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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

RICHARD FRANK PAISLEY

ENTITLED........ EVALUATION OF A THERMAL GRADIENT LAMP FOR APPLICATIONS

IN FAST TIME-RESOLVED ATOMIC ABSORPTION ANALYSIS

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF...... BACHELOR OF SCIENCE IN CHEMISTRY

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Instructor in Charge

APPROVED:

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O-1564

EVALUATION OF A THERMAL GRADIENT LAMP FOR APPLICATIONS

IN FAST TIME-RESOLVED

ATOMIC ABSORPTION ANALYSIS

BY

RICHARD FRANK PAISLEY

THESIS

for the

DEGREE OF BACHELOR OF SCIENCE

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Introduction

An ongoing study of various selenium compounds via use of a shock tube, has resulted in a search by Professors John R. Marquart (Eastern Illinois University) and R. Linn Belford (University of Illinois) for an intense source of illumination suitable for fast time-resolved atomic absorption studies of selenium. Most commercially available lamps display unacceptable degrees of self-reversal when pushed for maximum intensity. This is especially true for the more volatile elements such as selenium and cadmium.

The purpose of this paper is to compare and discuss the advantages and disadvantages of the new thermal gradient lamps (TGL's) manufactured by Scientific Glass Engineering (SGE) Pty. Ltd., Victoria, Australia relative to other sources of atomic emission, i.e., the electrodeless discharge lamp (EDL), the demountable cathode lamp (DCL), and the hollow cathode lamp (HCL). Lamp intensity over time have been analyzed for purposes of studying stability for the TGL and the EDL. Studies have been performed employing a single beam atomic absorption instrument in order to determine the extent of self-reversal of the TGL and the EDL. We do not have a selenium HCL at our disposal.

The TGL and the EDL will be discussed independently in this report and then comparison of the TGL will be made to the EDL, DCL, and HCL. Recommendations for further studies will also be commented upon.

Experimental

Apparatus

For studying lamp intensity over time, the selenium TGL light was focused onto the slits of a McPherson (Model 218) monochromator by a fifty millimeter focal length suprasil lens. The TGL was mounted 168 mm. above the table itself. There was a distance of 45.5 mm. from the face of the monochromator to the center of the lens and there was a distance of 81.3 mm. from the center of the lens to the selenium TGL. The lens was at a seven degree angle from parallel to the face of the monochromator. This slight alteration of the lens from parallel resulted in more light being passed through the vertical slits of the monochromator. The monochromator was fitted with a IP28A photo-multiplier tube. The signal was displayed on a Sargent recorder (Model-SR). For all scans, the recorder was set at 25 mV full scale. The chart rate was four inches per minute and the scan rate on the monochromator was always 200 $\overset{\circ}{A}$ per minute. The slit width on the monochromator was 0.1 mm. All scans were initiated at 1950 $\overset{\circ}{A}$ and were terminated at 2200 $\overset{\circ}{A}$. The temperature of the selenium TGL was varied from 140 $\overset{\circ}{C}$ to 163 $\overset{\circ}{C}$. After each scan, the TGL power supply was shut down according to the manuals' procedure (1) and the equipment was allowed to cool down for ten minutes before the lamp was restruck and heated to the desired temperature. The heating element generally required at least ten minutes before the heat indicator light on the power supply would dim signifying that the lamp had reached an

equilibrium point and was considered to be stable. The temperature of the room was also monitored so that the only parameter being varied would be the temperature of the TGL itself. Data for the various temperature settings are shown in Table 1. Peak heights are in millimeters. Data were collected over a two day period and the temperatures were varied at random in order to reduce systematic errors in data evaluation.

Results and Discussion

Figure 1 is a plot of intensity (mm.) vs. temperature (°C) for the 1960 Å atomic line for the selenium TGL. Figure 2 is a plot of intensity (mm.) vs. temperature (°C) at the 2040 Å atomic line for the selenium TGL. As one can readily see from these two figures, an increase in temperature causes an increase in the intensity with only four exceptions in twenty four data points (i.e. 143, 144, 147, and 149 °C). A large intensity increase is noted for the 1960 Å and the 2040 Å atomic lines when one compares the 152 °C and 153 °C data. A 27.9 % increase is observed for the 1960 Å peak and a 34.1 % increase in intensity is observed for the 2040 Å peak. There are at least three reasons that could be contributing factors in the increase in intensity mentioned above:

1) As the temperature is raised, the heat given off by the walls of the lamp may reduce the number of cold collisions that are occurring along the walls of the lamp (2). This would tend to decrease the probability that self reversal could occur.

Table 1. Data for Intensity (mm. chart pen displacement) versus

Temperature (°C) for the Selenium Thermal Gradient Lamp

Temperature (°C) of Selenium TGL	Height of Peaks (mm.)					Temperature of Room (°C)
	1960 Å	2040 Å	2063 Å	2075 Å	2167 Å	
140	52.0	34.2	10.2	24.4	3.9	27.5
141	53.0	37.8	14.0	27.2	6.0	26.0
142	55.3	36.2	12.1	15.3	4.0	27.9
143	65.0	45.0	16.4	32.3	7.3	25.0
144	52.4	36.8	13.4	26.5	6.0	25.1
145	60.0	40.0	14.7	29.1	6.4	24.9
146	61.4	42.9	15.8	30.3	7.0	25.0
147	52.3	36.2	13.6	26.9	5.8	25.2
148	69.7	49.0	18.2	36.6	8.0	25.4
149	65.9	45.3	16.0	31.3	6.9	25.8
150	72.2	49.6	18.6	35.2	7.9	25.8
151	76.7	53.4	19.8	37.7	8.1	26.0
152	81.6	56.3	21.1	40.3	8.8	26.0
153	104.4	75.5	28.0	53.5	11.2	26.1
154	104.6	73.5	27.1	52.7	10.8	26.2
155	113.7	81.8	31.2	59.1	12.3	26.6
156	128.8	95.7	35.6	66.0	14.7	26.4
157	135.9	102.9	38.0	70.5	15.1	26.2
158	155.0	117.3	44.3	80.0	17.3	26.7
159	158.0	123.0	46.0	84.3	19.1	26.9
160	179.0	139.7	53.9	98.1	20.5	26.5
161	186.3	154.2	57.9	107.0	21.4	29.0
162	224.5	209.6	88.5	155.2	32.0	28.1
163	226.0	220.7	108.4	170.0	35.3	28.0

2) As the temperature is raised, there is an increase in the concentration of selenium in the vapor state due to increased vapor pressure.

3) An Ar(II) line may possibly be contributing to the overall intensity of the 2040 Å line of selenium. This is highly doubtful because even though the argon line is found at 2039.1 Å, it is a first ionized argon line. It is improbable that argon could exist in a charged state at such low temperatures.

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Figure 1. Plot of intensity versus temperature for TGL at 1960 Å.

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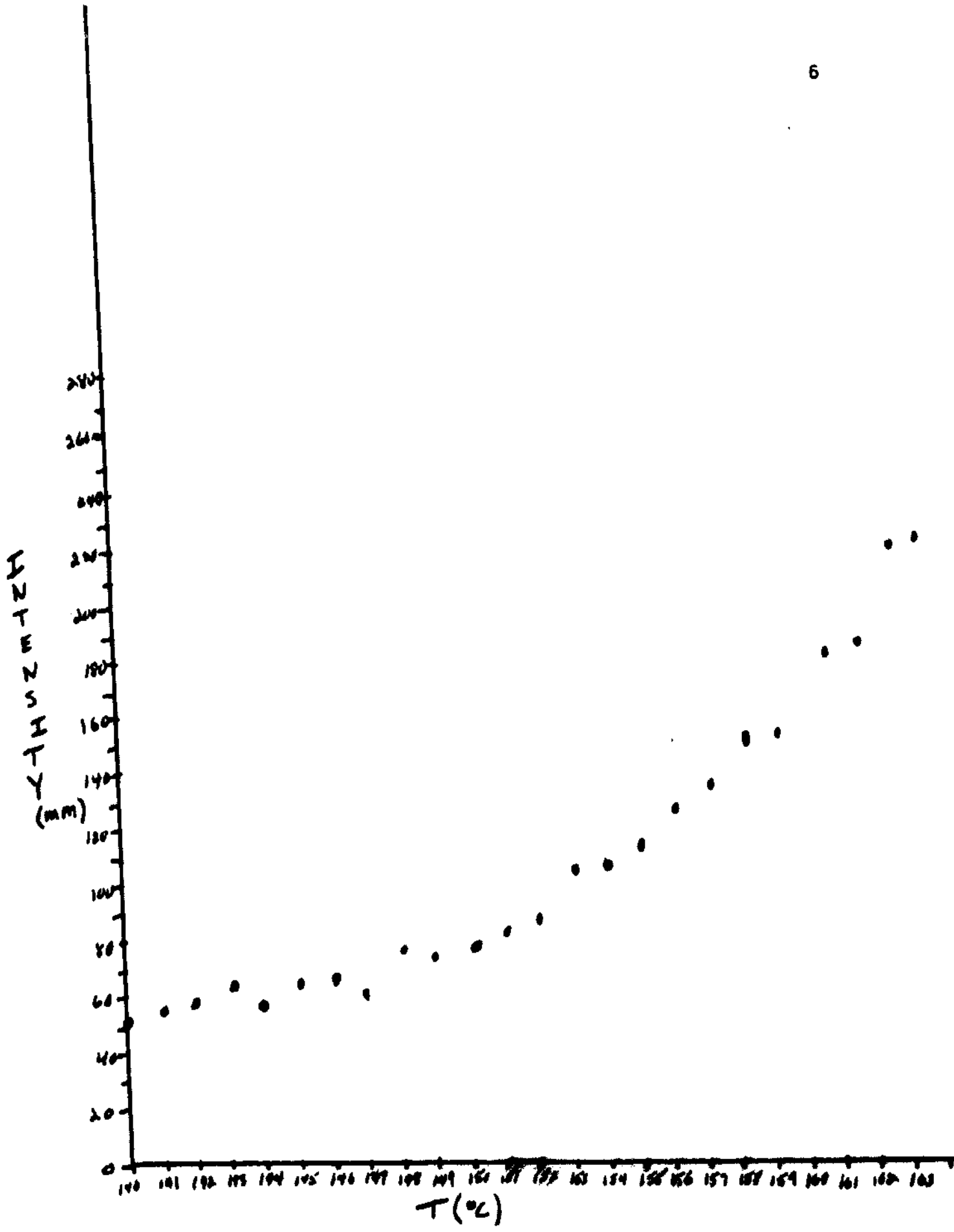
Figure 2. Plot of intensity versus temperature for TGL at 2040 Å.
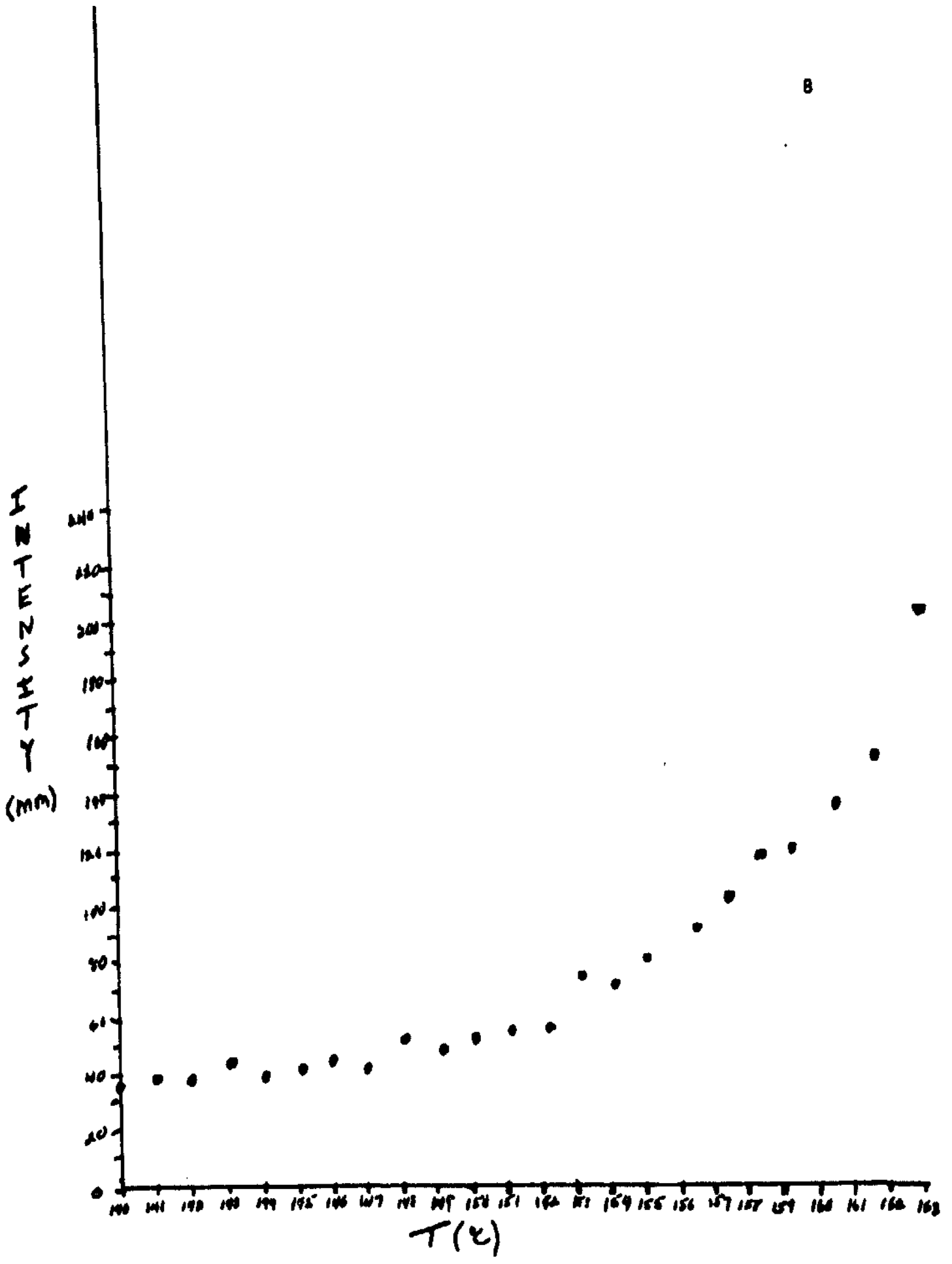
Several other things are worth mentioning here in regards to the temperature of the TGL lamp itself. As the temperature was increased from 153°C to 163°C, the relative intensities of the five peaks began to change drastically. For example, the relative ratio of the 1960 Å peak to the 2040 Å peak is approximately 3:2 at 140°C. By 163°C, the two peaks are roughly equivalent in height. The relative height of the 1960 Å peak and the 2063 Å peak is initially 5:1 at 140°C. This decreases to a factor of 2:1 at 163°C. The relative ratio of the 1960 Å to the 2075 Å peak is 2:1 at 140°C and decreases to 4:3 at 163°C. Finally, the relative ratio of the 1960 Å peak to the 2167 Å peak is initially 13:1 at 140°C. It decreases to a ratio that is slightly larger than 6:1 at the 163°C heater setting on the TGL power supply.

These facts lead one to conclude that the Boltzmann populations of the various ^3P states (i.e. $^3P_0$, $^3P_1$, and $^3P_2$) are rapidly changing inside the lamp. The selenium atom possesses a $^3P_2$ ground state. A diagram published by C. S. Rann and A. N. Hambly (3) is a good depiction of the lower energy level transitions to the more stable triplet P states of selenium. See figure 3 of this report for a reproduction of that diagram.

Although the ^5S transitions are considered to be spin forbidden, Rann and Hambly noted that they did make a moderate contribution to the intensity in the emission spectrum of their sources.

A second point worth noting, is a characteristic of the lamp itself. As temperatures reached the 160°C range, the lamp became much more difficult to restrike after a scan had been made and the

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Figure 3. Transitions between lower energy levels of Se atom.

S

S_5

$2144\overset{\circ}{A}$

$1960\overset{\circ}{A}$

$2063\overset{\circ}{A}$

$2040\overset{\circ}{A}$

$2075\overset{\circ}{A}$

sp_0

sp_1

sp_2
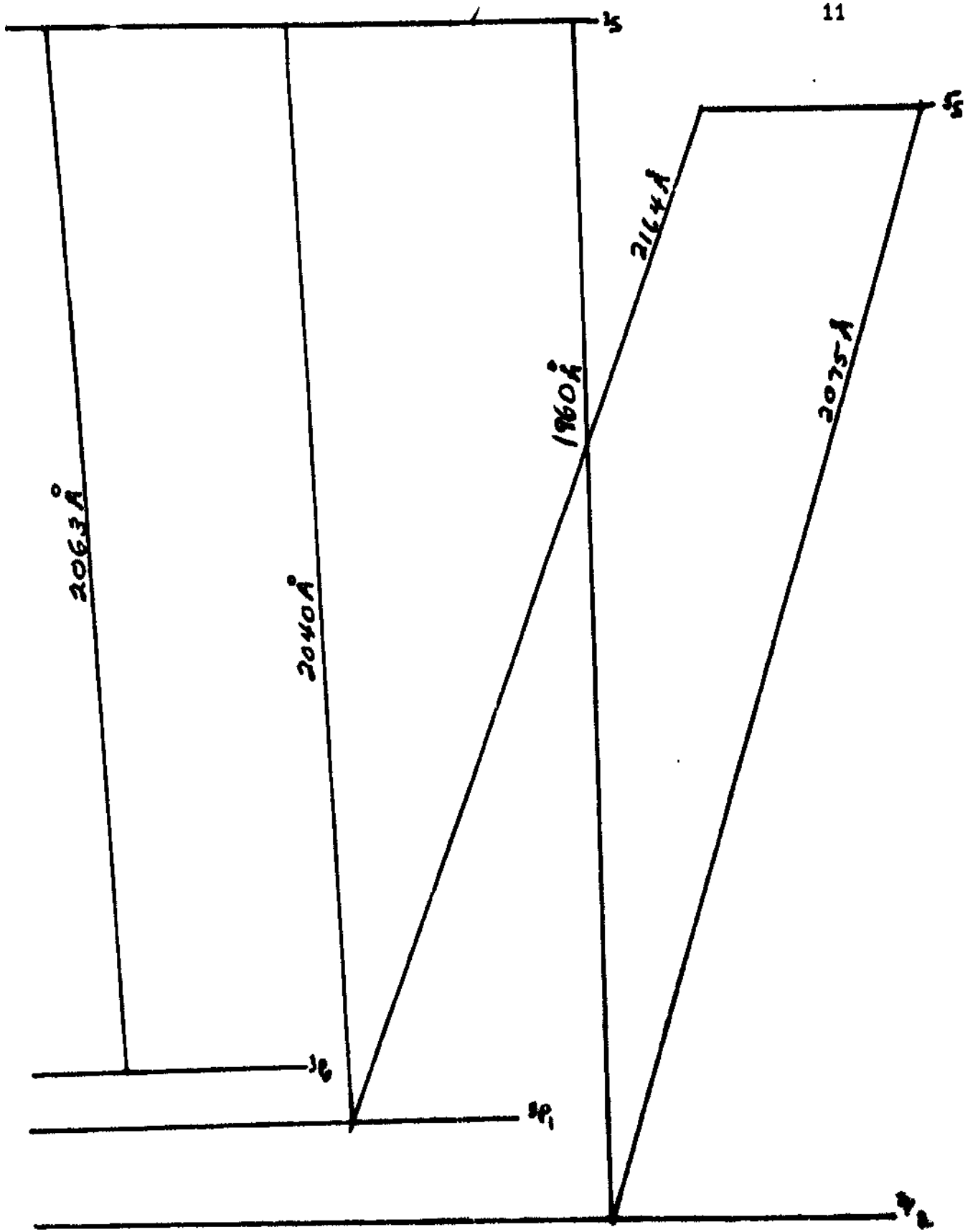
lamp had been allowed to cool and then turned off for the ten minute period stated previously. This may be due to poisoning of the electron emitter coating on the filament resulting from the presence of a high selenium concentration (4).

It is therefore recommended that the selenium TGL should never be heated over 159 °C. The lamp appears to be unstable above that temperature. The recommended temperature range, according to this writer, would be 150-152 °C, with 151 °C and 152 °C being more advantageous to use than the 150 °C that is recommended in the procedural manual provided by SGE. The lamp will give more intensity at 151 °C and 152 °C without a serious reduction in lamp life that one would probably experience if the heater were set at or above 159 °C. Stability and reproducability of emission lines were in evidence at 152 °C. No problems were experienced while attempting to restrike the lamp after several scans with the heater setting at 152 °C.

Intensity versus Time for the Selenium TGL

The equipment used for this study was identical to that used for the intensity versus temperature study. A heater setting of 150 °C was chosen for this study because 150 °C is the temperature specified in the manual provided by SGE. A description of the experimental conditions is described in the paragraph which follows.

The lamp was struck, the heater setting was dialed to 150 °C, and the heater was turned on. Eight minutes later, the heater light on the power supply dimmed, signifying that the desired temperature had

been attained. A scan from 1950 Å to 2200 Å was made every five minutes
for the first hour and then every ten minutes for the next three hours.
Data collected during this study are shown in Table 2. The temperature
of the room was again monitored and the intensity of all five atomic
lines of selenium in the 1950 Å to 2200 Å range were transformed into
tabular data using their maximum height from the baseline as a means for
making computations and comparisons. All conditions were the same as
those of the intensity versus temperature study (i.e. scan rate,
monochromator rate, millivolts full scale, etc.).

Results and Discussion

Figure 4 is a plot of intensity (mm.) versus time (min.) for the
1960 Å atomic line using the conditions stated above. Figure 5 is a
plot of intensity (mm.) versus time (min.) for the 2040 Å atomic line.

As one can readily see from figure 4, the selenium TGL at 150 °C
is unstable during the first two hours of operation. A 30 % increase
in intensity was observed during the first thirty minutes of the time
study. Maximum intensity was observed during the second thirty
 minute period of the time study. After the first hour of scans, the
TGL appeared to lose intensity until a relatively stable peak height
of 62 mm. was obtained at the end of the second hour of the time
study. The average height of 62 mm. was maintained for the remaining
two hours of the time study.

Figure 5 shows the same general trends that appear in figure 4.
The intensity in figure 5 shows an 85 % increase over the first hour

Table 2. Data for Intensity versus Time Study for Selenium Thermal
Gradient Lamp

Time (min.)	Run number	Height of Peaks (mm.)					Temperature of Room (°C)
		1960 Å	2040 Å	2063 Å	2075 Å	2167 Å	
0	1	59.6	41.0	14.9	30.1	5.0	25.6
5	2	66.4	46.6	17.1	32.0	6.1	24.0
10	3	73.3	51.0	18.0	35.6	7.8	23.7
15	4	72.8	50.7	17.8	36.4	7.0	23.5
20	5	70.5	49.6	17.1	35.2	6.7	23.0
25	6	72.3	52.9	19.3	37.4	7.2	22.9
30	7	85.0	60.8	22.0	41.7	7.7	22.8
35	8	83.9	60.0	21.2	42.0	8.1	23.0
40	9	84.2	61.9	23.0	42.9	8.1	23.0
45	10	86.0	63.0	22.6	44.0	8.3	23.0
50	11	76.1	56.3	20.3	40.9	8.1	23.0
55	12	97.0	72.9	26.0	48.7	9.0	24.2
60	13	90.8	65.6	23.8	45.0	8.8	24.0
70	14	73.9	59.3	20.0	39.4	7.4	23.9
80	15	79.4	58.3	20.8	40.2	7.7	25.0
90	16	80.2	59.7	21.1	41.8	8.0	24.5
100	17	72.9	51.2	18.4	35.5	7.0	24.0
110	18	66.3	46.3	16.3	32.0	5.8	24.0
120	19	62.0	43.5	15.5	30.9	5.6	23.5
130	20	65.8	46.9	16.3	34.0	6.4	23.4
140	21	64.5	45.6	16.3	31.0	5.5	23.1
150	22	65.2	46.3	16.9	33.0	6.4	24.1
160	23	61.1	40.9	14.0	28.0	4.8	24.5
170	24	66.3	44.0	15.9	32.1	4.8	24.0
180	25	62.4	43.0	15.0	30.0	5.6	24.1
190	26	62.9	42.4	15.3	30.8	6.0	24.1
200	27	64.2	45.1	15.8	31.0	5.3	24.2
210	28	64.9	43.0	15.4	31.3	6.0	24.1
220	29	65.0	44.0	15.8	31.1	5.9	24.2
230	30	65.2	45.9	16.0	31.9	6.4	24.0
240	31	69.0	47.0	17.0	33.3	7.1	24.1

of the study. During the second hour of the study, the relative peak
heights decrease to about 44 mm. and this average height is maintained
throughout the remaining two hours of the time study.

As one can easily see, the 1960 Å line is more intense than the
2040 Å line by a factor of 3:2.

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Figure 4. Time assay for TGL at 1960 Å.
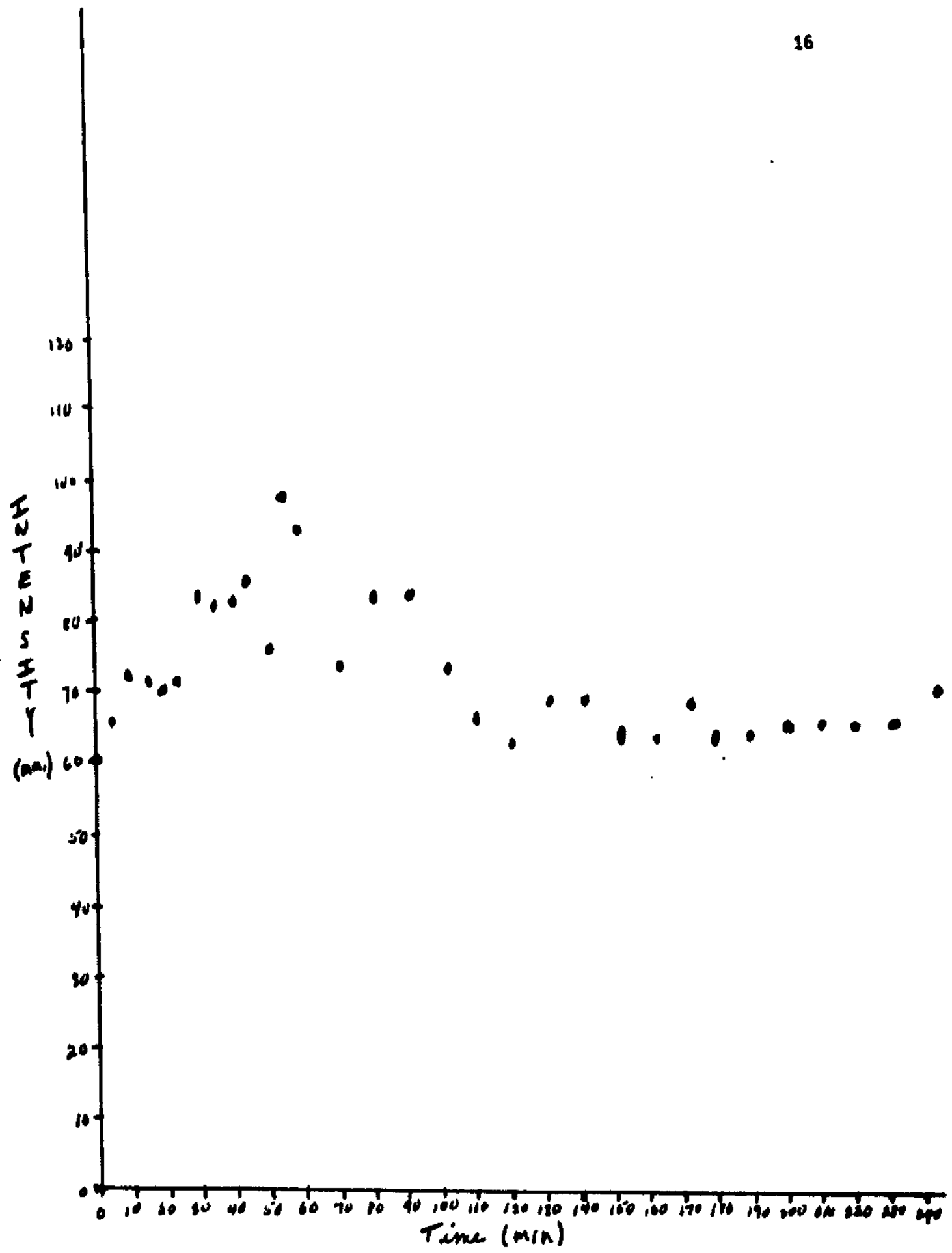
Figure 5. Time assay for TGL at 2040 Å.
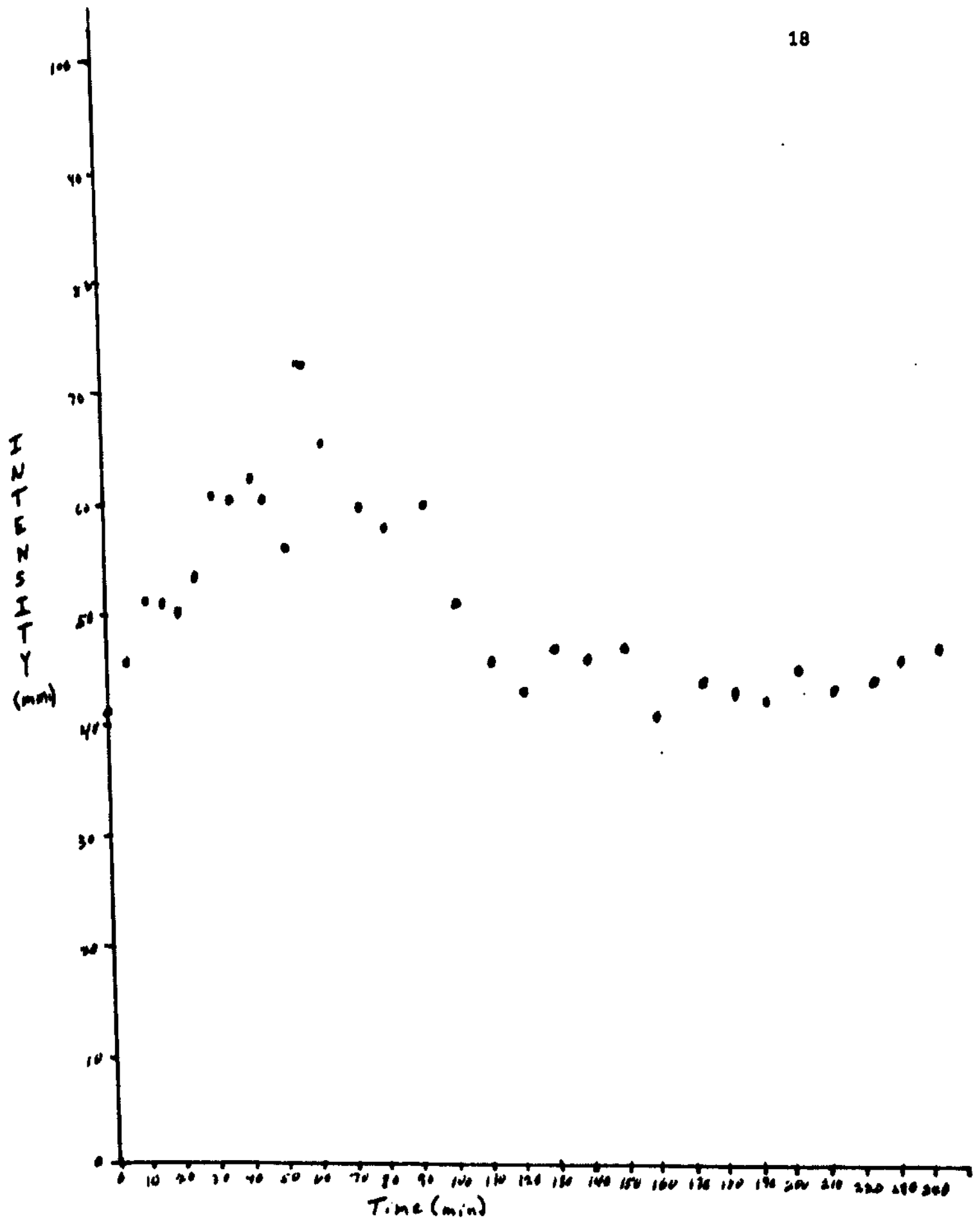
If one is looking at selenium in any environment, I would recommend that he choose the 1960 Å line to study selenium rather than the 2040 Å line. I will substantiate my reasoning later in this report.

TGL Studies Using Single Beam Atomic Absorption (AA) Instrument
Experimental

Shown below is a listing of the settings used in the AA portion of this experiment:

Temperature of selenium TGL: 150 ℃

GCA/McPherson AA Model number: EU-703

Heath Monochromator: EU-700

Heath Photomultiplier Module: EU-701-30 with R7328 UV Photomultiplier Tube

Slit Width: Variable (will be shown with each table used)

Heath Chart Recorder: Heath Log/Linear Current Module EU-20-B

Chart Recorder Settings:

% T Dial: 2×10^{-8}

Linear Mode

Millivolt Range: External

Chart Rate: three inches per minute

Path Length Through Flame: 100 mm.

Aspiration Rate: 5.1 mls./min.

Relative intensity of all table data is shown in millimeters.

Some arbitrary designations must now be stated in order to simplify some of the calculations involved in this section. They are listed on page twenty of this thesis.

Se : concentration of selenium in parts per million

M_b: $I_{D,b} - I_{e,b} - I_{stray}$ where;

$I_{D,b}$: intensity (mm.) read by detector using the blank,

$I_{e,b}$: intensity (mm.) of emission by the blank,

I_{stray}: intensity (mm.) of stray light.

M_c: $I \quad - I_{e,b} - I_{stray}$ where;

I : intensity of a certain concentration of selenium.

Key formulas for this section are:

$$\ln\left(\frac{M_b}{M_c}\right) = e^{K_3} + [Se]^{\aleph}$$

$$\ln\left[\ln\left(\frac{M_b}{M_c}\right)\right] = K_3 + \aleph\ln[Se]$$

The significance of $\aleph$ and K_3 will be explained later in this thesis. Both formulas will be used for graphs in this section and also later in this thesis when the atomic absorption studies using the EDL are presented.

Attempts by Dr. Marquart to determine the amount of stray light involved, led him to believe that for all calculations I could assume that I_{stray} was equal to zero. Dr. Marquart actually determined that the amount of stray light was less than 19 % of that which was being sensed by the detector.

The air-acetylene mixture used for the burner was a ratio of 5:1 respectivel . The solution which was used in these studies was developed om a combination of techniques employed by Varion Techtron Pty. Ltd. of Springvale, Australia (5) and Nakahara, Munemori, and

Musha (6).   The solution had the following reagents mixed in it:

                        1.996 g. of grey selenium

                        130 mls. of 70 % nitric acid

                        10 mls. bromine

                        Addition of millipore water to one liter

Millipore water is water which has been passed through cationic and

anionic columns in order to attempt to remove all ions from the water

before it is used in an experiment.   The water is also passed through

a special filter which is used to remove any undesirable impurities

which may be present.   The stock solution was then diluted in order to

obtain a large range of concentrations.   Table 3 shows the data

obtained with the slits on the monochromator at 34 um. at the 1960 Å

selenium line.

Table 3. TGL Data Using AA Instrumentation for 1960 Å line

$[Se]$ (ppm.)	M_b^*	M_c^*	$\ln\left(\dfrac{M_b}{M_c}\right)$	$\ln\left[\ln\left(\dfrac{M_b}{M_c}\right)\right]$	$\ln[Se]$
1.5	225.0	205.5	0.0907	-2.4010	0.4055
3.7	223.4	199.0	0.1157	-2.1571	1.3083
7.5	228.0	179.5	0.2392	-1.4306	2.0150
15.0	219.0	164.7	0.2849	-1.2555	2.7081
30.0	218.0	129.9	0.5177	-0.6583	3.4012
75.0	216.0	75.0	1.0578	0.0562	4.3175
102.0	214.0	49.5	1.4640	0.3812	4.6250
150.0	207.0	28.5	1.9828	0.6845	5.0106
299.9	207.5	7.4	3.3337	1.2041	5.7030

(* mm.)

Sensitivity at the 2040 Å line could not be noted until the

400 ug./ml. solution was used.   This is the reason that I stated

earlier in my report as to why one would benefit from using the 1960 Å line rather than the 2040 Å line when using the TGL.

Results and Discussions

Figure 6 is a plot of $\ln(M_b/M_c)$ versus $[Se]$ for the 1960 Å data obtained in the AA study of the TGL. The slope of this line would correspond to the ξ value of a Beer's law formula.

Figure 7 is a plot of $\ln\left[\ln(M_b/M_c)\right]$ versus $\ln[Se]$ for the 1960 Å data collected for this portion of the experiment. The slope of the y-intercept of this plot correspond to f and K_3 of the formula shown earlier in this report. The f function corresponds to a modified Beer's law formula which places a second parameter as an exponential governing the path length and the concentration in the Beer's law formula. The modified Beer's law formula is shown below:

Absorbance = $\xi(b[Se])^f$

b = path length

ξ = absorption coefficient

The linear regression correlation data for figures 6 and 7 were obtained on a TI 59 calculator. Values are shown below.

Figure 6	Figure 7
plot of $\ln(M_b/M_c)$ versus $[Se]$	plot of $\ln\left[\ln(M_b/M_c)\right]$ versus $\ln[Se]$
correlation = .8640	correlation = 0.9929
slope = 1×10^{-3}	slope = 0.7066
y-intercept = 0.4093	y-intercept = -2.9351 = K_3

Better sensitivity was obtained using the 1960 Å peak in this experiment. I did not run into the problems that Willard, Merritt, and Dean (7) mentioned that probably would occur when one

Figure 6. Plot of ln (M_b/M_c) versus $[Se]$ for AA study at 1960 Å.

$ln\left(\frac{n_b}{n_{bc}}\right)$

4.0

3.5

3.0

2.5

2.0

1.5

1.0

0.5

0 2.5 5   50   75   102   150   2.4.9
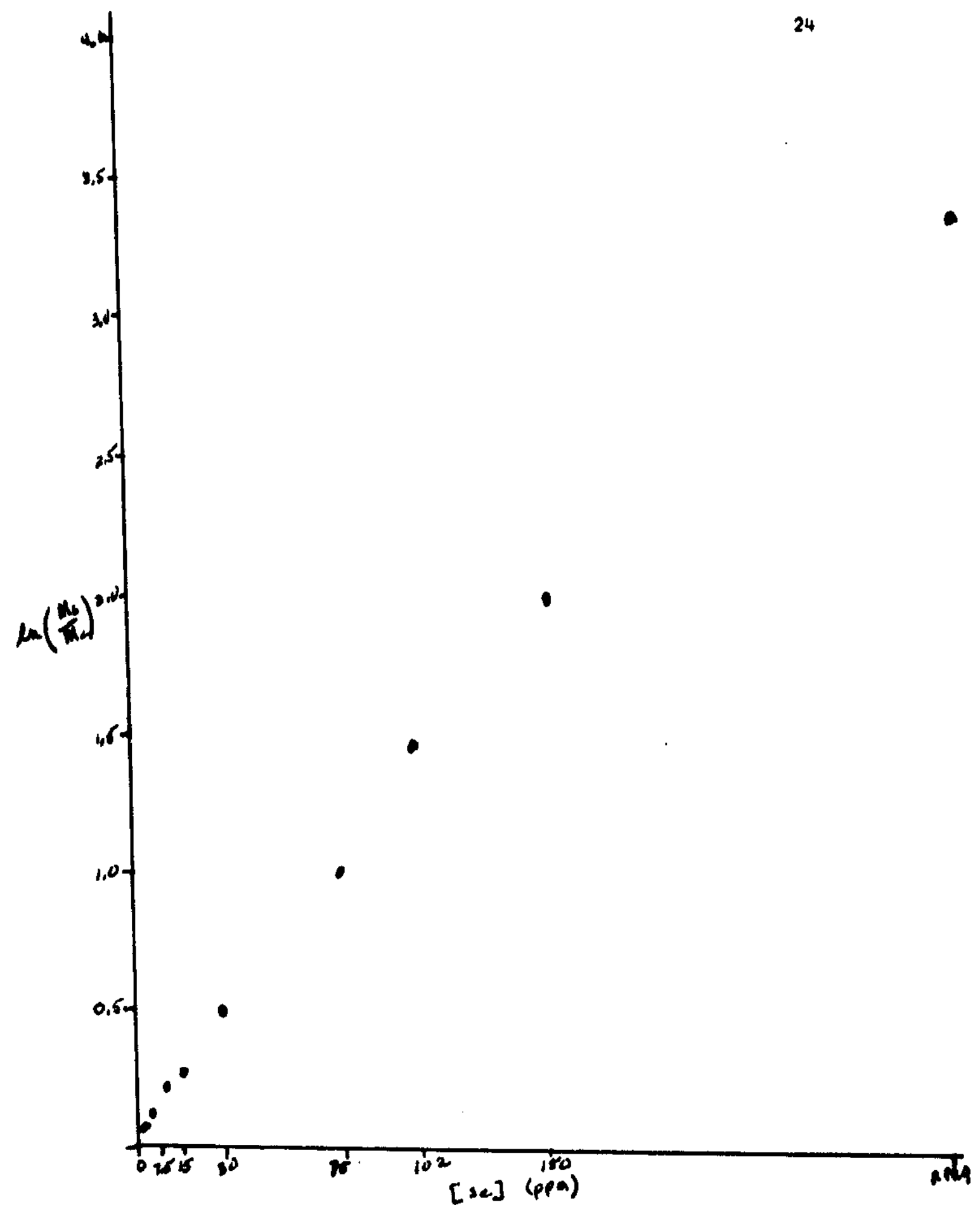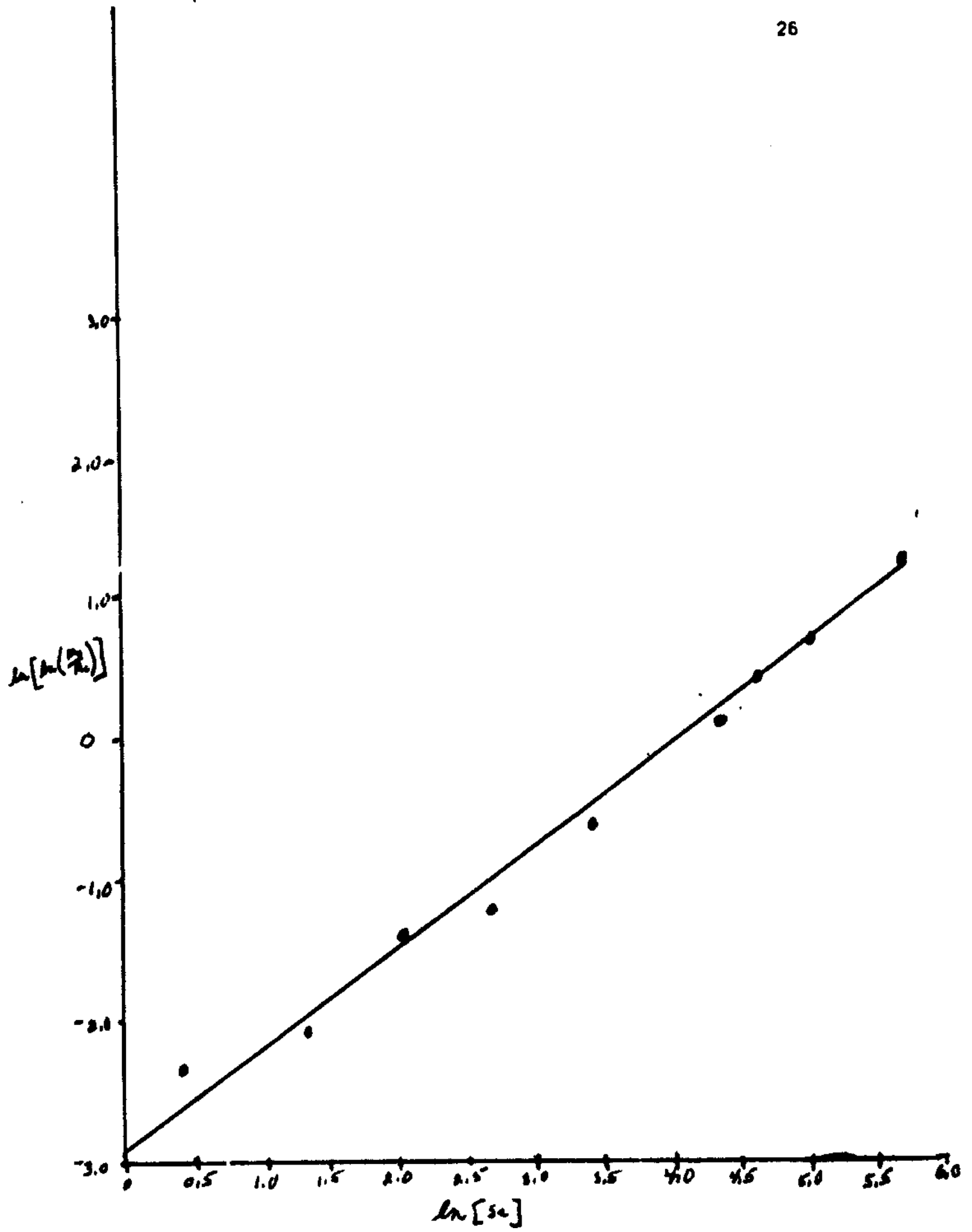
$[sc]$ (ppm)

25

Figure 7. Plot of $\ln\left[\ln(M_b/M_c)\right]$ versus $\ln[Se]$ for AA study at 1960 Å.

attempted to look at flames using wavelengths under 2000 Å. Some curvature is noted in figure 6. This is an expected course but not enough samples were used to verify it.

EDL Studies

Experimental for Blue EDL

All of the same equipment which was used in the TGL studies of intensity and temperature versus time was used again in the EDL studies. Two differently visible appearances of light emitted by the EDL were used. The color only changes with the amount of total power generated by the microwave source, and the amount of cooling air which is passed over the EDL. I used a selenium EDL and the operating colors which were chosen to study were pink and blue. Pink corresponds to a much lower % power supplied by the microwave source.

The microwave diathermy used for this portion of the experiments was manufactured by Burdick (Model ^{MW}/200) i.e., 100% power equals about 200 milliwatts. Dr. Marquart and I found no reliable way to determine the actual temperature of the ED1 accurately although we did not attempt to apply the method which R.F. Browner [6] had mentioned in one of his published studies. One major difference in these studies relative to the TGL studies of intensity versus time, is that the EDL studies were done over a three hour period and the TGL study was done over a four hour period.

The first EDL study of intensity over time was done using the selenium EDL with the power high enough to cause the lamp to appear blue. A complete listing of the settings on the equipment used for this study are shown below

Monochromatic slits = 0.1 mm

Chart rate = 4"/minute

Volts full scale = 0.01

Diathermy % power = 56%

No cooling air forced over EDL

A total of ten minutes passed after the EDL was struck with a Tesla coil before the desired color was obtained. The data which were collected in this portion of the experiment has been compiled and is shown in Table 7.

Figure 8 is a plot of intensity versus time for the 1960 $\overset{\circ}{A}$ selenium line. Figure 9 is a plot of intensity versus time for the 2040 $\overset{\circ}{A}$ selenium line. The data for both plots were taken from Table 4. Results and discussions will be deferred until the pink EDL data and figures are shown. The pink EDL studies of intensity versus time follow directly after this section of my thesis.

Experimental for Pink EDL

The conditions used for this portion of the experimentation are as follows

Monochromatic slits = 0.09 mm

Chart rate = 4"/ minute

Volts full scale = 0.01

Diathermy % power = 40%

Air being passed over the pink EDL

Table 5 is a compilation of all data taken during this portion of the experimentation. Figures 10 and 11 are figures of intensity versus time for the 1960 $\overset{\circ}{A}$ line and the 2040 $\overset{\circ}{A}$ line respectively.

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Figure 8. Plot of intensity versus time for blue EDL at 1960 Å.
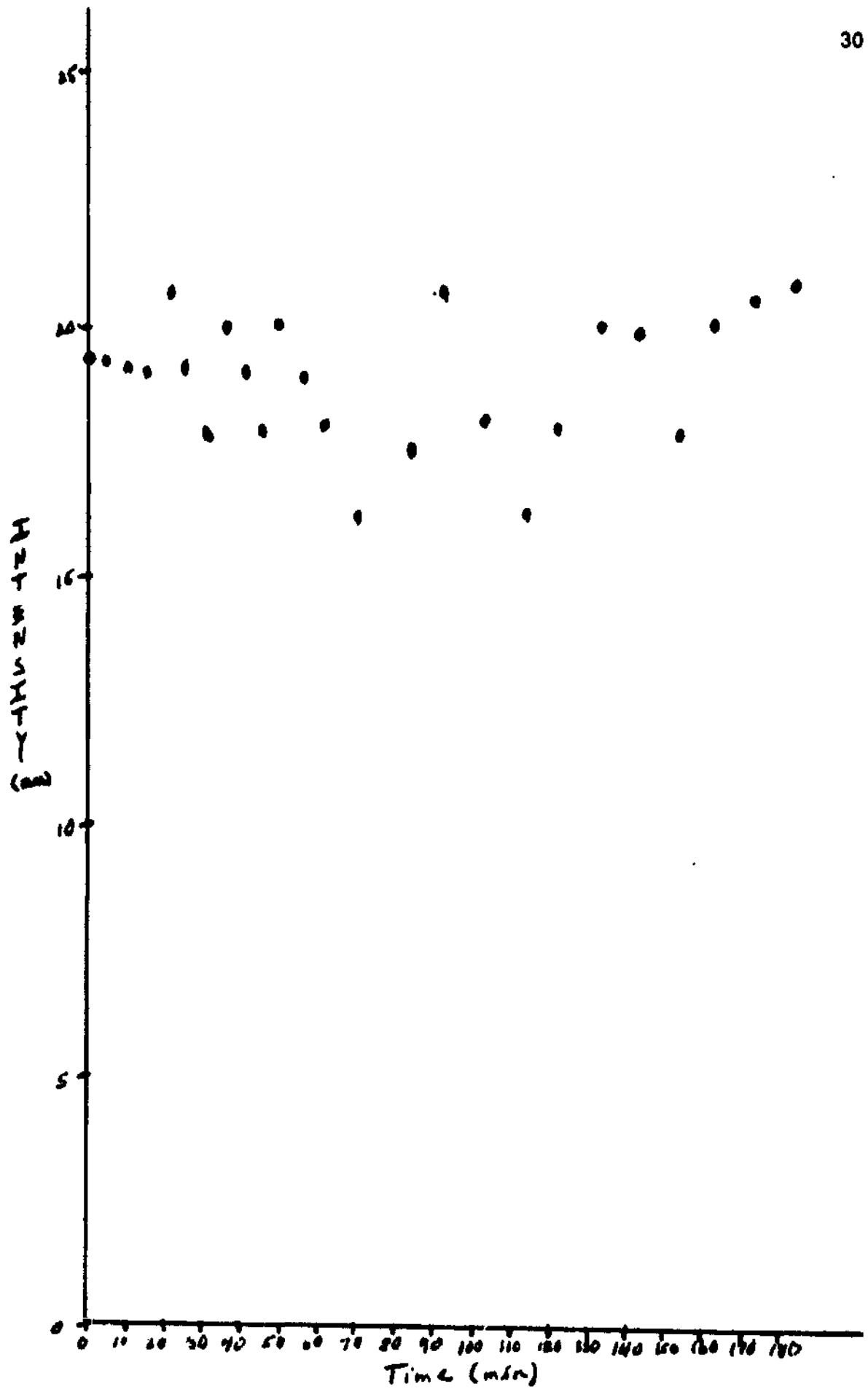
31

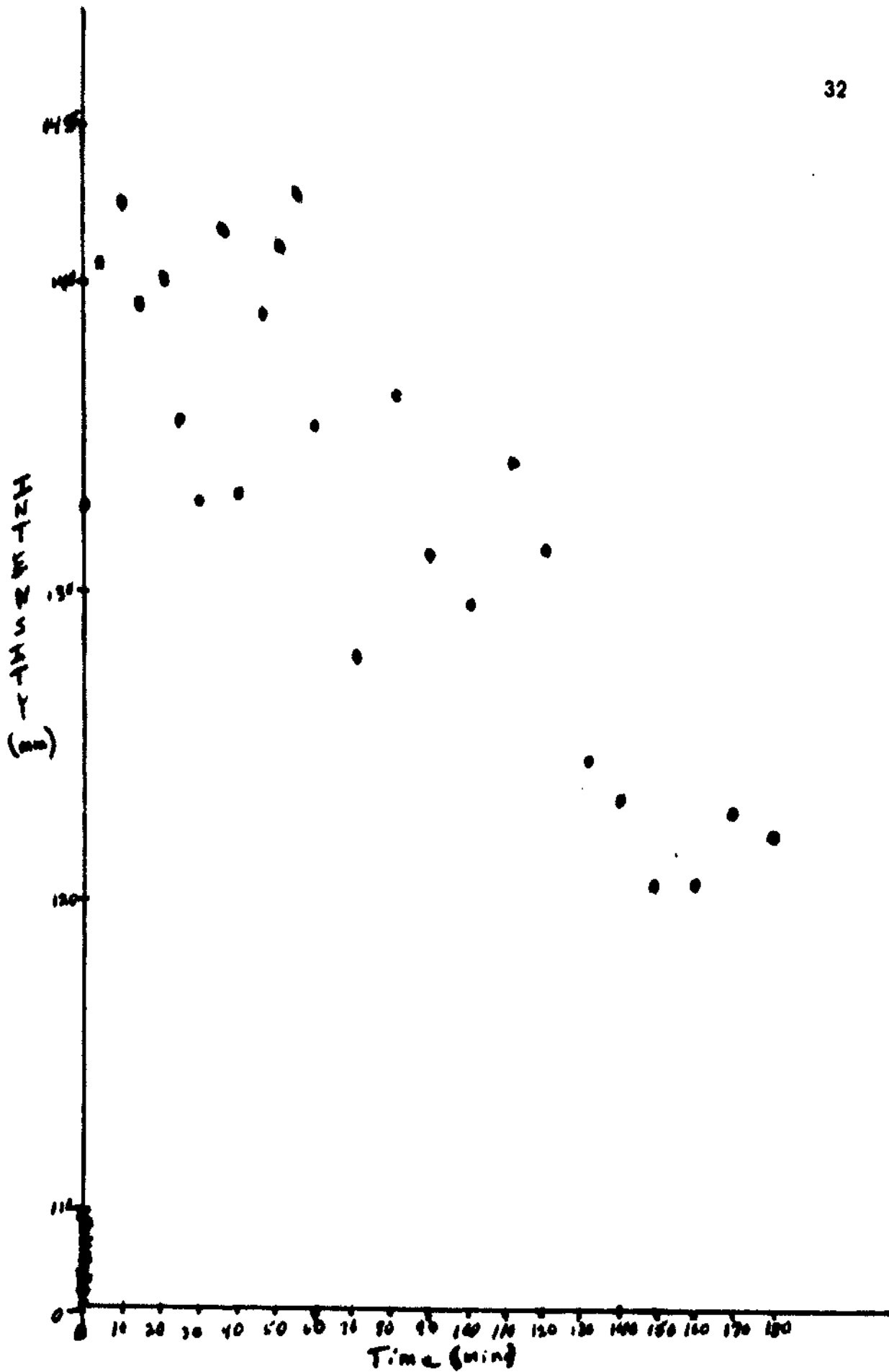Figure 9. Plot of intensity versus time for blue EDL at 2040 Å.

Table 4. Intensity versus Time Data Using the Blue EDL

Time (min.)	Run #	Height of Peaks (mm.)					Temperature of Room (°C)	% Power
		1960 Å	2040 Å	2063 Å	2075 Å	2167 Å		
0	1	19.1	132.8	214.9	19.2	65.3	26.0	56.0
5	2	18.9	140.3	227.3	20.8	67.7	26.0	56.0
10	3	18.6	142.7	234.9	21.0	68.4	25.9	56.0
15	4	18.4	139.3	222.3	20.0	65.8	25.9	56.0
20	5	21.1	140.0	218.5	19.5	66.2	25.8	57.0
25	6	18.4	135.4	213.9	18.8	65.9	26.0	58.0
30	7	17.7	133.1	212.1	19.1	65.7	25.9	58.0
35	8	20.0	141.7	221.3	20.2	66.6	25.8	58.0
40	9	18.4	133.3	218.9	19.7	66.3	25.9	58.0
45	10	17.6	139.0	216.0	19.9	66.4	25.9	58.0
50	11	20.1	141.0	220.5	20.1	68.7	25.8	58.0
55	12	18.9	142.8	222.3	20.0	67.9	25.9	58.0
60	13	17.7	135.6	211.1	18.4	66.0	25.8	58.0
70	14	16.3	127.8	205.2	18.1	64.9	25.9	58.0
80	15	18.6	136.2	207.7	18.4	65.7	26.0	58.0
90	16	20.6	131.0	211.8	18.9	66.0	25.9	58.0
100	17	18.0	129.3	203.0	17.9	64.0	25.8	58.5
110	18	16.3	134.0	206.7	17.8	64.4	25.6	58.5
120	19	17.9	131.2	200.6	18.1	64.3	25.8	59.0
130	20	20.1	123.9	191.8	17.0	62.7	25.8	60.0
140	21	18.8	122.7	190.9	16.6	62.9	25.8	60.0
150	22	17.9	119.7	183.0	15.6	61.0	25.7	60.0
160	23	20.0	119.7	191.0	16.9	62.3	25.7	59.5
170	24	20.6	123.0	194.1	17.2	64.0	25.8	59.0
180	25	21.0	122.0	189.2	16.8	61.9	25.5	60.5

Results and Discussions

It should be mentioned here that there was a significant amount of drift in the % power of the diathermy during this portion of the experimentation. This was especially prominent in the blue EDL study (See Tables 5 and 6). A sincere attempt was also made to control the temperature of the room itself. A listing of the temperature of the room at the initiation of each scan is also included in Tables 4 and 5.

Figure 8 (Intensity versus Time for Blue EDL at 1960 line) is a good example of why a more reliable source of illumination is necessary

Table 5. Intensity versus Time Data Using the Pink EDL

Time (min.)	Run #	Height of Peaks (mm.)					Temperature of Room (C)	% Power
		1960 A	2040 A	2063 A	2075 A	2167 A		
0	1	44.0	82.5	80.6	153.3	44.2	26.0	41.0
5	2	47.4	84.1	84.1	159.6	44.9	26.5	40.5
10	3	44.1	85.7	87.7	163.0	46.3	26.0	41.0
15	4	44.3	87.8	91.7	167.5	47.9	25.7	40.5
20	5	46.7	88.8	92.9	169.0	48.8	25.8	40.5
25	6	39.9	91.2	92.7	173.5	50.3	25.8	41.0
30	7	45.5	90.4	95.9	168.7	49.8	25.5	40.3
35	8	43.1	89.0	95.1	175.0	49.8	25.4	39.9
40	9	44.9	91.8	97.7	174.0	50.7	25.7	39.9
45	10	50.2	90.3	99.1	173.7	50.6	25.4	39.8
50	11	49.2	91.1	88.0	173.6	50.8	25.9	39.9
55	12	46.6	92.9	101.8	176.8	51.5	25.9	39.9
60	13	44.3	92.2	101.0	176.4	51.3	26.1	40.0
70	14	47.1	93.1	102.0	178.0	51.5	26.0	39.9
80	15	46.2	93.1	98.9	173.6	50.4	25.9	40.0
90	16	51.2	91.7	98.8	173.2	50.8	25.7	40.5
100	17	44.1	91.6	98.0	170.7	49.9	25.8	41.0
110	18	45.9	93.0	97.7	171.3	49.3	25.3	40.0
120	19	48.0	91.5	96.4	169.2	48.0	25.8	41.0
130	20	46.6	92.7	97.9	171.3	49.3	25.5	40.5
140	21	42.9	89.6	92.0	164.3	46.9	25.7	40.0
150	22	46.6	87.0	88.5	156.0	45.5	25.8	40.0
160	23	44.1	90.5	92.6	163.9	47.4	26.0	40.0
170	24	43.0	88.1	90.5	159.0	44.9	26.0	40.2
180	25	45.0	83.8	85.8	153.4	43.0	26.0	40.0

because the Edl intensity varies by 25% after the first fifteen

minutes of operating time. Figure 9 (Blue EDL at 2040 Å line) shows

the same kind of erratic distribution that is persent in Figure 8.

Figure 9 doesn't even show much stability during the first thirty

minutes of operating time. Figure 10 (Pink EDL at 1960 Å line) is

probably the most stable representation of the four figures involving

intensity versus time for the EDL. The largest deviation from a

mean line would be less than 15% of the total intensity for every point

plotted during the three hour period. It is my opinion that the best

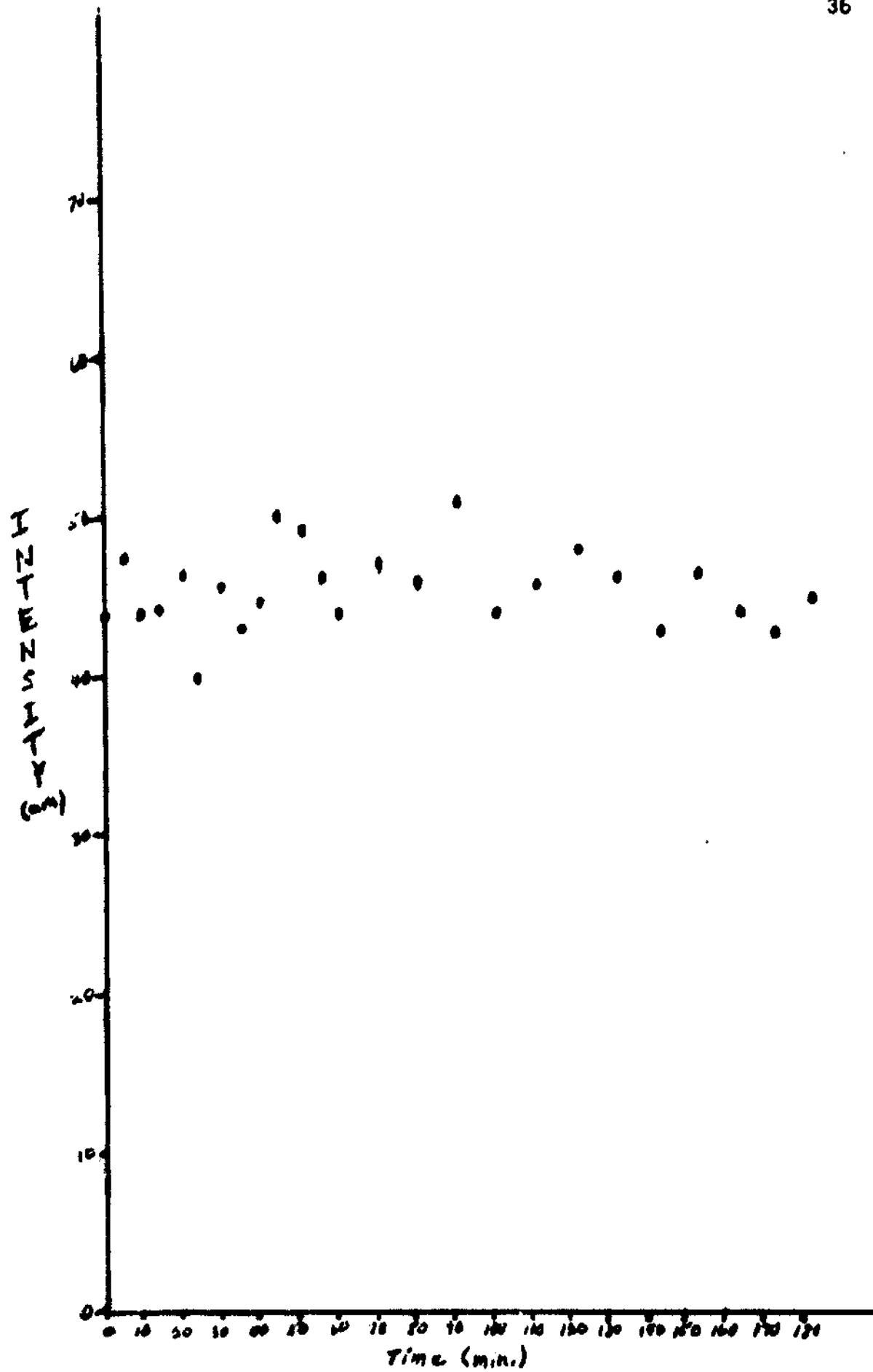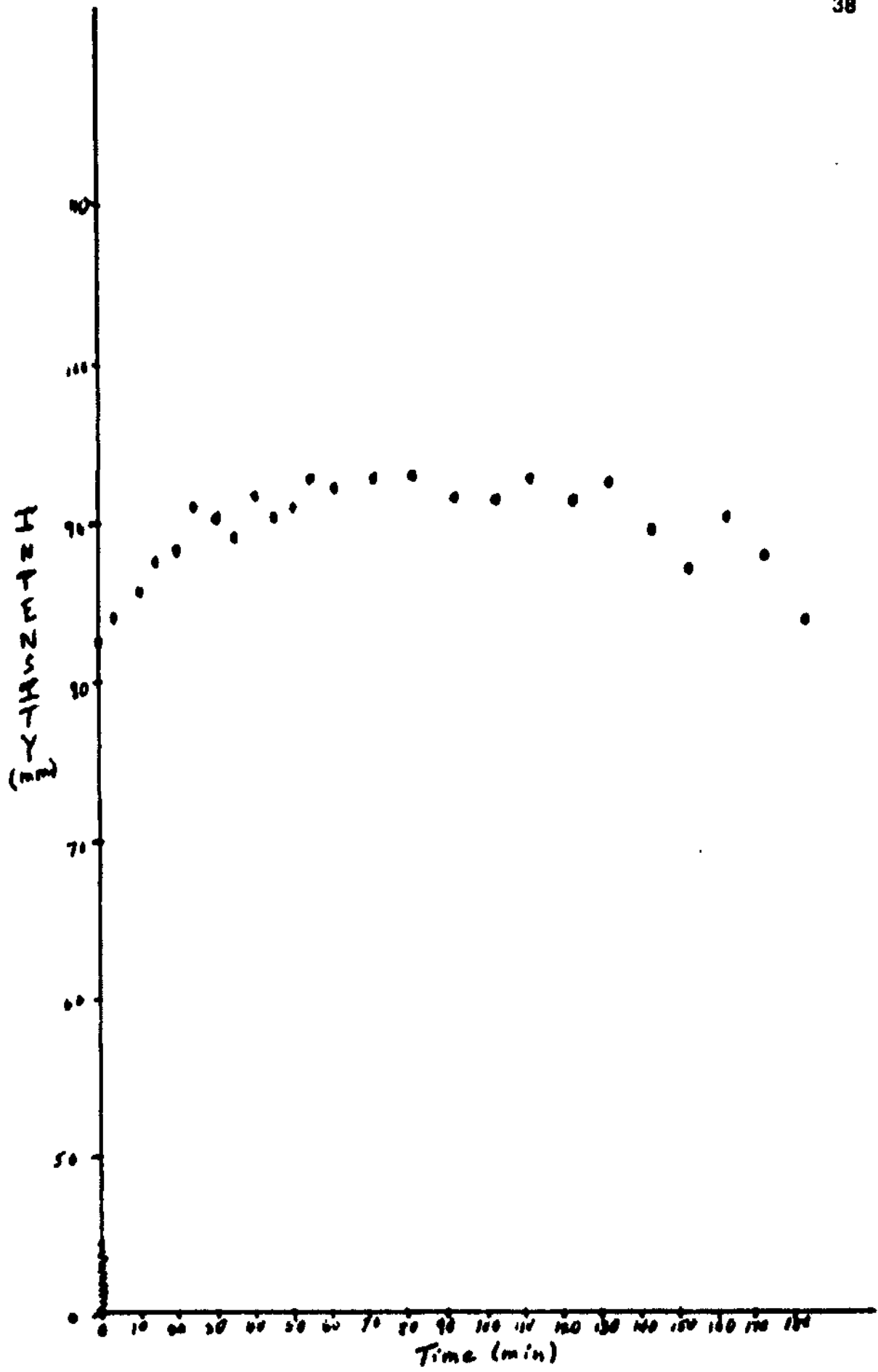Figure 10. Plot of intensity versus time for pink EDL at 1960 Å.

Figure 11. Plot of intensity versus time for pink EDL at 2040 Å.

way to study the 1960 A line of selenium with an EDL is to use less power and find a pink color that you can maintain for a length of time without sacrificing stability. The pink EDL showed more than twice the peak intensity that was obtained with the blue EDL at the 1960 Å setting on the monochromator.

Figure 11 (Pink EDL at 2040 Å line) shows stability and reproducability between the first and second hour of the time study. It is this writer's recommendation, that if one desires to observe phenomena regarding selenium at the 2040 Å line, the pink EDL would still be more advantageous to use relative to the blue EDL. Even though greater intensity can be achieved using the blue EDL, the stability and reproducability of the second hour of the pink EDL makes it more desirable to draw generalizations from when experiments are being performed.

Atomic Absorption Studies with Pink and Blue EDL

Experimental

All of the equipment described previously for the AA studies using the TGL were used again for the EDL studies. All chart recorder dials remained in the same place. The flame composition was also kept constant. The pink EDL will be discussed first.

Pink EDL

The only difference in equipment settings are shown below

Monochromatic slits = 2.2 μm

Diathermy % power = 25%

Data,Results and Discussions for Pink EDL

Table 6 is a compilation of information that was derived from the study of the pink EDL at the 1960 Å line of selenium. Data was

reduced by the same method which was explained previously in the section involving the AA studies employing the TGL as an illumination source.

Table 6   Data for Pink EDI at 1960 Å Line Using AA

[Se]	M_b	M_c	$\ln(\frac{M_b}{M_c})$	$\ln \ln(\frac{M_b}{M_c})$	$\ln [Se]$
1.5	169.0	155.0	0.0865	-2.4480	0.4055
7.5	167.0	153.0	0.0876	-2.4355	2.0150
75.0	172.0	137.0	0.2275	-1.4810	4.3175
150.0	170.0	97.0	0.5611	-0.5779	5.0106
299.9	186.0	56.0	1.2004	0.1827	5.7034

Figures 12 and 13 are plots of $\ln(\frac{M_b}{M_c})$ versus [Se] and $\ln\left[\ln(\frac{M_b}{M_c})\right]$ versus $\ln$ [Se] respectively for the 1960 Å line. Correlation data for figure 12 and 13 are shown below.

Figure 12(Plot of $\ln(\frac{M_b}{M_c})$ versus [Se]

Correlation = 0.9923

Slope = 3.78 x 10^{-3}

y-intersept = 0.029

Figure 13(ln $\ln(\frac{M_b}{M_c})$ versus $\ln$[Se])

Correlation = 0.9231

Slope = 0.4823

y-intersept = -3.035

Figure 12 shows less linearity than what would be considered desirable. Figure 13 is a vivid demonstration that all linearity is lost.

Table 7 is a compilation of information obtained while using the pink EDL at the 2040 Å selenium line. Slit width for this portion of the experiment was 17 μm.

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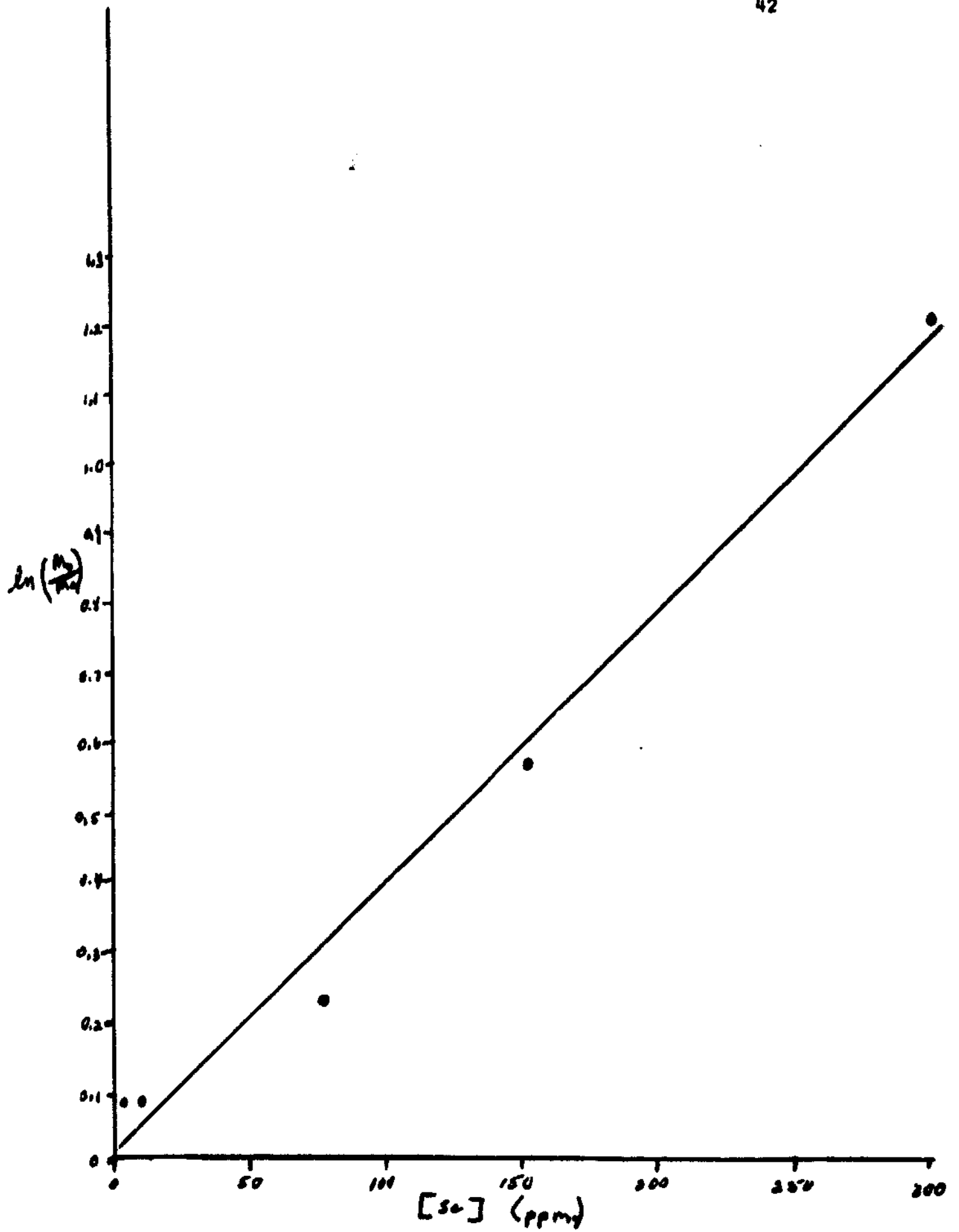Figure 12. Plot of $\ln(M_b/M_c)$ versus $[Se]$ for 1960 Å AA study with pink EDL.

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Figure 13. Plot of $\ln\left[\ln(M_b/M_c)\right]$ versus $\ln\left[Se\right]$ for 1960 Å AA study with pink EDL.
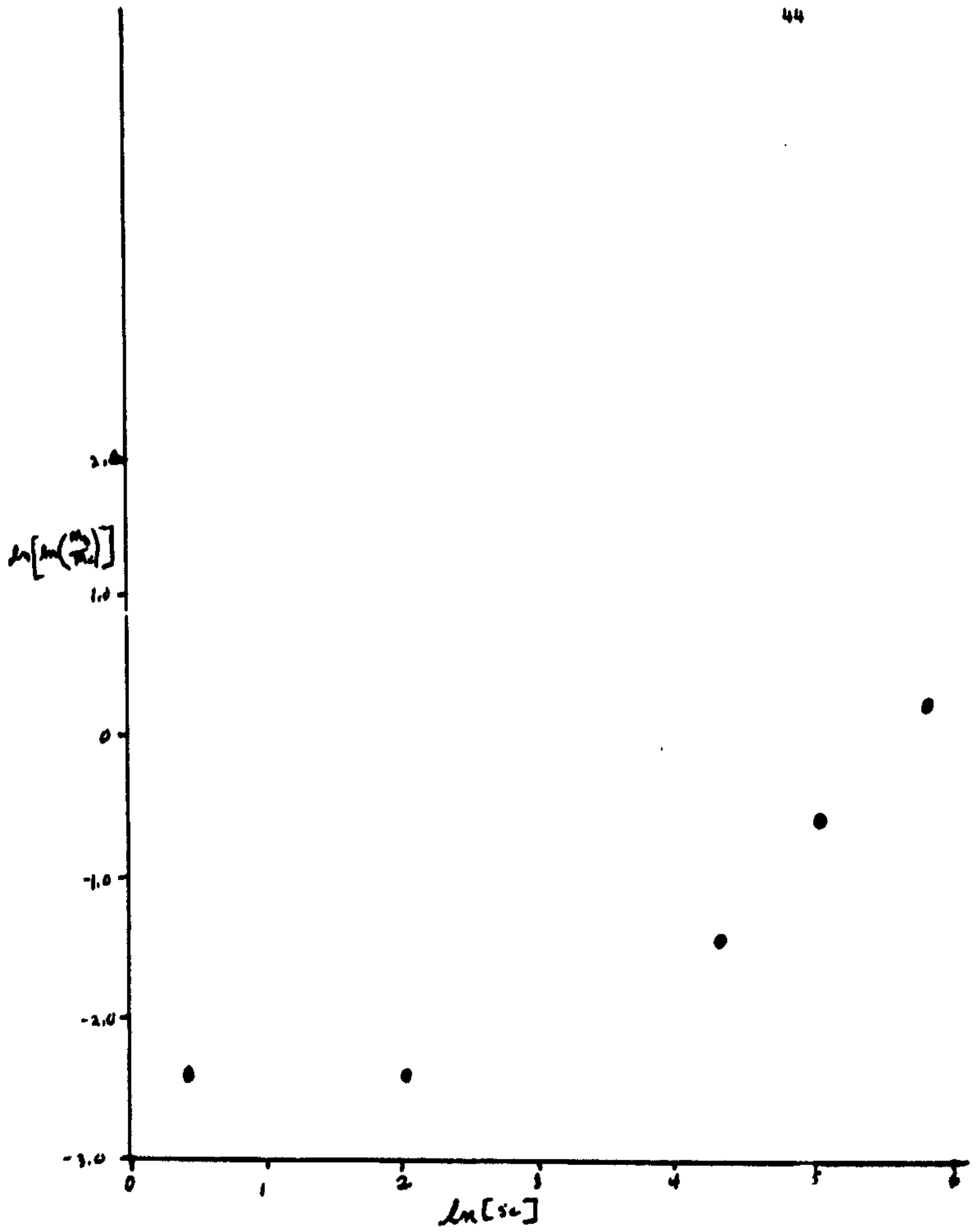
Table 7-Data For Pink EDL at 2040 $\overset{o}{A}$ Line Using AA

$[Se]$	M_b	M_c	$\ln\left(\frac{M_b}{M_c}\right)$	$\ln\ \ln(\frac{M_b}{M_c})$	$\ln [Se]$
30.0	199.0	195.0	0.0203	-3.8970	0.4055
102.0	186.5	167.0	0.1104	-2.2033	4.6250
150.0	188.0	161.5	.1519	-1.8843	5.0106
299.9	188.5	146.0	0.2555	-1.3646	5.7034

Correlation data for Figures 14 and 15 are shown below.

Figure 14- $\ln\left(\frac{M_b}{M_c}\right)$ versus $[Se]$

Correlation = 0.9875

Slope = 8.4×10^{-4}

y-intersept = 0.012

Figure 15-$\left(\ln\left[\ln(\frac{M_b}{M_c})\right]\right)$ versus $\ln [Se]$

Correlation = 0.9974

Slope = 0.4796

y-intersept = -4.204

Data, Results and Discussion for Blue EDL

The only differences in equipment setting are shown below.

Diathermy % power = 56%

Monochromator slit width = 29 μm

Table 8 is a compilation of data reduced to tabular form.

Table 8 - Data for Blue EDL at 1960 $\overset{o}{A}$ on AA Equipment

$[Se]$	M_b	M_c	$\ln(\frac{M_b}{M_c})$	$\ln\left[\ln\ (\frac{M_b}{M_c})\right]$	$\ln [Se]$
7.5	170.0	168.0	0.0118	-4.437	2.015
15.0	173.0	170.0	0.0175	-4.406	2.708
75.0	173.0	165.0	0.0473	-3.050	4.317
299.9	174.0	159.0	0.0902	-2.406	5.703

Figures 16 and 17 are plots of $\ln(\frac{M_b}{M_c})$ versus $[Se]$ and $\ln\ \ln(\frac{M_b}{M_c})$ versus $\ln [Se]$ respectively. The baseline was the least stable of

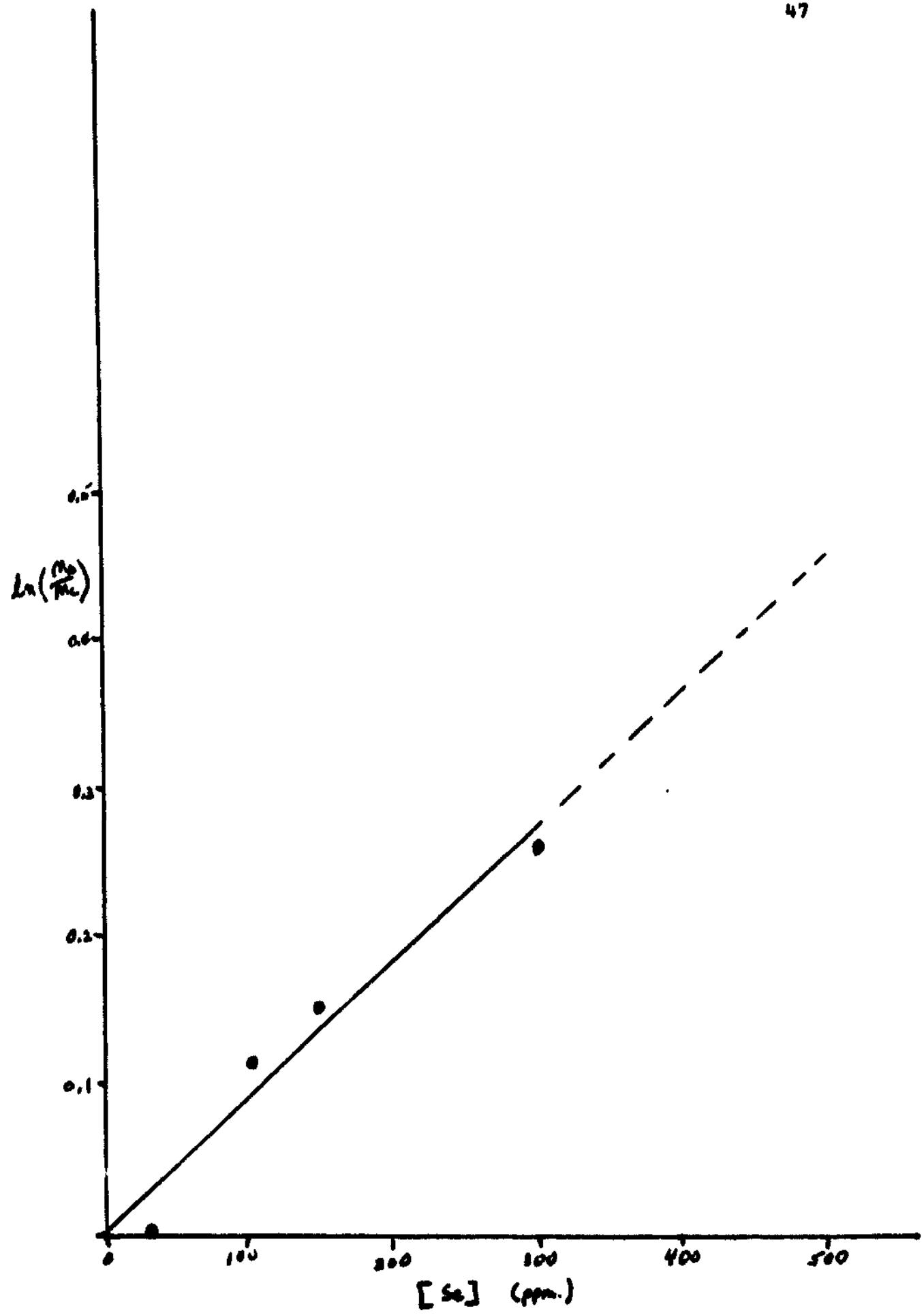Figure 14. Plot of $\ln(M_b/M_c)$ versus $[Se]$ at 2040 Å using pink EDL.

$ln\left(\frac{n_0}{n_e}\right)$

$[Se]$ (ppm.)

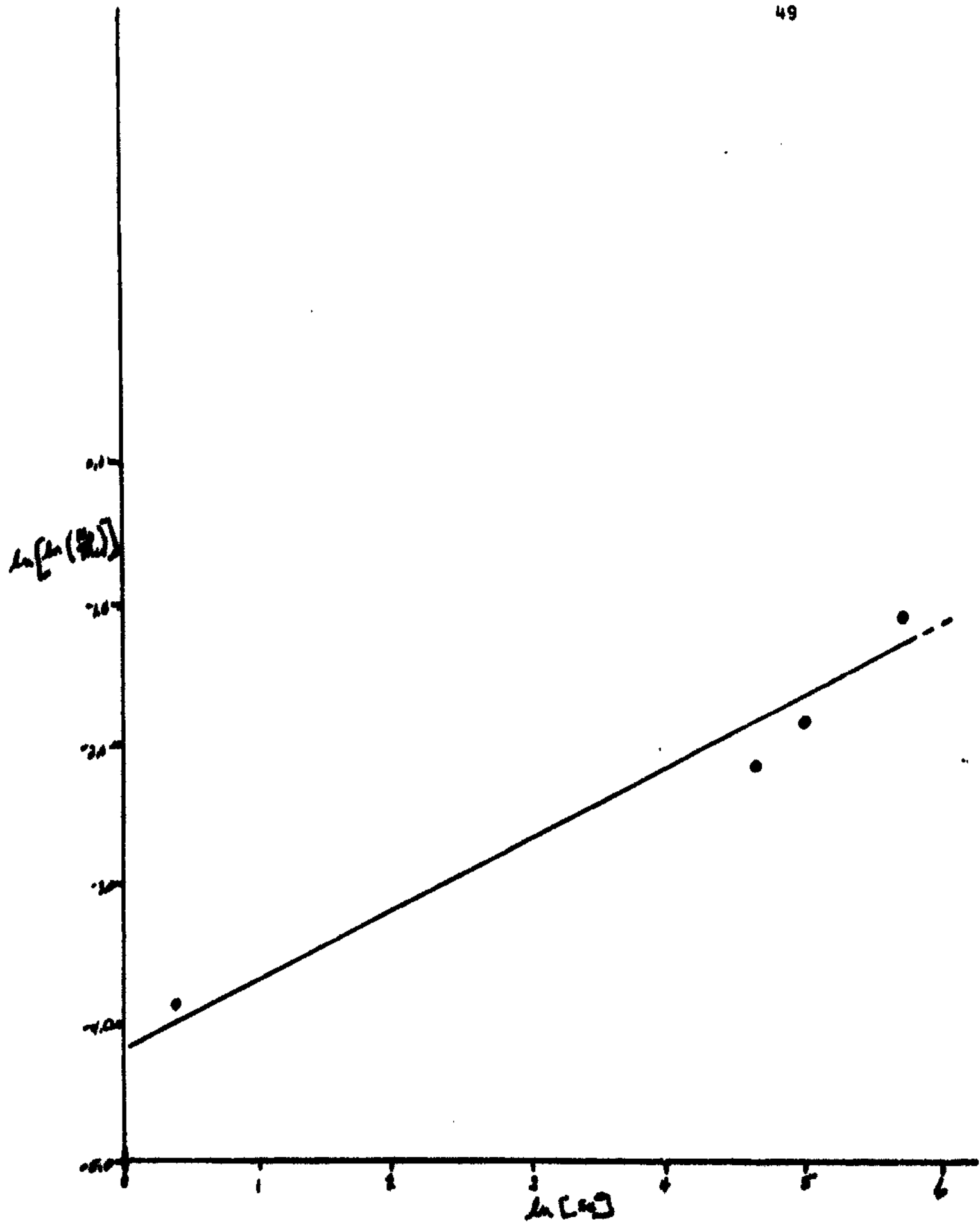Figure 15. Plot of $\ln\left[\ln(M_b/M_c)\right]$ versus $\ln\left[Se\right]$ at 2040 Å using the pink EDL.

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Figure 16. Plot of $\ln(M_u/M_c)$ versus [Se] at 1960 Å using the blue
EDL in the AA.

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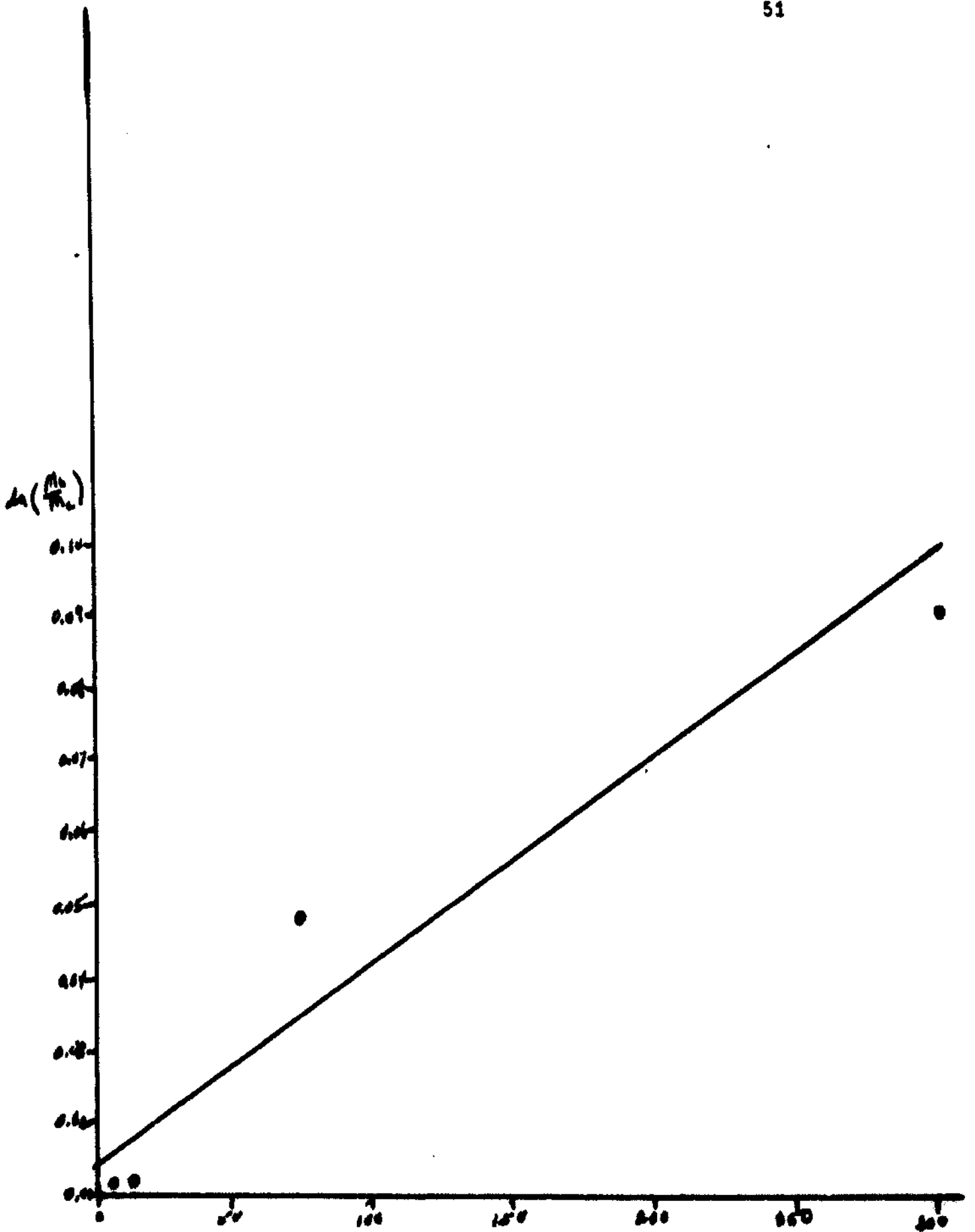
Figure 17. Plot of $\ln\left[\ln(M_b/M_c)\right]$ versus $\ln\left[\mathrm{Se}\right]$ at 1960 Å using the blue EDL in the AA.
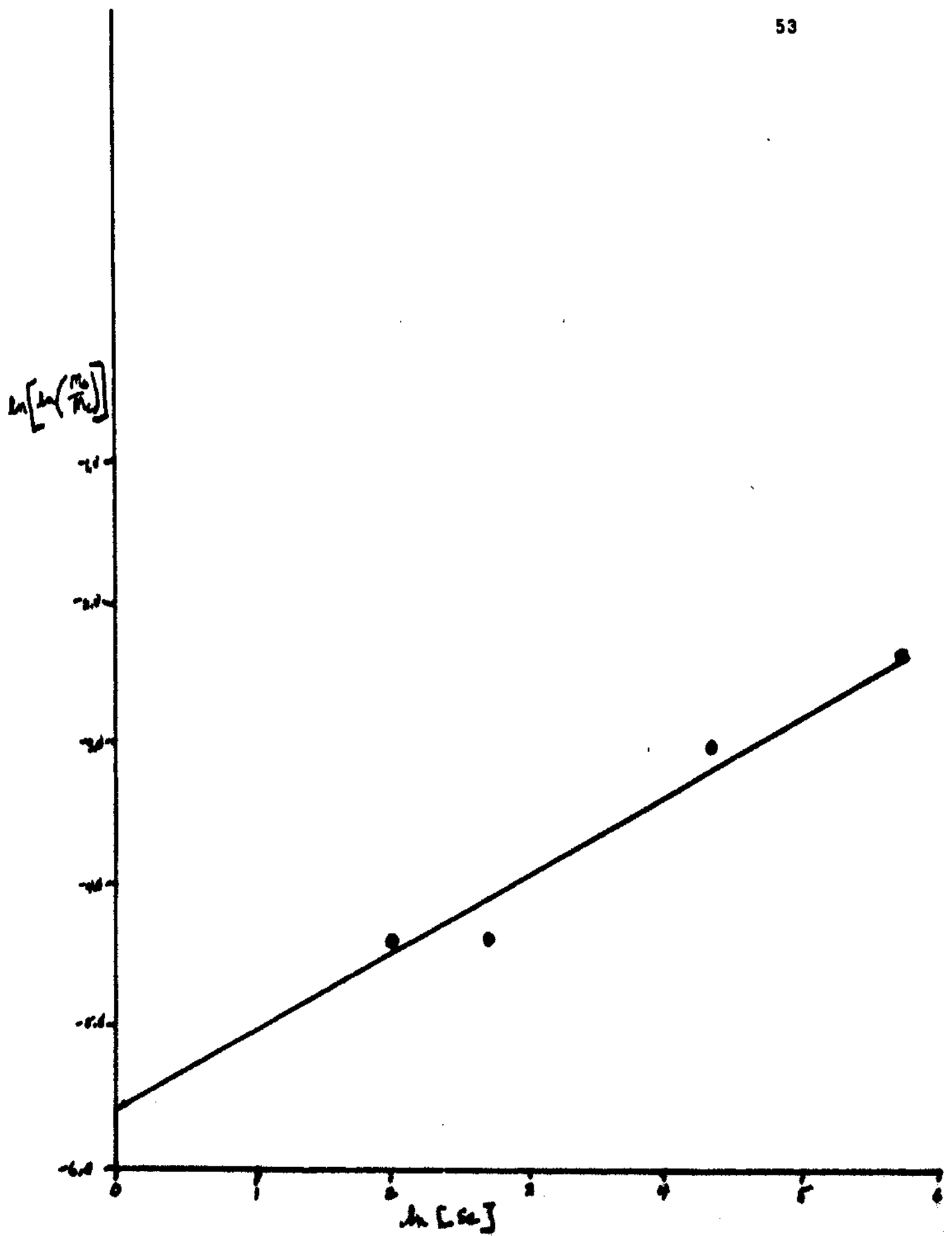
any baseline during the AA portion of this experiment. Figures 16 and 17 had the following least squares correlations.

Figure 16 $\ln(\frac{M_b}{M_c})$ versus $[Se]$

Correlation = 0.9744

Slope = 2.6×10^{-4}

y-intercept = 0.0164

Figure 17 ln $\ln(\frac{M_b}{M_c})$ versus ln $[Se]$

Correlation = 0.9981

Slope = 0.5590

y-intercept = -5.544

A reasonably good correlation was obtained in figure 17.

The 2040 $\overset{\circ}{A}$ line study using the blue EDL required a much larger concentration of selenium than what I would have expected before I obtained a reliable reading on the chart recorder. This could have been because I was using a much narrower slit width than what I was using during the rest of the AA studies. The slit width was 0.11 µm and the first concentration of selenium that gave a reproducable reading was 299.9 ppm.

Comparison of TGL to EDL

~ With regard to ease of use the TGL is far superior to the EDL. This is for several reasons.

1.) The EDL power supply will drift over a period of time.

2.) The TGL lamp assembly is fully enclosed and is much easier to obtain reproducable data at a given temperature.

3.) The temperature of the TGL can be regulated without requiring a complicated cumbersome apparatus as would be required to maintain a constant temperature for the EDL.

4.) The intensity of an EDL varies as it's position is altered in the microwave cavity of the diathermy.

5.) The intensity of the TGL will stabillize after a period of

time but the EDL never maintained a relatively constant
intensity for more than one hour during the course of the
experimentation.

The EDL may have several advantages over the TGL. For one,
the cost of an EDL source is less than the cost of a TGL lamp.
Second, it could be possible that the EDL has a much longer "life"
in terms of hours of usage. I cannot specifically say that the TGL
lamp will malfunction after thirty hours of use, but it's longevity
has not been determined because it is a relatively new piece of
equipment. The manufacturer (SGE) guarantees that it will strike
and operate for 500 hours of usage. Our test lamp failed to strike
after only thirty hours of operation. Whether or not such short
lifetime is an anomaly remains to be seen. Note, TGL's are limited
to relatively volatile elements, i.e., 0^{-5} to 10^{-4} at up to 200 C.
Currently only As, Se, Zn, and Te TGLs are commercially made.

The EDL's in our laboratory at the University of Illinois have
been used for years without any problems unless they were mishandled
or mis treated. Only time will tell future researchers whether the
TGL has the capabilities for this type of long term use.

Comparison of TGL to DCL

In theory, the DCL would be a distinct improvement over any type
of lamp which has been previously developed. The problem with it
appears to be that insufficient testing and research on the DCL and
the methods of preparation of cathodes for the DCL, make it an arduous
task at times to do any lengthy experimentation. Attempts by John
McGee, Dr. Marquart, Nathan Henshaw (8), and myself never culminated
in a workable cathode for studying selenium. The DCL does appear to

be at least adequate for cathodes comprised of materials which possess low vapor pressures (i.e. copper, etc.).

We found that the TGL was more intense than the selenium cathodes that we prepared for the DCL. I am very confident that the DCL will be a much better piece of equipment once the techniques of cathode preparation are improved on.

Comparison of TGL to HCL

Dr. Marquart and associates have previously worked with the HCL and have found that it does not conform to the intensity requirements that he needs for his fast time-resolved atomic absorption studies. We did not have a selenium HCL at our disposal so this comment is put forth from previous experience.

References

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6. T. Nakahara, M. Munemori, and S. Musha, Anal. Chim. Acta, 50, 51-57 (1970).

7. Willard, Merritt, and Dean, Instrumental Methods of Analysis (1954).

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