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The Radiolysis of Aqueous Chloroform Solutions

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THE RADIOLYSIS OF AQUEOUS CHLOROFORM SOLUTIONS

by

Francis John Simone UC 1969

Senior Thesis Submitted

in Partial Fulfillment
of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

MAY 1969



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This Thesis

Submitted by

Francis John Simone

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

John L. Festa

ABSTRACT

Saturated aqueous chloroform solutions have been irradiated with a 250 Curie gamma source. G-values for the production of hydrogen gas in neutral and acidic solutions have been determined.

ACKNOWLEDGEMENT

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guidance and encouragement.

TABLE OF CONTENTS

	Page
LIST OF TABLES	vi
LIST OF FIGURES	vii
I. INTRODUCTION	1
II. EXPERIMENTAL	3
A. Materials	3
B. Irradiations	4
C. Dosimetry	7
D. Hydrogen Gas Analysis	11
III. RESULTS	13
IV. SUGGESTIONS FOR FURTHER WORK	14
V. BIBLIOGRAPHY	19

LIST OF TABLES

	Page
I. Fricke Dosimeter Determination	8
II. Standardization Curve for Hydrogen	8
III. Hydrogen Yield Determination at pH 1.1	15
IV. Hydrogen Determination Under Neutral Conditions	15
V. Hydrogen Yield Determination at pH 2.25	17

LIST OF FIGURES

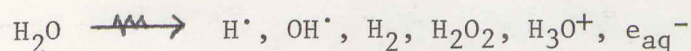
	Page
I. Toepler Pump and Hydrogen Transfer Vessel	5
II. Radiation Source and Holding Device	6
III. Absorbancy Fe^{+3} vs. Irradiation Time	9
IV. Standardization Curve for Hydrogen	10
V. Peak Height of Hydrogen vs. Irradiation Time ...	16
VI. Peak Height of Hydrogen vs. Irradiation Time ...	18

INTRODUCTION

Teply(1)-(5) as well as others(6),(7) have studied the effects of ionizing radiation on neutral, aqueous chloroform solutions. His studies demonstrated that the major product formed is hydrochloric acid, along with the secondary products of hydrogen peroxide and carbon dioxide. Through his observations, Teply concluded that the reaction involved a free radical mechanism.

Hayon and Allen(8), in their studies on the interaction of ionizing radiation with chloroacetic acid, suggested that the reaction cannot simply be explained by a free radical mechanism. By varying pH, they were able to change the major product formed. Under neutral conditions the major product was hydrochloric acid. When the pH was lowered to two, the major product formed was hydrogen gas.

The radiolysis of pure water(9)-(13) may be summarized by the equation:

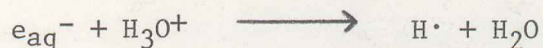


With this in mind, Allen's findings can be interpreted in the following way.

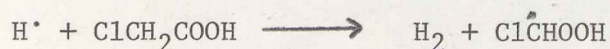
Under neutral conditions e_{aq}^- , the hydrated electron, reacts as follows:



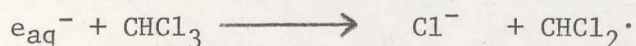
When the solutions are acidic, the hydronium ions compete with chloroacetic acid for e_{aq}^- :



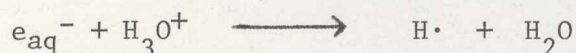
The hydrogen atoms then react with the chloroacetic acid:



Similarly Teply's findings can be explained by the following equation:



It is expected that under acidic conditions these reactions will take place:



The actions of the hydrated electron are of prime importance in this study. It has been found that this species reacts 3.4 times faster than the hydrogen atom when involved in similar reactions(8),(14). It resembles in many ways the solvated electron in metal-ammonia solutions and has been shown to be the primary reacting intermediate for many radiation induced reactions(15),(16),(17).

H.D. Kutz studied the production of hydrogen chloride under various conditions(18) and started work on hydrogen gas analysis(19). This study undertook the analysis of the major product yield under acidic conditions.

EXPERIMENTAL

A. MATERIALS

Eastman Kodak spectral grade chloroform was washed ten times with pure water to remove undesired materials. The pure water was prepared by passing distilled water through two ion exchange columns, the first removing ionic material, the second, organic. This is necessary due to the fact that impurities, even in minute amounts, can affect the yield of hydrogen, which is in micromoles.

Solutions to be irradiated were deaerated by bubbling nitrogen(Matheson "PREP" with an appropriate cotton filter) through for at least a half hour. This is done because oxygen can react with the $H\cdot$ radical formed and produce a new species, $HO_2\cdot$.

The solutions are made acidic with sulfuric acid. The pH is taken on a standard pH meter.

B. IRRADIATIONS

Pyrex ampules(20) were filled with ten milliliters of 7×10^{-3} molar chloroform solutions(5). These ampules are thoroughly washed with pure water to avoid any chance of contamination. They are filled in a glove bag under nitrogen. The bag is evacuated and filled with nitrogen so that there is no trace of oxygen. The acid and chloroform solutions are prepared in the glove bag and the ampules are filled by means of a hypodermic syringe. After removal from the bag, break seals are formed on the ampules.

Solutions were irradiated with gamma-rays from a Cobalt-60 source. The ampules are placed in an aluminium holder, which is then lowered into the core of the source. This is illustrated in Figure II.

Figure I Toepler Pump and Hydrogen Transfer Vessel(21)

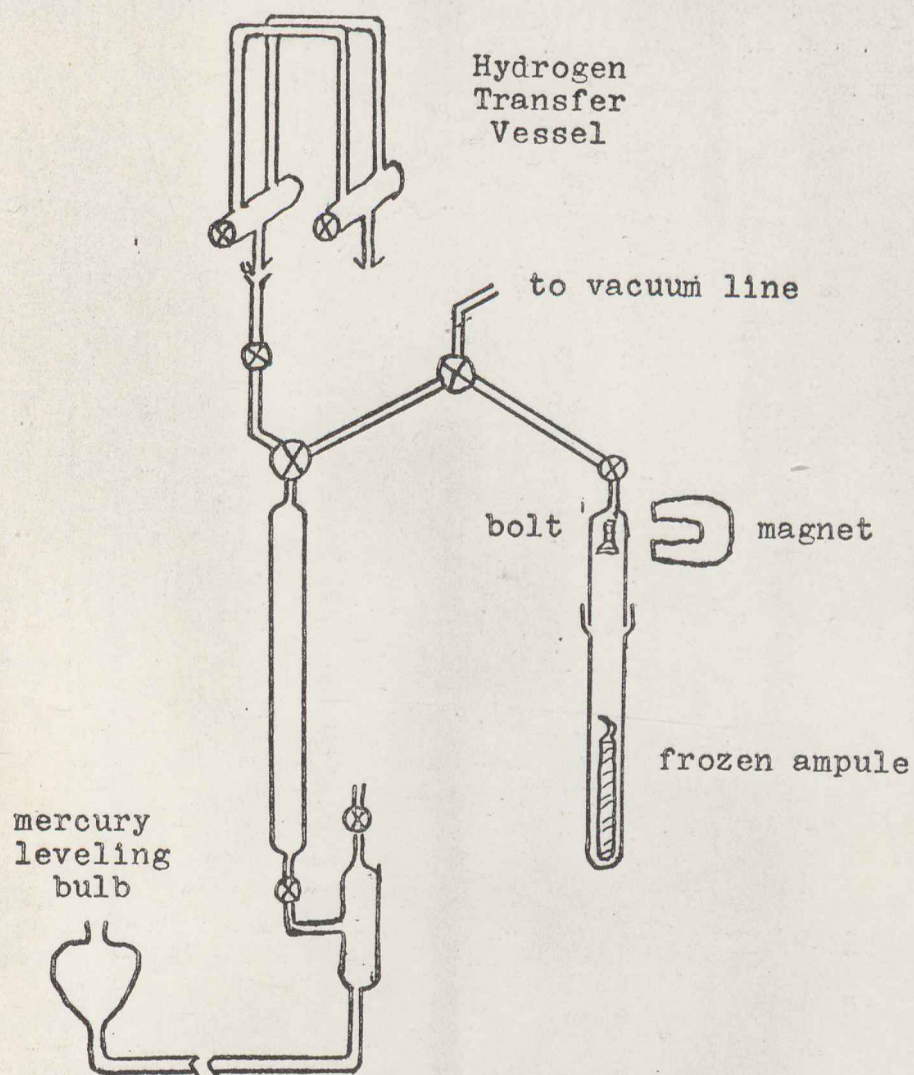
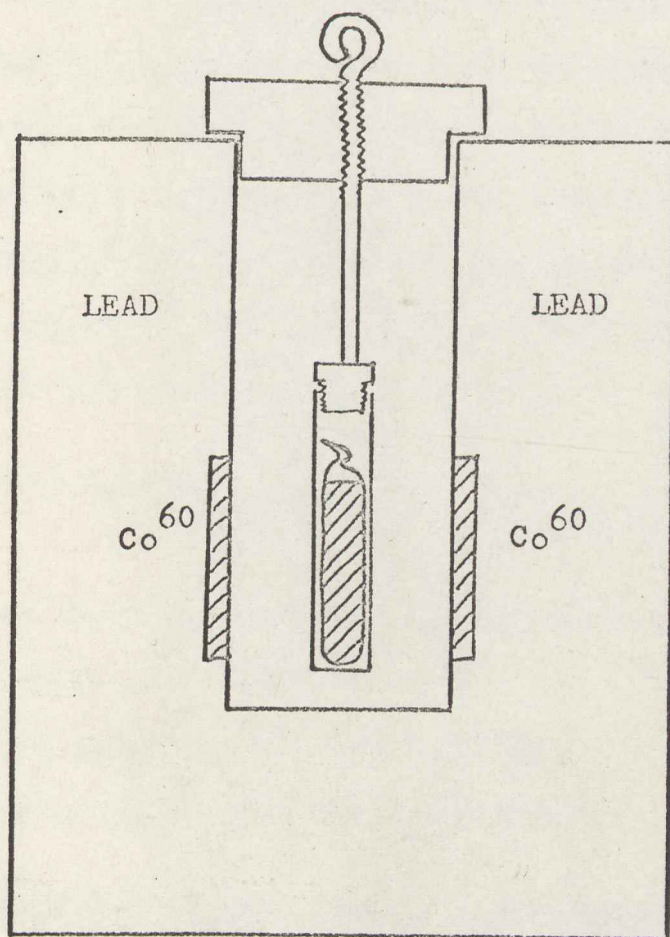


Figure II Radiation Source and Holding Device (22)



C. DOSIMETRY

TABLE I
Fricke Dosimeter Determination

In order to obtain a G-value for hydrogen later on, the exact dose rate coming from the source must be calculated. This is done by means of a technique evolved by Fricke(23). Aqueous ferrous ions are changed into ferric ions at the rate of 15.6 Fe^{3+} ions formed for every 100 electron-volts of energy absorbed. Since they have a molar absorbancy index of 2201, Fe^{3+} ions can be detected at 305 millimicrons on a Beckman model DU spectrophotometer. By irradiating the Fricke solution for various lengths of time, one can construct a line graph(see Figure III), the slope of which is needed to solve the dose rate equation.

$$\text{Dose Rate} = \frac{1}{G} \times \frac{m}{2201} \times \frac{N_o}{p}$$

G = G-value of the Fricke dosimeter: 15.6 atoms/100 electron-volts

m = slope of line: .06034 minutes⁻¹

N_o = Avogadro's number: 6.023 x 10²³ atoms/mole

p = density of solution: 1.0102 grams/milliliter

$$\text{Dose Rate} = \frac{100 \text{ ev}}{15.6 \text{ at}} \times \frac{.06034}{\text{min}} \times \frac{1}{2201} \times \frac{6.023 \times 10^{23} \text{ at/mole}}{1.0102 \text{ g/ml}}$$

$$\text{DOSE RATE} = 1.05 \times 10^{17} \text{ ev/g-min}$$

TABLE IFricke Dosimeter Determination

<u>Sample</u>	<u>Irrad. Time(min)</u>	<u>Absorbancy</u>
R-1	5	.335
R-2	10	.657
R-3	15	.970
R-4	20	1.237

TABLE IIStandardization Curve For Hydrogen

<u>Sample</u>	<u>Peak Height</u>	<u>Micromoles of Hydrogen</u>
S-1	48	.80
S-2	59	1.00
S-3	66	1.10
S-4	67	1.21
S-5	81	1.42

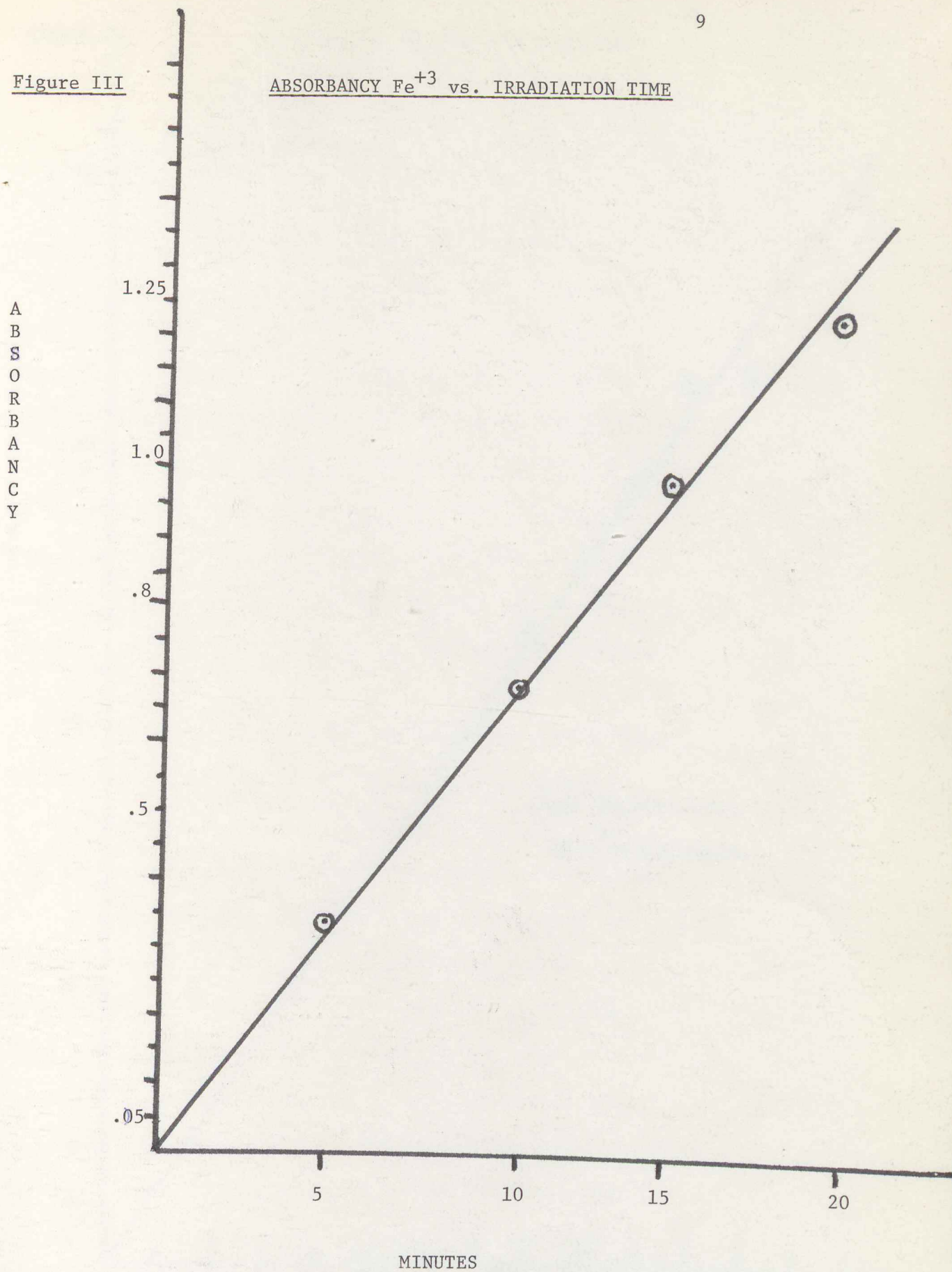
Figure IIIABSORBANCY Fe^{+3} vs. IRRADIATION TIME

Figure IV

STANDARDIZATION CURVE FOR HYDROGEN

Column Press. 10
" Temp. 33
Detector Volt. 8
Range 4

P
E
A
K

H
E
I
G
H
T

80

60

40

20

8

4

0.1

0.5

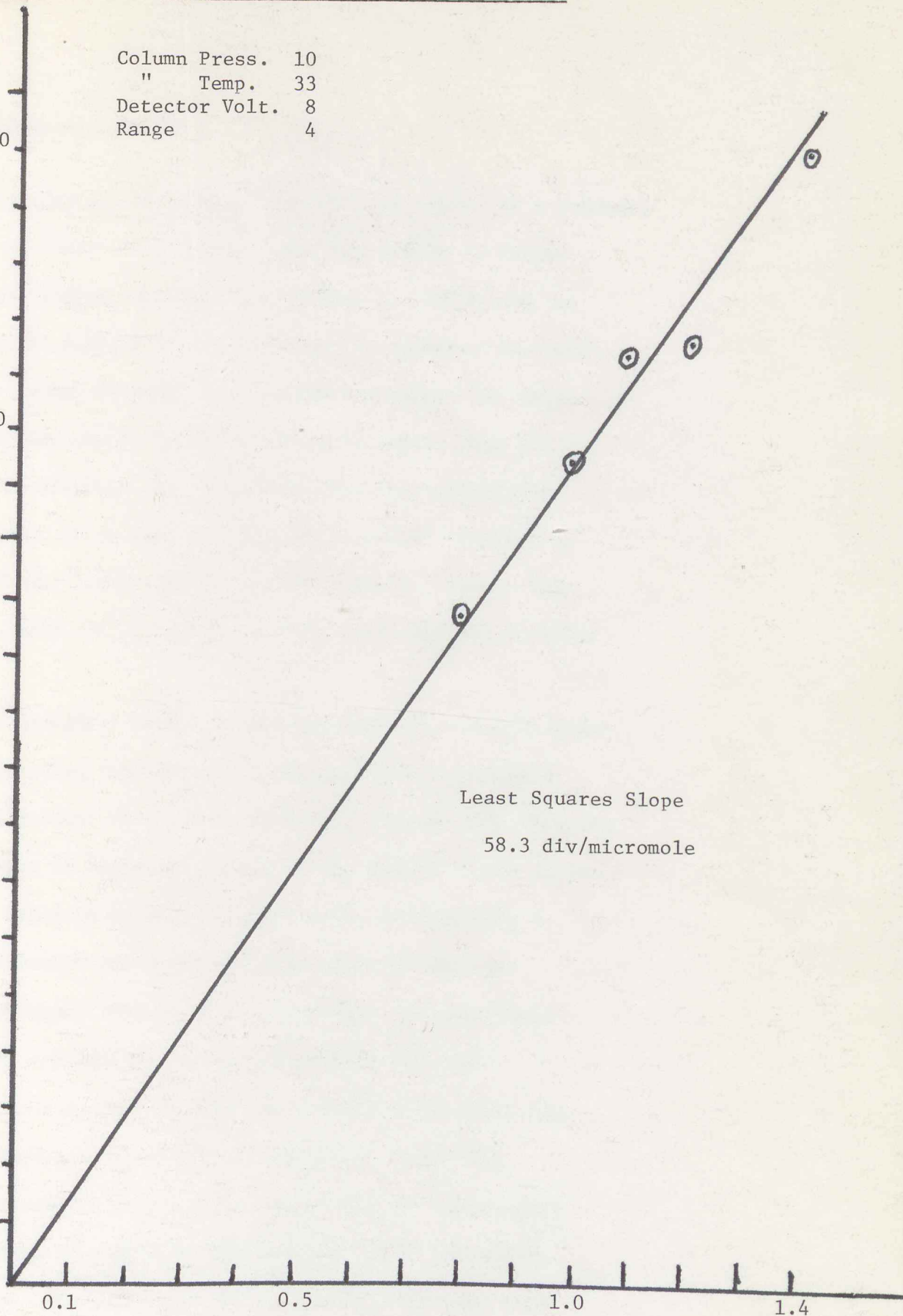
1.0

1.4

micromoles of Hydrogen

Least Squares Slope

58.3 div/micromole



D. HYDROGEN GAS ANALYSIS

Hydrogen gas is transferred from the ampule to a transfer vessel by means of a Toepler pump. The sample is frozen once with liquid nitrogen, the chamber is sealed and the pressure is reduced to 5×10^{-3} torr or greater. The break seal is broken by means of a weight (see Figure I). After thawing, the ampule is again frozen to ensure that all gas is out of solution. Next the stopcocks are manipulated (see Figure I) so that the gas can be pumped manually by means of the Toepler pump into the transfer vessel. This is done eight to ten times to ensure the complete transfer of gas.

The transfer vessel is then attached to a Perkin Elmer 154 vapor phase refractometer equipped with a molecular sieve 5A column. Nitrogen is used as a carrier gas. Thus the peak height of hydrogen present in the sample can be found.

In order to relate this into moles of hydrogen, a standardization curve must be made. This is done by injecting known amounts of hydrogen into the receptacle where the ampules are placed and pumping them into the transfer vessel. In this way a calibration curve can be prepared (see Figure IV). It should be noted that the molar volume is gotten by correcting for temperature and pressure according to the gas laws. Only one standardization curve was used instead of standardizing each

time a sample was run. It was found that, by using fresh batteries and keeping a check on the VPC running conditions, the variance was well within experimental error.

RESULTS

Figures V and VI show the results of peak height versus irradiation time for solutions of pH 1.1, 2.25 and neutral. From these graphs a slope is obtained and then a G-value determined.

$$G = \text{slope} \times N_0 / \text{Dose rate} \times \text{density} \times \text{volume of sample}$$

$$\text{Slope at pH 1.1} = 8.124 \times 10^{-3} \text{ micromoles/min}$$

$$N_0 = \text{Avogadro's number: } 6.023 \times 10^{23} \text{ atoms/mole}$$

$$\text{Dose rate} = 1.05 \times 10^{17} \text{ ev/g-min}$$

$$\text{Density} = 1.009 \text{ grams/milliliter}$$

$$\text{Volume} = 10 \text{ milliliters}$$

$$G(\text{pH 1.1}) = 0.46 \text{ molecules/100 ev}$$

Similar calculations were made on the graphs of hydrogen production versus the pHs of 2.25 and neutral.

$$G(\text{neutral}) = 0.33 \text{ molecules/100 ev} \quad \text{slope} = 5.9 \times 10^{-3}$$

$$G(\text{pH 2.25}) = 0.41 \text{ molecules/100 ev} \quad \text{slope} = 7.2 \times 10^{-3}$$

The G-value of 0.33 for neutral solutions is slightly higher than the one reported by Kutz(24). However upon searching his work, he never reported a pH reading of the neutral solution. My readings indicate that the solutions are slightly acidic and this could explain the discrepancy.

The only G-value for hydrogen reported in the literature that is useful in this study is the one reported for hydrogen

production in water. There is no value reported for hydrogen production in aqueous chloroform solutions. The literature value for hydrogen from water is 0.45(25). The value obtained from this study suggests that the solute chloroform dissolved in water is interfering with the hydrogen yield. However with a change in pH, the yield of hydrogen gas increases, until at the lowest pH read, it exceeds the literature value under neutral conditions, thus suggesting that the competing reaction involving the hydrated electron does exist.

Several difficulties were encountered. Great care must be exercised in deaerating the solutions. We are almost sure however that there is no oxygen in solution from the air at irradiation time. Also the factor of time is great here. Each sample takes about three hours to evaluate with numerous chances for error. It might be possible to modify the analytical procedure so that less time is required to prepare samples. Finally, we have no control over the temperature at which the sample is irradiated. It is regulated as best as possible, however due to physical plant limitations, this is not at optimum.

SUGGESTIONS FOR FURTHER WORK

Teply's experiments should now be carried out with regard to the production of hydrogen peroxide.

TABLE III Hydrogen Yield Determination at pH 1.1

<u>Sample</u>	<u>Irrad. Time(min)</u>	<u>Peak Height</u>	<u>micromoles of Hydrogen</u>
C1-A	30	11	.18
C2-A	60	25	.48
C3-A	90	41	.81
C4-A	120	49	.84
C5-A	150	71	1.23
C6-A	180	83	1.43

TABLE IV Hydrogen Determination Under Neutral Conditions

<u>Sample</u>	<u>Irrad. Time(min)</u>	<u>Peak Height</u>	<u>micromoles of Hydrogen</u>
D1-W	30	12	.20
D2-W	60	22	.38
D3-W	90	33	.57
D4-W	120	40	.69
D5-W	150	50.5	.87
D6-W	180	65	1.12

Figure V

PEAK HEIGHT OF HYDROGEN vs. IRRAD. TIME

pH 1.1 upper line(circles)

neutral lower line(squares)

P
E
A
K

H
E
I
G
H
T

60

40

20

4

30

60

90

120

150

180

MINUTES

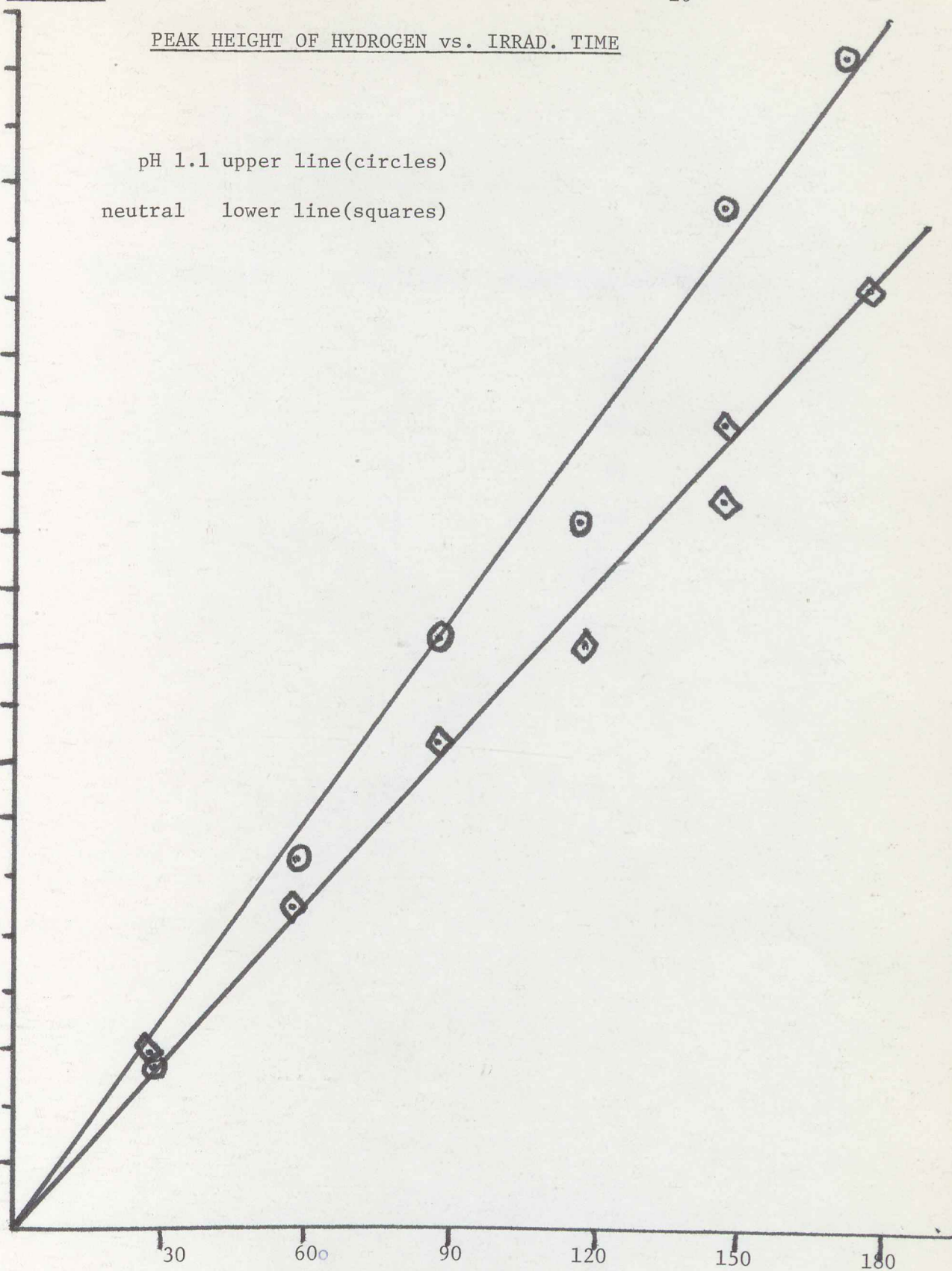
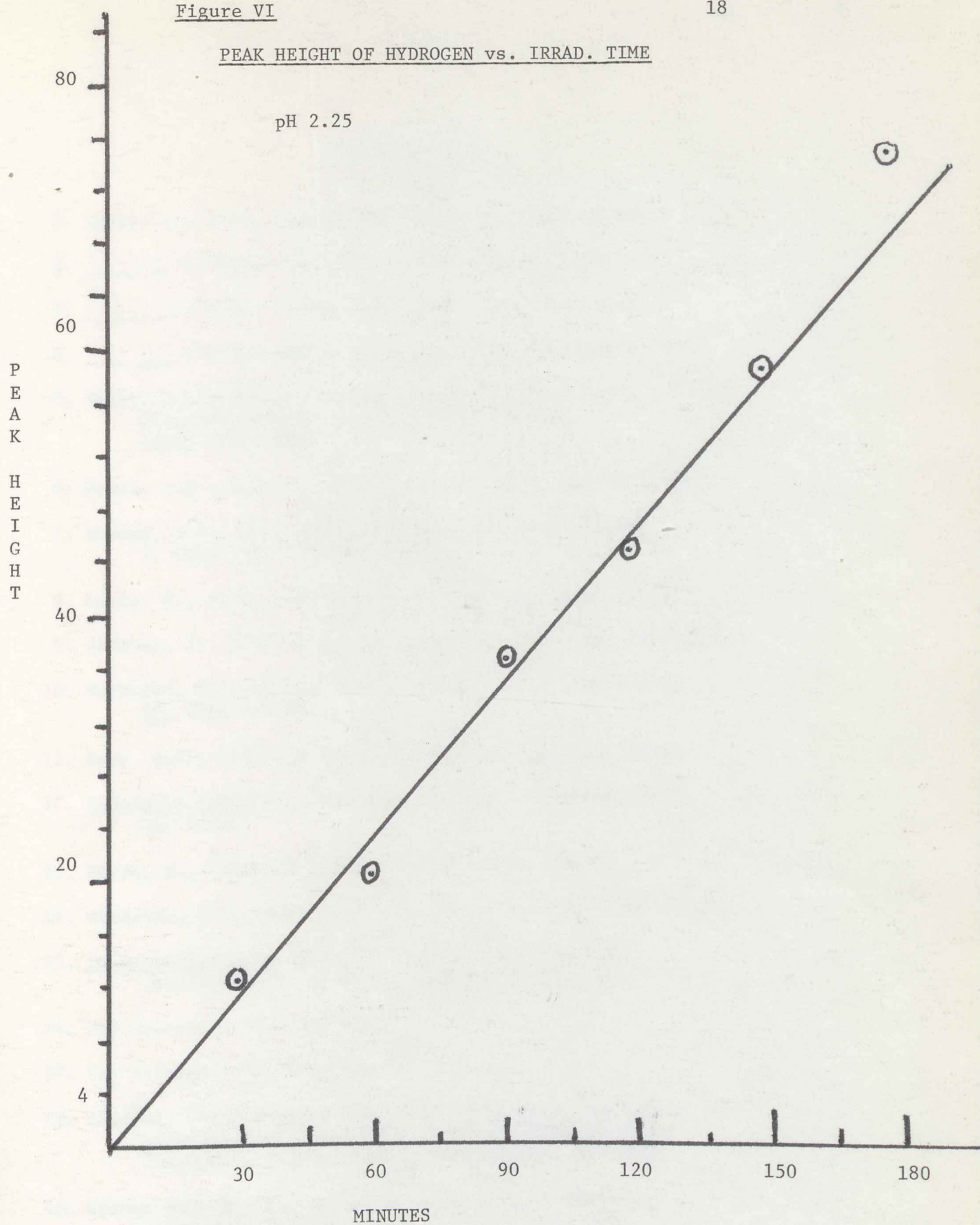


TABLE V Hydrogen Yield Determination at pH 2.25

<u>Sample</u>	<u>Irrad. Time(min)</u>	<u>Peak Height</u>	<u>micromoles of Hydrogen</u>
G1	30	12	.20
G2	60	21	.41
G3	90	38	.65
G4	120	47	.81
G5	150	62	1.06
G6	180	76	1.30

PEAK HEIGHT OF HYDROGEN vs. IRRAD. TIME

pH 2.25



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