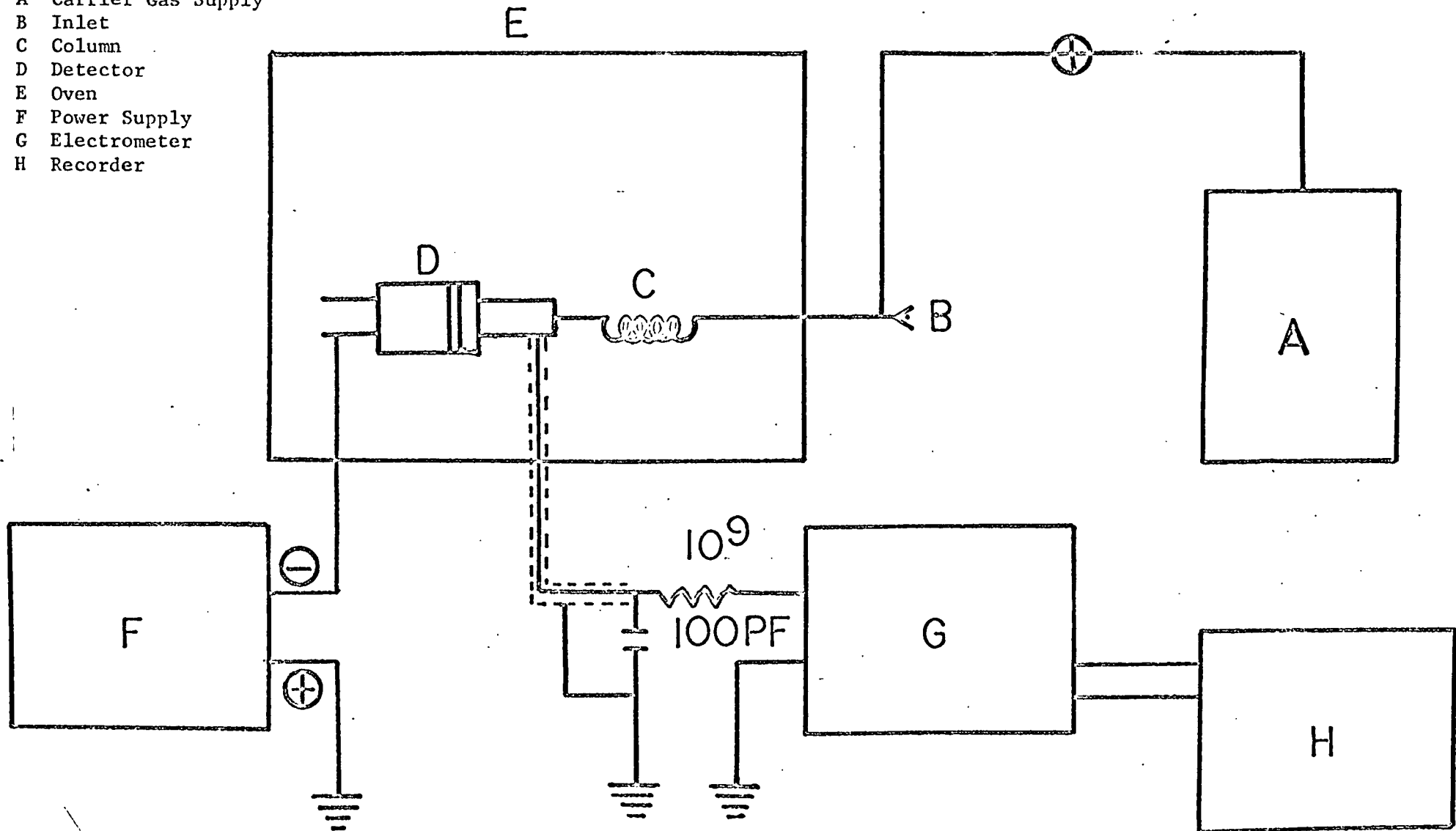


FIGURE 1

RADIATION SOURCE SELECTION

III.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Table I is a summary of the general characteristics of eight isotopes considered acceptable by the author as radiation sources for ionization detectors. Krypton-85 and Promethium-147 were omitted from the group because of technical difficulties encountered in incorporating these isotopes into a source adaptable to our particular cell design. The Krypton-85 presented the problem of leak proof gas encapsulation. A clathrate of Krypton-85 was not evaluated because it did not lend itself well to an acceptable geometry. The Promethium-147 was encapsulated in microspheres (registered trade mark, Minnesota Mining and Manufacturing Company) which had a tendency to be lost from the metallic backing. In addition enclosure of this radioisotope in glass reduced the effective ionization efficiency. Because of the low thermal neutron cross section of Nickel-62 the production of Nickel-63 was found to require long exposures at a high neutron flux in a reactor to obtain the desired amount of material. This made Nickel-63 undesirable from an economic point of view. Strontium-90, though still sometimes used, is generally considered to be hazardous because of the relatively high energy betas and the associated bremsstrahlung.

Table II outlines the general observations made with the four remaining isotopes. The surface dose rate at the detector body was noted to be higher than desired with Americium-241 and Radium-226 due to the gamma radiation accompanying the alpha emission of these elements. However, when the detector was placed in a standard gas chromatographic oven

TABLE I

GENERAL CHARACTERISTICS OF POSSIBLE RADIATION SOURCES

Source	Approximate Strength, mc	Particle	Energy MeV	γ , MeV	$t^{1/2}$ years
^3H	130	beta	.018	none	12.5
^{99}Tc	0.3	beta	.292	none	5×10^5
^{226}Ra	0.05	alpha	4.795 4.611 4.21	.64 .420 .260 .188	1622
^{241}Am	10	alpha	5.476 5.433	.06 .04 .10	457
^{90}Sr	---	beta	.55	none	28
^{63}Ni	---	beta	0.06	none	85
^{85}Kr	---	beta	0.67	.52	10.3
^{147}Pm	---	beta	.23	.121	2.6

TABLE II
OPERATING CHARACTERISTICS OF RADIATION SOURCES

Source	Carrier Gas	Surface Dose Rate, mr/hr*	Maximum Operating Temperature, °C	dc Saturation Current, amperes	dc** Noise, amperes	Pulse*** Current, amperes	Pulse** Noise***, amperes	Current Noise Ratio
^3H	Ar-5%CH ₄	0.02	200	9.5×10^{-9}	1.4×10^{-12}	1.0×10^{-9}	1.1×10^{-12}	6.8×10^3
^{99}Tc	Ar-5%CH ₄	0.06	500	2.9×10^{-11}	1.4×10^{-12}	2.7×10^{-11}	1.4×10^{-12}	21
^{226}Ra	Ar-5%CH ₄	25	500	1.14×10^{-8}	3.6×10^{-12}	8.0×10^{-9}	2.2×10^{-12}	3.2×10^3
^{241}Am	Ar-5%CH ₄	20	500	3.6×10^{-8}	4.8×10^{-12}	8.0×10^{-9}	3.6×10^{-12}	7.5×10^3

*Measurements made with a standard geiger tube at the surface of the detector body

**Measurements made with a band pass of 0 to 1 cycle per second

***Pulse characteristics: 50 microsecond period, 0.5 microsecond width, 40 volts amplitude

the dose rate at the surface of the oven was found to be less than 0.5 mr. per hour.

Noise level measurements indicate that the total electronic and chromatographic noise of the system is approximately 1×10^{-12} amperes. With Radium-226 and Americium-241 this value was increased by a factor of 3.6 and 4.8 respectively, which is still quite acceptable in most instances.

A comparison of the ratio of d.c. saturation current versus noise level indicates only minor differences between Tritium, Radium-226 and Americium-241. The low value noted for Technetium-99 was due to the small amount of the isotope present. According to the supplier (4) the foil contained all the activity practical for this application. This is based upon the amount of material that may be electroplated on a metal foil and the low specific activity of elemental Technetium-99. Since the noise level observed was essentially that of the system, the low d.c. saturation current gave rise to an unfavorable ratio.

Other data indicates that the amount of Americium-241 used in the test foils was in excess of that actually needed. Further studies are presently being carried out by the supplier to determine optimum source strength.

It appears from the foregoing data that Tritium, Americium-241 or Radium-226 would work about equally well as radiation sources for ionization detectors. Radium-226 is undesirable because its first daughter product is radon, a gas. Americium-241 offers the advantage

of having a lower energy associated gamma than the Radium-226. Tritium would appear to be the least hazardous and unless otherwise restricted would seem to be the best choice.

TRITIUM EVALUATION

I.

INTRODUCTION

INTRODUCTION

In this and other laboratories commonly employing ionization detection devices the source of radiation selected is often the relatively stable hydrogen isotope, Tritium, a pure beta emitter. The Tritium is usually available as the titanium tritide, with either copper or stainless steel backing. Detailed descriptions of the foil proper have been given by Vanderschmidt (5) and Wilson (6). The tritium betas with a mean energy of 5 Kev. are not sufficiently energetic to penetrate even a thin layer of restraining material. Bremsstrahlung from these weak betas should be negligible. For these reasons, a source contained within a detector cell should not constitute a hazard due to surface activity at the detector body.

The hazards involved with initial loading and subsequent modification of any ionization device should be of little concern to the average operator since by law this procedure is to be carried out only by qualified, licensed personnel. It has been shown (6) that the action of sample components upon the source will be minor in nature owing to their presence in such minute amounts. The most noticeable action would be from components having a corrosive effect upon the metal backing of the foil. A more detailed treatment of possible hazards arising from use of radioactive foils has been given by Taylor (7).

The National Aeronautics and Space Administration contemplate the use of gas chromatography employing ionization detectors in some of their interplanetary probes. Quite often it is necessary to operate these devices under varying conditions. For this reason it would be desirable to know

the effect of temperature, carrier gas and reduced pressure upon the stability of these foils since Tritium is a very attractive source in the laboratory development program of most of these devices. If losses should occur anomalous results would most likely be encountered without frequent calibration. Further, extreme losses might lead to hazardous conditions unless proper ventilation was provided, due to the enrichment of effluent vapor from the system in Tritium gas.

TRITIUM EVALUATION

II.

EXPERIMENTAL

EXPERIMENTAL

Apparatus: The radioactive foils used in all of these studies were obtained from U.S. Radium Corporation, Morristown, New Jersey.

The polarizing potential was provided by a Kepco Model 1500M regulated d.c. power supply.

The ionization currents were measured using a Cary Model 31 vibrating reed electrometer, in terms of the potential developed across a known high resistance.

The recorder was a Leeds and Northrup Model G potentiometric recorder.

Procedure: The data for the temperature-carrier gas were obtained from the experimental arrangement shown in Figure 2. A known flow of clean dry carrier gas was passed into a glass chamber containing the radioactive foil. The glass chamber was stationed in a furnace capable of elevating the temperature to 300°C. The effluent gas was lead through a short section of narrow diameter tubing into a large volume ionization chamber and from there to a fume hood. Figure 3 is a diagram of the actual ion chamber used in the experimental operations. The collection electrode is a 3 centimeter diameter brass tube isolated from the body of the chamber by a teflon supporting rod. The chamber body is a cylindrical brass tube 13.5 centimeters in diameter. Gas enters the chamber through a gas tight connection in the lower section and exits through a similar connection in the upper section. The total volume was measured and found to be 2 liters. The necessary electrical connections are made through the body of the chamber using gas tight teflon insulators

EXPERIMENTAL ARRANGEMENT FOR TEMPERATURE-CARRIER GAS STUDY ON TRITIUM LOSS RATE

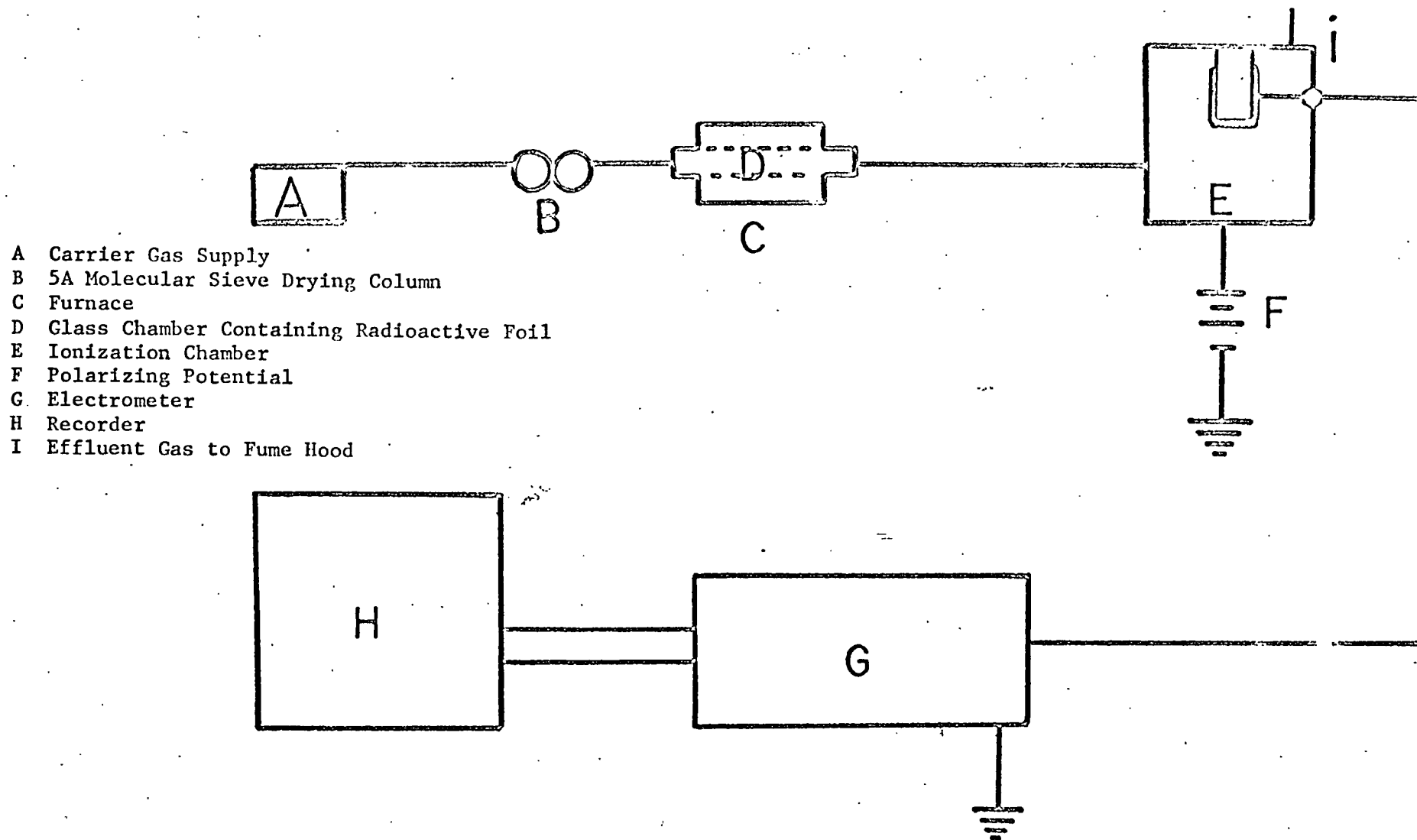


FIGURE 2

IONIZATION CHAMBER FOR TRITIUM LOSS RATE

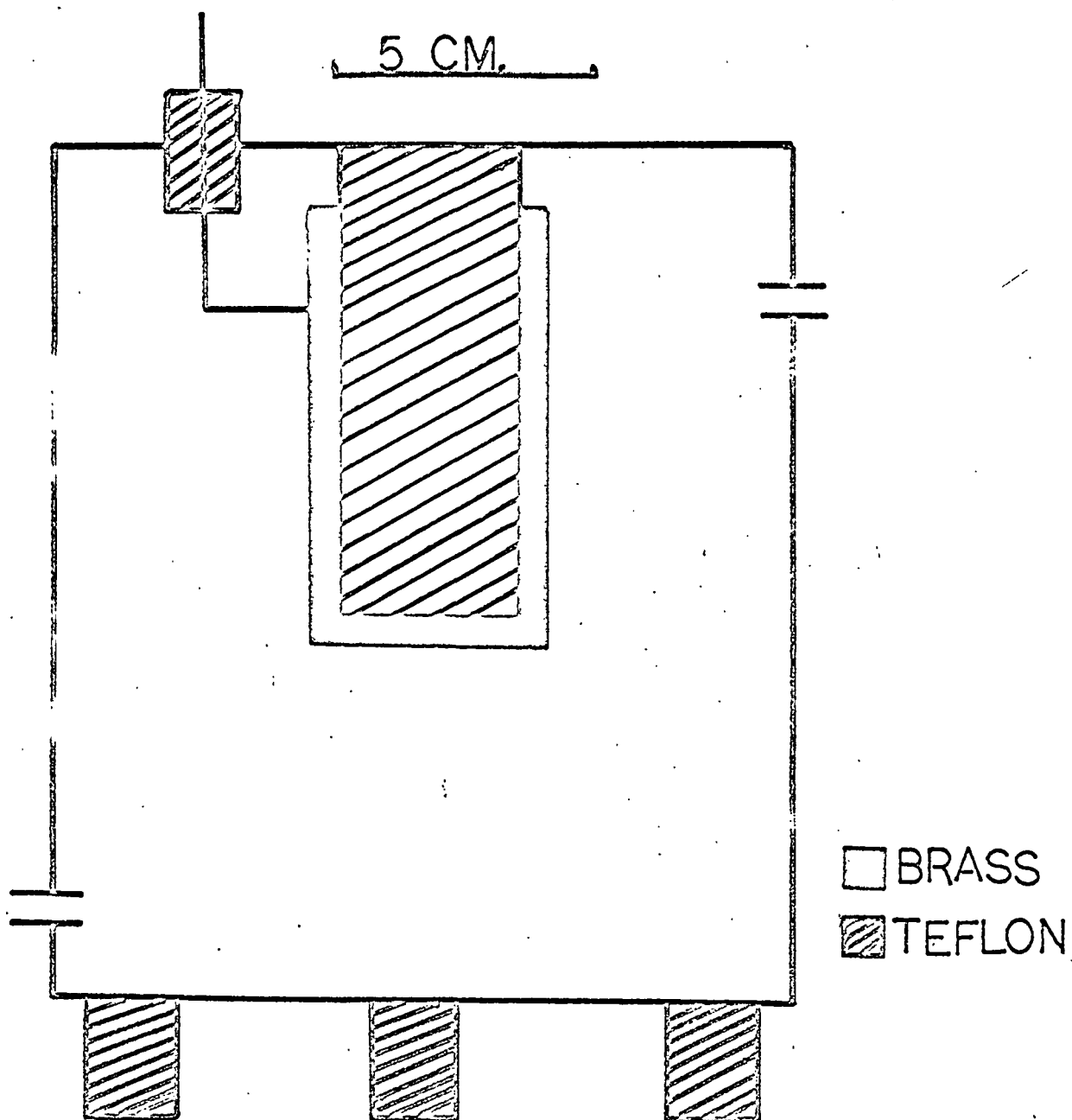


FIGURE 3

to minimize electrical leakage. A polarizing potential is developed between the detector body and the collection electrode. The electrical signal generated was fed into a high gain electrometer and subsequently recorded on the potentiometric recorder. Details of the considerations to be made in measurements of this type as well as construction details of ionization chambers in general have been given by Overman and Clark (8) and Nuclear of Chicago (9). Figure 4 is a sketch of the furnace used. It consists of a block of stainless steel properly drilled to accomodate the glass envelope, a thermocouple probe and cartridge heaters. Figure 5 shows the glass envelope. The length is chosen so that approximately one inch extends out of the furnace on either end to allow for closure using standard silicone rubber septums. This forms a gas tight system.

A voltage versus current relationship was determined to establish the proper operating conditions for the system. Figure 6 demonstrates that the chamber is operating as a simple ionization chamber at 300 volts and that all of the ions are being collected before there is a chance for recombination to occur. A measured volumetric flow of carrier gas, 100 milliliters per minute, was allowed to pass through the system for several hours until equilibrium was reached. The signal generated indicated a normal background. The furnace temperature was adjusted to the desired level and several hours were required to reach a steady state equilibrium whereby the amount of tritium gas being expelled was equivalent to the amount of tritium gas entering the chamber. The signal thus obtained indicated the concentration of radioactive species within the chamber.

EXPERIMENTAL FURNACE

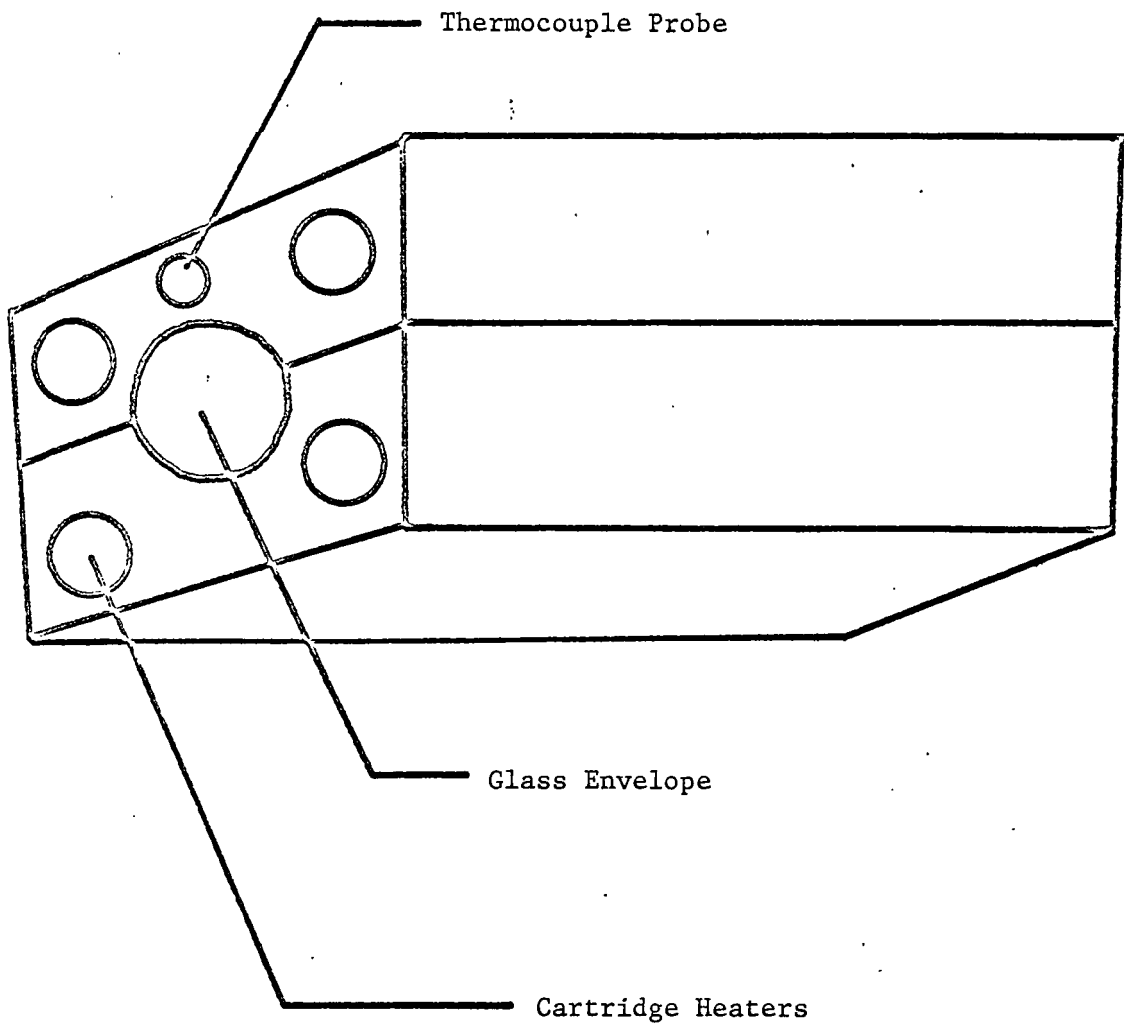


FIGURE 4

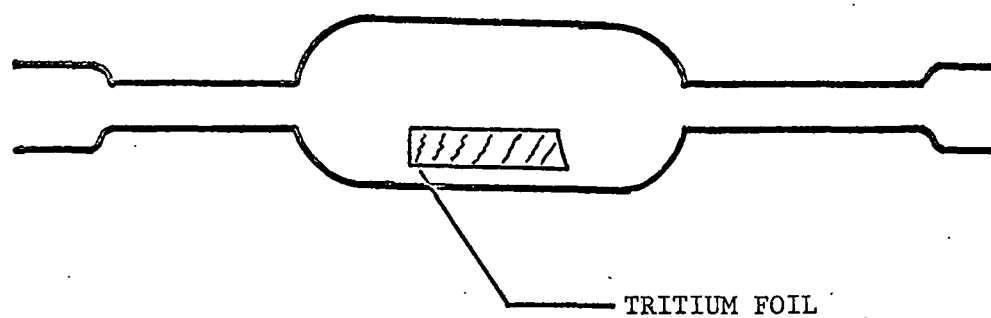


FIGURE 5

VOLTAGE VERSUS CURRENT FOR THE IONIZATION CHAMBER

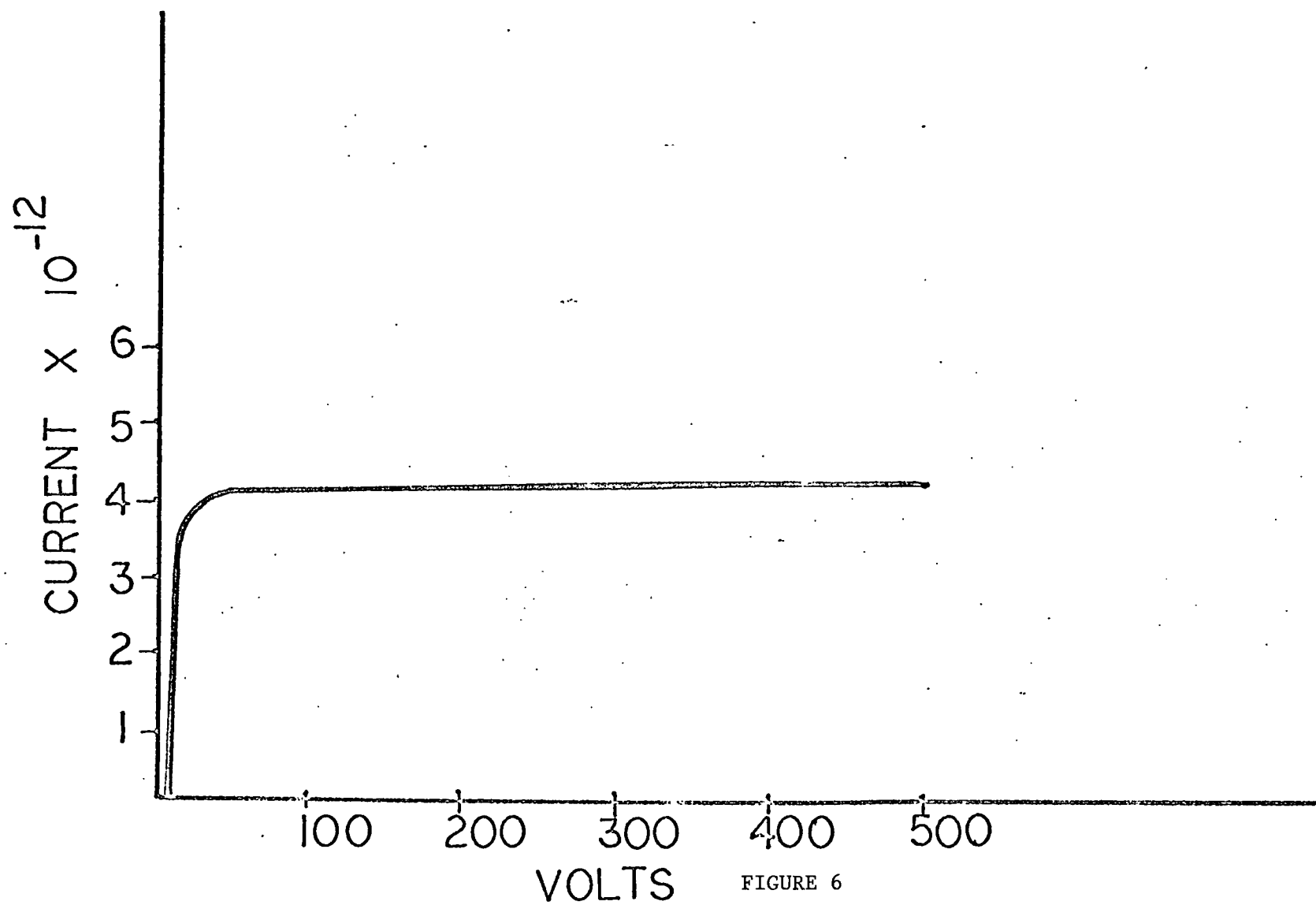


FIGURE 6

Tritium betas have a maximum range of about 1 centimeter in air at S.T.P.. The dimensions of the ionization chamber were so arranged that the distance between electrodes far exceeds this value. This would imply that the total energy of the tritium betas should be dissipated in the gas phase. The number of ion pairs formed per beta particle should, to a very close approximation, be equal to the average energy of the tritium beta divided by the specific ionization energy of the gas under consideration. Values for specific ionization energies have been presented by Sharpe (10). The average value is around 30 ev.. The concentration of radioactive species within the chamber at equilibrium was obtained from the following relationship.

$$I = \frac{c}{t}$$

where: I = current, amperes

c = coulombs

t = time, seconds

Since 1 coulomb is equal to 6.281×10^{18} electrons:

$$I = 6.281 \times 10^{18} \text{ electrons per second.}$$

The total number of ion pairs (electrons) formed should be to a very close approximation the average energy of the tritium betas divided by the ionization potential of the gas under consideration. This yields the following:

$$Z = \frac{5 \times 10^3}{P}$$

where: Z = number of ion pairs formed

5×10^3 = average energy of tritium betas, ev.

P = ionization potential of the gas

Combining the above equations:

$$Y = \frac{I (6.281 \times 10^{18}) P}{5 \times 10^3}$$

where: Y = tritium disintegrations per second

Since 1 microcurie is equal to 3.70×10^4 disintegrations per second:

$$C = \frac{I P (6.281 \times 10^{18})}{(5 \times 10^3)(3.70 \times 10^4)} \text{ microcuries}$$

where: C = concentration of radioactive species.

Then,

$$R = \frac{C F}{V}$$

where: F = flow rate of gas, milliliters per second

V = chamber volume, milliliters

R = loss rate of Tritium

A single radioactive foil was used in all of the experiments herein reported. Its activity was measured before and after each investigation in terms of the current it provided in a small ionization chamber under a standard set of conditions. Allowances were made in the calculations for any change in the observed activity. Table III shows the measurements made and the calculated source strength before each determination.

TABLE III

CALCULATED SOURCE STRENGTH

Gas	Current amps.	Proportion	Source Strength millicuries
Hydrogen	4.25×10^{-9}	1.00	50.0
Helium	3.95×10^{-9}	1.08	46.5
Nitrogen	3.55×10^{-9}	1.20	41.7
Air	3.30×10^{-9}	1.29	38.4
Argon-5% Methane	2.75×10^{-9}	1.54	33.4
Argon-Water	2.50×10^{-9}	1.70	30.0

In the study of Tritium loss at reduced pressures in a hydrogen atmosphere the apparatus in Figure 7 was utilized. A Tritium foil was cut to the dimensions 1.1 by 0.8 centimeters and placed in a conventional parallel plate ionization chamber. The specific activity of the Tritium was 1 curie per square inch so that a foil of these dimensions would be approximately 130 millicuries. The ionization current in hydrogen was determined. This current value was used as an indication of the source strength. Having been tested as to approximate activity the source was placed in the glass capsule, C, and this in turn connected to a hydrogen cylinder, vacuum pump and absolute pressure indicator, as indicated in Figure 7. The capsule was completely evacuated, then filled with hydrogen gas three separate times to assure the removal of most of the gaseous contaminants. The capsule was next evacuated until the absolute pressure was 1 millimeter of mercury. Hydrogen was slowly admitted until the desired pressure was reached. The system was allowed to come to equilibrium and the capsule was sealed, at A. Thus prepared the radioactive sources were allowed to stay for six months, at which time they were removed and the current again measured as previously outlined. The samples were again encapsulated and left for an additional three months. A final current measurement was performed at the end of this period.

EXPERIMENTAL ARRANGEMENT FOR REDUCED PRESSURE STUDY
ON TRITIUM LOSS RATE

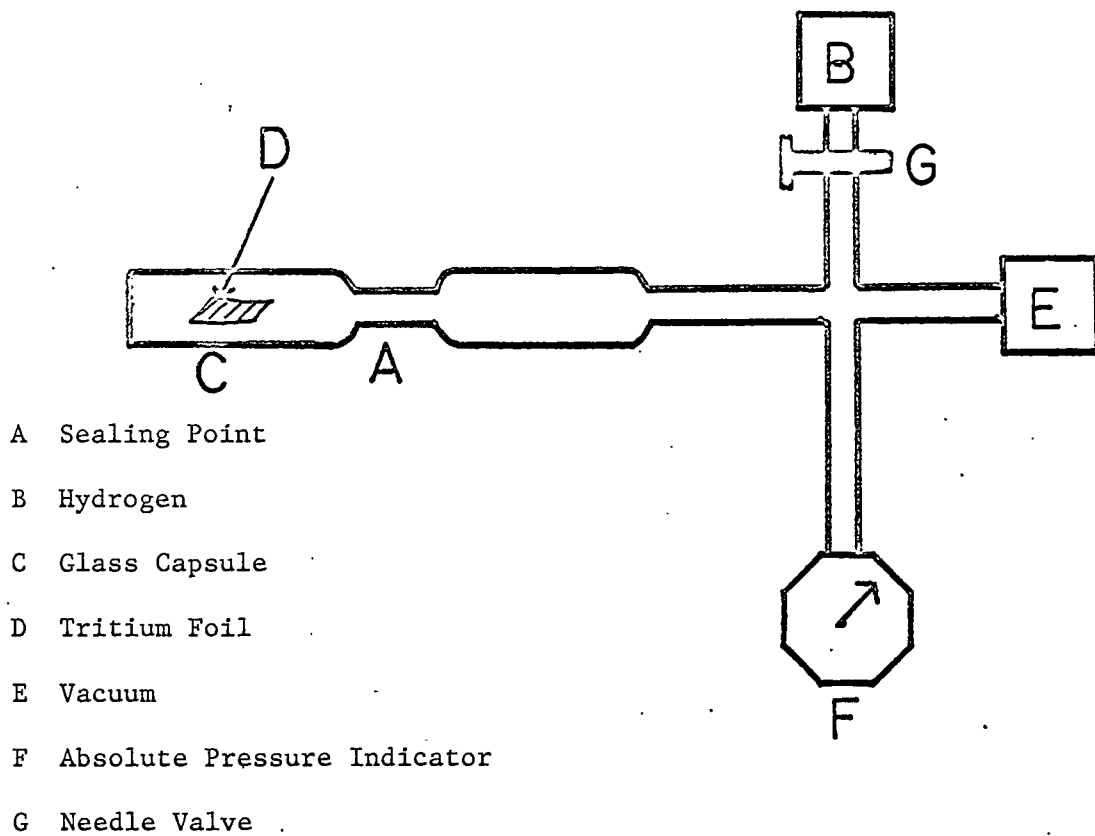


FIGURE 7

TRITIUM EVALUATION

III.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

In observing the effect of temperature and carrier gas on the loss rate of tritium the gases studied were hydrogen, helium, nitrogen, air, argon-5% methane, and argon saturated with water vapor. The temperature ranged from ambient to 290°C. Figure 8 shows the ion current observed versus temperature for the above gases. As might be expected, the current rises very rapidly above 200°C indicating an appreciable loss of Tritium from the radioactive foil. The exception noted was with hydrogen. In this case noticeable losses occur above 140°C. This observation could be accounted for if an exchange occurred between the hydrogen gas and the Tritium contained on the foil as titanium tritide. Such an observation would appear to be reasonable since similar observations could not be made with the other gases.

Table IV lists the calculated loss rate of Tritium in various carrier gases with respect to temperature. The loss rate, R , is given in units of microcuries per second and the more practical units of millicuries per day. R is seen to range in value from 10^{-2} to 6 millicuries per day depending upon the gas used and the operating temperature. These values are in close agreement with those given by Wilson (6). The concentration, C , of Tritium gas in air, assuming a 1000 cubic foot room with a turnover rate of one volume per hour is presented. The assumed enclosure and ventilation conditions are worse than those normally encountered. Nevertheless, it should be noted that the maximum permissible concentration in air for tritium is not exceeded.

ION CURRENT VERSUS TEMPERATURE FOR VARIOUS CARRIER GASES:

BEFORE CORRECTION FOR CHANGES IN SOURCE STRENGTH

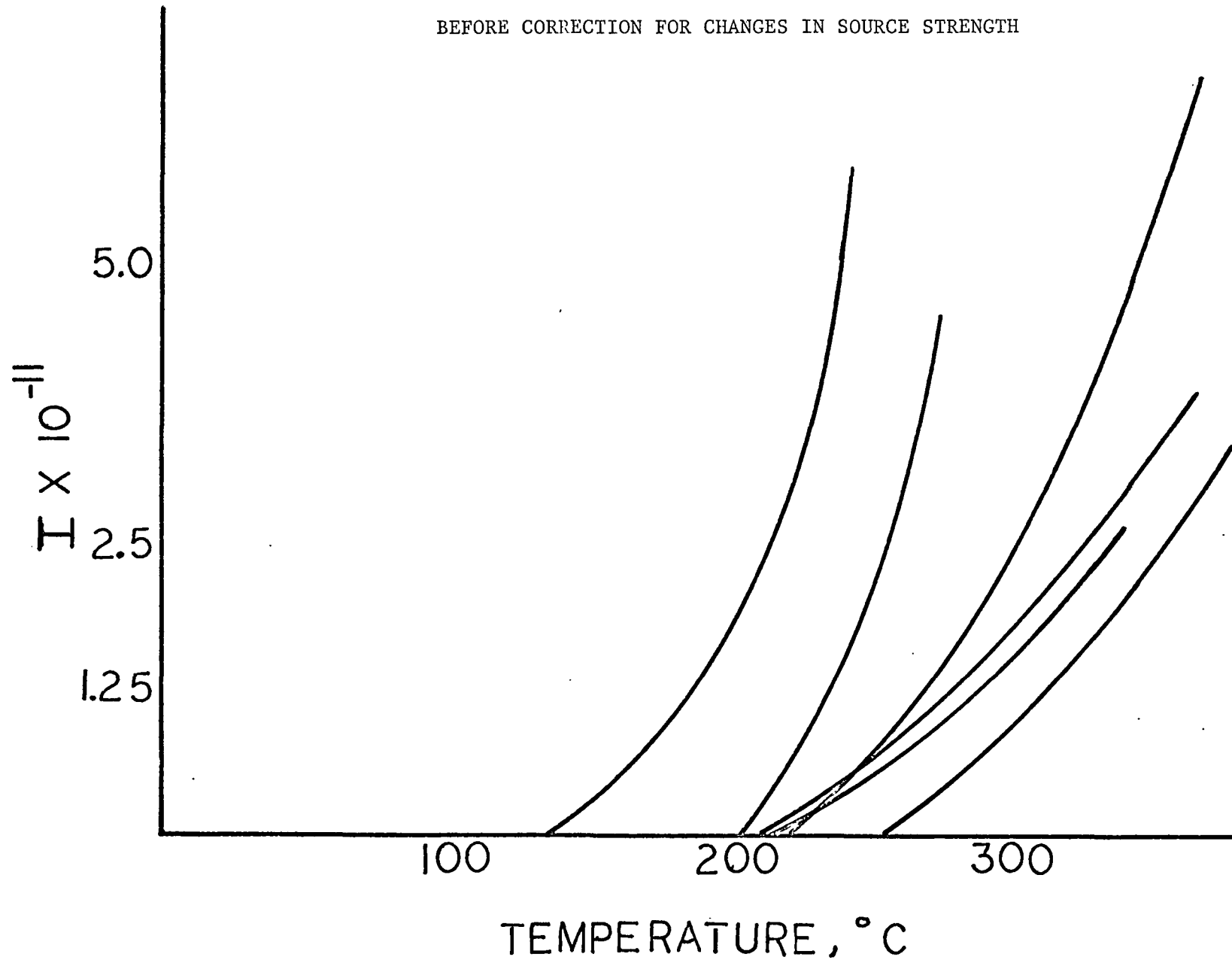


FIGURE 8

TABLE IV
LOSS RATE OF TRITIUM FOR VARIOUS GASES AT DIFFERENT
TEMPERATURES BASED ON A 50 MILLICURIE SOURCE

Gas	Temperature °C	R $\mu\text{C}/\text{sec}$	R mC/day	C $\mu\text{C}/\text{cm}^3$
Helium	190	0.73×10^{-3}	6.31×10^{-2}	0.93×10^{-7}
	243	5.72×10^{-3}	4.94×10^{-1}	7.26×10^{-7}
	290	2.38×10^{-2}	2.05	3.02×10^{-7}
Argon- 5% Methane	190	6.10×10^{-4}	5.27×10^{-2}	7.75×10^{-8}
	240	5.20×10^{-3}	4.49×10^{-1}	6.60×10^{-7}
	290	2.60×10^{-2}	2.24	3.30×10^{-6}
Argon- Water	240	6.50×10^{-3}	5.61×10^{-1}	8.25×10^{-7}
	280	2.20×10^{-2}	1.90	2.79×10^{-6}
Nitrogen	185	4.22×10^{-4}	3.64×10^{-2}	5.35×10^{-8}
	240	5.93×10^{-3}	5.12×10^{-1}	7.55×10^{-7}
	285	4.49×10^{-2}	3.87	5.70×10^{-6}
Air	240	3.63×10^{-3}	3.13×10^{-1}	4.60×10^{-7}
	285	6.50×10^{-2}	5.61	8.25×10^{-6}
Hydrogen	148	4.57×10^{-4}	3.94×10^{-2}	5.80×10^{-8}
	195	1.05×10^{-2}	9.00×10^{-1}	1.33×10^{-6}
	250	4.62×10^{-2}	3.99	5.85×10^{-6}
	290	4.29×10^{-2}	3.70	5.35×10^{-6}

Table V gives the calculated half life of an average Tritium foil in various gases at the indicated temperature. The calculated half life is based on the assumption that the loss is exponential and therefore obeys simple first order kinetics. This may be expressed:

$$-\frac{1}{c} \frac{dc}{dt} = K$$

Having obtained the value for K one may write:

$$t^{1/2} = \frac{\ln 2}{K} = \frac{0.69}{K}$$

where: $t^{1/2}$ = calculated half life

c = concentration of activity on the foil

K = constant

$\frac{dc}{dt}$ = loss rate of tritium

The half life is based solely on the loss rate and does not indicate the decrease in activity due to normal radioactive decay. The decrease in activity due to radioactive decay will not be of the same order of magnitude as the loss rate at elevated temperatures and therefore may be disregarded. Calculated half life values due to leakage range from 960 days at 185°C to 6.16 days at 285°C, again depending on the gas present. A slight discrepancy in the data for hydrogen is noted between 250°C and 290°C. This may be accounted for by considering the rapid decrease in source activity at these temperatures. From the calculated half life values one would predict that the observed saturation current of a detection device should decrease to one

TABLE V
ESTIMATED HALF LIFE OF TRITIUM FOIL FOR VARIOUS GASES
AT THE TEMPERATURES INDICATED

Gas	Temperature °C	Calculated Half Life days
Helium	190	547.
	243	71.2
	290	16.9
Argon-	190	650.
5% Methane	240	72.6
	290	14.7
Argon-	240	61.5
Water	280	18.2
Nitrogen	185	960.
	240	67.6
	285	8.96
Air	240	109.
	285	6.16
Hydrogen	148	887.
	195	38.4
	250	8.64
	290	9.35

half of its original value in one half life of the associated radioactive foil. In practice this has not always been found to be true. This apparent contradiction can best be explained by considering the characteristics of each individual source, which can reasonably be expected to vary from one source to another.

The data obtained in this investigation provide a guide for the selection of operating parameters when using tritium foils at elevated temperatures. Minor variations might occur for a given source. However, the general observations should remain valid.

The generally accepted maximum operating temperature for Tritium foils is around 225°C. This study confirms this value except when using hydrogen as the test gas. For molecular Tritium, the occupation maximum permissable concentration in air is 2×10^3 microcuries per cubic centimeter. Thus if the ventilation conditions for a given site are known, the foregoing guide may be used to determine approximate concentration levels.

Table VI is a summary of the data for Tritium loss at reduced pressure in a hydrogen atmosphere. The loss was not significant. Minor losses do indeed occur but they will not be of sufficient order of magnitude to warrant further consideration.

TABLE VI
CURRENT MEASUREMENTS INDICATING TRITIUM LOSS
AT REDUCED PRESSURE IN A HYDROGEN ATMOSPHERE

Source Notation	Approximate Activity	Initial Current (amp)	Pressure*	Final Current (amp)	
				t = 6m	t = 9m
#1	130 mc	9.0×10^{-9}	1 mm (3)	5.6×10^{-9}	5.6×10^{-9}
#2	130 mc	8.5×10^{-9}	21 mm (24)	4.7×10^{-9}	4.5×10^{-9}
#3	130 mc	7.8×10^{-9}	158 mm (163)	5.0×10^{-9}	4.7×10^{-9}
#4	130 mc	7.2×10^{-9}	200 mm (202)	4.6×10^{-9}	4.6×10^{-9}
#5	130 mc	7.2×10^{-9}	508 mm (511)	4.1×10^{-9}	4.2×10^{-9}
#6	130 mc	8.0×10^{-9}	694 mm (689)	5.3×10^{-9}	4.9×10^{-9}

Note: The experimental error for these measurements is estimated to be no better than $\pm 10\%$ due to contamination of carrier gas and geometry factors involved in the measurement of currents in a simple ionization chamber such as the 1 mm parallel plate cross section detector.

*Numbers in parentheses indicate pressures for the additional 3 months testing.

IONIZATION CROSS SECTION

I.

INTRODUCTION

INTRODUCTION

The ionization cross section detector is recognized to be the only cathodic ionization detector which is precise, reliable, robust and linear in its response. As described by Pompeo and Otvos (11) it is in all respects one of the closest approaches so far to the perfect gas chromatography detector. It is rugged, insensitive to changes in carrier gas flow rate and does not require a precisely regulated source of polarizing potential. The only weakness to this otherwise nearly perfect detector is that it is insensitive both in terms of the smallest quantity detectable and in terms of the signal output for a given unit mass of detectable substance. Following a suggestion by A. J. P. Martin (12) the mass sensitivity of this detector has been increased more than 100 fold by the simple expedient of reducing the sensing volume.

The physical basis underlying the operation of the ionization cross section detector is examined and extensively developed to ascertain the absolute aspect.

The development of this detector was also stimulated by a practical need for a rugged, reliable and reproducible detection system for the proposed planetary atmosphere measurements of the National Aeronautics and Space Administration (13). In particular, a detector with a sensing volume of only 8 microliters with an even higher sensitivity to small masses is described. Also, an integrated pair of detectors arranged to provide compensation for large changes in ambient temperature, pressure and composition of the carrier gas has been studied.

Examples of the practical use of the detector in gas chromatography are given, for it appears to have potentialities in gas chromatography generally.

IONIZATION CROSS SECTION

II.

PHYSICAL BASIS

PHYSICAL BASIS

The ionization cross section detector is a concentration sensitive device rather than a mass sensitive one. Sensitivity with respect to concentration of a gas is dependent upon the number of molecules present per unit volume within the detector whereas mass sensitivity is dependent upon the total amount of test substance present. Following Martin's suggestion the mass sensitivity has been increased by the simple expedient of properly reducing the sensing volume. To perhaps illustrate this important point we will refer to Figure 9. As the volume is decreased to positions 2, 3, 4, etc., it is seen that the radiation field intensity will be increased because the number of beta particles per unit volume is increased. Simply stated the number of beta particles is unchanged but the volume has been decreased. The concentration is not changing because the number of gas molecules per unit volume is not altered. If the radiation source intensity is adjusted slightly so that the observed current remains the same as the volume is reduced then the mass sensitivity is increased. Obviously the total number of gas molecules in position 4 is less than in position 1 but the current is unchanged. To better illustrate this difference consider a detector with a volume such that only a single molecule can be accommodated at any time. From a concentration standpoint, this detector would be totally insensitive because anything less than 100% vapor concentration would not be detected. However, from the standpoint of mass sensitivity this detector would be the ultimate because it would have the ability to detect the presence of a single molecule.

ILLUSTRATION OF PROPER VOLUME REDUCTION IN DETECTOR CELL

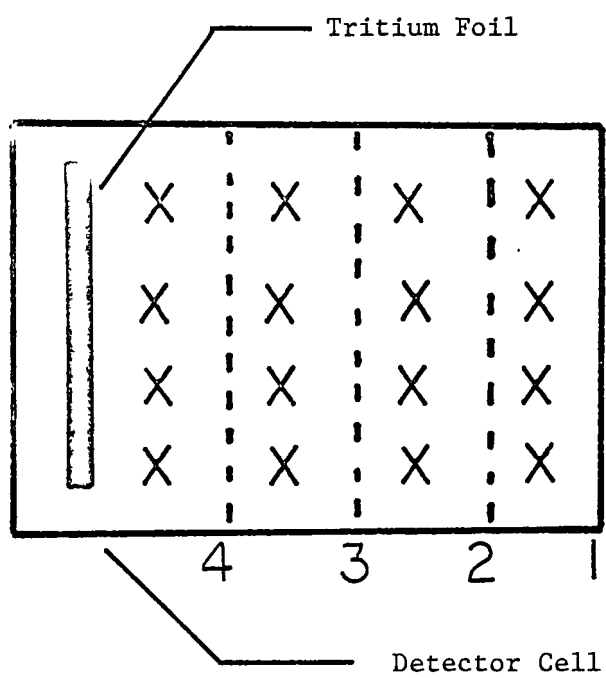


FIGURE 9

The general physical basis of ionization cross section measurements in chemical analysis has been comprehensively described by Otvos and Stevenson (14). These authors report that the total molecular cross section for ionization by a given radiation is the simple addition of the constituent atomic cross sections for the molecule for the same radiation and is almost completely independent of the nature of the chemical combination. The validity of such predictions are discussed in length in the work of Deal, et.al. (15) and of Boer (16).

An ionization cross section detector consists of an ionization chamber connected to a source of potential and some means of measuring the current flow within it. The gas in the chamber is irradiated with ionizing radiation from either an external or internal source. The ionization current when the chamber contains a light gas such as hydrogen or helium is small but increases on the addition of any other gas or vapor.

The physical principles on which the improved detectors are based are as follows: Consider the model of a single beta particle as it passes between two plates separated by a gas. The number of ion pairs formed due to ionization will be some function of the ionization cross section of the gas molecules present, assuming that the beta particle traverses the entire distance between the plates and dissipates only a minor portion of its energy during the journey. This may be expressed:

$$i = f(Q)$$

where: i = the number of ion pairs formed per unit length of travel of the beta particle.

Q = ionization cross section of the gas.

Since the number of ion pairs formed is also obviously dependent upon the number of gas molecules present we may write:

$$i = k n Q$$

where: k = constant

n = number of moles of gas present

If the gas separating the plates is hydrogen or helium and other components present are in low concentration we may use the ideal gas relationship to a very close approximation.

This yields the relationship:

$$i = k \frac{PV}{RT} Q$$

where: P = absolute pressure

V = volume of cell

R = gas constant

T = absolute temperature

If we now have ℓ beta particles that traverse the distance between the plates per second the rate of ion production will be:

$$\ell i = \ell k \frac{PV}{RT} Q$$

If a sufficient electrical potential is applied across the plates the drift rate of the ions formed will be such that they are collected before recombination can occur. If this is true then the rate of ion production will be equal to the current flow in the system, i.e.

$$I = \ell i = \ell \frac{PV}{RT} Q$$

However, since the beta particle itself is indistinguishable from the secondary electrons from ion production they will also be a contributing factor in the total current flow through the system. To illustrate this point refer to Figure 10. If the space between A and B is completely devoid of gas and a beta radiation source is attached at either electrode A or B a potential will develop across R_i . Polarity depends upon the source position and is independent of the applied potential P_i . If the source is at A, B will be negative due to the arrival of the beta particles at B. If the source is at B, A will be positive due to the positive nuclei left embedded in the radiation foil. Therefore the total current flow due to both ionization of the gas and collection of the primary beta particles will be:

$$I = \left[k \ell \frac{PV}{RT} Q \right] \pm \ell$$

It has been shown that for a gas mixture the current in an ionization cross section detector will be a function of the summation of the products of the mole fraction and ionization cross section for each component:

$$I = \left[k \ell \frac{PV}{RT} \sum X_i Q_i \right] \pm \ell$$

where: X_i = mole fraction.

When an ionization device is used as a detector in gas chromatography it is usual to offset the signal due to the ionization of the carrier gas and observe only the current due to the presence of test substance. For the carrier gas alone:

$$I_o = \left[k \ell \frac{PV}{RT} Q_c \right] \pm \ell$$

since $X_c = 1$.

REFERENCE DIAGRAM FOR RADIATION SOURCE CONTRIBUTION
TO CURRENT FLOW WITHIN CELL

SOURCE OF POTENTIAL P_i

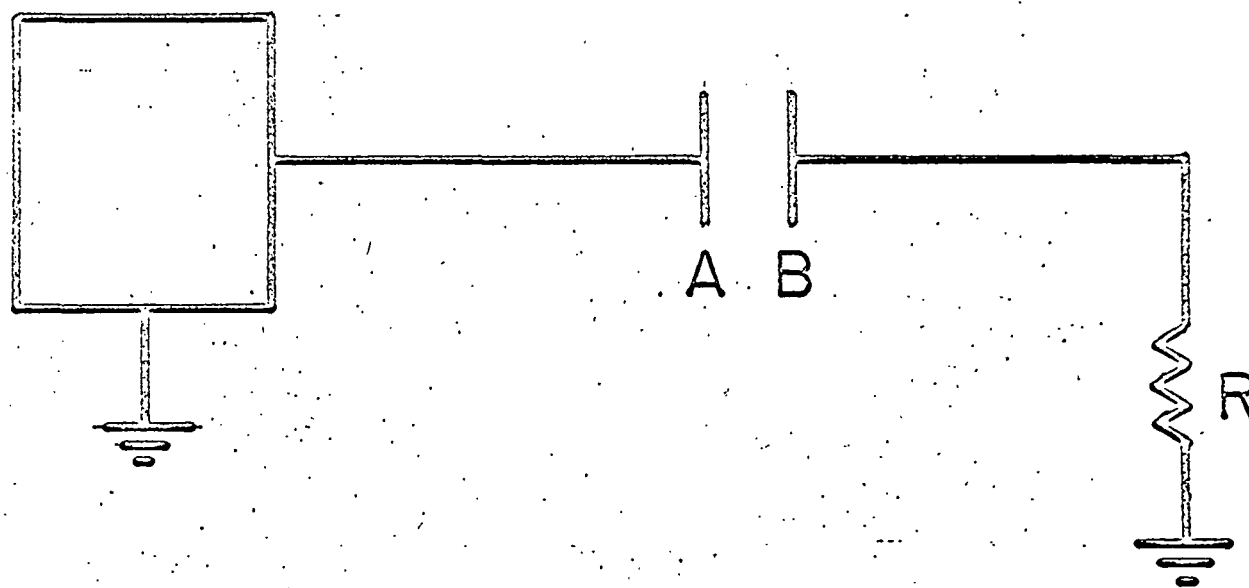


FIGURE 10

For the carrier gas plus a single test substance (where X_c is the mole fraction of carrier gas and X_s is the mole fraction of test substance):

$$X_c + X_s = 1 \quad \text{or} \quad X_c = (1 - X_s)$$

The total current will be given by:

$$I_t = \left[k \ell \frac{PV}{RT} X_s Q_s + k \ell \frac{PV}{RT} (1 - X_s) Q_c \right] \pm \ell$$

The signal due to the test substance alone will be:

$$I_s = I_t - I_0$$

$$I_s = \left[k \ell \frac{PV}{RT} X_s Q_s + (1 - X_s) k \ell \frac{PV}{RT} Q_c \right] \pm \ell - \left[k \ell \frac{PV}{RT} Q_c \pm \ell \right]$$

$$I_s = k \ell \frac{PV}{RT} X_s Q_s + k \ell \frac{PV}{RT} Q_c - k \ell \frac{PV}{RT} X_s Q_c - k \ell \frac{PV}{RT} Q_c$$

$$I_s = k \ell \frac{PV}{RT} X_s Q_s - k \ell \frac{PV}{RT} X_s Q_c$$

$$I_s = k \ell \frac{PV}{RT} X_s (Q_s - Q_c)$$

Let us now consider the diagrammatic representation of an eluted chromatographic peak in Figure 11. The area A will be given by

$$A = \int_{t_1}^{t_2} I_t dt = \int_{t_1}^{t_2} I_0 dt + \int_{t_1}^{t_2} I_s dt$$

Substituting in the appropriate values for I_0 and I_s we obtain:

$$A = \int_{t_1}^{t_2} \left[k \ell \frac{PV}{RT} Q_c \pm \ell \right] dt + \int_{t_1}^{t_2} \left[k \ell \frac{PV}{RT} X_s (Q_s - Q_c) \right] dt$$

Removing the constant term from inside the integral:

MODEL OF ELUTED GAS CHROMATOGRAPHIC PEAK

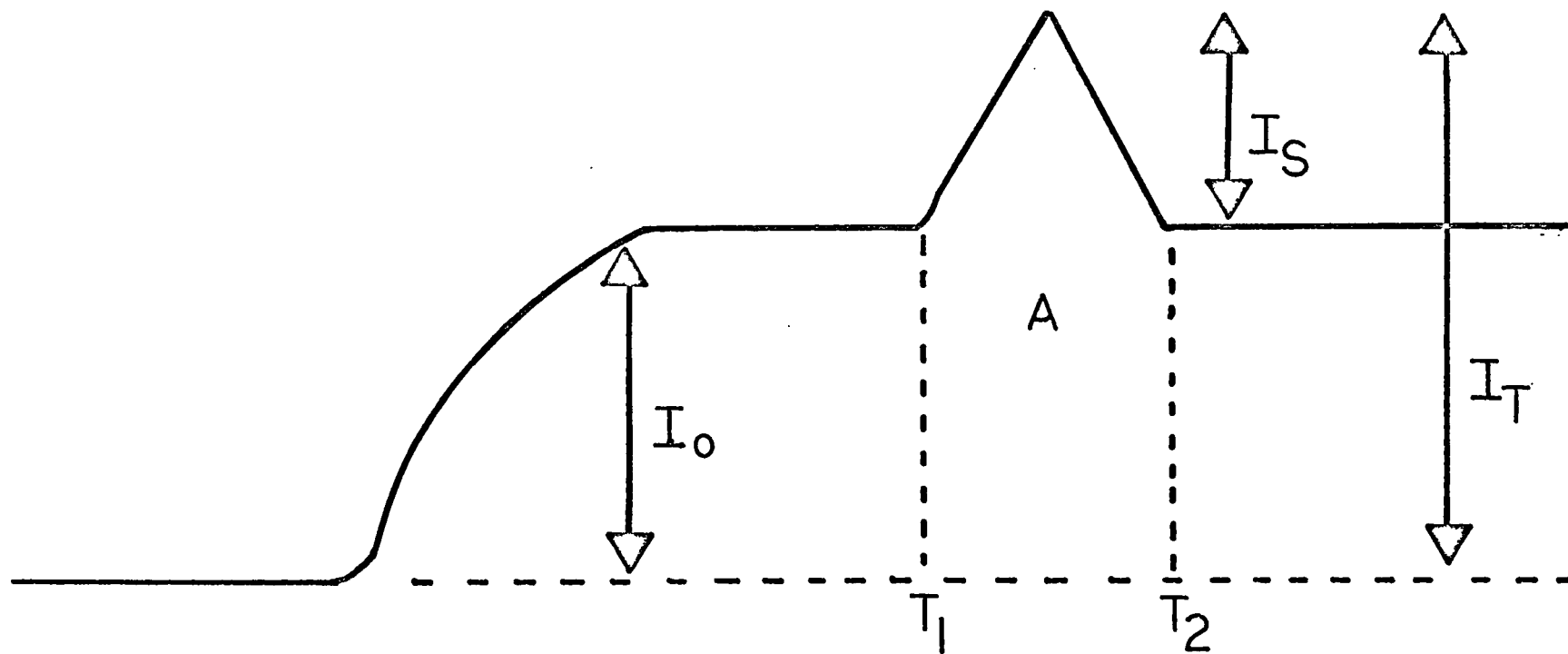


FIGURE 11

$$A = \left[k \ell \frac{PV}{RT} Q_c \pm \ell \right] \int_{t_1}^{t_2} dt + \left[k \ell \frac{PV}{RT} (Q_s - Q_c) \right] \int_{t_1}^{t_2} X_s dt$$

Simply as a matter of simplification let us make the substitution $n = \frac{PV}{RT}$

$$A = \left[k \ell n Q_c \pm \ell \right] \int_{t_1}^{t_2} dt + \left[k \ell n (Q_s - Q_c) \right] \int_{t_1}^{t_2} X_s dt$$

Rearranging the above:

$$A - \left[k \ell n Q_c \pm \ell \right] \int_{t_1}^{t_2} dt = k \ell n (Q_s - Q_c) \int_{t_1}^{t_2} X_s dt$$

$$A - \left[k \ell n Q_c \pm \ell \right] \int_{t_1}^{t_2} dt = \int_{t_1}^{t_2} X_s dt$$

$$k \ell n (Q_s - Q_c)$$

Separating the terms:

$$\frac{1}{k \ell n (Q_s - Q_c)} A - \frac{\left[k \ell n Q_c \pm \ell \right] \int_{t_1}^{t_2} dt}{k \ell n (Q_s - Q_c)} = \int_{t_1}^{t_2} X_s dt$$

If we now differentiate both sides of the equation to determine X_s

$$\frac{dA/dt}{k \ell n (Q_s - Q_c)} - \frac{k \ell n Q_c \pm \ell}{k \ell n (Q_s - Q_c)} = X_s$$

$$X_s = \frac{dA/dt - k \ell n Q_c \pm \ell}{k \ell n (Q_s - Q_c)}$$

Resubstituting $n = \frac{PV}{RT}$:

$$X_s = \frac{dA/dt - k \ell \frac{PV}{RT} Q_c}{k \ell \frac{PV}{RT} (Q_s - Q_c)}$$

$$X_s = \frac{RT \frac{dA}{dt} - k \ell n Q_c}{k \ell PV (Q_s - Q_c)}$$

The last expression represents the mole fraction of substance present in a chromatographic peak. It is interesting to note that this relationship is equally valid for integral as well as differential detection.

By definition we know that:

$$X_s = \frac{N_s}{N_s + N_c}$$

where: N_s = number of moles of test substance

N_c = number of moles of carrier gas

Solving for N_s :

$$X_s (N_s + N_c) = N_s$$

$$X_s N_s + X_s N_c = N_s$$

$$X_s N_c = N_s - X_s N_s$$

$$X_s N_c = N_s (1 - X_s)$$

$$N_s = \frac{X_s N_c}{1 - X_s}$$

The mass of substance present will simply be the product of the number of moles of substance and its molecular weight, i.e.,

$$M_s = N_s W_s$$

Where: W_s = molecular weight of substance

M_s = mass of substance

Making the proper substitutions:

$$M_s = \frac{X_s N_c W_s}{1 - X_s}$$

Since we are using ideal gas approximations:

$$N_c = \frac{PV_c}{RT}$$

However in a flowing system the volume of carrier gas, V_c , is equivalent to the volumetric flow rate multiplied by the time required for the sample to be eluted, Δt ,:

$$V_c = F_c \Delta t$$

where F_c = volumetric flow of carrier gas.

The previous expression for mass now becomes:

$$M_s = \frac{X_s}{1 - X_s} \frac{PF_c \Delta t}{RT} W_s$$

Substituting in the values previously obtained for X_s gives rise to the following expression for the mass:

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{\frac{RT}{k} \frac{dA}{dt} - k \ell PV Q_c \pm \ell RT/k \ell PV (Q_s - Q_c)}{1 - \frac{RT}{k \ell PV (Q_s - Q_c)} \left(\frac{dA}{dt} - k \ell PV Q_c \pm \ell RT \right)} \right]$$

Substituting $n = \frac{PV}{RT}$ and reducing:

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{RT \, dA/dt - k \ell n RT Q_c \pm \ell RT/k \ell n RT (Q_s - Q_c)}{k \ell n RT (Q_s - Q_c) - RT \, dA/dt + k \ell RT Q_c \pm \ell RT} \right]$$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{RT \, dA/dt - k \ell n RT Q_c \pm \ell RT}{k \ell n RT (Q_s - Q_c) - RT \, dA/dt + k \ell n RT Q_c \pm \ell RT} \right]$$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - k \ell n Q_c \pm \ell}{k \ell n (Q_s - Q_c) - dA/dt + k \ell n Q_c \pm \ell} \right]$$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - k \ell n Q_c \pm \ell}{k \ell n Q_s - k \ell n Q_c - dA/dt + k \ell n Q_c \pm \ell} \right]$$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - k \ell n Q_c \pm \ell}{k \ell n Q_s - kA/dt \pm \ell} \right]$$

Resubstituting for the value of n

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - k \ell PV/RT Q_c \pm \ell}{k \ell PV/RT Q_s - dA/dt \pm \ell} \right]$$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{RT \, dA/dt - k \ell PV Q_c \pm \ell RT}{k \ell PV Q_s - RT \, dA/dt \pm \ell RT} \right]$$

Since both k, ℓ and n are constant terms they may be combined into a single constant, i.e.,:

$$K = k \ell n = k \ell \frac{PV}{RT}$$

Now we may write the expression:

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - KQ_c \pm \ell}{KQ_s - dA/dt \pm \ell} \right]$$

The constant K is often referred to as the all constant.

A simpler approach may be made by making the valid assumption that $N_c \gg N_s$. Therefore:

$$X_s = \frac{N_s}{N_c}$$

As before:

$$N_c = \frac{PV_c}{RT} = \frac{PF_c \Delta t}{RT}$$

and,

$$M_s = N_s W_s = X_s \frac{PF_c \Delta t W_s}{RT}$$

The new expression for mass now becomes:

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{RT dA/dt - k \ell PV Q_c \pm \ell RT}{k \ell PV (Q_s - Q_c)} \right]$$

Making the substitution $n = \frac{PV}{RT}$:

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{kA/dt - k \ell n Q_c \pm \ell}{k \ell n (Q_s - Q_c)} \right]$$

Again letting $K = k \ell n$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - KQ_c \pm \ell}{K(Q_s - Q_c)} \right]$$

If by choice we select two radioactive sources of the same beta intensities for the two electrodes the contribution from primary radiation will exactly cancel. We may now calculate analogous expressions to the foregoing.

The total current will now be due to the ionization of gaseous components alone with no direct contribution from the primary radiation. The signal from carrier gas alone will be:

$$I_o = k \ell \frac{PV}{RT} Q_c$$

since $X_c = 1$

For a gas mixture:

$$I_t = k \ell \frac{PV}{RT} \sum X_i Q_i$$

For carrier gas plus a single test substance

$$I_t = k \ell \frac{PV}{RT} X_s Q_s + (1 - X_s) k \ell \frac{PV}{RT} Q_c$$

I_s , the signal due to test substance alone will be

$$I_s = I_t - I_o$$

$$I_s = k \ell \frac{PV}{RT} X_s Q_s + (1 - X_s) k \ell \frac{PV}{RT} Q_c - k \ell \frac{PV}{RT} Q_c$$

$$I_s = k \ell \frac{PV}{RT} X_s Q_s + k \ell \frac{PV}{RT} Q_c - X_s k \ell \frac{PV}{RT} Q_c - k \ell \frac{PV}{RT} Q_c$$

$$I_s = k \ell \frac{PV}{RT} X_s Q_s - k \ell \frac{PV}{RT} X_s Q_c$$

$$I_s = k \ell \frac{PV}{RT} X_s (Q_s - Q_c)$$

Again referring to Figure 11, the area A will be given by:

$$A = \int_{t_1}^{t_2} I_t dt = \int_{t_1}^{t_2} I_0 dt + \int_{t_1}^{t_2} I_s dt$$

Substituting in the new values

$$A = \int_{t_1}^{t_2} k \ell \frac{PV}{RT} Q_c dt + \int_{t_1}^{t_2} k \ell \frac{PV}{RT} X_s (Q_s - Q_c) dt$$

Removing the constant terms from inside the integral:

$$A = k \ell \frac{PV}{RT} Q_c \int_{t_1}^{t_2} dt + k \ell \frac{PV}{RT} (Q_s - Q_c) \int_{t_1}^{t_2} X_s dt$$

Rearranging yields:

$$\frac{A - k \ell \frac{PV}{RT} Q_c \int_{t_1}^{t_2} dt}{k \ell \frac{PV}{RT} (Q_s - Q_c)} = \int_{t_1}^{t_2} X_s dt$$

Again, for simplification let $n = \frac{PV}{RT}$

$$\frac{A - k \ell n Q_c \int_{t_1}^{t_2} dt}{k \ell n (Q_s - Q_c)} = \int_{t_1}^{t_2} X_s dt$$

Separating the terms:

$$\frac{1}{k \ell n (Q_s - Q_c)} A - \frac{k \ell n Q_c}{k \ell n (Q_s - Q_c)} \int_{t_1}^{t_2} dt = \int_{t_1}^{t_2} X_s dt$$

Differentiating with respect to t to obtain a value for X_s :

$$\frac{dA/dt}{k \ell n (Q_s - Q_c)} - \frac{k \ell n Q_c}{k \ell n (Q_s - Q_c)} = X_s$$

$$X_s = \frac{dA/dt - k \ell n Q_c}{k \ell n (Q_s - Q_c)}$$

Replacing the value for n , i.e., $n = PV/RT$

$$X_s = \frac{dA/dt - k \ell PV/RT Q_c}{k \ell PV/RT (Q_s - Q_c)}$$

$$X_s = \frac{RT dA/dt - k \ell PV Q_c}{k \ell PV (Q_s - Q_c)}$$

As before:

$$M_s = \frac{X_s}{1 - X_s} \quad \frac{PF_c \Delta t W_s}{RT}$$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \quad \frac{\frac{dA/dt - k \ell n Q_c}{k \ell n (Q_s - Q_c)}}{1 - \frac{dA/dt - k \ell n Q_c}{k \ell n (Q_s - Q_c)}}$$

Reducing:

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - k \ell n Q_c}{k \ell n (Q_s - Q_c) - dA/dt + k \ell n Q_c} \right]$$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - k \ell n Q_c}{k \ell n Q_s - k \ell n Q_c - dA/dt + k \ell n Q_c} \right]$$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - k \ell n Q_c}{k \ell n Q_s - dA/dt} \right]$$

Letting $K = k \ell n$:

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - KQ_c}{KQ_s - dA/dt} \right]$$

If we again assume $N_c \gg N_s$ then:

$$M_s = N_s W_s = X_s \frac{PF_c \Delta t W_s}{RT}$$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - k \ell n Q_c}{k \ell n (Q_s - Q_c)} \right]$$

and since $K = k \ell n$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{dA/dt - KQ_c}{K (Q_s - Q_c)} \right]$$

Since we have defined $K = k \ell n$ we may return to the initial considerations and define a more practical model. We have previously shown:

$$I = k \ell \frac{PV}{RT} Q = k \ell n Q = KQ$$

If we consider the primary radiation

$$I = KQ \pm \ell$$

For a gas mixture

$$I = K X_i Q_i \pm \ell$$

For the carrier gas alone:

$$I_0 = KQ_c \pm \ell$$

For the carrier gas plus a single test substance:

$$I_t = KX_s Q_s + (1 - X_s) KQ_c \pm \ell$$

I_s , the signal due to test substance alone will be:

$$I_s = KX_s Q_s + (1 - X_s) KQ_c \pm \ell - KQ_c \pm \ell$$

$$I_s = KX_s Q_s + KQ_c - X_s KQ_c \pm \ell - KQ_c \pm \ell$$

$$I_s = KX_s Q_s - KX_s Q_c$$

$$I_s = KX_s (Q_s - Q_c)$$

Let us now consider a slightly different model as shown in Figure 12.

To a very close approximation:

$$A_1 = I_0 \Delta t$$

$$A_2 = 1/2 \Delta t I_s$$

The correct area for the chromatographic peak will now be:

$$A_t = A_1 + A_2 = I_0 t + \frac{I_s \Delta t}{2}$$

Substitution for A , I_0 , I_s yields:

$$A_2 = \frac{I_s \Delta t}{2}$$

$$A_2 = \frac{KX_s (Q_s - Q_c) t}{2}$$

SIMPLIFIED MODEL OF ELUTED GAS CHROMATOGRAPHIC PEAK

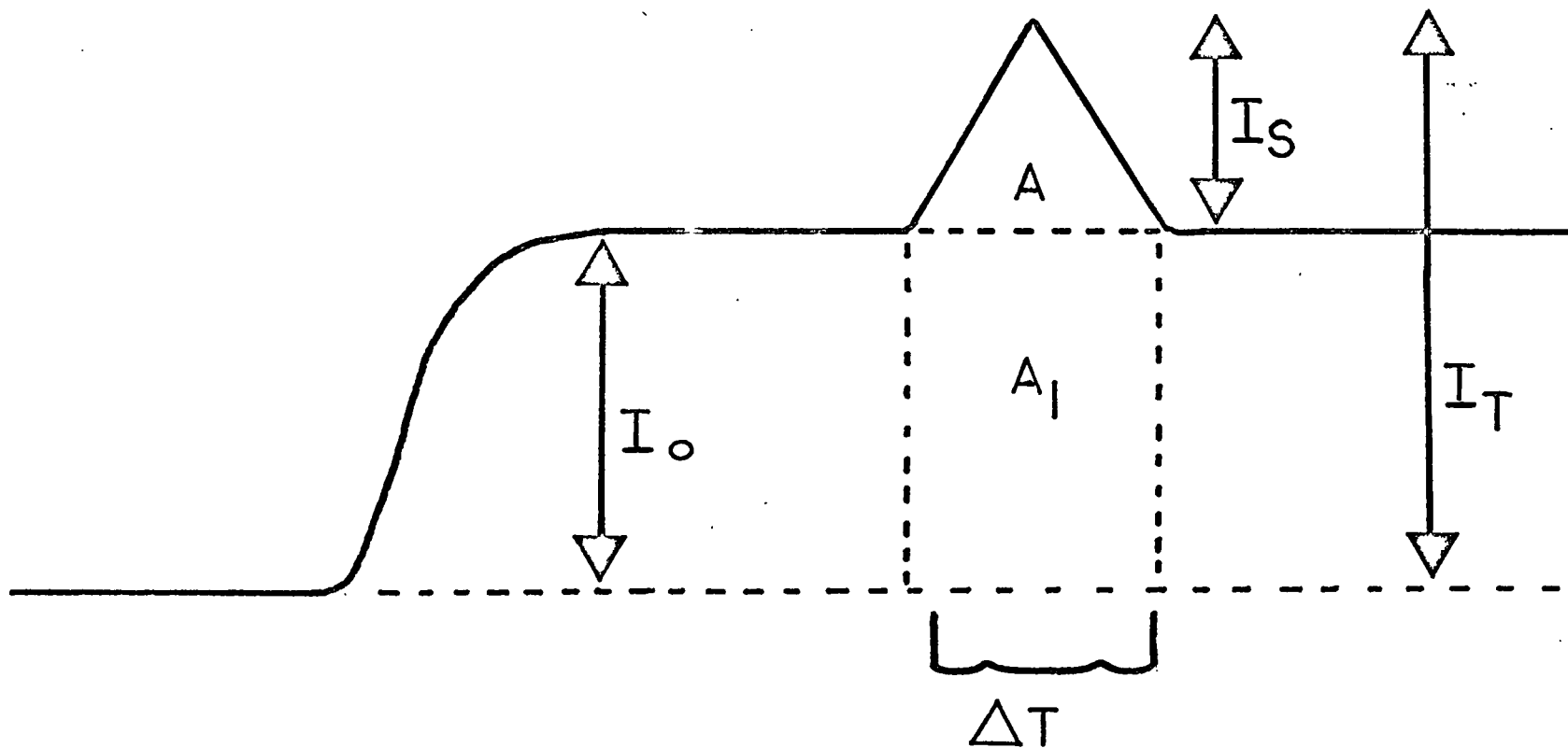


FIGURE 12

Solving for X_s :

$$X_s = \frac{2A_2}{K (Q_s - Q_c) \Delta t}$$

Similar to the previous treatment

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{\frac{2A_2}{K \Delta t (Q_s - Q_c)}}{1 - \frac{2A_2}{K \Delta t (Q_s - Q_c)}} \right]$$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{2A_2}{K \Delta t (Q_s - Q_c) - 2A_2} \right]$$

writing in terms of the operational variables

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{2(1/2 \Delta t I_s)}{k \ell n \Delta t (Q_s - Q_c) - 2(1/2 \Delta t I_s)} \right]$$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{(PVQ_c \pm RT) \Delta t I_s}{I_0 PV \Delta t (Q_s - Q_c) - (PVQ_c \pm RT) \Delta t I_s} \right]$$

If as before we assume $N_c \gg N_s$:

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{2A_2}{K \Delta t (Q_s - Q_c)} \right]$$

Writing in terms of the operational variables

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{(PVQ_c \pm RT) (\Delta t I_s)}{I_0 PV \Delta t (Q_s - Q_c)} \right]$$

$$M_s = \frac{PF_c W_s}{RT} \left[\frac{(PVQ_c \pm RT) (\Delta t I_s)}{I_0 PV (Q_s - Q_c)} \right]$$

We may now select two matched beta sources. The current will now reflect no contribution from the primary radiation. The solution of similar expressions to those previously presented yields:

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{2A_2}{K \Delta t (Q_s - Q_c) - 2A_2} \right]$$

Writing in terms of the operational variables:

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{I_s Q_c}{I_0 (Q_s - Q_c) - I_s Q_c} \right]$$

Again assuming $N_c \gg N_s$

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{2A_2}{K \Delta t (Q_s - Q_c)} \right]$$

Or in terms of the operational variables:

$$M_s = \frac{PF_c \Delta t W_s}{RT} \left[\frac{I_s Q_c}{I_0 (Q_s - Q_c)} \right]$$

Dimensional analysis of this last expression yields:

$$\frac{\text{atm} \cdot \frac{\text{ml}}{\text{sec}} \cdot \text{sec} \cdot \frac{\text{g}}{\text{mole}}}{\frac{\text{ml atm}}{\text{mole } ^\circ\text{k}} \cdot ^\circ\text{k}} \left[\frac{\text{amp}}{\text{amp}} \right] = \text{g}$$

Dimensional analysis of all of the foregoing was found to give the proper units. These calculations have been experimentally verified in a report by Simmonds and Lovelock (17).

To further extend the considerations of the ionization cross section detector as an absolute device, calculations have been made to demonstrate its use irrespective of incorporation into a gas chromatographic system (18).

Note: The mathematical approach taken on pages 46 and 47 is allowed because the function is known to be finite and continuous throughout the interval under consideration.

IONIZATION CROSS SECTION

III.

EXPERIMENTAL

EXPERIMENTAL

In practice the ideal conditions previously described are not difficult to meet. The factors affecting the lower limits of detection by the ionization cross section method are apparent from the foregoing relationships. There will be a background current attributable to the ionization of the carrier gas and this will fluctuate with changes in ambient temperature and pressure. The production and collection of ions are stochastic processes and will cause random fluctuations in the current flow. The sum of these random changes in the detector current constitutes the noise level and sets the limit for the least detectable signal.

The noise due to temperature and pressure changes is to a considerable extent controllable and so long as it is less than the noise from the production and collection of ions can be disregarded. The noise level from temperature and pressure changes however increase directly with increasing ionization, whereas the stochastic noise from ion production and collection increases only with the square root of the rate of ion production. It follows that the performance of the detector will improve as the radiation intensity is increased until the noise from the temperature and pressure changes is as great as that from ion production. Experience indicates that this point is reached at an ion current in the region of 10^{-7} amperes. It is assumed that the detector geometry and applied potential are appropriate for the efficient collection of all the ions produced before recombination can occur. This is not difficult to achieve with a detector of the type to be described later.

The experimental conditions corresponding to this ideal limit of detection for the cross section detector are as follows: An ionization current of 10^{-7} amperes in hydrogen would in the most favorable circumstances be associated with a noise level of 10^{-13} amperes. A noise level of this magnitude would be generated by a pressure fluctuation of one microbar per second or by a temperature change of 10^{-3}°C per second. The total noise would be in the region of 1 to 3×10^{-13} amperes so that a signal of 10^{-12} amperes should be discernible. Such a signal would be given by CO_2 at a concentration of one part per million.

Apparatus: The polarizing potential in all of these studies was provided by a Kepco Model 1500M regulated d.c. power supply.

The ionization current of the detector was measured using a Cary Model 31 vibrating reed electrometer, in terms of the potential developed across a known high resistance.

Chromatograms were obtained and measurements were recorded using a Leeds and Northrop Model G potentiometric recorder.

The Tritium radiation sources were obtained from the U.S. Radium Corporation, Morristown, New Jersey.

Carrier gases were obtained from Big Three Welding Supply, Houston, Texas.

Test gases were Matheson lecture bottle gases.

Figure 13 shows the dimensions and materials of construction of the first experimental detector. The ion chamber is formed by a rectangular sectioned teflon ring of 1 centimeter internal diameter.

SMALL VOLUME PLANE PARALLEL IONIZATION CROSS SECTION DETECTOR

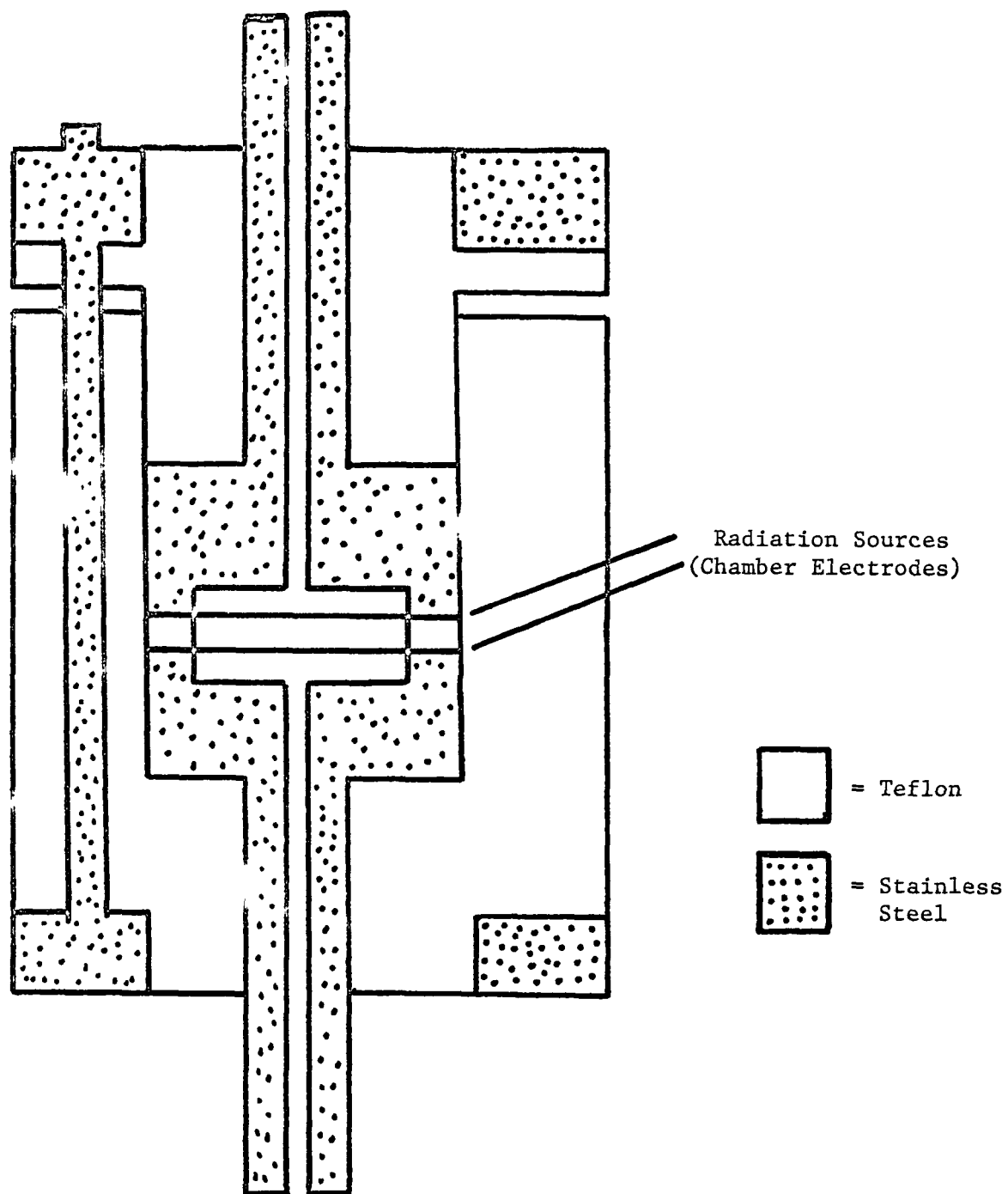


FIGURE 13

The ring is enclosed between two parallel sheets of metal foil, each 1.1 by 0.8 centimeters. The small openings between the inside of the ring and the edge of the foil are to permit the passage of gas through the chamber. The foil is held firmly in place against the ring and the whole assembly mounted inside a closed end cylindrical teflon tube. The stainless steel discs each include a hollow coaxial tube which passes through the outer teflon body of the detector. These tubes serve the dual purpose of gas and electrical conduction. The sheets of foil enclosing the detector chamber are cut from thin stainless steel sheet onto which is coated a thin film of titanium or zirconium containing occluded tritium. They serve therefore both in the production of ions as the radioactive source and in the collection of ions as the chamber electrodes. The volume of the detector was measured and found to be 80 microliters. The plane parallel design for the detector chamber was initially chosen because of the ease with which changes in the thickness or diameter of the teflon ring would permit equivalent changes in the electrode separation or chamber volume. It was soon found however that it possessed other more important advantages. When used with two identical electrodes the chamber is electrically symmetrical so that the development of spurious signals from contact potentials which can occur with dissimilar electrodes is no longer a problem.

Figure 14 shows the dimensions and materials of construction of an 8 microliter ionization cross section detector. The ion chamber is formed from 1.6 millimeter diameter tubing which encloses the radiation

8 MICROLITER VOLUME IONIZATION CROSS SECTION DETECTOR

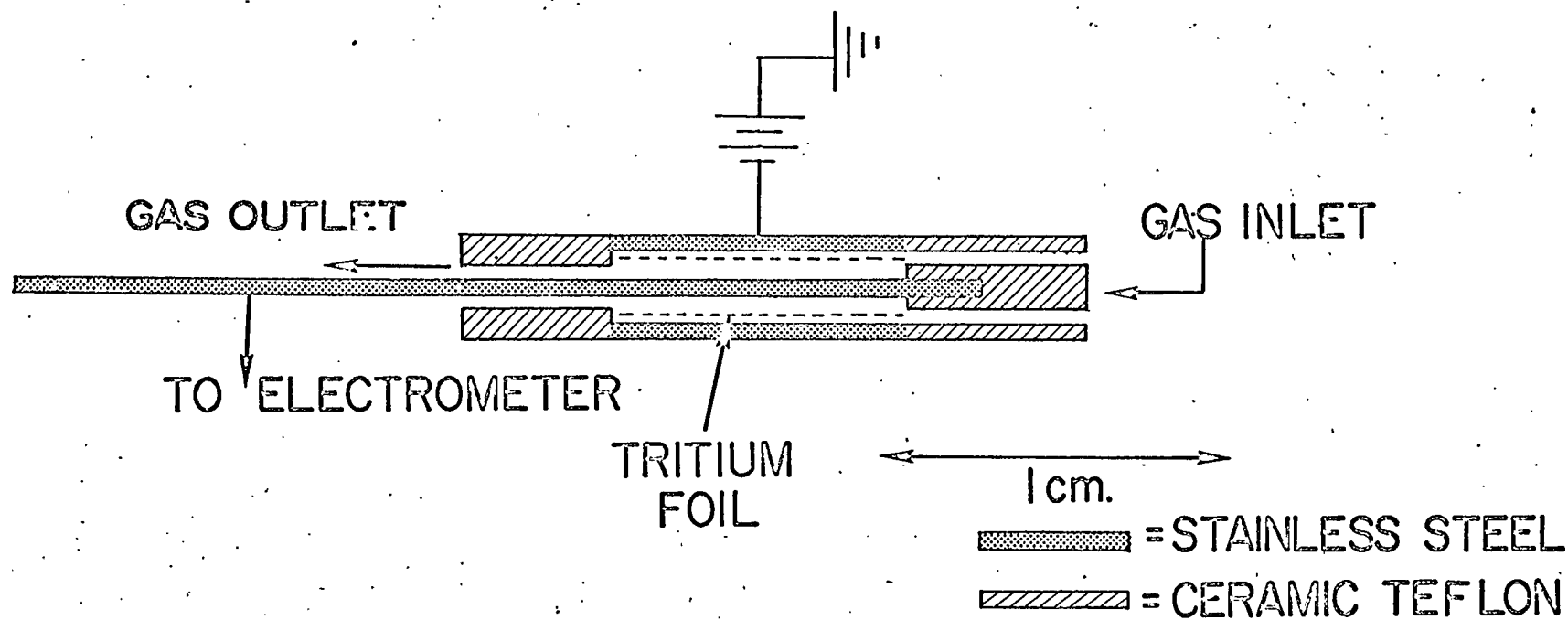


FIGURE 14

source. The source is a sheet of stainless steel foil 0.002 inches thick with a surface layer of 200 millicuries titanium tritide. The collecting electrode, made of 0.8 millimeter diameter stainless steel rod is mounted axially along the chamber. Carrier gas enters the chamber through channels in a plug of teflon which also serves to insulate and support the ion collecting electrode. The gas exit is through a second teflon plug through which the ion collecting electrode extends for external electrical connections.

Figure 15 shows the dimensions and materials of construction of a compensated pair or "dual" ionization cross section detector. In this construction the two ion chambers are integrally connected and mounted within a single external body. The common ion collecting electrode is an axial rod in the left chamber and the inner cylindrical wall of the right chamber of the pair. The rod section is hollow and serves to conduct the gas from the chamber and also, where it extends through a teflon bushing in the outer metal body of the detector, as an external electrical connection to the electrometer. At the end of the left chamber the axial rod passes through a teflon insulation and expands to form the second ion chamber. Gas enters the chamber through another axial rod which also serves as the external connection to the negative supply of potential. This rod is threaded where it passes through an insulated supporting metal plate. This provides a fine adjustment of the volume of the right chamber so that the final electrical balancing can be made with the detector assembled. The external supporting metal case also functions as the second electrode of the left chamber to which is

BALANCED PAIR IONIZATION CROSS SECTION DETECTOR

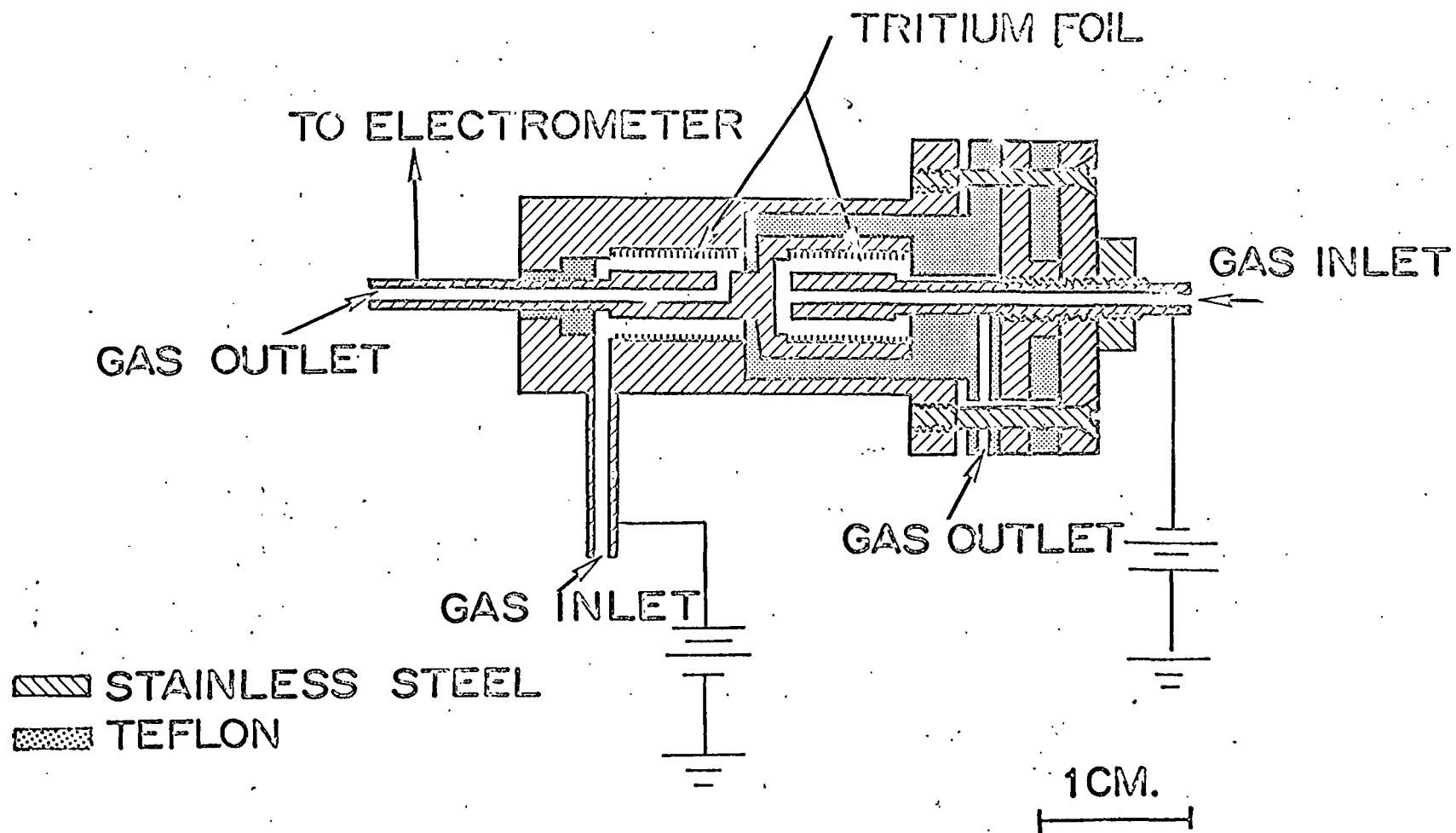


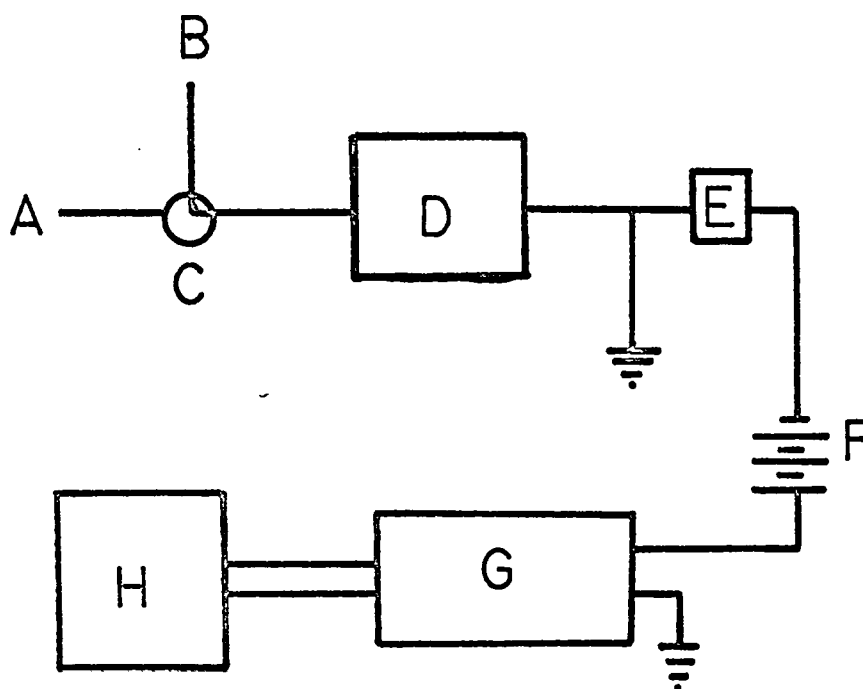
FIGURE 15

connected the positive supply of potential. The radiation sources are again stainless steel foils with a layer of titanium tritide on the surface. They are mounted on the inner surface of the outer walls of both chambers.

Procedure: The performance of the 80 microliter detector was investigated using the experimental arrangement shown in Figure 16. An accurately known flow of carrier gas was passed into a 250 milliliter mixing vessel containing a magnetically driven stirrer. The mixing vessel was modeled after that previously described by Lovelock (19) and is shown in Figure 17. The outlet from the mixing chamber was passed directly to the detector. The ionization current of the detector was measured using a vibrating reed electrometer, in terms of the potential developed across a known high resistance. At the commencement of the calibration experiment the supply of carrier gas was temporarily disconnected and test gas passed into the mixing vessel until the steady signal from the detector indicated the presence of undiluted test gas throughout the system. The supply of test gas was then cut off and the carrier gas flow restored. This flow was maintained until the detector by its steady state signal indicated the presence of uncontaminated carrier gas within the detector volume. During the progressive dilution of the test gas the detector signal was recorded graphically by the potentiometric recorder. At any time, t , after the commencement of an experiment the concentration of the test gas, C , remained in the mixing chamber is given by the expression:

$$C = C_0 e^{-ut/v}$$

EXPERIMENTAL ARRANGEMENT FOR THE MEASUREMENT OF DETECTOR PERFORMANCE
FOR PLANE PARALLEL IONIZATION CROSS SECTION DETECTOR



- A Carrier gas inlet
- B Test gas inlet
- C Three way valve
- D Mixing chamber
- E Detector
- F Polarizing potential
- G Electrometer
- H Recorder

FIGURE 16

EXPONENTIAL DILUTION CHAMBER

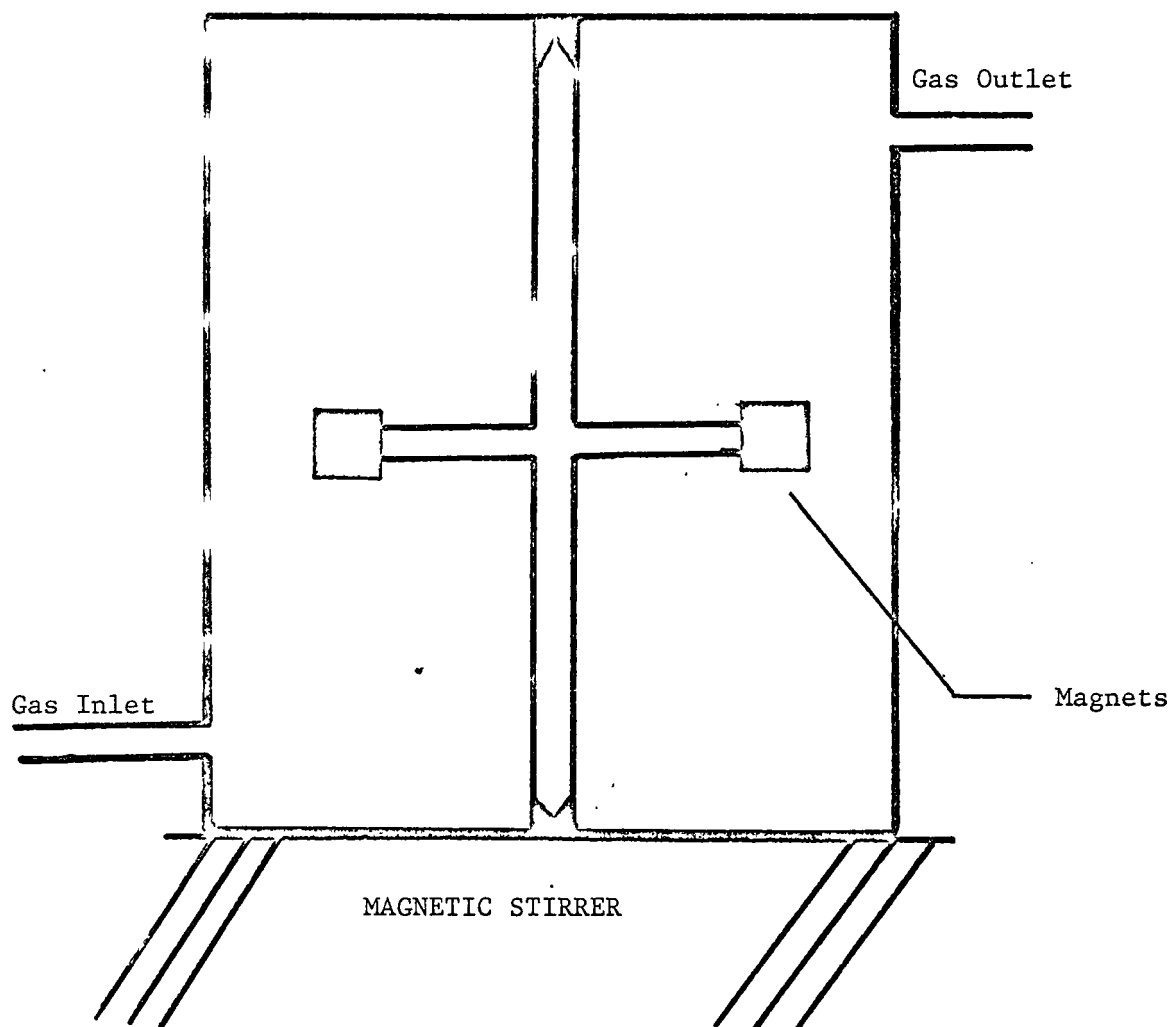


FIGURE 17

where: C_0 = initial concentration, i.e., 100%

v = mixing chamber volume, ml.

u = carrier gas flow rate, ml. per sec.

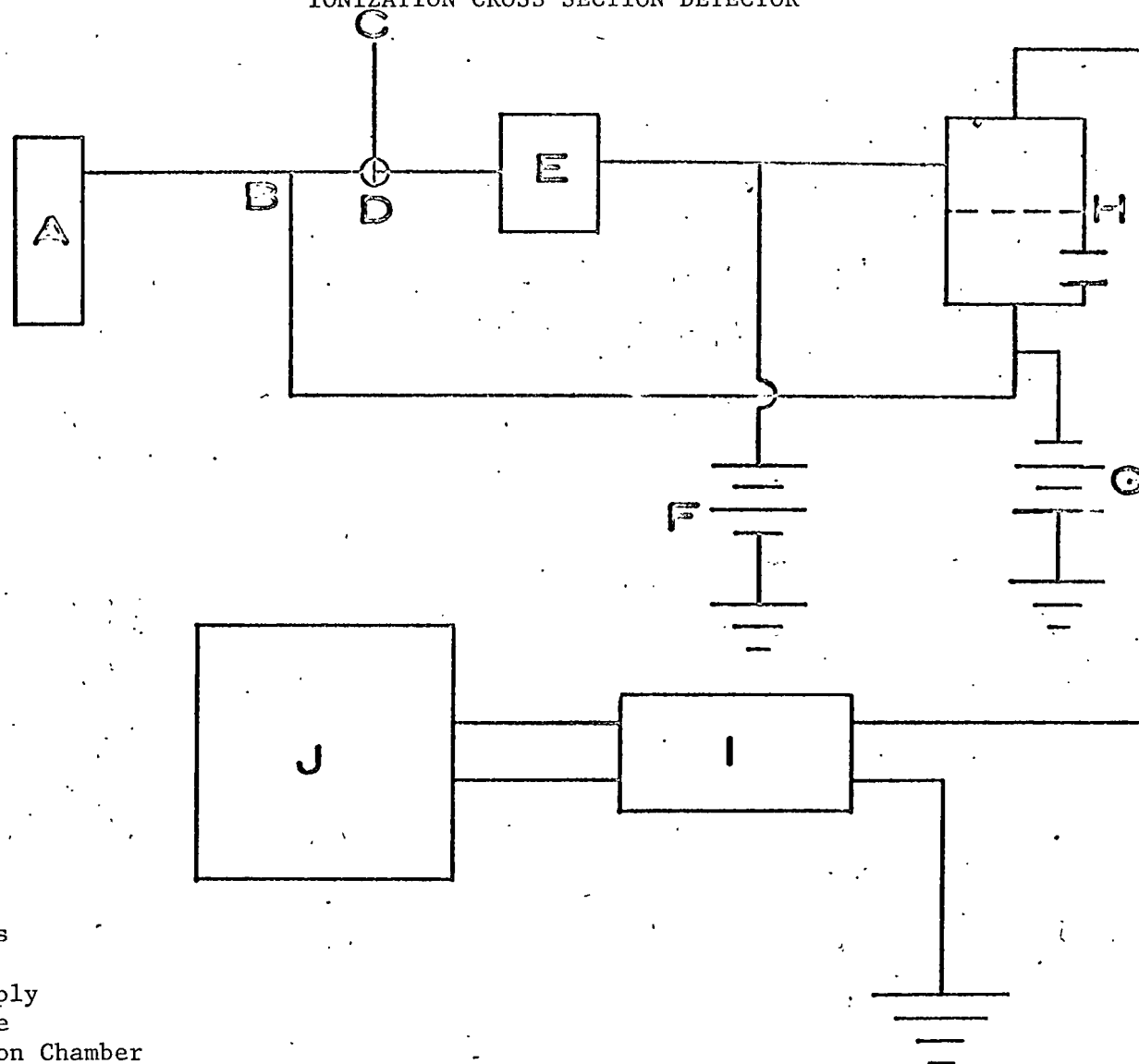
t = time, sec.

From the recorded signal the response of the detector to any test gas concentration can readily be discovered. A more detailed description of the calibration method and the precautions necessary for precise measurements are given by Lovelock (19). Measurements were made using the following test gases: argon, methane, nitrogen, oxygen, carbon dioxide, sulfur hexafluoride, carbonyl sulfide, propylene, ethane and butane with hydrogen and helium as the carrier gases. The effects of variations of the electrode separation and applied potential on the response of the detector to different gases were also measured by this method.

The performance of the 8 microliter volume detector was measured using the same apparatus and procedure described above. The practical performance of the detector was also observed when it was used to monitor the effluent from a 0.01 inch diameter capillary column.

The characteristics of the balanced pair detector at S.T.P. were measured as before using the logarithmic dilution method. The experimental arrangement is shown in Figure 18. However this detector was designed for use at pressures considerably different from atmospheric, i.e., in the range 5 to 250 millimeters of mercury. Low pressure measurements of the detector performance were made using the apparatus illustrated in Figure 19. The detector was mounted within a plexiglass vacuum

EXPERIMENTAL ARRANGEMENT FOR INVESTIGATION OF OPERATING CHARACTERISTICS OF THE BALANCED PAIR
IONIZATION CROSS SECTION DETECTOR



- A Carrier Gas
- B Gas Tee
- C Sample Supply
- D 3 Way Valve
- E Log Dilution Chamber
- F & G Polarizing Potential
- H Detector
- I Electrometer
- J Recorder

FIGURE 18

EXPERIMENTAL ARRANGEMENT FOR INVESTIGATION OF DETECTOR PERFORMANCE UNDER REDUCED PRESSURE

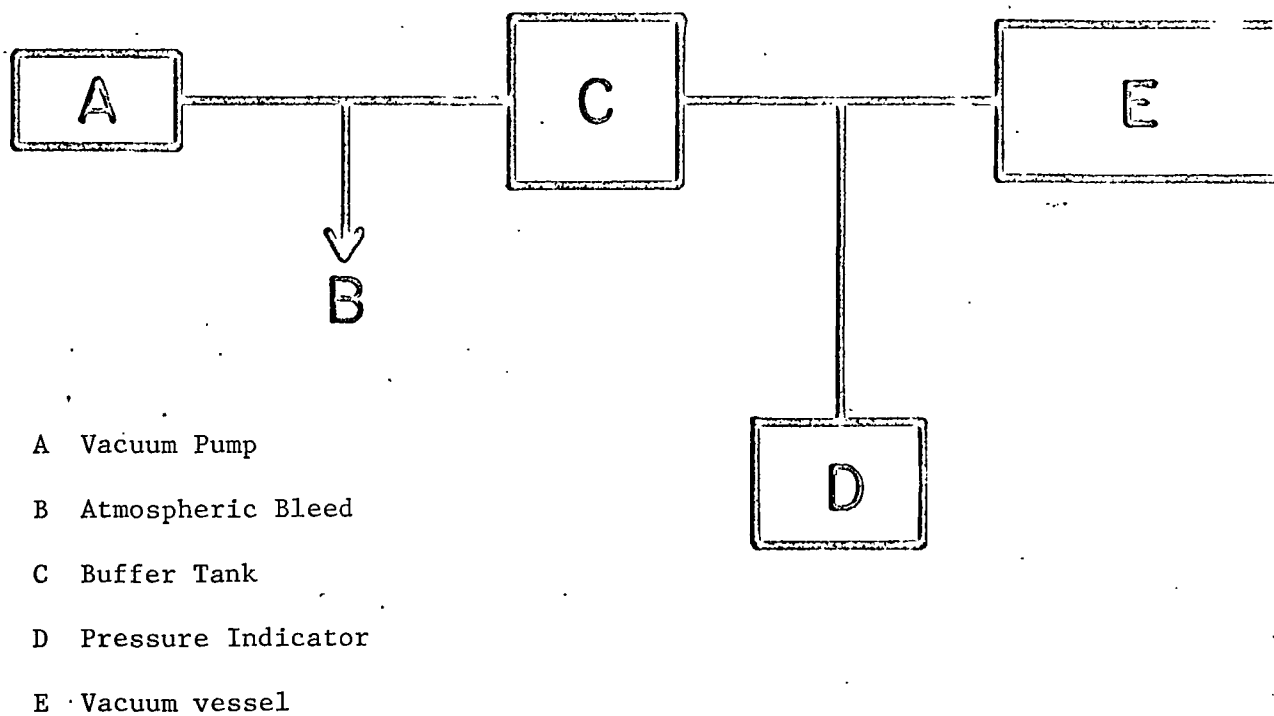


FIGURE 19

desiccator which was connected to a vacuum pump through a buffer storage volume, to reduce fluctuations, and to an absolute pressure indicator. When the detector was tested using a dilution vessel the vessel was operated at atmospheric pressure and a small portion of the effluent from the vessel passed through a capillary restrictor into the vacuum chamber. All necessary gas and electrical connections were made by passing such connections through the desiccator walls and sealing with epoxy resin. When the detector was tested at the end of a gas chromatographic column these were usually included with the detector inside the vacuum vessel.

Figure 20 shows the experimental arrangement used when the balanced pair detector is operated in the standard mode. Figure 21 illustrates the recommended experimental method for the balanced pair detector when used for temperature programming or dual column operation. For parallel column application the sample injection is at point (J), while for temperature programming the sample is injected at point (B).

Though not as desirable in most instances as parallel column operation, a series column arrangement may be used as illustrated in Figure 22. In either the parallel or series column application care must be exercised in column choice so that the sample components do not arrive in both cells simultaneously as one of the pair must be available to serve as the reference.

EXPERIMENTAL ARRANGEMENT FOR SINGLE COLUMN OPERATION OF THE BALANCED PAIR IONIZATION CROSS SECTION
DETECTOR

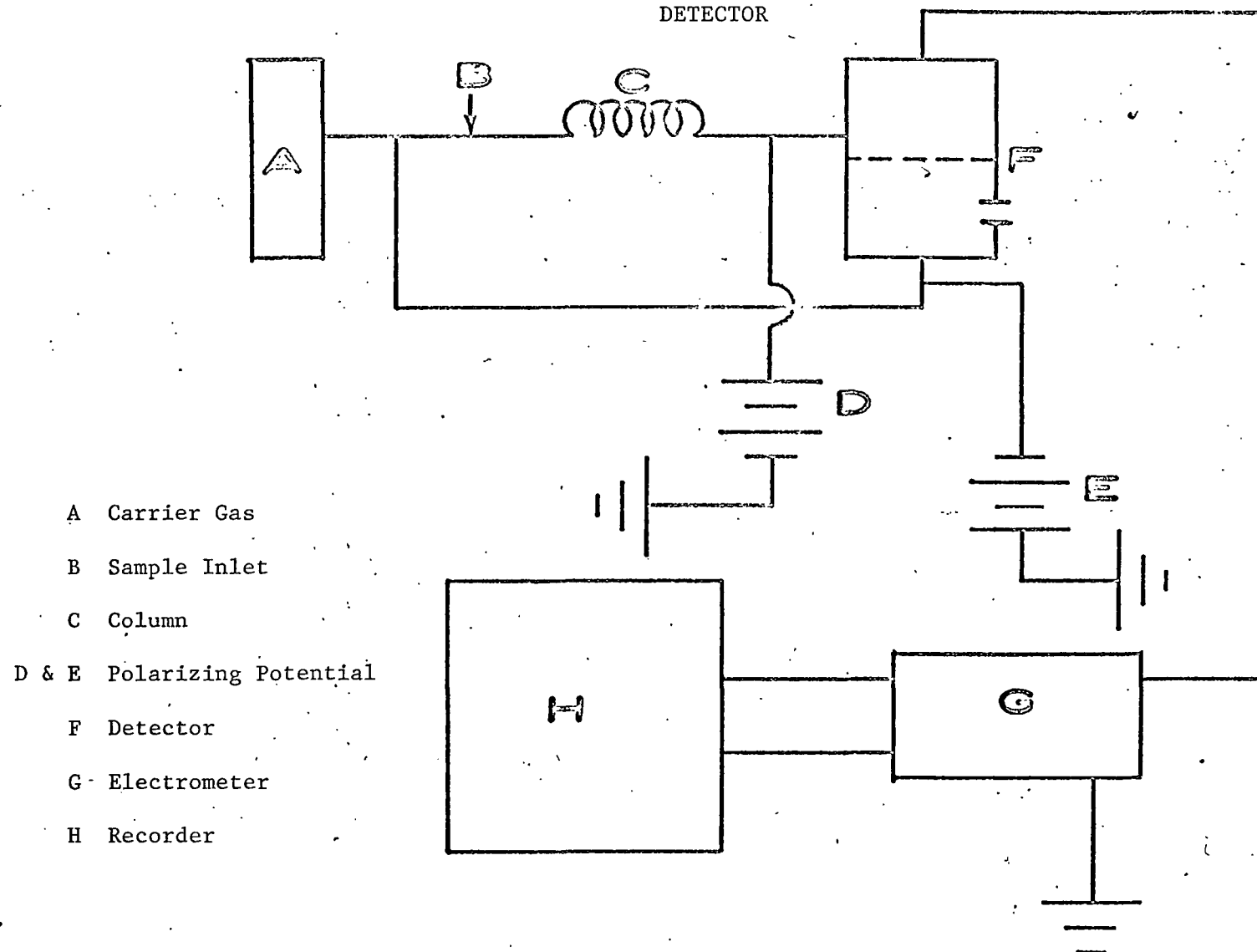
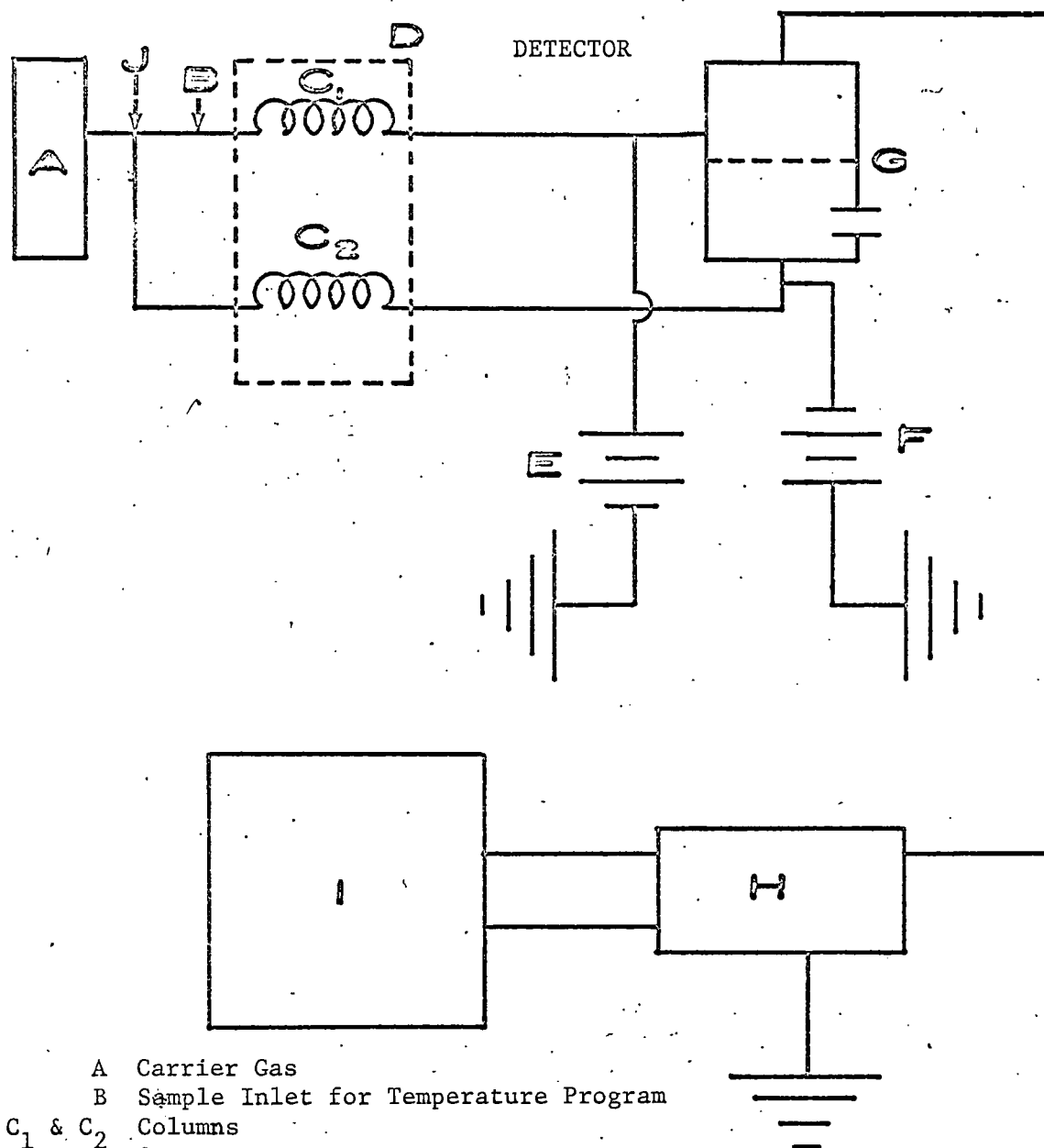


FIGURE 20

EXPERIMENTAL ARRANGEMENT FOR PARALLEL COLUMN OPERATION OR TEMPERATURE
PROGRAMMED OPERATION OF THE BALANCED PAIR IONIZATION CROSS SECTION



- A Carrier Gas
- B Sample Inlet for Temperature Program
- C₁ & C₂ Columns
- D Oven
- E & F Polarizing Potential
- G Detector
- H Electrometer
- I Recorder
- J Sample inlet for parallel column operation

FIGURE 21

EXPERIMENTAL ARRANGEMENT FOR SERIES COLUMN OPERATION OF THE BALANCED PAIR
IONIZATION CROSS SECTION DETECTOR

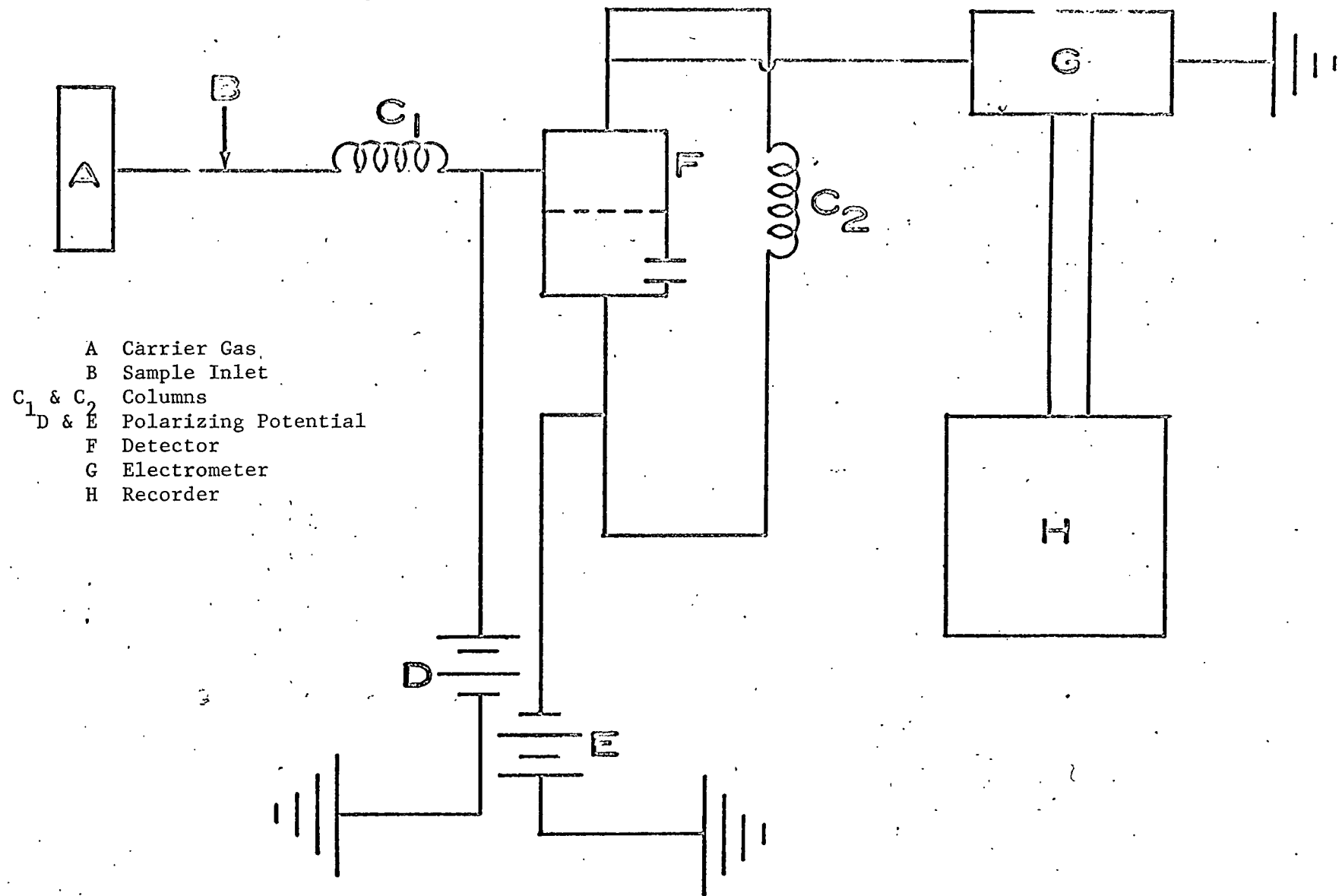


FIGURE 22

IONIZATION CROSS SECTION

IV.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Plane Parallel Detector: Figure 23 shows the ionization current in different gases at various applied potentials for the plane parallel ionization cross section detector. Here the electrode separation was constant at 1 millimeter. In all of these experiments the quantity of tritium used was between 100 and 200 millicuries.

Figure 24 shows the ionization current in hydrogen and nitrogen at S.T.P. for various electrode separations all at an applied potential of 300 volts d.c.. It is noteworthy that even with as close a separation as 0.5 millimeters no field intensified ionization is observed even with an applied potential of 300 volts (6000 volts per centimeter). Also, in the strong electron absorbing gas, sulfur hexafluoride, no loss of ions by recombination is seen above 100 volts applied potential. In practical gas chromatography recombination losses as severe as those to be expected in undiluted SF_6 are most unlikely to be encountered. It may be safely assumed therefore that a polarizing potential of 100 volts is sufficient to avoid errors from this cause. The chamber volume at 0.5 millimeters electrode separation is only 40 microliters. The ion current nevertheless even with the modest amount of tritium used still exceeds 10^{-9} amperes in hydrogen. This leads to the obvious conclusion that an even smaller detector is possible and practical, especially by reducing the internal diameter of the chamber. Table VII lists the general performance characteristics of the detector. Those for a typical cross section detector are also listed for purposes of comparison. They were measured under the following conditions: electrode

RELATIONSHIP BETWEEN IONIZATION CURRENT AND APPLIED POTENTIAL FOR THE PLANE PARALLEL IONIZATION
CROSS SECTION DETECTOR: 1 MILLIMETER ELECTRODE SEPARATION

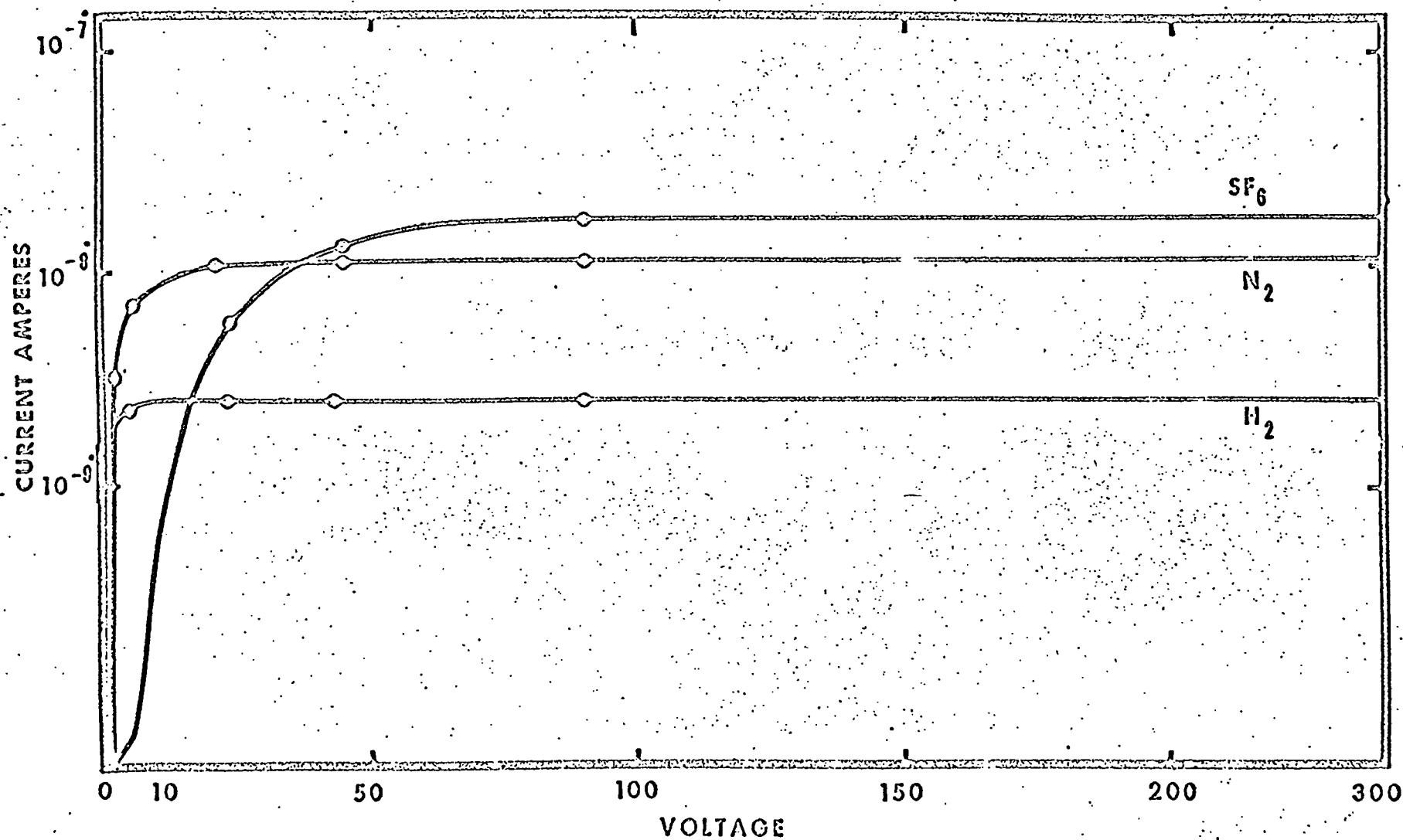


FIGURE 23

RELATIONSHIP BETWEEN IONIZATION CURRENT AND ELECTRODE SEPARATION FOR THE PLANE PARALLEL

IONIZATION CROSS SECTION DETECTOR: HYDROGEN AND NITROGEN

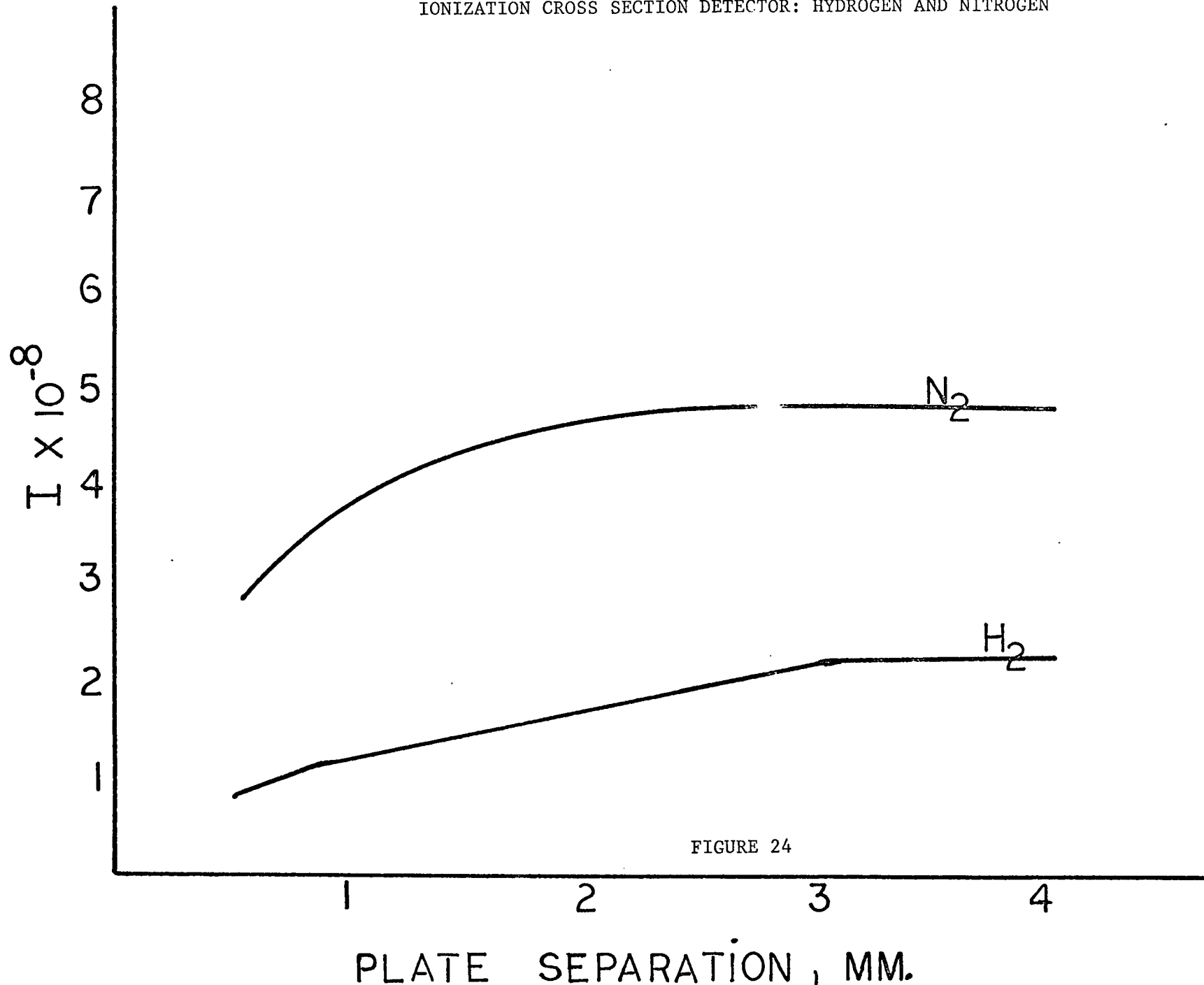


FIGURE 24

TABLE VII
 PERFORMANCE CHARACTERISTICS OF THE SMALL PARALLEL PLATE IONIZATION
 CROSS SECTION DETECTOR COMPARED WITH THOSE OF A TYPICAL IONIZATION
 CROSS SECTION DETECTOR

CHARACTERISTIC	SMALL DETECTOR	TYPICAL DETECTOR
Ionization efficiency	10^{-7}	2×10^{-9}
Linear dynamic range	3×10^5	10^4
Noise level (amperes)	10^{-13}	10^{-13}
Background current in hydrogen (amperes)	5×10^{-9}	5×10^{-11}
Minimum detectable quan- tity (gms per sec.)	10^{-9}	2×10^{-7}
Minimum detectable concen- tration by volume	5×10^{-6}	2×10^{-5}
Carrier gas	H ₂	H ₂
Detector volume (ml)	0.08	5
Substances detectable	All	All

separation of 1 millimeter, polarizing potential 300 volts and with hydrogen as the carrier gas.

The apparent ionization efficiency of the detector assuming a flow rate of 80 microliters per second (4.8 milliliters per minute) is 1 in 10. Though small this is still at least 50 times greater than with previous versions of this detector. The detectivity for small vapor concentrations, which is independent of detector volume, has increased modestly in the range 3 to 10 times. This improvement is attributable to the improved signal to noise ratio accompanying the use of a more intense radiation source. The detectivity for small masses shows the greatest improvement and at 10^{-9} grams per second is beginning to encroach upon the province of the more sensitive ionization detectors. Fortunately, most of the recent advances in gas chromatography, such as capillary tube and lightly coated column present their small vapor samples to the detector at higher concentrations than hitherto. They need from the detector the ability to see small masses and a fast response time. The small cross section detector readily satisfies needs.

The results of the "exponential" dilution experiments with different test gases as shown in Figures 25 and 26. The detector signal is given in logarithmic units so that a linear response to varying gas concentration will appear as a straight line. It can be seen that even with "heavy" gases such as SF_6 and C_3H_6 the response is linear to a concentration of 60% by volume and that an increasing although non-linear response is retained to 100%. This slight departure from linearity above 60% is attributable to the total absorption of an increasing

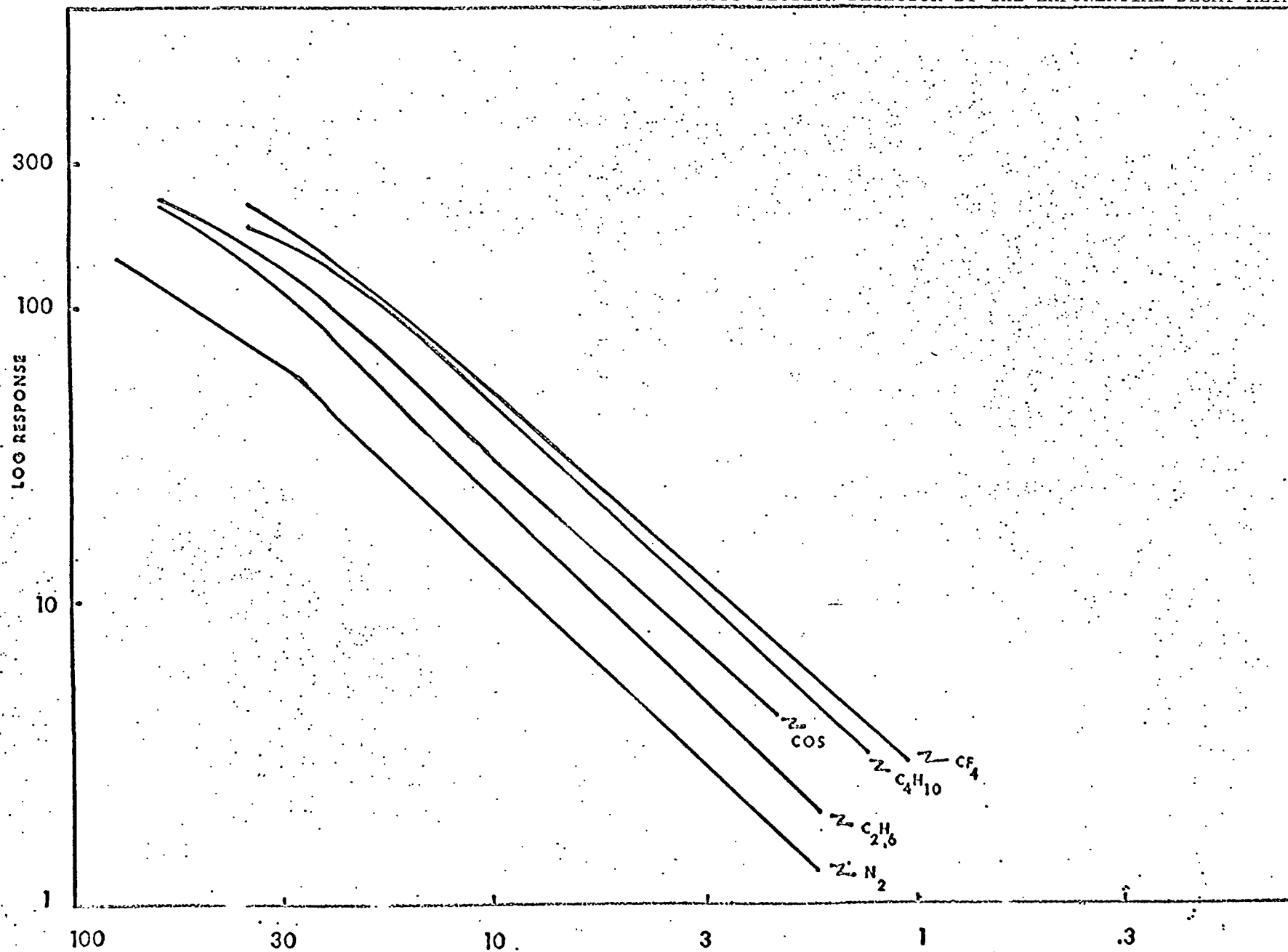


FIGURE 25

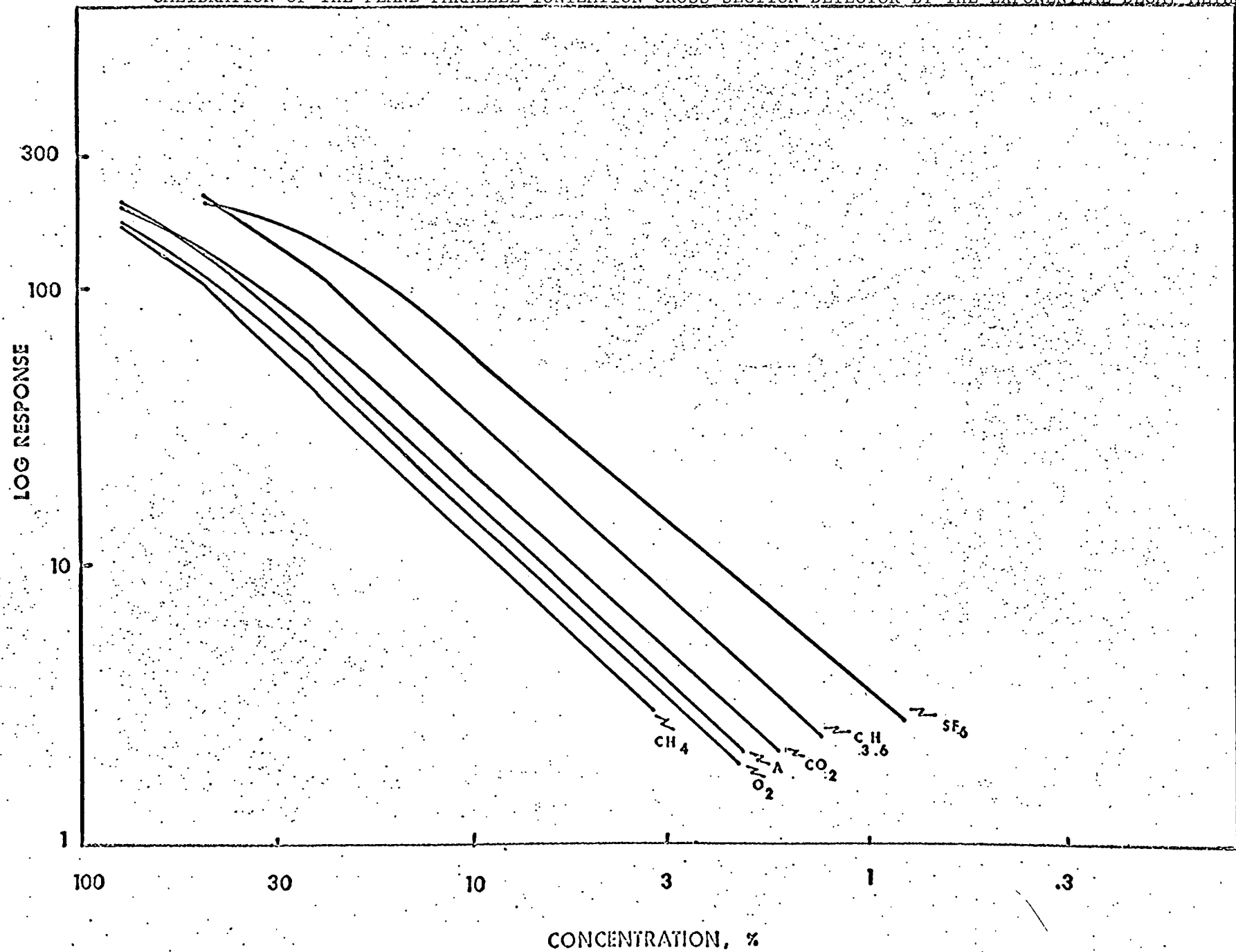


FIGURE 26

portion of the tritium betas in the heavier gases. Figure 27 illustrates the effect of electrode separation on the concentration at which a non-linear response occurs. At 0.5 millimeters the response is linear to nearly 90% by volume, whereas at 2 millimeters the departure from linearity is apparent at 50% by volume of the test gas. A more energetic radiation source than the very weak Tritium beta particles would of course completely avoid this small departure from linearity at high gas concentrations. In practical gas chromatography a non-linear response at concentrations above 50% is hardly of any consequence. Vapor concentrations this high are rarely, if ever, observed.

Otvos and Stevenson (14) measure molecular ionization cross sections using electrons with mean energies of approximately 0.1, 30, and 600 Kev. The ionization cross section varied for any given compound with the energy of the impacting electrons, but for each of the three electron energies the total molecular cross section was consistently the sum of the constituent atomic cross sections of the molecule. The mean energy of the Tritium beta particles is 5 Kev. which is different from the electron energies previously studied. As expected the molecular and atomic cross sections for ionization by Tritium radiation are different from those found with other electron energies. Nevertheless, the total molecular ionization cross section is still simply the sum of the constituent atomic cross sections. Table VIII lists the atomic ionization cross sections for Tritium beta particles relative to hydrogen which is arbitrarily taken as unity. These values are derived by extrapolating the exponential dilution curves to 100% vapor concentration.

THE EFFECT OF ELECTRODE SEPARATION ON THE LINEARITY OF RESPONSE FOR THE PLANE PARALLEL IONIZATION
CROSS SECTION DETECTOR

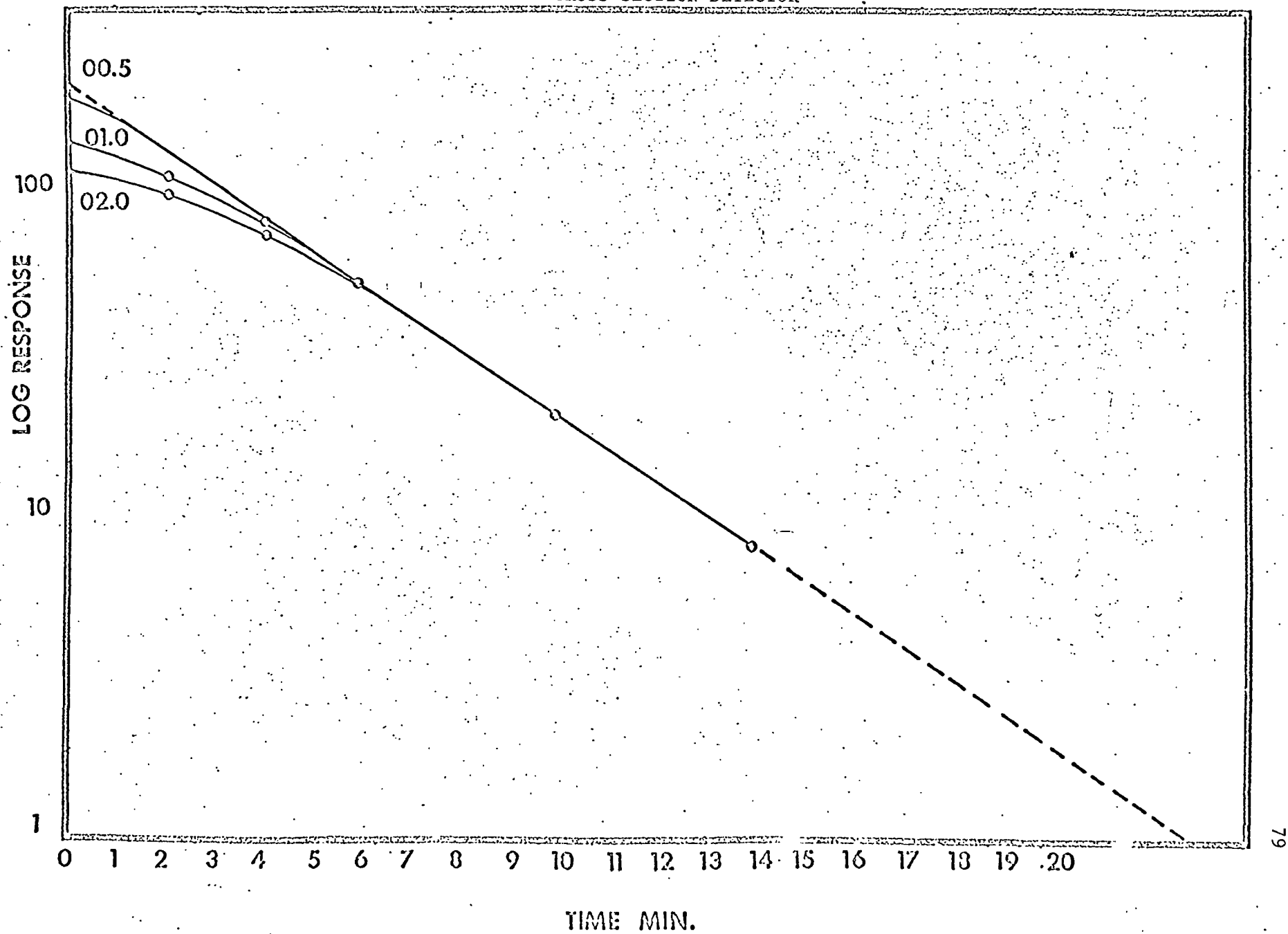


FIGURE 27

TABLE VIII

RELATIVE ATOMIC IONIZATION CROSS SECTIONS FOR TRITIUM RADIATION.

THE CROSS SECTION OF THE HYDROGEN ATOM TAKEN AS UNITY.

Atom	Relative Ionization Cross Section
H	1.00
C	3.69
N	3.20
O	4.56
F	4.08
S	8.75
Ar	9.98

Lovelock (20) has verified these factors in a study of the composition of an ASTM blend of hydrocarbons. The results he obtained are given in Table IX.

Boer (16) discussed the relationship between the response of the detector to equal masses of different compounds in terms of the molecular and atomic ionization cross sections. He showed that a simple, practical response factor was given by the expression:

$$f = \frac{Q_x - Q_c}{M_x}$$

where: f = response factor

Q_x = ionization cross section of the compound

Q_c = ionization cross section of the carrier gas

M_x = molecular weight of the compound

Boer's results were with ^{90}Y radiation but as discussed above are in practice applicable to tritium radiation also. This relationship correctly predicts that in a homologous series the response factor will tend towards a constant value when the ionization cross section of the compound is large compared with that of the carrier gas. With hydrogen or helium as the carrier gas this essentially constant response is reached for relatively simple compounds. With other carrier gases such as N_2 , Ar or CO_2 the difference, $(Q_x - Q_c)$, will for simple compounds be much smaller, or even negative. This means that the detector sensitivity is less with those other carrier gases. No adverse effects on the precision of measurement result however from their use.

TABLE IX
ANALYSIS OF ASTM TEST MIXTURE

	nC7	MCH	Bz	Tol
Synthesis composition	19.8	36.1	14.4	29.7
Analyses; Sample load microliters				
0.03	19.2	36.0	15.7	29.0
0.06	18.9	35.1	15.4	30.6
0.20	18.9	34.2	14.9	32.1
1.0	19.6	34.1	14.3	32.2
3.0	19.6	34.0	14.0	32.3
4.0	20.0	34.7	14.3	31.0
1.0	19.5	35.6	14.6	30.0
0.4	19.3	35.2	14.7	30.6
	19.38	34.86	14.74	30.98

The current flow in the detector has been previously shown to vary directly with the pressure and inversely with the absolute temperature of the gas within it. When used with hydrogen or helium as the carrier gas the detector is not a sensitive thermometer or manometer. With the detector described in this section the temperature and pressure fluctuations which would equal the stochastic noise level are 0.03°C and 0.1 millibar per second respectively. These are comparatively large rates of change of temperature and pressure so that in normal use it is quite unnecessary to use a compensating ionization chamber to offset noise or drift. The detector is unaffected by changes in gas flow rate unless these are accompanied by turbulence sufficient to generate temperature and pressure fluctuations within the detector. However, the observed response may be less for increasing flow rates due to the dilution of sample with excess carrier gas.

Carrier gases other than hydrogen or helium have relatively large molecular ionization cross sections. Q_c for nitrogen for example is 6.40 compared with $Q_c = 2$ for hydrogen. The use of a carrier gas with a large molecular cross section for ionization increases the background current and noise level and decreases the signal given by compounds whose own cross sections are not greatly different from that of the carrier gas. A change from hydrogen to nitrogen or argon as carrier gas decreases sensitivity by a factor of 3 to 10 times according to the conditions and compounds to be measured.

The rare gases argon or helium should never be used as carrier gases in their pure or partially pure state if accurate measurements

are desired. The radiation in the detector is sufficient to produce metastable helium or argon and cause the detector to function simultaneously as a "helium" or "argon" and an ionization cross section detector. In the latter case the ionization is brought about by collision of the test substance with the metastable helium or argon. This phenomenon is vividly demonstrated in Figure 28, which is the exponential decay plot of nitrogen with pure helium as the carrier gas. Considerable deviation from linearity is noted beginning at approximately 3% by volume of nitrogen in the helium carrier gas. In such circumstances high sensitivity would be found but at the price of an unpredictable response to different substances. If the applied potential is relatively high (above 500 volts) these anomalous effects with the rare gases will be greatly increased due to the field intensified multiplication of metastables. At 1000 volts applied potential the observed response is "negative" or current reducing and at least one order of magnitude above that which is observed for normal cross section when using pure helium as the carrier gas. This observation has not been satisfactorily explained but could well deserve further investigation. Helium or argon saturated with water vapor or containing 3%-5% by volume of methane seems to be free of these objections to their use as carrier gases in the cross section detector. In Figure 28 the dashed portion of the curve is the response noted for helium plus 3% methane as the carrier gas. Evidently this quantity of methane is sufficient to completely quench the excess helium metastable energy thereby causing the detector to respond in a normal ionization cross section mode.

EXPONENTIAL DECAY CURVE OF NITROGEN WITH PURE HELIUM AS THE CARRIER GAS:
PLANE PARALLEL IONIZATION CROSS SECTION DETECTOR

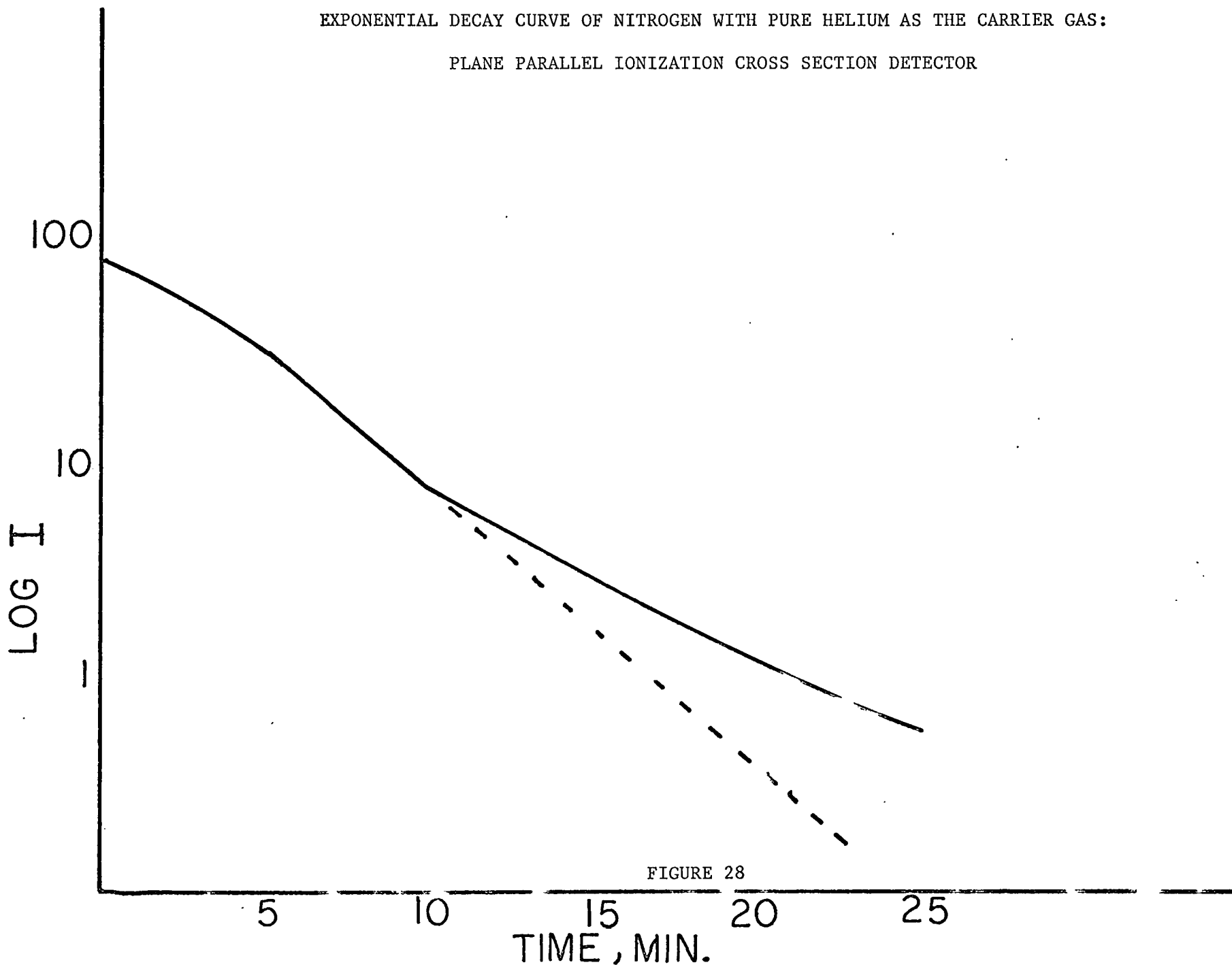


FIGURE 28

The three chromatograms in Figures 29, 30, and 31 illustrate the use of the detector in some of the more severe problems of gas chromatography. Figure 29 is a capillary column chromatogram illustrating that the detector volume is small enough and the sensitivity high enough for it to function in a region commonly thought to be the special province of the more sensitive ionization detectors with a very fast response time. Figure 30 is a series of chromatograms illustrating the separation of oxygen and nitrogen in air on a 5A molecular sieve column. The column loads range from one to thirty microliters. Figure 31 is a chromatogram of the separation of three steroids and one tetracyclic aromatic hydrocarbon at 240°C on a 12 foot SE 30 stationary phase column. Here the detector was operated, as the fast noise level indicates, near the limits of detection. Nevertheless a few micrograms only of these steroids and one microgram (4×10^{-9} moles) of chrysene provided a signal from which an estimate of the loss of steroid by irreversible adsorption on the column could be made. No other detector at present available could have provided such information.

Previous theoretical considerations indicate that if the radiation intensity of the detector is adjusted to maintain the ionization current constant then the pressure or volume can be reduced without changes in performance. This implies that although the lower limits of detectable concentration is unaltered the lower limits of mass detection can be improved. Thus a detector with a volume of one microliter at atmospheric pressure or of one milliliter at a pressure of one millibar could detect as little as 10^{-12} grams of CO_2 (one part per million in this reduced

CHROMATOGRAM SHOWING SEPARATION OF LOW BOILING ORGANIC COMPOUNDS

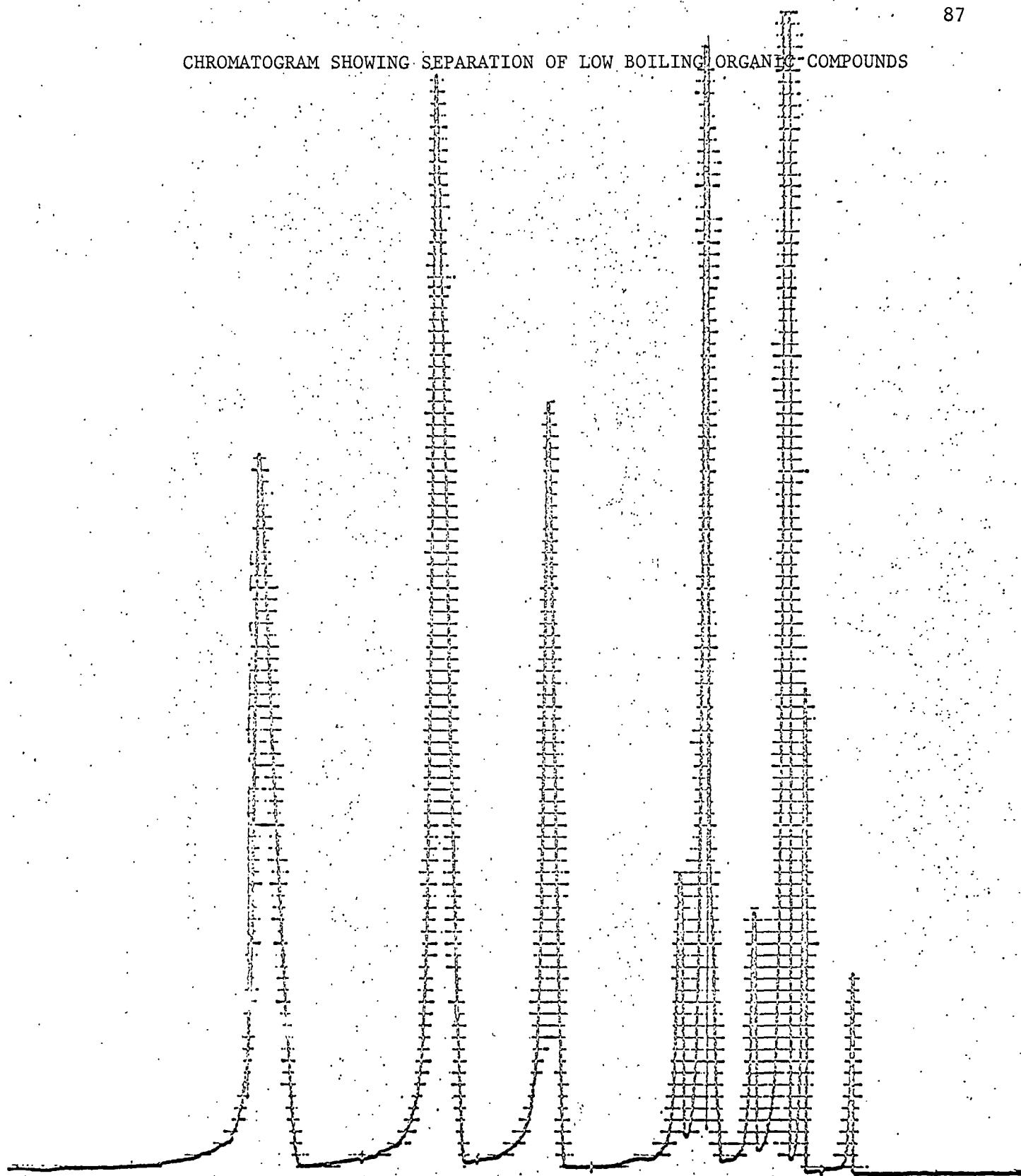


FIGURE 29

SERIES OF CHROMATOGRAMS FOR VARIOUS QUANTITIES OF
AIR APPLIED TO A 5A MOLECULAR SIEVE COLUMN

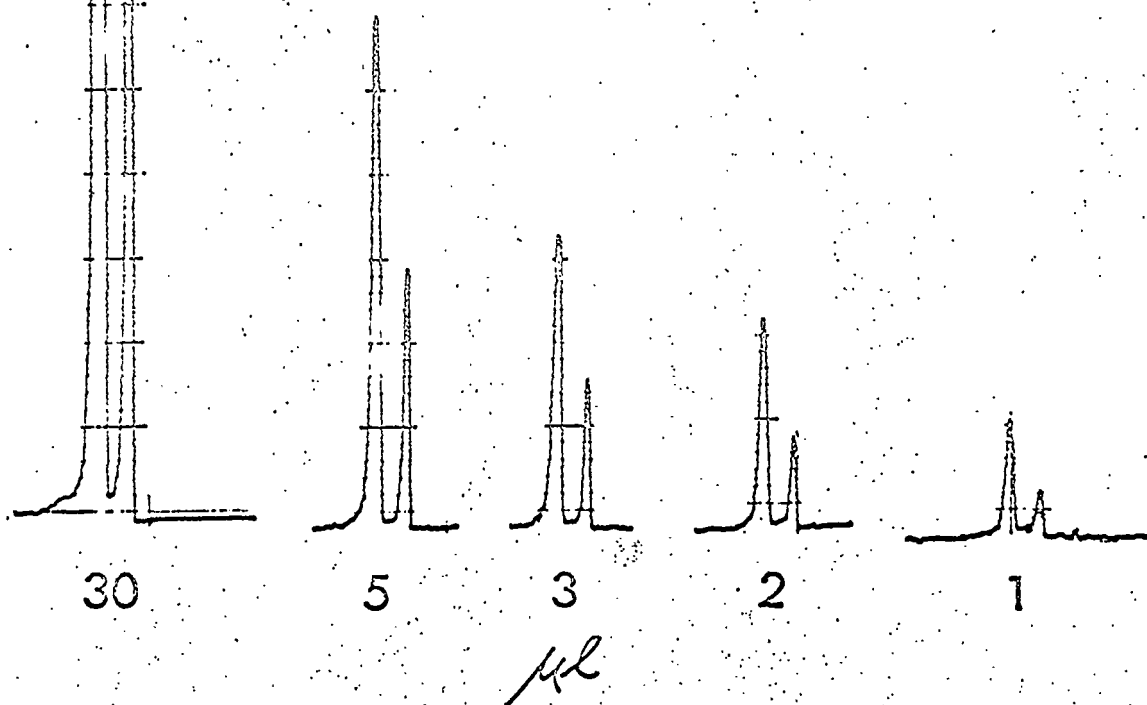


FIGURE 30

THE SEPARATION OF THREE STEROIDS AND ONE TETRACYCLIC AROMATIC HYDROCARBON

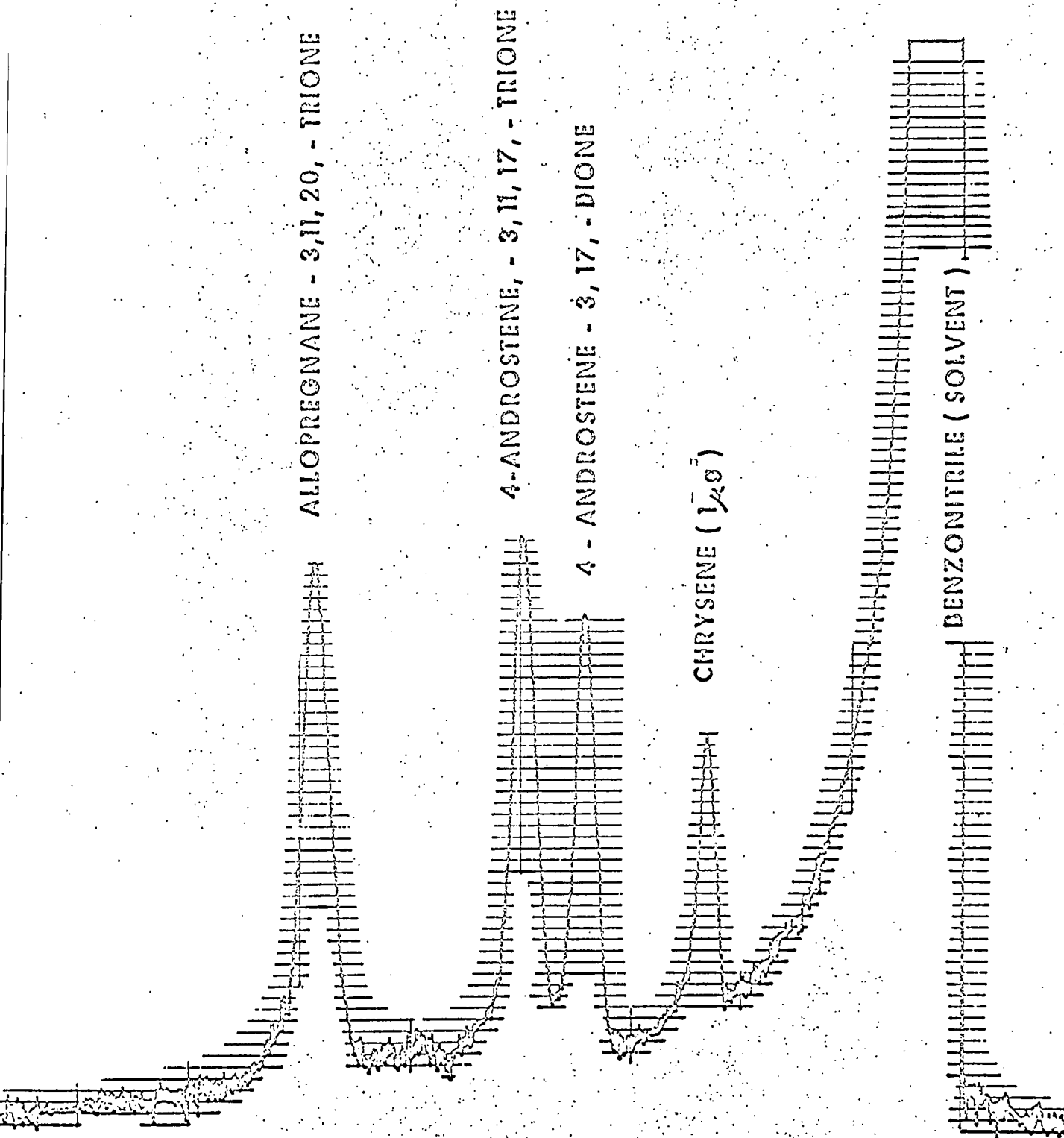


FIGURE 31

volume). These conditions are not far beyond practical reach and it is interesting to observe that they imply an ionization efficiency of 0.05% and a detectivity at least as good as that which can be achieved with the flame ionization detector which is usually considered to be highly sensitive.

8 Microliter Ionization Cross Section Detector: The potentialities of the 8 microliter total volume detector are perhaps best illustrated by the chromatogram in Figure 32, made with an 0.01 inch diameter capillary column. The optimum flow rate with such columns is in the region of 16 microliters per second so that the operating time constant of the detector is only 0.5 seconds. This is fast enough for nearly all of the practical needs of gas chromatography. Where faster analyses are contemplated even shorter operating time constants are possible by an increase in gas flow rate through the detector. This may, however, require a price to be paid in terms of resolution or detectability. The ionization processes within the detector are in gas chromatography terms instantaneous so that the time constant is uniquely determined by the detector volume and gas flow rate.

Table X lists the performance characteristics at S.T.P. for the 8 microliter detector. The characteristics for the previously described plane parallel ionization cross section detector as well as the balanced pair detector are included for purposes of comparison.

Balanced Pair Ionization Cross Section Detector: The sensitivity of the ionization cross section detector to changes in the ambient temperature or pressure is sufficiently low for a single uncompensated detector

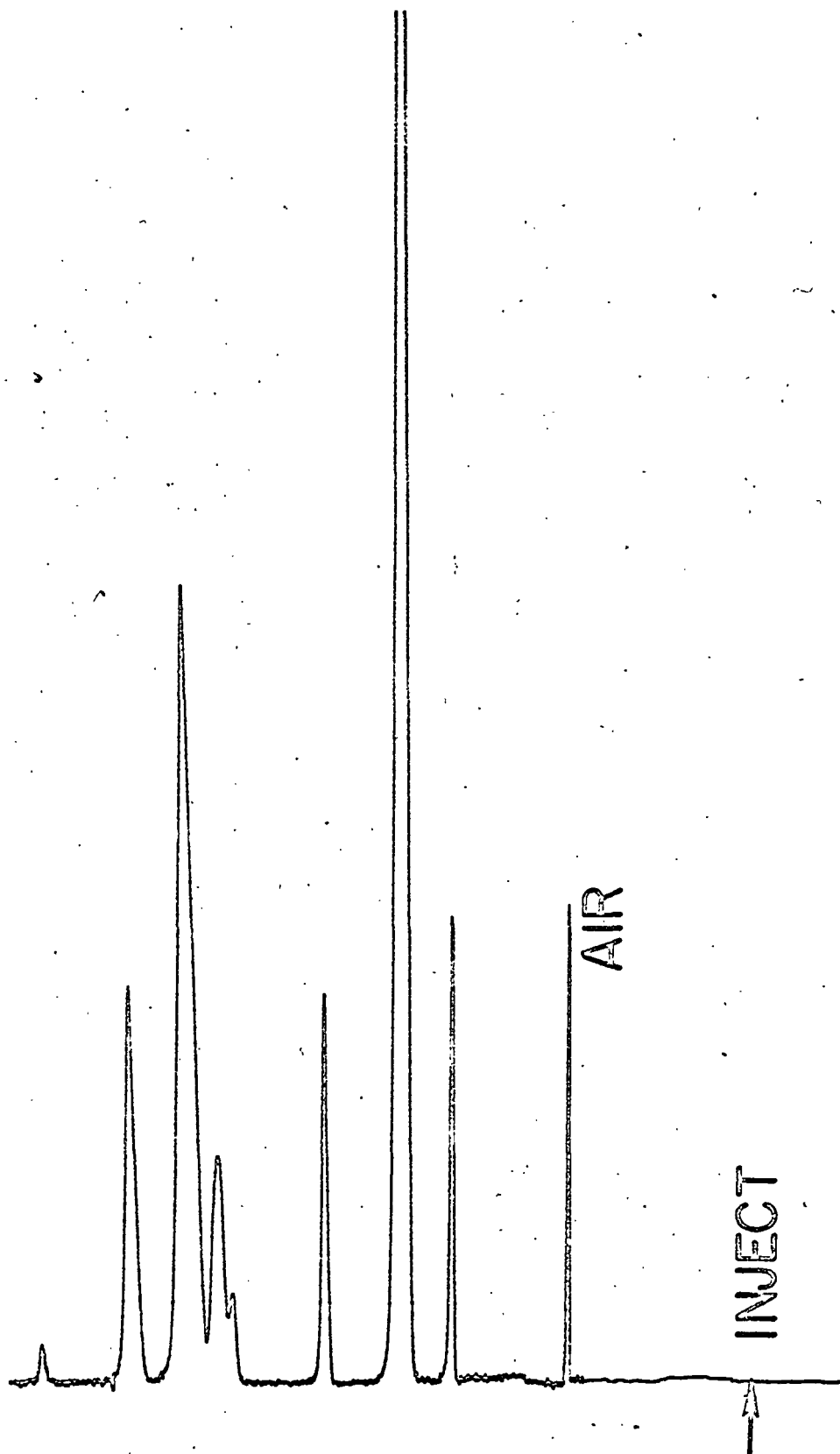


FIGURE 32

TABLE X

PERFORMANCE CHARACTERISTICS OF THE BALANCED PAIR IONIZATION CROSS SECTION DETECTOR AND 8 MICROLITER IONIZATION CROSS SECTION DETECTOR COMPARED WITH THE PLANE PARALLEL IONIZATION CROSS SECTION DETECTOR

(Measurements made with a band pass of 0 to 1 cycle per second)			
Characteristic	Balanced Pair** Detector	80 Microliter Detector	8 Microliter Detector
Ionization Efficiency	10^{-8}	10^{-7}	3.7×10^{-7}
Linear Dynamic Range	1.5×10^5	3×10^5	3×10^5
Noise Level (Ampere)			
H ₂ or He-5% CH ₄	10^{-13}	10^{-13}	10^{-13}
Background Current in Hydrogen (Ampere); Per Single Channel			
H ₂	2.5×10^{-8}	5×10^{-9}	1.3×10^{-9}
He-CH ₄	2.5×10^{-8}		
Minimum Detectable Quantity (gm. per sec.)*	1.6×10^{-9}	3.2×10^{-10}	3.2×10^{-11}
Minimum Detectable Concentration by Vol.	3.2×10^{-6}	2×10^{-6}	2×10^{-6}
Carrier Gas	H ₂ or He 5% CH ₄	H ₂ or He 5% CH ₄	H ₂ or He 5% CH ₄
Detector Volume (ml.)	.250	0.08	.008
Substances Detectable	All	All	All

*Assuming an operating time constant of 1 second

**These parameters determined at 760 mm. Operation at 250 mm. will provide an approximate three fold improvement in characteristics.

to meet the needs of routine isothermal gas chromatography. When the temperature, pressure or composition of the carrier gas in the detector is subject to large changes, for example in temperature programmed gas chromatography, or in the sampling of a planetary atmosphere by a descending probe, a pair of identical detectors can be used in a circuit design to compensate against drift of the base line or false signals from unknown changes in the ambient variables. The notion of compensation using a pair of identical detectors is not new. It was introduced early in the history of ionization cross section detectors by Boer (16) and has recently been demonstrated by Abel and de Schmertzing (21). The theory and practice of compensation, particularly where large changes in gas pressure are to be cancelled have not been previously described.

Figure 33 shows two possible circuit arrangements for a balanced pair detector. In the parallel arrangement of Figure 33A a perfect balance under almost all conditions is readily achieved. Small differences between the standing currents of the two detectors under otherwise identical conditions can be cancelled by equivalent changes in the individual resistors, R ., in series with the detectors. With both detectors the current flows which are compared come from the collection of the same species of charge carriers which may be either negative or positive. In spite of these apparent desirable features the parallel balance circuit is somewhat impractical because of the inherent high impedance of ionization detectors. The arrangement shown in Figure 33A would require an electrometer with both sides of the input floating or alternately two electrometers with the signal comparison made at low impedance outputs which is, of course, expensive.

TWO POSSIBLE CIRCUIT ARRANGEMENTS FOR BALANCED PAIR IONIZATION DETECTOR

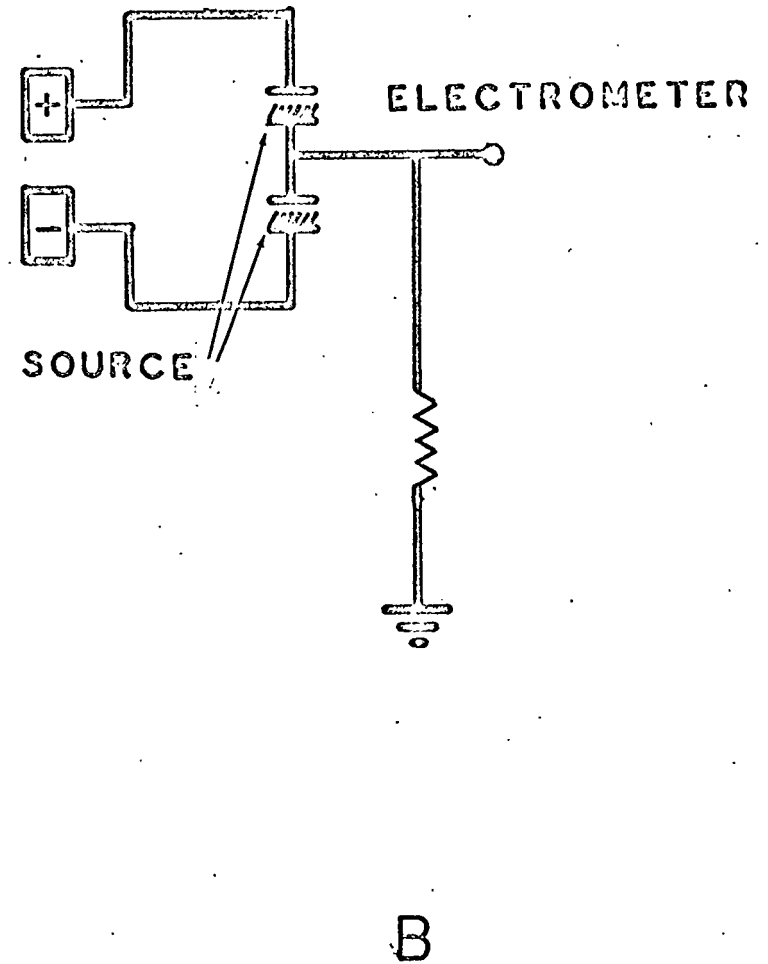
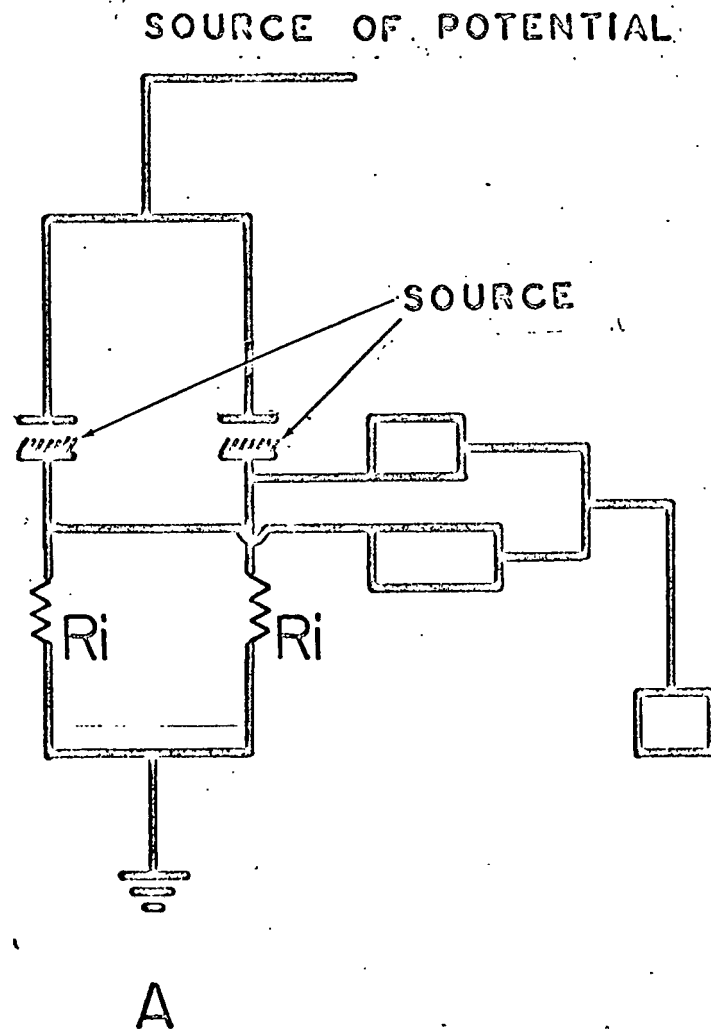


FIGURE 33

The series balanced circuit in Figure 33B is more practical and requires only one conventional electrometer. Its disadvantage is that balancing must be done by the tedious initial adjustment of the radioactive source intensities when the detectors are evacuated and subsequently balancing the pair by small changes in the cell geometry of one of the detectors. In either mode, failure to observe the correct site and polarity of the radiation sources with the balanced pair detectors can give rise to erroneous and even negative signals for a change in gas composition.

Table X lists the performance characteristics for the balanced pair at S.T.P. The detectivities are expressed as the static concentration parameter, grams per milliliter, which is seen to be the same for all three detectors, and as the much more useful dynamic parameters apparent ionization efficiency, in units of grams per second, with an operating time constant of one second. We do not apologize for wishing to include the sensitivities of these concentration measuring detectors, in the dynamic units mass per unit time, for a stated volumetric time constant. The gas chromatograph is a dynamic method of analysis and when detector capability and comparison are considered, the dynamic mass transfer expression, mass or moles per unit time at unit operating time constant is a convenient single parameter. For the three detectors listed in Table X the sensitivities in the mass units are seen to improve as the volume of the detector is reduced. The other performance and operating characteristics listed in the table are less controversial and for the most part self explanatory.

Figure 34 is an illustration of a chromatogram obtained with the balanced pair detector utilizing the parallel column operation previously discussed. Figure 35 shows a similar analysis carried out with the balanced pair detector operating with the column in series.

To demonstrate the usefulness of the balanced pair detector in temperature programming a chromatogram, Figure 36, was obtained showing a complex hydrocarbon mixture. The deviation of the baseline due to bleeding of the liquid substrate becomes quite apparent and calculation of peak areas made somewhat difficult. Figure 37 shows the identical analysis made with the balanced pair detector utilizing the temperature programmed mode of operation. No shift in baseline is observed due to loss of liquid substrate from the column. Any temperature change on the detector itself is found to have negligible effect on the baseline since a change of 200°C on the detector resulted in a net baseline shift of less than 3% of full scale deflection. This minor change due to detector characteristics would be eliminated if the cells were exactly balanced as previously described.

Figure 38 shows the extent to which the balanced pair detector fails to achieve complete cancellation of the signals due to pressure changes. Ideally this residual error signal should vary linearly with the pressure change. In practice where the change is large, for example, a pressure change from 760 mm Hg to 20 mm Hg, the effects shown in Figure 38 may occur. That these are attributable to differences in intensities of the beta sources is shown by exchanging the two sources between the two chambers (dotted line). This effect is not a serious

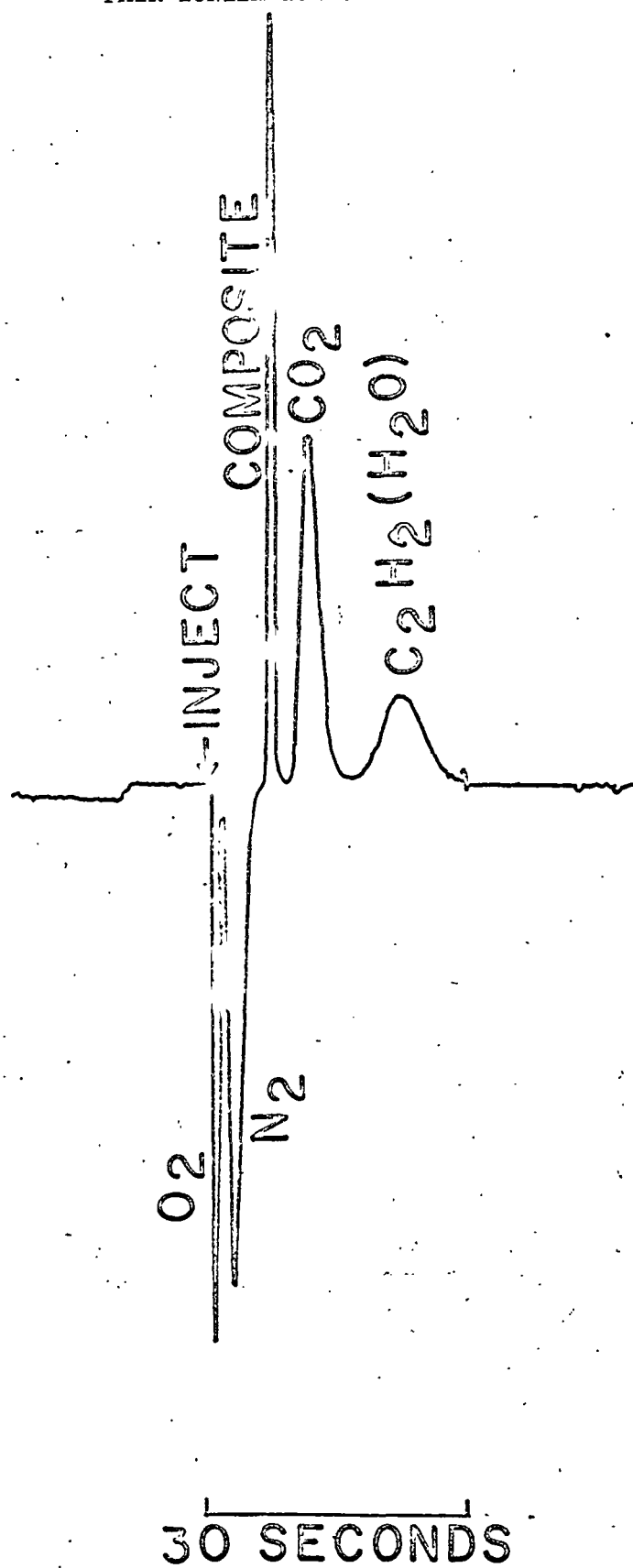


FIGURE 34

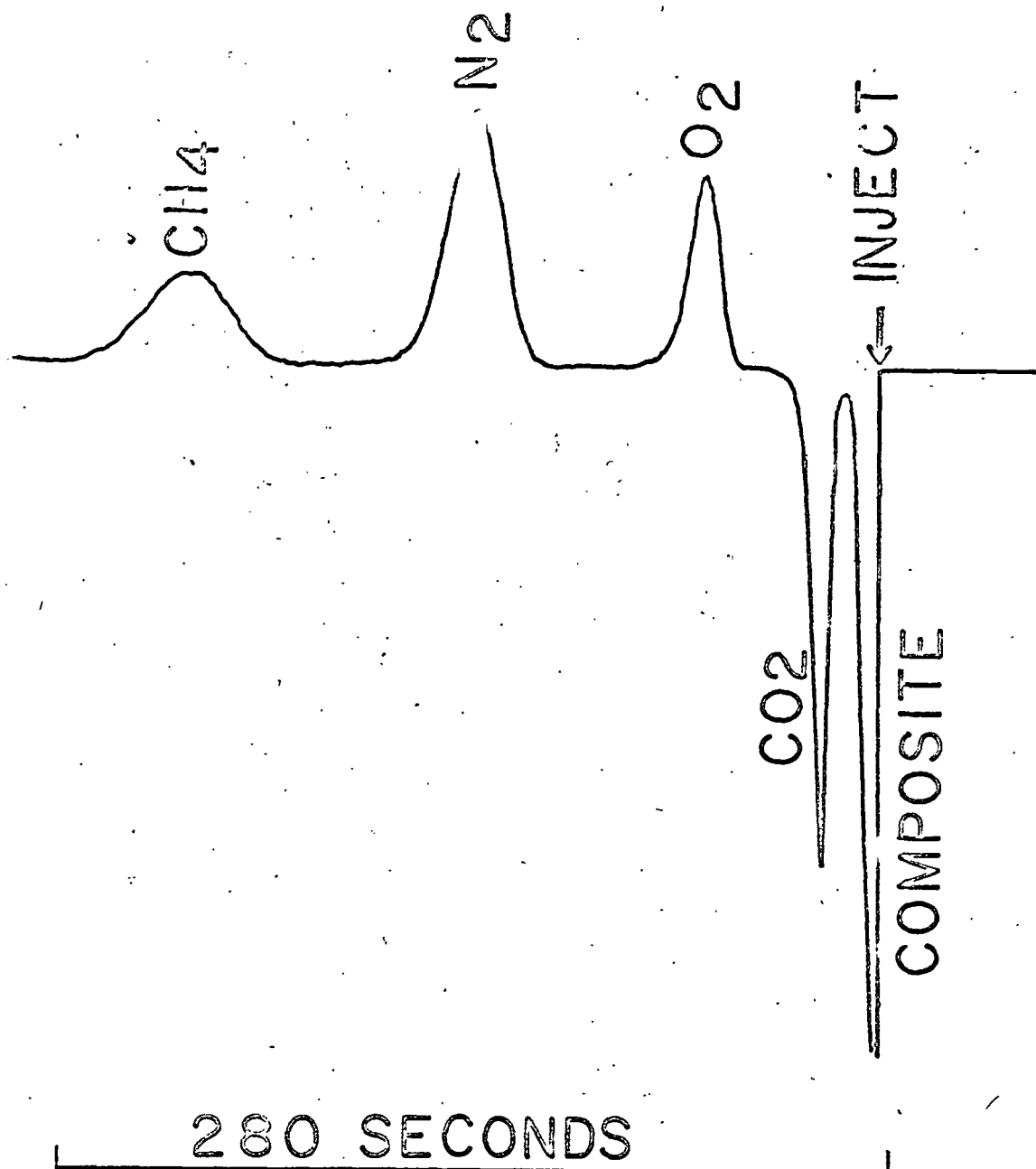


FIGURE 35

CHROMATOGRAM OF TEMPERATURE PROGRAMMED OPERATION OF THE PLANE PARALLEL IONIZATION

CROSS SECTION DETECTOR

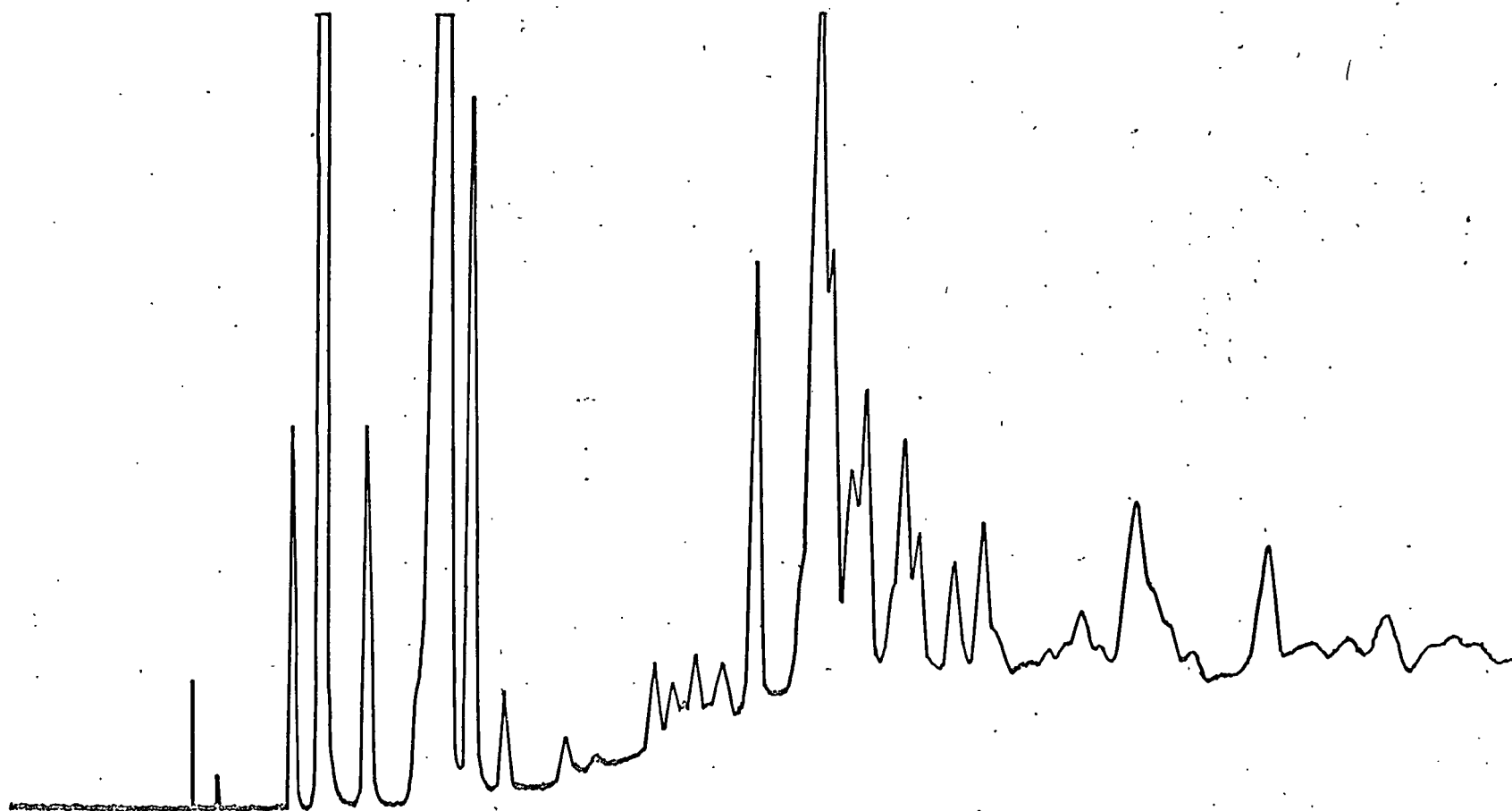


FIGURE 36

CHROMATOGRAM ILLUSTRATING TEMPERATURE PROGRAMMED OPERATION OF THE BALANCED PAIR

IONIZATION CROSS SECTION DETECTOR

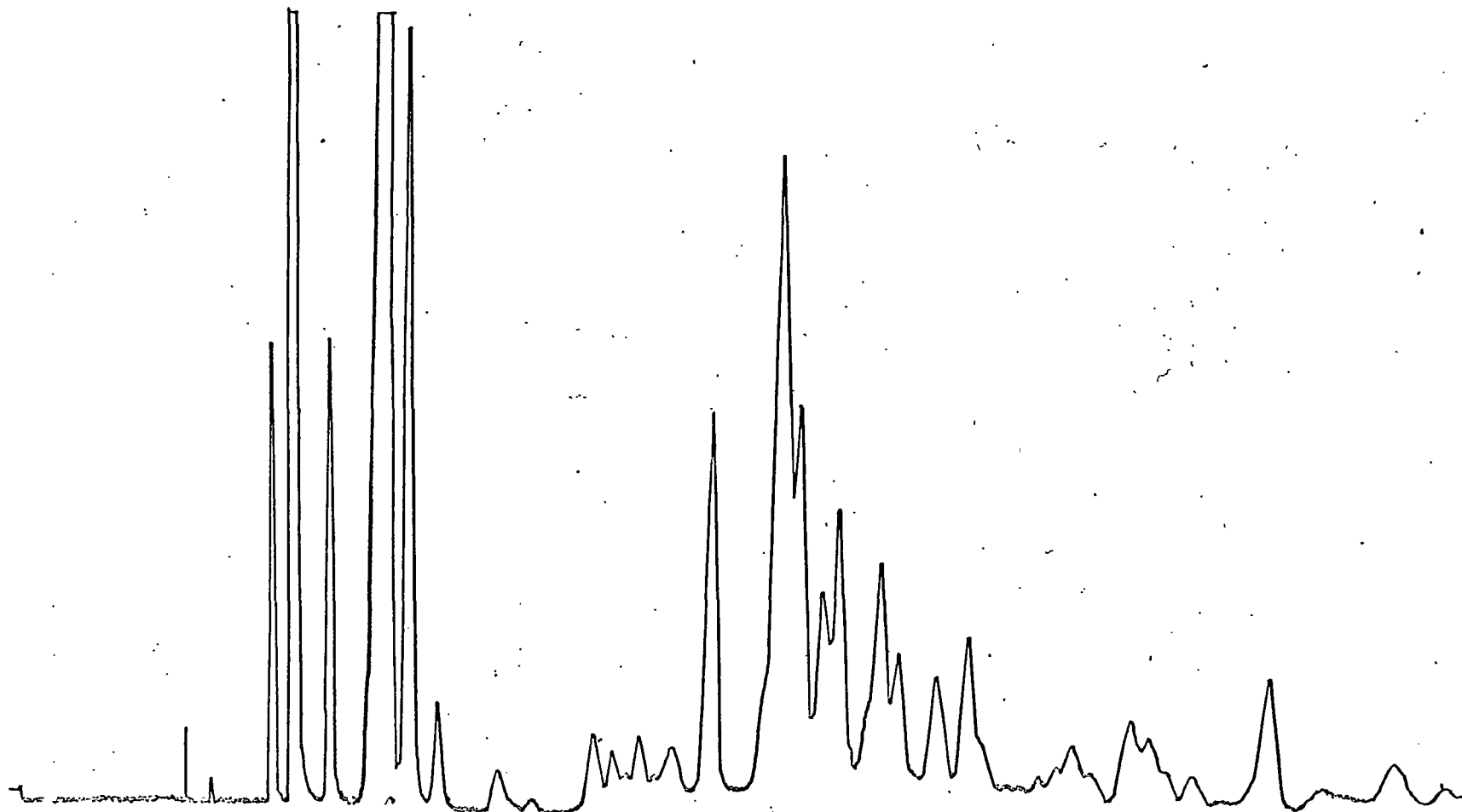


FIGURE 37

EFFECT OF PRESSURE ON THE RESPONSE OF THE BALANCED PAIR IONIZATION CROSS SECTION DETECTOR

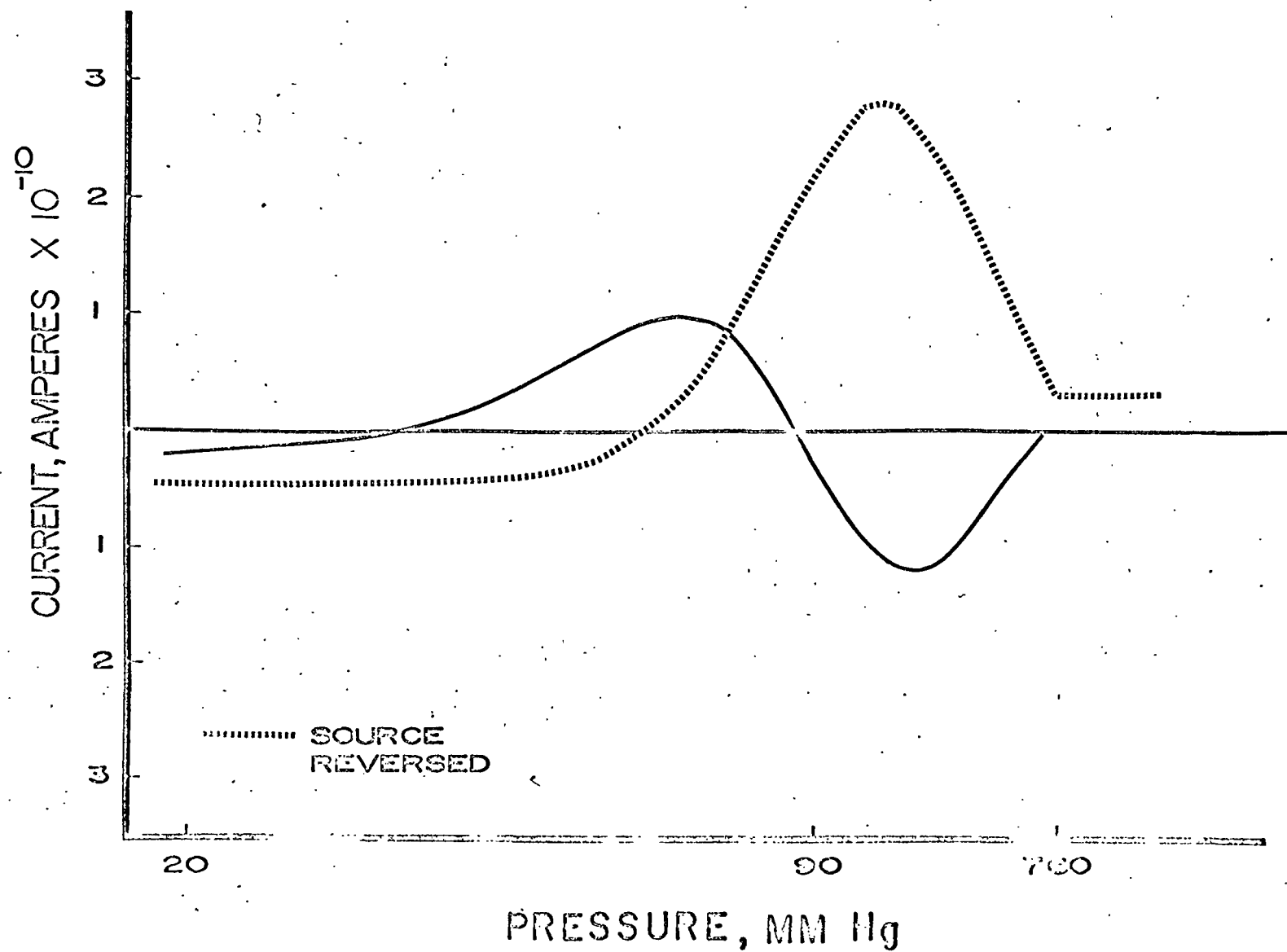


FIGURE 38

source of error for the error signal is only one percent of the standing current at the worst point of the pressure change between 760 mm Hg and 20 mm Hg. It is, however, worthwhile ensuring that the Tritium sources are as similar as possible.

The cross section detector can be regarded as the ionization equivalent of the gas density balance of Martin and James (5) which is probably the most precise and reliable detector for gas chromatography. In the past neither of these detectors have received the attention their good qualities merited largely because their sensitivity was barely sufficient for the advanced applications of gas chromatographic technique. The results here reported show that the sensitivity to small masses for the ionization cross section detector can be improved 100 fold without any loss in its other desirable characteristics. There is also no reason in principle against a further 100 fold improvement in sensitivity which would set the limit of detection in the region of 10^{-11} to 10^{-12} grams per second.

The present version provides a precise and reliable detection method for all applications of gas chromatography except extreme dilution trace analysis. For this a detector with a high sensitivity to low gas or vapor concentrations is needed. It is important to note however that a cathodic detector with a high sensitivity to low vapor concentration is very difficult to handle. The contamination of the system with water vapor in the range one to one hundred parts per million is almost impossible to avoid and would cause noise and drift with such a detector. The fact that the small cross section detector is sensitive to

small masses rather than to small concentrations is for most purposes therefore an advantage. These detectors, differing perhaps in their mode of construction and radiation source, would seem well suited to the needs of lunar and planetary gas chromatography.

IONIZATION CROSS SECTION - ELECTRON CAPTURE

I.

INTRODUCTION

INTRODUCTION

With the introduction of "electron affinity spectroscopy" into the already active field of chromatography a further stimulus was provided which has lead to extension of gas chromatographic techniques to new and different chemical disciplines.

In classical physics complex, sometimes extremely rigid methods are employed to determine precisely the electron affinities of certain compounds. Lovelock (22) simplified the determination with the use of a simple ionization chamber containing a source of ionizing radiation and some means of measuring the current which flows in the chamber at different applied potentials. This method was chosen in an attempt to make detection qualitative as well as quantitative. For this purpose apparent electron affinities were all that was needed, thereby permitting the use of a much less refined measuring technique.

The electron affinity of a molecule is defined as the energy liberated by the attachment of a free electron to that molecule or that energy required to dissociate the resulting negative ion. The electron affinities of different molecular species were known to vary widely, sometimes as much as several orders of magnitude, thus the measurement of apparent electron affinities should be all that is needed for a qualitative indication in a gas chromatographic scheme.

Further work by Lovelock (23)(24)(25)(26)(27) indicated that the attachment process may not be as simple as originally anticipated but that the ultimate potential of the study of such processes and the use

of devices utilizing this phenomenon in detection was astounding and offered an entirely new dimension to the field of gas chromatography.

That the latter statement is valid is evidenced by the rapid appearance in the literature of reports where this new technique was used. To date this trend has continued, increasing at an almost exponential rate. References (28-77) are but a few selected to indicate the present areas of study making use of electron capture studies.

As more use was made of electron capture measurements in chemical studies it was soon realized, however, that interpretation of data was not as straightforward as some had tried to make it. Quite often questionable, if not completely erroneous conclusions were drawn from data that had been painstakingly collected over a long period of time. Unfortunately this is the price sometimes paid when dealing with a method that is jointly extremely sensitive and highly specific.

In an attempt to obviate the aforementioned difficulties a system has been devised simultaneously utilizing both electron affinity and ionization cross section methods. The ionization cross section being absolute, in that it is directly related to a molecular parameter, serves as a nonselective guide to the interpretation of electron affinity measurements as well as providing unique quantitative data. The following section will describe the development and utilization of such a system.

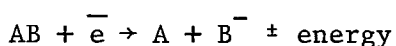
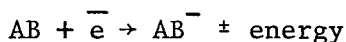
IONIZATION CROSS SECTION - ELECTRON CAPTURE

II.

PHYSICAL BASIS

PHYSICAL BASIS

The physical process occurring in electron affinity measurements are the reactions of free electrons and molecules to form stable negative ions by either of two methods:



Lovelock (23) indicates that in the first reaction, the energy released may escape as radiation from the negative molecular ion or be shared with other molecules during subsequent collisions. In the second, dissociative capture, the energy balance is maintained by the following factors: the relative kinetic energy of the reactants before and after collision; the energy released by the formation of the negative ion from a constituent atom or radical of the compound; and the energy required or released during dissociation of the molecule. Whichever of the two reactions occurs, free electrons are lost and negative ions are formed. Owing to the difference in mobility of the two species, i.e., free electrons and negative molecular or atomic ions, this loss may be measured.

The response of an electron capture detector was initially believed to be related to vapor concentration of a given compound in approximately the same manner as light absorption is related to the Beer-Lambert Law. This would lead to the following expression for

the response of the detector in the presence of an electron absorbing vapor:

$$I = I_0 e^{-EcX}$$

where: I_0 = ionization current in the presence of carrier gas only

I = ionization current in the presence of test vapor

e = natural function

E = electron absorption coefficient of the vapor

c = vapor concentration

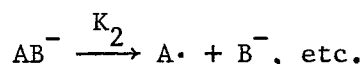
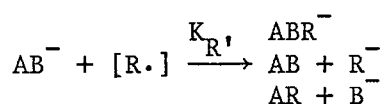
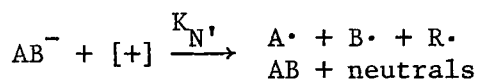
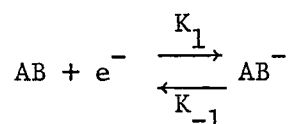
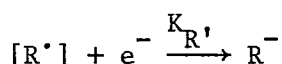
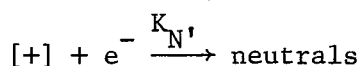
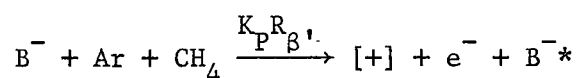
X = geometry constant

It was noted at the time that not all compounds followed this relationship; indeed, some showed a considerable deviation. Therefore this relationship was not strictly correct, possibly because it did not take into account all of the possible interactions occurring during the reaction.

Wentworth, et al., (78) has recently examined very carefully the total electron attachment process and devised a model based on kinetic considerations which more completely describes the actual interactions occurring. Briefly the model is based on the following assumptions: First, the rate of ion production of thermal electrons is constant and is not affected by the presence of any foreign gaseous materials; further it is assumed that the actual reaction zone is a cloud of electrons localized in a narrow region about the radioactive foil, this cloud being positive due to the presence of excess positive species. Since the cloud is considered homogeneous, the kinetic treatment is

justified. Finally it is assumed that the major loss of electrons in the presence of pure carrier gas is brought about by recombination of the electrons with the positive species and/or the reaction of electrons with radicals. Subsequent experimental evidence has supported these assumptions, therefore in all probability they are acceptable.

The authors have placed most of their emphasis to date upon the non-dissociative reaction, so this is the case we will consider. They describe the reactions occurring in the cloud as follows:



By appropriate kinetic treatment, which provides the basis for their excellent publication, they are able to drive kinetic expressions for the reactions occurring in the presence of a non-dissociative capturing species. In each case studied the corrected response was found to be

proportional to the concentration of the electron capturing species under investigation. The corrected response and concentration relationship may be expressed as:

$$\frac{b - e^-}{e^-} = K_M a$$

where: $b - e^-$ = peak height at given time

e^- = electron capture current in absence of capturing species

e^- = electron capture current remaining after peak subtraction

K_M = total reaction rate constant

a = $[AB]$ = concentration of capturing species

This expression can be understood better by reference to Figure 39. Thus the capture coefficient, K , can be determined by plotting the corrected response as a function of the concentration of capturing species and obtaining the slope. In the use of this model only the total sample injected was known so that it was necessary to integrate the corrected response with respect to the volume of gas passed through the cell since the concentration dependency of the corrected response is given in terms of instantaneous concentrations, i.e.,

$$\int \frac{b - e^-}{e^-} = KA$$

where: A = peak area.

The modification suggested by this author is that a dual system be incorporated in the measurements to determine simultaneously the electron

DESCRIPTION OF TERMS USED IN THEORETICAL MODEL

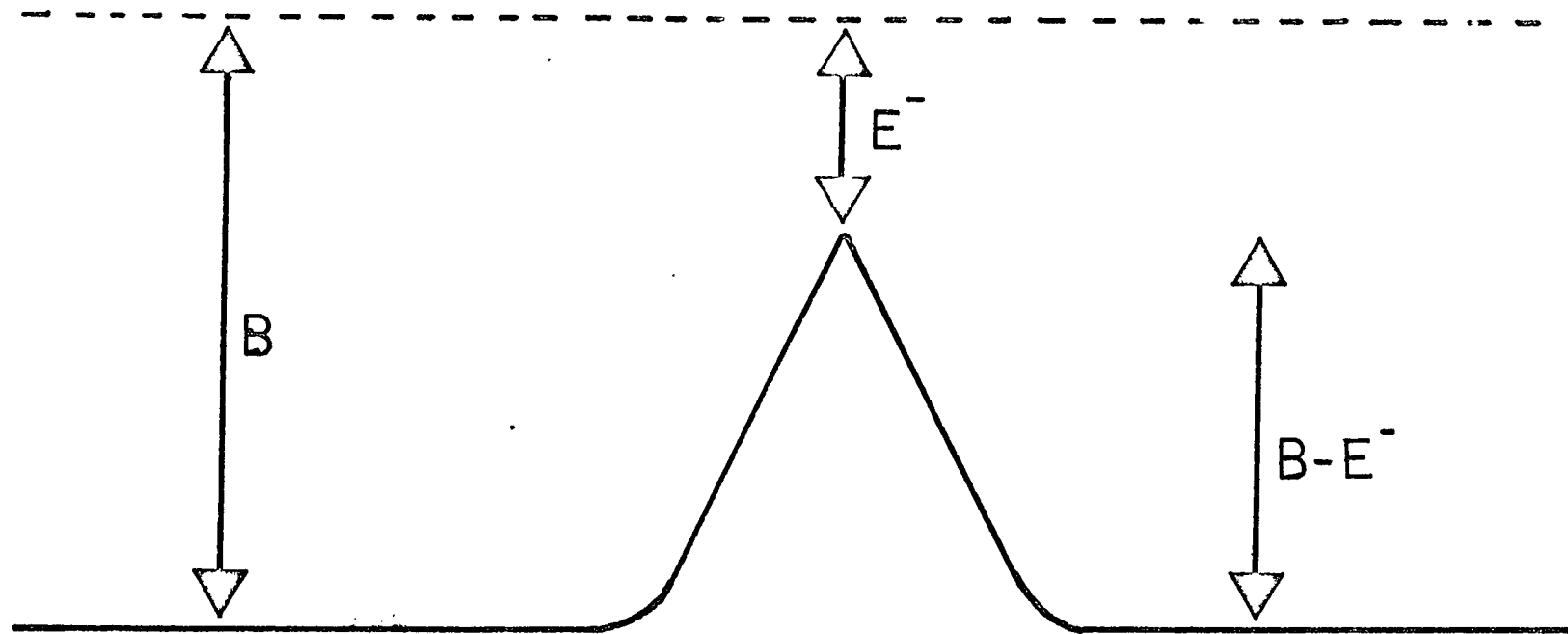


FIGURE 39

capturing signal and some nonselective signal related to a molecular parameter, i.e., ionization cross section signal. Since the capture coefficient, K , is a function of the change in peak response with varying concentration of capturing species a measurement of peak height of the cross section peak is all that is necessary to determine response versus concentration. If the chromatographic peaks are assumed to be triangular and since the peak width at the base remains essentially constant for a given compound being eluted from a chromatographic column, the change in peak height will directly reflect the change in sample concentration in a series of determinations.

The other advantage in this measurement scheme is that there is more conclusive evidence that the peak under consideration is indeed that suspected. In the previous method a prior knowledge of sample composition is assumed.

If relative capture coefficients are all that is required the aforementioned experiments suffice. However, if the results are to be tabulated and actual electron affinities are to be calculated, we may calculate the actual weight of sample represented by the ionization cross section peak as previously outlined. This information along with a knowledge of the relative amount of sample going into each detector will yield information regarding the actual amount of sample present in the electron capture cell. Thus decomposition, sample losses due to adsorption in the column and other unaccountable losses in the chromatographic process, introduce little or no error into our determinations. If the latter, more involved calculations are made then, as suggested by

Wentworth, et al., a plot of $\ln KT^{3/2}$ versus $1/T$ is a linear function with a slope of EA/k , where k is the equilibrium rate constant. Thus the electron affinities in absolute values may be obtained.

IONIZATION CROSS SECTION - ELECTRON CAPTURE

III.

EXPERIMENTAL

EXPERIMENTAL

Apparatus: The electron capture detector was that described by Lovelock (3).

The ionization cross section detector was the plane parallel design discussed in the foregoing section.

The polarizing potential for the ionization cross section detector was provided by a Kepco Model 1500M regulated d.c. power supply.

The polarizing potential for the electron capture detector was provided by a Datapulse Model 102 d.c. pulse generator.

Chromatograms were obtained and measurements recorded using a Westronics dual channel recorder.

The oven units were a modified Barber Colman Model 150 Gas Chromatograph.

Ionization currents were measured using a Cary Model 31 vibrating reed electrometer, in terms of the potential developed across a known high resistance.

All carrier gases were commercial grade obtained from Big Three Welding Supply, Houston, Texas.

Chemicals were the purest grades available from commercial sources.

Procedure: Figure 40 is a schematic representation of the experimental system used in this study. A mixture of Helium-5% Methane is used as the carrier gas in the column. Both the Helium-Methane and Argon-5% Methane are dried by passing these through a chamber filled with 5A molecular sieve. The inlet pressures were accurately measured by means of the gauges shown. The chromatographic column employed was

EXPERIMENTAL ARRANGEMENT FOR DUAL SYSTEM

114

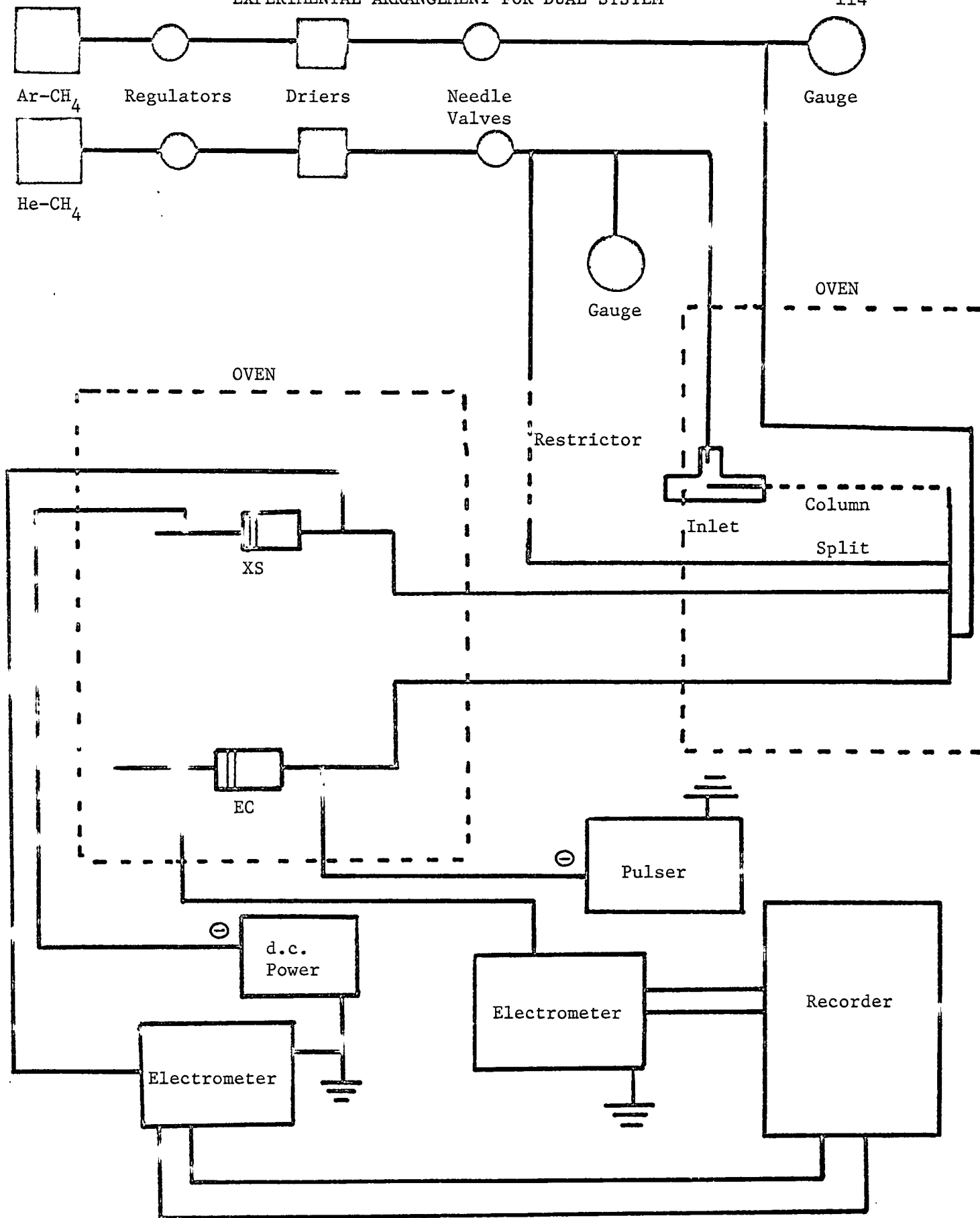


FIGURE 40

10 feet 1/8 inch 3% SE 30 on Gas-Chrom Q to avoid loss of the liquid substrate at elevated temperatures. The effluent from the gas chromatographic column was divided by means of a simple tee arrangement having been adjusted by crimping one arm to yield the desired split ratio, and portions of the sample sent to both the ionization cross section and electron capture detectors. Mass flow through the splitting system was maintained at a suitable level by an additional flow of Helium-5% Methane admitted to the system just prior to the sample division. Argon-5% Methane for the electron capture operation is added prior to the divided sample entering the detection cell. The additional Helium-5% Methane added serves another purpose of maintaining the proper pressure balance, thus restricting Argon-Methane from flowing into the ionization cross section system. The ionization cross section detector was operated at 200 volts d.c. in all of the experiments.

The proper operating conditions for the electron capture detector were established by varying the pulse width and pulse interval in addition to the pulse amplitude and noting the corresponding changes in output signal from the cell. The proper operating conditions having been determined, the system was next evaluated as an entity: all carrier gases were admitted, the column heated and the detector temperature varied to note any temperature effects. Only when temperature independence was observed were the experiments attempted. It should be noted that in order for the system to perform properly it must be completely free from contamination and devoid of any gas leaks that could result in diffusion of air into the system. If these precautions are not taken

the data obtained will be of little or no value due to the presence of oxygen and other foreign matter which has an unpredictable effect upon the response of the electron capture detector.

IONIZATION CROSS SECTION - ELECTRON CAPTURE

IV.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

As previously mentioned, the system used in this study is outlined in Figure 40. To ascertain that the electron capture detector was functioning properly and the results obtained were compatible with the theoretical model the following tests were run: the current was measured as a function of the pulse period (t_p). In the model employed it is necessary that the electron concentration does not vary. Since the current, I , in amperes is equal to coulombs per second or electrons per second, the product of the pulse period and current will yield the electron concentration, i.e.,:

$$t_p \text{ (seconds)} \times I \text{ (electrons/second)} = \text{electrons.}$$

Table XI is a tabulation of the results obtained. The carrier gas was Helium-5% Methane, the scavenger gas was Argon-5% Methane, the pulse amplitude was 50 volts; the pulse width was one microsecond. The data is presented graphically in Figure 41. It is noted that the electron concentration reaches a constant value at approximately 500 microseconds. The hump in the curve is best explained by considering the recombination rate for electrons with the positive species in the reaction cloud.

The proper pulse width was selected by studying the variation in current with pulse width. The data obtained is presented in Table XII. Figure 42 is a plot of this data. From this information it may be concluded that a pulse width of 0.3 to 2.0 microseconds is sufficient

ELECTRON CONCENTRATION VERSUS PULSE INTERVAL

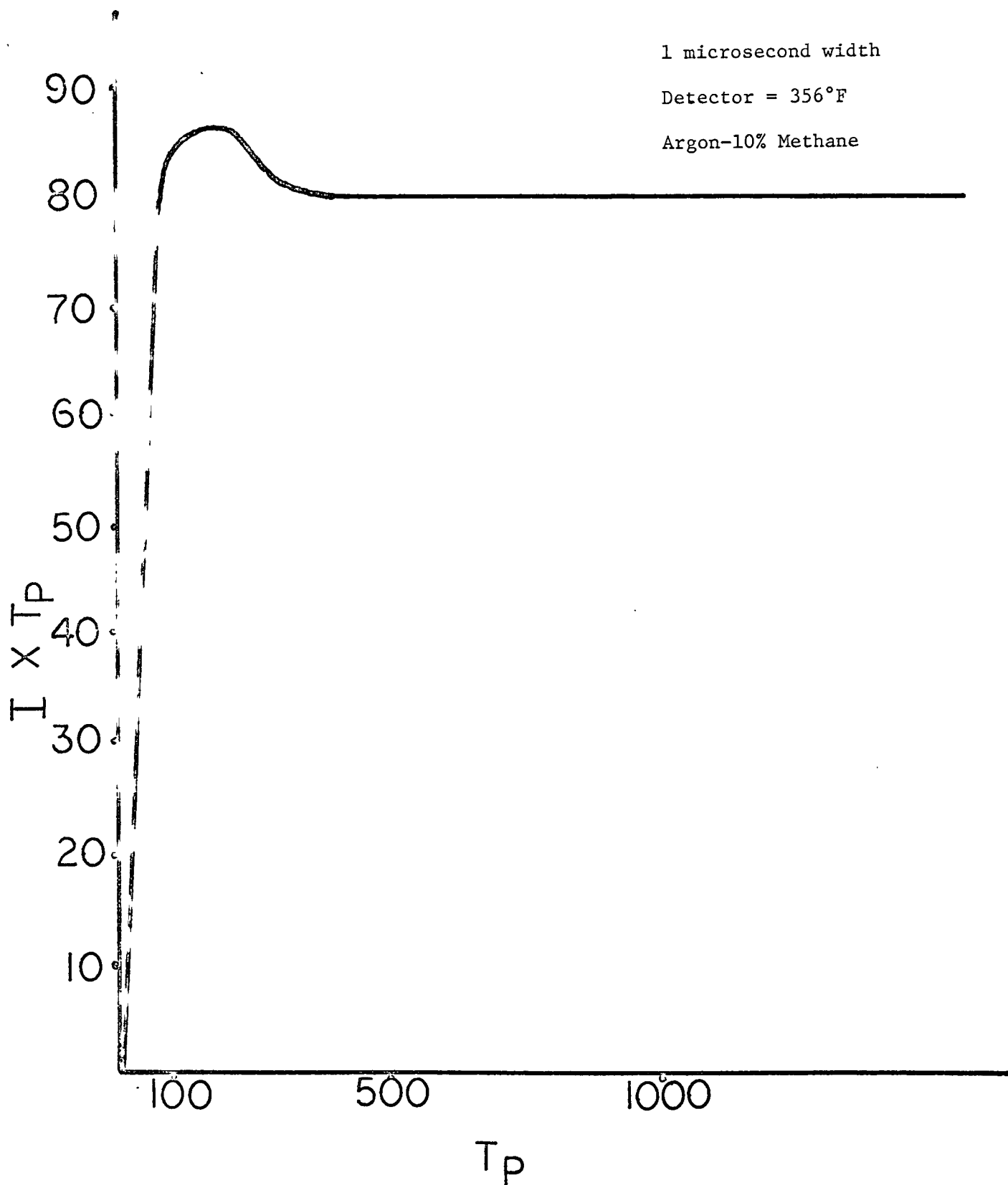


FIGURE 41

SATURATION CURRENT VERSUS PULSE INTERVAL

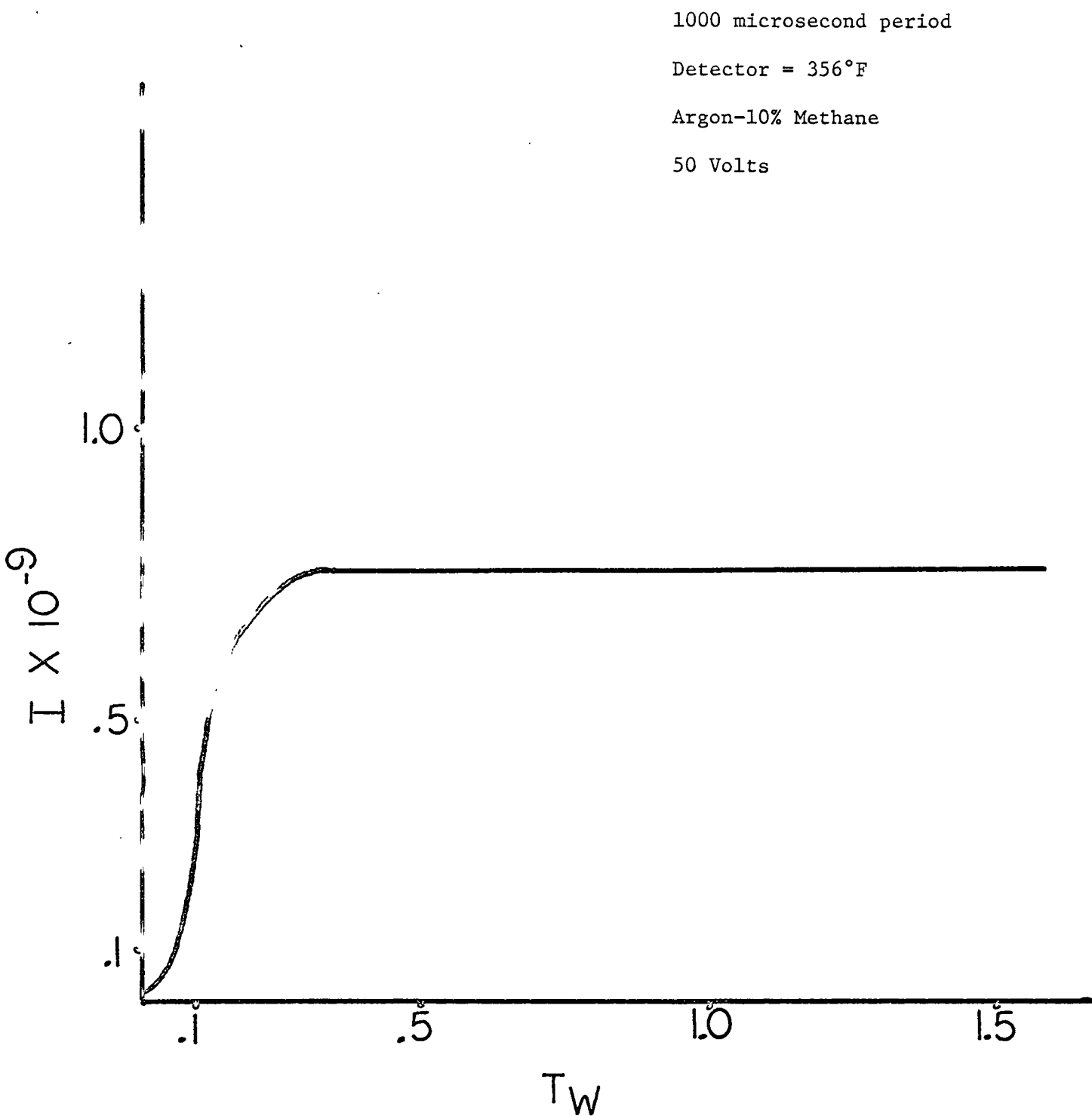


FIGURE 42

TABLE XI
ELECTRON CONCENTRATION VERSUS PULSE INTERVAL

$\frac{t_p}{\text{microseconds}}$	$\frac{I}{\text{amperes}}$	$\frac{I \cdot t_p}{\text{electrons}}$
10	1.39×10^{-8}	13.9×10^{-8}
20	1.32×10^{-8}	26.4×10^{-8}
50	1.10×10^{-8}	55.0×10^{-8}
100	0.84×10^{-8}	84.0×10^{-8}
200	0.43×10^{-8}	86.0×10^{-8}
300	0.27×10^{-8}	81.0×10^{-8}
400	0.20×10^{-8}	80.0×10^{-8}
500	1.50×10^{-9}	75.0×10^{-8}
1000	0.75×10^{-9}	75.0×10^{-8}
2000	0.40×10^{-9}	80.0×10^{-8}
4000	2.58×10^{-10}	103.0×10^{-8}
6000	2.45×10^{-10}	147.0×10^{-8}
10,000	2.00×10^{-10}	200.0×10^{-8}
20,000	1.90×10^{-10}	380.0×10^{-8}

TABLE XII
SATURATION CURRENT VERSUS PULSE WIDTH

t_w microseconds	I amperes
0.1	0.27×10^{-9}
0.2	0.66×10^{-9}
0.3	0.74
0.7	0.74
1.0	0.75
2.0	0.76
5.0	0.79
10.0	0.84
20.0	0.94
50.0	1.38
100.0	2.03
200.0	pulse overload
500.0	pulse overload

for the collection of all of the electrons generated. Above 2 microseconds pulse width the electrons generated during the application of the pulse begin to give rise to a current increase. Since we are attempting to study the system during equilibrium conditions the pulse width selected was 1.0 - 1.5 microseconds. The carrier gas again was Helium-5% Methane, the scavenger gas was Argon-5% Methane, the pulse amplitude was 50 volts and the pulse period was 1000 microseconds.

A voltage versus current determination was carried out to predict the proper pulse amplitude. The results are presented in Figure 43. The plateau region extends from 10 to 60 volts. Therefore any pulse amplitude within this region will be acceptable. In the description to follow 40 volts was selected as the operating pulse voltage. The temperature of the detectors in the foregoing tests was 350°F.

If the system is performing properly, the electron capture cell current should exhibit temperature independence. The shape of the charge cloud where the reaction is occurring will be somewhat altered at elevated temperatures but should not exhibit a noticeable effect upon the standing current with the cell. To verify this condition the cell temperature was increased stepwise and the current measured. The initial results are shown in Table XIII. As can readily be seen the data does not indicate temperature independence but instead shows a high degree of dependence. Changing the operating conditions, i.e., voltage, pulse period, pulse width and gas flows did not substantially change the results. The overall temperature dependence shown is illustrated in Figure 44. A closer examination of the curve suggested what

PULSE VOLTAGE VERSUS CURRENT

2 microsecond width

1000 microsecond period

Detector = 356°F

Argon-10% Methane

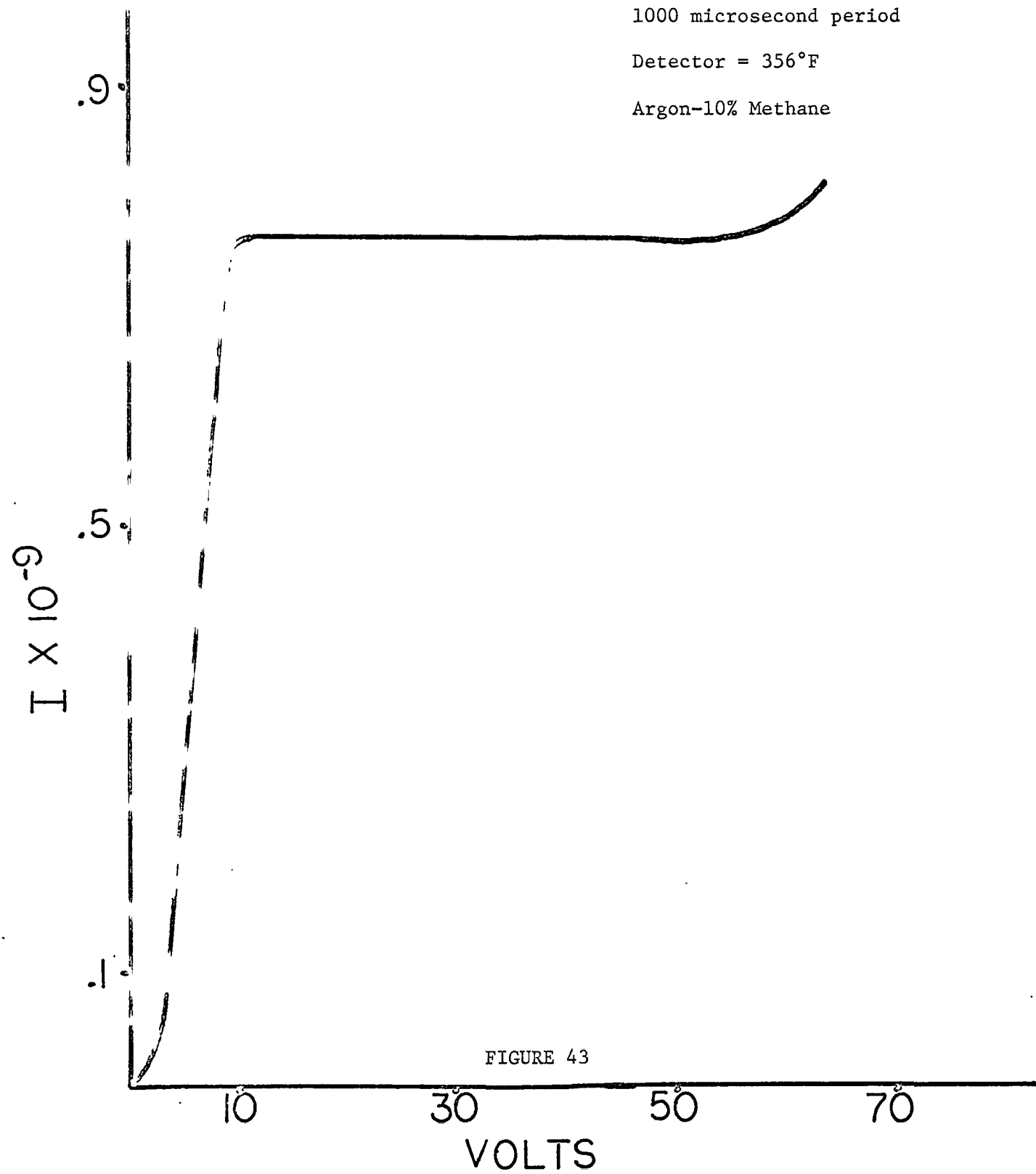


FIGURE 43

TEMPERATURE DEPENDENCE OF SATURATION CURRENT

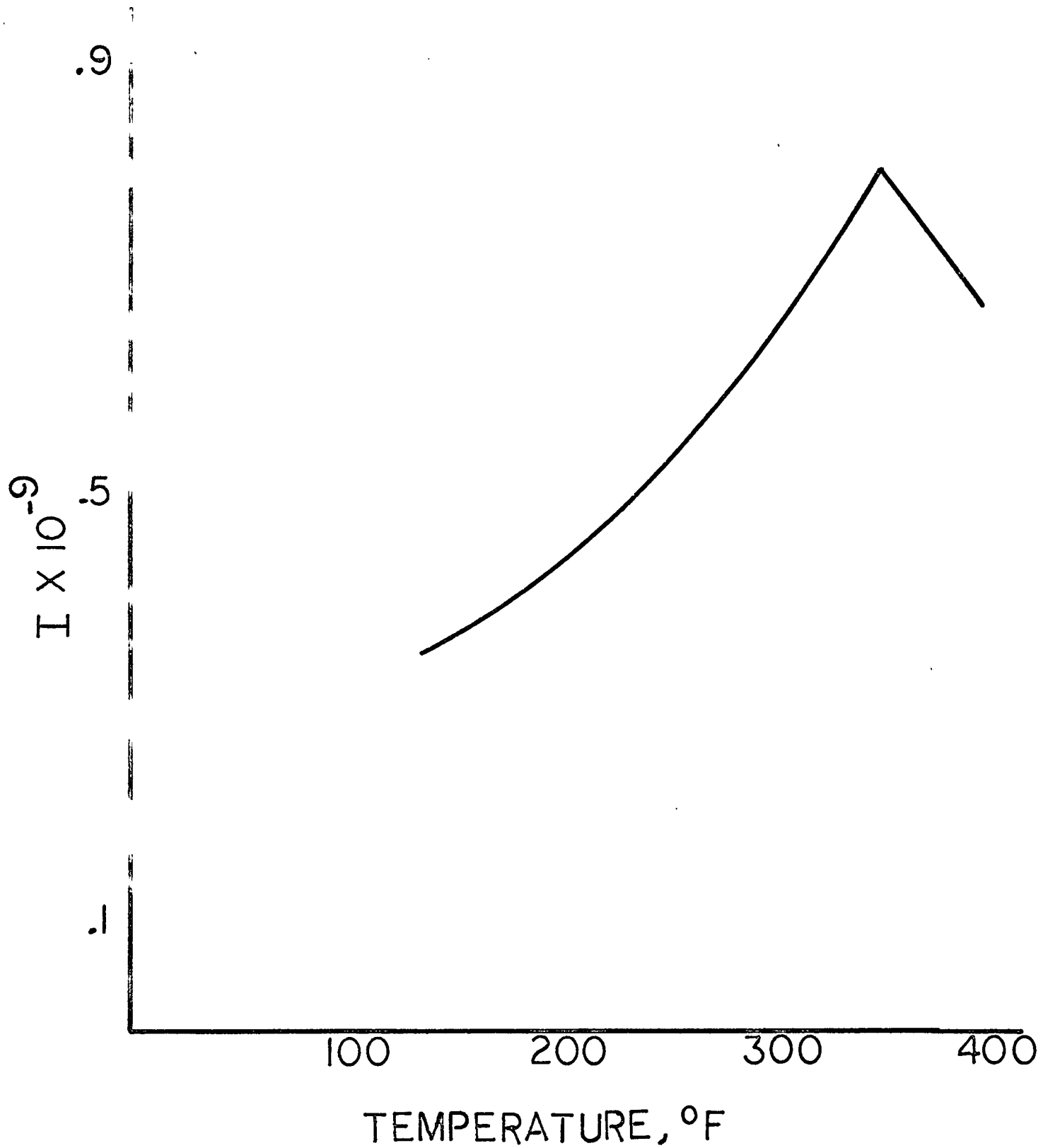


FIGURE 44

TABLE XIII
TEMPERATURE DEPENDENCE OF SATURATION CURRENT

Temperature			I
°F	°C	°K	Amperes
105	41	319	0.37×10^{-9}
150	66	339	0.36×10^{-9}
200	104	377	0.40×10^{-9}
250	121	394	0.56×10^{-9}
300	129	422	0.68×10^{-9}
350	176	449	0.74×10^{-9}
400	204	477	0.54×10^{-9}

appeared to be the same general shape as had previously been determined by other investigators (78) for temperature dependence of response for compounds. This would lead to the conclusion that an impurity was present in the system that was causing such anomalous results. In an attempt to clarify the situation the system was disassembled and completely cleaned; the column was replaced; the cells were also replaced and the system, after reassembly, was purged with gas overnight at 200°C to remove all traces of cleaning solvent. The system was now again checked for temperature dependence. The results are given in Table XIV. The results, though still not satisfactory, show improvement. Further heating while flowing gas through the system reduced the deviation from the mean current value to less than 0.06×10^{-9} amperes. It should be pointed out that the cleanliness of the system proved to be the single most perplexing problem encountered during this phase of the investigation. If all components are not scrupulously clean or if the column is losing substrate the results obtained will be completely useless. The justification for this statement is that since our model is based upon kinetic considerations any reactions taking place that involve any reaction intermediates will invalidate our theoretical model if the exact nature of the foreign reaction is not known. In most instances the latter is indeed the case.

In order that the data obtained might be interpreted and calculations made it was imperative that the amount of sample entering each detector be known. This necessitated the measurement of the split ratio, the volumetric flows and the temperature dependence that

TABLE XIV
TEMPERATURE DEPENDENCE OF SATURATION CURRENT

Temperature	I	Mean Current	Deviation from Mean
°F	amperes	amperes	amperes
400	1.71×10^{-9}	1.80×10^{-9}	$.09 \times 10^{-9}$
350	1.50×10^{-9}	1.80×10^{-9}	$.30 \times 10^{-9}$
300	1.95×10^{-9}	1.80×10^{-9}	$.15 \times 10^{-9}$
250	2.05×10^{-9}	1.80×10^{-9}	$.25 \times 10^{-9}$
200	1.90×10^{-9}	1.80×10^{-9}	$.10 \times 10^{-9}$
150	1.71×10^{-9}	1.80×10^{-9}	$.09 \times 10^{-9}$

might be present. The data is summarized in Table XV. The column and split temperature was 172°F. The inlet and transfer line was approximately 200°C. It was determined that changes in the detector bath temperature did not alter the split ratio or the total volumetric flow of gas. The Argon-Methane flow at different pressures was as follows: 42.9 ml/min at 5.1 psig; 90.9 ml/min at 10.0 psig; 142.9 ml/min at 15.0 psig and 193.6 ml/min at 20.0 psig. Also, it was noted that the Argon-Methane flow had a negligible effect on the Helium-Methane flow and therefore reflected no change on the split ratio. The flow characteristics are illustrated in Figures 45 and 46. Figure 47 is a simplified schematic of the system indicating the measured volumetric flows.

The other consideration of prime importance is the chemical purity of the compounds under investigation. In the past experiments it was assumed that the chromatographic peak of the greatest magnitude on electron capture measurements was the compound under study. Our experience has shown that this assumption is totally invalid. In fact this is the exception rather than the general rule. Consider Figure 48 which is a capillary chromatogram of "pure" mesityl oxide. The detector used was flame ionization. These results alone are rather startling, however not as much as when this same sample is observed on the dual system. Figure 49 is the chromatogram obtained on the dual system. The upper trace is the cross section response. It can easily be seen that if only electron capture responses were observed misinterpretation of the data would be an almost certainty. Other examples of the same nature are shown in Figures 50 and 51, which are chromatograms of

FLOW VERSUS PRESSURE

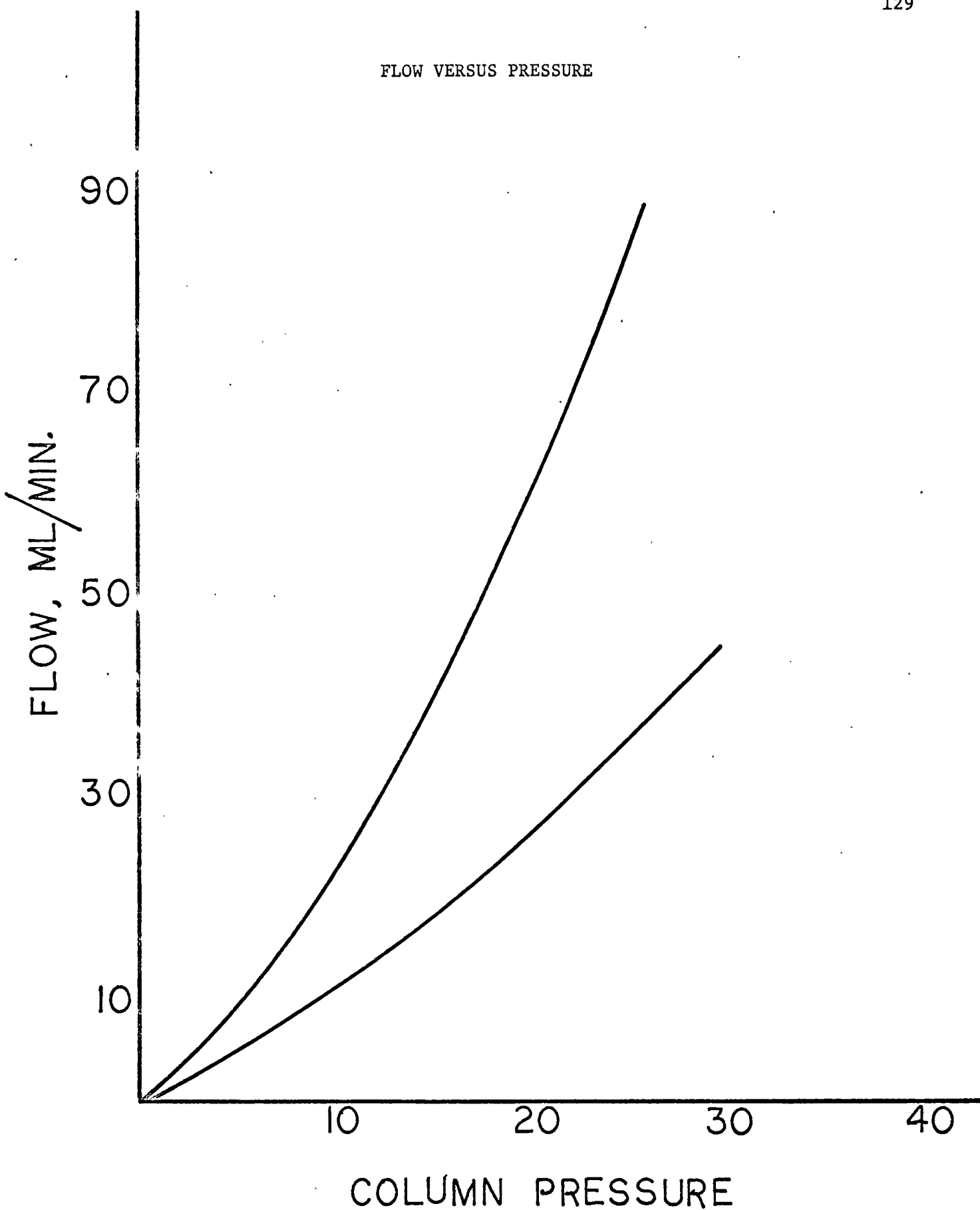


FIGURE 45

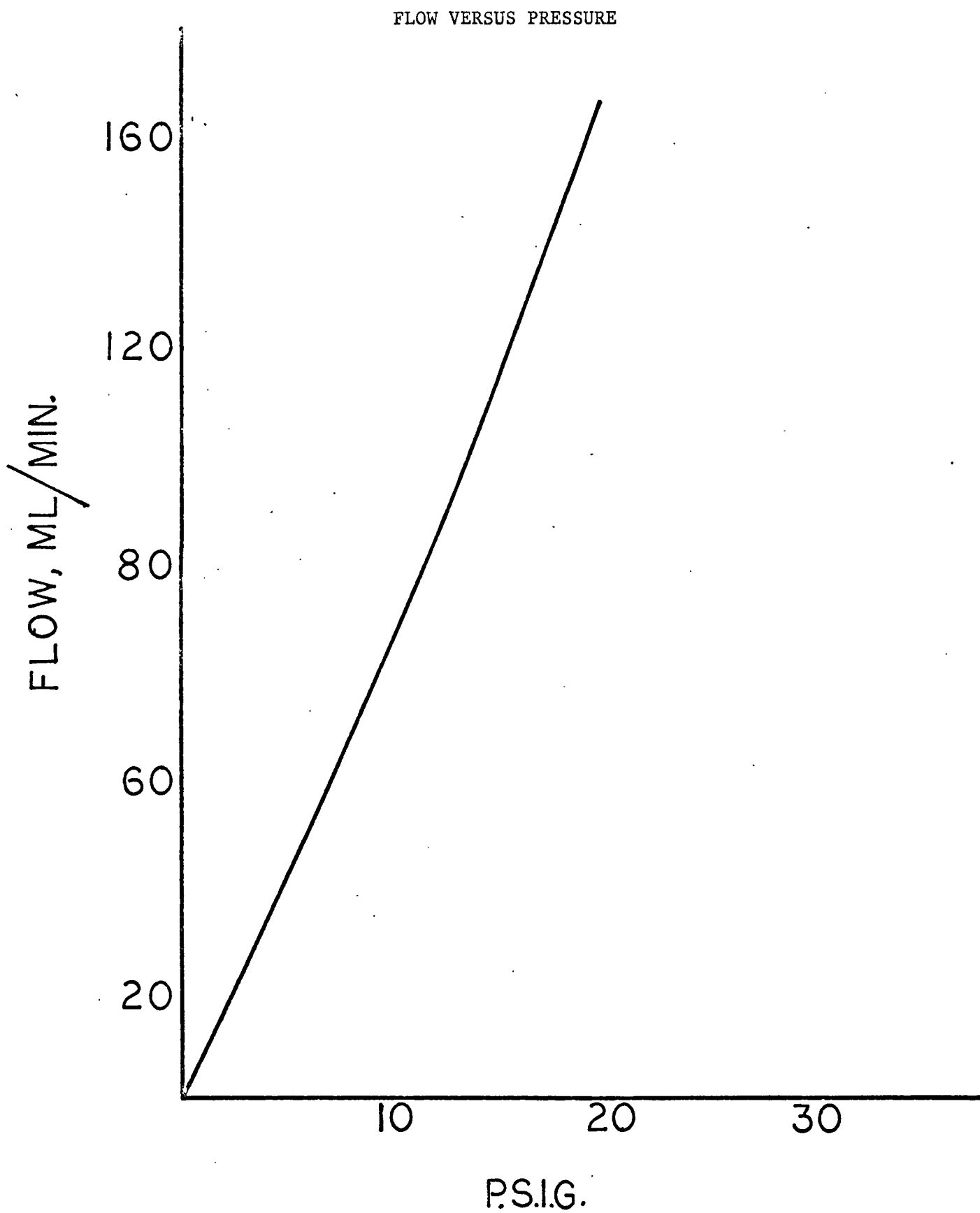


FIGURE 46

SCHEMATIC OF FLOW SYSTEM

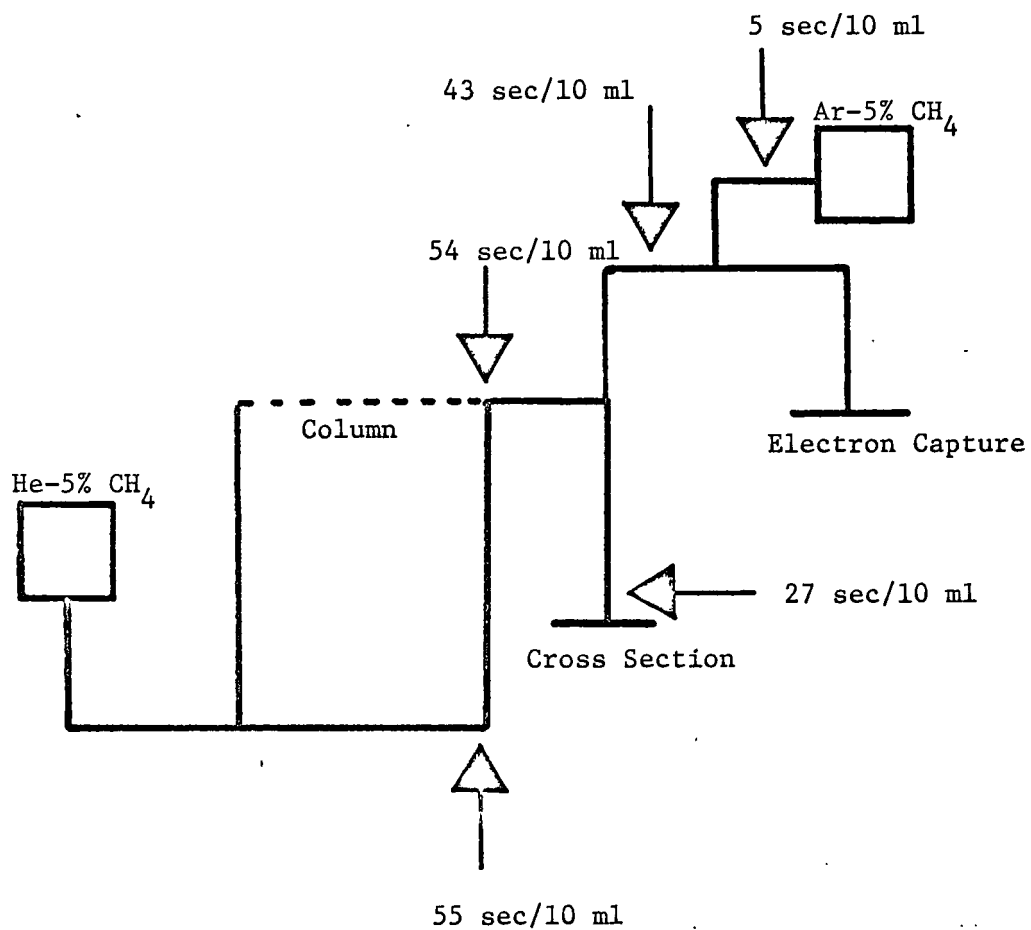


FIGURE 47

CHROMATOGRAM OF MESITYL OXIDE

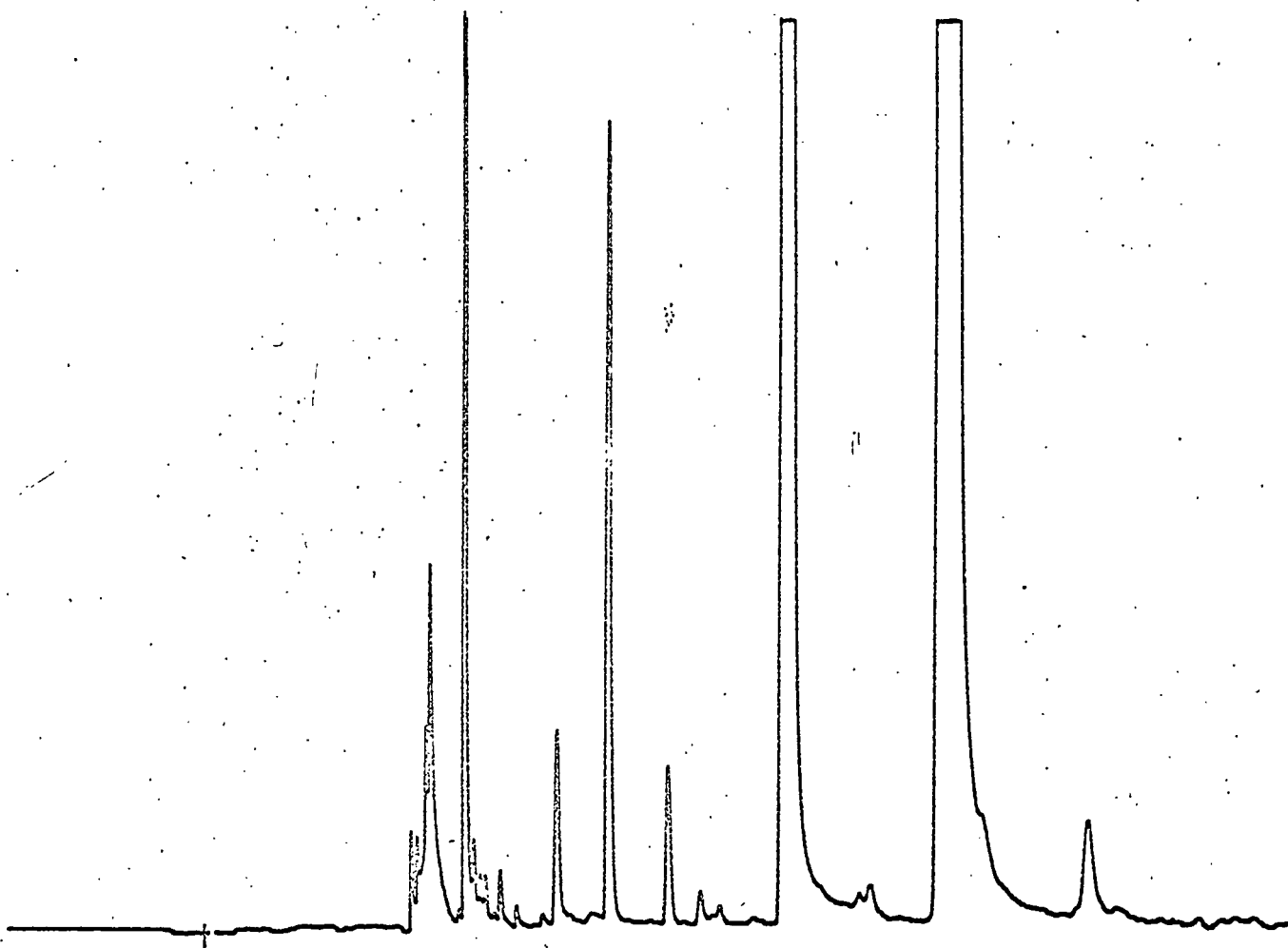


FIGURE 48

CHROMATOGRAM OF MESITYL OXIDE ON DUAL SYSTEM

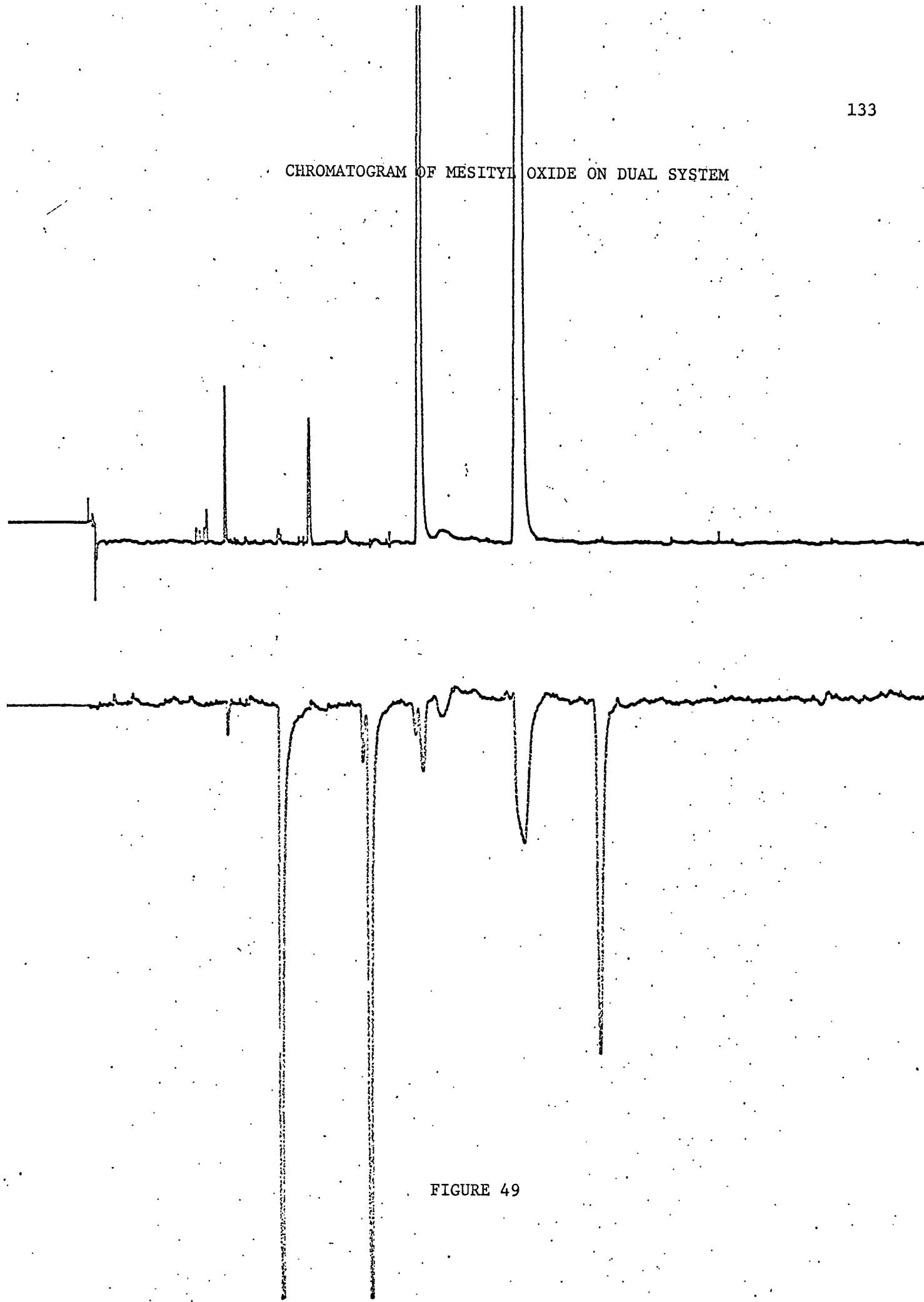
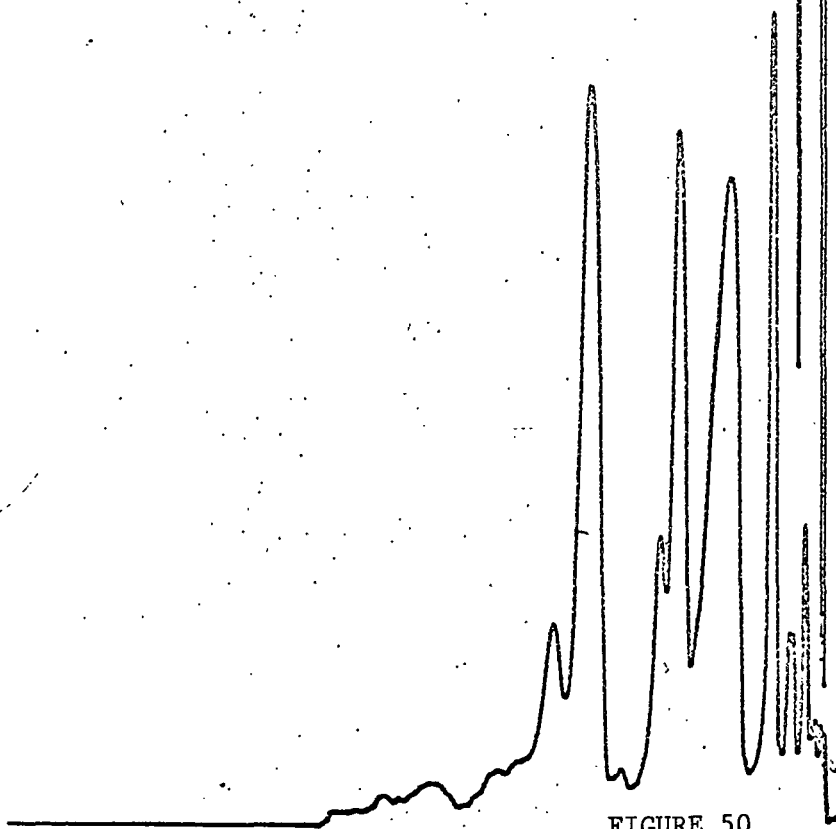


FIGURE 49

CHROMATOGRAM OF CHLOROCYCLOHEXANE

FIGURE 50



CHROMATOGRAM OF DI-TERTIARYBUTYL KETONE

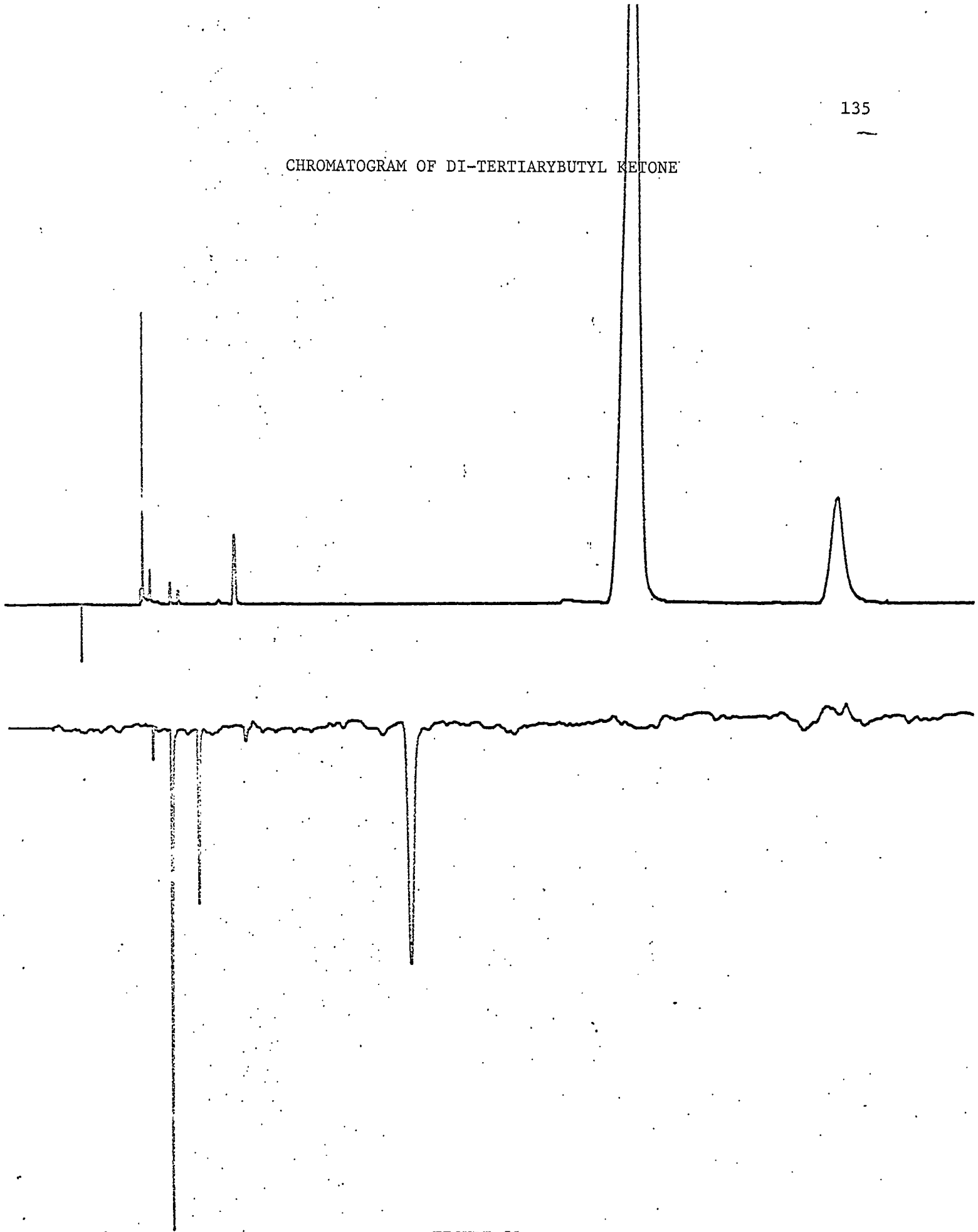


FIGURE 51

TABLE XV
FLOW RELATIONSHIPS

<u>He-CH₄ Pressure</u>	<u>Cross Section</u>	<u>Electron Capture</u>	<u>Split Ratio</u>
psig	ml/min	ml/min	
5.2	11.7	5.0	2.34 : 1
10.1	25.6	10.9	2.35 : 1
14.9	42.9	18.3	2.34 : 1
20.1	63.2	27.6	2.29 : 1
25.2	87.0	37.7	2.31 : 1

chlorocyclohexane and di-tertiarybutyl ketone, respectively. Observations of this type were prominent throughout the entire investigation. For this reason chromatographic purity for each compound ultimately used in the study was verified prior to its use.

The data obtained for the determination of relative electron affinities is summarized in Tables XVI through XVII. The data is for the compounds benzaldehyde, α -chlorotoluene and cyclooctatetraene. Figures 52 through 54 are graphical representations of $\frac{b - e^-}{e^-}$ versus the relative sample size. The slope obtained by least squares adjustment of the data is presented in Table XIX. It is noted that these three compounds represent dissociative (α -chlorotoluene), non-dissociative (benzaldehyde) and mixed (cyclooctatetraene) types of capture phenomenon.

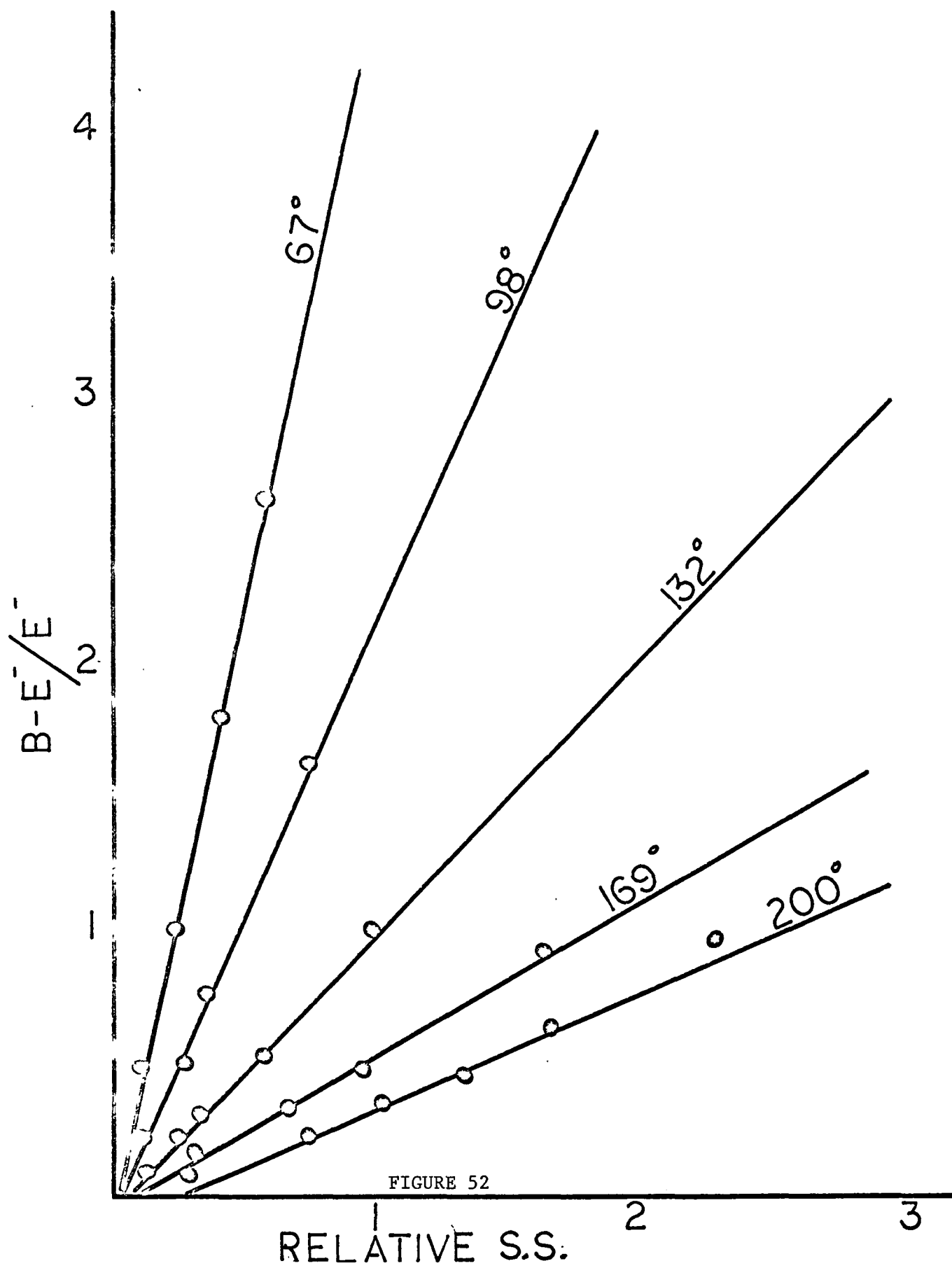
PLOTS OF $b - e^-/e^-$ VERSUS RELATIVE SAMPLE SIZE - BENZALDEHYDE

FIGURE 52

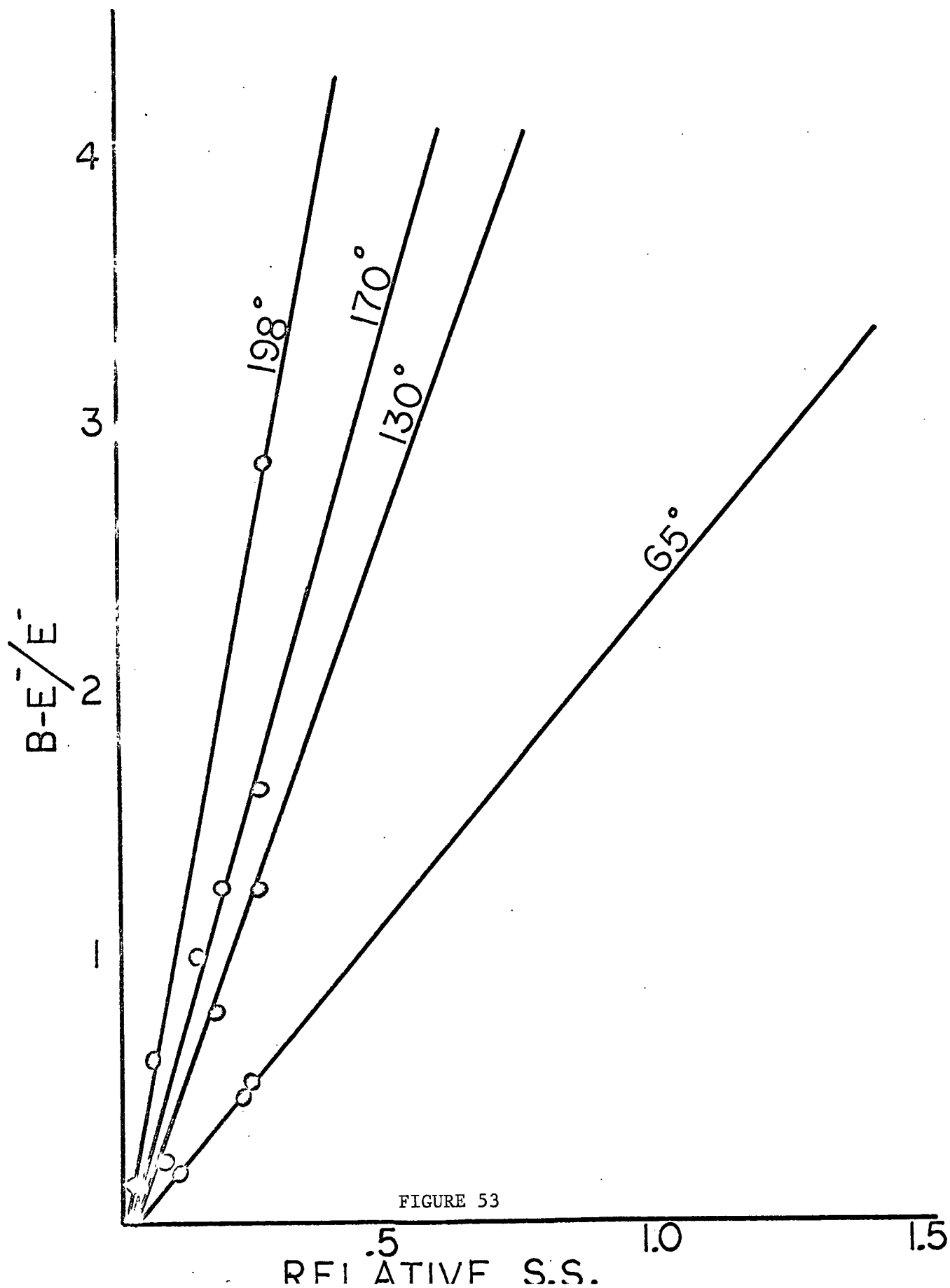
PLOTS OF $b - e^-/e^-$ VERSUS RELATIVE SAMPLE SIZE - α -CHLOROTOLUENE

FIGURE 53

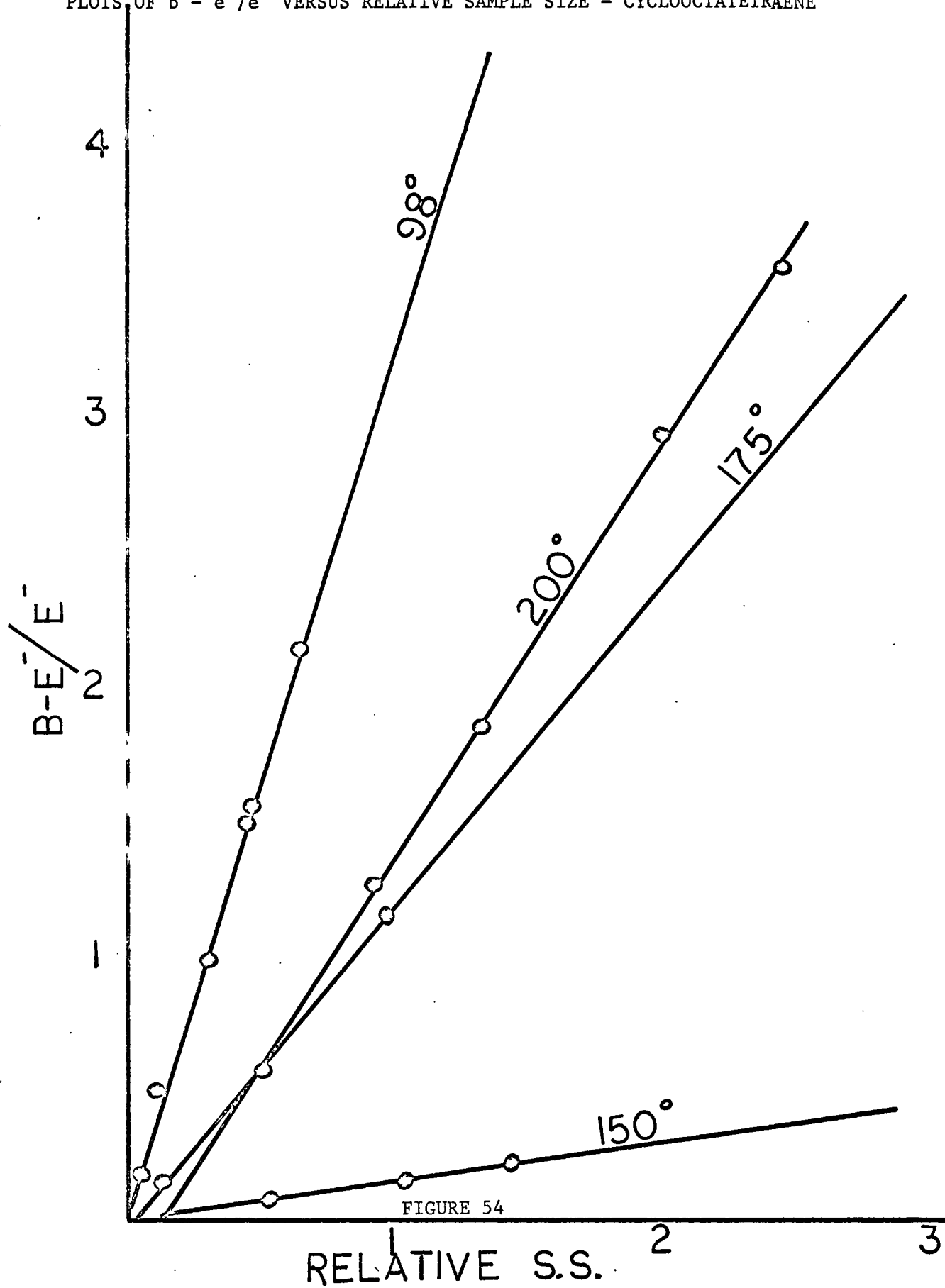
PLOTS OF $b - e^-/e^-$ VERSUS RELATIVE SAMPLE SIZE - CYCLOOCTATETRAENE

FIGURE 54

TABLE XVI
SUMMARY OF DATA - BENZALDEHYDE

Temperature	#	Peak Height	F.S.D.	Corr.	Rel. S.S.	Peak Height
67°	1	5.25	3×10^{-10}	$.122 \times 10^{-9}$	.028	2.65
	2	5.75	3×10^{-10}	$.133 \times 10^{-9}$	.030	2.50
	3	7.10	1×10^{-9}	$.548 \times 10^{-9}$	.124	10.20
	4	13.80	1×10^{-9}	1.066×10^{-9}	.242	16.25
	5	7.70	3×10^{-9}	1.784×10^{-9}	.405	7.05
	6	11.05	3×10^{-9}	2.560×10^{-9}	.582	7.45
	7	19.00	3×10^{-9}	4.400×10^{-9}	1.000	8.95
98°	1	4.60	3×10^{-10}	$.106 \times 10^{-9}$	.024	1.20
	2	17.70	3×10^{-10}	$.410 \times 10^{-9}$	.093	4.10
	3	6.85	1×10^{-9}	$.529 \times 10^{-9}$	.120	5.45
	4	15.15	1×10^{-9}	1.170×10^{-9}	.266	10.70
	5	7.05	3×10^{-9}	1.633×10^{-9}	.371	4.60
	6	14.20	3×10^{-9}	3.290×10^{-9}	.748	6.65
	7	5.75	1×10^{-8}	4.440×10^{-9}	1.009	7.55
132°	1	6.05	3×10^{-10}	$.140 \times 10^{-9}$	.032	0.40
	2	14.80	1×10^{-9}	1.143×10^{-9}	.260	5.30
	3	6.40	3×10^{-9}	1.483×10^{-9}	.337	7.10
	4	10.80	3×10^{-9}	2.502×10^{-9}	.569	10.95
	5	12.60	3×10^{-9}	4.309×10^{-9}	.979	5.35
	6	8.50	1×10^{-8}	6.564×10^{-9}	1.492	6.65

TABLE XVI
SUMMARY OF DATA - BENZALDEHYDE

F.S.D.	$b - e^-$	b	e^-	$\frac{b - e^-}{e^-}$
1×10^{-9}	$.205 \times 10^{-9}$	2.55×10^{-9}	2.345×10^{-9}	.087
1×10^{-9}	$.193 \times 10^{-9}$	2.55×10^{-9}	2.357×10^{-9}	.082
1×10^{-9}	$.788 \times 10^{-9}$	2.55×10^{-9}	1.762×10^{-9}	.447
1×10^{-9}	1.255×10^{-9}	2.55×10^{-9}	1.295×10^{-9}	.969
3×10^{-9}	1.633×10^{-9}	2.55×10^{-9}	$.917 \times 10^{-9}$	1.780
3×10^{-9}	1.842×10^{-9}	2.55×10^{-9}	$.708 \times 10^{-9}$	2.602
3×10^{-9}	2.073×10^{-9}	2.55×10^{-9}	$.477 \times 10^{-9}$	4.346
1×10^{-9}	$.093 \times 10^{-9}$	2.50×10^{-9}	2.407×10^{-9}	.039
1×10^{-9}	$.317 \times 10^{-9}$	2.50×10^{-9}	2.183×10^{-9}	.145
1×10^{-9}	$.421 \times 10^{-9}$	2.50×10^{-9}	2.079×10^{-9}	.202
1×10^{-9}	$.826 \times 10^{-9}$	2.50×10^{-9}	1.674×10^{-9}	.493
3×10^{-9}	1.066×10^{-9}	2.50×10^{-9}	1.434×10^{-9}	.743
3×10^{-9}	1.540×10^{-9}	2.50×10^{-9}	$.960 \times 10^{-9}$	1.604
3×10^{-9}	1.749×10^{-9}	2.50×10^{-9}	$.751 \times 10^{-9}$	2.329
1×10^{-9}	$.031 \times 10^{-9}$	2.50×10^{-9}	2.469×10^{-9}	.012
1×10^{-9}	$.409 \times 10^{-9}$	2.50×10^{-9}	2.091×10^{-9}	.196
1×10^{-9}	$.548 \times 10^{-9}$	2.50×10^{-9}	1.952×10^{-9}	.281
1×10^{-9}	$.846 \times 10^{-9}$	2.50×10^{-9}	1.654×10^{-9}	.511
3×10^{-9}	1.239×10^{-9}	2.50×10^{-9}	1.261×10^{-9}	.982
3×10^{-9}	1.540×10^{-9}	2.50×10^{-9}	$.960 \times 10^{-9}$	1.604

TABLE XVI CONTINUED
SUMMARY OF DATA - BENZALDEHYDE

Temperature	#	Peak Height	F.S.D.	Corr.	Rel. S.S.	Peak Height
169°	1	5.65	1×10^{-9}	$.436 \times 10^{-9}$	.099	1.10
	2	5.85	3×10^{-9}	1.355×10^{-9}	.308	3.40
	3	12.45	3×10^{-9}	2.884×10^{-9}	.655	7.45
	4	5.35	1×10^{-8}	4.131×10^{-9}	.939	10.15
	5	9.30	1×10^{-8}	7.181×10^{-9}	1.632	5.05
	6	13.05	1×10^{-8}	10.077×10^{-9}	2.290	6.20
200°	1	15.70	1×10^{-9}	1.212×10^{-9}	.275	1.95
	2	13.65	3×10^{-9}	3.162×10^{-9}	.719	5.45
	3	5.75	1×10^{-8}	4.440×10^{-9}	1.009	7.60
	4	7.55	1×10^{-8}	5.830×10^{-9}	1.325	9.75
	5	9.40	1×10^{-8}	7.259×10^{-9}	1.650	11.90
	6	12.95	1×10^{-8}	10.000×10^{-9}	2.273	5.10
	7	14.10	1×10^{-8}	10.888×10^{-9}	2.474	6.00

TABLE XVI CONTINUED
SUMMARY OF DATA - BENZALDEHYDE

F.S.D.	$b - e^-$	b	e^-	$\frac{b - e^-}{e^-}$
1×10^{-9}	$.085 \times 10^{-9}$	2.45×10^{-9}	2.365×10^{-9}	.036
1×10^{-9}	$.262 \times 10^{-9}$	2.45×10^{-9}	2.188×10^{-9}	1.20
1×10^{-9}	$.575 \times 10^{-9}$	2.45×10^{-9}	1.875×10^{-9}	.301
1×10^{-9}	$.784 \times 10^{-9}$	2.45×10^{-9}	1.666×10^{-9}	.470
3×10^{-9}	1.170×10^{-9}	2.45×10^{-9}	1.280×10^{-9}	.914
3×10^{-9}	1.436×10^{-9}	2.45×10^{-9}	1.014×10^{-9}	1.416
1×10^{-9}	$.150 \times 10^{-9}$	2.40×10^{-9}	2.250×10^{-9}	.067
1×10^{-9}	$.421 \times 10^{-9}$	2.40×10^{-9}	1.919×10^{-9}	.213
1×10^{-9}	$.587 \times 10^{-9}$	2.40×10^{-9}	1.813×10^{-9}	.324
1×10^{-9}	$.753 \times 10^{-9}$	2.40×10^{-9}	1.647×10^{-9}	.451
1×10^{-9}	$.919 \times 10^{-9}$	2.40×10^{-9}	1.481×10^{-9}	.620
3×10^{-9}	1.181×10^{-9}	2.40×10^{-9}	1.219×10^{-9}	.969
3×10^{-9}	1.390×10^{-9}	2.40×10^{-9}	1.010×10^{-9}	1.376

TABLE XVII
SUMMARY OF DATA - α -CHLOROTOLUENE

Temperature	#	Peak Height	F.S.D.	Corr.	Rel. S.S.	Peak Height
65°	1	1.60	1×10^{-9}	$.124 \times 10^{-9}$	.021	.50
	2	8.05	1×10^{-9}	$.622 \times 10^{-9}$	.106	4.60
	3	17.20	1×10^{-9}	1.328×10^{-9}	.226	11.10
	4	6.15	3×10^{-9}	1.425×10^{-9}	.243	3.95
	5	11.85	3×10^{-9}	2.745×10^{-9}	.468	6.25
	6	7.60	1×10^{-8}	5.869×10^{-9}	1.000	8.70
130°	1	7.20	3×10^{-10}	$.167 \times 10^{-9}$	.028	1.95
	2	19.90	3×10^{-10}	$.461 \times 10^{-9}$	.078	6.80
	3	13.85	1×10^{-9}	1.069×10^{-9}	.182	15.70
	4	6.25	3×10^{-9}	1.448×10^{-9}	.247	6.50
	5	9.15	3×10^{-9}	2.120×10^{-9}	.361	7.95
	6	20.75	3×10^{-9}	4.807×10^{-9}	.819	10.00
170°	1	5.70	3×10^{-10}	$.132 \times 10^{-9}$	.022	2.10
	2	6.65	3×10^{-10}	$.154 \times 10^{-9}$	.026	2.65
	3	1.75	1×10^{-9}	$.135 \times 10^{-9}$	.023	2.45
	4	4.65	1×10^{-9}	$.359 \times 10^{-9}$	.061	6.40
	5	19.60	1×10^{-9}	1.514×10^{-9}	.258	20.45
	6	14.45	1×10^{-9}	1.116×10^{-9}	.190	18.25
198	1	6.20	3×10^{-10}	$.144 \times 10^{-9}$	.024	2.60
	2	16.20	3×10^{-10}	$.375 \times 10^{-9}$	.064	6.45
	3	10.55	1×10^{-9}	$.815 \times 10^{-9}$	.139	13.45
	4	6.75	3×10^{-9}	1.564×10^{-9}	.266	6.70
	5	14.00	3×10^{-9}	3.243×10^{-9}	.552	8.50

TABLE XVII
SUMMARY OF DATA - α -CHLOROTOLUENE

F.S.D.	$b - e^-$	b	e^-	$\frac{b - e^-}{e^-}$
1×10^{-9}	$.039 \times 10^{-9}$	2.65×10^{-9}	2.611×10^{-9}	.015
1×10^{-9}	$.355 \times 10^{-9}$	2.65×10^{-9}	2.295×10^{-9}	.155
1×10^{-9}	$.857 \times 10^{-9}$	2.65×10^{-9}	1.793×10^{-9}	.478
3×10^{-9}	$.915 \times 10^{-9}$	2.65×10^{-9}	1.735×10^{-9}	.527
3×10^{-9}	1.448×10^{-9}	2.65×10^{-9}	1.202×10^{-9}	1.205
3×10^{-9}	2.015×10^{-9}	2.65×10^{-9}	$.635 \times 10^{-9}$	3.173
1×10^{-9}	$.150 \times 10^{-9}$	2.70×10^{-9}	2.550×10^{-9}	.059
1×10^{-9}	$.525 \times 10^{-9}$	2.70×10^{-9}	2.175×10^{-9}	.241
1×10^{-9}	1.212×10^{-9}	2.70×10^{-9}	1.488×10^{-9}	.814
3×10^{-9}	1.506×10^{-9}	2.70×10^{-9}	1.194×10^{-9}	1.261
3×10^{-9}	1.842×10^{-9}	2.70×10^{-9}	$.858 \times 10^{-9}$	2.147
3×10^{-9}	2.317×10^{-9}	2.70×10^{-9}	$.383 \times 10^{-9}$	6.050
1×10^{-9}	$.162 \times 10^{-9}$	2.55×10^{-9}	2.388×10^{-9}	.068
1×10^{-9}	$.205 \times 10^{-9}$	2.55×10^{-9}	2.345×10^{-9}	.087
1×10^{-9}	$.189 \times 10^{-9}$	2.55×10^{-9}	2.361×10^{-9}	.080
1×10^{-9}	$.494 \times 10^{-9}$	2.55×10^{-9}	2.056×10^{-9}	.240
1×10^{-9}	1.579×10^{-9}	2.55×10^{-9}	$.971 \times 10^{-9}$	1.626
1×10^{-9}	1.409×10^{-9}	2.55×10^{-9}	1.141×10^{-9}	1.235
1×10^{-9}	$.201 \times 10^{-9}$	2.10×10^{-9}	1.899×10^{-9}	.106
1×10^{-9}	$.498 \times 10^{-9}$	2.10×10^{-9}	1.602×10^{-9}	.311
1×10^{-9}	1.039×10^{-9}	2.10×10^{-9}	1.061×10^{-9}	.979
3×10^{-9}	1.552×10^{-9}	2.10×10^{-9}	$.548 \times 10^{-9}$	2.832
3×10^{-9}	1.969×10^{-9}	2.10×10^{-9}	$.131 \times 10^{-9}$	15.030

TABLE XVIII
SUMMARY OF DATA - CYCLOOCTATETRAENE

Temperature	#	Peak Height	F.S.D.	Corr.	Rel S.S.	Peak Height
98°	1	2.90	1×10^{-9}	$.224 \times 10^{-9}$	.055	5.90
	2	7.45	1×10^{-9}	$.575 \times 10^{-9}$	.142	12.90
	3	5.75	3×10^{-9}	1.332×10^{-9}	.328	6.85
	4	8.30	3×10^{-9}	1.923×10^{-9}	.474	8.00
	5	7.90	3×10^{-9}	1.830×10^{-9}	.451	7.85
	6	11.60	3×10^{-9}	2.687×10^{-9}	.663	8.95
	7	17.50	3×10^{-9}	4.054×10^{-9}	1.000	9.85
	8	7.90	3×10^{-9}	$.183 \times 10^{-9}$	.045	6.15
150°	1	9.50	3×10^{-9}	2.201×10^{-9}	.543	1.20
	2	17.85	3×10^{-9}	4.135×10^{-9}	1.020	1.85
	3	7.35	1×10^{-8}	5.676×10^{-9}	1.400	2.50
	4	11.45	1×10^{-8}	8.842×10^{-9}	2.181	4.05
	5	14.25	1×10^{-8}	11.004×10^{-9}	2.714	5.45
	6	16.40	1×10^{-8}	12.664×10^{-9}	3.123	6.90
175°	1	8.70	3×10^{-9}	2.015×10^{-9}	4.97	5.50
	2	17.20	3×10^{-9}	3.984×10^{-9}	.983	8.30
	3	7.15	1×10^{-8}	5.521×10^{-9}	1.362	9.95
	4	10.85	1×10^{-8}	8.378×10^{-9}	2.067	11.75
	5	13.25	1×10^{-8}	10.232×10^{-9}	2.524	12.30
	6	6.75	1×10^{-9}	$.521 \times 10^{-9}$	.128	1.80
200°	1	8.05	3×10^{-9}	1.865×10^{-9}	.460	5.15
	2	16.30	3×10^{-9}	3.776×10^{-9}	.931	8.20
	3	6.90	1×10^{-8}	5.328×10^{-9}	1.314	9.60
	4	10.45	1×10^{-8}	8.069×10^{-9}	1.990	11.10
	5	12.85	1×10^{-8}	9.923×10^{-9}	2.448	11.60
	6	15.20	1×10^{-8}	11.737×10^{-9}	2.895	12.15

TABLE XVIII
SUMMARY OF DATA - CYCLOOCTATETRAENE

F.S.D.	$b - e^-$	b	e^-	$\frac{b - e^-}{e^-}$
1×10^{-9}	$.456 \times 10^{-9}$	3.05×10^{-9}	2.594×10^{-9}	.176
1×10^{-9}	$.996 \times 10^{-9}$	3.05×10^{-9}	2.054×10^{-9}	.485
3×10^{-9}	1.587×10^{-9}	3.05×10^{-9}	1.463×10^{-9}	1.085
3×10^{-9}	1.853×10^{-9}	3.05×10^{-9}	1.197×10^{-9}	1.548
3×10^{-9}	1.818×10^{-9}	3.05×10^{-9}	1.232×10^{-9}	1.476
3×10^{-9}	2.073×10^{-9}	3.05×10^{-9}	$.977 \times 10^{-9}$	2.122
3×10^{-9}	2.281×10^{-9}	3.05×10^{-9}	$.769 \times 10^{-9}$	2.966
1×10^{-9}	$.475 \times 10^{-9}$	3.05×10^{-9}	2.575×10^{-9}	.184
3×10^{-9}	$.278 \times 10^{-9}$	3.40×10^{-9}	3.122×10^{-9}	.089
3×10^{-9}	$.428 \times 10^{-9}$	3.40×10^{-9}	2.972×10^{-9}	.144
3×10^{-9}	$.579 \times 10^{-9}$	3.40×10^{-9}	2.821×10^{-9}	.205
3×10^{-9}	$.938 \times 10^{-9}$	3.40×10^{-9}	2.462×10^{-9}	.381
3×10^{-9}	1.262×10^{-9}	3.40×10^{-9}	2.138×10^{-9}	.590
3×10^{-9}	1.598×10^{-9}	3.40×10^{-9}	1.802×10^{-9}	.887
3×10^{-9}	1.274×10^{-9}	3.60×10^{-9}	2.330×10^{-9}	.545
3×10^{-9}	1.923×10^{-9}	3.60×10^{-9}	1.677×10^{-9}	1.147
3×10^{-9}	2.305×10^{-9}	3.60×10^{-9}	1.295×10^{-9}	1.780
3×10^{-9}	2.722×10^{-9}	3.60×10^{-9}	1.878×10^{-9}	3.100
3×10^{-9}	2.849×10^{-9}	3.60×10^{-9}	1.629×10^{-9}	1.749
3×10^{-9}	$.417 \times 10^{-9}$	3.60×10^{-9}	3.183×10^{-9}	.131
3×10^{-9}	1.193×10^{-9}	3.45×10^{-9}	2.257×10^{-9}	.528
3×10^{-9}	1.900×10^{-9}	3.45×10^{-9}	1.550×10^{-9}	1.226
3×10^{-9}	2.224×10^{-9}	3.45×10^{-9}	1.226×10^{-9}	1.814
3×10^{-9}	2.571×10^{-9}	3.45×10^{-9}	$.879 \times 10^{-9}$	2.925
3×10^{-9}	2.687×10^{-9}	3.45×10^{-9}	$.763 \times 10^{-9}$	3.522
3×10^{-9}	2.815×10^{-9}	3.45×10^{-9}	$.635 \times 10^{-9}$	4.833

TABLE XIX
RELATIVE K VALUES

Compound	Temperature	K
Cyclooctatetraene	98	3.181
	150	.119
	175	1.195
	200	1.533
α -Chlorotoluene	65	2.387
	130	5.508
	170	6.912
	198	11.729
Benzaldehyde	67	4.618
	98	2.202
	132	1.035
	169	.577
	200	.451

IONIZATION CROSS SECTION - ELECTRON CAPTURE

V.

CONCLUSIONS

CONCLUSION

The electron capture detector has been previously shown to possess a high sensitivity and a large degree of selectivity for organic molecules, depending upon the molecular structure of the compound under investigation. However, to date, very little correlation has been established between molecular structure and electron attachment cross sections or electron affinities. This is due primarily to the uncertainties connected with the measurement of electron affinities. With the methods herein outlined this uncertainty should be eliminated.

As noted by Lovelock (25), it has been observed that the affinities of compounds for electrons with thermal energies are frequently associated with their biological activity. Also, an examination to determine the effect of structure and substituent groups on electron affinities might be related to the compound's reactivity, particularly when the mechanism is suspected to be electron transport. This type of information would be of prime importance in biological systems. The techniques herein reported should allow such studies to be carried out with a minimum of experimental hazard and inconvenience and a high yield of useful scientific information.

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