

THE APPLICATION OF A LOGARITHMIC
SECTOR OF MANY STEPS TO PLATE
CALIBRATION AND QUANTITATIVE
SPECTRUM ANALYSIS

THE APPLICATION OF A LOGARITHMIC SECTOR OF MANY STEPS TO PLATE CALIBRATION
AND QUANTITATIVE SPECTRUM ANALYSIS

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Table of Contents

	Page
1. Review of the Literature and Theory - - - - -	1
2. The Problem - - - - -	6
a. Construction of Sector	
3. Plate Calibration - - - - -	13
4. Test Analysis - - - - -	22
5. The Problem in Quantitative Analysis- - - - -	26
6. Analysis by Densitometer Method - - - - -	49
7. Conclusions - - - - -	57
8. Bibliography- - - - -	61
a. Books	
b. Periodicals	

Review of the Literature and Theory

The development of this thesis required a review of standard works on quantitative and qualitative analyses by means of the emission spectrum. Special study was given to sections of these works dealing with quantitative analysis by means of the logarithmic sector.^{1/} Quantitative spectrographic analysis is based on the assumption that the intensity of a light source containing any one element is proportional to the number of atoms of that element radiating energy. This has been established in practice for comparatively small concentrations of an element in a matrix of some other elements or compounds.

The density or blackening of a photographic plate has been found to be proportional to the logarithm of the intensity ^{of the incident light}. It can be stated quantitatively as (over linear part of characteristic curve)

$$d \propto \log_{10} I$$

where d is the density and I is the intensity ^{of the incident light}. Quantitative spectrographic analysis applies the comparison of the intensities of the spectrum lines of a sample of unknown concentration with spectrum lines of samples of known concentration. Since there exists a linear relation between density and \log_{10} of intensity, the density of spectrum lines can be used as an indication of the number of atoms or the concentration.

Since the constituents of every substance used as a source of light for a spectrograph definitely influence the intensity of the emission of

^{1/} See Bibliography.

any element constituent, there can be no quantitative analysis on the basis of absolute density measurements. Therefore, it has been the practice, in quantitative analysis by this means, to compare the densities of lines from an element of unknown concentration with the densities of lines from an element of known concentration. A further condition for quantitative determination of concentration is that these lines representing elements of known concentration shall have densities proportional to those of certain lines of the unknown element within practical range of excitation conditions. This is the basis of the Internal Standard Method which is common practice.

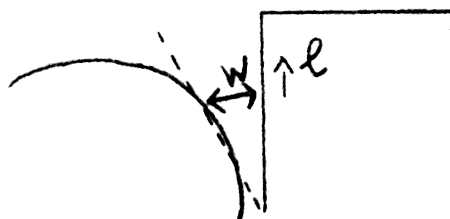
The rotating log stepped sector causes the exposure to vary along the length of the slit, as will be shown below, and produces a spectrum line image of graded density.

Scheibe and Neuhäusser first applied this device to quantitative spectrum analysis.^{1/} These results were published in 1928. In 1930 Twyman and Fitch^{2/} published the results of analysis of steels using the sector. Twyman and Hitchen used the sector for an analysis of solutions.^{3/} These investigators also showed that in the case of many of the solutions analyzed, the linear relation existed between the length of the line as given by the sector and the logarithm of the percentage of concentration.

^{1/} Twyman, F. "The Practice of Spectrum Analysis" p. 40. Adam Hilger, Ltd., 98 Kings Road, London.
^{2/} Ibid.
^{3/} Ibid.

A paper on the theory of the sector and its use was published by Twyman and Simeon in 1930.^{1/} The theory of the sector method is as follows:^{2/}

1. The blackening of the plate is governed by the relation, IT^P where I is the intensity, T is the time of exposure, and P is Schwarzschild's constant.
2. $\delta \propto \log I$.
3. The sector should be formed so that the logarithm of its opening should be proportional to the distance from the zero point to the point on the sector.



This can be expressed as follows:

$$\log W = B \times L'$$

where W is the opening of the sector in degrees, B' is a constant, and L' is the distance ^{toward} to the outer circle of the disc.

4. According to Schwarzschild's law two spectrum lines present equal blackening when:

$$\frac{I_1 T_1^P}{I_2 T_2^P} = 1 \text{ or } \frac{I_1}{I_2} = \left(\frac{T_2}{T_1} \right)^P, \text{ where } I_1 \text{ and } I_2 \text{ and } T_1 \text{ and } T_2 \text{ are the}$$

intensities and exposure times of the respective lines. Since W is

^{1/} Twyman, F. and Simeon, F. Trans. Opt. Soc. 31, 169 (1929-30).
^{2/} Gerlach, Dr. Walther and Schwertzer, Dr. Eugen. "Foundations and Methods of Chemical Analysis". Adam Hilger, Ltd., 24 Rochester Place, Camden Rd., London.

proportional to T,

$$\frac{I_1}{I_2} = \left(\frac{W_2}{W_1}\right)^P \text{ and } \log\left(\frac{I_1}{I_2}\right) = P (\log W_2 - \log W_1) = PB [L_2 - L_1],$$

Now, the length of the line appearing on the photographic plate will be the distance to any point of extinction (L') modified by the optical system of the apparatus. Therefore HL can be expressed as,

$$HL = B^1 L$$

where B^1 is a new constant and L is the length of the line on the photographic plate. Therefore $B[L_2 - L_1]$ can be expressed in terms of the length of the line on the plate as

$$\log \frac{I_1}{I_2} = B^1 P (L_2 - L_1).$$

Assuming that the intensity of radiation of an element in a source is proportional to the concentration, a spectrogram of $P+a\%A$ and $P+b\%A$ made through a rotating sector can be evaluated thus:

I_1	= intensity of Primary Substance P.	<i>radiation</i>	<i>incident upon the plate</i>
I_2	= intensity of $a\%A$.	"	"
I_2^1	= intensity of $b\%A$.	"	"

$$\log \frac{I_1}{I_2} = B^1 P (L_2 - L_1) \text{ and } \log \frac{I_1}{I_2^1} = B^1 P (L_2^1 - L_1).$$

Subtracting.

$$\log \frac{I_1}{I_2} - \log \frac{I_1}{I_2^1} = B^1 P [L_2 - L_1 - L_2^1 + L_1].$$

$$\log \frac{I_2^1}{I_2} = B^1 P [L_2 - L_1 - L_2^1 + L_1] = \log b/a.$$

If L_1 is the length of line due to an internal standard of known concentration then the expression for any one spectograph becomes

$$\log\left(\frac{L_1\%}{X\%}\right) = B^1P [L_X - L_1].$$

Since $L_1\%$ is a constant,

$$\log X\% = \log \frac{L_1}{X\%} + B^1P [L_1 - L_X].$$

Therefore a linear relation exists between the common logarithm of percentage concentration and the difference between the length of the internal standard line and the "unknown" line.

This relation holds only for relatively small concentrations of one element in a matrix of other substances which make the major part of a sample. This has been established by empirical data and general practice. The reason is given in general discussions of the theory of spectrographic analysis and is beyond the scope of this work.

The Problem

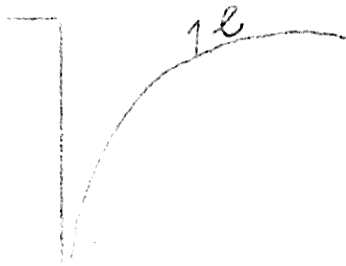
The application of the sector to quantitative spectrum analysis has resulted in a rapid and accurate method of analysis which has seen wide use, and become generally accepted. The method consists of plotting the difference between the length of lines resulting from an element of known concentration and the length of an internal standard line against the common logarithm of the percentage concentration. This is known as a working curve. The log. % of an unknown can be read from the curve when the difference between the unknown and internal standard line is determined from a spectrogram of the sample. The measurement of lines is usually made by means of a lens with an eyepiece graduated in millimeters.

It has been considerably difficult to determine the exact termination of the line. Direct measurement by means of a graduated eyepiece becomes fatiguing. It is not necessary to find the line termination for comparison. An examination of the theory presented above will show that the difference between two points of equal density will quantitatively describe the ratio between the density of two lines. Bausch and Lomb have available an eyepiece with a built in scale and inverted comparison line. This facilitates comparison of density and measurement between points of equal density.

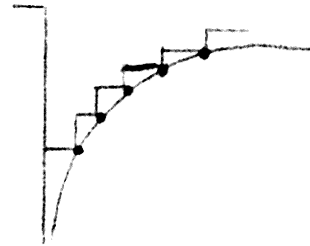
This research was undertaken to determine with what success the method of reducing the intensity in steps, rather than in continuous gradation, could be applied to the problem. It was also believed that steps could be more easily counted, and therefore be made a fairly accurate indication of line length. The aim of the present work was to determine the percentage

concentration of unknown by the difference between the number of steps from a point of equal density or the termination of the line. The use of steps would increase the area of points of equal density and therefore facilitate comparison.

The construction of a logarithmic stepped sector is in effect, establishing certain points for density determination along the logarithmic curve. In other words, the logarithmic sector can be thought of as having an infinite number of steps.



logarithmic sector



logarithmic stepped sector

The placing of steps was predicated on the theory that a line terminating in a step could be definitely terminated between the lengths represented by the values indicated by the terminating step and the step representing the next longer length. The various degrees of density and values of line length could be easily seen because of a sharp density change indicating another value of exposure. The step terminated on the logarithmic curve, therefore the length of line could easily be translated into so many easily discerned steps.

Obviously the steps more accurately bracket the end of the line if they are closer together. The ideal for this, of course, is the log sector since it represents an infinite number of steps. However that

destroys the definition which is necessary for locating the end of the line. Sectors have been built containing 7-9 steps. This number achieves distinction between steps, but does not define the end of the line with sufficient accuracy. The number of steps which can be built into any sector is limited by physical dimensions and mechanical considerations.

Since the spectrograph for which the sector was designed had a 20 m.m. slit, it was feasible to build a 20-step sector, each step being of the order of 1 m.m. This number of steps was expected to allow a determination of the end of the spectrum line with a fair degree of accuracy.

It was required that the sector be constructed so as to conform to the relation

$$\log W = BL',$$

as stated above. It was convenient to construct W in degrees, or units of circular measure. It was more convenient to work with W than with $\log W$, therefore the sector equation was written,

$$W = 10^{BL'}.$$

According to this relation, $W = 1^\circ$ when $L' = 0$. But, from mechanical consideration, the first step was required to be 2° . It was obvious that a sector constructed according to the relation, $W = K 10^{BL'}$, where K is a constant, could be used to apply the theory previously developed. The values of L' for a stepped sector are measured in terms of equal divisions of the slit length available, since the length of the slit determines the number of steps that can be built into the sector. (L') , therefore, takes on integer values as follows:

$$\text{step 1, } \dot{L} = 0^*, W = K (10^B)^0$$

$$\text{step 2, } \dot{L} = 1, W = K (10^B)^1$$

$$\text{step n, } \dot{L} = n-1, W = K (10^B)^{n-1}, \text{ where } n = \text{number of steps.}$$

This at once suggests that the values of W can be expressed as the terms of a geometric progression, any one term of which can be found by the relation

$$S = ar^{n-1},$$

where S is any term of the series, a is the first term, r is a constant, and n is the number of the terms in the series. By comparison,

$$W = K(10^B)^{n-1}, \text{ where } n = \text{number of steps.}$$

From the construction of the sector, it was obvious that W for the first step was 2° and 360° for the last or twentieth. Also, a consideration of boundary conditions can establish the values as follows:

$$n = 1, W = 2, K = 2$$

$$n = 19, W = 360^\circ$$

$$360^\circ = 2 \times (10^B)^{19}$$

$$\log 360 = \log 2 + 19 \log (10^B)$$

$$2.5563 = .30103 + 19 \log (10^B)$$

$$\log (10^B) = \frac{2.25527}{19} = .1186984$$

$$(10^B) = 1.13143.$$

Therefore,

$$W = 2 \times (1.13143)^{(n-1)}.$$

The openings of each step was computed according to this formula. The values are shown in the table which follows.

* Divisions of available slit length in any convenient units.

Step	log W	W
1	.30103	2°
2	.41996	2.63°
3	.53908	3.46°
4	.65801	4.55°
5	.76716	5.85°
6	.89542	7.86°
7	1.01410	10.33°
8	1.13322	13.59°
9	1.25261	17.89°
10	1.37199	23.55°
11	1.49122	30.98°
12	1.60906	40.65°
13	1.72835	53.50°
14	1.84757	70.40°
15	1.96614	92.50°
16	2.08565	121.80°
17	2.20412	160.00°
18	2.32222	210.50°
19	2.44217	276.80°
20	2.55630	364.00°*

* 4° distributed error in 20 calculations. [slide rule calculations]

A hole was cut in a square sheet of 18-gauge thickness aluminum. This was fitted with a collar which was fitted for $\frac{1}{4}$ " shaft. The aluminum was secured to the collar and the collar placed on a $\frac{1}{4}$ " mandril. This was turned to size in a lathe. A fine pointed threading tool was placed in the cross feed perpendicular to the path of the feed. This system was brought up to the outside diameter. By advancing the horizontal feed $1/32$ " and advancing upon the disc with the parallel feed, the disc was laid out in concentric circles of radii/increments of $1/32$ ". The method of filing and the optical system of the spectrograph caused the steps on the spectrogram to be exactly 1 m.m. ($1/32$ " = .794 m.m.) in region used. The center of the disc was filled with a doweling and centered with a centering rule. A protractor was selected which allowed enough space on the periphery for marking. After the first two steps from the outside circle, there was no necessity of moving the protractor. The protractor read 0.5 for least count. The steps were defined by using a centering rule and connecting the points on the periphery and the center. This avoided the necessity of relying on the center of the doweling.

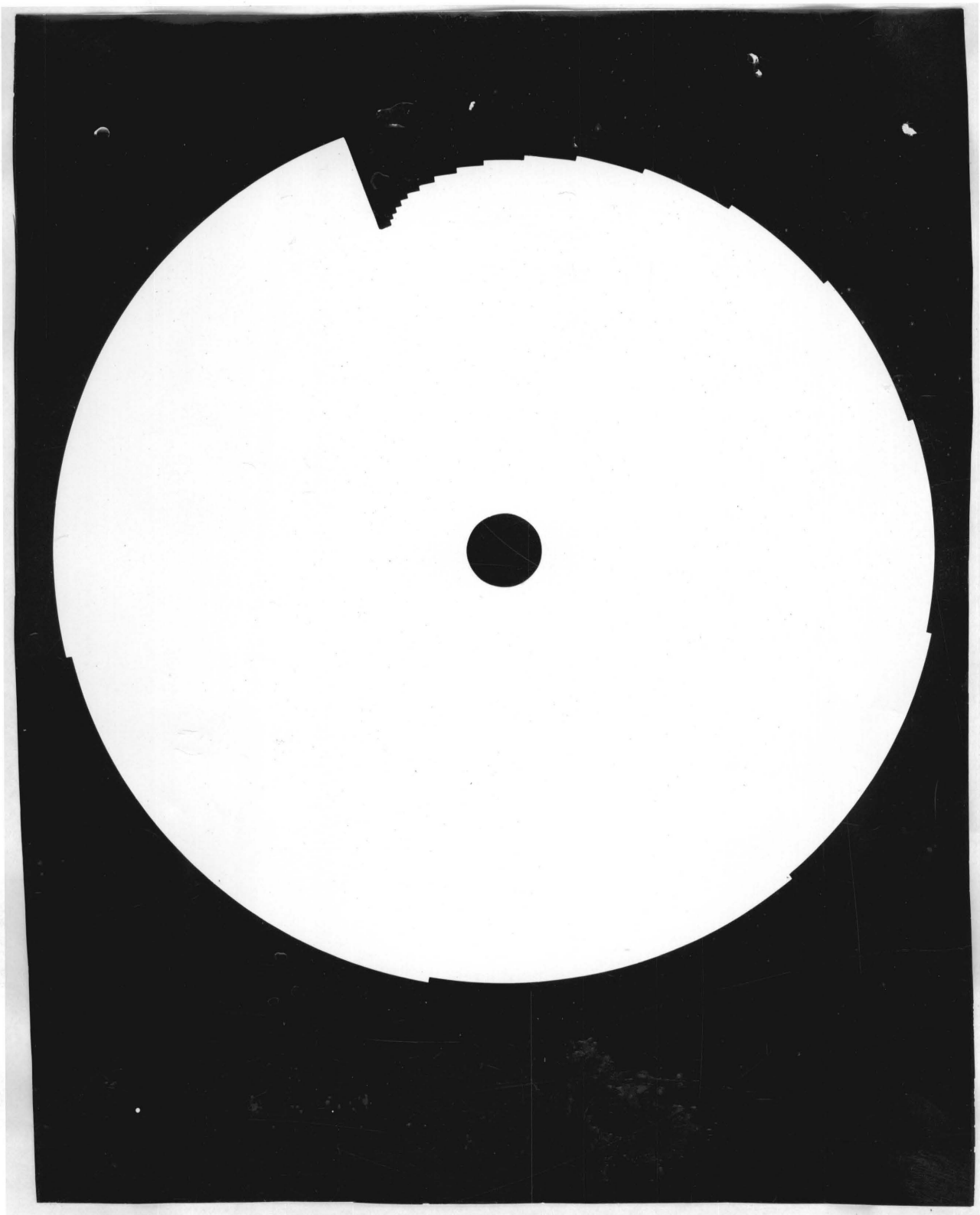
The disc was laid flat on an elevated platform and clamped with wooden clamps. Care was taken to have support flush with the surface being filed. As the line was approached a finer file was used. After the lines were reached by filing by eye, the disc was mounted under a microscope and filing was done with a set of jewelers files. Care was taken to leave no rounded corners. As the center of the line was approached the change in the metal crystals made by the lathe tool could be detected because it offered less resistance to filing and seemed to crumble away. This material was removed and clinging particles were removed by going over the surface with a scriber or smooth surface tool.

The finished sector was lacquered to hold bits of metal in place and to prevent scattering of light.

A mixture of thinner and a few drops of lacquer was poured into the container of an ordinary flit gun. This was sprayed upon the sector as it was turned by the high speed of a lathe. This gave a hard even surface, and avoided uneven distribution of lacquer and piling up in the corners.

The sector was mounted on a series motor to which ^{could be} ~~was~~ ^{to} attached a shaft. ~~mounting~~. A shaft of the proper size was threaded and a heavy cast iron base was tapped for the shaft. This gave movement of the motor vertically and laterally. The sector was placed directly before the slit of the large quartz spectrograph.

The image of the flame was focused upon the collimator lens by a weak lens covering the slit.



Contact Print of Sector

Plate Calibration

The calibration of the photographic plate is usually not necessary for the ordinary sector method. However a spectrogram made through this sector appeared to the unaided eye almost like one made with a log sector. A closer examination, even by unaided eye revealed definite steps in the weaker and shorter lines. These same weak lines showed a tendency to fade out much like those made through a log sector. Some of the stronger lines maintained the entire length but faded at the end so that it was difficult to decide between the last two steps. The strongest lines, of course, terminated abruptly in the last step, but there were five to eight steps which could not be distinguished with the lens provided for this purpose. It was decided, therefore to determine the characteristic curve of the plate.

The plate used was the Eastman 33 4" x 10" plate. The large Bausch and Lomb Spectrograph is calibrated for a range of 2,000-7,000 A° . All this work was done in the range of 2,600-3,900 A° . The spectrum of copper was used. Electrodes of pure copper were placed in the arc electrode holder, and an exposure of approximately 30 seconds was made through the sector. The slit width was set at 10 μ which is optimum slit width for this instrument.

The most intense lines of this range were chosen for this calibration. Since the behavior of the sector through the entire range of intensities could be observed, only two lines of these faded at the end. These lines can be observed in the print shown. The curve for these lines shows a flattening out for the last few steps. This effect can be consistently observed. The curves for lines which terminate abruptly in the last step

do not show this tendency to flatten out in the last steps. It was also discovered that the range of steps which were not easily distinguished was in the over-exposed part of the characteristic curve. This was represented by a flattening of the curve in the higher values of exposure which represent the larger openings of the sector. Each step in the line was easily defined by the nearby weak lines or the background which existed in the region of the large openings. There was negligible background after the first ten steps. As the lines increase in wave length, it can be seen that their characteristic curves have a steeper slope. This caused the steps to become more easily distinguished at both high and low values of exposure.

The fading out of the weak lines is explained at once by the abrupt trend of the characteristic curve for low values of exposure. Reasoning from this, one would expect the line to continue indefinitely. Actually this effect is only observed through one or two steps.

The use of the sector was at once restricted to lines which faded, or a comparison of steps of equal density. These steps were restricted to the linear portion of the curve. This is at once apparent from densitometer readings of the first few steps. It is worth repeating that more steps are on the curve as the wave length increases. This particular plate was blue-light sensitive.

Later during this investigation, a Process Panchromatic plate was used. This plate was a fast plate with high (β). It also was fine grained. The terminal of the line was much more evident. The characteristic curve

was not taken for this plate, but it is evident that the curve is steeper in the underexposed region.

The densitometer readings are tabulated for reference.

Densitometer Readings

Line No. 1 2766 A°

Step	S ₁	S ₀	S ₁	$\frac{S_0 - S_1}{S_1 - S_1}$	$\log \frac{S_0 - S_1}{S_1 - S_1}$
1	---	---	---	---	---
2	2.25	16.5	13.4	$\frac{14.25}{11.15}$.1065
3	2.25	16.5	13.7	$\frac{14.25}{11.45}$.0951
4	2.25	16.75	12.0	$\frac{14.5}{9.75}$.1729
5	2.30	17.00	10.48	$\frac{14.7}{8.18}$.255
6	2.25	16.65	9.05	$\frac{14.4}{6.8}$.326
7	2.25	16.50	7.60	$\frac{14.3}{5.4}$.424
8	2.25	16.90	6.15	$\frac{14.65}{3.90}$.575
9	2.30	17.00	5.10	$\frac{14.7}{2.8}$.72
10	---	---	---	---	---
11	2.20	16.8	4.30	$\frac{14.6}{2.1}$.841
12	2.25	16.65	3.80	$\frac{14.4}{1.55}$.969
13	2.20	14.00	2.51	$\frac{11.8}{.31}$	1.585
14	2.20	14.20	2.45	$\frac{12.0}{.25}$	1.686
15	2.20	13.50	2.40	$\frac{11.3}{.2}$	1.758
16	2.20	13.4	2.35	$\frac{11.2}{.15}$	1.875
17	2.10	13.4	2.20	$\frac{11.3}{.1}$	2.06
18	2.00	12.25	2.15	$\frac{12.05}{.15}$	1.907
19	2.10	11.40	2.15	$\frac{9.3}{.05}$	2.27
20	2.15	12.4	2.05	$\frac{10.25}{-.05}$	---

Steps numbered from least to greatest exposure.

Densitometer Reading
Line No. 2 2824A°

Step	S_i	S_o	S_1	$\frac{S_o - S_i}{S_1 - S_i}$	$\log \frac{S_o - S_i}{S_1 - S_i}$
1	1.90	12.0	1.95	$\frac{10.1}{.05}$	
2	1.90	13.7	2.00	$\frac{11.6}{.02}$	
3	2.00	11.5	2.00	$\frac{9.5}{0.0}$	
4	2.00	15.1	2.10	$\frac{13.1}{.1}$	
5	2.10	15.6	2.20	$\frac{13.5}{.1}$	
6	---	---	---	---	
7	---	---	---	---	
8	---	---	---	---	
9	---	---	---	---	
10	---	---	---	---	
11	2.35	17.15	3.50	$\frac{14.8}{1.25}$	
12	2.40	16.90	3.85	$\frac{14.5}{1.45}$	
13	2.40	17.20	4.65	$\frac{14.8}{2.25}$	
14	2.40	17.00	5.90	$\frac{14.6}{3.5}$	
15	2.40	16.90	6.40	$\frac{14.9}{4.0}$	
16	2.50	17.10	7.70	$\frac{14.6}{5.2}$	
17	2.50	17.20	9.45	$\frac{14.7}{6.95}$	
18	2.40	17.30	10.85	$\frac{14.9}{8.45}$	
19	2.40	17.10	12.70	$\frac{14.7}{10.3}$	
20	---	---	---	---	

Densitometer Readings

Line No. 3 2858

Step	S_1	S_0	S_1	$\frac{S_0 - S_1}{S_1 - S_1}$	$\log \frac{S_0 - S_1}{S_1 - S_1}$
1	- - -	- - -	- - -	- - -	
2	3.60	32.8	25.1	<u>29.20</u>	
				21.50	
3	3.65	32.5	21.4	<u>28.95</u>	
				17.75	
4	3.65	32.9	18.8	<u>26.25</u>	
				15.15	
5	3.70	32.5	16.1	<u>28.80</u>	
				12.40	
6	3.70	32.85	12.7	<u>29.15</u>	
				9.00	
7	3.50	32.90	10.5	<u>29.40</u>	
				7.0	
8	3.50	33.3	8.58	<u>29.80</u>	
				5.08	
9	3.50	33.5	7.15	<u>30.00</u>	
				3.65	
10	3.50	33.75	6.00	<u>30.25</u>	
				1.50	
11	3.50	33.4	5.20	<u>29.9</u>	
				1.70	
12	3.60	33.4	4.70	<u>29.8</u>	
				1.1	
13	3.60	33.3	4.40	<u>29.7</u>	
				0.8	
14	3.50	33.8	4.00	<u>30.3</u>	
				.15	
15	3.50	33.85	4.00	<u>30.65</u>	
				0.8	
16	3.50	33.3	3.65	<u>30.1</u>	
				0.45	
17	3.20	32.5	3.50	<u>29.3</u>	
				0.3	
18	3.10	29.9	3.35	<u>26.8</u>	
				0.25	
19	3.00	28.1	3.10	<u>25.1</u>	
				0.1	
20	3.20	26.4	3.15	<u>23.2</u>	
				-.5	

Densitometer Readings
Line No. 4 2961

Step	S1	S0	S ₁	$\frac{S_0 - S_1}{S_1 - S_1}$	$\log \frac{S_0 - S_1}{S_1 - S_1}$
1	---	---	---	---	
2	3.85	34.4	29.9	$\frac{30.55}{26.05}$	
3	3.80	35.1	30.0	$\frac{31.30}{26.20}$	
4	3.80	35.2	29.2	$\frac{31.40}{25.40}$	
5	3.70	34.5	25.85	$\frac{30.80}{22.15}$	
6	3.75	34.7	23.3	$\frac{30.95}{19.55}$	
7	3.70	36.0	19.4	$\frac{32.30}{15.70}$	
8	3.70	36.5	16.55	$\frac{32.80}{12.85}$	
9	3.65	36.0	13.8	$\frac{32.35}{10.15}$	
10	3.60	35.85	11.2	$\frac{32.25}{7.60}$	
11	3.60	37.30	9.35	$\frac{33.70}{5.75}$	
12	3.55	35.60	7.8	$\frac{32.05}{4.25}$	
13	3.45	36.30	6.9	$\frac{32.80}{3.45}$	
14	3.50	36.00	5.85	$\frac{32.50}{3.35}$	
15	3.40	36.50	5.3	$\frac{32.10}{1.90}$	
16	3.30	35.2	4.5	$\frac{31.90}{1.20}$	
17	3.30	33.8	4.1	$\frac{30.50}{0.80}$	
18	3.60	32.5	3.8	$\frac{29.90}{0.20}$	
19	3.50	33.6	3.7	$\frac{30.10}{0.20}$	
20	3.30	27.0	3.55	$\frac{23.70}{0.25}$	

Densitometer Readings

Line No. 5 3010 A°

Step	S_1	S_0	S_1	$\frac{S_0 - S_1}{S_1 - S_1}$	$\log \frac{S_0 - S_1}{S_1 - S_1}$
1	---	---	---	---	
2	3.40	32.0	32.72	<u>28.60</u>	
				28.60	
3	3.40	32.6	29.10	<u>29.20</u>	
				25.70	
4	3.40	32.9	26.40	<u>29.50</u>	
				23.00	
5	3.40	32.3	24.60	<u>28.90</u>	
				21.20	
6	3.30	30.4	22.60	<u>27.10</u>	
				19.30	
7	3.30	33.2	20.40	<u>29.90</u>	
				17.10	
8	3.30	31.1	16.20	<u>27.80</u>	
				12.90	
9	3.20	33.1	14.20	<u>29.90</u>	
				11.00	
10	3.20	33.3	11.80	<u>30.10</u>	
				8.60	
11	3.20	33.5	9.30	<u>30.30</u>	
				6.10	
12	3.25	33.4	8.00	<u>30.15</u>	
				4.75	
13	3.30	33.7	7.00	<u>30.40</u>	
				3.70	
14	3.30	33.4	6.40	<u>30.10</u>	
				3.10	
15	3.40	33.5	5.40	<u>30.10</u>	
				2.00	
16	3.40	32.3	4.30	<u>28.90</u>	
				0.90	
17	3.40	30.5	4.00	<u>27.10</u>	
				0.60	
18	3.30	36.0	4.00	<u>32.70</u>	
				0.70	
19	3.25	34.2	3.90	<u>30.95</u>	
				0.65	
20	3.25	31.2	3.90	<u>27.95</u>	
				0.65	

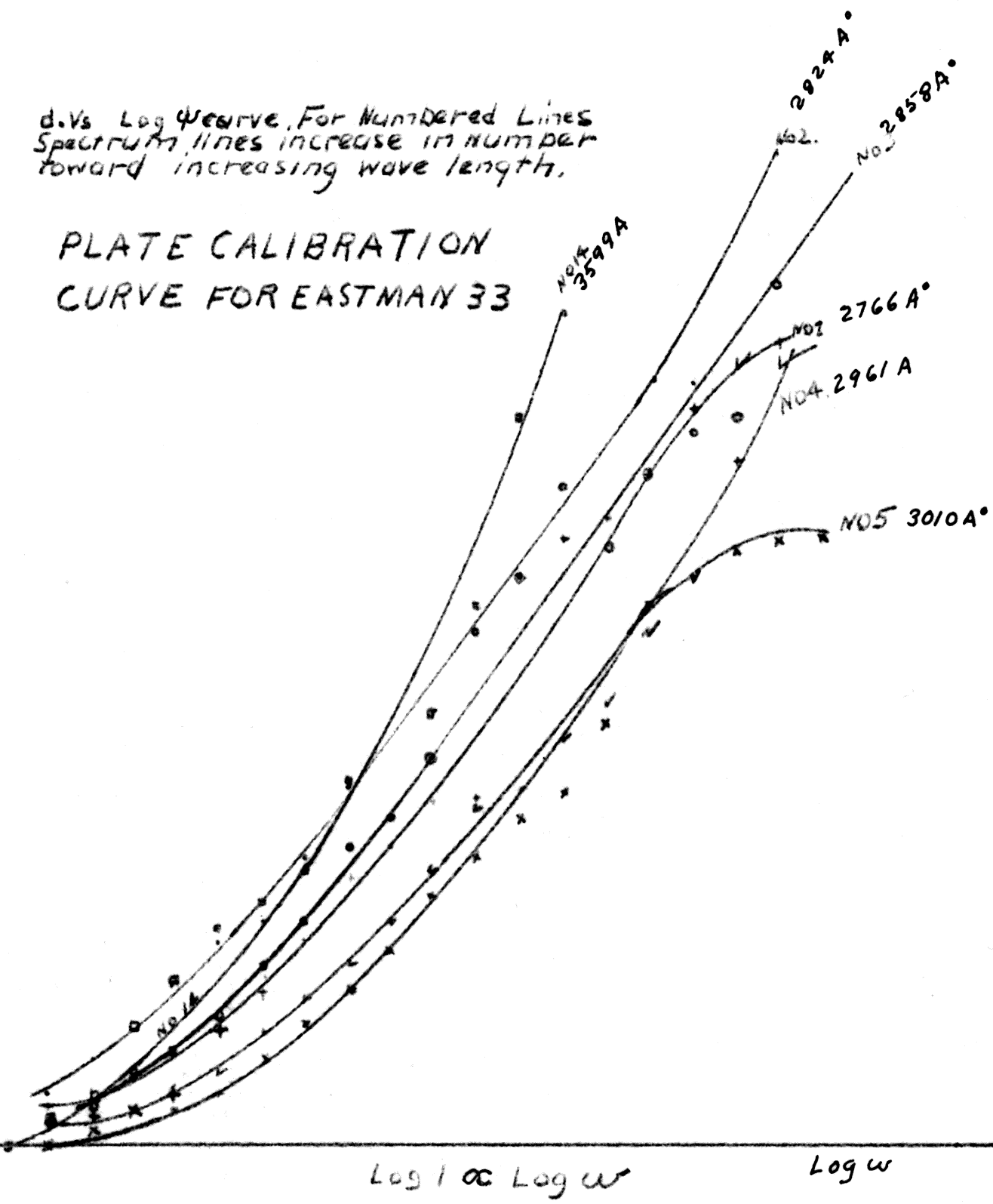
Densitometer Readings
Line No. 14 3599A.

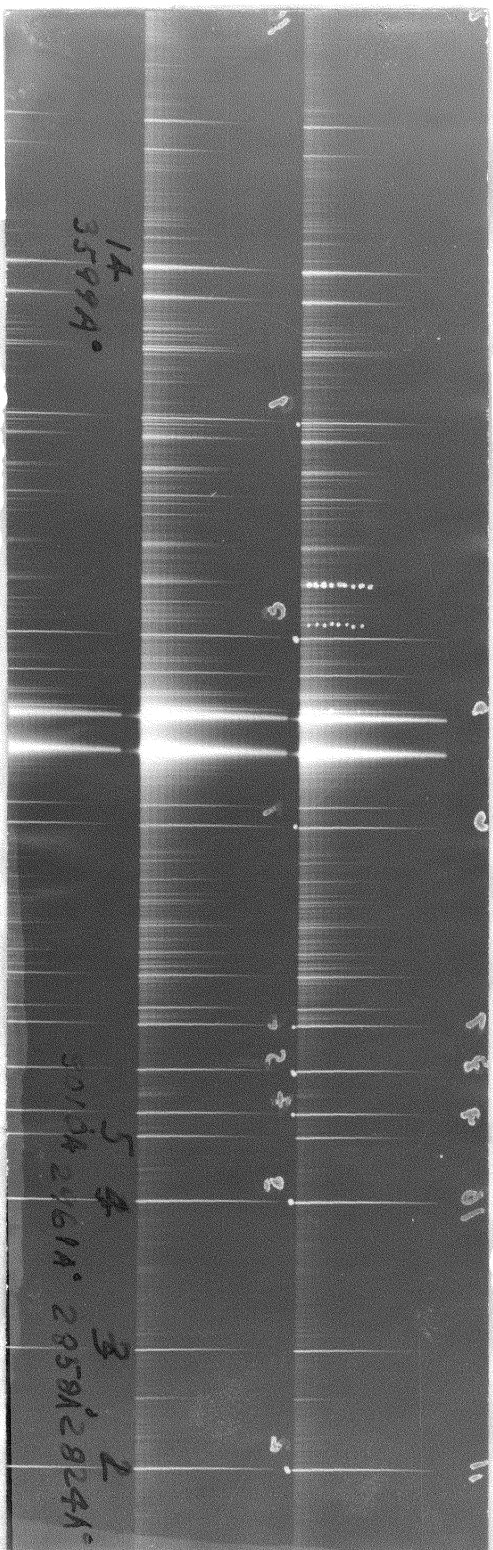
Step	S_1	S_0	S_1	$\frac{S_0 - S_1}{S_1 - S_1}$	$\log \frac{S_0 - S_1}{S_1 - S_1}$
1	3.10	25.1	21.7	<u>22.00</u> 18.60	.07225
2	3.20	25.5	21.2	<u>22.30</u> 18.00	.09482
3	3.30	25.4	18.75	<u>22.10</u> 15.45	.15927
4	3.20	25.6	14.15	<u>22.40</u> 10.95	.30069
5	3.30	26.2	11.15	<u>22.90</u> 7.85	.46583
6	3.30	26.4	8.90	<u>23.10</u> 5.60	.61595
7	3.20	25.7	8.00	<u>22.50</u> 4.80	.67210
8	3.30	26.5	7.20	<u>23.20</u> 3.90	.77815
9	3.30	26.1	5.50	<u>22.80</u> 2.20	1.01536
10	3.20	26.1	4.60	<u>22.90</u> 1.40	1.21352
11	3.40	25.75	4.10	<u>22.35</u> 0.70	1.50420
12	3.30	25.00	3.50	<u>21.70</u> 0.20	2.02840
13	3.20	24.30	3.10	<u>21.10</u> 0.10	2.32482
14	3.10	23.50	2.90	<u>20.40</u> -0.20	
15	3.20	21.3	2.70	<u>18.40</u> -0.50	
16	3.20	20.9	2.70	<u>17.70</u> -0.50	
17	3.00	19.0	2.40	<u>16.00</u> -0.60	
18	2.85	15.7	2.30	<u>12.85</u> -0.55	
19	2.60	13.2	2.20	<u>10.00</u> -0.40	
20	2.90	11.3	2.5	<u>8.40</u> -0.40	

d. Vs Log ψ curve. For Numbered Lines Spectrum lines increase in number toward increasing wave length.

PLATE CALIBRATION CURVE FOR EASTMAN 33

d = 10y/0 5e-30





Spectrogram of Copper Electrodes used for Plate calibration

Test Analysis

After the above information had been secured, and by it the limits of intensities defined, the next step was to proceed with a preliminary analysis. For the first analysis, there was no information concerning the number of steps which would appear in the spectrogram of samples of various concentrations. It was necessary, therefore, to use the whole length of the slit. Only four spectrograms of this magnitude could be put on the four-inch plate of the large quartz spectrograph. Prepared samples were selected containing 0.5%, 0.8%, 2%, and a known but undisclosed concentration of copper in a matrix of calcium. Each of these samples contained 5% lead and 5% tin. This allowed the use of calcium, lead, and tin as internal standards. The lead, tin, and calcium lines were located by means of a comparator and a chart of comparator readings and corresponding wave lengths prepared by using the spectrum of iron as a secondary standard^{1/}. The copper lines were identified by comparison with the plate containing the copper spectrum from which the plate calibration data was taken. The samples were burned in graphite electrodes according to standard procedure. The exposure was of the order of one minute, therefore, only the persistent lines, or lines of highest intensity were expected to appear in the spectrogram. The entire length of the slit was used and the plate was racked down. The same part of the slit was used to expose each sample.

Since the calibration curves indicated a fairly uniform response to exposure throughout a great length of the plate, two lines fairly close

^{1/} Tsein (thesis).

together could be compared with satisfactory accuracy without calibration curves for each spectrum line. Such pairs as Cu 2824^{1/2}-Sn 2850.6, Cu 2824-Zn 3075.9, Cu 2961.2-Pb 2980, and Cu 2961-Sn 3032.8 and 3009.1 have been used. These pairs were used along with others selected by the investigator. The lines were first measured by graduated eyepieces according to standard practice. Then the number of steps was recorded for comparison. Regardless of the line fading, the length of line resulting from the exposure was terminated with some one step. This was from consideration of the known sector dimensions and construction. It was observed at once that measurements gave such millimeter values, that differences in line lengths were integers of the same value of the difference between the number of steps in each line. The values are recorded below:

Cu 2824.4 A.U.
Sn 2850.0 A.U.

	.5% Cu-Sn	.8% Cu-Sn	2% Cu-Sn	X% Cu-Sn
m.m.	5.5-18.5 = -13	*7.5-18.5 = -11	8.5-18.5 = -10	6.5-18.5 = -12
steps	5-18 = -13	7-18 = -11	8-18 = -10	6-18 = -12.

These readings were given by comparing distance between steps of equal density. The curve of difference between lengths of unknown and control line vs log. % concentration is the same curve for the number of steps between points of equal density on control and unknown vs log. % concentration.

^{1/2} Brode, Wallace R. Chemical Spectroscopy. p. 475-476, Table IV, John Wiley and Sons, Inc., New York, New York.

* Estimated since the shutter of the plate holder was accidentally left in such a position as to cut off the lower part of the line along with the short part of the spectrum.

Cu 2961 A.U
Pb 28940 A.U

	.5% Cu-Pb	.8% Cu-Pb	2% Cu-Pb	X% Cu-Pb
m.m.	12-13 = -1	13-13 = 0	17-17 = 0	13-13 = 0
steps	13-14 = -1	14-14 = 0	18-18 = 0	14-14 = 0

It is hoped that the prints to accompany this data are distinct. It can be seen by examination of the spectrogram that there is an interfering line in the 2% sample. The lead line seems to be definitely within another line. A plot of the readings are given, along with one based on the assumption that the control line is constant at 13 m.m.

Sometimes the measurement of certain low range lines do not reveal a difference between certain concentrations which are of relatively close values. In spite of the erratic behavior of the curve the unknown is reasonably close to the value of the first curve.

Since both lines terminated within the upper limit of the sector, their lines were compared at the terminal.

Cu 3290 A.U
Ca 3215 A.U

	.5% Cu-Ca	.8% Cu-Ca	2% Cu-Ca	X% Cu-Ca
m.m.	14.5-19.5 = -4	15.5-19.5 = -4	17.5-19.5 = -2	16.5-19.5 = -3
steps	16-20 = -4	16-20 = -4	18-20 = -2	17-20 = -3

These values represent comparison between points of equal density. The copper line was in the immediate vicinity of the calcium lines 3215 and 3225.

Cu 3290A.U
Ca 3225 A.U.

	.5% Cu-Ca	.8% Cu-Ca	2% Cu-Ca	X% Cu-Ca
m.m.	13-19 = -6	14-19 = -5	16-19 = -3	15-19 = -4
steps	14-20 = -6	15-20 = -5	17-20 = -3	16-20 = -4

Cu
Ca

	.5% Cu-Ca	.8% Cu-Ca	2% Cu-Ca	X% Cu-Ca
m.m.	9.5-19.5 = -10	10.5 - 19.5 = -9	13.5-19.5 = -6	11.5-19.5 = -8
steps	10-20 = -10	11-20 = -9	14-20 = -6	12-20 = -8

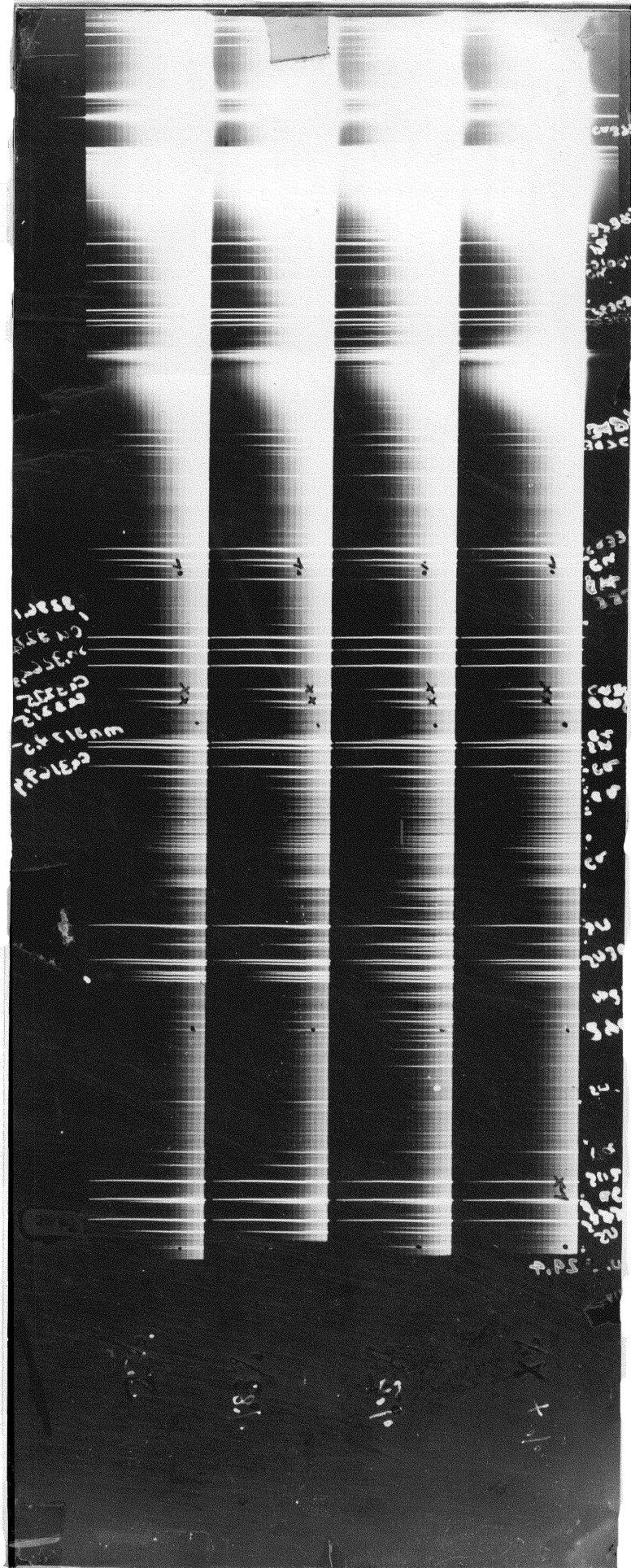
Cu
Ca

	.5% Cu-Ca	.8% Cu-Ca	2% Cu-Ca	X% Cu-Ca
m.m.	10-16 = -6	10-15 = -5	17-17 = 0	11-16 = -5
steps	11-17 = -6	11-16 = -5	18-18 = 0	12-17 = -5

The above data is of two copper-calcium combinations, one of which is found between 2890 Å⁰ and 2961 Å⁰.

The best lines indicated that the copper concentration in the sample which was used for an unknown was 1%. This was verified by the director of this research.

Cu in Ca 5% Pb 5% Sn Internal Standard
 Tests were made of many pairs of lines not indicated. Insufficient
 data on plate is cause of some uncertainty of identification.



x Ca 3215
 • Cu 3194
 x Ca 3225
 • Cu 3194
 • Cu 3350
 • Cu 3349

• Cu 2824 A
 x Sn 2850 A
 L Pb 2840 A

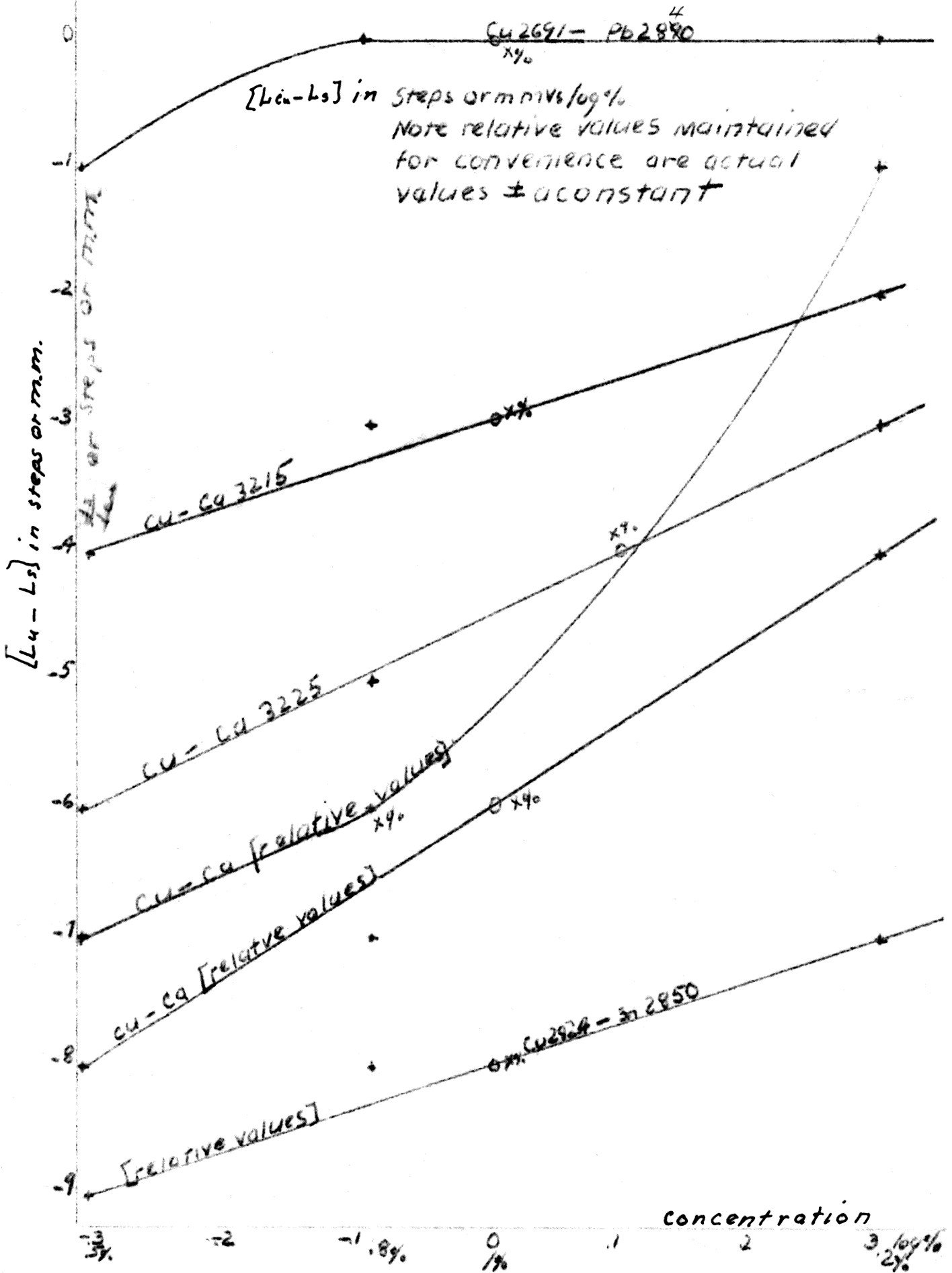
Reading down.

2% Cu

.8% " 5% Pb, 5% Sn

.5% " Internal Standard

X% "



The Problem in Quantitative Analysis

Since the sector yielded excellent results in a problem involving known concentrations, it was decided to apply it at once to an analysis of materials containing various elements in unknown quantities. A piece of hard sand-rock was picked up on Brush Mountain. This was broken up and ground to a fine flour with a mortar and pestle. A piece of white rock consisting of practically pure SiO_2 was picked up from the stream bed at Crockett Springs. This was also ground to a white flour. A spectrogram was made of the graphite electrodes, the white rock (designated as X_1), the hard sand rock (designated as X_2), and a sample of SiO_2 flour which had been furnished to the spectroscopy lab by the ceramics department.

A qualitative analysis was first required, therefore the large grating instrument was used. This instrument required 2-inch plates, which were fitted to the focal curve by means of clamps. This instrument gave a large plate dispersion, which was constant over the whole plate.

In order to be sure that all the material was burned up, each sample was given an exposure of six or eight minutes. The arc current was maintained at about an average of seven amperes. A diaphragm allowing a slit length of about 1 m.m. was used. This instrument is not provided with any means of racking the plate, since the plate holder is stationary and it is impractical to enter the room containing the plates while exposures are being made. The spectrograms are placed upon the plate by using a ~~device~~, which opens different parts of the slit.

Two plates were used for each series of exposures. These exposures were made of a range of 2200 Å - 3500 Å°. This practically covered the range for which the calibration had been made for the Eastman 33 plate.

The plates were developed six minutes, placed in the fixing bath for 15 minutes, washed 30 minutes, and rinsed with distilled water. This procedure was followed for all spectrograms made during this investigation. Rinsing with distilled water was not rigorously observed for plates which were to be used for qualitative work.

The lines of the various elements were identified by using a comparator and chart of the readings of the principle lines appearing in this range. Lines not charted were identified by interpolating between the nearest known lines. The most prevalent impurity lines were manganese, magnesium, iron, calcium, and copper.

Another negative was made containing spectrograms of eight samples. They were in the order of their appearance from bottom to top:

1. Cadmium (First suspected but none found in samples.).
2. Manganese.
3. Magnesium.
4. A sample of $\text{SiO}_2 \times \text{H}_2\text{O}$ procured from the chemistry stockroom.
5. The SiO_2 flour.
6. The sand rock X_2 .
7. The white rock X_1 .
8. Iron filings.

Lines of all these elements appeared in all spectrograms, but they were more intense in some than in others. Aluminum lines appeared in all silicon samples except the sample procured from the chemistry stockroom. ($\text{SiO}_2 \times \text{H}_2\text{O}$). The lines 2568, 2575, 2669, 3082, and 3092 A were present in all but this sample of silicon. Since all the other impurities were impurities in the electrodes, it was decided that aluminum was definitely

identified as a constituent of the sand rock as well as the other silicon samples.

The investigator did not know of the existence of any conveniently available working curves of aluminum in silicon, therefore, the first problem was to establish the range of concentration which would include the unknown and over which the curve of line density vs log. % concentration would be linear. The lines which appeared were the most persistent lines of aluminum, therefore relatively low concentrations were suspected.

An investigation of what was known about the concentration of aluminum in local rocks revealed that the concentration was represented by an upper limit of about 6% aluminum oxide.

The first range concentration which was investigated included .001% and .1% as upper and lower limits. The first aluminum compound used was anhydrous aluminum chloride. It was decided to make up 10-gram samples to improve the accuracy of measuring the aluminum. The amount of aluminum compound was computed on the basis of aluminum concentration required as follows:

$$\frac{X \frac{\text{Al}}{\text{AlCl}_3}}{W} \times 100 = \%$$

X = weight of compound used.

Al = atomic weight of aluminum = 26.97.

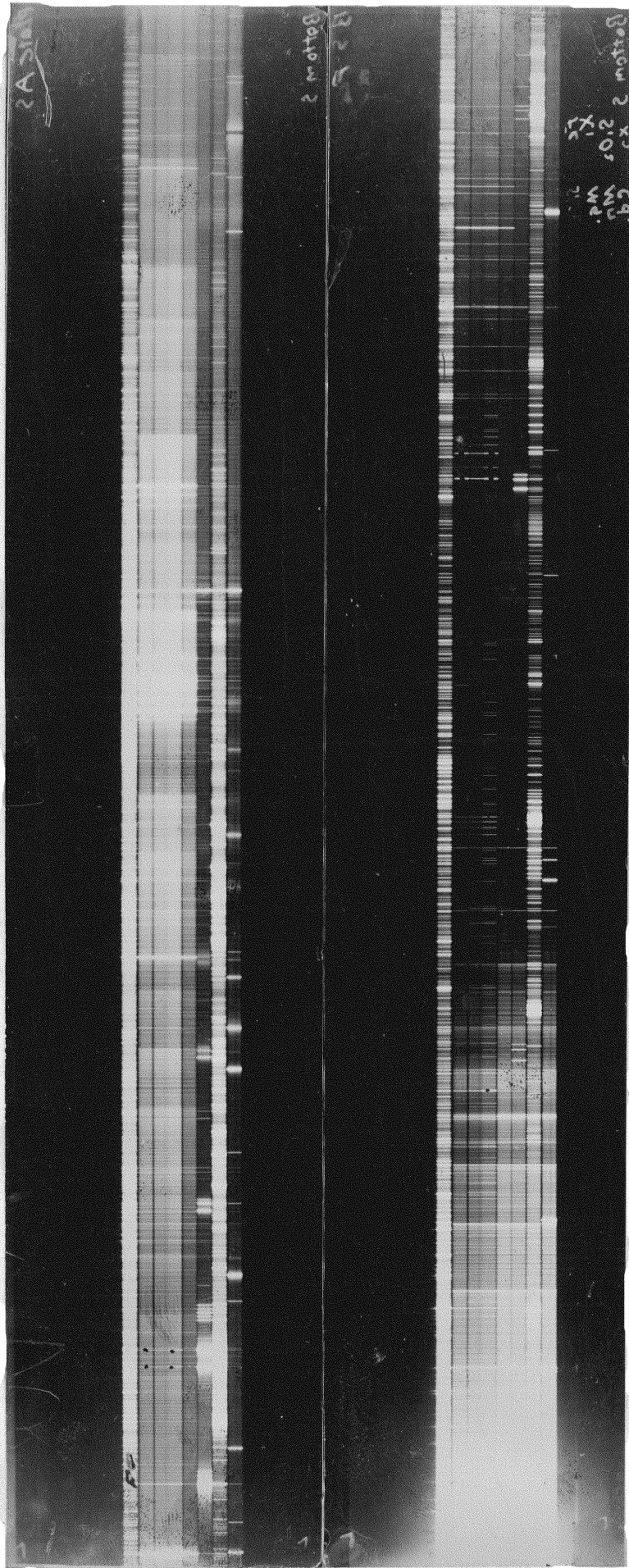
AlCl₃ = molecular weight of aluminum chloride = 133.34.

W = entire weight of the sample = 10 gm.

spectrogram of elements listed

2890A

2200A



3550A

Top to Bottom

Fe

X₁

SiO₂ [Spec Lab]

X₂

SiO₂ [Chem Lab

Mg

Mn

Cd

• A1 3082

• " 3092

2890A

Bottom 2 motor
B 2
Bottom 2

$$X \frac{26.97}{\frac{133.34}{10}} \times 100 = .1\%$$

$$X \frac{269.7}{133.34} = .1\%$$

$$X = \frac{13.334}{269.7} = .04945 \text{ gm. AlCl}_3.$$

.1% Al requires .04945 gm. = 49.45 mg.

.01% " requires .004945 gm. = 4.945 mg.

.001% " requires .0004945 gm. = .4945 mg.

.005% " requires .0024725 gm. = 2.4725 mg.

.05% " requires .024725 gm. = 24.725 mg.

.08% " requires .039560 gm. = 39.560 mg.

Anhydrous AlCl_3 was secured. All preparations were made so that weighing could proceed immediately upon breaking the container seal. This compound takes up water rapidly, and therefore accuracy in weighing depends upon rapid weighing. Paper was placed on both pans of the balance and a balance was made by the method of equal swings. A gram mass was put on the left balance and this was balanced by adding material from the bottle which was unsealed only after these preparations were made. The weighed material was put in a 125 ml. beaker and water was added. The water was poured over the paper containing the AlCl_3 . This paper had been carefully guarded against contamination and loss of material until it could be washed into the beaker. The paper was glazed and therefore the contamination of the water by contact with the paper was reduced. The flask was filled with water up to the 125 ml. mark. This gave a solution of

$$\frac{1000 \text{ mg.}}{125 \text{ ml.}} = \frac{8 \text{ mg.}}{\text{ml.}}$$

50 ml. of this solution were then placed in a 100 ml. graduate. This gave, when water was added to the 100 ml. mark,

$$\frac{50 \times 8 \text{ mg.}}{100 \text{ ml.}} = \frac{4 \text{ mg.}}{\text{ml.}}$$

A third solution was made by putting yet another 50 mg. of $4 \frac{\text{mg.}}{\text{ml.}}$ solution in the 100 ml. graduate and the whole brought up to 100 ml. by adding water. This gave

$$\frac{50 \times 4 \text{ mg.}}{100 \text{ ml.}} = \frac{2 \text{ mg. AlCl}_3}{\text{ml. H}_2\text{O}}$$

This roundabout method of obtaining a solution of desired concentration was necessary because of the element of haste in weighing the anhydrous compound. It was necessary to have a dilute solution in order to thoroughly immerse approximately 10 gm. of dry $\text{SiO}_2 \times \text{H}_2\text{O}$, and allow complete mixture with the solution containing the internal standard. As the samples were made up the AlCl_3 solution was further diluted from $2 \frac{\text{mg.}}{\text{ml.}}$ to $.2 \frac{\text{mg.}}{\text{ml.}}$ and $.02 \frac{\text{mg.}}{\text{ml.}}$ by pipetting 10 ml. of the high concentration into a 100 ml. graduate and bringing the total up to 100 ml. The solutions were added as follows:

.1% required 49.45 mg. AlCl_3 received 24.73 ml. $2 \frac{\text{mg.}}{\text{ml.}}$ solution.

.01% required 4.945 mg. AlCl_3 received 24.73 ml. $.2 \frac{\text{mg.}}{\text{ml.}}$ solution.

.001% required .4945 mg. AlCl_3 received 24.73 ml. $.02 \frac{\text{mg.}}{\text{ml.}}$ solution.

This allowed sufficient and equal volume of liquid for mixture of each concentration. If the solution is of such volume that it can be measured accurately, much labor can be avoided by adding water to approximately the same level in each sample.

Zinc was used as an internal standard. Zinc sulphate was chosen as a source of zinc. A supply was procured from the chemistry stockroom.

The samples were made up to contain 1% zinc by the following data:

$$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} = 287.55 \text{ M.W.}$$

$$\text{Zn} = 65.38 \text{ A.W.}$$

1% of a 10 gm. sample was computed as follows:

$$X \frac{65.38}{287.55} \times 100 = 1\%.$$

$$X \frac{653.8}{287.55} = 1.$$

$$X = \frac{287.55}{653.8} = .4398 \text{ gm. ZnSO}_4 \cdot 7\text{H}_2\text{O}.$$

The ZnSO_4 crystals were large, therefore 10 grams were weighed and placed in a 100 ml. graduated cylinder. Water was added as the crystals were dissolved until the whole was brought up to 100 ml. This gave a solution of

$$\frac{10,000 \text{ mg.}}{100 \text{ ml.}} = \frac{100 \text{ mg.}}{\text{ml.}}, \text{ which was diluted to}$$

$$\frac{10 \times 100 \text{ mg.}}{100 \text{ ml.}} \text{ by pipetting 10 mg. of the}$$

$$\frac{100 \text{ mg.}}{\text{ml.}}$$

solution into the graduated cylinder and bringing the volume up to 100 ml. This latter solution was prepared for addition to 1-gram samples as will be described later.

Since the dry $\text{SiO}_2 \times \text{H}_2\text{O}$ comprised the bulk of the sample, it was weighed according to the following prepared table.

Conc.	AlCl ₃ mg.	+	ZnSO ₄ ·7H ₂ O mg.	= Total mg.	(10,000-Total) =	SiO ₂ ·xH ₂ O mg.
.1%	49.45 mg.	+	439.8 mg.	= 489.25 mg.	(10,000-Total) =	9510.75 mg.
.01%	4.95 mg.	+	439.8 mg.	= 444.75 mg.	(10,000-Total) =	9555.25 mg.
.001%	.495 mg.	+	439.8 mg.	= 440.30 mg.	(10,000-Total) =	9559.70 mg.
.005%	2.47 mg.	+	439.8 mg.	= 442.27 mg.	(10,000-Total) =	9557.73 mg.
.05%	24.73 mg.	+	439.8 mg.	= 464.53 mg.	(10,000-Total) =	9535.47 mg.
.08%	39.56 mg.	+	439.8 mg.	= 479.36 mg.	(10,000-Total) =	9520.64 mg.

The silicon was weighed, placed in a porcelain container and the solution added by pipette. Three pipettes were used. Unit measure was delivered from a large pipette which measured 10 ml. Full measure was used twice and 4 ml. delivered from it from the third filling. A second pipette was used to deliver .7 ml. and a third was used to deliver .03 ml. 439.8 mg. ZnSO₄ were delivered from the 100 $\frac{\text{mg.}}{\text{ml.}}$ solution by the same procedure. 4.398 ml. of the solution was used. The third decimal place was estimated on the pipette delivering .01 as least count.

Since there was not any large amounts of the unknown, a 1-gram sample was made up as follows:

$$43.98 \text{ mg. ZnSO}_4 \cdot 7\text{H}_2\text{O for 1\% Conc.}$$

$$1000 \text{ mg.} - 43.98 \text{ mg.} = 956.02 \text{ mg. SiO}_2 \cdot x\text{H}_2\text{O.}$$

.4398 ml. of 100 $\frac{\text{mg.}}{\text{ml.}}$ solution were added to the sample.

After this treatment, the samples were placed in an oven and then evaporated to dryness at about 50° C. The sides of the containers were carefully scraped with a spatula. The samples were dried in a mortar, so they could be ground and mixed without removal from the container.

Graphite electrodes were prepared according to standard procedure. A spoon of about 10 mg. capacity was used to measure the samples and transfer

them to the crater of the electrode. In order to insure uniform measurement, the material was pressed into the spoon and leveled off with a stainless steel spatula. A second smaller tool was used to work the material into the electrode in order that uniform transfer might be achieved. The spoon and all tools used were cleaned with tissue paper after each transfer.

All precautions against contamination and inaccuracy of measurement which have been described were rigidly followed throughout the investigation.

Only four full length spectrograms could be made on the plate, so the unknown, .1%, .01%, and .001% samples were selected. The cratered electrode was made positive with respect to the pointed smaller electrode. A direct current of six amps. was used to maintain an arc between these two electrodes.

The unknown concentration was expected to lie within the range described. It was intended to establish a curve with the samples named, and then make spectrograms of the samples of intermediate samples to see whether or not they were on the same curve. This would establish the consistency of sample preparation and the behavior of the sector when evaluated in terms of the method desired.

A glance at the developed negative showed that the unknown was not in the range used, and therefore new samples were required.

The curve was plotted however, since it yielded data on the use of the sector. The curve is shown along with data.

Data for .001-.1 range.

.1%	.01%	.001%	X%
l_1-C_1	l_1-C_1	l_1-C_1	l_1-C_1
m.m. 17-17 = 0	16-12 = -1	15-17 = -2	19-16 = +3
l_1-C_2	l_1-C_2	l_1-C_2	l_1-C_2
m.m. 14.5-19.5	13.4-19.5	13.5-19.5	19.5-19.5

spectrogram of unknown and .001% Al = .1% Al in silicon

Zn 1% internal standard

$I_{Al} = 3283$
 $I_{Zn} = 3302$
 $I_{Si} = 3345$

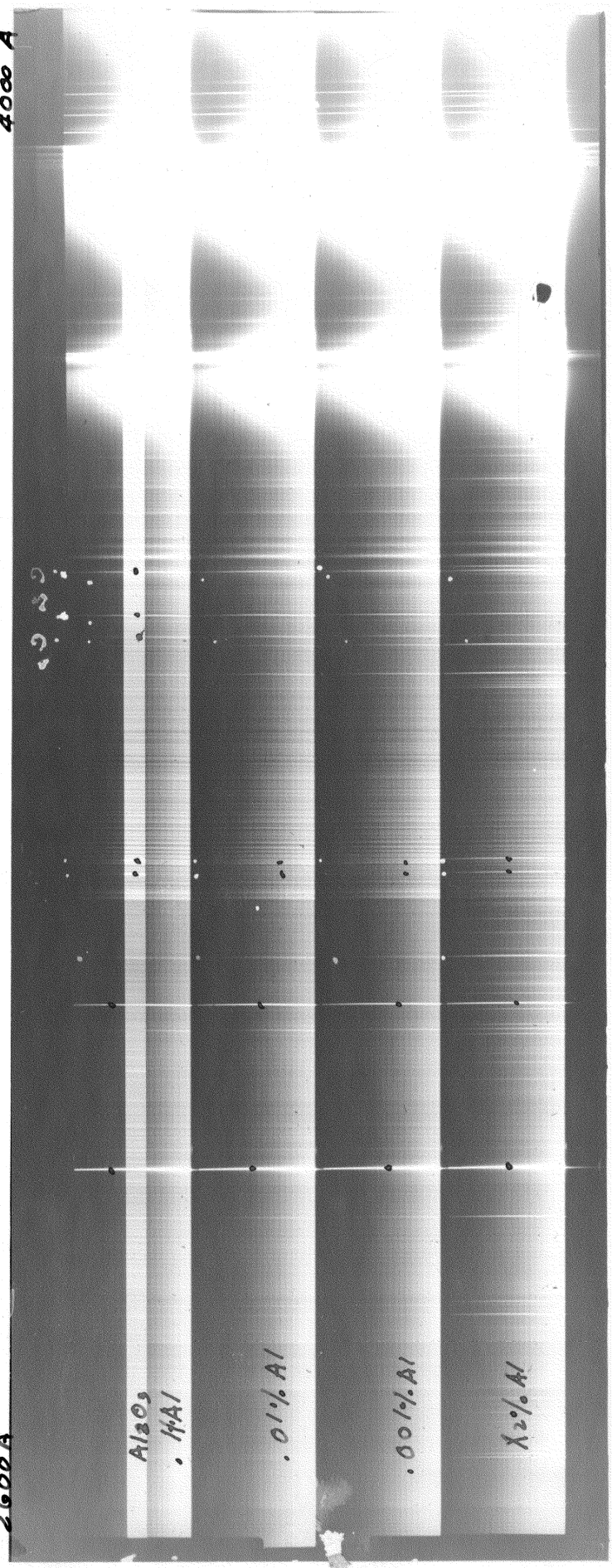
Al 3092
Al 3082

Si 2987

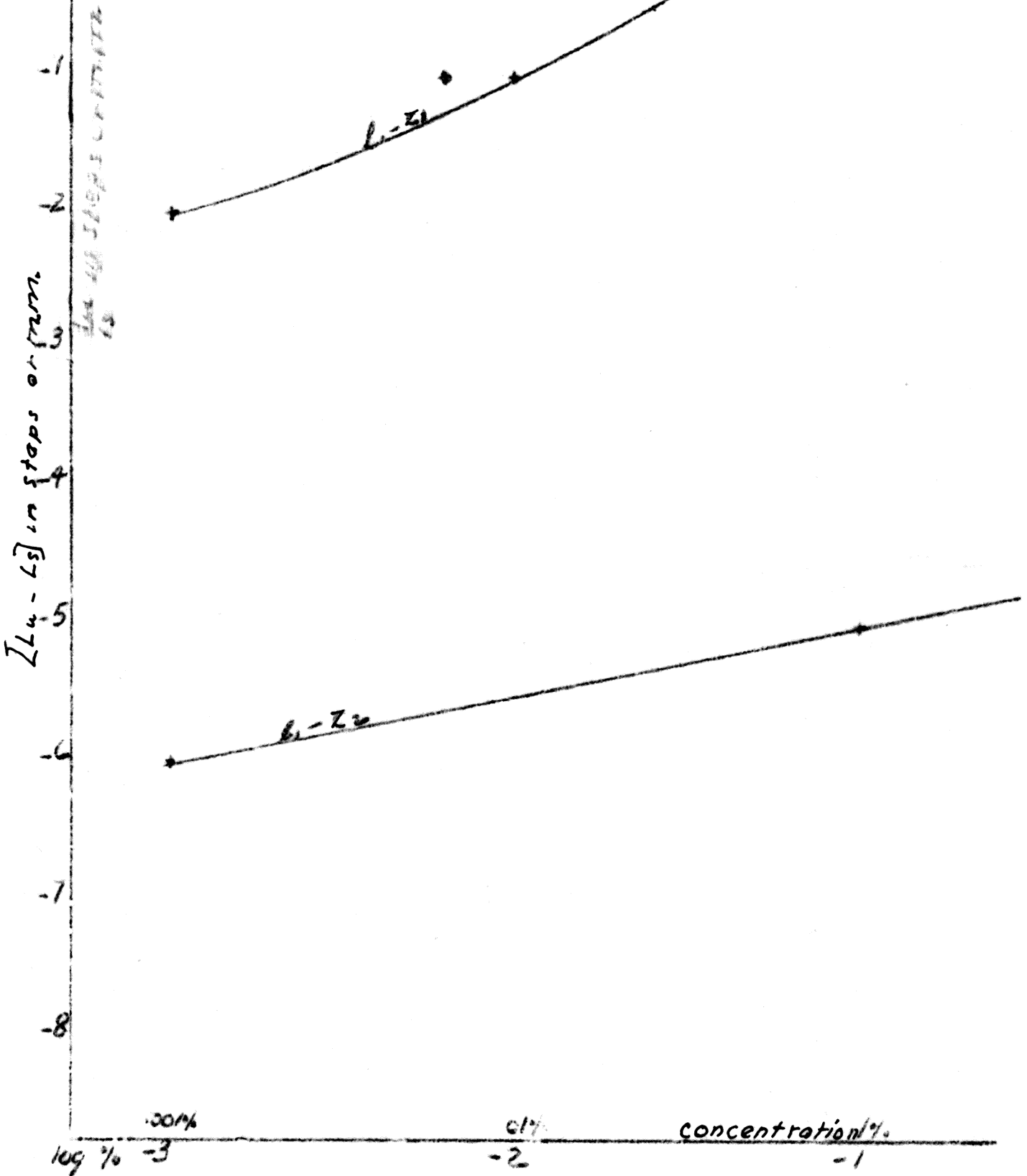
(Si) 2881

4000 A

2600 A



LL₁ - L₂ vs log. % conc.
LL₂ - L₂ " " " "
For range .001% - .1%



l_1 is the aluminum line; C_1 and C_2 are zinc lines which were identified by means of the comparison spectrum. The comparison of C_1 and l_1 were direct measure as can be seen by an examination of the plate. C_2 and l_1 comparisons were made by points of equal density.

It became apparent at once that the only lines within the range used, available for analysis were at 3092 \AA and 3082 \AA , and 3944 \AA and 3961 \AA . The former pair are listed as subject to self reversal by some tables, but the M.I.T. wave length tables do not indicate reversal. The latter pair were close to the cyanogen bands, and background is quite prevalent, but they could be analyzed by the sector method. Several lines were used as control lines, some of them far enough away from two unknowns to cause question concerning the accuracy of the analysis, but they were valuable in evaluating the use of the sector.

Since it was intended to make up several samples in order to test consistency of behavior and accuracy of making up samples, a new set of samples were prepared within the range of concentration, including .1% and 2% as limits.

Aluminum nitrate was used as a source of aluminum for the second set of samples. The samples were prepared according to the methods previously outlined.

Since the samples were to be of the order of 1 gm., a more concentrated solution was required. The crystals of aluminum nitrate were coarse, therefore it was decided to weigh 10 gm. of this compound in order to insure accuracy.

The 10 gms. were placed in a graduated cylinder and water was added to bring the solution up to 100 ml. Care was taken that all crystals were

dissolved before the final volume was added. This gave a solution of

$$\frac{10,000 \text{ mg.}}{100 \text{ ml.}} \text{ or } \frac{100 \text{ mg.}}{\text{ml.}} \text{ from which a } \frac{10 \text{ mg.}}{\text{ml.}}$$

solution was prepared. This required 1.39 ml. of solution to be added in each case.

A new zinc solution was made up according to the first specifications. 43.98 mg. were required for a gram sample.

When a spectrogram was made of these samples, the unknown concentration was yet far beyond the range used as shown by an attempt at extrapolation of the curve. The uncertainty of results obtained by extrapolating such a curve was recognized, but it was hoped that some indication could be obtained. The data is shown below.

The .05% sample was taken from the samples made up for the first or lowest range of concentrations.

Since it was apparent that all concentrations used appeared above the tenth step, the sector was raised above the slit until only part of the eleventh step was visible. This allowed room for more spectrograms on the plate. Spectrograms of .05%, .1%, 1%, and 2% samples were made. A spectrogram of ZnSO_4 and one of $\text{Al}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ was also made on this plate.

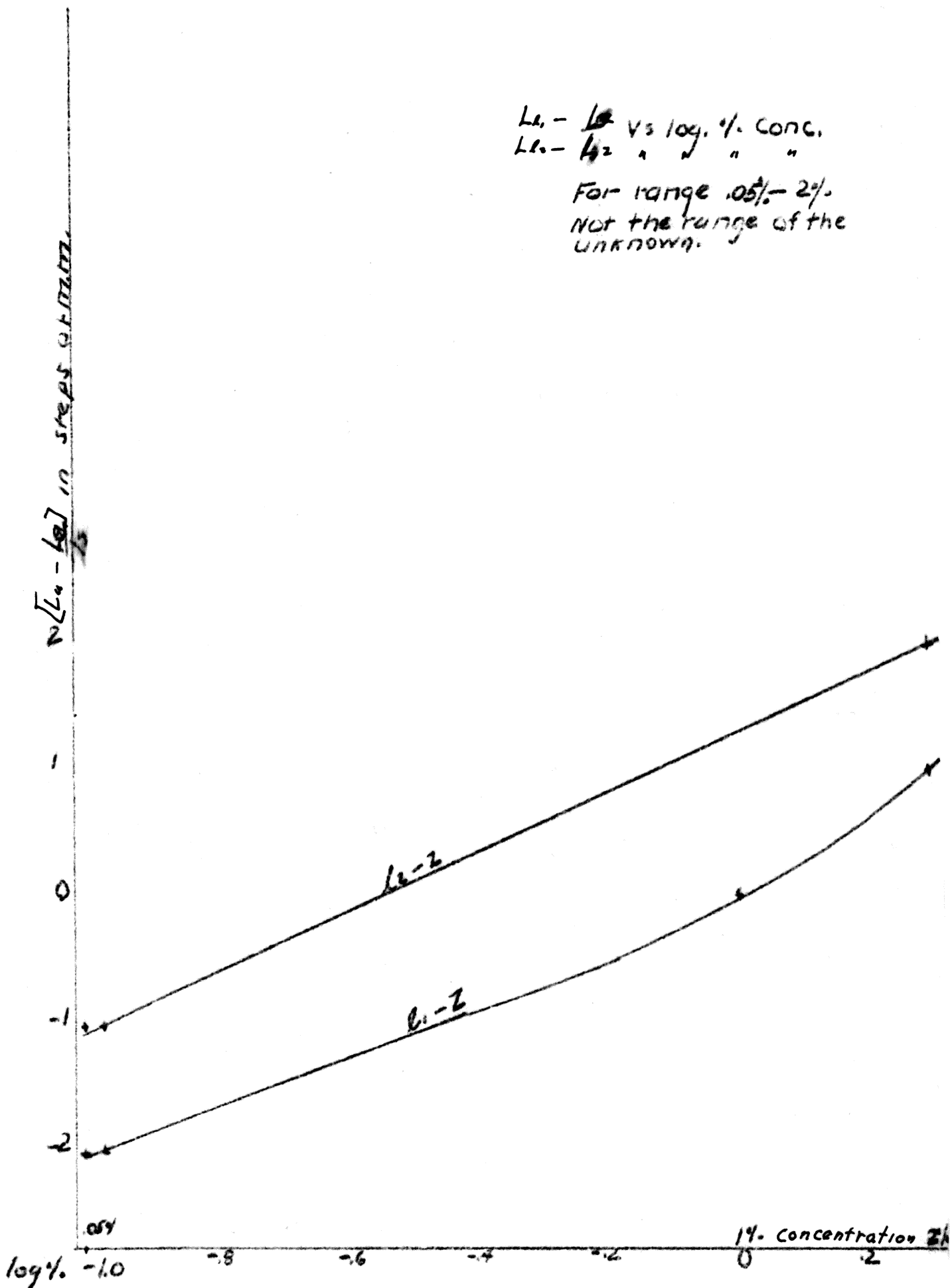
An examination of this plate showed a zinc line within the same region as the two aluminum lines which were used for analysis. This control line is designated as "Z".

.05%	.1%	1%	2%	X%
1 ₁ -Z	1 ₁ -Z	1 ₁ -Z	1 ₁ -Z	1 ₁ -Z
m.m. 6-8	6-8	6-6	7-8	9-3*
steps 16-18	16-18	16-16	17-18	19-13

* Density comparison.

L₁ - ~~L₁~~ vs log. % Conc.
 L₂ - ~~L₂~~ " " " "

For range .05% - 2%
 Not the range of the
 unknown.



Zn 3282
Zn 3302
Zn 3345

500 = 2997 Zn 3015

X% Al

2% Al

1% Al

.1% Al

.05% Al

A13948
A13960

A1.3082
A1.3092

$I_1 = 213082$ $I_2 = 3092$
 $Z = Zn 3075$

	.05%	.1%	1%	2%	X%
	I_2-Z	I_2-Z	I_2-Z	I_2-Z	I_2-Z
m.m.	9-8	9-8	8-6	9-7	9- -1 †

† Estimate (close).

Again the unknown was out of the range of concentrations used.

According to analyses thus far, the concentration of aluminum in the unknown was beyond 10%. It was decided to investigate the range from 1% to 20%. This, according to established practice was well out of the range of concentration for which spectrographic analysis is practical. Some techniques have been used for analysis of high concentrations, but this investigation continued with methods used in the investigation of low concentrations.

Aluminum compounds, suitable for solutions, were not available in sufficient concentrations for high concentration samples. Therefore it was decided to use Al_2O_3 in powder form.

Samples were made up according to the procedure described above.

The zinc concentration in each sample was increased to 5%. Since a 2% sample had already been made, it was used as the lower limit and samples were prepared ranging from 4%-20%.

The zinc was added from the solution used in making up the previous or second range of samples. For 5%, 5 x 43.98 mg. or 219.90 mg. $ZnSO_4$ were required.

The silicon was weighed, placed in a mortar, the Al_2O_3 weighed and added, and the mixture was thoroughly ground. The mortar was carefully scraped and emptied into a porcelain crucible. The zinc solution was measured into the mixture. A measured quantity of water was poured into the mortar to wash down any remaining materials. This was then poured into the crucible containing the samples. The mortar was dried each time in an oven.

The samples were evaporated to dryness. The sides of the crucibles were carefully scraped and the mixture mixed and powdered with the end of a glass rod.

Six samples were used for spectrograms, and spectrograms of Zn, Al, Cu, and the carbon electrodes were put above the spectrograms of the samples.

The range of concentration of the unknown was believed to be exceeded by the samples used. In the previous spectrograms, the lines of the unknown had terminated sharply, therefore it was decided to use a sector to reduce the intensity to the straight portion of the curve. A sector was used which reduced the light to one-eighth of the source. The resulting spectrograms were thought to be unsatisfactory because of the appearance of the internal standard lines. During the exposure, a beat effect of the light between the openings of the two sectors was noticed. The effect was such that the stepped sector appeared to be rotating at a very low speed.

Spectrograms of 2%, 4%, 8%, 12%, 16%, and unknown concentration were made. The spectrograms of copper, aluminum, zinc, and the electrodes were put on the plate for comparison purposes. The aluminum lines in the 12% and 16% concentration were less intense than they were in the spectrograms of the 2% and 4% samples. The data given below describes the situation quantitatively.

	2%	4%	8%	12%	16%	X%
(1 ₁ -Z)	Indistinct	0-6	2-6	0-6	0-6	7- *
(1 ₂ -Z)	4-6	3-6	4-6	-6	-6	8- *

* The unknown contained 1% Zn instead of 5%.

1/8 of over-all value. Note the length of lines [Al] in 12% Al and 16% Al samples. This confirms identification of Zn lines

$\lambda_3 = 3944A$
 $\lambda_4 = 3960A$

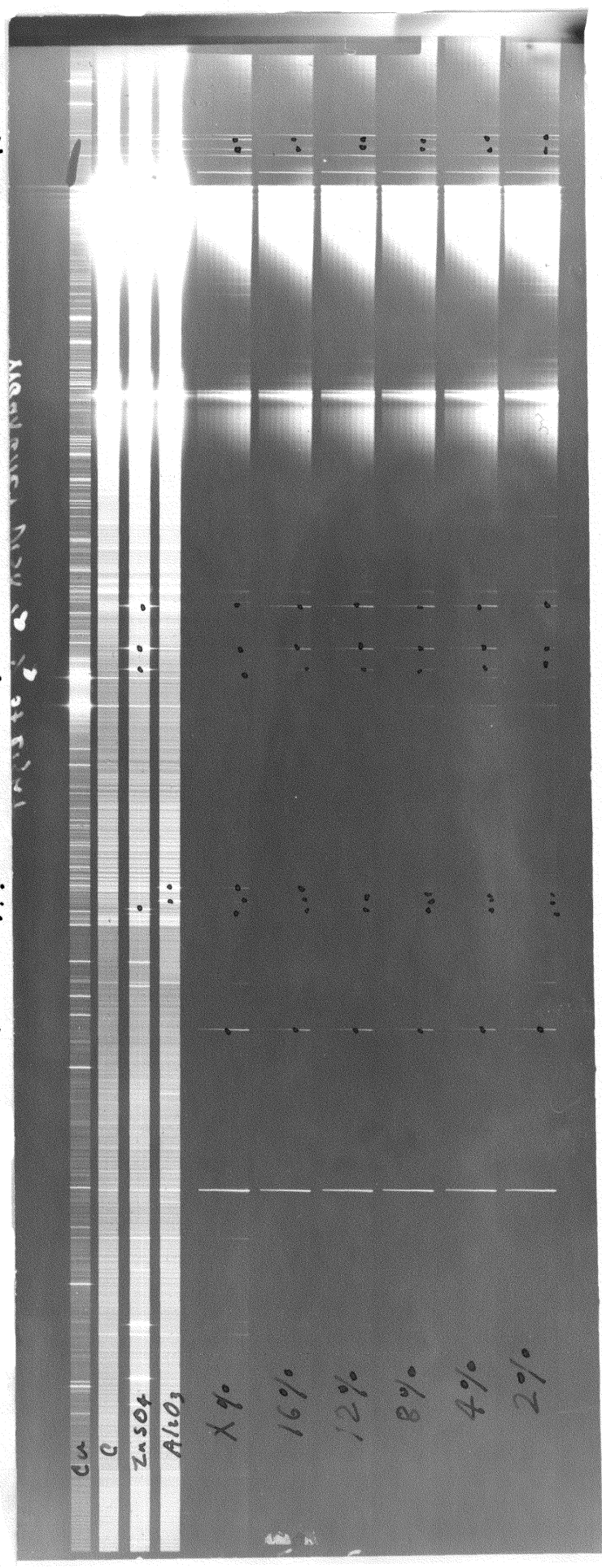
$Z_1 = Zn\ 3282$
 $Z_2 = Zn\ 3362$
 $Z_3 = Zn\ 3345$

$S_1(O) = Si\ 2987\ 2 = 3075$
 $\lambda_1 = Al\ 3082$
 $\lambda_2 = Al\ 3092$

i_3, i_4

Z_1, Z_2, Z_3

$S_1(O), i_1, i_2$



Cu

C

ZnSO₄

Al₂O₃

X 9%

16%

12%

8%

4%

2%

The appearance of the Al lines in these two samples were attributed to error in sample preparation. The intensity of the source for these spectrograms was probably reduced below the value required for accuracy. However, this erratic behavior was observed in the Al lines of spectrograms of high concentration samples through the entire investigation.

The sector method of reducing the intensity of light incident upon the stepped sector was abandoned because of the appearance of the above spectrogram, and the increased probability of stroboscopic effect suggest by the observation of the two sectors operating simultaneously. The next device employed to reduce overall intensity was the reduction of the diaphragm before the prism. The spectrograph had been operated with the smallest diaphragm provided by the makers of the instrument. This diaphragm provided an aperture about $\frac{1}{2}$ " in height. A cardboard diaphragm with an aperture about $\frac{1}{8}$ " high was strapped across the diaphragm platform.

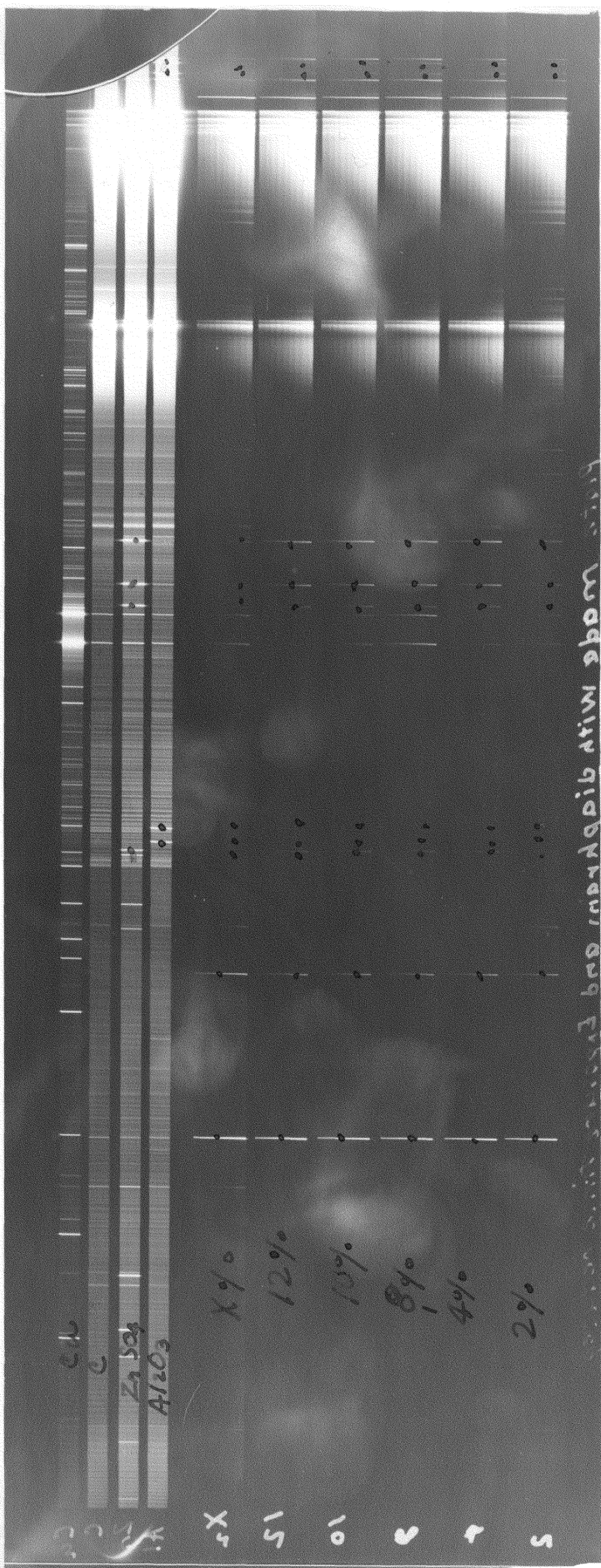
Spectrograms of the same samples described above were made with this diaphragm in position. The surface was blackened to prevent scattering of light. This plate was also unsatisfactory, as can be observed from data taken from it.

	2%	4%	8%	12%	X ₂
Cu ₁ -1 ₁	7-4	7.5-4	7-4.5	indistinct	0-8.5
Cu ₁ -1 ₂	4-5	6.5-3.5	6.5-5	- - - -	5.5-8.5

This second spectrogram seemed to indicate that the behavior of the 12% sample was due to error in making up the sample. At this time, it was also discovered that the appearance of the internal standard lines was due to the use of the 2% sample from the previous range, which had a concentration of 1% Zn instead of 5%.

Note appearance of Al lines in X% and 12% sample

Si 2881 Si(D) = 2987 Zr 2102 Zr 2103



made with gibberite and FeO

This exhausted the supply of No. 33 plates, and the investigation was continued using a process panchromatic plate.

Since this plate was much more sensitive than the 33, it was thought wise to use the diaphragm which had been contrived as described above. It was also decided to include copper as an internal standard.

450 milligrams of the samples which had already been prepared was weighed and to this was added 50 milligrams of CuSO_4 crystal which had been thoroughly ground in a mortar and pestle. This added a constant, but unknown amount of copper to the samples. A new 12% Al sample was made up as follows:

$$12\% \text{ of } 500 \text{ mg.} = 60 \text{ mg. Al.}$$

$$\frac{2 \times 26.97}{101.94} \times 100 = 52.91\% \text{ Al in } \text{Al}_2\text{O}_3.$$

$$\frac{60}{.5291} = 113.4 \text{ mg. } \text{Al}_2\text{O}_3.$$

Therefore:

$$450 \text{ mg.} - 113.4 = 336.6 \text{ mg. } \text{SiO}_2.$$

The sample was then prepared by the following:

$$336.6 \text{ mg. } \text{SiO}_2 \times \text{H}_2\text{O.}$$

$$113.4 \text{ mg. } \text{Al}_2\text{O}_3.$$

$$50.0 \text{ mg. } \text{CuSO}_4.$$

These compounds were weighed and mixed by grinding with a mortar and pestle.

The concentrations of aluminum in the samples was evaluated as follows:

- 1% Al = 4.5 gm. $\frac{4.5}{500} \times 100 = .9\% \text{ Al} + 1\% \text{ Zn} + \text{SiO}_2 + \text{X}\% \text{ Cu.}$
- 2% Al = 9.0 gm. $\frac{9.0}{500} \times 100 = 1.8\% \text{ Al} + 1\% \text{ Zn} + \text{SiO}_2 + \text{X}\% \text{ Cu.}$
- 4% Al = 18.0 gm. $\frac{18}{500} \times 100 = 3.6\% \text{ Al} + 5\% \text{ Zn} + \text{SiO}_2 + \text{X}\% \text{ Cu.}$
- 8% Al = 36.0 gm. $\frac{36}{500} \times 100 = 7.2\% \text{ Al} + 5\% \text{ Zn} + \text{SiO}_2 + \text{X}\% \text{ Cu.}$
- 12% made up new.
- 20% Al = $\frac{90}{500} \times 100 = 18\% \text{ Al} + 5\% \text{ Zn} + \text{X}\% \text{ Cu.}$

Spectrograms of .9-12% were made with the abovementioned diaphragm in place. It was a considerable surprise to the investigator to find that the plate, when processed, showed that there was not light of sufficient intensity incident upon the plate.

Another plate was exposed to the same range of samples. This plate did not show the degree of blackening expected of such a sensitive plate. However, the steps were more easily distinguished, the termination was more definite, and the whole spectrogram was generally improved. This has been explained in a preceding part of this work.

The aluminum lines in the 12% sample showed the same behavior as it had in previous exposures. A third 12% sample was prepared with twice the amount of material specified above, and another exposure was made immediately. In this plate, the lines in the 12% sample fell into line as expected, but the unknown spectrum was abnormally reduced in length and blackening.

Extreme care was taken that conditions of exposure and excitation were kept uniform. The material was burned for same amount of time regardless of the fact that the flame color indicated that it had all been

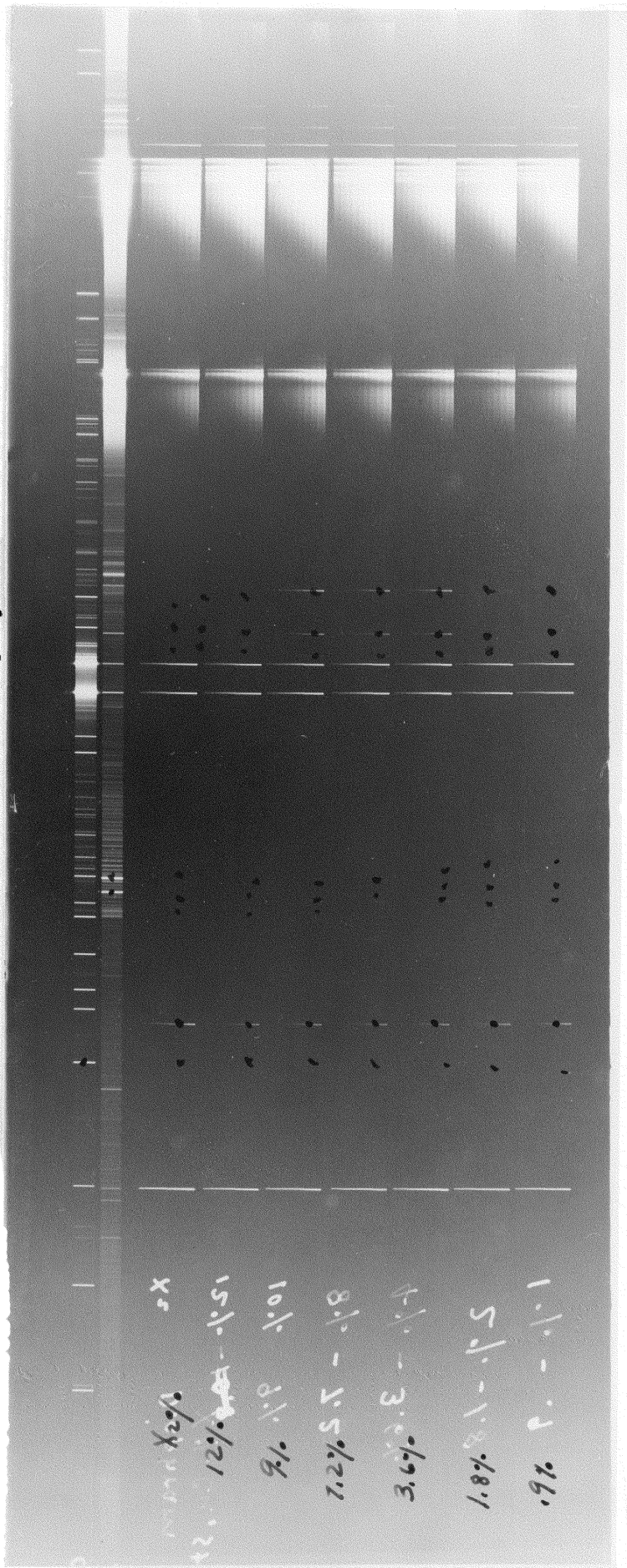
consumed. This time was set by the greatest amount of time required for burning any one sample, which was consistently that of the unknown.

Data was taken for a comparison of the four lines available in the wave length range used with all possible control lines. More time was spent on the 3092 \AA and 3082 \AA ^{lines} because of the background and cyanogen bands in the region of 3940 \AA and 3960 \AA .

Tables and curves from both plates follow:

Print of spectrogram made with 2g unapertured
in front of the prism.

Cu. Zn. Zn.



Note behavior of 12% sample

Cu3 = 4022

034 Cu3

Cu1 = 2961
510

Z 1. L2

Z 2. Z3

1.59

1.11

	1.59	1.11	Z 1. L2	Z 2. Z3	
X2	.	.	0.1	0.0	0.0
12%	.	.	0.0	0.55	0.0
9%	.	.	0.0	0.0	0.0
7.2%	.	.	0.0	0.0	0.0
3.6%	.	.	0.0	0.0	0.0
1.8%	.	.	0.0	0.0	0.0
.9%	.	.	0.0	0.0	0.0

	.9%	1.8%	3.6%	7.2%	9%	12%	X ₂
l_1-Cu_1							
m. m.	5-16	2-5	2-5	3-5	4-5	2-4	7-5
steps	0-16	12-15	12-15	13-15	14-15	12-14	17-15
l_1-Si							
m. m.	-1-9	0-9	1-9	2-9	4-9	-1-9	3-9
steps	20-10	11-20	11-20	13-20	14-20	10-20	13-20
l_2-Cu_1							
m. m.	4-4	3-5	4-5	4-4	6-5	5-4	9-5
steps	15-14	14-16	15-16	15-15	16-15	16-15	20-16
l_2-Si							
m. m.	1-9	1-9	2-9	3-9	5-9	3-9	5-9
steps	12-20	20-12	13-20	14-20	15-20	14-20	16-20
l_1-Zn_1							
m. m.	0- -	1- -	2-7	3-7	4-7	2- -	7- -
steps	11- -	12	13-18	14-18	15-18	13- -	17- -
l_1-Zn							
m. m.	0- -	1- -	2-6	3-7	4-7	2- -	7- -
steps	10- -	11- -	12-16	13-17	14-17	13- -	17- -
l_1Zn_2							
m. m.	0- -	0- -	1-9	2-9	4-9	2- -	7- -
steps	0- -	0- -	12-20	20-13	15-20	13- -	17- -
l_1-Zn_3							
m. m.	- - -	- - -	0-9	1-9	3-9	2- -	5- -
steps	- - -	- - -	11-20	12-20	14-20	13- -	16- -
l_2-Zn							
m. m.	- - -	4- -	5-7	5-7	7-7	4- -	9- -
steps	- - -	15- -	15-18	15-18	18-18	15- -	20- -

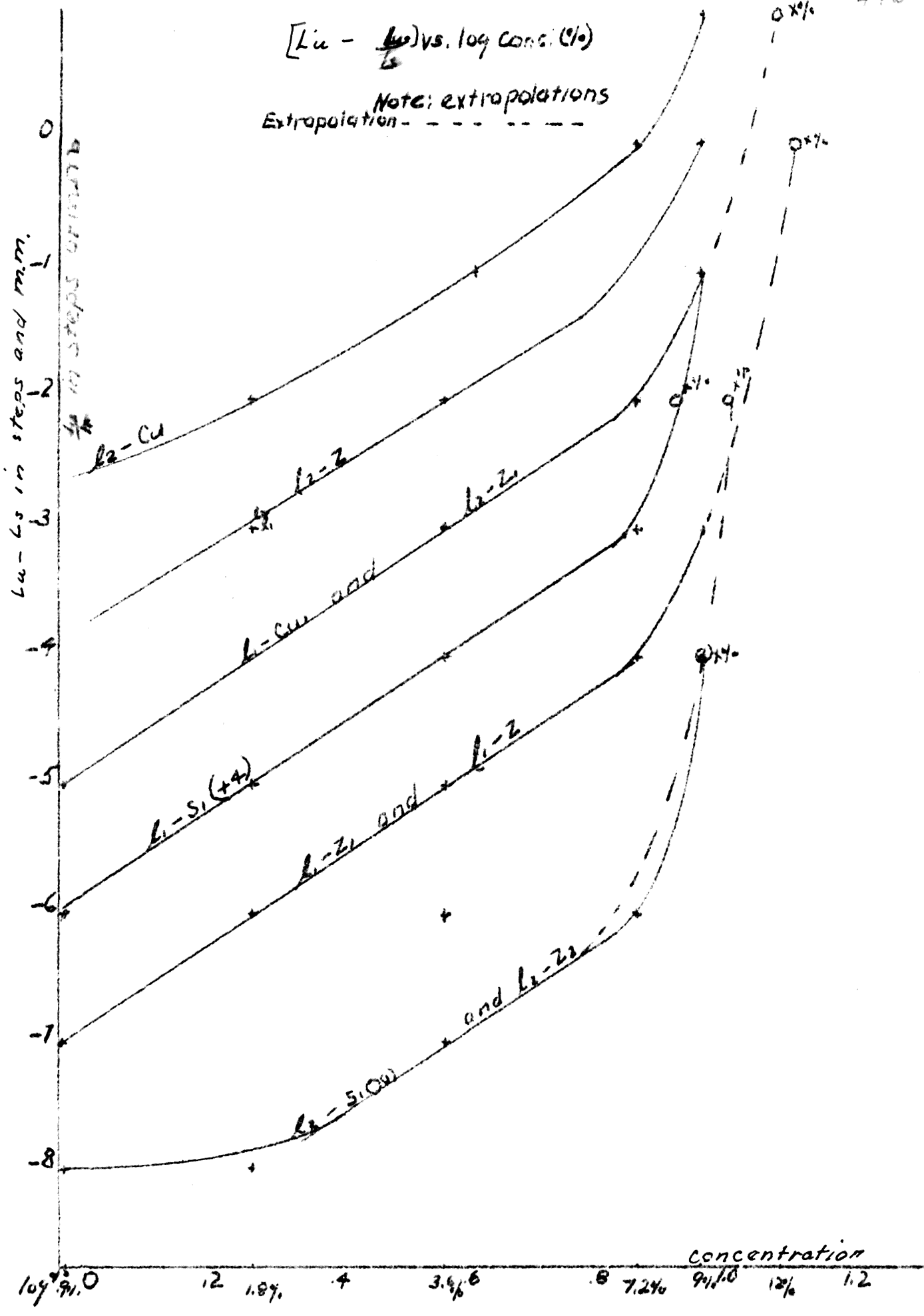
	.9%	1.8%	3.6%	7.2%	9%	12%	X ₂
l₂-Zn₁							
m. m.	- - -	- - -	4-7	5-7	6-7	- - -	8- -
steps	- - -	- - -	14-17	15-17	16-17	- - -	19- -
l₂-Zn₂							
m. m.	- - -	1-9	3-9	3-9	5-9	- - -	7-9
steps	- - -	12-80	13-20	13-20	15-20	- - -	17-20
l₄-Cu₂							
m. m.	3-5	3-5	4-5	5-5	7-5	- - -	9-3
steps	13-15	13-15	14-15	15-15	17-15	- - -	20-14
l₃-Cu₂							
m. m.	4.5-5.5	4.5-5.5	6.5-5.5	5.5-5.5	7-5.5	- - -	9.5-4.5
steps	14-15	14-15	16-15	16-16	17-15	- - -	20-14

An attempt at extrapolation was based on an assumption that 10% concentration was the extreme of the range in which the investigation was being undertaken. This assumption seemed justified when for this set of curves, the values for 9% were out of line upward from the other values. The intensity of the unknown was not reached nor exceeded by the upper limit of the range of concentration.

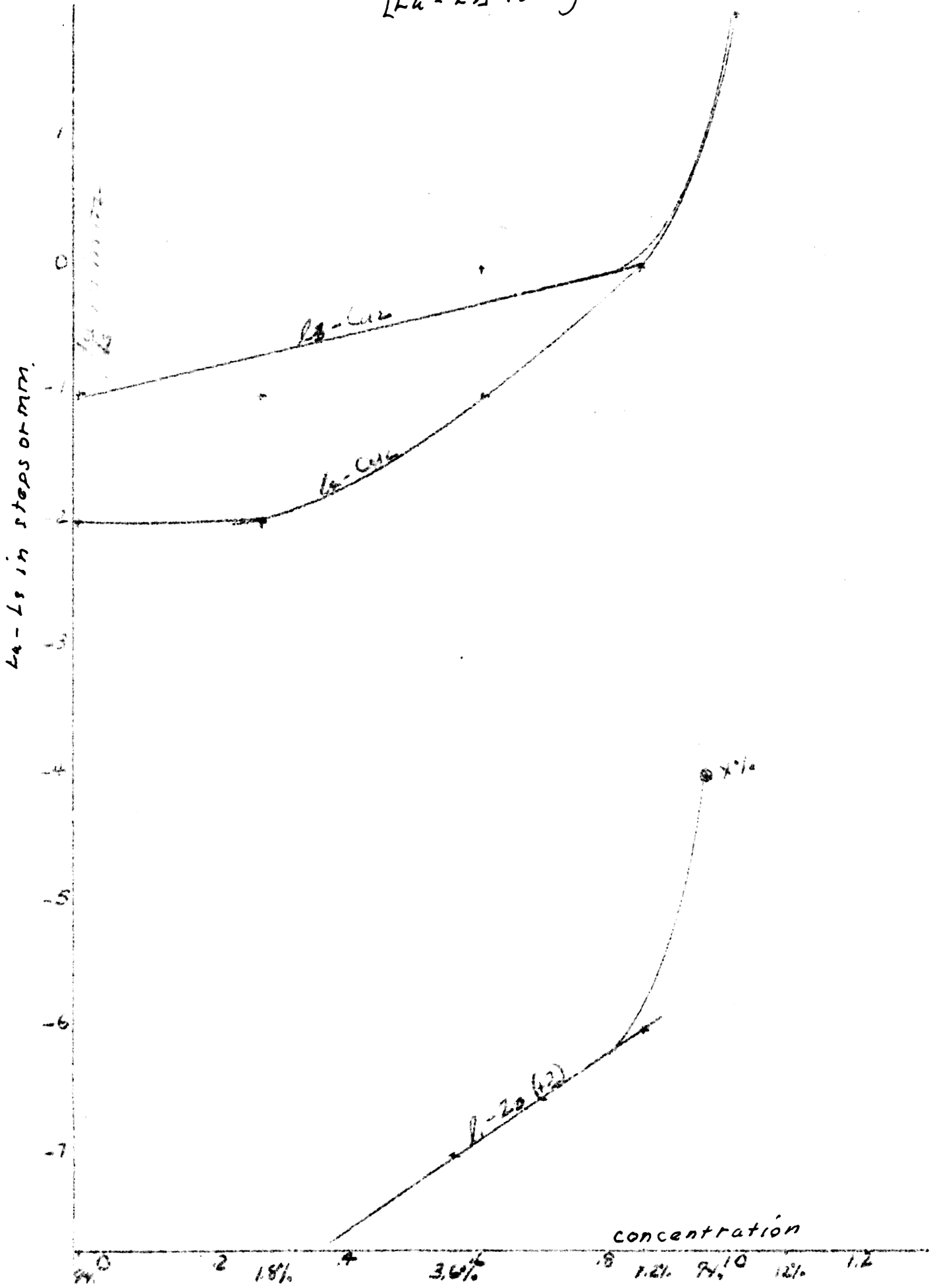
Attention is called to the values for 12%. The spectra of Al, Cu, and Zn were not put on the next plate and a spectrogram of an 18% Al was put in its place. As was mentioned, the unknown showed the tendency of the aluminum lines to disappear. With this exception the plate yielded valuable data on the operation of the sector. The data follows:

$[Li - \frac{L_i}{L_j}]$ vs. log Conc. (%)

Note: extrapolations
Extrapolation - - - - -

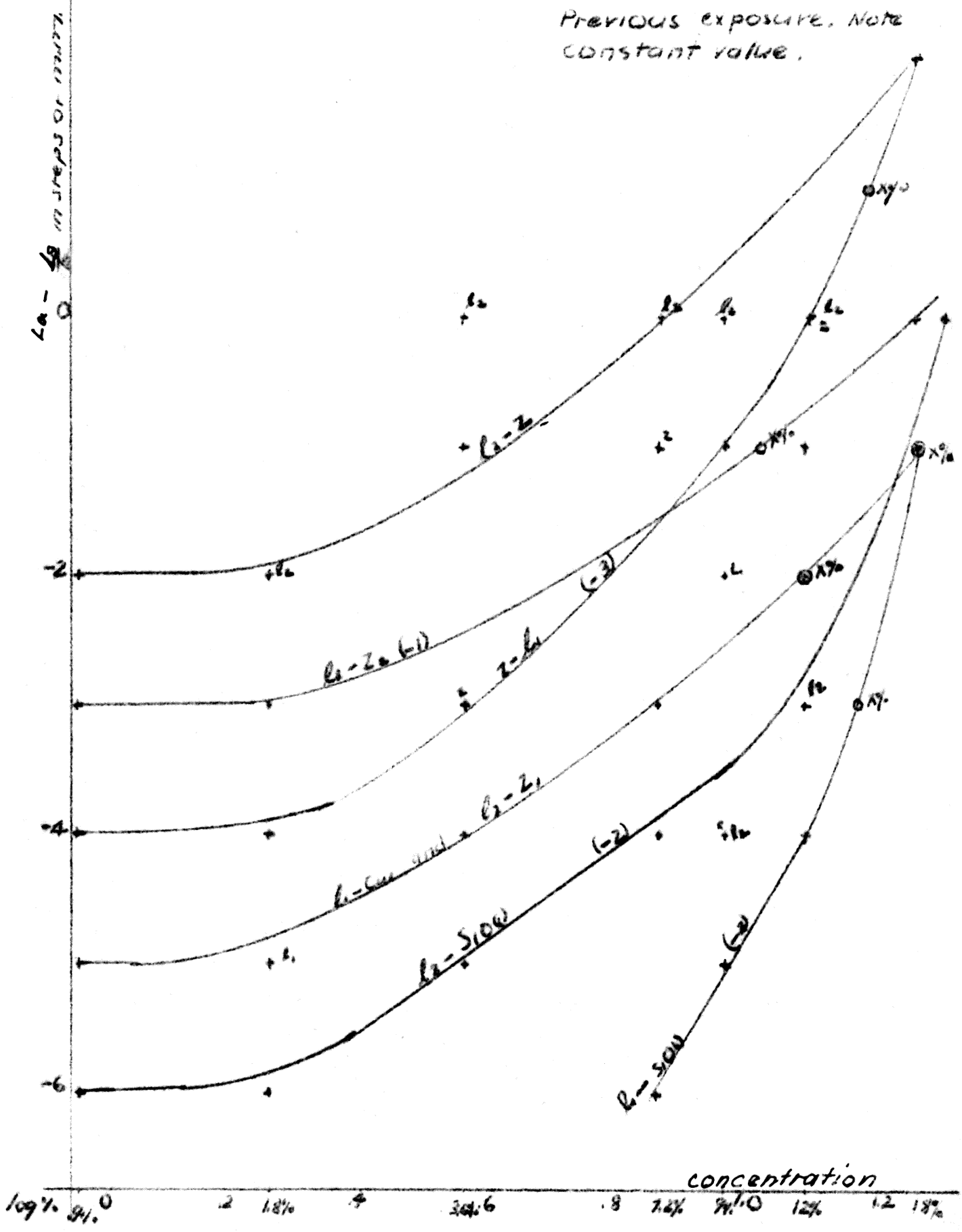


[L_u - L_s] vs log. concentration



	.9%	1.8%	3.6%	7.2%	9%	12%	X ₂	18%
<i>l₁-Cu₁ Al. 3082 - Cu 2961</i>								
m. m.	0-5	0-5	2-6	3-6	4-6	4-6	1-6	5-6
steps	10-15	10-15	12-16	13-16	14-16	14-16	11-16	15-16
<i>l₂-Cu₁ Al. 3092 - Cu 2961</i>								
m. m.	3-5	3-6	5-6	5-5	5-5	5-5	2-5	7-5
steps	13-15	13-16	15-16	15-15	15-15	15-15	12-5	17-15
<i>l₁-Si_p Al. 3082 - Si. 2987</i>								
m. m.	- - -	- - -	-1-9	0-9	1-9	2-9	-1-9	5-9
steps	- - -	- - -	12-20	10-20	12-20	13-20	10-20	16-20
<i>l₂-Si₁ Al. 3092 - Si. 2987</i>								
m. m.	1-9	1-9	2-9	3-9	3-9	4-9	0-9	7-9
steps	12-20	12-20	20-13	14-20	14-20	15-20	20-20	16-20
<i>l₁-Zn Al. 3082 - Zn 3075</i>								
m. m.	0- -	0- -	1-7	3-7	3-7	4- -	- - -	5-6
steps	0- -	10- -	11-17	13-7	13-17	14- -	- - -	15-16
<i>l₂-Zn Al. 3092 - Zn 3075</i>								
m. m.	3- -	2- -	3-7	5-7	5-7	5- -	- - -	6-6
steps	13- -	12- -	13-17	15-17	15-17	15- -	- - -	16-16
<i>l₁-Zn₁ Al. 3082 - Zn 3282</i>								
m. m.	- - -	0- -	2-6	3-8	4-8	4- -	- - -	4-8
steps	- - -	10- -	12-18	13-18	14-18	14- -	- - -	14-18
<i>l₂-Zn₁ Al. 3092 - Zn 3282</i>								
m. m.	1- -	3- -	4-8	5-8	5-8	5- -	- - -	7-8
steps	4- -	13- -	14-18	15-18	15-18	15- -	- - -	17-18

$L_u - L_a$ vs $\log \% \text{ Conc}$
If unknown selected from
Previous exposure. Note
constant value.



A comparison of the internal standard of the two plates showed that they were of the same value, therefore the value of the unknown could be used on the latter spectrogram, provided the erratic effect noticed was confined to specific causes and conditions, and when observed, was present, and when not observed, its influence could be considered negligible. It is well to point out that the work was done in a range in which spectrographic analysis is entirely empirical. This data seemed to indicate an unknown concentration of 18% or less.

Another plate of spectrograms of this same range of samples seemed to indicate that all the samples appeared to exhibit normal behavior. Data was therefore taken for a second set of curves as shown below.

A comparison of the two previous sets of curves, showed that the assumption concerning the trend of the curve was not justified completely. The curve did rise with a steep slope but not as steep as predicted, and therefore the concentration of the unknown was greater than predicted.

The sector stopped due to a broken wire while the 18% sample was being arced. The slit was closed before the sector stopped, but since the failure occurred about one minute after the exposure had started, part of the sample was burned without reaching the plate. The control lines used, however, all showed a decrease relative to the same lines in the other spectrograms. There was some question as to whether or not each element was excited in the same relative way because the exposure was of such short time. Data from this plate indicates about the same unknown concentration as did the data from the previous plate.

	.9%	1.8%	3.6%	7.2%	9%	12%	X ₁	18%
l_1-Cu_1	<i>Al. 3082 - Cu. 2961</i>							
m. m.	0-5	2-6	4-7	4-6	4-6	5-6	7-6	4-4
steps	10-15	12-16	14-17	14-16	14-16	15-16	17-16	14-14
l_2-Cu_1	<i>Al. 3092 - Cu 2961</i>							
m. m.	2-4	4-5	5-6	5-5	5-5	6-5	7-6	6-4
steps	12-14	14-15	15-16	15-15	15-15	16-15	17-16	16-14
l_1-Si_2	<i>A 1 3082 - S. 2987</i>							
m. m.	- - -	-1-9	2-9	2-9	2-9	3-9	4-9	4-7
steps	- - -	10-20	13-20	12-20	13-20	13-20	14-20	14-17
l_2-Si_2	<i>Al. 3092 - S. 2987</i>							
m. m.	0-9	2-9	3-9	3-9	4-9	5-9	7-9	6-8
steps	10-20	12-20	13-20	13-20	14-20	15-20	17-20	16-18
l_1-Zn	<i>Al. 3082 - Zn 3075</i>							
m. m.	- - -	1- -	3-7	2-6	3-7	4- -	6- -	4-5
steps	- - -	11- -	13-17	12-16	13-17	14- -	16- -	14-15
l_2-Zn	<i>Al. 3092 - Zn 3075</i>							
m. m.	2- -	4- -	5-7	4-6	5-7	6- -	7- -	5-5
steps	12- -	14- -	15-17	14-16	15-17	16- -	17- -	15-15
l_1-Zn_1	<i>Al 3082 - Zn 3282</i>							
m. m.	0- -	1- -	3-8	3-8	3-7	4- -	6- -	4-6
steps	11- -	12- -	13-18	13-18	13-17	14- -	16- -	14-16
l_2-Zn_1	<i>Al 3092 - Zn 3282</i>							
m. m.	2- -	3- -	5-8	5-8	5-7	6- -	8- -	6-6
steps	12- -	13- -	15-18	15-18	15-17	16- -	18- -	16-16

	.9%	1.8%	3.6%	7.2%	9%	12%	X ₁	18%
l_3 -Cu _g	Al. 3944 - Cu 4022							
m. m.	3-6	4-6	6-6	6-6	5-5	6-4	8-5	7-4
steps	13-16	14-16	16-16	16-16	15-15	16-14	18-15	17-14
l_4 -Cu _g	Al. 3960 - Cu 4022							
m. m.	4-6	5-6	7-6	7-6	6-5	7-4	9-5	8-4
steps	14-16	15-16	17-16	17-16	16-15	17-14	20-15	18-14
Si (2)- l_3	Al. 3944 - Si. 3905							
m. m.	- - -	-1-9	1-9	1-9	1-9	2-9	3-9	3-9
steps	- - -	10-20	11-20	11-20	11-20	12-20	13-20	13-20
Si (2)- l_4	Al. 3960 - Si. 3905							
m. m.	- - -	0-9	2-9	2-9	2-9	3-9	4-9	4-9
steps	- - -	10-20	12-20	12-20	12-20	13-20	14-20	14-20

Some control lines chosen were of questionable distance from the unknown, but the primary interest of this investigation was the behavior of spectrum lines under the operation of the sector upon intensity values. There was also considerable question as to whether or not the step chosen on two intense silicon lines was on the linear portion of the curve. The step available in the weaker line, ^{of} lower concentrations of Al could well have been on the underexposed parts of the curve. These considerations were not of importance to analysis by the sector, but they were considerable when an analysis was made by the densitometer method and compared with that of the sector.

Analysis By Densitometer Method

Since the analysis by sector had been concluded, ~~or pursued to the limits where it had any meaning,~~ the next step was to make an analysis by the densitometer method as a check against the method introduced. It was first suggested that density measurements of various steps be made for comparison. This, however, was only a refinement of the sector method. The densitometer method is fundamentally a measurement of equal segments of two lines. In measuring segments of lines of uniform density, care must be taken that the ^{value} line density is on the linear portion of the $d \log I$ curve. There is considerably more freedom of choice in a spectrogram made through a stepped sector, since one can find such conditions by taking steps well up on a line of high intensity. If the same steps on each line are measured, a correct evaluation of the relative intensities of the two lines can be obtained.

Another emergency arose when readings were made of the 18% sample. The four-inch plate came against the upper frame of the plate holder carriage, and could not be positioned so that the proper steps for readings could be placed in the beam. Readings were taken by turning the plate upside down. Outside of causing confusion of the lines, no inaccuracy could result. However, there was some question as to the position of the plate for a proper focus. Readings were carefully taken, clear plate and dark line.

So and Si were taken at every line. The slit was carefully prepared by covering the entire area with dark paper. A V-shaped notch was cut so that the length of the step could be accurately defined. The line was brought close to the slit and then moved through a position which gave maximum deflection. The clear plate reading was noted. It was recorded after a

reading taken for the line of infinite blackness. After the S_0 reading the line was moved across the slit and the deflection recorded.

The density of a line is given by the following relation between the readings:

$$d = \log_{10} \frac{S_0 - S_1}{S_1 - S_1} \quad \text{where}$$

d = density,

S_0 = clear plate reading,

S_1 = reading with dark line over slit, and

S_1 = reading with spectrum line over slit.

This formula corrects for background. The working curve for the densitometer method is the plot of $d_l - d_s$ vs log. % concentration where d_s is the density of the internal standard line and d_l is the density of the spectrum line used for analysis. Therefore,

$$d_l - d_s = \log_{10} \frac{S_{0l} - S_{1l}}{S_{1l} - S_{1l}} - \log_{10} \frac{S_{0s} - S_{1s}}{S_{1s} - S_{1s}} =$$

$$\log_{10} \frac{S_{0l} - S_{1l}}{S_{1l} - S_{1l}} \times \frac{S_{1s} - S_{1s}}{S_{0s} - S_{1s}}$$

Densitometer readings and corresponding values are given below.

A plot of the difference in steps and millimeters between unknown lines and standard lines vs percentage concentration was made for each pair of lines used. Then, on the same graph, a plot of the above expression for the density vs. percentage concentration was made on the same page. Of course, the comparison necessarily was to be between trends of curves and the relation of corresponding values to the curves. The tables of readings and values are shown below.

Densitometer Analysis on Final Plate

		.9%			Sc-Si Sl-Si
		Si	Sc	Sl	
Cu ₁	2961	3.1	20.8	17.5	<u>17.7</u>
					14.2
Si (1)	2987	3.0	21.0	6.7	<u>18.0</u>
					2.7
Zn	3075	--	--	--	--
l ₁	Al.3082	3.2	20.8	20.5	<u>17.6</u>
					17.3
l ₂	Al.3092	3.2	20.2	18.8	<u>17.0</u>
					15.6
Zn ₁	3282	3.1	20.5	16.1	<u>17.4</u>
					13.0
Zn ₂	3302	3.1	20.5	13.3	<u>17.4</u>
					10.2
Zn ₃	3345	--	--	--	--
Si (2)	3905	2.1	16.3	2.4	<u>14.2</u>
					0.3
l ₃	Al.3944	2.7	20.7	15.7	<u>18.0</u>
					13.0
l ₄	Al.3960	--	--	16.1	<u>18.0</u>
					13.4
Cu ₂	4022	--	--	--	--
		1.8%			Sc-Si Sl-Si
		Sc	Si	Sl	
Cu ₁	2961	20.6	2.8	15.75	<u>17.8</u>
					13.0
Si ₁	2987	20.5	2.8	5.6	<u>17.7</u>
					2.8
Zn	3075	20.3	2.9	19.0	<u>17.4</u>
					16.1
l ₁	Al.3082	20.3	2.9	19.3	<u>17.4</u>
					16.4
l ₂	Al.3092	20.3	2.9	17.2	<u>17.4</u>
					14.3
Zn ₁	3282	--	--	--	--
Zn ₂	3302	--	--	--	--
Zn ₃	3345	--	--	--	--

3.6%

	Sc	Si	Si	<u>Sc-Si</u> Si-Si
Cu ₁ 2961	20.9	3.0	15.3	<u>17.9</u>
Si (1) 2987	21.5	2.9	6.4	<u>12.3</u>
Zn 3075	--	--	12.4	<u>18.4</u>
l ₁ Al. 3082	--	--	17.6	3.5
l ₂ Al. 3082 Al. 3092	20.7	2.9	14.0	<u>17.6</u>
Zn ₁ 3282	21.0	2.6	16.6	9.5
Zn ₂ 3302	--	--	5.6	<u>17.8</u>
Zn ₃ 3345	20.0	2.8	4.3	<u>14.7</u>
				<u>17.8</u>
				11.1
				<u>18.4</u>
				14.0
				<u>18.4</u>
				3.0
				<u>17.2</u>
				1.5

7.2%

Cu ₁ 2961	20.8	2.9	15.7	<u>17.9</u>
Si (1) 2987	21.8	2.8	6.4	<u>12.6</u>
Zn 3075	20.1	2.9	13.1	<u>19.0</u>
l ₁ Al. 3082	--	--	19.0	3.6
l ₂ Al. 3092	--	--	15.3	<u>17.2</u>
Zn ₁ 3282	20.9	2.6	11.1	<u>10.2</u>
Zn ₂ 3302	--	--	5.9	<u>17.2</u>
Zn ₃ 3345	20.5	2.7	4.5	16.1
				<u>17.2</u>
				12.4
				<u>18.3</u>
				8.5
				<u>18.3</u>
				3.3
				<u>17.8</u>
				1.8

9%

Cu ₁ 2961	22.7	2.7	15.9	<u>20.0</u>
Si (1) 2987	22.6	2.8	6.7	<u>13.2</u>
Zn 3075	--	--	13.2	<u>19.8</u>
l ₁ Al. 3082	--	--	19.6	3.9
l ₂ Al. 3092	22.6	2.7	16.6	<u>19.9</u>
				<u>10.5</u>
				<u>19.9</u>
				16.9
				<u>19.9</u>
				13.9

			9%		Sc-Si
	Sc		Si	Sl	<u>Sl-Si</u>
Zn ₁ 3282	--		--	11.8	<u>18.7</u>
Zn ₂ 3302	21.4		2.7	6.0	<u>9.7</u>
Zn ₃ 3345	20.5		2.7	4.5	<u>18.7</u>
					<u>3.3</u>
					<u>17.8</u>
					<u>1.8</u>
12%					
Cu ₁ 2961	21.3		2.8	14.8	<u>18.5</u>
Si (1) 2987	20.4		2.8	6.5	<u>12.0</u>
Zn 3075	--		--	--	<u>17.6</u>
					<u>3.7</u>
l ₁ Al. 3082	21.0		2.6	15.5	<u>18.5</u>
l ₂ Al. 3092	--		--	11.7	<u>12.9</u>
Zn ₁ 3282	--		--	--	<u>18.5</u>
Zn ₂ 3302	--		--	--	<u>9.1</u>
Zn ₃ 3345	--		--	--	--
					--
12%					
Cu ₁ 2691	21.7		2.7	15.7	<u>19.0</u>
Si ₁ 2987	20.1		2.7	4.0	<u>13.0</u>
l ₁ Al. 3082	20.1		2.6	12.1	<u>17.4</u>
l ₂ Al. 3092	--		--	8.8	<u>1.3</u>
					<u>17.5</u>
					<u>9.5</u>
					<u>17.5</u>
					<u>6.2</u>
18%					
Cu ₁ 2961	22.4		2.7	11.7	<u>19.7</u>
Si 2987	22.2		2.8	10.8	<u>14.3</u>
Zn 3075	--		--	15.1	<u>19.4</u>
					<u>8.0</u>
l ₁ Al. 3082	--		--	16.8	<u>18.3</u>
l ₂ Al. 3092	21.0		2.7	12.8	<u>12.2</u>
Zn ₁ 3282	--		--	12.0	<u>18.3</u>
Zn ₂ 3302	22.6		2.7	6.5	<u>14.1</u>
Zn ₃ 3345	20.7		2.5	4.7	<u>14.1</u>
					<u>18.3</u>
					<u>10.1</u>
					<u>19.9</u>
					<u>9.3</u>
					<u>19.9</u>
					<u>3.8</u>
					<u>18.2</u>
					<u>2.2</u>

La - vj

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
I₁-CuI	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log
A1.3082-Ca2961	17.614.2	17.413.0	17.812.3	17.212.6	19.913.2	18.412.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0
	log .816 =	log .775 =	log .8325 =	log .752 =	log .777 =	log .927 =	log 1.261 =	log 1.008 =	log 1.09 =	log .883 =	log .795 =	log .752 =	log .777 =	log .777 =	log .777 =	log .777 =	log .777 =	log .777 =
	-.0883	-.1092	-.0795	-.1232	-.1095	-.0329	+.1008	+.1008	+.0374									
I₂-CuI	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log
A1.3092-Ca2961	17.014.2	17.413.0	17.812.3	17.212.6	19.913.2	18.412.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0	17.513.0
	log .875 =	log .89 =	log 1.11 =	log .977 =	log .946 =	log 1.312 =	log 1.945 =	log 1.318 =	log .875 =	log .875 =	log .875 =	log .875 =	log .875 =	log .875 =	log .875 =	log .875 =	log .875 =	log .875 =
	-.053	-.0505	+.0436	-.011	-.0245	+.118	+.288	+.12										
I₁SI (1)	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log
A1.3082-S12987	17.62.7	17.42.8	17.83.5	17.23.6	19.93.9	18.43.7	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3
	log .147 =	log .1678 =	log .231 =	log .2025 =	log .2075 =	log .298 =	log .375 =	log .535 =	log .832 =	log .832 =	log .832 =	log .832 =	log .832 =	log .832 =	log .832 =	log .832 =	log .832 =	log .832 =
	-.832	-.776	-.636	-.645	-.6825	-.526	-.865	-.272										
I₂-S₀₁	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log
A1.3092-2997	17.02.7	17.42.8	17.83.5	17.23.6	19.93.9	18.53.7	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3	17.51.3
	log .1635 =	log .1923 =	log .305 =	log .263 =	log .282 =	log .428 =	log .211 =	log .747 =	log .79 =	log .79 =	log .79 =	log .79 =	log .79 =	log .79 =	log .79 =	log .79 =	log .79 =	log .79 =
	-.79	-.715	-.515	-.58	-.55	-.38	-.675	-.1265										
I₁-Zn	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log
A1.3082-Z13675	17.610.1	17.410.1	17.89.5	17.210.2	19.910.5	18.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1
	log .562 =	log .585 =	log .654 =	log .634 =	log .621 =	log .7925 =	log 1.015 =	log .855 =	log .25 =	log .25 =	log .25 =	log .25 =	log .25 =	log .25 =	log .25 =	log .25 =	log .25 =	log .25 =
	-.25	-.233	-.185	-.1985	-.207	-.1015	+.00646	-.068										
I₂-Zn	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log	log
A1.3092-Z13075	17.010.1	17.410.1	17.89.5	17.210.2	19.910.5	18.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1	17.510.1
	log .602 =	log .671 =	log .865 =	log .8225 =	log .756 =	log 1.121 =	log 1.51 =	log 1 =	log .22 =	log .22 =	log .22 =	log .22 =	log .22 =	log .22 =	log .22 =	log .22 =	log .22 =	log .22 =
	-.22	-.173	-.0631	-.085	-.1215	+.0496	+.182	0										

Observations were written on each graph. It will be observed that the loci of the two curves were practically the same. A further study of densitometer and sector readings showed that the same values were off the curves by an amount which could be expressed by a constant factor relating a sector reading with a densitometer reading. The readings from sector data would have followed the densitometer data more closely, but for operator prejudice in taking readings from sector data.

^{A/.}
The lines in spectrograms of low concentrations were sometimes as dense, or more dense than ^{*the same lines in spectrograms of*} higher concentrations. This caused any doubt in comparing density or line termination to be given to lower values. Densitometer readings for such values are relatively much farther from the theoretical loci of the curve than sector readings.

It will be observed, that with one exception which is a questionable reading due to difficulties mentioned, the densitometer data gives a higher value for the unknown than 18%.

and readings made by densitometer. The spectrograms used for comparison were omitted in favor of the 18% sample

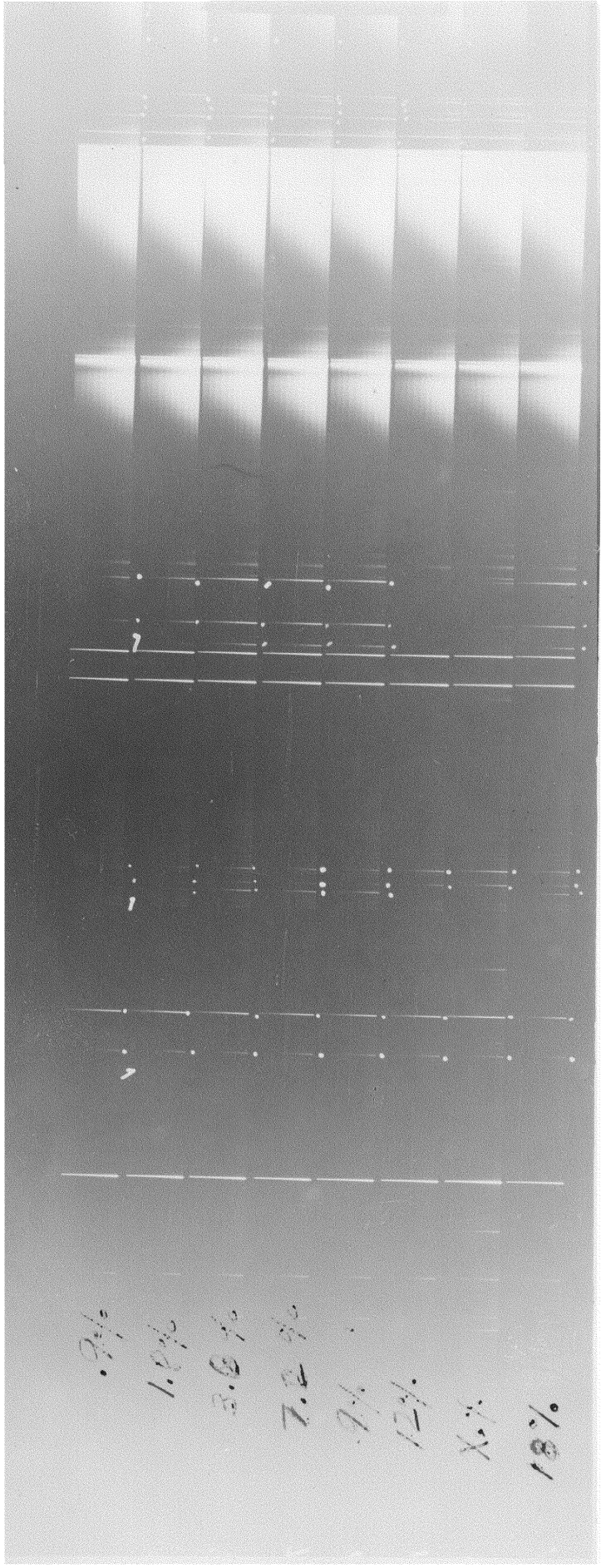
Si(1) = 3905
1004 Ca3

Zn1Zn2Zn3

Zn1Zn2

Cu Si(1)

0.7%
1.8%
3.6%
7.2%
14%
12%
X%
18%

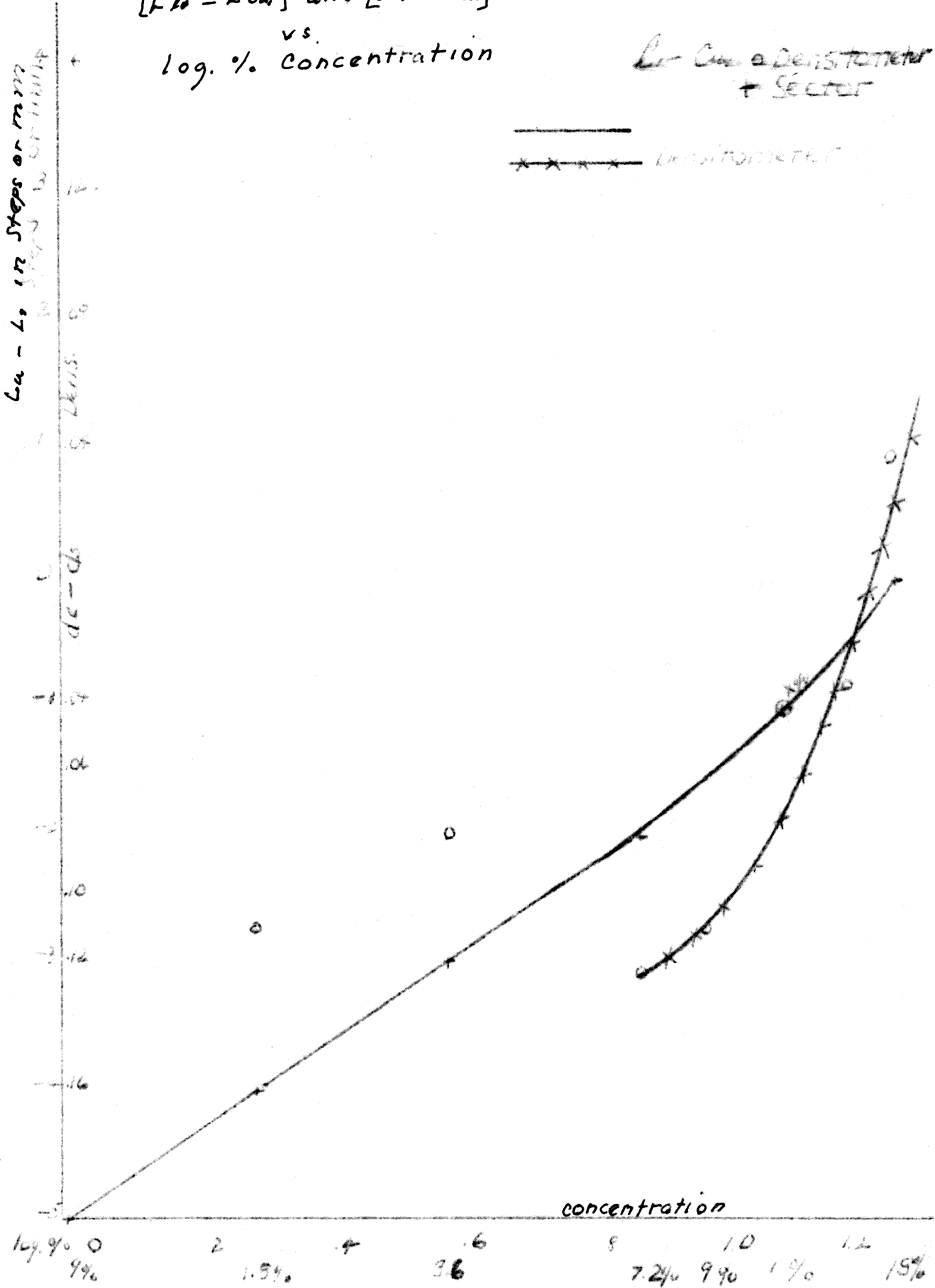


$[L_{10} - L_{cu}]$ and $[d_{10} - d_{cu}]$

vs.
log. % Concentration

For Cur a Densitometer
+ Sector

$L_{cu} - L_{10}$ 172 Steps or more
Steps of 1/1000

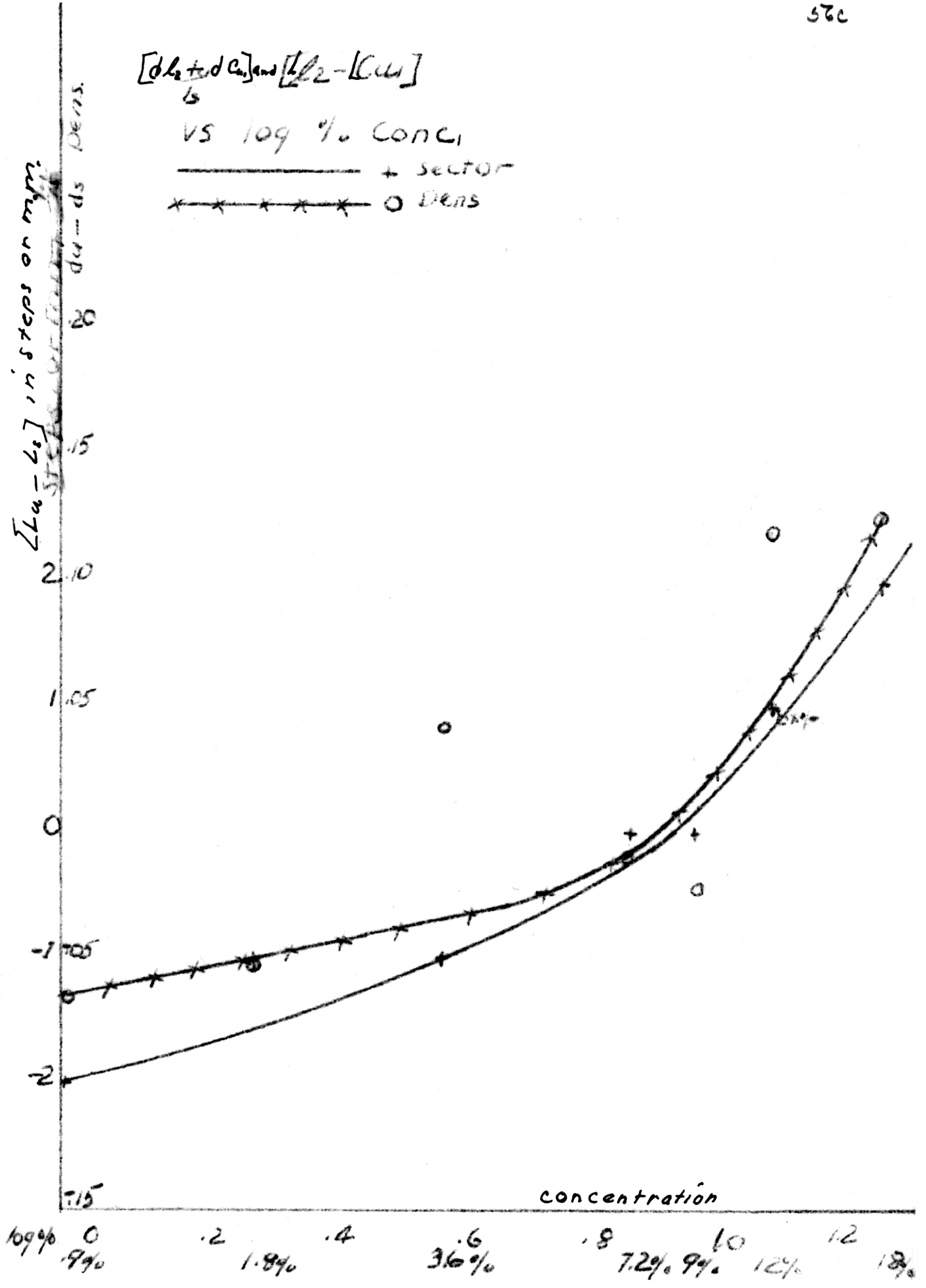


$[\frac{dI_2 + dC_2}{I_2}]$ and $[\frac{dI_2}{I_2} - \frac{dC_1}{C_1}]$

VS $\log \% \text{ Conc}_1$

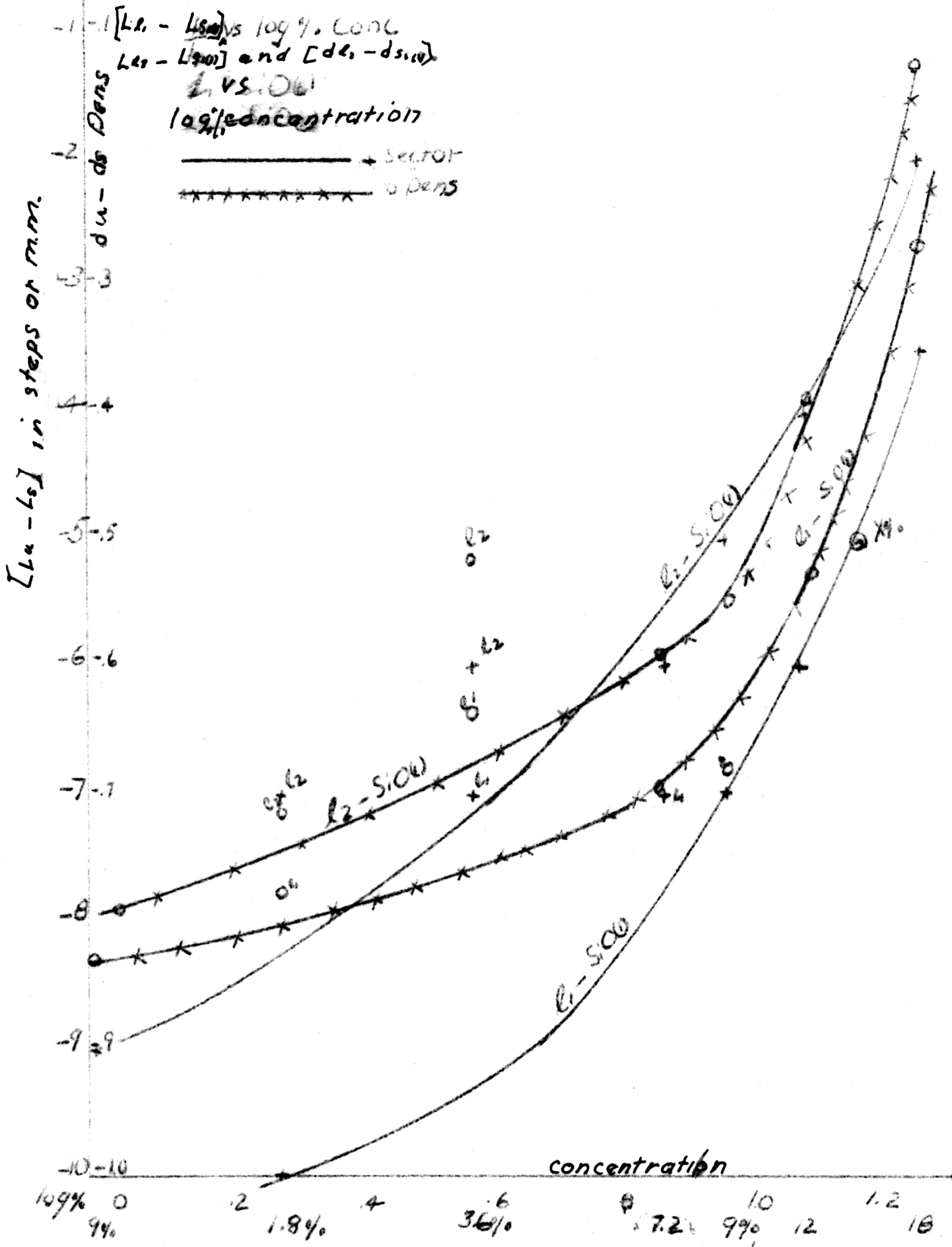
— + sector
* * * * * O Dens

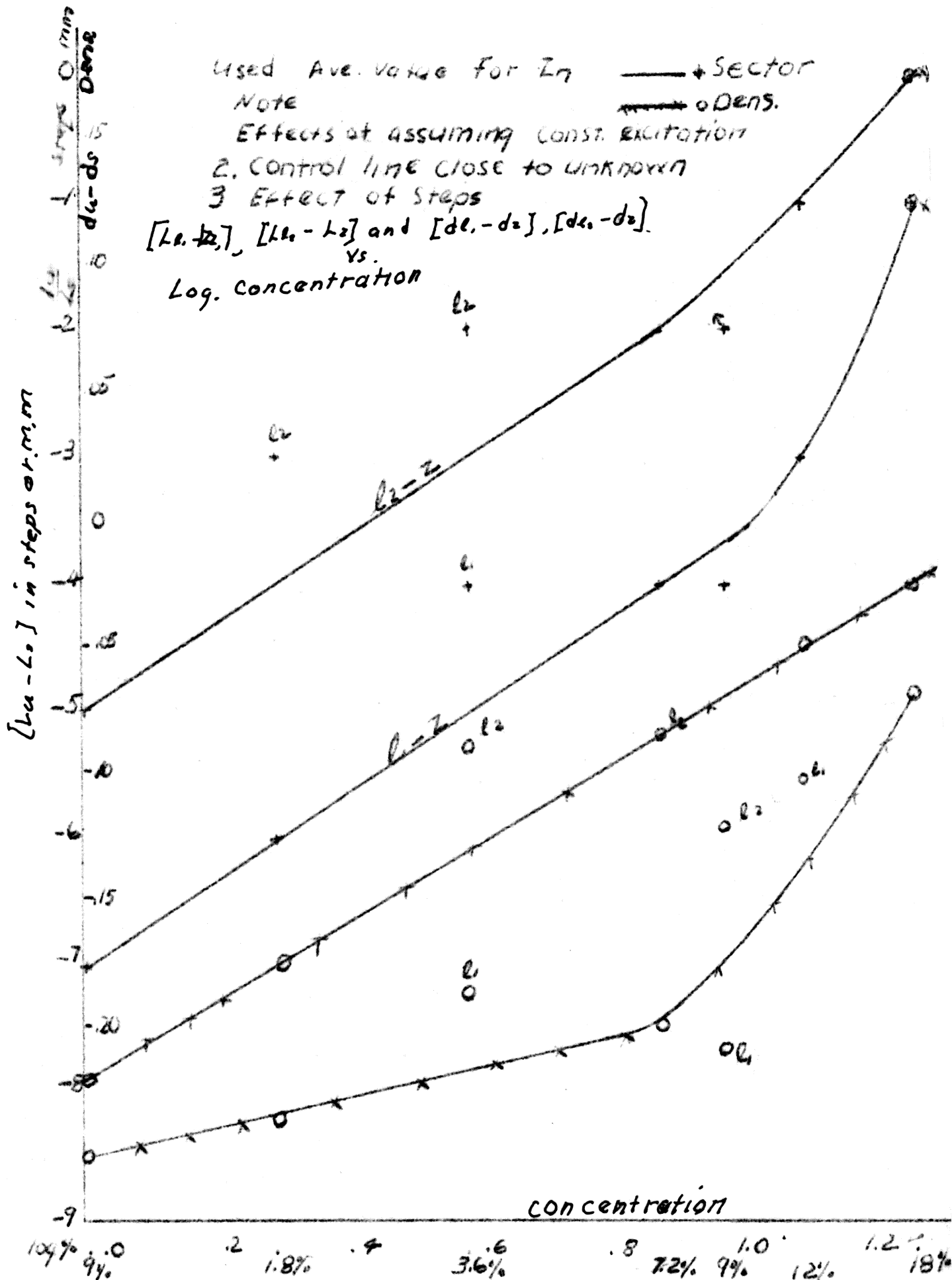
$[\frac{dI_2 + dC_2}{I_2}]$ in steps or m.m.



and $[d_{e_1} - d_{s_{10}}]$

56d

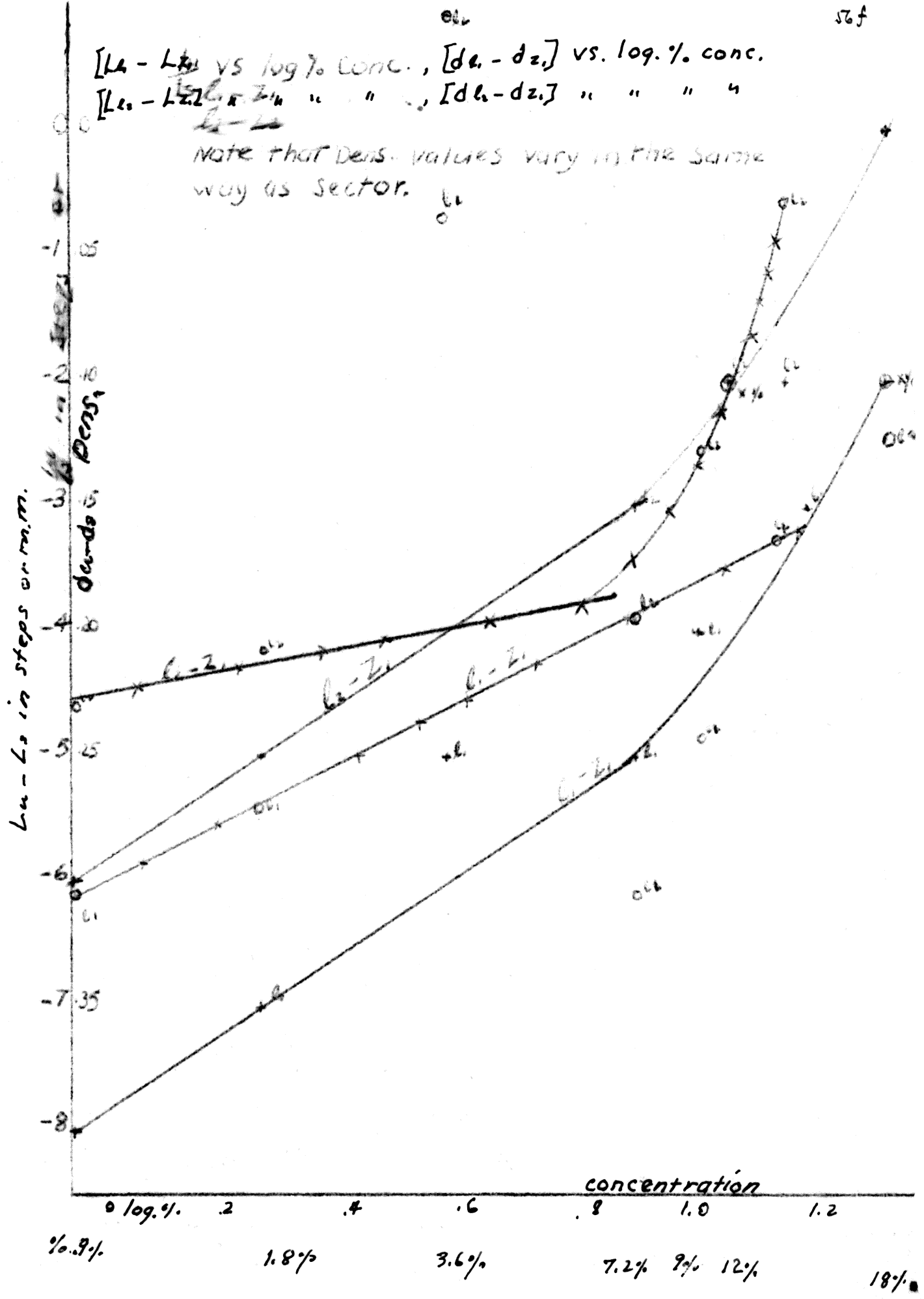




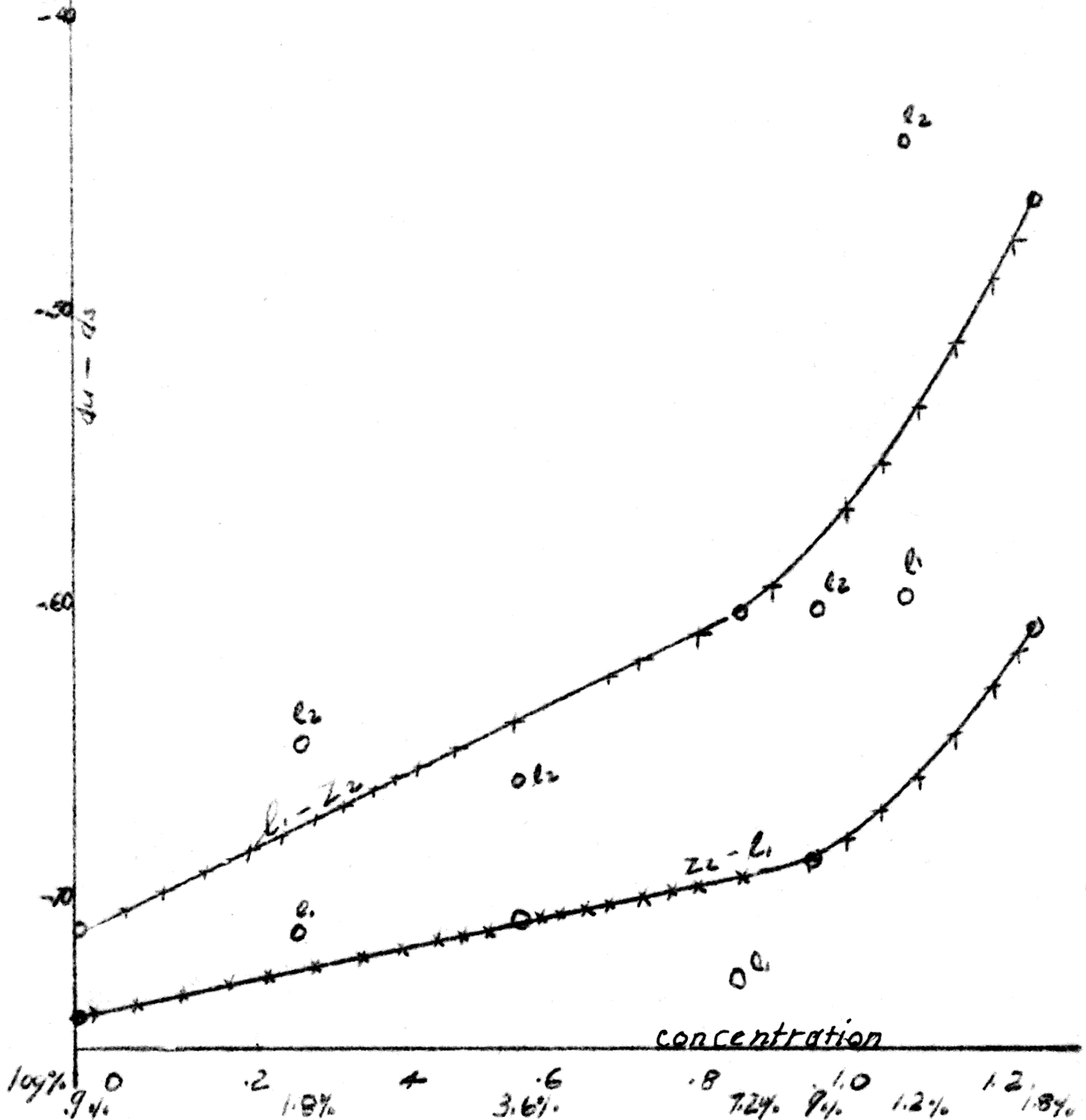
$[L_1 - L_2]$ vs $\log \% \text{ conc.}$, $[d_1 - d_2]$ vs. $\log \% \text{ conc.}$

$[L_1 - L_2]$ vs $\log \% \text{ conc.}$, $[d_1 - d_2]$ vs. $\log \% \text{ conc.}$

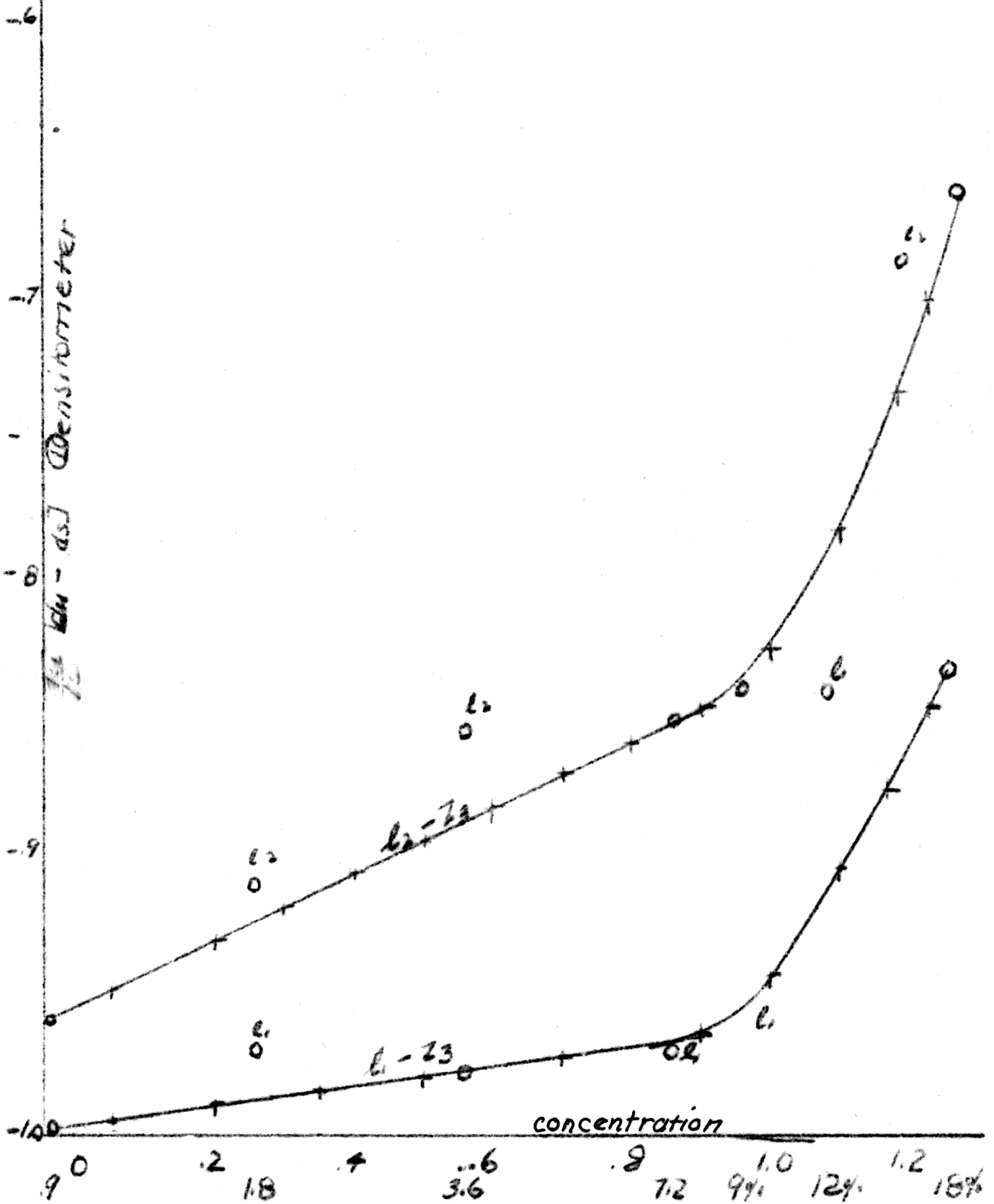
Note that dens. values vary in the same way as sector.



$[d_{l_1} - d_{z_2}]$ vs. log. % conc. ($l_1 - z_2$)
 $[d_{l_2} - d_{z_1}]$ " " " "
 For Densitometer ($l_1 - z_2$)
 Only

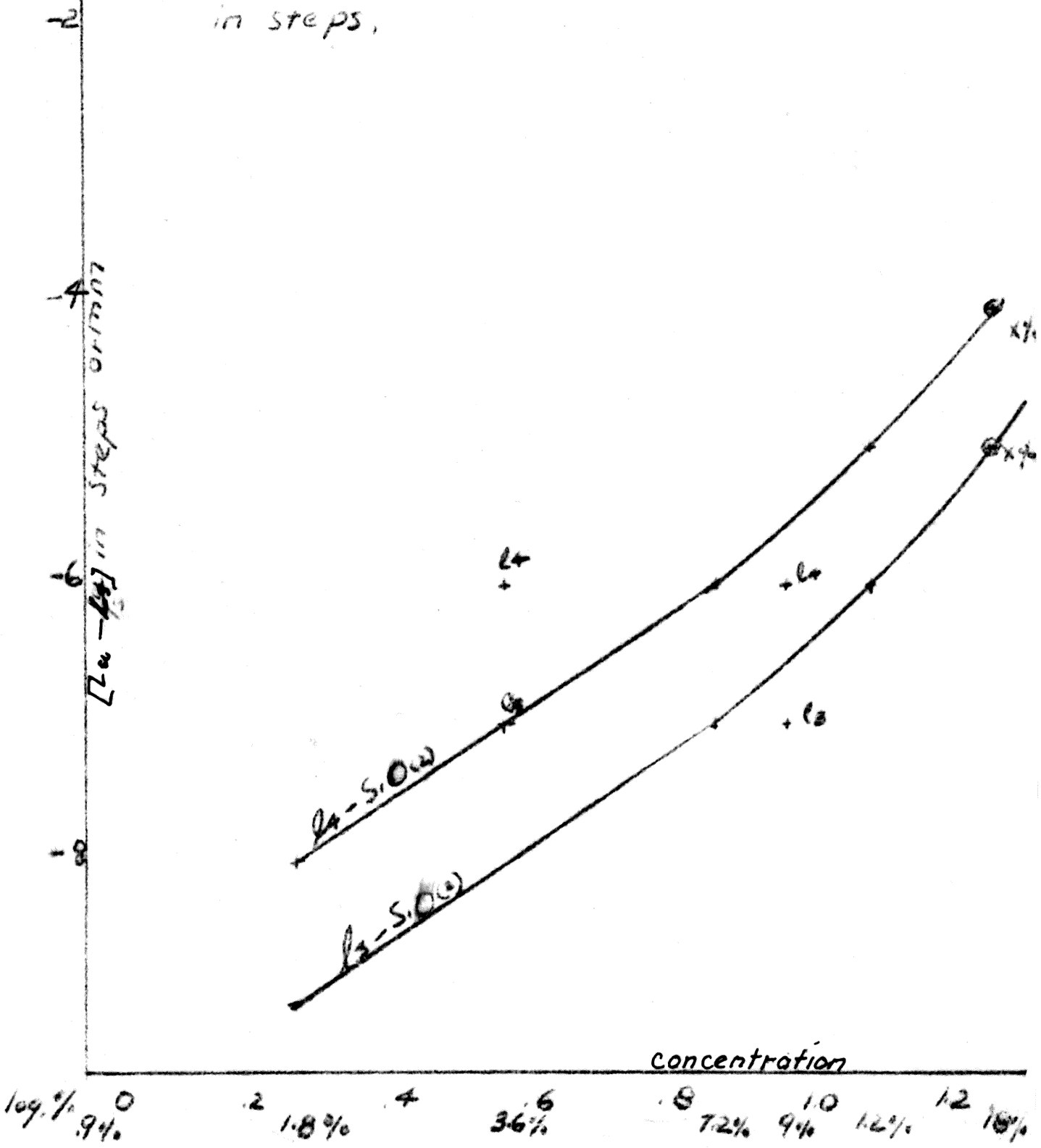


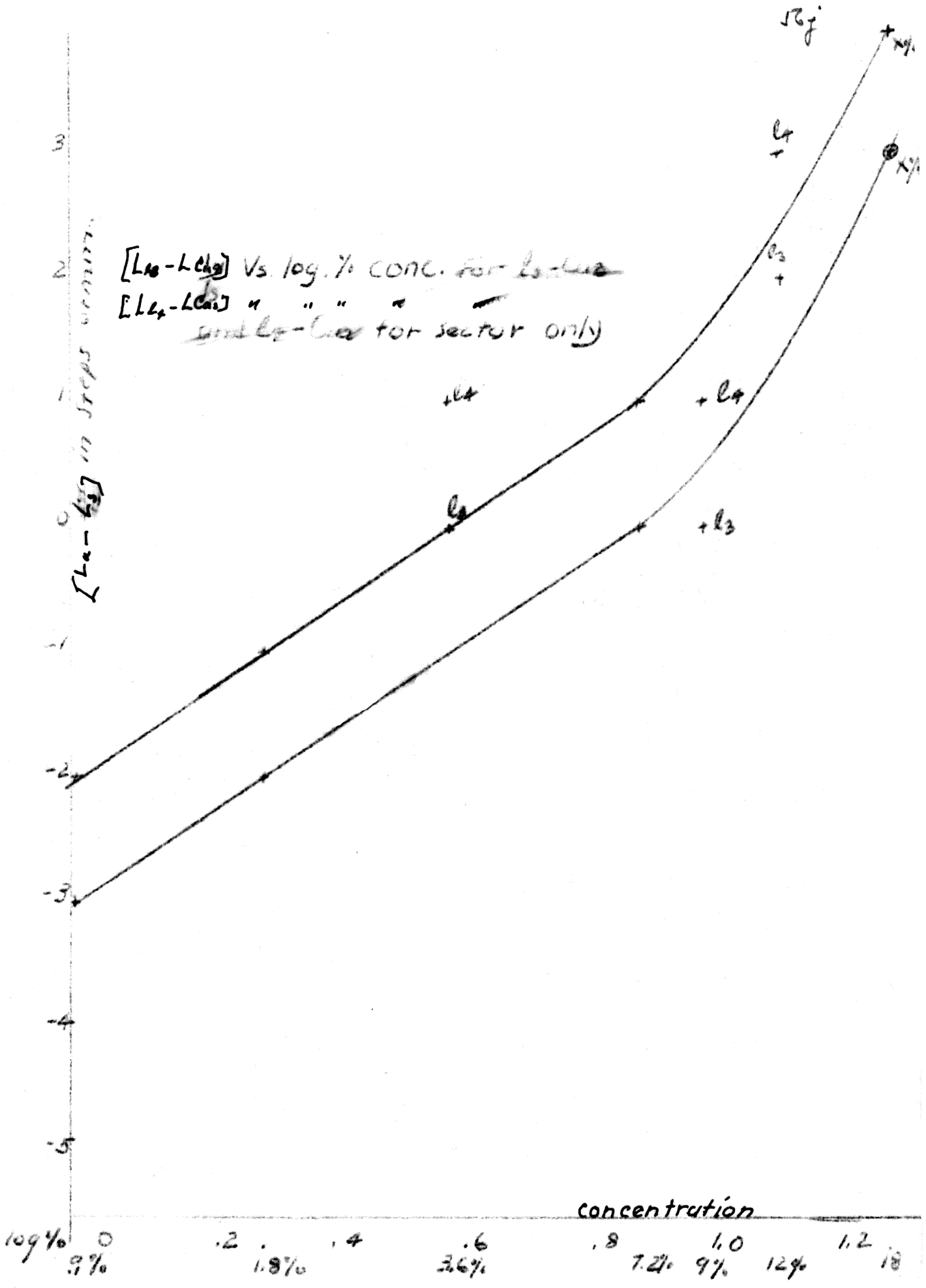
$[d_1 - d_2]$ vs log% For Densitometer only
 $d_1 - d_2$ " " " " " "
 $l_1 - z_3$ " " " " " "
 $l_2 - z_2$ " " " " " "



$[L_4 - L_{50}]$ vs log % Conc.
 $[L_4 - L_{50}]$ " " " "
 FOR Sector Only

Note:
 1. Control near unknown.
 2. Match of densities in steps.





Conclusions

The method thus presented is the use of a device which presents in the spectrogram not the continuous line, but a series of steps of certain density values from zero to its full value of intensity*, which values it separates from values infinitesimally close and compares them with values of such magnitude that the difference in density can be distinguished. It has been established that within certain limits there is a linear relation between the distance between such points of equal density on two lines compared and the logarithm of % concentration. Such distance is a measure of relative values, and can be expressed in terms of constants, predetermined by sector construction such as certain points for measurement or a certain number of steps. The termination of two lines by this device is a point of equal density. The log sector depends with some few exceptions †, upon the terminal point for a comparison of densities. The method thus devised allows the comparison of densities within a greater range of values.

At first, the definition of line termination or zero value of density by this device was disappointing, but the construction of the sector allowed only an error of one step or unit of measure greater, and this was at once evident when the curve was plotted.

Conclusions concerning the slope of the curve of measure and steps vs log. % concentration should be made after further work with carefully prepared samples and choice of lines for comparison. For the materials

* The qualifications stated in the section on plate calibration should be reviewed here.

† See discussion of Bausch and Lomb's special eyepiece.

tested, it seems that for some lines a difference of one step will appear between .05% and .1%. The fact that in some cases no discernable increments appeared between 9% and 7.2% and sometimes, in the case of the last plate discussed, within a range of 3.8-9, cannot at this stage be called an indication of a lack of sensitivity of the method.

Conversely, a study of the curves from data derived by both methods, shows that the sector method is as sensitive as the densitometer method within the limits set by the construction of the sector.

So far, it seems that a sector of 20 steps is fine enough to define most intensity values. In other words, the degree of accuracy obtained by using a stepped sector is as great as can be expected from the use of a smooth sector, and the ease and rapidity of taking data is much greater.

This sector can be applied to a method of quantitative analysis comparable to the densitometer method. The densitometer method requires for its success uniform excitation conditions. If such can be assumed, a spectrogram of a sample can be made and from a working curve of the particular material under test, the percentage concentration can be determined by the number of steps in the unknown line. Actually, the counting of steps is much more fatiguing than measurement with an eyepiece, but this investigation demonstrated how, that after the range of concentration is estimated, many steps can be counted or cut off by any convenient device. A slide with a diagonally cut end can be fitted to the slit of the spectrograph. The horizontal movement of this slide can be calibrated in millimeters or steps cut out as it moves over the slit. This demands that the operating position of the sector be well defined so that it can be in the same position relative to the diagonal line of the slide.

If constant excitation conditions can be achieved, the intensity of the line can be determined by the step in which it appears or disappears in a series of spectrograms. By this method, many spectrograms can be made on one plate.

Since the internal standard can be added with a little more time and trouble in most cases, a more practical and reliable method would be to cut steps off the bottom of the spectrogram with such a slide. The step in which the unknown disappeared could be more easily defined and the steps or length of the internal standard line read for the difference or vice versa.

When it is desirable to consider the whole length of such line in a spectrogram, a slide can be devised with a slot cut perpendicular to its horizontal movement, and this slot crossed with fine wires to cross the slit at termination of sector steps. This will define each step clearly.

The investigator has considerable ~~doubt~~ ^{concentration} concerning the value of aluminum present in the unknown sample. However, it has been demonstrated by the samples used, that the concentration is of the order of 10-20%. Within this range, an analysis by routine chemical means would be more accurate. Verification by this method has been considered.

If the exact ~~concentration~~ ^{concentration} were a major concern, as it would be in the case of the mineralogist, a careful consideration of methods of making up samples could be checked by finding yet another matrix. However, the use of this sector and the method of applying it is the major concern of this investigation. It is respectfully submitted that the value, sensitivity, and accuracy of this method has been shown to be comparable to accepted methods.

It is realized that this method is based on the same theory as other accepted methods, and that it is only a variation of such. The aim ~~was~~ to ~~increase~~ facilitate the application of such established methods.

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