A preliminary investigation of a submerged electrode for quantitative spectroscopic analysis
by Douglas N Stewart

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University

Abstract:
The possibility of using submerged 60 cycle alternating current electrodes as a light source for quantitative Chemical analyst was investigated. The Intensities of the spectral lines produced were measured hy means of a multiplier phototube. The studies were made using the internal standard method. A series of teste were made with lithium as the Internal standard and adding Mg, Ca, Zn and Cu in varying amounts.

A series of tests were also made using cadmium as the internal standard and adding Li, Mg, Ce, Zn end Cu In varying amounts.

A PRELIMINARY INVESTIGATION OF A SUBMERGED ELECTRODE FOR QUANTITATIVE SPECTROSCOPIC ANALYSIS

By

DOUGLAS N. STEWART

A THESIS

Submitted to the Graduate Committee

in

partial fulfillment of the requirements

for the degree of

Master of Science in Chemistry

at

Montana State College

Approved:

B. L. Johnson

Head, Major Department

Ray Woodriff

Chairman, Examining Committee

J. A. Nelson

Chairman, Graduate Division

Bozeman, Montana
July 1949

TABLE OF CONTENTS

Pg.

Graduate Committee

I. ABSTRACT

The possibility of using submerged 60 cycle alternating current electrodes as a light source for quantitative chemical analysis was investigated. The intensities of the spectral lines produced were measured by means of a multiplier phototube. The studies were made using the internal standard method. A series of tests were made with lithium as the internal standard and adding Mg, Ca, Zn and Cu in varying amounts. A series of tests were also made using cadmium as the internal standard and adding Li, Mg, Ca, Zn and Cu in varying amounts.

II. INTRODUCTION

The submerged electrode used in this study was first investigated by Todd[1]. He used it for qualitative determinations. A list of the elements and the lower limits of concentrations that can be detected visually was given by him.

During previous work at this institution some changes had been made in the apparatus suggested by Todd. From those changes and observations it was thought that further investigation of the relation between concentration and intensities of the spectral lines produced, might result in a quantitative method of analysis of solutions.

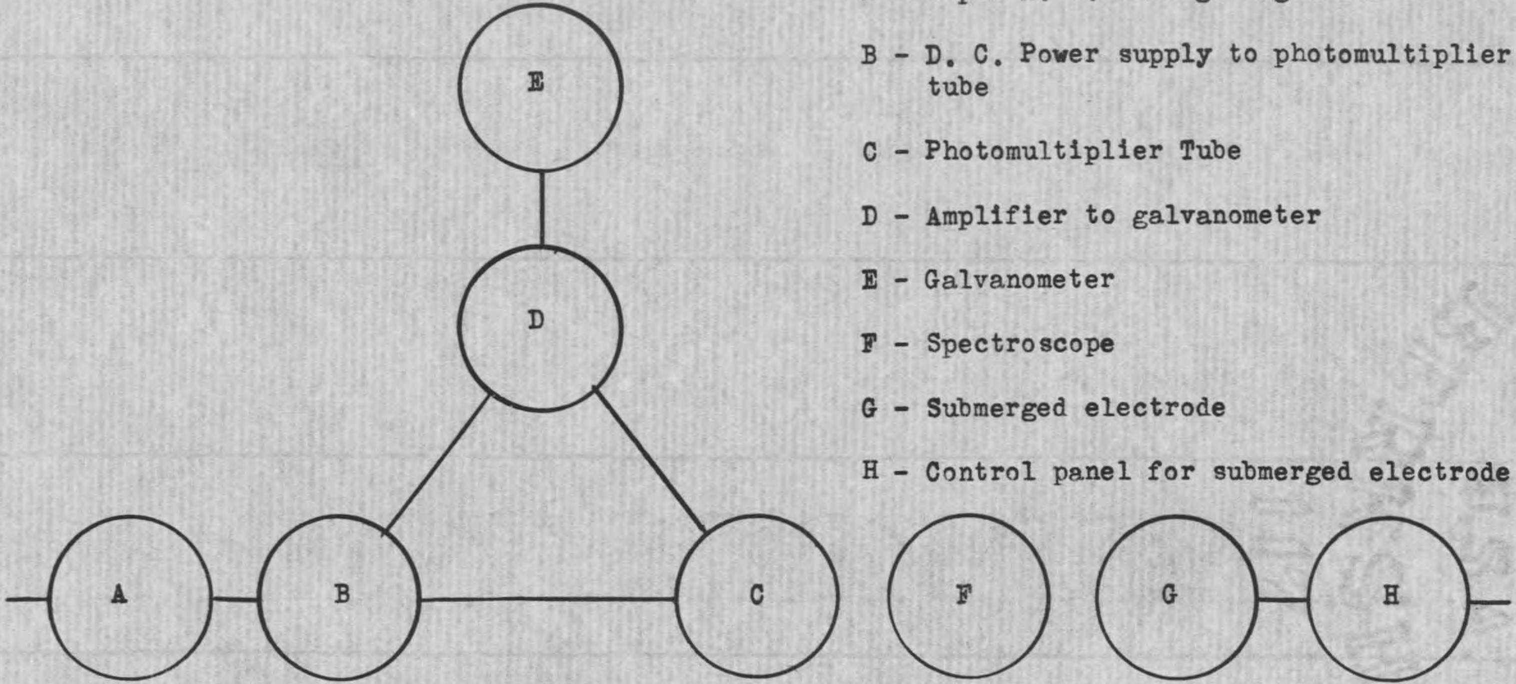
With the possibility of a method for quantitative determination of elements in solutions in mind, it was decided to construct the necessary apparatus needed to operate a multiplier phototube, and a preliminary study of the effects of additional elements in the solutions was also to be made if the intensity of the light source was found to be adequate.

It has long been recognized that a light source capable of giving a homogeneous light for a considerable length of time would increase the usefulness of the spectroscope.

The possibility of obtaining additional information on the behavior of ions in solution was recognized in planning this study.

---

[1] J. Chem. Ed. V 15, p 241 (1938)



A - Input A. C. voltage regulator

B - D. C. Power supply to photomultiplier tube

C - Photomultiplier Tube

D - Amplifier to galvanometer

E - Galvanometer

F - Spectroscope

G - Submerged electrode

H - Control panel for submerged electrode

Arrangement of Instruments

Figure 1

III. APPARATUS

Input Constant Voltage Regulator:

The large daily fluctuations of line voltage and amperage made it necessary to stabilize the power source for both the direct current power supply and the alternating current supply to the submerged electrodes. Any change in the d. c. voltage supplied to the multiplier phototube would have changed the amplification factor of the tube. To check the voltage regulator, a variable transformer was placed in the supply line to the voltage regulator. For a 10 volt change in the variable transformer no change in the output voltage of the d. c. power supply could be detected with a 7½ inch Triplett volt-ohm-milliammeter, 20,000 ohms/volt d. c.

Direct Current Power Supply:

The power supply, Figure 2, consisted of a high-voltage transformer, T_2, 1500-0-1500 volts, 115 volts primary; two half-wave mercury rectifier tubes, RCA 816; a filtering system of two condensers, C_1, C_2, 4 mu-f, 3000 volts d. c.; two chokes, L_1, L_2, 12 henerys, 80 ma. d. c.; and a bank of voltage regulator tubes, RCA VR90, to serve as a voltage divider for the multiplier phototube. A 100,000 ohms, 30 watt resistor, R_1, served as a means of discharging the condensers when the power supply was turned off.

A similar power supply was used by Dieke and Crosswhite[1].

Multiplier Phototube:

The multiplier phototube used with this work was a RCA 1P22 having a spectral response of about 4000 A° to 7000 A°. It is capable of multi-

---

[1] J. Opt. Soc. of Am. V 35, p 471 (1945)

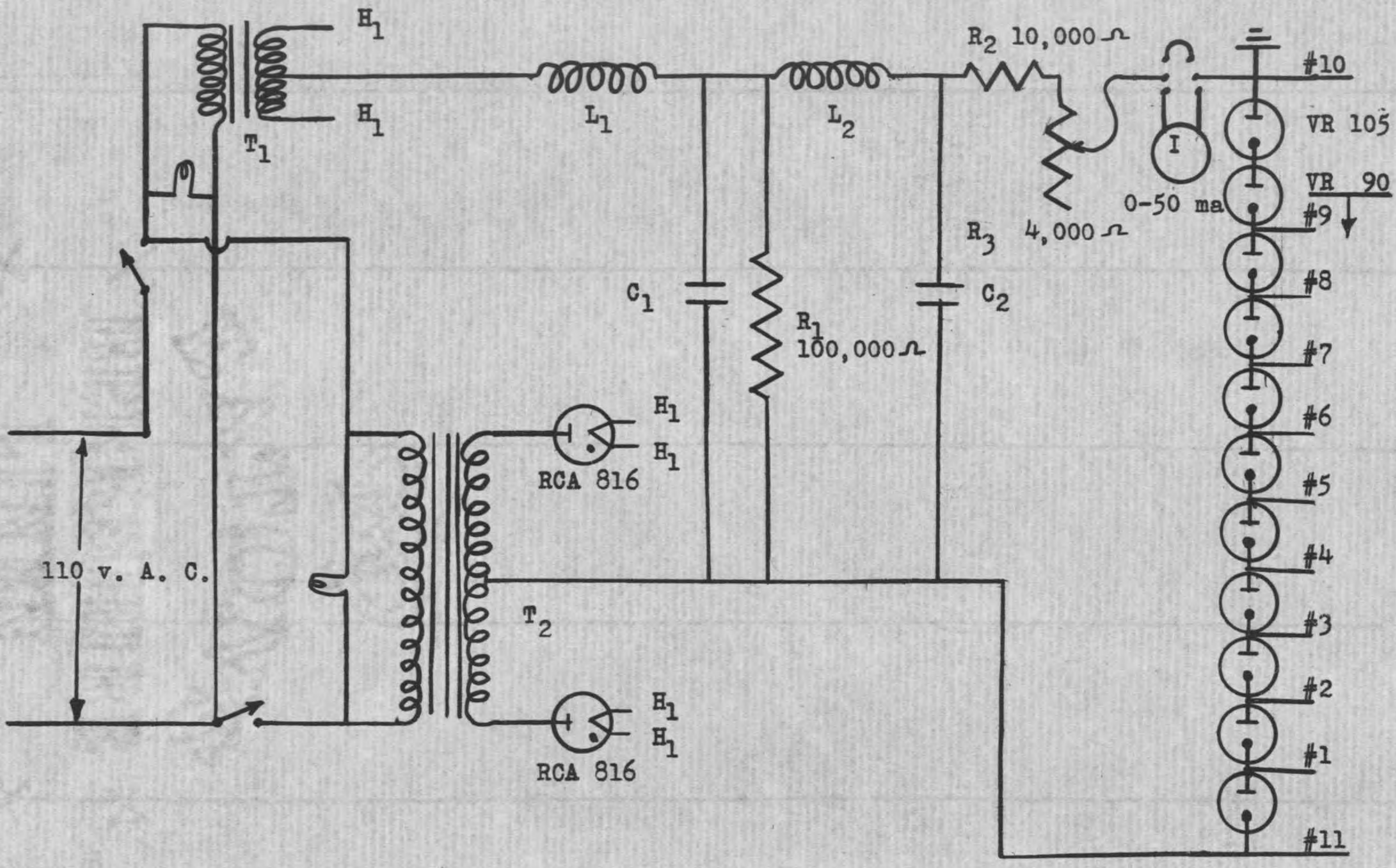


Figure 2

Direct Current Power Supply

plying feeble currents produced under weak illumination by an average value of 200,000 times when operated at 100 volts per stage. A good review on the behavior of a multiplier tube is given by Engstrom[1]. The characteristics of the tube itself are presented in tentative data published by RCA[2].

An electron multiplier is a vacuum tube in which the electrons emitted from the illuminated cathode are directed by fixed electrostatic fields to the first dynode (secondary emitter). The electrons impinging on the dynode surface produce many other electrons. These secondary electrons are directed to a second dynode and these produce many more electrons. This process is repeated until the final stage is reached where they are collected and constitute the current utilized in the output current.

Amplifier, Phototube to Galvanometer:

The amplifier tube was a RCA 959[3] acorn type tube wired as a reduced grid current tube in which G_2 is the space charge grid (screen) and G_3 the control grid. The circuit in which it was used was a Dubridge and Brown[4] balanced circuit. Only slight changes were made to fit the existing conditions. A 70 meg.[5] resistor was used as the grid bias resistor. The voltages used on the 959 tube were filament .65 volts, plate and screen 6 volts each. After the installation was completed the circuit

---

[1] J. Opt. Soc. of Am. V 37, p 420 (1947)
[2] RCA Victor Division, Radio Corporation of America
[3] RSI V 18, p 18 (1947)
[4] RSI V 4, p 532 (1933)
[5] S. S. White Dental Mfg. Co.

the circuit was balanced as recommended by Dubridge and Brown[1]. In Figure 3, R_2 was set at 25 ohms, R_3 adjusted to give the desired filament voltage and R_4 the desired plate and screen voltage. R_7 decreased the scale reading by 5 times, R_8 adjusted the position of the galvanometer reading on its scale. The lead wire "A" was from the anode, No. 10, of the multiplier phototube. Lead "B", the return wire, to the d. c. power supply.

Submerged Electrodes and Controls:

The submerged electrodes, Figure 4, consisted of a short platinum wire and a longer one. When the system was turned on a sputtering glow appeared on the shorter electrode. The light from the short electrode is the light source that is used with the spectroscope. It is presumed that the light produced is from the burning of the oxygen and hydrogen generated by the alternating cycles of the a. c. used on the electrodes and the metallic ion being carried into the flame by the current.

The control to the electrodes was a resistor in series with it. Its purpose was to adjust the amperage drawn by the electrodes to the desired value.

---

[1] RSI V 4, p 532 (1933)

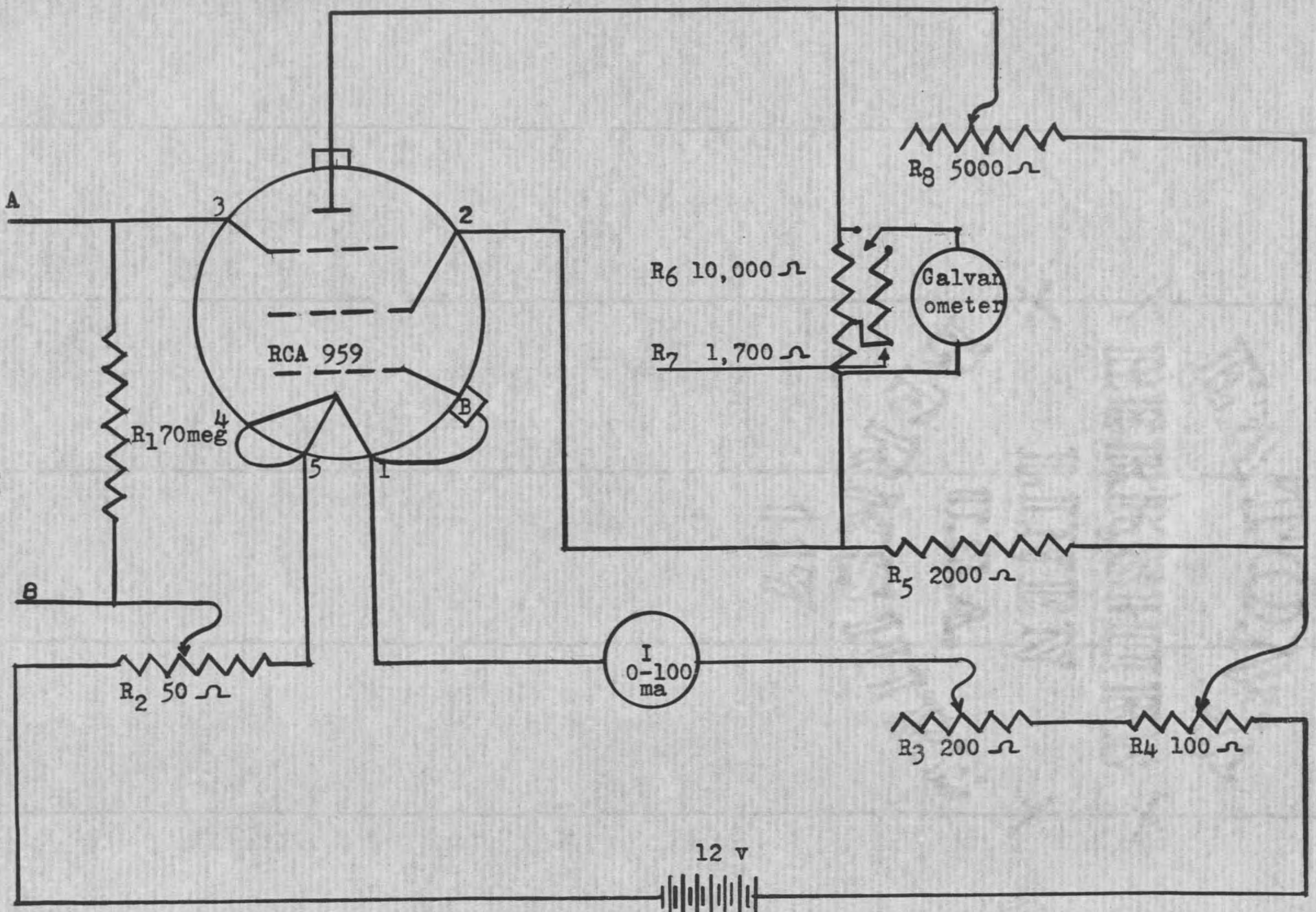


Figure 3

Amplifier, Multiplier Phototube to Galvanometer

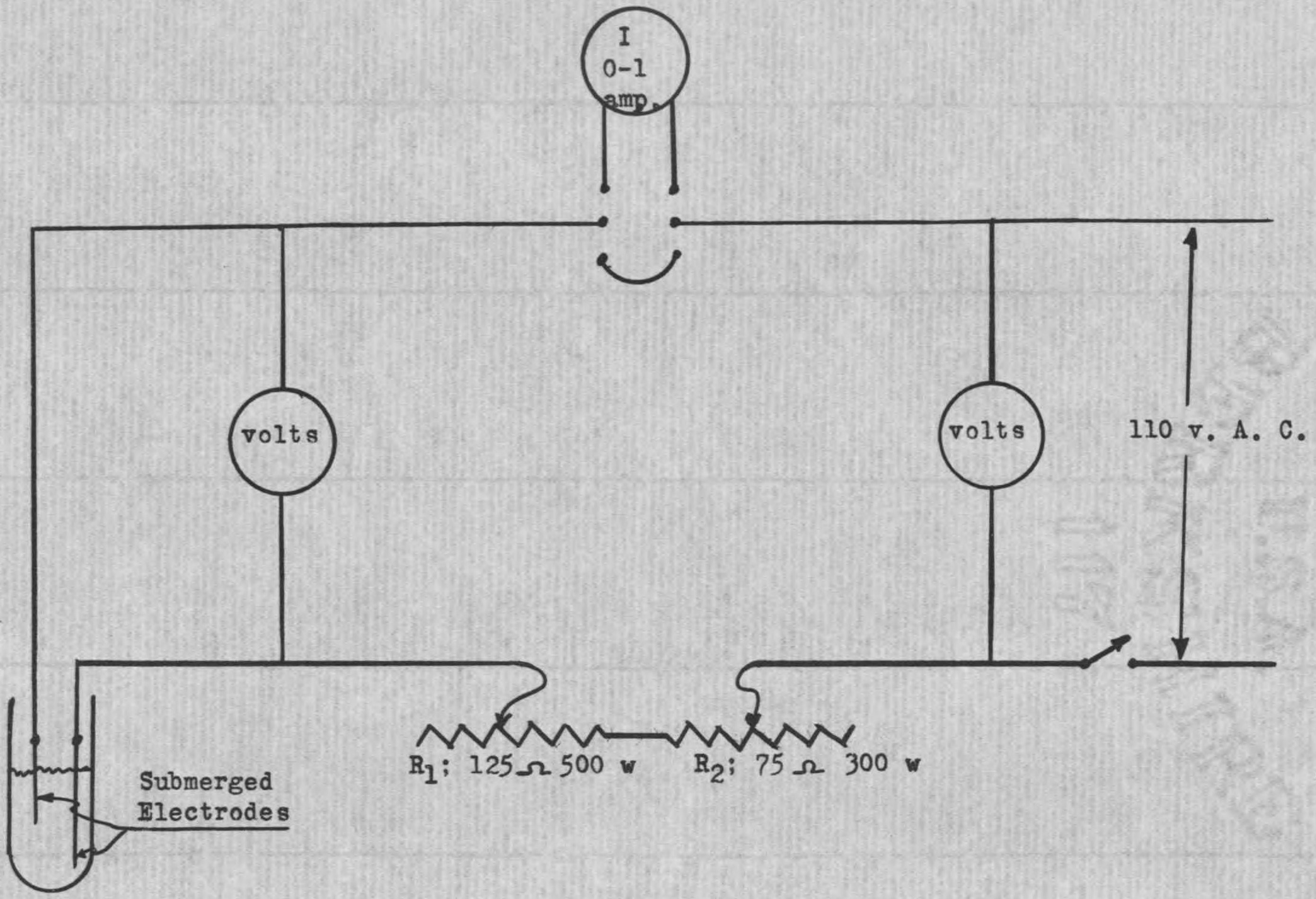


Figure 4

Submerged Electrodes and Controls

IV. EXPERIMENTAL PROCEDURES

The following conditions and procedures were followed for the various pieces of equipment for all tests that were made. They are not in chronological order.

1. All power used was drawn through the constant voltage transformer.
2. The amperage supplied to the bank of V. R. tubes of the d. c. power supply was 20 ma.
3. The voltages of the 959 tube were, filament .65 volts, plate and screen 6 volts each.
4. The resistance R_2, Figure 3, was set at one-half of its rated value.
5. The 12 volt battery was recharged after each 10-12 hours of use.
6. The d. c. power supply and amplifier were given a 3 hour warm up period before any tests were made.
7. The 959 tube was kept shielded from light and all pieces of equipment were grounded and shielded at all times.
8. Twenty ml of solution were used with the submerged electrode.
9. One cm of the short electrode was submerged when readings were being taken.
10. The temperature of the solution being tested must be allowed to reach equilibrium with the cooling water before any readings are taken.
11. The setting of the internal standard was 250 cm on the galvanometer scale. The amperage necessary to give this deflection was obtained by adjusting the resistance in series with the electrodes.
12. When igniting the electrode, the less the short electrode is submerged, the less the possibility of the burning off of the tip of the electrode.

As soon as possible after the electrode had been ignited, the electrode was submerged to the desired depth and the resistance in series with it was increased until the electrode had lost its red-hot color. The amperage to the electrode was later adjusted to the desired value after the light source had been placed in line with the optical system of the spectroscope.

13. The final test solutions were 4 N with respect to nitric acid.

14. The following lines were used in taking the readings:

Lithium	6708 A°	Cadmium	5086 A°
Copper	5218 A°	Zinc	4722 A°
Magnesium	5184 A°	Calcium	4228 A°

15. The continuous light spectrum, background light, produced by the hot electrode, was subtracted from the average maximum deflection of the galvanometer reading labelled "difference" in the tables.

16. In order to obtain the average maximum deflection reading of the galvanometer scale, it was necessary to consider the length of time the light beam from the galvanometer spent at a given setting, i. e. 10 seconds at 265 cm would be more important than .1 second at 270 cm. The sputtering of the electrode caused the galvanometer to be unstable.

17. The following standard solutions were made from the weighed-out stock solutions of .10 mg/ml: 5, .5, .05, 2, .2, .02, 1, .1 mg/ml of each element. The standard solutions were in turn used to make the following concentrations when made up with the 20 ml of the HNO_3 used on the electrodes: .5, .25, .1, .05, .025, .01 mg/ml of each element.

V. GENERAL CONSIDERATION OF THE DATA

In any 20 ml of solution the concentrations of the elements present were the same except for the internal standards which was .2 mg/ml in all cases, whereas the lithium of Tables II through V and the copper in Table XII, both of which were five times the concentration of the others. It was not possible to detect the lithium and copper in the same concentration as the other elements.

The graphs of the data were grouped. Figures 5 through 9 are those in which cadmium was used as the internal standard. Figures 10 through 13 are those with lithium as the internal standard. Each figure is a plot of a single element. The Roman numerals that identify each curve also represent the table from which the data for the curve was obtained. The legend on each graph gives first, the element used as the internal standard; second, the element plotted is underlined; third, any additional elements that were present in the same solution. The amperages appearing in Figure 14 were the amperages required by the internal standard in order to produce a deflection of 250 cm on the galvanometer scale.

TABLE I. Readings of Mg: Cd Internal Standard

Cd .2 mg/ml					Mg							
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
5	255	.32	95	45	.1	off scale						
5	255	.25	95	52	.05	75	245	170				
5	260	.27	96	45	.025	80	145	65				
10	260	.3	99	37	.01	95	120	25				

TABLE II. Readings of Li, Mg; Cd Internal Standard

Cd .2 mg/ml					Li				Mg			
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
0	250	.37	94	43	.5	off scale			.1	off scale		
0	250	.29	95	48	.25	30	275	245	.5	70	275	205
0	250	.29	95	45	.1	35	140	105	.025	75	160	85
0	260	.27	98	45	.05	35	95	55	.01	75	100	25

TABLE III.* Readings of Li, Mg, Cu; Cd Internal Standard

Cd .2 mg/ml					Li				Mg			
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
0	250	.40	94	44	.5	15	190	175	.1	off scale		
0	250	.32	94	47	.25	25	220	195	.05	65	280	215
10	260	.29	95	47	.1	40	115	75	.025	70	150	80
4	255	.28	98	40	.05	37	95	58	.01	80	135	55

* Continued on next page

TABLE IV.* Readings of Li, Mg, Zn, Ca; Cd Internal Standard

Cd .2 mg/ml					Li				Mg			
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
0	250	.43	96	36	.5	20	200	180	.1	off scale		
3	250	.33	94	49	.25	25	200	175	.05	65	290	225
0	250	.29	96	47	.1	25	120	95	.025	70	180	110
0	250	.24	96	47	.05	30	85	55	.01	70	100	30

*Continued on next page

TABLE III. Continued

Ca											
mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
.1	5	120	115								
.05	6	43	37								
.025	8	30	22								
.01	20	30	10								

TABLE IV. Continued

Zn				Ca							
mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
.1	70	170	100	.1	10	180	170				
.05	45	110	65	.05	10	65	55				
.025	55	85	30	.025	14	35	21				
.01			4	.01	12	18	6				

TABLE V.* Readings of Li, Cu, Mg, Zn, Ca; Cd Internal Standard

Cd .2 mg/ml					Li				Cu			
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
0	250	.5	100	24	.5	60	190	130	.1	70	150	80
10	260	.32	97	62	.25	40	190	150	.05	85	120	35
3	250	.28	94	53	.1	34	125	91	.025	78	110	32
5	250	.29	95	46	.05	40	95	55	.01	84	112	28

*Continued on next page

TABLE VI. Readings of Mg, Ca; Cd Internal Standard

Cd .2 mg/ml					Mg				Ca			
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
0	250	.26	91	63	.1	off scale			.1	8	105	97
6	255	.25	94	57	.05	65	250	185	.05	15	58	43
5	255	.24	96	52	.025	65	155	90	.025	15	30	15
5	255	.26	98	44	.01	78	115	37	.01	15	25	10

TABLE V. Continued

Mg				Zn				Ca			
mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
.1	off scale			.1	40	235	195	.1	5	270	265
.05	80	320	240	.05	55	125	70	.05	20	78	58
.025	85	178	93	.025	52	85	33	.025	15	34	19
.01	84	116	32	.01	65	74	16	.01	27	33	6

mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference

TABLE VII.* Readings of Mg, Zn, Ca; Cd Internal Standard

Cd .2 mg/ml					Mg				Zn			
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
0	250	.41	89	53	.1	off scale			.1	20	190	170
5	255	.32	90	57	.05	65	290	225	.05	40	112	72
5	255	.27	96	47	.025	70	160	90	.025	55	70	15
5	250	.27	96	49	.01	70	100	30	.01	45	65	25

*Continued on next page

TABLE VIII.* Readings of Cu, Mg, Zn, Ca; Cd Internal Standard

Cd .2 mg/ml					Cu				Mg			
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
5	255	.36	89	57	.1	45	75	30	.1	off scale		
5	255	.34	91	53	.05	65	95	30	.05	60	285	225
0	250	.31	95	46	.025	70	105	35	.025	70	155	85
5	260	.31	96	43	.01	85	110	25	.01	75	105	30

*Continued on next page

TABLE VII. Continued

Ca											
mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
.1	5	90	85								
.05	14	38	24								
.025	17	35	18								
.01	5	14	9								

TABLE VIII. Continued

Zn				Ca							
mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
.1	30	215	185	.1	7	130	123				
.05	45	120	75	.05	10	40	30				
.025	48	80	32	.025	5	25	20				
.01	60	70	10	.01	14	20	6				

TABLE IX. Readings of Mg; Li Internal Standard

Li .2 mg/ml					Mg							
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
12	270	.36	99	35	.1	off scale						
5	255	.3	101	28	.05	80	215	135				
5	260	.27	101	24	.025	90	130	40				
10	260	.24	101	93	.01	80	80	0				

TABLE X. Readings of Ca; Li Internal Standard

Li .2 mg/ml					Ca							
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
0	250	.34	102	25	.1	50	220	170				
0	250	.32	102	27	.05	16	78	62				
5	255	.23	101	37	.025	20	37	17				
3	255	.25	101	35	.01	12	20	8				

TABLE XI. Reading of Zn; Li Internal Standard

Li .2 mg/ml					Zn							
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
0	250	.34	98	37	.1	72	250	178				
4	255	.28	99	31	.05	75	150	75				
8	260	.22	100	43	.025	70	88	18				
10	250	.24	101	37	.01	80	85	5				

TABLE XII. Reading of Cu; Li Internal Standard

Li .2 mg/ml					Cu							
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
0	250	.29	97	45	.5	50	145	95				
5	255	.31	100	31	.25	75	145	70				
0	250	.29	100	35	.1	80	120	40				
5	260	.26	100	37	.05	75	115	40				

TABLE XIII. Readings of Mg, Ca; Li Internal Standard

q	Li .2 mg/ml				Mg				Ca			
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
10	260	.52	100	24	.1	off scale			.1	22	180	150
10	260	.37	100	32	.05	85	215	130	.05	20	70	50
10	260	.33	101	30	.025	75	140	65	.025	15	48	33
2	255	.33	101	26	.01	80	90	10	.01	11	18	7

TABLE XIV.* Readings of Mg, Zn, Ca; Li Internal Standard

Li .2 mg/ml					Mg				Zn			
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
5	255	.5	99	29	.1	off scale			.1	off scale		
8	260	.36	99	30	.05	90	305	215	.05	55	175	120
0	250	.31	100	22	.025	80	165	85	.025	55	85	30
3	255	.36	100	27	.01	75	105	30	.01	55	68	13

*Continued on next page

mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference

TABLE XIV. Continued

Ca											
mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
.1	20	240	220								
.05	15	80	65								
.025	10	42	32								
.01	11	20	9								

TABLE XV.* Readings of Cu, Mg, Zn, Ca; Li Internal Standard

Li .2 mg/ml					Cu				Mg			
Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
0	250	.41	97	30	.1	110	200	90	.1	off scale		
0	250	.33	99	37	.05	110	155	45	.05	115	315	200
0	250	.24	100	39	.025	90	128	38	.025	80	185	105
5	260	.25	101	34	.01	85	105	20	.01	80	104	24

*Continued on next page

Galvanometer Zero	Average Maximum Deflection	Amperage Applied to Electrodes	Voltage Across Electrodes	Ohms in Series with Electrodes	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference

TABLE XV. Continued

Zn				Ca							
mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference
.1	off scale			.1	11	270	259				
.05	68	170	102	.05	10	95	85				
.025	60	120	60	.025	10	50	40				
.01	63	80	17	.01	17	33	16				

mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference	mg/ml	Background Light	Average Maximum Deflection	Difference

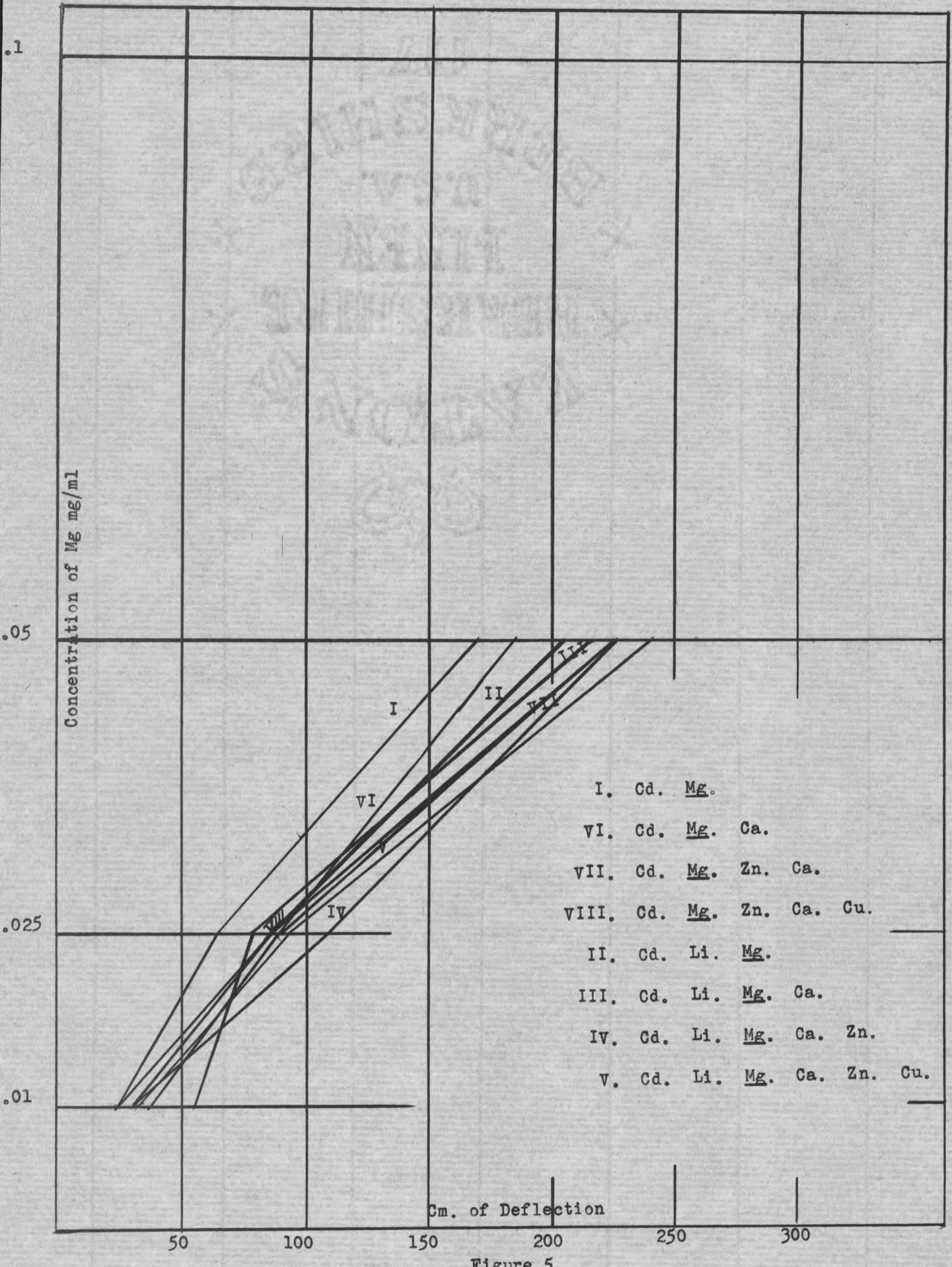

.1
.05
.025
.01
Concentration of Mg mg/ml
50
100
150
200
250
300
Cm. of Deflection
I
II
III
IV
V
VI
VII
VIII
I. Cd. Mg.
VI. Cd. Mg. Ca.
VII. Cd. Mg. Zn. Ca.
VIII. Cd. Mg. Zn. Ca. Cu.
II. Cd. Li. Mg.
III. Cd. Li. Mg. Ca.
IV. Cd. Li. Mg. Ca. Zn.
V. Cd. Li. Mg. Ca. Zn. Cu.

Figure 5

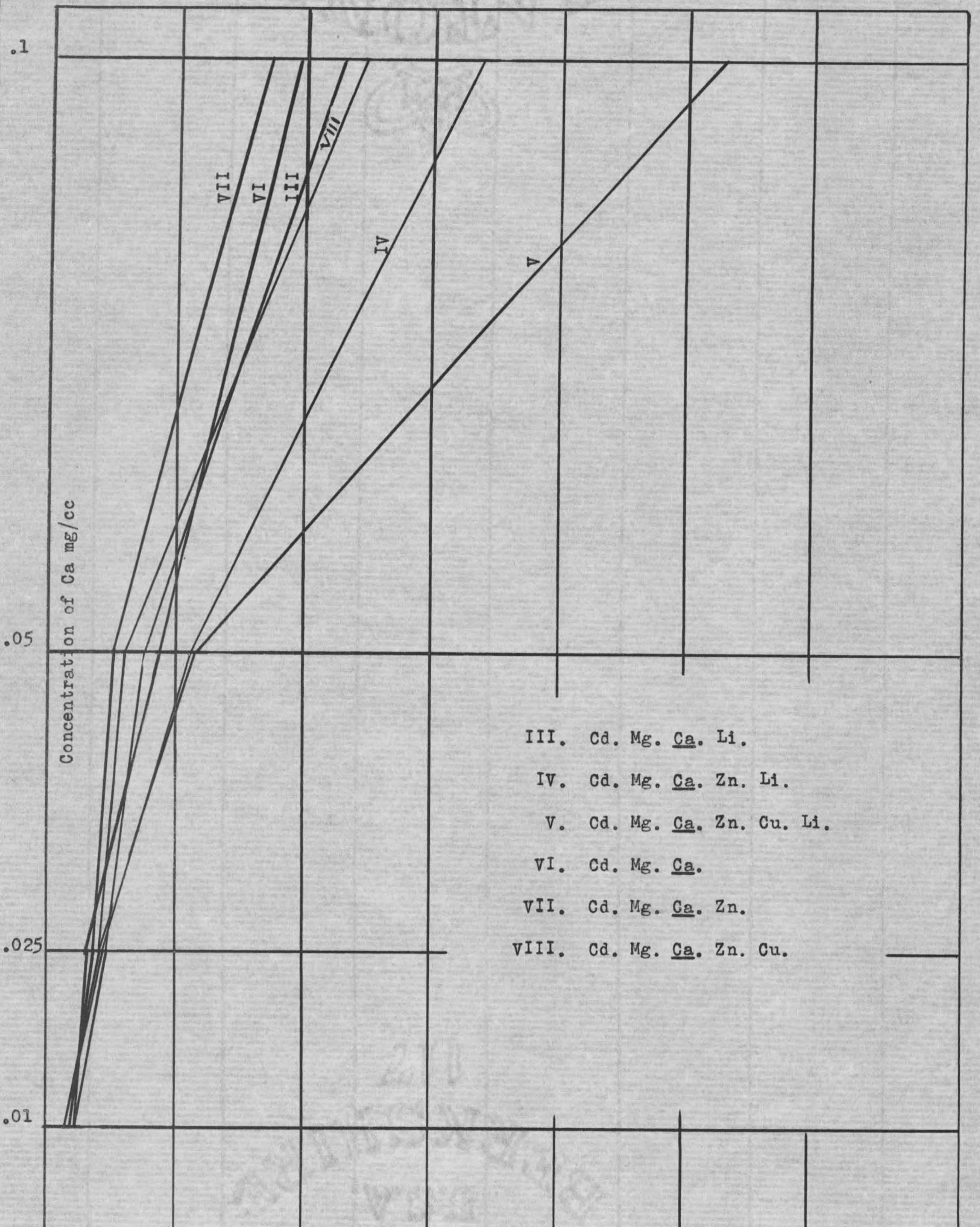

.1
.05
.025
.01
Concentration of Ca mg/cc
Cm. of Deflection
50
100
150
200
250
300
VII
VI
III
VIII
IV
V
III. Cd. Mg. Ca. Li.
IV. Cd. Mg. Ca. Zn. Li.
V. Cd. Mg. Ca. Zn. Cu. Li.
VI. Cd. Mg. Ca.
VII. Cd. Mg. Ca. Zn.
VIII. Cd. Mg. Ca. Zn. Cu.

Figure 6

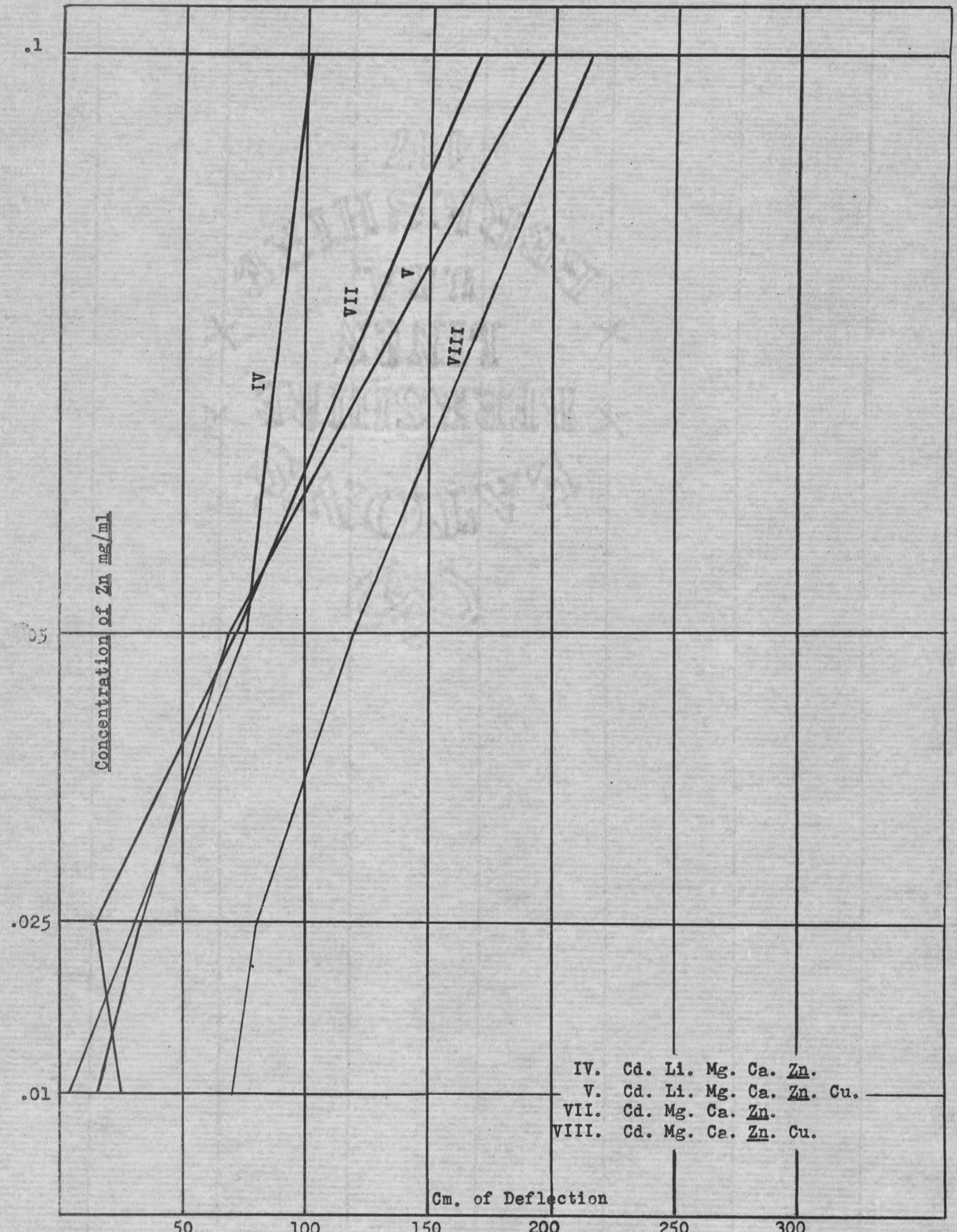

.1
.05
.025
.01
Concentration of Zn mg/ml
IV
V
VII
VIII
IV. Cd. Li. Mg. Ca. Zn.
V. Cd. Li. Mg. Ca. Zn. Cu.
VII. Cd. Mg. Ca. Zn.
VIII. Cd. Mg. Ca. Zn. Cu.
Cm. of Deflection
50
100
150
200
250
300

Figure 7

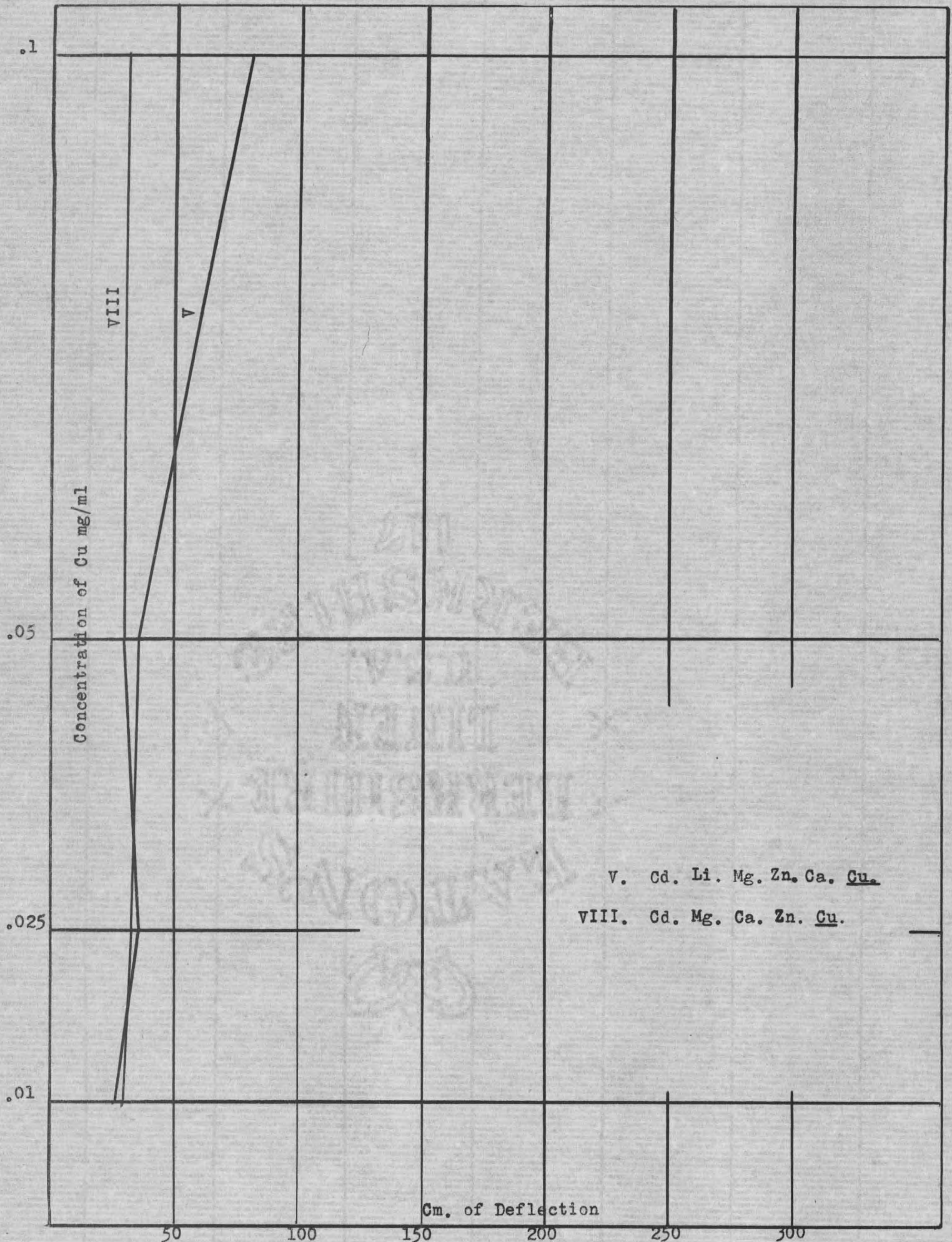

.1
.05
.025
.01
Concentration of Cu mg/ml
VIII
V
V. Cd. Li. Mg. Zn. Ca. Cu.
VIII. Cd. Mg. Ca. Zn. Cu.
Cm. of Deflection
50
100
150
200
250
300

Figure 8

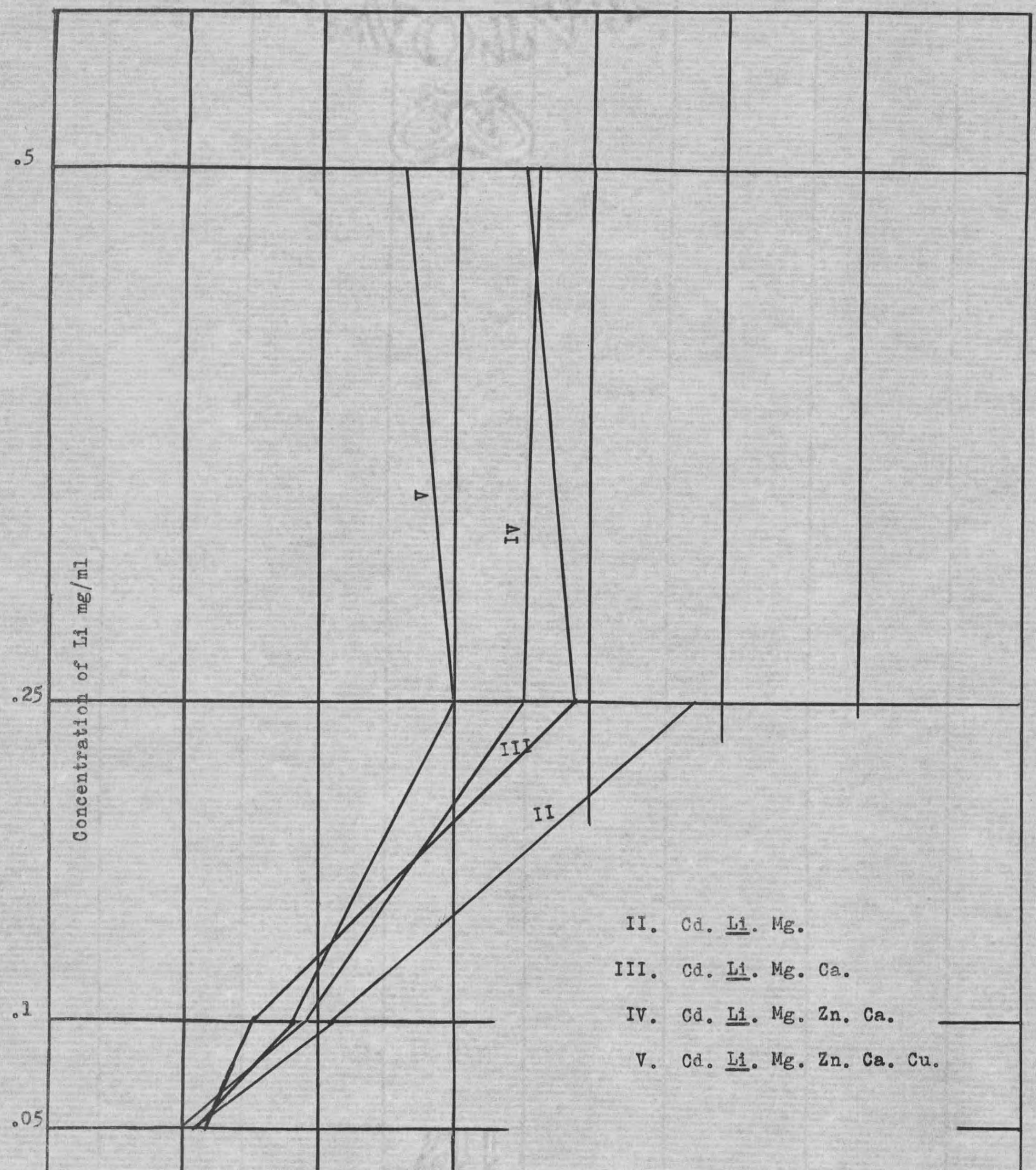

.5
.25
.1
.05
0
Concentration of Li mg/ml
V
IV
III
II
II. Cd. Li. Mg.
III. Cd. Li. Mg. Ca.
IV. Cd. Li. Mg. Zn. Ca.
V. Cd. Li. Mg. Zn. Ca. Cu.
Cm. of Deflection
50
100
150
200
250
300

Figure 9

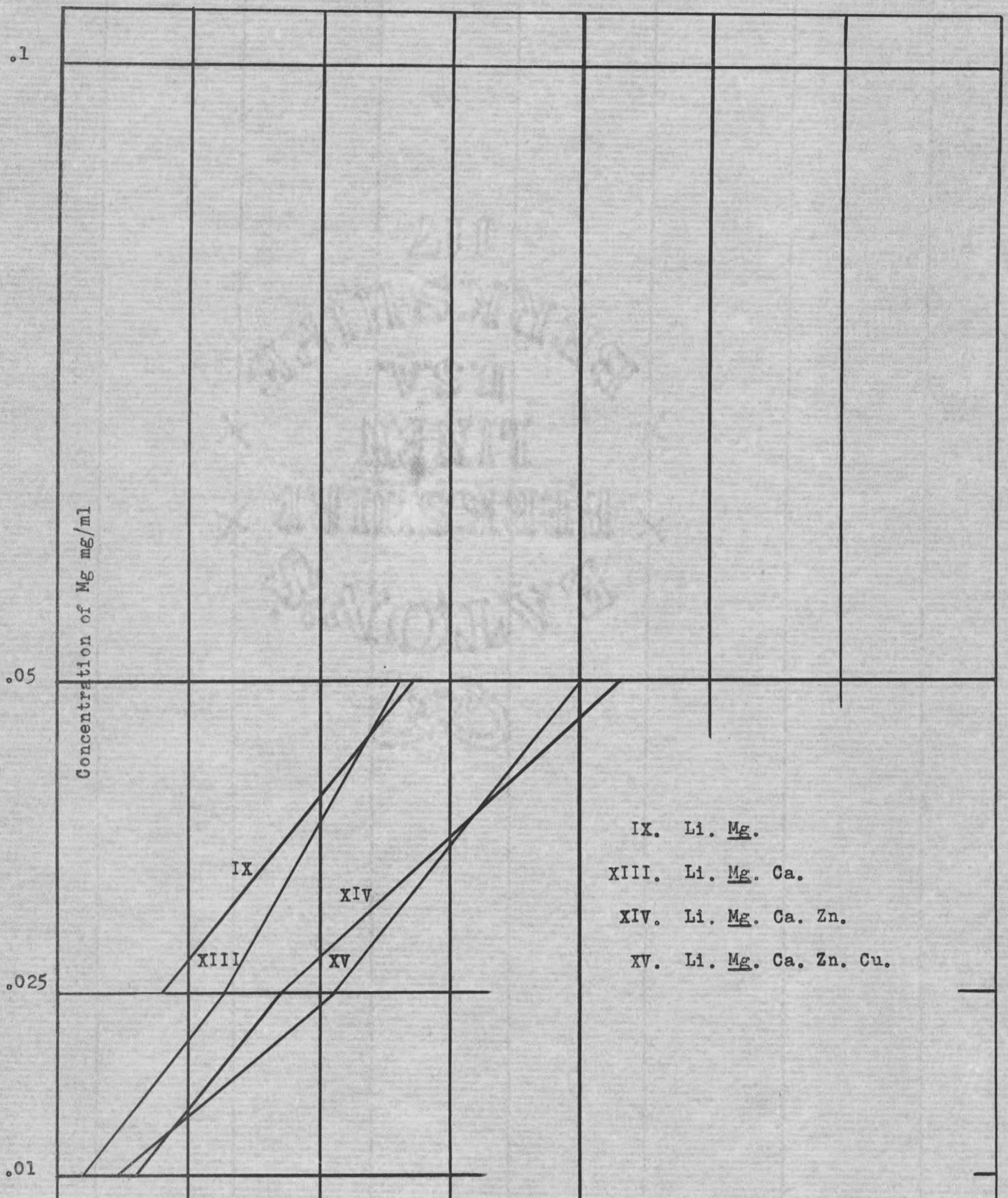

.1
.05
.025
.01
Concentration of Mg mg/ml
IX
XIII
XIV
XV
IX. Li. Mg.
XIII. Li. Mg. Ca.
XIV. Li. Mg. Ca. Zn.
XV. Li. Mg. Ca. Zn. Cu.
Cm. of Deflection
50
100
150
200
250
300

Figure 10

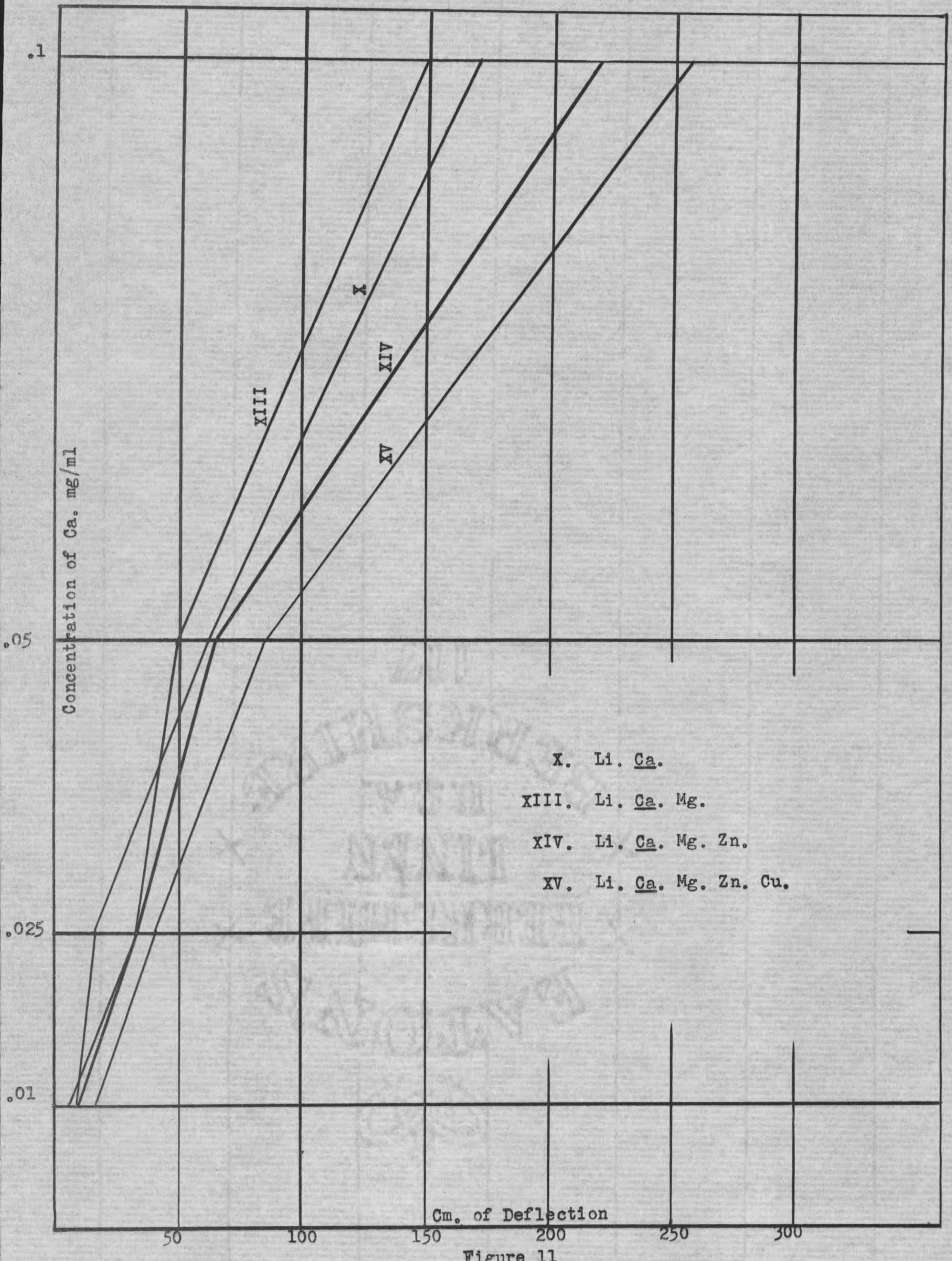

.1
.05
.025
.01
Concentration of Ca. mg/ml
Cm. of Deflection
50
100
150
200
250
300
XIII
X
XIV
XV
X. Li. Ca.
XIII. Li. Ca. Mg.
XIV. Li. Ca. Mg. Zn.
XV. Li. Ca. Mg. Zn. Cu.

Figure 11

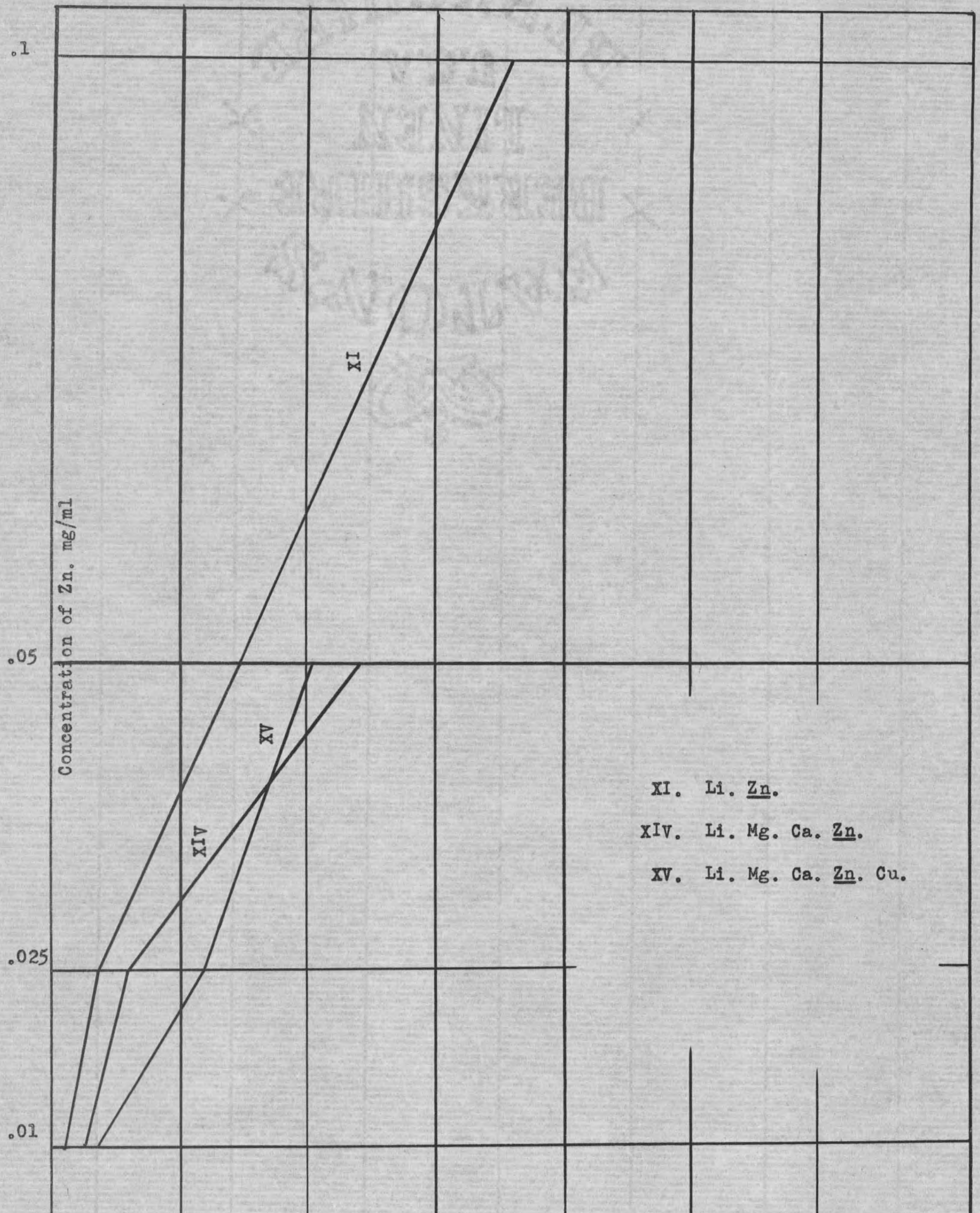

.1
.05
.025
.01
Concentration of Zn. mg/ml
50
100
150
200
250
300
Cm. of Deflection
XI
XV
XIV
XI. Li. Zn.
XIV. Li. Mg. Ca. Zn.
XV. Li. Mg. Ca. Zn. Cu.

Figure 12

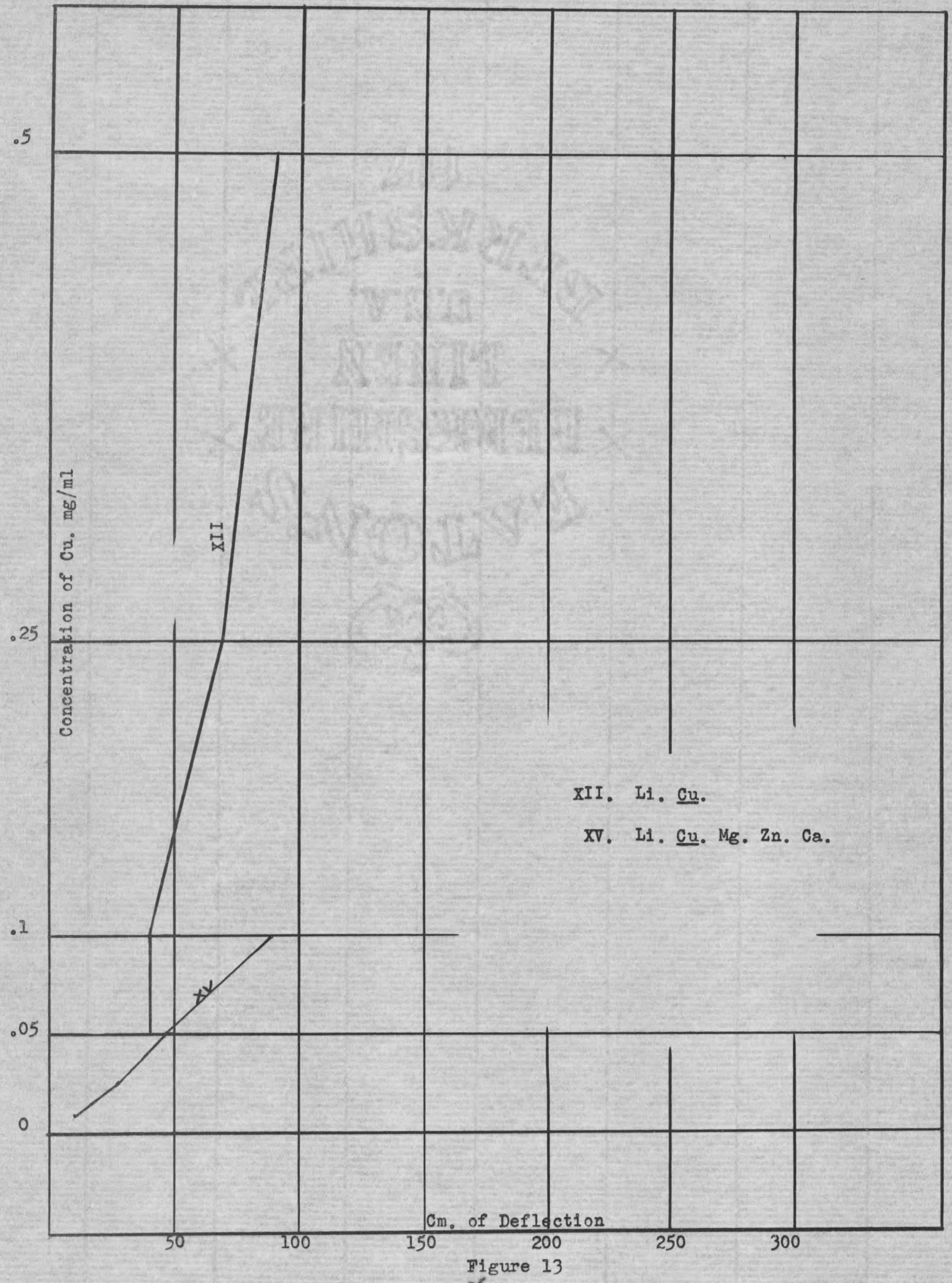

.5
.25
.1
.05
0
Concentration of Cu. mg/ml
XII
XV
XII. Li. Cu.
XV. Li. Cu. Mg. Zn. Ca.
Cm. of Deflection
50
100
150
200
250
300

Figure 13

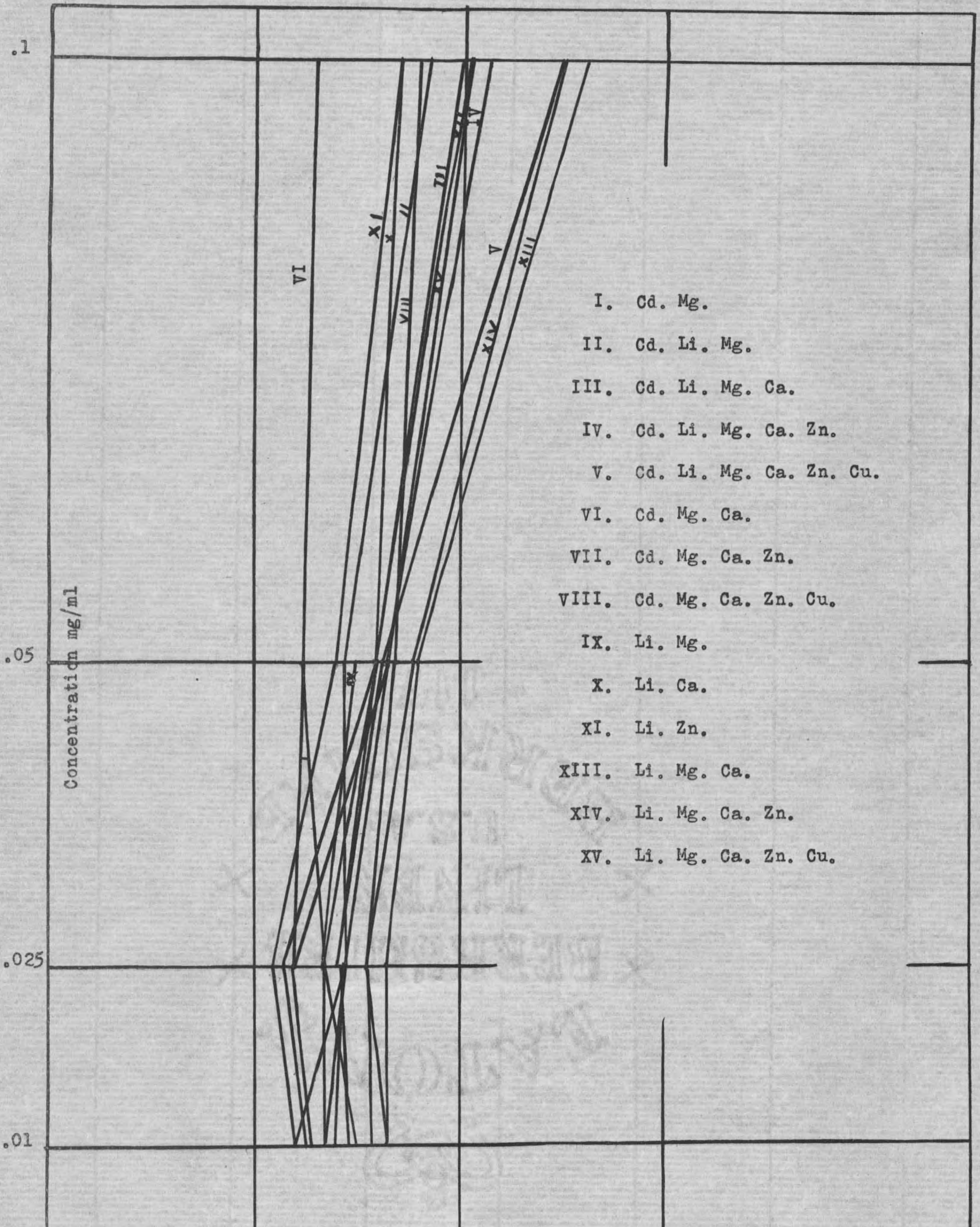

.1
.05
.025
.01
Concentration mg/ml
0
.1
.2
.3
.4
.5
.6
Amps.
VI
XI
X
II
VIII
VII
IV
III
V
XIII
XIV
IX
I. Cd. Mg.
II. Cd. Li. Mg.
III. Cd. Li. Mg. Ca.
IV. Cd. Li. Mg. Ca. Zn.
V. Cd. Li. Mg. Ca. Zn. Cu.
VI. Cd. Mg. Ca.
VII. Cd. Mg. Ca. Zn.
VIII. Cd. Mg. Ca. Zn. Cu.
IX. Li. Mg.
X. Li. Ca.
XI. Li. Zn.
XIII. Li. Mg. Ca.
XIV. Li. Mg. Ca. Zn.
XV. Li. Mg. Ca. Zn. Cu.

Figure 14

VII. DISCUSSION

The data of Tables IX through XV were obtained first. In general analytical procedures lithium is not encountered and for this reason it was chosen for the internal standard. In choosing the internal standard method as a basis of comparison, it was hoped that by adjusting the electrode system to produce a constant intensity of light that the energy carried by other elements would be compensated for and a single curve obtained; i. e., the addition of Mg, Zn and Cu, curves XIII, XIV and XV, Figure 11, to the Li-Ca solution, curve X, would possibly have produced identical curves within experimental error. The curves obtained from the plotting of the calcium data, Figure 11, will illustrate what was found to take place. There is, undoubtedly, some experimental error present but it could in no way account for the results. At the .05 mg/ml concentration of Ca, curve X, a deflection of 62 cm was obtained. The addition of .05 mg/ml of Mg resulted in only a deflection of 50 cm. In other words, the addition of Mg decreased the intensity of light produced by the calcium or increased the light produced by the lithium. From Figure 14, it can be seen that the amperage needed to produce the 62 cm deflection of calcium was .32 amps. The amperage required to produce the 50 cm deflection in the presence of Mg was .37 amps.

To have to increase the current in order to get the same amount of light from the internal standard, as more ions are added, to the solution could be expected. In curve XIV, Zn had been added to the Li-Ca-Mg solution. At the concentration of .05 mg/ml of Ca, a deflection of 65 cm was obtained, an increase of 15 cm in deflection when Zn was added. At the

.1 mg/ml concentration of Ca, the difference between curves XIII and XIV is an increase in deflection of 70 cm. From Figure 14, curve XIV shows less amperage used - .01 amp. less - than curve XIII at the .05 mg/ml of Ca. At the .01 mg/ml of Ca the curve XIII required .02 amp. more than the curve XIV. Curve XV is an additional increase in deflection of 20 cm at the .05 mg/ml of Ca and also an additional increase at the .1 mg/ml of Ca of 49 cm. The amperage used to produce the deflections of curve XV was .03 amp. less at the .05 mg/ml of Ca and .09 amp. less at the .1 mg/ml of Ca.

An examination of the Mg curves, Figure 10, that was added to the Ca of Figure 11 shows a very similar behavior to the Ca of Figure 11. As more elements are added to the solution the amount of deflection is increased, i. e., the Mg ions result in the production of more light. The crossing over of curves XIV and XV of Figure 10 does not readily lend itself to an explanation. The same crossing over occurs on Figure 12, curves XIV and XV, which is the graph of Zn. In general, the same shifting occurs in Figure 12.

The curves of Cu, Figure 13, are of two widely differing concentrations and consequently do not lend themselves to a great deal of interpretation. The fact that they represent data of such widely differing concentrations may point to a need of getting more conclusive data. Some of the erratic character of the other curves may be due to their being plotted on such a large scale. Any slight error would be greatly magnified. It is desirable to obtain data that would cover a much wider range of concentrations before any definite conclusions are drawn.

In general, to summarize the preceding Figures 10, 11, 12, 13, the increase in number of elements present increases the sensitivity (cm of deflection) of all elements present. The current needed to produce this increase in sensitivity decreases as more elements are added. If the presence of the added elements had carried more of the current which had originally been used by the internal standard, it would seem logical that it should have been necessary to increase the current supplied to the electrode in order to re-establish the desired intensity of the internal standard. Since the current used was actually less as more elements were added, some other explanation is necessary. An explanation of how one element could act upon another to cause them both to produce more light for an emission spectra could not be found. However, a study of the nature of the light source may possibly reveal an explanation.

The data summarized in the curves produced from Tables IX through XV indicated that part of the irregularities could be due to the presence of the lithium. As a result, cadmium was chosen as the next internal standard and lithium was used as an additional element along with Mg, Ca, Zn and Cu. Curves II, III, IV and V, Figure 9, are the plots of Li, as the additional elements were added. It is easily seen that as the number of elements in the solution increased, the intensity of the Li decreased. The fact that the Li values seemed to approach a constant value of deflection was probably due to the spectral response of the multiplier phototube. An examination of Figure 14 will show that an <u>increase</u> in amperage was required to produce the desired spectral intensity of the internal standard as the number of elements in the solution increased. This is a contradiction of the results obtained from data of Tables IX through XV. An examination of curves II, III, IV and V of Figures 5, 6, 7 and 8 shows an increase in sensitivity of the elements Mg, Ca, Zn and Cu as each of these additional elements was added to the solution.

A review of the results of these two groups of data will show that with Li as the internal standard, the addition of different elements to the solution, causes an increase in sensitivity of all the elements present. The amperage needed to produce this increase in sensitivity <u>decreases</u> as more elements are added. With cadmium as the internal standard, the sensitivity of the elements present is again increased as more elements are added, but in this case the amperage required to produce the normal internal standard had been increased. While the Mg, Ca, Zn and Cu were increasing in intensity, the intensity of the Li was decreasing as the number of elements in the solution increased.

In order to gain further information on what the effect of Li might be, the data in Tables I, VI, VII and VIII were obtained. In these tables the elements present are the same as in Tables II, III, IV and V except that Li is absent in all cases. In the data shown, the amperages are seen to increase as the number of elements in the solution was increased, and the increase in the intensity of the light produced, as more elements were added, was not nearly so great as it was when Li was present.

VIII. SUMMARY

1. The light source was more than adequate for the spectroscope available for this investigation.
2. The lower limits of detection was limited by the background light produced by the submerged electrode. Further experimentation could probably reduce this limiting factor.
3. When lithium is used as the internal standard, the addition of the elements studied, and increasing their concentration, increases the sensitivity of all elements present.
4. If cadmium is used as the internal standard, the sensitivity of lithium decreases with addition of the elements studied and with their increasing concentration. If lithium is not present the increase in sensitivity of the elements studied is not nearly so great.
5. With a single element in a solution, its concentration could be readily determined from a known concentration curve.
6. From the behavior of the elements studied, it is thought that due to the shifting of the curves caused by the additional elements, a group of unknowns from closely related sources, having the same elements present, could be analyzed quantitatively by this method. Each group of unknowns would probably need a different set of known curves.
7. It is apparent from the curves presented in this work that each element has a characteristic curve.

IX. ACKNOWLEDGMENT

The author wishes to acknowledge the valuable assistance given throughout this investigation by Dr. R. Woodriff. He also wishes to thank the Research Corporation of New York for making this investigation possible through a grant.