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**INTERFERING IONS IN THE FLAME PHOTOMETRIC
DETERMINATION OF CERTAIN CATIONS**

by

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B. S., University of Notre Dame, 1947

**Presented in partial fulfillment
of the requirements for the degree of
Master of Arts**

MONTANA STATE UNIVERSITY

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TABLE OF CONTENTS

| | Page |
|---------------------------------------|------|
| INTRODUCTION | 1 |
| Chapter | |
| I. STATEMENT OF PROBLEM | 4 |
| II. DISCUSSION OF PROCEDURE | 6 |
| III. EXPERIMENTAL | 9 |
| IV. SUMMARY | 33 |
| BIBLIOGRAPHY | 36 |

INTRODUCTION

The development of the flame photometric method for the quantitative determination of metallic elements has been hindered greatly due to the interference in the flame intensity caused by the presence of extraneous cations and anions. For several years workers in this field have been aware of this interference. Not only have opinions been advanced as to the cause, but several techniques have been developed to minimize the error in the determinations of certain solutions.

Duffendack, Wiley, and Owens¹ made the general statement that the effect of one element on the determination of another is due to "changes in the characteristics of the solution, and changes in the nature of the vapor and in the interactions within the vapor." So that more accurate determinations could be made of a solution of cations, they proposed two methods. In the "method of excess," the interfering ion was added in excess since it was found that, above certain concentrations, small variations in the concentration of the interfering ion no longer affected the determination of a particular ion. And, in the "method of successive approximations," working curves for each element were developed with various concentrations of the interfering ions. From these working curves, successive approximations of the concentrations of the elements present could

be obtained until the desired degree of precision was reached.

In their work on developing a flame photometer, upon which the Model 18 Perkin-Elmer flame photometer is based, Berry, Chappell, and Barnes^{3,4} have projected from spectrography to flame photometry the use of the internal standard method. The principle of this method is that any factor which will cause a change in the intensity of the light transmitted by any one element will cause a similar change in the intensity of the element used as the internal standard. By the use of this method they were able to correct, to a certain degree, the errors in the absolute method due to detrimental effects which they said could be divided into at least four classes: effect of variation of gas pressure, effect of variation of air pressure, effect of foreign molecules and ions, and effect of viscosity of the sample.

Parks, Johnson, and Lykken⁵ pointed out possible contributing factors for the large errors found in the determination of sodium and potassium. Those suggested were: the shape and temperature of the flame cone, the size of the droplets of the mist entering the flame, the surface tension and viscosity of the solutions, and the complexing action of the ions on the alkali metal ions.

The use of "radiation buffers," as developed by West,

Folse, and Montgomery,⁶ is a procedure similar to the "method of excess."

A few of the observations recorded concerning errors caused by interfering ions are as follows: sulfuric, nitric, hydrochloric, and phosphoric acid, as well as ammonium chloride, sodium chloride, potassium chloride, magnesium sulfate, and cupric chloride, decrease the transmission of sodium and potassium;⁴ sulfuric, phosphoric, hydrochloric, oxalic, nitric, and boric acid, and most of the cations depress the readings of sodium and potassium.⁵ It was also reported that sulfate and chloride ion show little effect on sodium, potassium, and calcium; but sodium, potassium, and calcium enhance one another.^{2,6} Others report that neither calcium nor barium interfere with strontium but strontium interferes with calcium and calcium with barium and these interferences increase linearly with increasing concentration of the interfering ion.⁷

CHAPTER I

STATEMENT OF PROBLEM

Although considerable research has been done in the application of flame photometry to the rapid determination of metallic elements, apparently little progress has been made in explaining what actually takes place in the process of vaporizing the solution which would cause some ions to depress transmission readings and others to enhance the flame intensity. Perhaps the interfering ions cause a change in the physical characteristics of the solution and the flame, which would account for the errors in the flame intensity. However, one purpose of this study was to investigate the possibility of a correlation between the degree of interference and the chemical processes that could take place as the solution is passed through the flame. It was thought that with this knowledge it may be possible to predict what errors may be encountered if the chemical behavior of the constituents present were studied. Thus, determinations of mixtures could be made more accurately and perhaps more rapidly.

Because of the speed with which determinations can be made with the flame photometer, it would seem that this instrument would be extremely valuable in soils determinations. Therefore, it was a second purpose of this study to investigate the effect of certain ions commonly found in

soils on the flame photometric determination of calcium.
Particular emphasis was placed on the phosphates.

CHAPTER II

DISCUSSION OF PROCEDURE

I. INSTRUMENT USED.

All flame intensity data were obtained by the employment of a Model DU Beckman quartz spectrophotometer, with an acetylene flame attachment, Model 9200. Toward the end of the experimental work, a Beckman photomultiplier attachment, Model 4300, was used. During the earlier runs with the instrument, it was extremely difficult to obtain reproducible readings; but, after replacing the dry cell batteries, drying the desiccant within the instrument, disconnecting the charger from the storage battery while runs were being made, and replacing the atomizer-burner, the reproducibility of the readings was greatly improved. Through the use of the photomultiplier tube, slit widths could be reduced. This seemed to make the galvanometer needle much easier to read and to increase the reproducibility. All earlier data were checked using the photomultiplier.

II. PREPARATION OF SOLUTIONS.

(1) A stock solution of calcium chloride was prepared from reagent grade calcium carbonate. The sample of carbonate was heated for one hour at 100°C, accurately weighed, and treated with C. P. hydrochloric acid (37%). The excess acid was driven off and the calcium chloride was diluted to a concentration of 1000 p.p.m. of calcium.

(2) The following acids were used to furnish interfering ions: reagent grade phosphoric acid (86%), glacial acetic acid, perchloric acid (70%), sulfuric acid (96%), hydrochloric acid (37%), nitric acid (70%), and formic acid (88%).

(3) Reagent grade sodium chloride was used in making up solutions containing sodium.

The above solutions were stored in polyethylene bottles whenever there was a possibility of contamination from glass containers.

III. OPERATION OF INSTRUMENT.

The spectrophotometer was turned on and allowed to warm up for several minutes, up to an hour, until the dark current reading remained constant. Supplies of acetylene and oxygen were furnished in cylinders. Although some experimenting was done to observe the effect of a change of pressure of fuel and oxygen upon flame intensities, all the readings recorded herein were made at a pressure of 12 lbs. per sq. in. for oxygen and 3 lbs. per sq. in. for acetylene. These were the pressures recommended on the atomizer-burner.

During a particular run, a standard solution was set at a definite transmission reading. This setting was made roughly by adjusting the slit width and more accurately made by adjusting the sensitivity control knob. Frequently the transmission of this standard solution was checked. If

this reading seemed to vary at all, it was checked between each reading of the unknowns. Considerable difficulty was encountered at higher concentrations of calcium and phosphate, probably due to a "salting up effect," since the flame intensities continually decreased if the solution was allowed to enter the flame for a continued period of time. This difficulty was greatly reduced by cleaning the burner with dilute hydrochloric acid after each reading was made.

It was observed that an apparent mechanical defect in the selector switch of the instrument made it impossible to use the "check" position in setting the standard solution. The galvanometer needle would not return to the zero point after the selector switch had been changed from one position to any other.

IV. WAVE LENGTHS USED.

Except in certain cases, as are mentioned in Chapter III, the following wave lengths were used: calcium, 554 millimicrons; sodium, 589 millimicrons; and potassium, 404.6 millimicrons.

The wave length dial on the spectrophotometer was adjusted slightly at these wave lengths to give the maximum transmission.

CHAPTER III

EXPERIMENTAL

I. DETERMINING A CALCIUM WORKING CURVE.

Exact portions of the stock solution of calcium chloride were diluted with distilled water to give solutions whose concentrations were multiples of 10, ranging from 10 to 100 p.p.m. of calcium. The solution of 100 p.p.m. of calcium was used as the standard. Table I illustrates the consistency of readings observed for a particular run. In

TABLE I

| <u>Ca Conc.</u> <u>(P.P.M.)</u> | <u>Observed Readings</u> | <u>Corrected Readings</u> |
|------------------------------------|------------------------------|---------------------------|
| 10 | 15.8, 15.9, 15.8 | 10.3 |
| 20 | 25.0, 24.5, 24.2, 25.2, 25.1 | 19.6 |
| 30 | 35.0, 34.8, 34.6, 34.9, 34.6 | 29.1 |
| 40 | 44.9, 44.8, 44.8 | 39.3 |
| 50 | 53.7, 54.8, 54.9 | 49.4 |
| 60 | 65.7, 65.9, 65.0, 65.1, 65.1 | 59.6 |
| 70 | 75.5, 74.5, 75.5, 75.2, 75.2 | 69.7 |
| 80 | 85.5, 86.5, 85.8, 85.8 | 80.3 |
| 90 | 96.5, 95.0, 95.1 | 89.6 |
| 100 | 105.5 (set) | 100.0 |

order that concentrations of calcium would be read directly, the standard solution was set to read 100% plus the transmission of the background when distilled water was sent through the atomizer. In this particular case, the slit width was set at 0.86 mm. and a wave length of 622 millimicrons was used. For this instrument setting, the background gave a reading of 5.5% and the standard read 105.5%.

Separate readings were taken for each solution until the variation from the previous reading was not more than 0.1%. The column "corrected readings" was obtained by subtracting 5.5 from the most consistent observed reading.

It is seen that the data in Table I would represent a nearly linear curve (slightly concave upward). The above readings were made without use of the photomultiplier tube; but, after this attachment was received, a check was made on the same solutions. Table II shows the results of this check. With the increased sensitivity, it was possible to reduce the slit width to 0.03 mm. A wave length of 554 millimicrons was used. The distilled water background read 5.0%.

TABLE II

| <u>Ca Conc.</u> <u>(P.P.M.)</u> | <u>Observed Readings</u> | <u>Corrected Readings</u> |
|------------------------------------|--------------------------|---------------------------|
| 10 | 15.0, 15.0, 15.0 | 10.0 |
| 30 | 34.5, 34.5, 34.5 | 29.5 |
| 50 | 54.5, 54.5, 54.6 | 49.5 |
| 70 | 74.5, 75.3, 74.5 | 69.5 |
| 90 | 95.3, 95.5, 95.5 | 90.5 |
| 100 | 105.0 (set) | 100.0 |

The data in the two tables compare very favorably. A graphic representation of a calcium working curve is shown in Figure 1. Data for this curve was obtained before the photomultiplier tube was used at a wave length of 554 millimicrons. A slit width of 0.418 mm. was required and

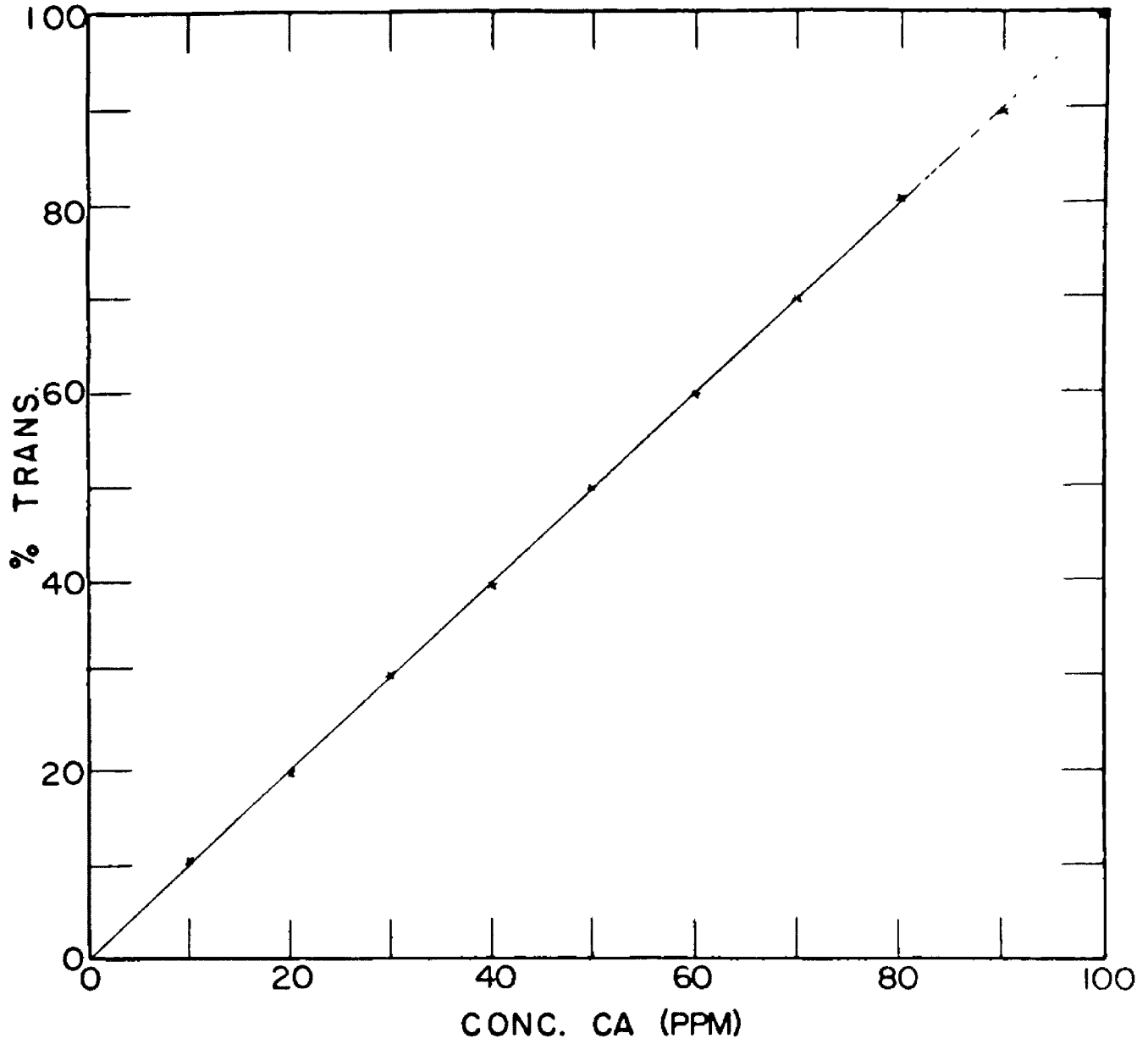


FIGURE 1

FLAME INTENSITY OF CALCIUM SOLUTIONS

at this setting the background reading was 9.5%. From a consideration of the readings in Table II, it is seen that the photomultiplier tube has improved the reproducibility.

II. THE EFFECT OF H_3PO_4 ON CALCIUM.

In order to determine the effect of the phosphate ion on various concentrations of calcium, a series of solutions was prepared in which the calcium concentrations varied from 50 to 200 p.p.m., and the ratio of the moles of H_3PO_4 to the moles of calcium varied from 0 to 52.0. In making transmission readings of these solutions, the solution of 100 p.p.m. of calcium with no phosphate was used as the standard and was set at a transmission of 50.0%. The average readings for one particular concentration of calcium are shown in Table III. No effort was made to correct the readings for the background intensity. A check was

TABLE III

| <u>Ca Conc.</u> <u>(P.P.M.)</u> | <u>Mole Ratio</u> <u>H_3PO_4/Ca</u> | <u>Observed</u> <u>Reading</u> |
|------------------------------------|---|-----------------------------------|
| 125 | 0.00 | 62.3 |
| " | 0.26 | 51.3 |
| " | 0.52 | 41.2 |
| " | 0.78 | 35.3 |
| " | 1.04 | 31.3 |
| " | 1.30 | 28.3 |
| " | 2.60 | 27.0 |
| " | 5.20 | 27.1 |
| " | 52.0 | 33.6 |

made on these readings using the photomultiplier. The slit

width was again reduced to 0.022 mm. and distilled water gave a background intensity of 2.0. Table IV shows the results of this check on the solutions of Table III. It is seen that, although the general effect of the increased phosphate concentration is the same as that recorded without the use of the photomultiplier tube, the transmission is less.

TABLE IV

| <u>Mole Ratio</u> <u>H₃PO₄/Ca</u> | <u>Observed Readings</u> | <u>Corrected Reading</u> |
|--|--------------------------|--------------------------|
| 0.00 | 65.0, 65.0, 65.1 | 63.0 |
| 0.26 | 53.5, 53.5, 53.5 | 51.5 |
| 0.52 | 41.2, 41.3, 41.2 | 39.2 |
| 0.78 | 34.8, 34.1, 34.6 | 32.6 |
| 1.04 | 30.6, 30.4, 31.2, 30.8 | 28.8 |
| 1.30 | 27.7, 27.1, 28.0, 27.8 | 25.8 |
| 2.60 | 24.9, 24.9 | 22.9 |
| 5.20 | 24.8, 24.8 | 22.8 |
| 52.0 | 29.1, 29.2 | 27.2 |

From the graphical representation of the work done on calcium and phosphate solutions, Figure 2, it is apparent that there is a considerable range in concentration of phosphate over which the depressive effect on the calcium transmission remains nearly constant. Also, on a larger scale graph, it appears that these curves are not smooth. A break seems to occur at a mole ratio of H₃PO₄ to calcium of approximately 0.6 and another break appears at a ratio of about 1.2. Unfortunately, the error involved in making the transmission readings without the photomultiplier tube

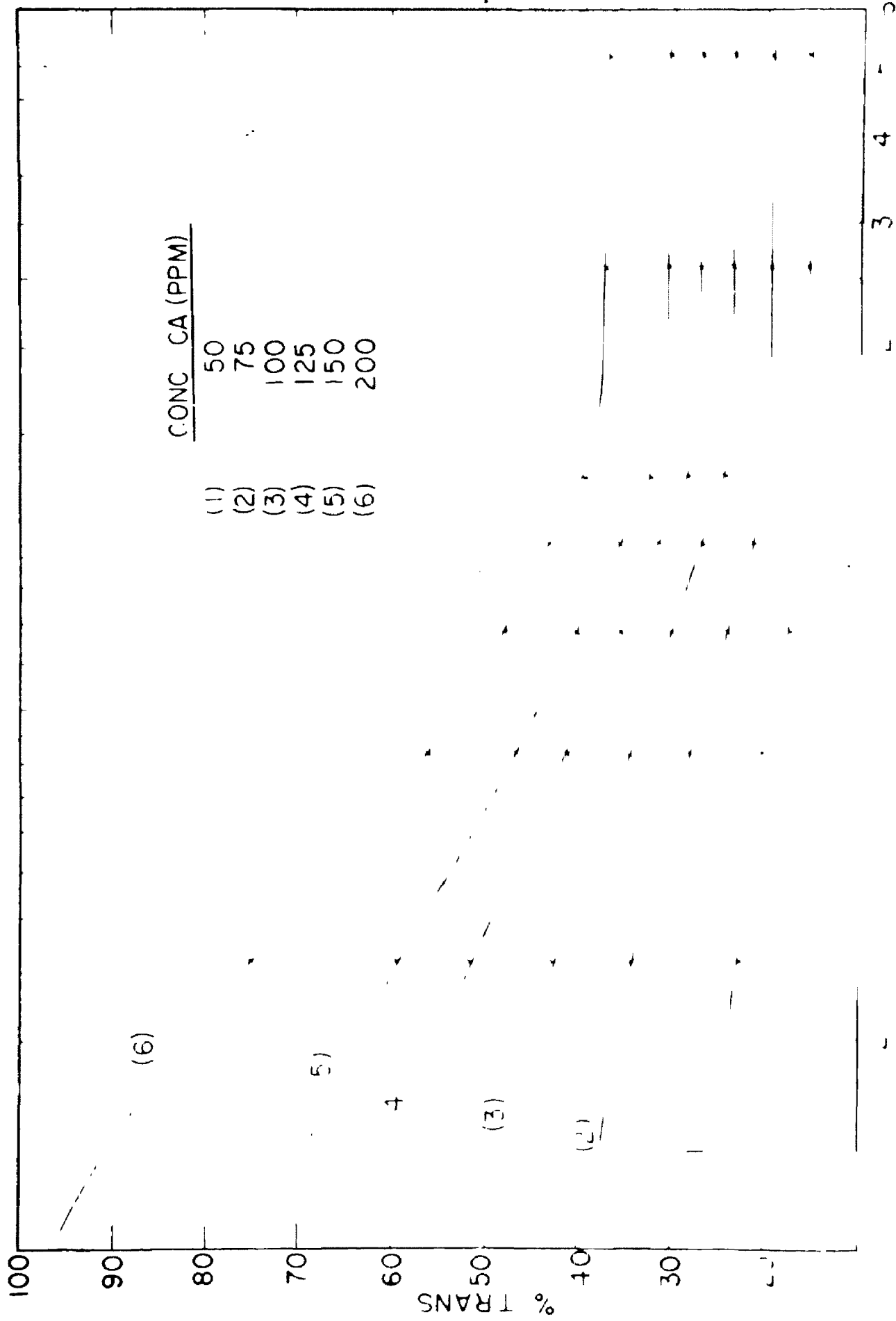


FIGURE 2
FLAME INTENSITY OF CALCIUM IN PHOSPHORIC ACID

prohibited the possibility of drawing any definite conclusions from a study of these breaks.

Because of the inconvenience in plotting, the mole ratio of H_3PO_4 to calcium is shown only up to 5.2 in Figure 2. However, a solution of ten times this concentration of H_3PO_4 was determined and was found to give a transmission reading somewhat higher than the plateau established in the curve by the two previous solutions. The magnitude of this increased intensity is shown in Table V.

TABLE V

| <u>Ca Conc.</u> <u>(P.P.M.)</u> | <u>Mole Ratio</u> <u>H_3PO_4/Ca</u> | <u>Observed</u> <u>Reading</u> |
|------------------------------------|---|-----------------------------------|
| 50 | 5.20 | 15.5 |
| | 52.0 | 17.8 |
| 75 | 5.20 | 19.7 |
| | 52.0 | 23.2 |
| 100 | 5.20 | 23.7 |
| | 52.0 | 28.7 |
| 125 | 5.20 | 27.1 |
| | 52.0 | 33.6 |
| 150 | 5.20 | 30.5 |
| | 52.0 | 38.6 |
| 200 | 5.20 | 37.0 |
| | 52.0 | 49.1 |

More points were obtained on the curve of the depression of the transmission of calcium by phosphoric acid using the photomultiplier tube. Increments in the ratio of phos-

phoric acid to calcium were 0.026. As shown in Figure 3, the curve is substantially the same as Figure 2, with a change in the slope of the curve appearing at mole ratios of 0.6 and 1.2. The successive readings were reproducible to $\pm 0.5\%$ on the transmission scale.

III. DETERMINING THE FLAME INTENSITIES OF H_3PO_4 SOLUTIONS.

Since the flame intensities of the calcium and H_3PO_4 solutions increased when a great excess of H_3PO_4 was added, it was thought that solutions of H_3PO_4 alone would show increasing intensities with increasing concentrations. Solutions of H_3PO_4 of concentrations varying from 0.0164M to 0.656M were prepared and the results of the transmission readings of these solutions are shown graphically in Figure 4. These readings were made without using the photomultiplier tube. The instrument was set with a standard of 100 p.p.m. of calcium at 110.0%; the background reading was 10.0%.

Because the transmission curve is linear, it is possible that this emission is due merely to incandescence of solid particles, probably HPO_3 or P_2O_5 , formed in the flame. This opinion seems to be substantiated by the evidence recorded in Table VI. To obtain this data, the 0.656M solution of H_3PO_4 was run at different wave lengths. Water was used as the standard and was set at a transmission reading of 10.0% at each wave length. As the slit width was

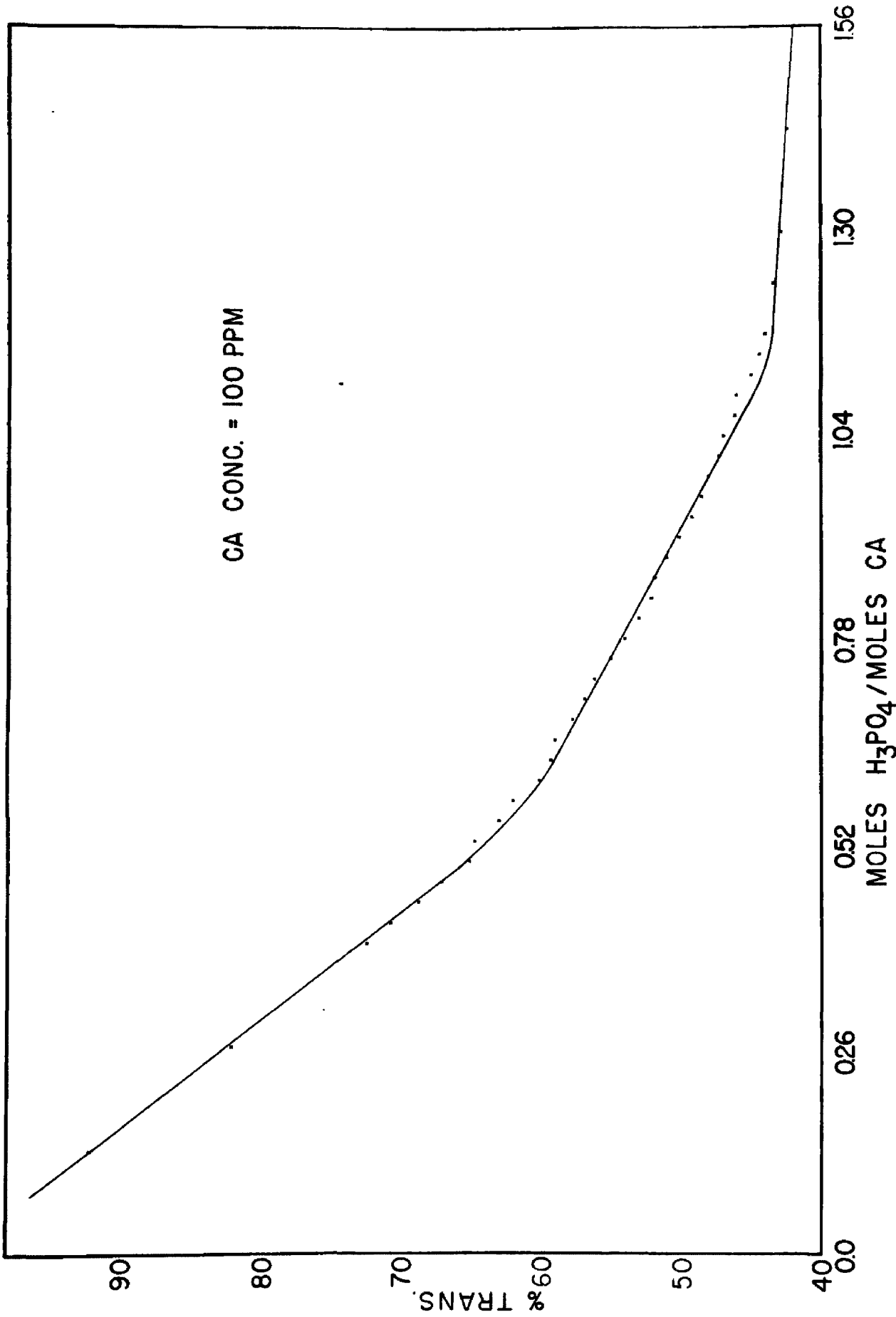


FIGURE 3

FLAME INTENSITY OF CALCIUM IN PHOSPHORIC ACID

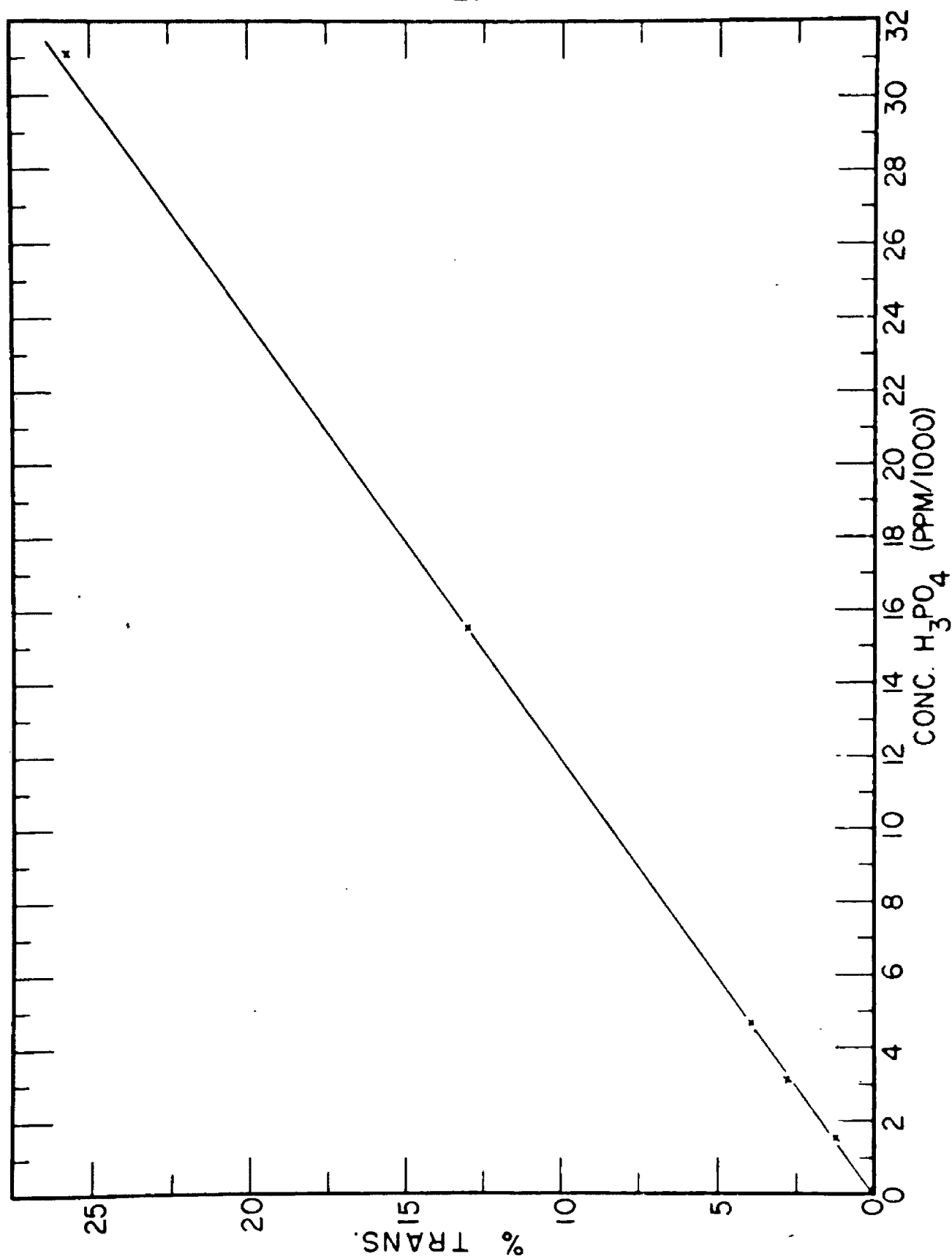


FIGURE 4

FLAME INTENSITY OF PHOSPHORIC ACID

increased, allowing more light to enter, the transmission increased. The ratio of the intensities at a wave length of 422.7 millimicrons and at 554 millimicrons was equal to the ratio of the square of the slit widths (approximately).

TABLE VI

| <u>Wave Length</u> (millimicrons) | <u>Slit Width</u> (mm.) | <u>Observed</u> <u>Reading</u> |
|--------------------------------------|----------------------------|-----------------------------------|
| 422.7 | 0.210 | 18.2 |
| 554 | 0.435 | 73.0 |
| 622 | 1.15 | 118 |

The reading at the longest wave length probably dropped off due to the insensitivity of the blue phototube at this wave length.

A study was also made of the relative flame intensities of other acids. The molar concentrations of all the acid solutions tested were approximately 0.65. In these tests a standard solution of 100 p.p.m. of calcium was set at 110% transmission. The slit width of 0.48 mm. gave a background intensity with distilled water of 10.0%. The 554 millimicron wave length was used. Table VII shows the relative flame intensities. Considering the formation of gaseous oxides, it is easily explained why all the acids except phosphoric acid should transmit very little light. The reason for the transmission of perchloric acid is not known. However, it is small compared to that of phosphoric acid.

TABLE VII

| <u>Acid</u> | <u>Corrected Reading</u> |
|--------------|--------------------------|
| Formic | 0.5 |
| Hydrochloric | 0.5 |
| Acetic | 0.5 |
| Nitric | 1.0 |
| Sulfuric | 2.0 |
| Perchloric | 4.0 |
| Phosphoric | 100 |

IV. DETERMINING CALCIUM IN EXCESS H_3PO_4 .

Since the depressive effect of the phosphate ion on calcium approached a limiting value, Figure 2, a study was made of the possibility of determining the concentration of calcium in which there was an unknown quantity of phosphate ion by adding an excess of H_3PO_4 . Solutions of varying concentrations of calcium were prepared in which the mole ratio of H_3PO_4 to calcium was held at 1.95. This was sufficient H_3PO_4 to be in the range where the slopes of the curves were zero. Figure 5 shows that a linear relationship was observed between the logarithm of the concentration of calcium and the logarithm of the percent transmission. This makes it possible to determine calcium in a phosphate medium. An approximation could be made of the calcium concentration by use of the flame photometer, omitting consideration of the depressive effect of any phosphate ion present, and this value could be used to determine the amount of H_3PO_4 which should be added to make possible the

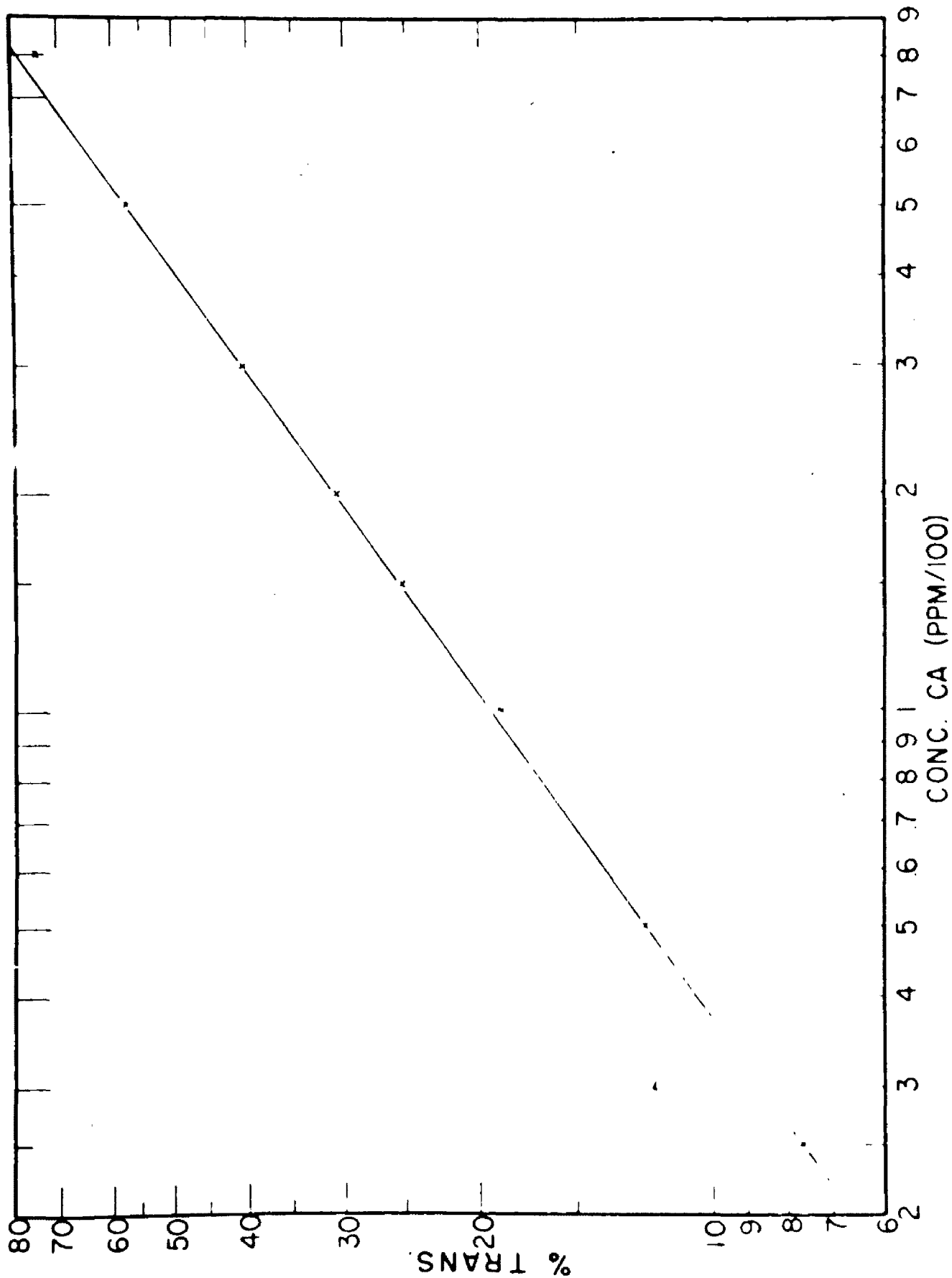


FIGURE 5

FLAME INTENSITY OF CALCIUM IN PHOSPHORIC ACID (MOLE RATIO $H_3PO_4/CA = 2$)

use of a curve similar to Figure 5. From such a curve, the unknown calcium concentration could be determined.

V. THE EFFECT OF SULFATE AND PERCHLORATE IONS ON CALCIUM.

Curves similar to those for phosphate ions were prepared for sulfate and perchlorate ions. The mole ratio of H_2SO_4 to calcium varied up to 51.2, and the calcium concentration varied up to 200 p.p.m. Again a depressive effect was observed on the transmission readings; however, the depression was not as great as that recorded with H_3PO_4 . Contrary to the phosphate solutions, the solutions most concentrated in sulfate ion did not show an increase in flame intensity. If, as was mentioned, this increase was due to incandescence, sulfate ion would not be expected to show it, since the decomposition products of the sulfate would be gaseous.

Solutions of calcium and $HClO_4$ were prepared by adding a standard acid solution to portions of the calcium chloride stock solution and diluting to the proper concentration. Contrary to all other anions studied, the perchlorate ion enhanced the transmission readings of the calcium solutions. The magnitude of enhancement reached a constant value.

Graphic representations of the effects of the sulfate and perchlorate ions are shown in Figures 6 and 7. The most concentrated acid solution, ten times the maximum recorded

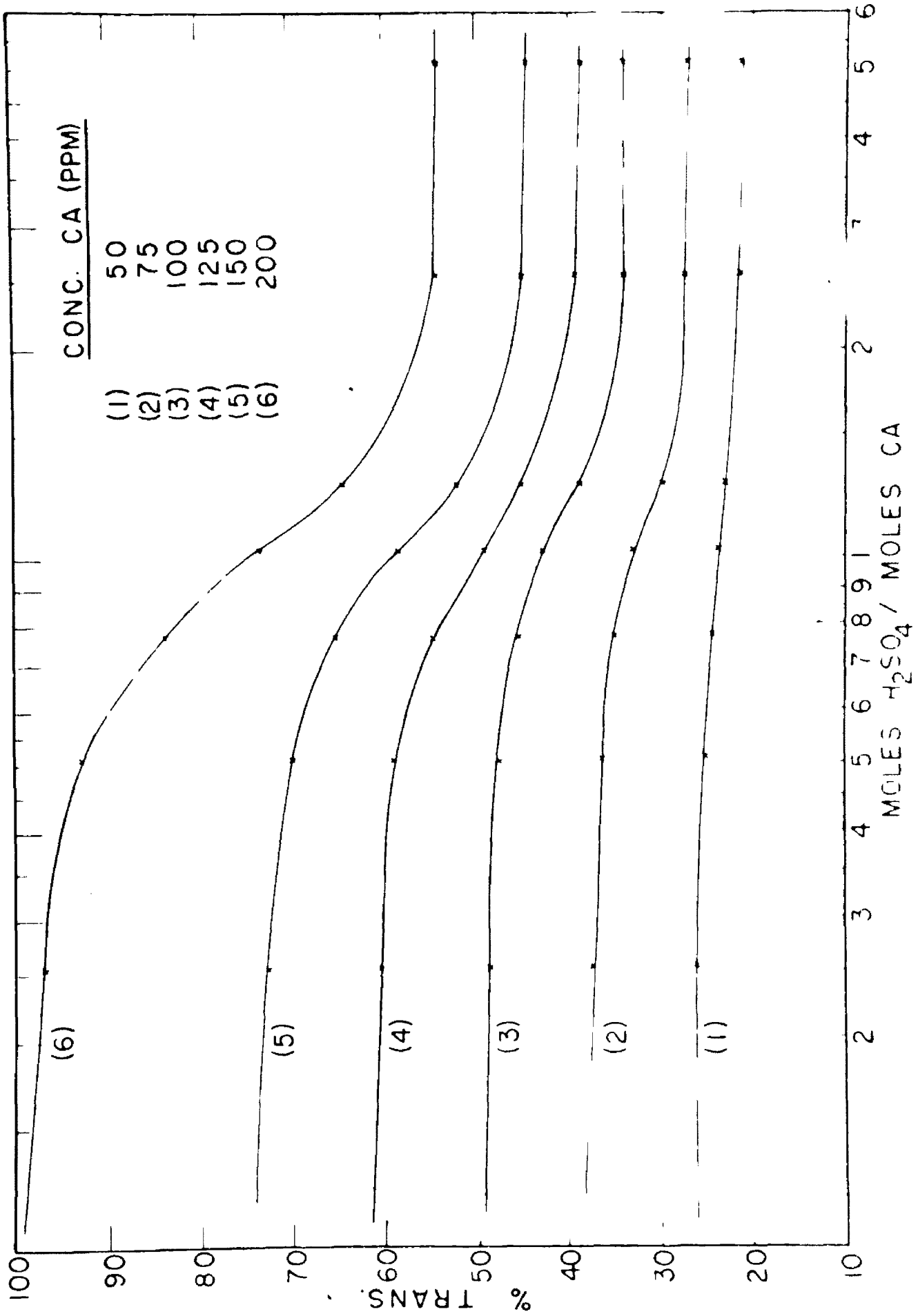


FIGURE 6

FLAME INTENSITY OF CALCIUM IN SULFURIC ACID

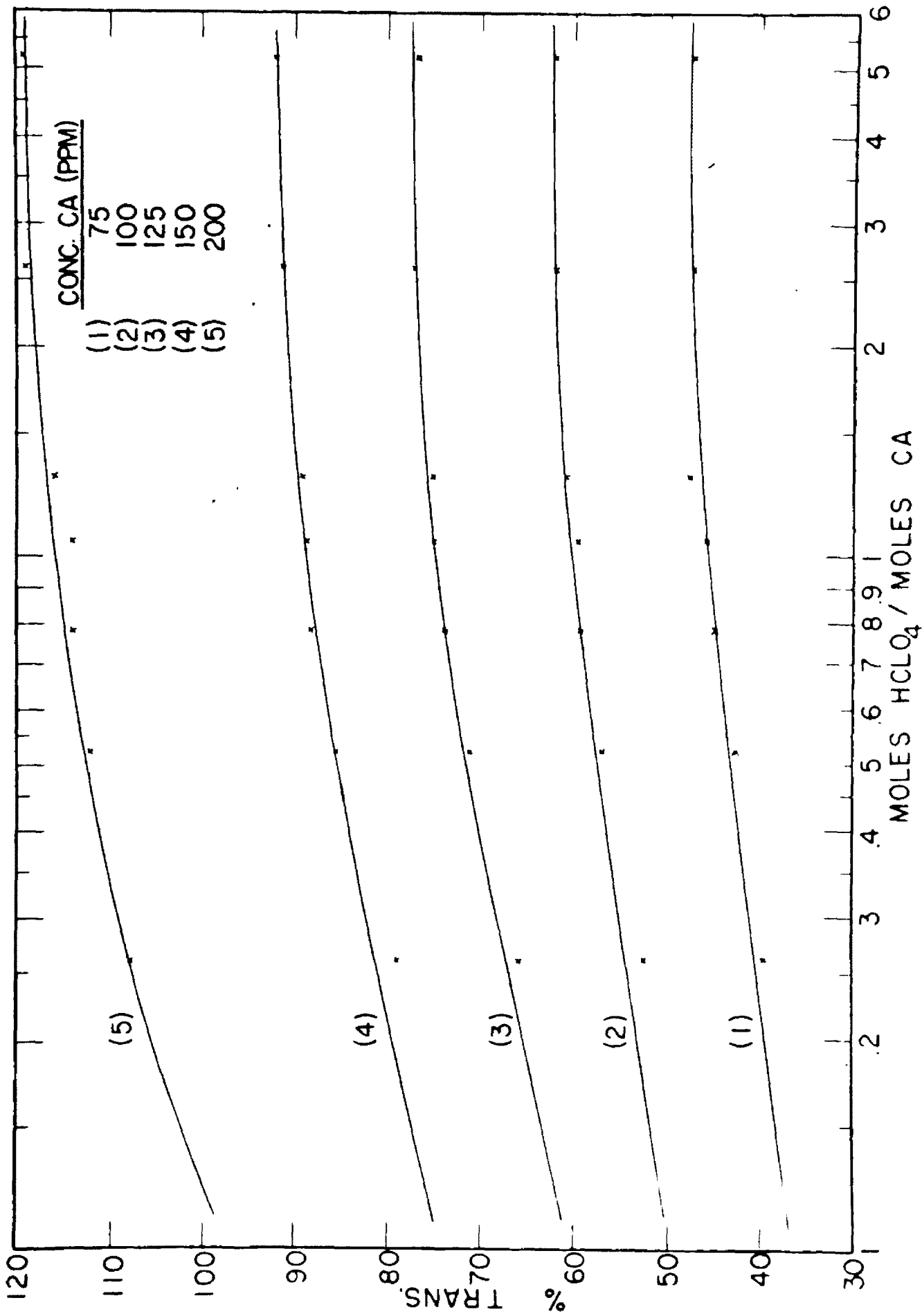


FIGURE 7

FLAME INTENSITY OF CALCIUM IN PERCHLORIC ACID

on the graphs, again is not shown; but, the transmission of this sulfate solution remained the same as the next less concentrated solution. However, the most concentrated perchlorate solutions, mole ratio of HClO_4 to calcium equal to 52.0, showed a slightly less transmission than the solutions of a 5.20 mole ratio. This decrease in transmission is recorded in Table VIII. These readings of sulfate and perchlorate solutions were made without the use of the photomultiplier tube but a check was made on the solutions of 100 p.p.m. of calcium with perchlorate ions. The magnitude of the enhancement using the photomultiplier tube was approximately 45% higher than without the attachment.

TABLE VIII

| <u>Ca Conc.</u> <u>(P.P.M.)</u> | <u>Mole Ratio</u> <u>HClO_4/Ca</u> | <u>Observed</u> <u>Reading</u> |
|------------------------------------|--|-----------------------------------|
| 50 | 5.20 | 33.2 |
| | 52.0 | 32.8 |
| 75 | 5.20 | 47.3 |
| | 52.0 | 46.7 |
| 100 | 5.20 | 62.0 |
| | 52.0 | 60.5 |
| 125 | 5.20 | 76.5 |
| | 52.0 | 74.4 |
| 150 | 5.20 | 91.8 |
| | 52.0 | 88.2 |
| 200 | 5.20 | 119 |
| | 52.0 | 114 |

VI. RELATIVE EFFECT OF ANIONS ON CALCIUM.

A series of solutions were prepared to study the relative magnitude of the effect of various anions on the flame intensities of calcium solutions. All solutions were made to a concentration of 100 p.p.m. of calcium from the stock solution of calcium chloride. Definite amounts of acid were added to vary the anion concentration up to approximately 0.026M. Tables IX and X show the results of these studies. Table IX gives the transmission readings for

TABLE IX

| <u>Acid Added</u> | <u>Corrected Reading</u> | <u>Deviation</u> | <u>% Error</u> |
|--------------------------------|--------------------------|------------------|----------------|
| HNO ₃ | 42.0 | - 8.0 | 16.0 |
| H ₂ SO ₄ | 29.5 | -20.5 | 41.0 |
| H ₃ PO ₄ | 20.3 | -29.7 | 59.4 |
| HClO ₄ | 62.3 | +12.3 | 24.6 |

the most concentrated solutions that were prepared. A standard solution of 100 p.p.m. of calcium was set at 51.0% transmission and the background showed an intensity of 1.0% at a slit width of 0.022 mm. The photomultiplier tube was used. A graph representing the relative effects of HCl, HNO₃, H₂SO₄, H₃PO₄, and HClO₄ is shown in Figure 8.

These results show the negligible effect of acetic, formic, and hydrochloric acids on the calcium intensities.

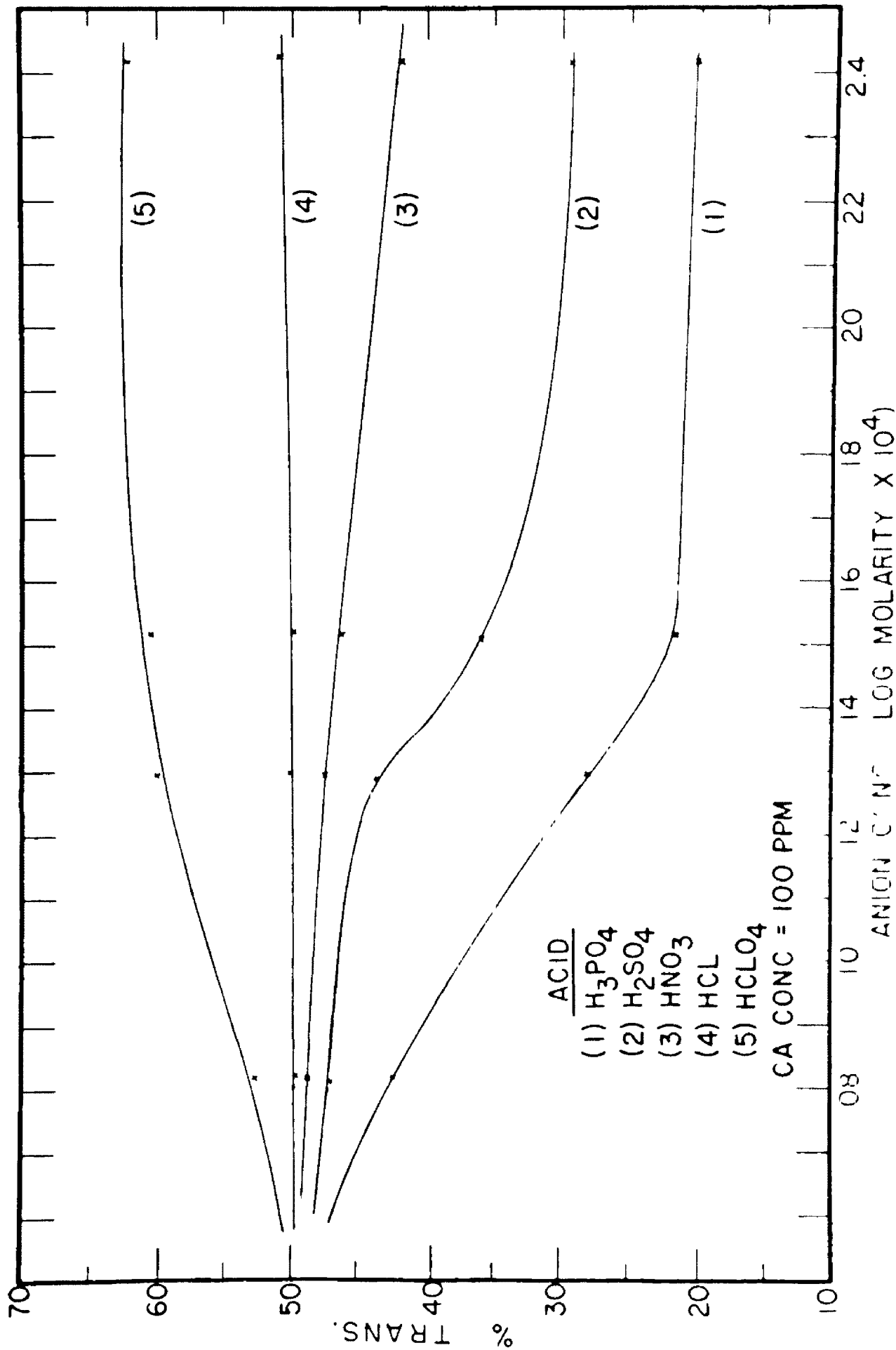


FIGURE 8

FLAME INTENSITY OF CALCIUM IN ACID SOLUTIONS

Since the solutions were made from CaCl_2 , the concentration of acid shown in Table X was not the true concentration of the chloride ion. Its maximum concentration was actually 0.0314M . Since chloride ion from the CaCl_2 was present in

TABLE X

| <u>Acid Added</u> | <u>Conc. of Acid (Molarity $\times 10^2$)</u> | <u>Corrected Reading</u> |
|-------------------|--|------------------------------|
| Acetic | 0.064 | 50.0 |
| | 0.193 | 49.3 |
| | 0.322 | 50.0 |
| | 2.57 | 49.5 |
| Formic | 0.064 | 50.4 |
| | 0.192 | 50.0 |
| | 0.321 | 50.0 |
| | 2.56 | 48.5 |
| Hydrochloric | 0.066 | 50.0 |
| | 0.197 | 50.0 |
| | 0.329 | 50.8 |
| | 2.64 | 51.3 |

all the solutions studied, it was thought that this ion might be taking part in the intensity deviations. Consequently, solutions were studied in which the calcium and phosphate ions were held at a constant concentration and the chloride ion concentration was varied from 0 to 0.01008M . This was done by treating a known amount of CaCO_3 with a known excess of standard H_3PO_4 and adding varying amounts of HCl to definite portions of this solution. The solution, whose chloride ion concentration was equal to 0.00504M , is identical to one of the original phosphoric acid solutions

used in previous studies which had a transmission reading of 23.3%. From the results recorded in Table XI, it is apparent that the chloride ion is not affecting the flame intensities of the calcium solutions.

TABLE XI

| <u>HCl Conc.</u> <u>(Molarity)</u> | <u>Observed</u> <u>Reading</u> |
|---------------------------------------|-----------------------------------|
| 0.00 | 23.2 |
| 0.00252 | 23.1 |
| 0.00504 | 23.2 |
| 0.01008 | 23.2 |

VII. EFFECT OF ANIONS ON SODIUM.

There seems to be some disagreement in the literature as to the effect on the flame intensity of sodium solutions when certain anions were added.¹ Solutions were prepared with 100 p.p.m. of sodium and various concentrations of H_2SO_4 , HNO_3 , H_3PO_4 , and $HClO_4$. The maximum concentration of H_2SO_4 was 0.008M; that for HNO_3 and $HClO_4$ was 0.065M; while the H_3PO_4 was made up to a concentration of 2.9M. There was no effect observed on the sodium transmission in the presence of sulfate, nitrate, or perchlorate ions. This is in agreement with the published results of West, Folse, and Montgomery. However, the results of the tests with phosphate ions, which are shown in Table XII, are not in

¹ Cf. ante, pp.2-3

agreement with the publication of Parks, Johnson, and Lykken. They observed a depressive effect on the percent transmission. Table XII shows an enhancement. Apparently

TABLE XII

| <u>H₂PO₄ Conc. (Molarity)</u> | <u>Observed Transmission</u> |
|---|------------------------------|
| 0.000325 | 101.2 |
| 0.00163 | 102.2 |
| 0.06522 | 104.0 |
| 0.559 | 113. |
| 2.9 | 109.5 |

the effects of sulfuric and nitric acid resulting from the studies herein are not in agreement with the works of Berry, Chappell, and Barnes; however, the anion concentration used by them was considerably higher than that used in this study. Further studies should be made before any comparison can be discussed. Although it does not seem probable, the inconsistencies reported may be due to the difference in the instruments that were used.

The readings recorded in Table XII were made with the photomultiplier attachment and a standard solution of 100 p.p.m. of sodium was set at a transmission reading of 100.0%. The background intensity, at a slit width of 0.07 mm., was zero percent.

VIII. MIXTURES OF SODIUM AND POTASSIUM.

In the publication of West, Folse, and Montgomery, it is reported that sodium enhances potassium and potassium

enhances sodium. This is contrary to the report of Parks, Johnson, and Lykken, who recorded a depressive effect in both cases.

To study this combination only one concentration was used. A solution of 50 p.p.m. of sodium and 50 p.p.m. of potassium was checked against two standards: one with a sodium concentration of 50 p.p.m., and another with a potassium concentration of 50 p.p.m. The sodium determination was run at a wave length of 589 millimicrons, and potassium was run at 404.6 millimicrons. It was found that potassium enhanced the sodium transmission by approximately 2.2%; and, sodium increased the potassium reading by approximately 2.6%. West, Folse, and Montgomery reported the enhancement to be 4% and 14% respectively.

IX. THE EFFECT OF SODIUM ON CALCIUM PHOSPHATE.

Solutions of standard CaCl_2 were diluted with standard phosphoric acid and sodium chloride solutions. All solutions contained 100 p.p.m. of calcium. The phosphoric acid concentration ranged up to 0.013M; and, for each concentration of phosphoric acid, the sodium concentrations were varied from zero to 0.00978M. From the observations made on the solutions containing only sodium and calcium ions, it is seen that sodium causes a decrease in the flame intensity of calcium. The magnitude of the error approached a maximum value at higher concentrations. This same effect

was observed when the solutions contained a low concentration of phosphate ions; as the concentration of phosphate ions was increased, the depressive effect of sodium became less. At a concentration of 0.013M H_3PO_4 the percent transmission was higher with sodium present than when only calcium and phosphate ions were present. Table XIII shows the percent transmissions of these solutions.

TABLE XIII

| <u>Na Conc.</u> <u>(P.P.M.)</u> | <u>H_3PO_4 Conc.</u> <u>(Molarity x 10³)</u> | <u>Corrected</u> <u>Reading</u> |
|------------------------------------|---|------------------------------------|
| 0 | 0.00 | 100.0 (set) |
| | 0.6556 | 83.1 |
| | 1.639 | 59.4 |
| | 3.278 | 42.1 |
| | 13.11 | 39.1 |
| 20 | 0.00 | 99.2 |
| | 0.6556 | 82.6 |
| | 1.639 | 58.3 |
| | 3.278 | 42.3 |
| | 13.11 | 41.8 |
| 100 | 0.00 | 88.5 |
| | 0.6556 | 76.0 |
| | 1.639 | 47.5 |
| | 3.278 | 39.8 |
| | 13.11 | 43.2 |
| 200 | 0.00 | 88.2 |
| | 0.6556 | 76.0 |
| | 1.639 | 48.6 |
| | 3.278 | 42.3 |
| | 13.11 | 41.1 |

CHAPTER IV

SUMMARY

Perhaps one of the most interesting points of this study is evident from the results of the calcium phosphate curves shown in Figure 1. It is obvious that the effect of phosphate on calcium follows a general pattern of depression; but, this pattern is not correlated with the concentration of phosphate ion but rather with the molecular ratio of phosphate to calcium. If this depressive effect were due to a change in the physical properties of the solution, such as viscosity or surface tension, then it would be expected that the magnitude of the depression would be related to the concentration of phosphoric acid and not to the ratio of its strength to that of calcium. However, if the effect were due to a chemical bonding of calcium ions to phosphate ions, then its magnitude would be expected to vary with the ratio of phosphate to calcium. This seems to support the opinion that chemical combination is the important factor.

Along with this idea is the slight evidence of breaks in the calcium phosphate transmission curves. It is possible that a relationship exists between these breaks and the formation of the compounds: $\text{Ca}_3(\text{PO}_4)_2$, CaHPO_4 , and $\text{Ca}(\text{H}_2\text{PO}_4)_2$. With the photomultiplier tube, readings were obtained which gave evidence of changes in the slope of the curve at mole ratios of phosphoric acid to calcium of 0.6

and 1.2. One of these occurs at a ratio slightly less than that of tertiary calcium phosphate (0.67). The second change in the slope occurs at twice the mole ratio of the first break (1.2) which is more than the ratio of secondary calcium phosphate (1.0). The explanations of this change in slope is not understood, and investigations of these phenomena is being continued.

Some study was done to determine a correlation between the heats of decomposition of the compounds involved and the flame intensities. It was thought that the intensity of the light transmitted would depend upon the temperature of the flame, and that this temperature would be lowered when energy was supplied to decompose the compound. Consequently, compounds of higher heats of decomposition would register lower transmission readings. A qualitative relationship does appear to exist between the heats of decomposition of the three calcium compounds and their positions on the calcium phosphate transmission curves. That is, the compound $\text{Ca}_3(\text{PO}_4)_2$, which would form first upon the addition of phosphoric acid to a calcium solution, has the lowest heat of decomposition per mole of CaO produced; and, the solutions, whose mole ratio of phosphate to calcium is in the neighborhood of 0.67, have higher flame intensities than those corresponding to the secondary or primary calcium phosphate.

The effects of acids on calcium, Figure 8, also appear to be related qualitatively to the heats of decomposition of the various salts formed. However, the values of the heats of decomposition at 25°C were compared, and obviously these would vary considerably at the high temperature of the acetylene flame. Further study would have to be made to determine whether or not a definite relationship exists between the heats of decomposition and the flame intensities.

No explanation is offered for the discrepancies found in the data observed and the data shown in the literature. It is evident that the data recorded herein compare favorably to that of other investigators who used a Beckman spectrophotometer but are not in agreement with the published data obtained by those using the Perkin-Elmer instrument.

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