



137
145
THS

THE COLORIMETRIC DETERMINATION
OF CADMIUM
BY MEANS OF DITHIZONE

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
George W. Armstrong
1939

[REDACTED]



82
11/1/72

**THE COLORIMETRIC DETERMINATION
OF CADMIUM
BY MEANS OF DITHIZONE**

by
George Willard Armstrong

A THESIS

**Submitted to the Graduate School of Michigan
State College of Agriculture and Applied
Science in partial fulfillment of the
requirements for the degree of**

MASTER OF SCIENCE

Department of Chemistry

1939

CHENIERE 0000

T543

A735

ACKNOWLEDGEMENT

The writer wishes to take this opportunity to express his sincerest appreciation to Mr. E. Leininger for his ever helpful suggestions and criticisms which have made possible the work which appears in this paper.

CONTENTS

	PAGE
INTRODUCTION	1
HISTORICAL SKETCH	3
THEORETICAL	5
MATERIALS, APPARATUS, REAGENTS	8
PROCEDURES AND DATA	14
INTERFERING SUBSTANCES	33

INTRODUCTION

In recent years the increasing importance of the detection of trace metals and the estimation of their amounts has demanded a sensitive method for their determination. The control of lead left upon fruit as spray residue and the detection of trace metals present in ores, alloys, etc., as impurities has stimulated research into the use of dithizone (diphenyl thiocarbazonone) as analytical reagent in such procedures.

Besides lead, zinc has perhaps received the most attention as to the possibilities of the dithizone methods in trace detection.

The analysis of traces of cadmium is one of the applications which, although the possibilities have been realized, has had little done toward its advancement. The field of research in cadmium then is still open. It will be the attempt of this paper to introduce new procedures in the dithizone methods for cadmium and, if possible, to improve upon any already existing.

Much may be learned of value to the detection of cadmium from a perusal of the literature for lead, zinc, and the other heavy metals. Since the amount of work done in

connection with cadmium has been small, this will be necessary, for it is beyond the scope of this paper to give a complete digest of all existing literature.

HISTORICAL SKETCH

In Germany in 1882 Emil Fischer (1) in his work upon the properties and reactions of phenyl hydrazine first came upon dithizone. At this time he recognized the fact that it formed a colored complex with zinc. It was nearly fifty years later, however, that anyone thought of the possibility of the use of dithizone as an analytical reagent.

Hellmut Fischer, also working in Germany, first studied the possibilities of the dithizone complexes in the qualitative detection of many heavy metals, among which were lead, copper, gold, silver, mercury, and cadmium. This was in 1924. A year later he published his findings in *Wiss. Veroff. Siemens-Kons.* (2) Very little interest was aroused however and except for a few scattered papers by Fischer himself, and a few authors in England, little was published of value upon the use of dithizone. In 1934 in *Angew. Chemie* (3) Fischer published another paper upon the use of dithizone in analysis, both in qualitative and quantitative microchemistry. Since that time more than fifty papers have been published dealing with the use of dithizone in analysis, most of which have dealt

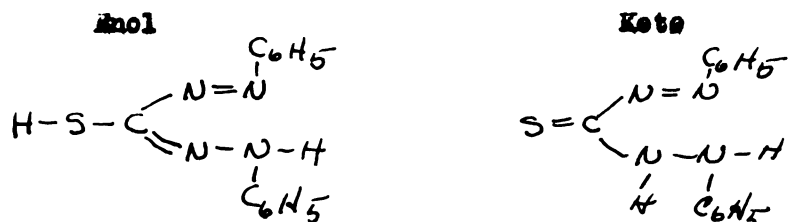
with lead and zinc.

In the time since 1925 several methods have been developed for the use of dithizone. Direct and indirect titration methods have been developed, as well as several colorimetric procedures which will be discussed later. Due to the insolubility of the dithizone complexes in water, an attempt was made to develop a gravimetric procedure. However, it was found that at temperatures sufficiently high to remove the water mechanically held, the dithizone complexes began to decompose necessitating final weighing as the oxide, sulfide, or sulfate. Under certain conditions mixtures of any two or all of these might occur. Since this was true and since the advantage of the high molecular weight of the dithizonate was lost, the attempt was discarded.

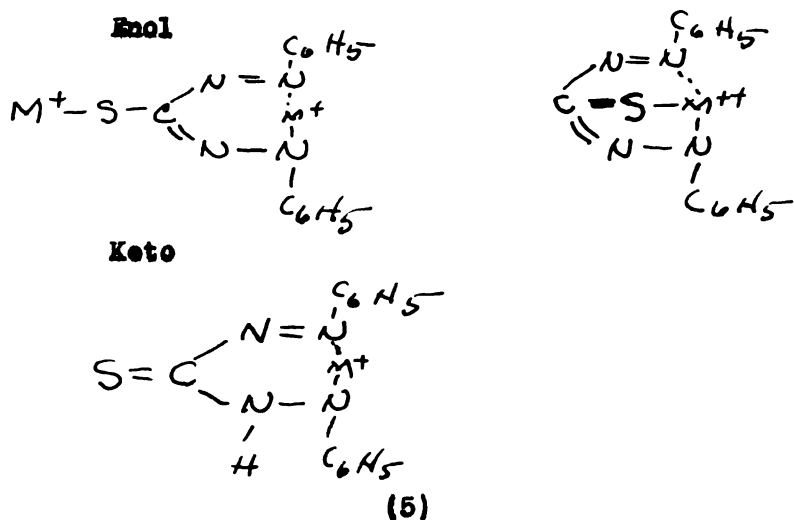
A complete bibliography of the work with dithizone up to 1937 was published in *Angewandte Chemie* (4) by Fischer along with the methods then in use. A partial list including papers published since 1937 may be found at the end of this report.

THEORETICAL

All the dithizone methods depend upon the fact that certain of the heavy metals form colored complexes with dithizone. These complexes are insoluble in water, but soluble in chloroform and other organic solvents. Fischer in his article in *Angewandte Chemie* (3) gave the following forms existing for dithizone:



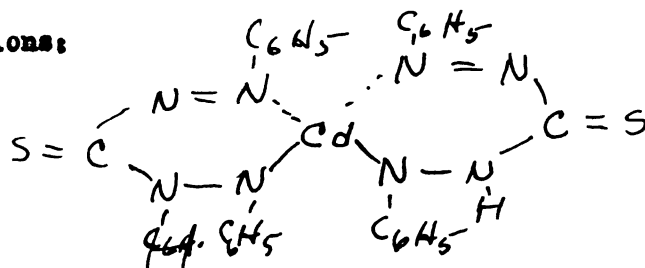
and postulated the following possibilities for the heavy metal complexes:



With the divalent metals the same linkage takes place, but another molecule of dithizone is used. Of the three valent metals reacting only the keto form has been found to exist at this writing. With these the bond type is the same, but the formula takes three molecules of dithizone.

According to Fischer (3) the keto forms are generally existant in neutral or acid solution with a few exceptions of which cadmium is one, while the enol form exists in basic solution.

For the cadmium complex the following form has been shown to exist in neutral to strongly alkaline solutions:



This has been contracted for convenience to CdD₂. The existence of an enol complex of cadmium has as yet not been proved.

According to Clifford and Wichmann (5) the most complete complexing of cadmium takes place above the pH value of twelve, with the complex first forming at a pH of around nine.

Fischer in his work found that an end concentration of five per cent sodium hydroxide gave the best results. It was noticed by this observer in corroboration of these workers that the extraction of cadmium with a twenty-five per cent excess of dithizone began at a pH between eight and nine and was most complete above a value of twelve. From this point to a concentration of approximately ten per cent sodium hydroxide there seemed to be no appreciable difference in the coloring of the dithizone-chloroform extract. However, above this concentration the colors again seemed to decrease in intensity.

This method is by no means specific for cadmium. Fischer and Leopoldi (6) claim, however, that only the following metals interfere: copper, silver, gold, mercury, palladium, nickel, cobalt, and zinc in large amounts. Also any ion precipitating in the alkaline solution will cause incomplete extraction of cadmium. Such ions are phosphate, ferric, chromic, aluminium, stannous, etc. Sandell in a recent paper (7) has said that manganese also interferes and, since the method as given by Fischer will not take care of this, gives a method for its elimination in small amounts.

MATERIALS, APPARATUS, REAGENTS

1. Separatory funnels

100 ml. size Kimball Exax funnels were used.

2. All pyrex glass still

3. Colorimeter

Klett-Bio instrument was used with the artificial light attachment.

4. Photometer

Cenco-Sheard-Sanford Photometer using the Cenco No. 2 green filter.

Solutions and Reagents:

1. Standard cadmium solution

2. Chloroform (redistilled from pyrex)

3. Carbon tetrachloride (redistilled from pyrex)

4. Dithizone in Chloroform (25 mg./ml.)

5. Dithizone in Carbon tetrachloride (25 mg./ml.)

6. Redistilled water (redistilled from pyrex)

7. Sodium hydroxide - 25% (C. P. chemical dissolved in redistilled water)

8. Hydrochloric acid solution - 1 N.

9. Sodium citrate - 25% (C. P. chemical in redistilled water)

10. Potassium sodium tartrate - 25% solution (C. P.
chemical in redistilled water)
11. Solutions of various foreign ions.

To prepare a standard cadmium solution the following method was found to be convenient: a solution of cadmium nitrate was made up so that fifty milliliters of solution were approximately equal to one-tenth gram of cadmium. This solution was standardized by several means.

Fifty-milliliter portions of the solution were evaporated to dryness with a milliliter of sulfuric acid (dilute) in platinum dishes. The excess acid was then fumed off and the cadmium sulfate thus formed ignited at five hundred degrees in a muffle furnace. It was found that traces of sulfuric acid might be left; this was, therefore, removed by moistening the residue with water and again fuming off any remaining sulfuric acid. This process was repeated until constant weights were obtained on the residue. This procedure is given in detail in Hillebrand and Lundell (8). A series of such determinations gave the following results:

Sample	1.	2.	3.	4.	5.
Cadmium/50 ml.	.1012	.1012	.1014	.1013	.1014

Since the results obtained from the cadmium sulfate method are likely to be in error due to the in-

complete removal of the sulfuric acid or due to loss by spattering, a second series was run by means of the electrolytic deposition of cadmium on a platinum gauze cathode from an alkaline complex cyanide solution. (Treadwell-Hall (9); Hillebrand and Lundell (10)). The results obtained on four samples were:

Sample	1.	2.	3.	4.
g. Cadmium/50 ml.	.1013	.1012	.1013	.1013

The value .1013 g./ml. was then taken as the cadmium content of the stock solution. A standard cadmium solution was prepared by diluting fifty milliliters of this solution to one liter in a volumetric flask. Twenty milliliters of the resulting solution were made up to a liter in another flask. The resulting solution contained two-millionths of a gram cadmium per milliliter or two micrograms of cadmium.

An additional series was run where the cadmium was precipitated as the cadmium ammonium phosphate. Since this method, due to inadequate pH control, is prone to give low results, these results were not included in the average, but were merely used to give

further evidence of the unreliability met with in this method. The following results were obtained with five samples:

Sample	1.	2.	3.	4.	5.
g. Cd/50 ml. .1000	.0999	.1001	.1002	.0997	

This procedure followed that given by Treadwell-Hall (11)

It was found by tests upon the carbon tetrachloride and chloroform obtained from stock that they were unsuited for determinations with dithizone, since they contained appreciable amounts of materials giving color with dithizone. Hence all chloroform and carbon tetrachloride used were redistilled from an all-pyrex glass still. Similar results were obtained in tests upon distilled water obtained from the taps due to the copper and lead taken up from the pipes. The distilled water must also be redistilled previous to use.

Solutions of sodium hydroxide, sodium citrate, potassium sodium tartrate and hydrochloric acid were made by diluting C. P. reagents with redistilled water. The sodium potassium tartrate and sodium citrate solutions were found to be sufficiently pure for

use if shaken with successive small portions of dithizone until the pure green of the dithizone is unmodified upon shaking. The sodium hydroxide and hydrochloric acid solutions could not be purified in this way; however, they were found to be sufficiently pure.

Since a strongly alkaline solution is used in the extraction of cadmium, it will be found that etching of the glass may take place slowly with subsequent deposition of traces of cadmium; hence, it will be necessary to clean the separatory funnels frequently with a strong acid solution. Ordinary cleaning solution was used for this purpose originally, but it was found that any slight traces of the chromate which may be left will oxidize the dithizone; consequently, a solution of nitric acid was used after this.

PROCEDURES

For the colorimetric determination of cadmium as the complex dithizonate only one method had been developed until the spring of 1939. In 1937 Fischer and Leopoldi (6) first worked with dithizone in connection with cadmium and used the following procedure:

To five to ten milliliters of approximately neutral cadmium solution an equal volume of ten per cent sodium hydroxide solution was added. Any ions which might precipitate with sodium hydroxide were held back by means of Rochelle salt. This solution was extracted repeatedly with dithizone in a separatory funnel until the carbon tetrachloride was no longer colored red. The combined extracts were then washed with three per cent sodium hydroxide twice and water once. The red cadmium dithizonate was decomposed by means of normal hydrochloric acid and the green color of the dithizone compared. An accuracy of within five per cent was claimed with this method.

Since the work with the above method, one other method for cadmium has been recorded in the published literature by E. B. Sandell (7). The procedure used

by Sandell is as follows: The sample was extracted with dithizone in carbon tetrachloride and the carbon tetrachloride layer drawn off. This extract was shaken with one-hundredth normal hydrochloric acid to remove the cadmium leaving the major portion of the other metals present behind. The water solution was then transferred to a flat bottomed tube. Two and five-tenths milliliters of twenty-five normal sodium hydroxide was then added and the solution shaken with dithizone. The carbon tetrachloride layer was then compared to standards prepared by diluting standard amounts of cadmium to the same volume as the unknown, adding the same amount of sodium hydroxide and then shaking with dithizone.

However, working with lead in connection with spray residue control on fruits, O. B. Winter, E. J. Miller, and others (12) at Michigan State College in 1935 developed a method using chloroform as solvent rather than carbon tetrachloride, which followed the procedure of Fischer and Leopoldi rather closely except in minor details until the final extraction of the dithizonate of lead. Rather than decomposing the red complex and comparing the green dithizone, they

compared the extracted dithizonate. The results obtained were claimed to be at least as accurate as those obtained by Fischer and Leopoldi and the procedure was shortened considerably. Chloroform was substituted for carbon tetrachloride because of the greater solubility of the complexes in chloroform.

In 1936 Clifford and Wichman (5) of the United States Department of Agriculture published in the J. Off. Ag. Chem. an article dealing with the methods for lead and submitted a new method whereby the separation of the excess dithizone was eliminated, hence shortening the procedure still further. The accuracy was increased, they claimed, due to the lack of necessity of repeated extractions to remove the excess dithizone. The optimum pH was chosen and a single extraction of the solution made with excess dithizone. This excess was allowed to distribute between the aqueous and the chloroform phase. The mixed dithizone-dithizonate was then compared with standards prepared in the same way.

The possibility of applying these last two methods to the determination of cadmium has given rise to

to the work in this report.

It was found by experiment however that at the alkalinity best suited for the greatest extraction of cadmium as the dithizonate, the excess dithizone went over into the aqueous phase too readily to permit the use of the mixed color method. At a lower pH it was found that the cadmium was not extracted quantitatively. The work in this paper is consequently limited to a review of the method of Fischer and Leopoldi, and to the development of an acceptable procedure for the use of the red cadmium dithizonate.

The procedure adopted for the work in this paper on the determination of cadmium differs slightly from that proposed by Fischer and Leopoldi. It was found by results in the laboratory that differences in volume of the aqueous solution when a constant volume of cadmium found in the chloroform extract. The effects of various amounts of water solution to twenty milliliters of chloroform solution are shown below. Each sample contained a constant amount of cadmium.

Volume of aqueous solution	Amount of cadmium present	Amount of cadmium found
10 ml.	20 microgr.	19.5 microgr.
15 ml.	20 "	19.8 "
20 ml.	20 "	20.0 "
25 ml.	20 "	19.6 "
30 ml.	20 "	19.3 "

Taking this fact into consideration the following procedure was developed:

To an approximately neutral aliquot of cadmium solution five milliliters of twenty per cent sodium hydroxide was added and the aqueous solution was made up to twenty milliliters with redistilled water. Sufficient dithizone in chloroform (25 mg./liter CHCl_3) was added from a buret in one-milliliter portions with shaking after each addition to cause a distinct excess to be present. The presence of the excess dithizone may be noticed by the yellow color imparted to the aqueous phase and a slight purplish color to the chloroform layer. Sufficient chloroform was then added from another buret to make the total chloroform-dithizonate extract up to twenty milliliters. The chloroform layer was then removed to a second separatory funnel con-

taining twenty milliliters of three per cent sodium hydroxide, shaken up and allowed to separate. The chloroform layer is again drawn off and washed with twenty milliliters of redistilled water. One washing with sodium hydroxide was found to be as effective as two washings. The washed dithionite was then drawn off and compared against a standard in a colorimeter. If foreign ions were present the procedure was carried out with the addition of sodium citrate or potassium sodium tartrate. The amount of cadmium present in the solution is read off of a calibration curve obtained by plotting the reading on the colorimeter against the concentration of known solutions. The following concentrations were taken to plot the curve:

.001 mg., .0025 mg., .0050 mg., .0100 mg., .0150 mg.,
.0200 mg., .0250 mg., .0300 mg., .0350 mg.

It was noticed that concentrations higher than those listed above when using a standard of .0200 mg. were out of the convenient working range of the colorimeter.

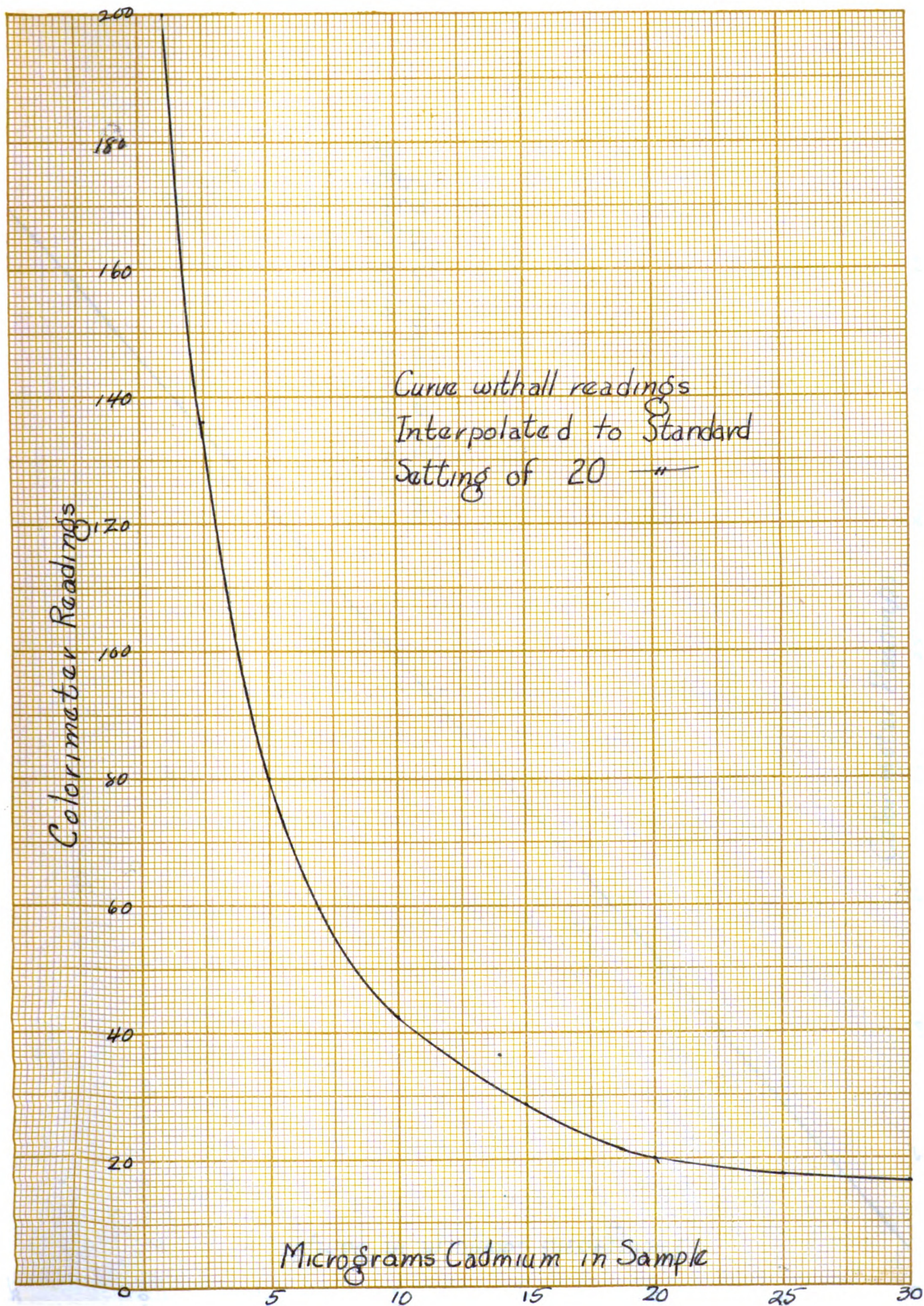
This calibration curve according to Fischer and Leopoldi (13) is a linear curve while Winter, Miller, and others (12) working with lead found the calibra-

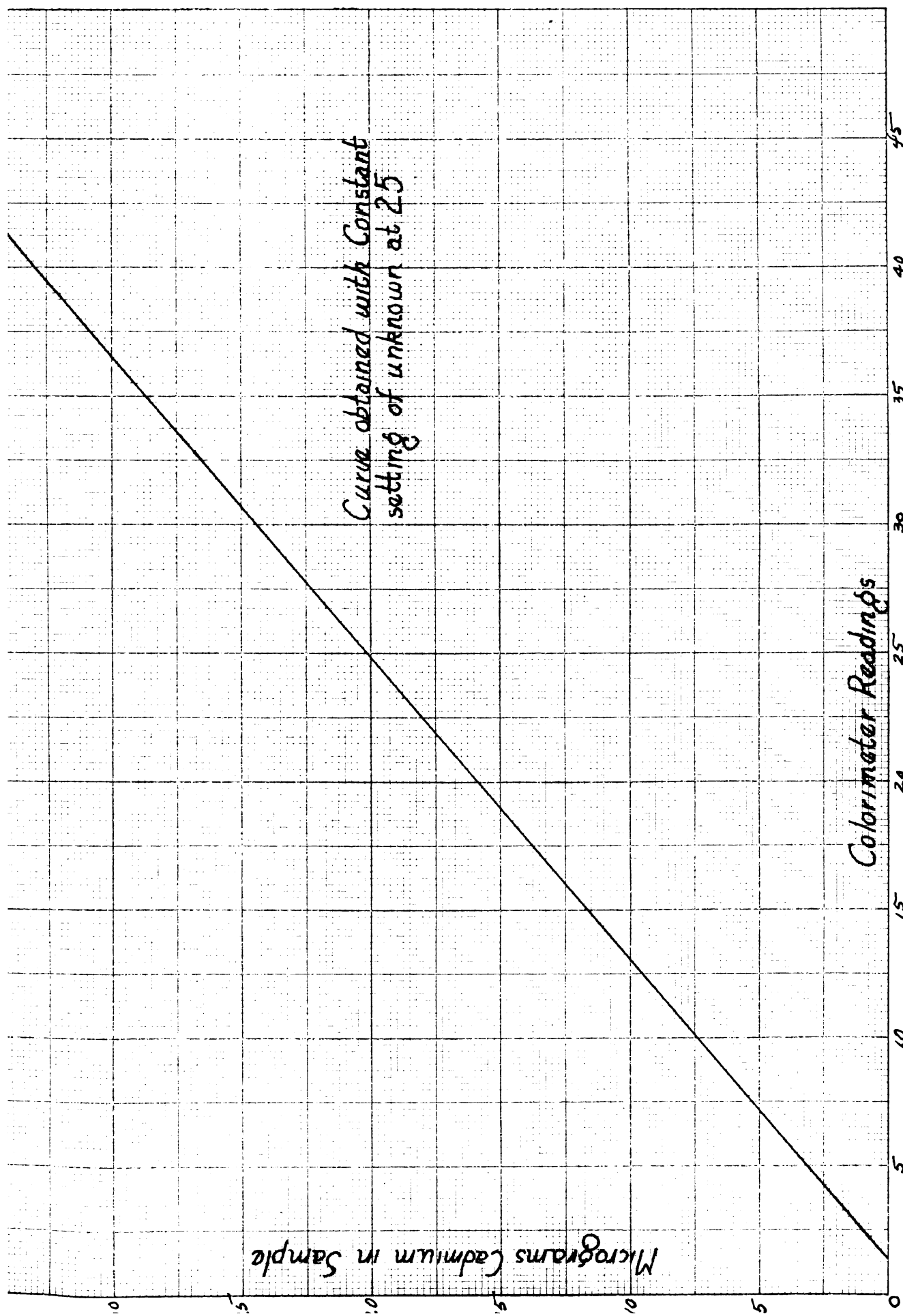
tion curve to be a hyperbolic function. It was found by this observer that if the standard was set at a constant reading and the sample varied that a curve was obtained similar to that obtained by Winter and Miller for lead, which was distinctly hyperbolic in character. The comparison of the complete range, however, was not possible without a change of standard setting and interpolation from that setting to the original setting which was taken as twenty. To eliminate this difficulty it was found sufficient to set the sample rather than the standard at a constant setting and vary the standard until matching is obtained. In this manner, choosing a setting of twenty-five for the sample, it was found possible to compare directly without interpolation samples between zero and thirty-five micrograms of cadmium. It was also found that by this means a linear graph was obtained, therefore facilitating reading and increasing the accuracy of reading the graph. The data obtained for plotting the curve is given below:

Colorimeter Readings

Curve with all readings
Interpolated to Standard
Setting of 20 —

Micrograms Cadmium in Sample





Cadmium Present mg.	Colorimeter Readings				
	1.	2.	3.	4.	average
.0010	2.4	2.3	2.3	2.5	2.4
.0025	3.8	3.9	4.0	3.9	3.9
.0050	7.3	7.1	7.0	7.4	7.2
.0100	13.0	12.8	12.6	12.5	12.7
.0150	18.5	18.3	18.5	18.4	18.4
.0200	25.0	25.0	25.0	25.0	25.0
.0250	30.0	30.3	30.8	30.5	30.4
.0300	36.2	36.5	35.9	36.4	36.2

Each of the series above was run on a different set of samples.

As a check up on the accuracy and reproducibility of the method several series of unknown samples in which the operator was unaware of the cadmium content were run. The table below gives the results of these series:

Cadmium Found ✓	Cadmium Present ✓	Error	
		%Cd	%Cd
7.8	8.0	-.2	-2.5
14.0	14.0	.0	.0
10.0	10.0	.0	.0
21.8	22.0	-.2	-1.0
6.3	6.0	+.3	+5.0
13.2	12.0	+1.2	+10.0

Cadmium Found ✓	Cadmium Present ✓	Error	
		✓Cd	✓Cd
20.3	20.0	+ .3	+1.5
27.9	28.0	- .1	- .4
2.0	2.0	.0	.0
9.7	8.0	1.7	21.0
16.1	16.0	+ .1	+ .7
22.1	22.0	+ .1	+ .5
10.1	10.0	+ .1	+1.0
3.9	4.0	- .1	-2.5
26.2	26.0	+ .2	+ .8
5.8	4.0	+1.8	+45.0
18.0	14.0	+4.0	+28.5
3.9	3.0	+ .9	+30.0
16.1	16.0	+ .1	+ .7
20.0	20.0	.0	.0
11.9	10.0	+1.9	+19.0
20.0	21.0	+1.0	-5.0
2.2	2.0	+ .2	+10.0
3.5	3.5	.0	.0
17.2	17.0	+ .2	+1.5
19.3	19.0	+ .3	+1.5
24.9	25.0	- .1	- .3
21.7	22.0	- .3	-1.5

Cadmium Found ✓	Cadmium Present ✓	Error	
		γCd	%Cd
8.0	7.5	+0.5	4.0
9.8	10.0	-0.2	-2.0
15.6	16.0	-0.4	-3.3
8.0	8.0	.0	.0
14.0	14.0	.0	.0
2.2	2.0	+0.2	10.0
6.1	6.0	+0.1	1.6
8.7	10.0	-1.3	-13.0
4.0	4.0	.0	.0
12.6	12.0	+0.6	5.5

Since the presence of an appreciable color in the blank determination will cause a variation in the amount of cadmium found, the effect of the aging of reagents upon the blank color was studied along with the development of a suitable procedure. The reagent under test was allowed to age in ordinary glass containers while all other reagents were made up fresh on the day of use. The following results were obtained:

1. Sodium hydroxide allowed to age; dithizone, chloroform, and redistilled water fresh every day.

1st day - no perceptible color

2nd day - no perceptible color

3d day - no perceptible color

one week - slight color

two weeks - blank of less than two-tenths microgram of cadmium.

2. Dithizone allowed to age other reagents fresh each day (dithizone kept in brown bottle in dark, at room temperature.)

1st day - no perceptible color

2nd day - no perceptible color

3d day - slight pinkish color about .2 microgram

one week - blank of about one microgram

two weeks - reagent oxidizes to the yellow
diazone upon shaking.

The chloroform and redistilled water could be used as long as two to three weeks with no perceptible color being noticed in the blank. The dithizone may be used for a longer period than found above if it is kept in the ice box. Dithizone preserved in a brown bottle at ice box temperatures was found to give only a slight blank after standing two weeks.

The magnitude of the blank obtained from the reagents may be fairly accurately measured by plotting the readings obtained from the comparison of the blank with decreasingly small amounts of cadmium. For this purpose samples containing 1.0, 0.7, 0.4, 0.1 micrograms of cadmium plus the blank in each case were compared to the blank. The comparisons gave the results listed below which when plotted in the manner for the main graph and extrapolated to zero reading gave a value of approximately 0.3 microgram for the blank. A standard setting of ten was used for the samples while the blank was varied.

Cadmium Present ✓	Colorimeter Readings		
	1.	2.	3.
1.0	50.0	49.9	50.0
0.7	36.1	36.0	36.0
0.4	26.7	26.8	26.9
0.1	13.1	13.0	13.2

Various workers have done their research into the detection of trace metals with dithizone using both carbon tetrachloride and chloroform. Therefore, a discussion of the relative merits of the two as a solvent for cadmium dithizonate is pertinent. It was noticed with carbontetrachloride that emulsions formed less readily due to the lower solubility of carbon tetrachloride in water. The greater difference in the hue of colors of the different dithizonates is a factor giving a greater detection possibility in carbon tetrachloride, but at the same time this advantage is offset by the fact that at higher concentrations many of the metallic complexes are less soluble than in chloroform. This is true of the cadmium complex. It was noticed that above about twenty-five micrograms of cadmium the readings obtained with the colorimeter were very nearly constant indicating saturation of the carbon tetrachloride. This difficulty is not encountered with chloroform.

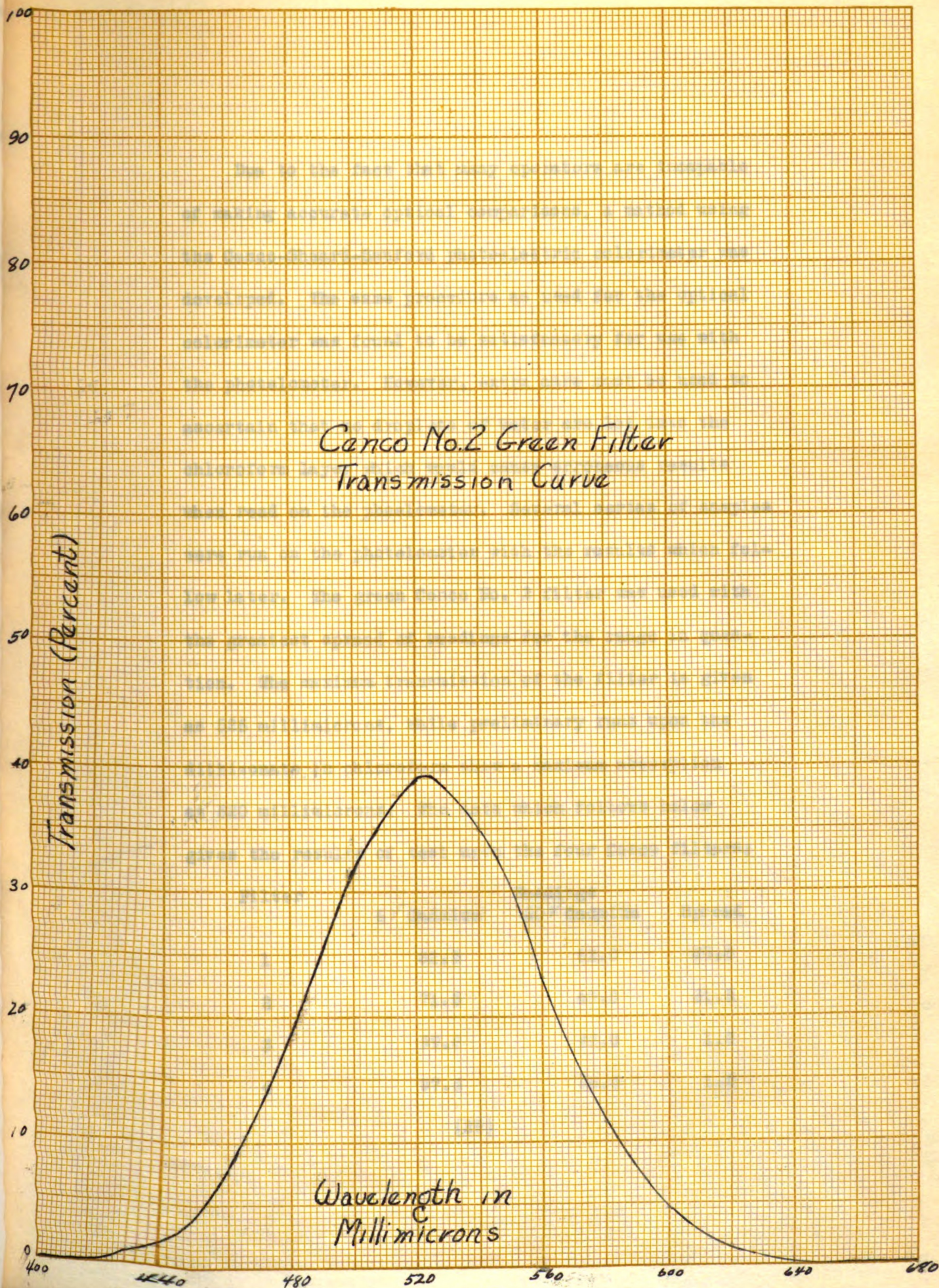
Because of the fact that the distribution ratio of dithizone between the water and carbontetrachloride phases is more favorable for the excess to go over into the water phase than with chloroform, the excess

dithizone can be more easily washed out when using carbon tetrachloride than when using chloroform. This, however, also eliminated the possibility of using the sensitive mixed color method for the comparison of the samples, since this method depends upon the distribution of the excess dithizone between the water and the organic phases. By the use of chloroform for the extraction, the pH range of stability of the metal complexes of dithizone is increased, at times aiding the separation of certain foreign ions from the desired metal. The deciding factor for the use of chloroform for the work in this paper was the fact of the greater solubility of the cadmium dithizonate in chloroform, hence increasing the working range.

Canco No. 2 Green Filter
Transmission Curve

Transmission (Percent)

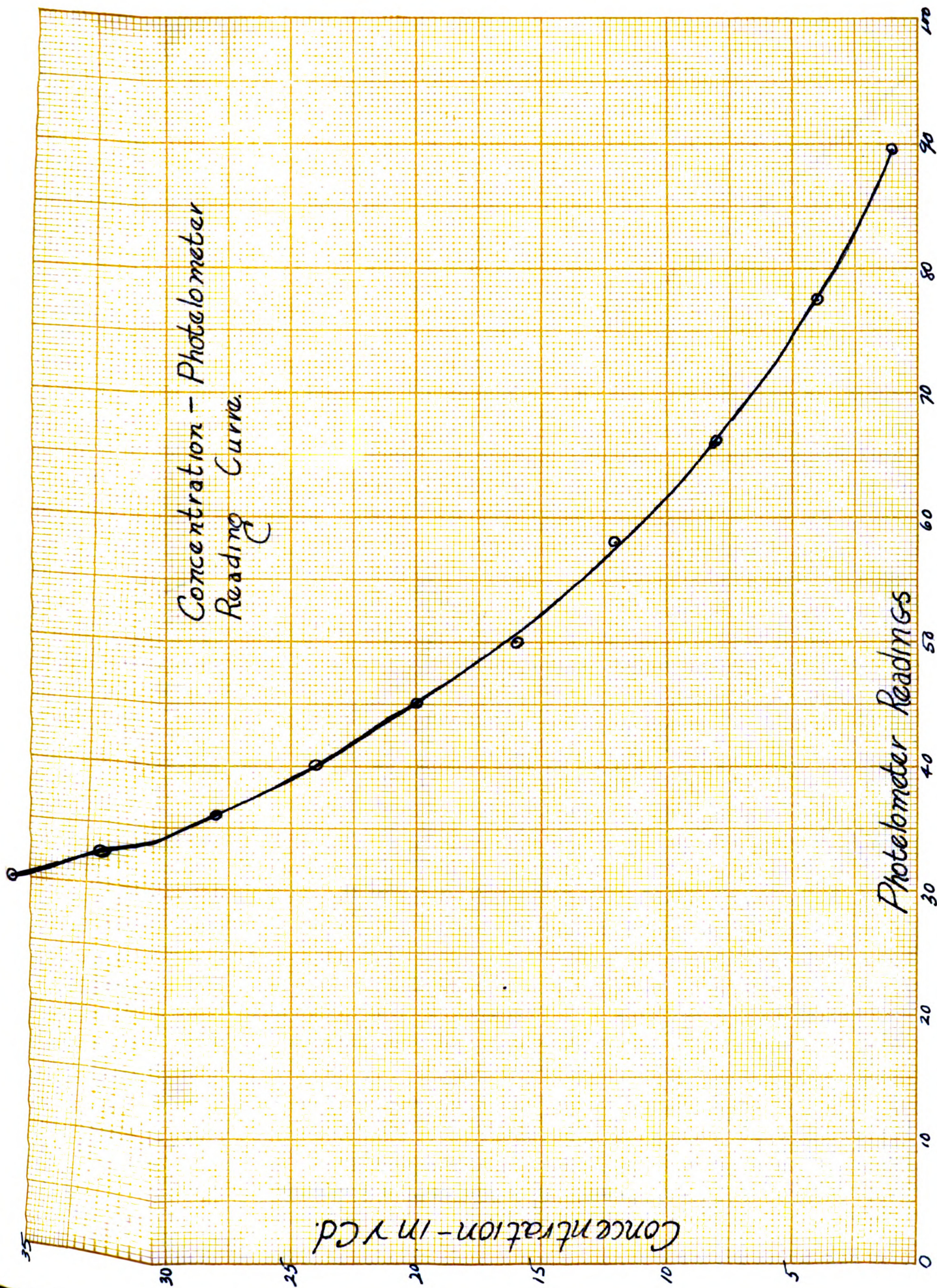
Wavelength in
Millimicrons



Due to the fact that many operators are incapable of making accurate optical comparisons, a method using the Cenco-Sheard-Sanford photoelectric colorimeter was developed. The same procedure as used for the optical colorimeter was found to be satisfactory for use with the photometer. However, extra care must be used to ascertain that no droplets of water are let into the chloroform layer which would cause erroneous results when read on the photometer. Several series of samples were run on the photometer with the results which follow later. The green Cenco No. 2 filter was used with the greatest spread of readings for the range in question. The maximum transmission of the filter is given as 525 millimicrons, while preliminary runs upon the dithizonate in chloroform show a maximum absorption at 520 millimicrons. The data which follows below gives the results of test upon the four Cenco filters:

Filter	Readings		
	67 Cadmium	207 Cadmium	Spread
1	82.5	62.0	20.5
2	71.5	40.0	31.5
3	99.8	98.0	1.8
4	97.5	96.0	1.5

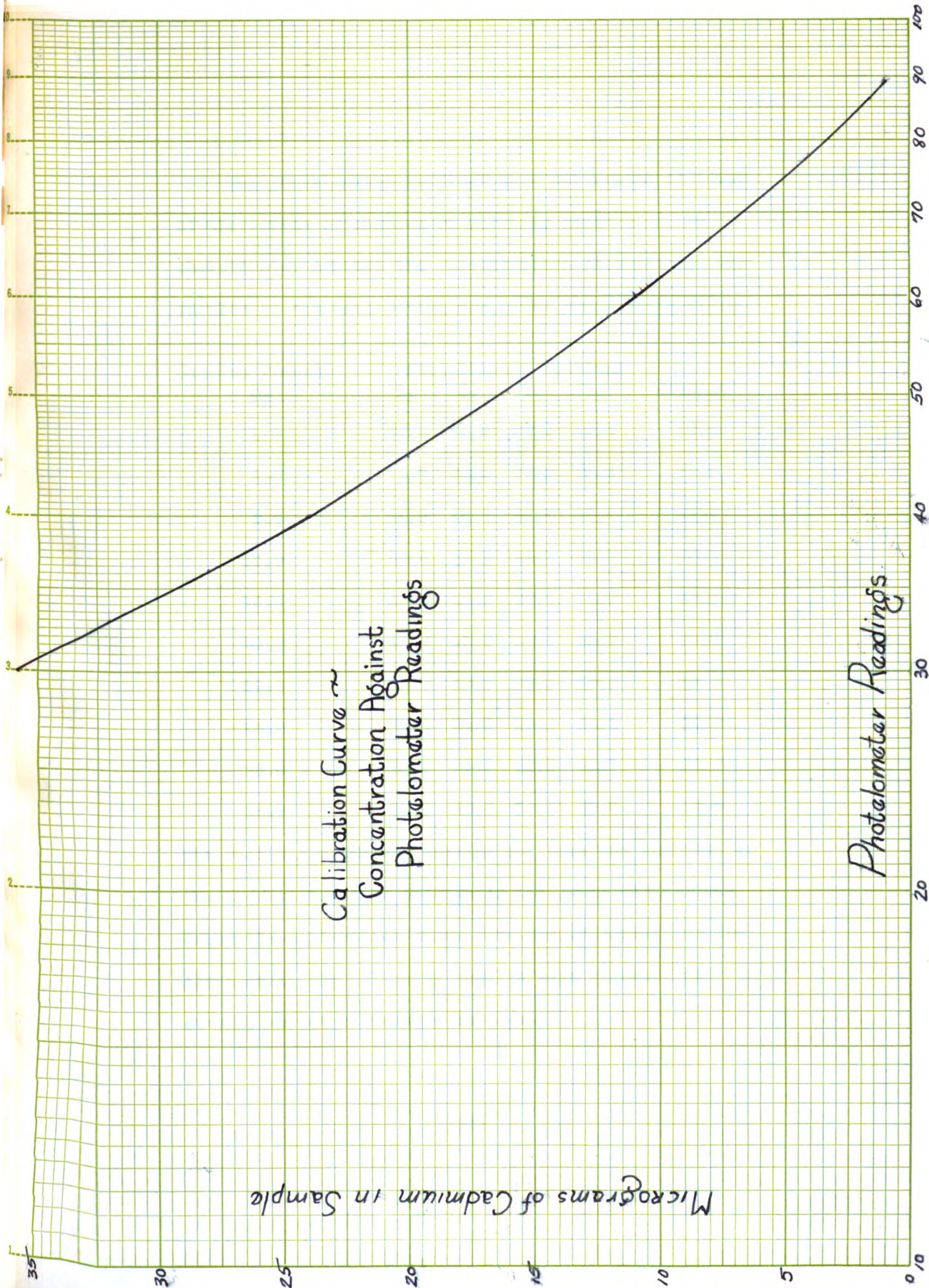
Concentration - Photometer
Reading Curve.



Micrograms of Cadmium in Sample

Calibration Curve ~
Concentration Against
Photometer Readings

Photometer Readings



The photelometer readings were calibrated in terms of micrograms of cadmium by plotting reading on the photelometer against the concentration of cadmium. The results of the calibration are given immediately below.

Cadmium Present Cd ✓	Phtelometer Readings				Average
	1.	2.	3.	4.	
1.0	89.5	89.8	87.0	89.4	89.4
4.0	76.7	78.0	77.2	76.6	76.7
8.0	66.9	66.9	66.7	67.0	66.8
12.0	58.0	58.2	59.1	58.0	58.1
16.0	50.0	50.0	50.0	51.0	50.0
20.0	45.0	45.0	45.0	45.0	45.0
24.0	39.7	39.8	39.5	39.9	39.8
28.0	36.0	35.9	39.2	36.5	36.2
32.0	32.6	33.0	33.0	32.7	32.8
36.0	30.0	30.0	30.0	30.0	30.0

The readings which are crossed out were not included in the average readings because of the great differences. Using the calibration curve obtained from plotting the above data, the following results were obtained on several series of unknown samples.

Cadmium Present ✓	Cadmium Found ✓	Error	
		✓Cd	%Cd
10.0	10.8	+ .8	+8.0
20.0	19.8	- .2	-1.0
2.0	2.1	+ .1	+5.0
4.0	4.2	+ .2	+5.0
8.0	8.0	.0	.0
6.0	6.0	.0	.0
30.0	29.0	-1.0	-3.3
16.0	14.8	-1.2	-8.0
20.0	22.0	+2.0	+10.0
20.0	20.0	.0	.0
10.0	10.1	+ .1	+1.0
10.0	10.1	+ .1	+1.0
6.0	6.0	.0	.0
8.0	11.5	+3.5	+45.0
16.0	17.0	+1.0	+6.3
22.0	22.0	.0	.0
6.0	6.0	.0	.0
10.0	10.5	+ .5	+5.0
18.0	18.5	+ .5	+1.7
16.0	16.4	+ .4	+2.5
2.0	2.2	+ .2	+10.0
8.0	8.3	+ .3	+3.6

Cadmium Present ✓	Cadmium Found ✓	Error	
		✓Cd	%Cd
4.0	4.0	.0	.0
4.1	4.0	-.1	-2.5
20.0	19.8	-.2	-1.0
8.0	8.2	+.2	+2.5
16.0	16.3	+.3	+1.8
12.0	12.0	.0	.0
6.0	5.8	-.2	-3.3
10.0	10.0	.0	.0
2.0	2.1	+.1	+5.0
14.0	14.5	+.5	+3.6
7.0	6.7	-.3	-4.3

As mentioned before in this report, Fischer and Leopoldi gave the following ions as interfering with the extraction of cadmium as the dithizonate: silver, gold, palladium, copper, mercury, nickel, cobalt, and zinc in large amounts, as well as any ions which would precipitate in the alkaline solution used for the extraction of the cadmium. Those metals which were found to precipitate were held back by the use of Rochelle salt. Sandell (7) found that this method was not satisfactory in holding up manganese which interfered with the complete precipitation of the cadmium dithizonate. Chromium as chromic ion was found to give the same difficulty in addition to giving a slight pinkish-purple color to the extract.

In the work that follows the following ions were examined for their effect on the extraction of cadmium and, where methods were not given by the literature for the removal of any interference, attempts were made at developing suitable procedures.

The ions were: calcium, phosphate, ferric, cupric, bismuth, lead, cobalt, nickel, zinc, strontium, barium, chromic, arsenious, and silver.

It was found that calcium did not give difficulties

with the procedure as developed originally in this paper. A series of determinations gave the following results:

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion ✓	Error %Cd	%Cd
20.0	20.0	10% Ca	.0	.0
20.0	20.0	50% Ca	.0	.0
20.0	20.0	100% Ca	.0	.0
20.0	20.5	150% Ca	.5	2.5
20.0	19.8	200% Ca	-.2	-1.0
20.0	19.8	250% Ca	-.2	-1.0
20.0	19.9	300% Ca	-.1	-.5
20.0	19.9	350% Ca	-.1	-.5
20.0	20.0	400% Ca	.0	.0
20.0	19.7	500% Ca	-.3	-1.5

The results above are all corrected for a blank on the calcium solution and reagents of two micrograms. All comparisons above were made on the photometer. No additional precautions appear to be necessary than those necessary in the ordinary procedure.

The presence of the phosphate ion also appeared to cause no difficulty. A series of determination made in the presence of phosphate ion gave good results with no additional precautions.

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors %Cd	%Cd
10.0	9.8	100 ✓ PO_4^{-3}	-.2	-2.0
20.0	19.9	200 ✓ "	-.1	-.5
10.0	10.0	300 ✓ "	.0	.0
14.0	14.0	400 ✓ "	.0	.0
10.0	10.2	500 ✓ "	.2	2.0
4.0	4.0	400 ✓ "	.0	.0
16.0	15.9	300 ✓ "	-.1	-.6
10.0	10.2	200 ✓ "	.2	2.0

7.0 (sample off color - no readings possible)

To ascertain the effects of larger amounts of phosphate ion upon the accuracy of the results the following series was run:

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors %Cd	%Cd
10.0	9.8	1.0 gra. PO_4^{-3}	-.2	-2.0
20.0	20.0	1.0 gra. "	.0	.0
18.0	18.2	1.0 gra. "	.2	1.1
2.0	3.0	1.0 gra. "	1.0	50.0
6.0	6.3	1.0 gra. "	.3	5.0
22.0	22.3	1.0 gra. "	.3	1.4
14.0	13.8	1.0 gra. "	-.2	-1.4
30.0	29.4	1.0 gra. "	-.6	-2.0
26.0	25.8	1.0 gra. "	-.2	-.8

Ferric iron, one of the ions precipitating in such alkaline solutions, causes great difficulties because of the fact that part of the cadmium dithionite is absorbed on the surface of the ferric hydroxide formed. The following data gives results obtained when nothing is added to hold up the iron:

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors % Cd	Errors % Cd
20.0	11.5	.5 mg Fe ⁺³	-8.5	-42.5
16.0	8.8	.5 mg "	-7.2	-45.0
8.0	4.0	.5 mg "	-4.0	-50.0
4.0	1.5	.5 mg "	-2.5	-62.5
2.0	.5	.5 mg "	-1.5	-75.0

By trying various concentrations of potassium sodium tartrate and sodium citrate, the best concentration was found to be five milliliters of 25% tartrate of citrate in the twenty milliliters of water solution. Using potassium sodium tartrate the following results for the determination of cadmium in the presence of a small amount of iron.

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors ✓ Cd	Errors %Cd
2.0	2.2	.5 mg Fe ⁺³	.2	10.0
8.0	8.1	.5 mg "	.1	1.3
10.0	10.0	.5 mg "	.0	.0
14.0	13.8	.5 mg "	-.2	-1.5
18.0	17.7	.5 mg "	-.3	-2.0
22.0	22.3	.5 mg "	.3	1.5
20.0	20.1	.5 mg "	.1	.5
16.0	15.6	.5 mg "	-.4	-2.5
12.0	12.1	.5 mg "	.1	.9

With larger concentrations of iron running as high as four milligrams per twenty milliliters of aqueous solution, the following results were obtained using five milliliters of 25% potassium sodium tartrate to tie up the iron:

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors ✓ Cd	Errors %Cd
10.0	9.8	1.0 mg Fe ⁺³	-.2	-2.0
10.0	9.5	1.5 mg "	-.5	-5.0
10.0	10.2	2.0 mg "	.2	2.0
10.0	10.1	2.5 mg "	.1	1.0
10.0	10.5	3.0 mg "	.5	5.0
10.0	10.4	4.0 mg "	.4	4.0

Since the citrates have been used with great success in tying up iron in the determination of nickel as the dimethyl glyoxime salt, sodium citrate was tried in this determination with the following results. Five milliliters of 25% sodium citrate were used.

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors ✓Cd	Errors %Cd
10.0	10.0	.5 mg Fe ⁺³	.0	.0
10.0	10.3	1.0 mg "	.3	3.0
10.0	10.2	1.5 mg "	.2	2.0
10.0	9.7	2.0 mg "	.3	3.0
10.0	9.8	2.5 mg "	.2	2.0
10.0	10.2	3.0 mg "	.2	2.0
10.0	10.0	3.5 mg "	.0	.0
10.0	9.7	4.0 mg "	.3	3.0

In an attempt to find if other poly-hydroxy organic compounds could be used to tie up the iron, a series of determination were run using glycerine. The following table shows the results obtained with various concentrations of iron.

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors ✓Cd	%Cd
2.0	2.1	.1 mg Fe^{+3}	.1	5.0
5.0	4.8	.2 mg "	.2	-4.0
7.0	6.7	.3 mg "	.3	-5.2
10.0	9.8	.2 mg "	.2	-2.0
20.0	20.3	.4 mg "	.3	1.5
30.0	29.6	.5 mg "	.4	-1.3
10.0	9.7	.5 mg "	.3	-3.0
10.0	9.5	1.0 mg "	.5	-5.0
10.0	9.3	1.5 mg "	.7	-7.0
10.0	9.5	2.0 mg "	.5	-5.0
10.0	9.2	2.5 mg "	.8	-8.0
10.0	10.0	3.0 mg "	.0	.0
10.0	10.0	3.5 mg "	.0	.0
10.0	9.5	4.0 mg "	.5	-5.0

One milliliter of glycerine which theoretically is many times that actually needed to tie up the iron present was used in each case. In both the tables above it can be seen that the predominant tendency is to be slightly low. However, no precipitate of ferric hydroxide was noted. The use of a higher concentration of glycerine was not tried due to the fact that a very large excess over that theoretically need-

ed was used. It is evident from these results that glycerine is not as satisfactory as either potassium sodium tartrate or sodium citrate.

With cupric copper and silver results were obtained similar to those found by Fischer and Leopoldi (6) who extracted small amounts of these ions by a previous extraction in an acid solution. The solution used for this extraction had an approximate pH value of 4.0. A subsequent extraction by the usual method for cadmium gave satisfactory results. However, with large amounts of silver and cupric copper, it was impossible to extract these interfering ions completely enough to get comparisons on the cadmium without losing the bulk of the cadmium along with them. The following results were obtained with a silver content up to one hundred micrograms:

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors %Cd ✓Cd	Errors %Cd %Cd
10.0	9.8	.01 mg Ag	-.2	-2.0
10.0	10.0	.04 mg Ag	.0	.0
10.0	9.7	.06 mg Ag	-.3	-3.0
10.0	10.4	.08 mg Ag	.4	4.0
10.0	9.9	.09 mg Ag	-.1	-1.0
10.0	10.3	.05 mg Ag	.3	3.0

Without this previous extraction of silver, the yellow of the silver dithizonate is preferentially extracted and obscures the cadmium color. The series run with copper present showed the same effect. Five samples were run without the acid extraction, and no comparisons were possible because the yellow cupric dithizonate obscured the red cadmium color. The results of five samples previously acid extracted showed the following results:

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors %Cd	%Cd
10.0	10.2	.02 mg Cu ⁺²	.2	2.0
10.0	9.8	.04 mg "	-.2	-2.0
10.0	10.0	.06 mg "	.0	.0
10.0	10.3	.08 mg "	.3	3.0
10.0	9.9	.10 mg "	-.1	-1.0

A few samples with larger amounts of copper were run using hypophosphorous acid to reduce the cupric ion to metallic copper which was filtered off. However, due to some influence, these samples were found to be sufficiently off color to prevent accurate comparison.

Bismuth and lead are both extracted in alkaline solution, but the dithizonates are theoretically decomposed at the alkalinity necessary for most complete

extraction of the cadmium. These two metals were run in a series using five milliliters of 25% potassium sodium tartrate in the strongly alkaline solution. The following results were obtained:

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors ✓Cd	Errors %Cd
10.0	10.1	.5 mg Pb	.1	1.0
10.0	10.3	1.0 mg Pb	.3	3.0
10.0	9.9	1.5 mg Pb	-.1	-1.0
10.0	9.7	2.0 mg Pb	-.3	-3.0
10.0	10.0	2.5 mg Pb	.0	.0
10.0	10.5	.5 mg Bi	.5	5.0
10.0	9.8	1.0 mg Bi	-.2	-2.0
10.0	10.3	1.5 mg Bi	.3	3.0
10.0	9.7	2.0 mg Bi	-.3	-3.0
10.0	10.0	2.5 mg Bi	.0	.0

Zinc in not too large amounts, strontium, barium, and arsenic (ious) seemed to give no difficulty in the extraction of the cadmium dithionite in the presence of either sodium citrate or potassium sodium tartrate. Zinc in large amounts, however, caused an increase in the intensity of color due to the extraction of some zinc along with the cadmium.

For relatively small amounts of zinc, the follow-

ing results were obtained using five milliliters of 25% potassium sodium tartrate or 25% sodium citrate as indicated.

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors ✓Cd	Errors %Cd
7.0	7.2	.10 mg Zn(cit)	.2	2.0
10.0	9.8	.20 mg Zn "	-.2	-2.0
20.0	20.4	.50 mg Zn "	.4	2.0
15.0	14.9	.80 mg Zn "	-.1	-1.0
2.0	2.3	.10 mg Zn "	.3	15.0
10.0	10.0	.20 mg Zn(tar)	.0	.0
5.0	4.8	.50 mg Zn "	-.2	10.0
25.0	25.5	.80 mg Zn "	.5	2.0

With larger amounts of zinc the following results were obtained:

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors ✓Cd	Errors %Cd
10.0	20.2	1.0 mg Zn	10.2	102.0
10.0	29.5	1.5 mg Zn	19.5	195.0
10.0	29.8	2.0 mg Zn	19.8	198.0
10.0	30.2	2.5 mg Zn	20.2	202.0

According to Fischer and Leopoldi (6), the cadmium may be precipitated as the sulfide and, after filtering off and redissolving, the cadmium may be extracted as

previously. This, however, was not attempted in the work of this paper.

A few additional samples were run with strontium, barium, and arsenic (ious) with the results given in the following table. Five milliliters of 25% sodium citrate were added in each case.

Cadmium Present ✓	Cadmium Found ✓	Interfering Ion	Errors %Cd	%Cd
20.0	20.4	5.0 mg Sr	.4	2.0
15.0	15.2	5.0 mg Sr	.2	1.5
10.0	9.9	5.0 mg Sr	-.1	-1.0
5.0	4.8	5.0 mg Sr	-.2	-4.0
20.0	20.0	5.0 mg Ba	.0	.0
15.0	14.8	5.0 mg Ba	-.2	-1.5
10.0	9.7	5.0 mg Ba	-.3	-3.0
5.0	5.3	5.0 mg Ba	.3	6.0
20.0	19.7	5.0 mg AsO ₃	-.3	-1.5
15.0	15.0	5.0 mg AsO ₃	.0	.0
10.0	10.2	5.0 mg AsO ₃	.2	2.0
5.0	5.0	5.0 mg As O ₃	.0	.0

Since no method has as yet been devised for accurately accounting for small amounts of cadmium in the presence of large amounts of nickel, an attempt was

made to solve this difficulty. Fischer (3) used stannous chloride to aid in the qualitative detection of cadmium in the presence of nickel and cobalt. This was tried with the quantitative determination, but was found to be unsuccessful, since appreciable amount of nickel and cobalt were extracted along with the cadmium giving a purplish color to the solution of cadmium dithionite. The excess tin also caused a change in the color of the extract; hence, this idea was discarded. The precipitation of nickel as the di-methyl glyoxime salt was also attempted. It was found that an excess of di-methyl glyoxime caused variations in colors which varied with the amount of di-methyl glyoxime present. Therefore, the excess dimethyl glyoxime must be removed by treating with nitric acid. Even after this was done, it was noticed that small amounts of nickel were left which caused an off coloring of the extract. Sandell in his paper (7) eliminated the difficulty attendant upon small amounts of nickel by extracting the cadmium in a slightly ammoniacal solution. However, he dealt with extremely small amounts of cadmium, about .2 micrograms. It was found that with larger amounts of cadmium complete extraction as the dithionite was not possible. The following table expresses results obtained by this

slightly ammoniacal extraction of cadmium. No nickel was present in these samples.

Cadmium Present γ	Cadmium Found γ	Errors			
			γ Cd	% Cd	
20.0	16.0	ammonia solution	4.0	20.0	
15.0	12.2	" "	2.8	21.0	
30.0	25.6	" "	4.4	14.0	
5.0	4.2	" "	.8	16.0	

The above results indicate about eighty per cent extraction at the pH obtained. However, the per cent extraction is not constant.

Since the precipitation of nickel dimethyl glyoxime is not complete enough to remove the last traces of nickel, and also that nickel is extracted under the same conditions as cadmium, this method cannot give results for the cadmium determination.

An attempt was made to precipitate the cadmium as cadmium sulfide leaving the nickel in solution using lead as a carrier for the small amount of cadmium present. However, it was found impossible to get complete precipitation of cadmium without precipitating a portion of the nickel; hence, the same difficulty is encountered here as in the precipitation of nickel as the dimethyl glyoxime salt.

Cobalt, which along with cadmium and nickel is extracted in the alkaline solution, could not be removed by any of the methods attempted. Methods for the precipitation of cobalt by hydroxylamine (14), and anthranilic acid (15) are given in the abstracts, but neither of these proved successful when tried. Cobalt then could not be removed from the extract and a purplish-brown color was always obtained.

Chromium as the chromic ion even in the presence of citrate or tartrate gives a purplish tint to the extract of cadmium dithizonate, preventing any comparison with the standard and gives erroneous results with the photometer. If present as the dichromate the dithione is oxidized almost immediately to the diazone. Large amounts of nitrate will also oxidize the dithione slowly as will pentavalent arsenic. Since this difficulty cannot be stopped by use of citrate or tartrate, cleaning solution must not be used to clean apparatus due to the danger of chromate being present. Large amounts of nitrate and arsenic though probably seldom encountered must be removed.

CONCLUSIONS

A method for the determination of cadmium as the cadmium dithizonate in which the red color of the dithizonate is compared directly has been developed both for the optical and the photoelectric colorimeters. The following ions were found not to interfere under the conditions of the experiment: calcium, phosphate, ferric, barium, strontium, arsenic (ious), manganous, bismuth, lead, zinc in not too large amounts, and cupric and silver in small amounts. Nickel and cobalt interfere, and no method was found which eliminated this difficulty.

BIBLIOGRAPHY

1. Fischer, E. Ann. 212, 316-24 (1882)
2. Fischer, H. Wiss. Veroff. Siemens-Konz.
4, 158, (1925)
reprinted in
Angewandte Chem.
42, 1025-9 (1929)
3. Fischer, H. Angew. Chem. 47, 685 (1934)
4. Fischer, H. Angew. Chem. 50, 919 (1937)
5. Clifford and Wichmann
J. Assoc. Off. Ag. Chem.
19, 130 (1936)
6. Fischer, H. and Leopoldi, G.
Mikrochemica Acta 1, 30-42 (1937)
7. Sandell, E. B.
Ind. & Eng. Chem. Anal. Ed.
31, 364 (1939)
8. Hillebrand and Lundell "Applied Inorganic Analysis"
John Wiley and Sons New York, N. Y.
1929 p.205.
9. Treadwell-Hall "Analytical Chemistry"
John Wiley and Sons New York, N. Y.
7th Ed. 1928 p. 189.

10. Hillebrand and Lundell; loc. cit. pp. 206-7
11. Treadwell-Hall; loc. cit. p. 192
12. Winter, O. B., Robison, Helen M., Lamb, Francis W.,
and Miller, E. J.
Ind. Eng. Chem. Anal. Ed. 27, 265 (1935)
13. Fischer, H. and Leopoldi, G.
Wiss. Veroff. Siemens-Kons. 12, 44 (1933)
14. Roldan, J. Casares
Anales Soc. Espan. fis quim.
28, 1080-3 (1930) C. A. 25, 261 (1931)
15. Funk, H. and Ditt, M.
Z. Anal. Chem. 93, 241-7 (1953)
C. A. 27, 4497 (1933)

CHEMISTRY LIBRARY

111

T543

CL
A735

126718

Armstrong



MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 02446 7536