SPECTROPHOTOMETRIC DETERMINATION

OF

CADMIUM AND MANGANESE

BY

LILY B. HAGOPIAN

submitted in partial fulfillment of the requirements

for the degree Master of Science

in the Chemistry Department of the

American University of Beirut

Beirut, Lebanon

June 1963

SPECTROPHOTOMETRIC DETERMINATION

OF

CADMIUM AND MANGANESE

BY

LILY B. HAGOPIAN

ACKNOWLEDGMENT

The author wishes to thank Professor Samir K. Thabet who suggested this problem and encouraged it with steady interest and counsel. She is also grateful to Professor Costas H. Issidorides for his helpful advice.

The author wishes to express her gratitude to the Arts and Sciences Research Committee for financial support.

ABSTRACT

A new spectrophotometric method for the determination of cadmium and manganese in presence of other cations is presented where a preliminary separation of cadmium and manganese is not required.

Both cadmium and manganese react with 2,6-dimethyl pyridinediimine N,N'-bis (o-hydroxy phenyl) to give a red complex which obeys Beer's law over the range 0 - 2000 p.p.m. of metal ion.

Colorimetric measurements were made at 460 mμ for cadmium and at 376 mμ for manganese. It was possible to detect cadmium and manganese in the presence of other cations such as Ca(II), Cu(II), Fe(III), Ni(II) and Co(II) all of which react with the reagent to give a red complex.

Only 0.05 ml of the cadmium sample and 0.1 ml of the manganese sample are required.

A new method for the rapid differentiation between the aminophenol isomers is also presented.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PART ONE: SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM AND MANGANESE

I. INTRODUCTION

2,6 dimethylpyridinediimine N,N'-bis (o-hydroxyphenyl) reacts with a large number of metal ions in alkaline solution to form intense red complexes which are extractable in chloroform.[1] Although the reagent is not specific, its reactions can be "conditioned" so that many highly selective and sensitive detections are possible. It was thus possible to detect cadmium and manganese qualitatively in the presence of ions such as Ni(II), Cu(II), Co(II), Zn(II), Fe(III), Ca(II), Al(III), Cr(III), Ba(II). The limits of identification were 0.025 ɣ per drop and 0.1 ɣ per drop for cadmium and manganese respectively.

The main objective of this work was to adapt the spot technique to the colorimetric determinations of cadmium and manganese. The extraction of the red complexes in chloroform, the success of the qualitative technique in presence of interfering ions suggested that the reagent could be of particular interest in colorimetric determinations. The methods which are proposedin the work aim at determining cadmium and manganese in the presence of foreign ions such as Ni(II), Co(II), Cu(II), Fe(III), Ca(II) without previous separation.

Cadmium and manganese were selected because at the time the work was initiated very few colorimetric methods were available for these

elements, in particular for manganese in the +2 oxidation state. Since then however, a number of methods have been proposed for cadmium and manganese, these are reviewed in the following section.

The cadmium methods require in the majority of cases repeated extraction of interfering ions, separation as sulfide or the absence of certain interfering ions.

The colorimetric methods for manganese based on the formation of permanganate are accurate and sensitive although certain precautions have to be taken in the selection of the oxidizing agent. The recent colorimetric methods involving complexes of Mn(II) are relatively few in number and require the separation of common ions such as Cd(II), Fe(III), Co(II), Ni(II).

In the methods which are presented in this work cadmium and manganese were determined in the presence of ions that were known to form colored complexes of their own with the reagent. No previous separation is required. In the presence of equal concentrations of cadmium and interfering ions a maximum deviation of 2% is obtained in the cadmium determination. For manganese, presence of interfering ions in the concentration ratios of 1:2, 1:5, 1:10 gave good results with a maximum deviation of 2% in the manganese determination; in certain cases presence of 40 fold concentration of foreign ions caused no interference. Mg(II) however interferes.

Attempts to determine the manganese content in sea water, blood serum and brass were however unsatisfactory.

The procedures which are described are simple and rapid, the determination of cadmium and manganese requiring 25 and 20 minutes

respectively of which, about 12 minutes are necessary for centrifugation.

In the course of the work it appeared that a sensitive test could be developed for aminophenols. Thus if o-aminophenol is added to pyridine 2,6 dialdehyde in the presence of cadmium ions and the solution is made alkaline, an intense red coloration is formed which is extractable in chloroform. With p-aminophenol a similar red coloration is formed but it is not extractable in chloroform, while with m-aminophenol no color is formed at all. This procedure was therefore developed to differentiate between the aminophenol isomers. The method proposed is very rapid requiring about 2 minutes and the limits of detection were 5 ɣ per drop of o- and p-aminophenol.

The procedures used to determine cadmium and manganese are presented in the first part of the thesis and the differentiation between the aminophenol isomers is described in the second part.

II. HISTORICAL

A. Cadmium Determination

1. Gravimetric Methods

Most of the methods for the determination of cadmium require preliminary separation of cadmium from almost all other elements, and thus result in lengthy, tedious procedures, involving many operations of precipitation, filtration, washing and drying of the precipitate. Methods employed most involve the precipitation of cadmium as the molybdate, quinaldinate, naphthaquinolinate[2], anthranilate[3] or pyridinethiocyanate[4]. Cadmium is also precipitated as the ammonium phosphate[5] which can be ignited and weighed as the pyrophosphate[6]. The method is inaccurate for concentrations of cadmium larger than 0.2 gr/ 100 ml.

Cadmium sulfide obtained as a result of cadmium separation can be converted to cadmium sulfate by addition of excess sulfuric acid, but it is difficult to expell all the acid, and the precipitate is often contaminated by adsorbed cadmium salts.[7]

2. Volumetric Methods

Cadmium can be determined volumetrically by addition of excess iodine to cadmium sulfide and the excess titrated with thiosulfate to a colorless starch end point, and then back titrated with iodine to a distinct blue.[8] The cadmium anthranilate precipitate is dissolved and titrated by excess bromate-bromide method.[9] The cadmium pyridine thiocyanate precipitate is filtered and the excess thiocyanate titrated with silver nitrate.[10]

These methods require a preliminary separation of cadmium as the

sulfide. They are not accurate, because the precipitate is not pure sulfide, some of it being in the form of cadmium sulfate, hence low results are apt to be obtained.

3.- Colorimetric Methods

The most recent methods for the determination of cadmium are colorimetric, and are few in number. Cadmium forms a red complex with dithizone[11] which can be extracted by carbon tetrachloride at pH values above 10, and determined colorimetrically at 515 mμ. The accuracy of the method is only fair, since the compound is not very stable particularly when dissolved in carbon tetrachloride. As little as 0.02 p.p.m. of cadmium can be determined and 1 part of cadmium can be separated from 1000 parts of zinc. Cu(II), Ag(I), Hg(II), Pd(II), Ni(II) and Co(II) interfere however. Cu(II) and Hg(II) are removed by a preliminary extraction with dithizone in acid solution, Ni(II) is removed by extraction with chloroform in ammoniacal citrate solution as the dimethylglyoxime complex, and Co(II) gives a stable complex with dimethylglyoxime which is not extractable and does not therefore interefere. Many extraction operations are necessary for elimination of interfering ions, and more than 500 γ of Zn(II) and 500 γ of Pb(II) interfere.

Colorimetric determination of cadmium at 600 mμ with sodium 1,8-dihydroxy-2-(2-hydroxy phenylazo)-3,6 naphthalenedisulfonate[12] requires a preliminary separation of cadmium as the sulfide because magnesium and zinc interfere. The maximum error is 3%.

Cadmium is determined spectrophotometrically with glyoxal bis-(2-hydroxy anil)[13] at 610 mμ, at which wavelength the reagent has a

negligible absorbance. The red color obtained is stable for 60 minutes, and Beer's law holds for 1 - 40 γ of cadmium per 10 ml of solution. Small amounts of nickel and cobalt interefere and should be masked with potassium cyanide.

Cadmium gives a colored complex with 1-(2-pyridyl azo)-2-naphthol[14] between pH values of 8.7 - 10. The complex is extracted in chloroform and the absorbance measured at 555 mμ. The solution should be free of the following interfering ions: As(III), Cr(III), Mg(II), Pb(II), Sb(III), Th(IV), Ti(IV) citrates, fluorides, phosphates and ortho vanadates.

Colorimetric determination of cadmium with Rhodamine B[15] is based on the reaction of CdI_2 with the reagent to form $[CdI_4]\ [C_{28}H_{31}O_3N_2]_2$ complex, with a maximum color intensity at 580 mμ. Cu(II), Bi(III), Sb(III), Hg(II) should be separated by sodium diethyldithiocarbamate; Zn(II), Co(II) and Ni(II) interfere in amounts greater than 10 mg. The interference of Fe(III) is reduced by addition of ascorbic acid.

B. Mangansese Determination

1. Gravimetric Methods

Most of the gravimetric methods for the determination of manganese require a preliminary separation of manganese as the dioxide by treating it with potassium chlorate.[16] Precipitation of the dioxide is never quantitative and fails with very small amounts of manganese. The manganese dioxide precipitate is contaminated by silicon, tungsten, colombium, tantalum, iron, antimony, cobalt and vanadium[17].

Volhard[18] proposed precipitation of manganese as the sulfate by addition of sulfuric acid on the oxide of manganese, provided no other

sulfates are present.

Gibbs[19] recommended precipitation of manganese as the phosphate or pyrophosphate, where the solution should not contain more than 0.2 gr of manganese per 200 ml.

These tests are very long; they involve many operations of pH adjustment and handling of precipitates.

2. Volumetric Methods

Volumetric determinations of manganese involve oxidation of Mn(II) to MnO_2 or MnO_4^- and subsequent titration of the permanganic acid formed by a reducing agent, when sodium bismuthate[20] is used as an oxidizing agent the excess bismuthate has to be removed by filtration and the permanganate formed titrated with ferrous sulfate. Ce(IV), Co(II), Cr(VI), and V(V) interfere.

Persulfate[21] oxidizes Mn(II) in acid solution in presence of silver nitrate to permanganic acid, which is titrated with arsenious acid. This method is less accurate than the bismuthate method and Cr(III) interferes at concentrations greater than 10 mg/100 ml.

Volhard's[22] method involves oxidation of Mn(II) to MnO_2 by titration with potassium permanganate, where the color of excess permanganate marks the end point of the titration. The determination is quantitative above pH of 3 to 4 but Cr(III), Ni(II), Co(II) and sulfates interfere.

Manganese is determined by potentiometric titration of Mn(II) with permanganate in neutral pyrophosphate solution.[23] The manganic pyrophosphate complex has an intense reddish-violet color. The

method is accurate and short, but the complex is unstable at a pH higher than 8. Large amounts of Mg(II), Cd(II) and Al(III) interfere by giving precipitates which may coprecipitate with manganese, and equal amounts of V(IV) interfere by being oxidized to V(V).

3. Colorimetric Methods

Most of the colorimetric determinations of manganese involve oxidation of Mn(II) to permanganate by sodium bismuthate or potassium or ammonium persulfate in presence of silver nitrate or by potassium periodate.[24] Colorimetry of permanganate is an accurate, specific and sensitive method but for some disadvantages: thus for instance excess of sodium bismuthate must be removed while persulfate oxidizes Mn(II) to permanganate incompletely and no more than 1.5% Mn(II) should be present for reliable results. The periodate method does not present these disadvantages, but no more than 2 mg/100 ml of Mn(II) should be present for accurate results. Phosphoric acid should be added to decolorize Fe(III).

There are very few colorimetric determinations of manganese in the oxidation state of +2 involving complex formation or chelation. Thioxine[25] forms a stable complex with Mn(II), the color intensity of which is determined colorimetrically at 413 mμ. Tl(I), Pb(II), Zn(II), Cd(II), V(IV) and Sn(II) interfere and so should be removed.

Salicylal-o-aminophenol[26] forms a brown complex at pH 9.6 - 11.6 with Mn(II), which is determined colorimetrically at 428 mμ. The sensitivity is 0.25γ per 5 ml of solution, but Fe(III), Cu(II), Ti(IV), Co(II) and Ni(II) interfere by giving similar colors.

Anthranilo hydroxamic acid (2-amino benzohydroxamic acid)[27] is used for complexing Mn(II) at a pH greater than 9.2, giving a wine red complex. The maximum color absorbance is at 490 - 500 mμ. Fe(III) interferes above a 250 fold concentration of Mn(II).

2,6 pyridine dialdoxime[28] chelates with Mn(II) at pH of 9.5 - 11.5 to form green or red chelates at low or high concentrations of Mn(II) respectively. The maximum absorbance is at 598 mμ, and 0.1 - 10 γ of Mn(II) per ml of solution can be determined. The color is stable for several hours, but reducing agents such as ascorbic acid, hydroxyl amine hydrochloride and $N_2H_4.H_2SO_4$ destroy the chelate. Fe(III), Co(II) and Ni(II) interfere by producing colored chelates of their own.

1-(2-pyridyl azo)-2-naphthol[29] reacts with Mn(II) giving a colored complex between pH 5 - 9. It is extracted in diethyl ether and has a maximum absorbance at 560 mμ. As(III), Cr(III), Mg(II), Pb(II), fluorides and ortho vanadates interfere.

III. EXPERIMENTAL

A. Spectrophotometric Determination of Cadmium

Apparatus

Spectrophotometric determinations were made with the Unicam S.P. 600 spectrophotometer using glass cells of 1 cm thickness.

A Hamilton Co., Inc., microsyringe was used for smaller than 0.1 ml volume measurements.

pH measurements were made with a Radiometer pH meter type PHM 4C.

An M.S.E. centrifuge was used for centrifugation.

Reagents

Reagent Solution

2,6 dimethylpyridinediimine N,N'-bis (o-hydroxyphenyl) was prepared by the following method: 0.44 gr of freshly sublimed o-aminophenol obtained from Fluka A.G. Buchs S.G., was dissolved in 75 ml of water at 100°C. To this was added 0.27 gr of pyridine 2,6 dialdehyde in 25 ml of water. The pyridine-2,6-dialdehyde was obtained by the University of Illinois from Raschig Co., Germany. The mixture was maintained in a water bath for 30 minutes, then stored overnight in the refrigerator. The yellow precipitate was filtered and washed with water, and recrystallized from methyl alcohol. 0.53 gr were obtained, corresponding to a 78% yield. The solid reagent was kept in the refrigerator.

The reagent solution was prepared daily by dissolving 20 mg of the solid reagent in 5 ml of ethyl alcohol and was kept in a dark brown glass bottle.

Sodium hydroxide solutions

10% NaOH solution and 1% NaOH solution were prepared.

Buffer solution

A buffer solution was prepared by adding 25 ml. of saturated $Na_2HPO_4.12H_2O$ solution to 25 ml of 10% NaOH solution.

All other reagents were of analytical grade and were used without further purification.

Standard cadmium solutions

A 1% cadmium solution was prepared by dissolving 1.7700 gr of $CdCl_2$ in 100 ml of water. The 1% solution was diluted to 0.1%.

Stock solutions of cadmium containing 100, 125, 200, 250, 333, 500, 555, 666, 714, 833 p.p.m. were prepared by adding to 1 ml portions of the 0.1% cadmium solution 9, 7, 4, 3, 2, 1, 0.8, 0.5, 0.4, and 0.2 ml of water respectively.

Stock solutions of cadmium containing 1111, 1428, 2000, and 3333 p.p.m. were also prepared by adding to 1 ml portions of the 1% cadmium solution 8, 6, 4, 2 ml of water respectively.

Solutions of foreign ions

A 1% solution of each of the following ions was prepared: Cu(II), Ca(II), Ni(II), Co(II), Mn(II), Fe(III) by dissolving 3.9098 gr of $CuSO_4.5H_2O$, 5.9261 gr of $Ca(NO_3)_2.4H_2O$, 4.3896 gr of $NiCl_2.6H_2O$, 4.9792 gr of $Co(NO_3)_2.6H_2O$, 3.7908 gr of $MnCl_2.4H_2O$ and 7.2290 gr of $Fe(NO_3)_3.9H_2O$ respectively in 100 ml of water.

1. Procedure for the determination of cadmium in the absence of foreign ions.

Before proceeding with the determination of cadmium in the presence

of other ions it was desirable to verify the validity of the method on cadmium alone. After many trials the following procedure was adopted.

To 0.05 ml of a cadmium sample solution transferred to a centrifuge tube by a microsyringe, 0.1 ml of the reagent solution was added with a microsyringe. The mixture was shaken well and 0.8 ml of 1% NaOH was added. These amountsof reagent and NaOH were chosen because they gave the best conditions of operation with minimum blank absorbance, good color formation and best separation of aqueous layer from chloroform. The pH of the solution was 13.2. 5 ml of chloroform were added and the centrifuge tube stoppered with a cork. The centrifuge tube was inverted 30 times and centrifuged at 3000 r.p.m. for 5 minutes. The lower chloroform layer was transferred into another centrifuge tube and centrifuged at 3000 r.p.m. for 5 minutes more, in order to get rid of the turbidity in the chloroform layer due to water adhering to the walls of the test tube. The clear chloroform layer was then transferred into a cell and the absorbance read by the spectrophotometer against a standard of pure chloroform. The same procedure was carried for a reagent blank containing 0.05 ml of water instead of the cadmium sample solution.

It was found that the absorbance varied with time; in order to obtain reproducible results it was necessary to fix the time at which the reading was taken. A preliminary investigation showed that maximum absorbance was around 460 mμ. Table 1 shows absorbance values taken at one minute intervals from the time NaOH is added to the solution. These values are plotted in Figure 1.

Table 1

Variation of Cadmium Complex Absorbance With Time After Addition

Of 0.8 ml of 1% NaOH

Time in minutes	Absorbance at 460 mμ
16	0.560
17	0.540
18	0.510
19	0.505
20	0.500
21	0.490
22	0.485
23	0.480
24	0.480
25	0.480
26	0.480
27	0.480
28	0.480
29	0.480
30	0.480
31	0.480
32	0.480
33	0.480
34	0.480
35	0.480

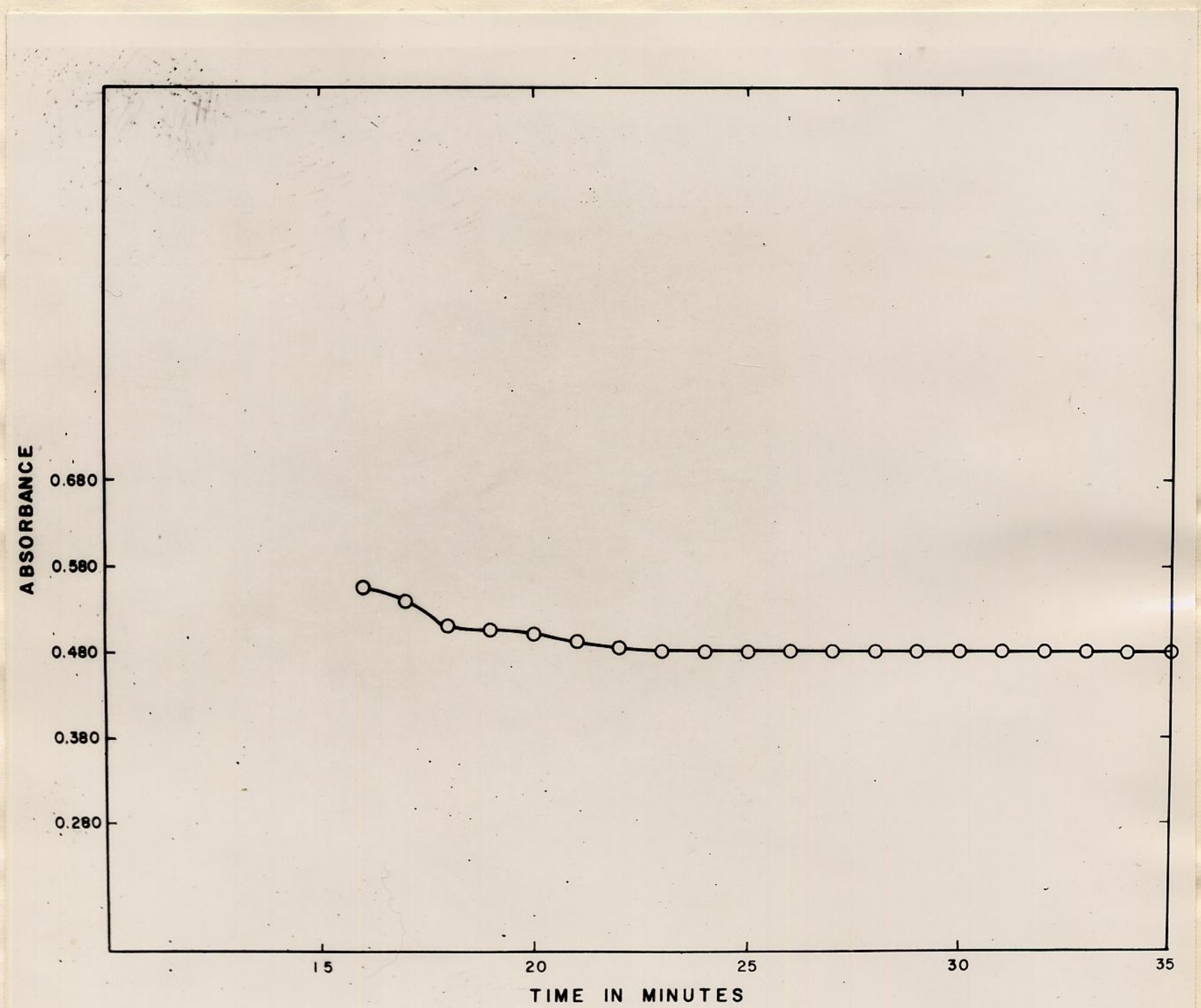


Figure 1 - Variation of Cadmium Complex Absorbance with time

Therefore readings were taken 25 minutes after addition of NaOH.

Absorbance values at different wavelengths for the blank and the cadmium complex are shown in Table 2. The procedure described above was followed and the time for taking the reading was 25 minutes after addition of the NaOH. The values are plotted in Figure 2.

Table 2

Absorbance Values for Cadmium Complex and Reagent Blank

λ in mμ	Absorbance	
	Reagent Blank	Cadmium Complex
350	0.155	0.461
360	0.145	0.419
370	0.120	0.305
380	0.100	0.245
390	0.090	0.242
400	0.095	0.278
410	0.100	0.335
420	0.105	0.412
430	0.130	0.490
440	0.140	0.560
450	0.145	0.618
460	0.155	0.645
470	0.150	0.635
480	0.135	0.595
490	0.125	0.530
500	0.096	0.441
510	0.075	0.345
520	0.055	0.260
540	0.020	0.145
560	0.005	0.080
600	0.000	0.022
650	0.000	0.015
700	0.000	0.005

Maximum absorbance for the cadmium complex is between 450-470 mμ.

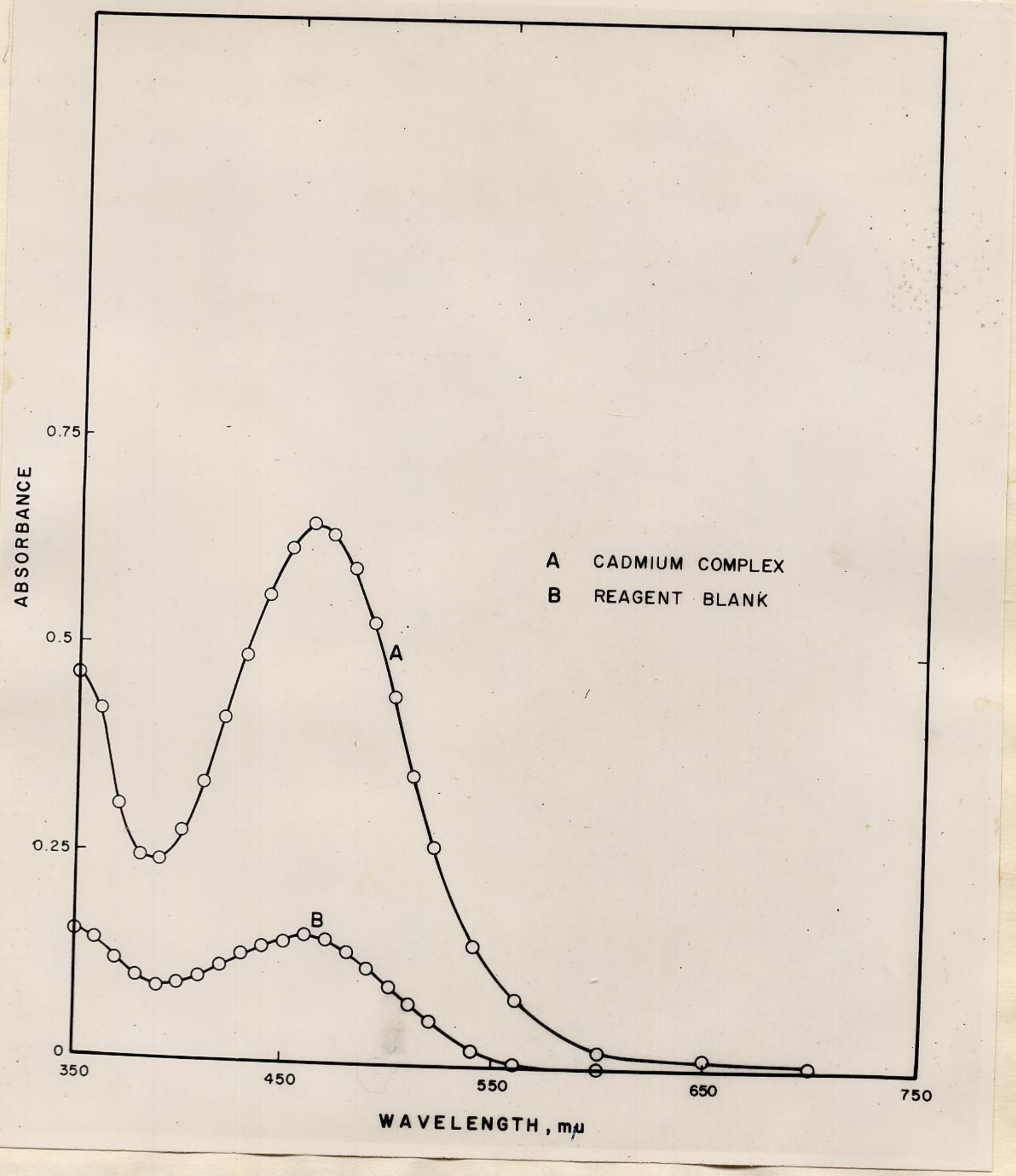


Figure 2 - Absorbance Curves for Cadmium Complex and Reagent Blank

A further breakdown was made between these values in order to determine accurately the maximum absorbance. The values are shown in Table 3 and the results plotted in Figure 3.

Table 3

Cadmium Complex Absorbance Between 450 and 470 mμ

λ in mu	Absorbance of Cadmium Complex
450	0.618
452	0.624
454	0.630
456	0.635
458	0.642
460	0.645
462	0.643
464	0.642
466	0.640
468	0.638
470	0.635

Therefore maximum absorbance for the cadmium complex is at 460 mμ. At this wavelength the reagent blank has an absorbance of 0.155.

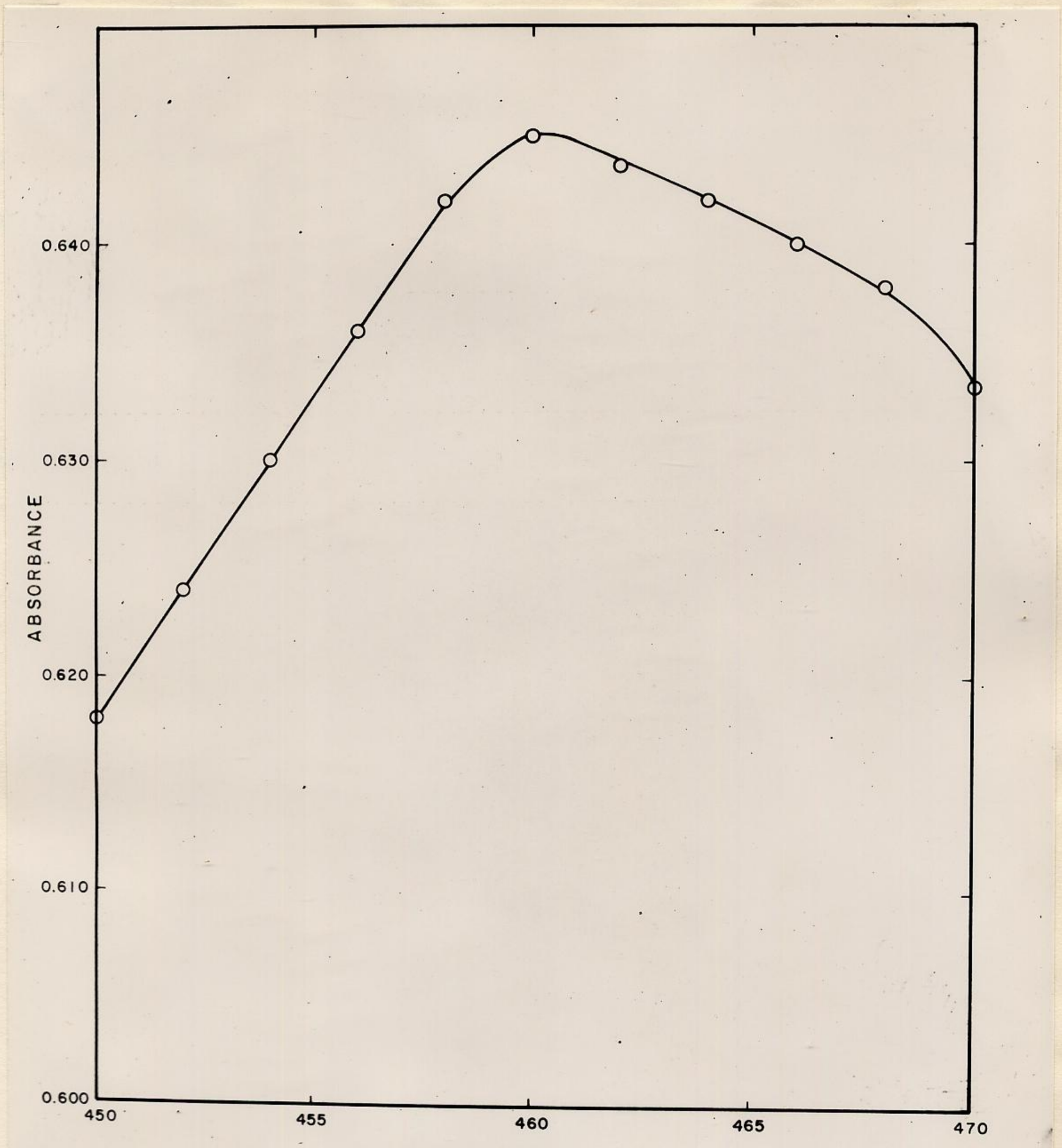


Figure 3 - Absorbance Curve for Cadmium Complex

Between 450 and 470 mμ.

Absorbances were obtained for the different stock solutions of cadmium by following the procedure proposed for the determination of cadmium in the absence of foreign ions. The values for the absorbance are shown in Table 4 and the calibration is plotted in Figure 4.

For cadmium concentrations above 2000 p.p.m. turbid solutions were obtained resulting in very high absorbance values.

Figure 4 shows that the colored system obeys Beer's law over the range 0 - 2000 p.p.m. or 0 - 0.2% of cadmium.

Table 4

Absorbance Calibration Values

p.p.m. of Cadmium	Absorbance	Abs. - Blank
blank	0.155	0.000
100	0.205	0.050
125	0.220	0.065
200	0.283	0.128
250	0.307	0.152
333	0.350	0.195
500	0.480	0.325
555	0.520	0.365
666	0.560	0.405
714	0.622	0.467
833	0.675	0.520
1000	0.790	0.635
1111	0.850	0.695
1428	1.070	0.915
2000	1.450	1.295
3333	> 1.5	--
10000	> 1.5	--

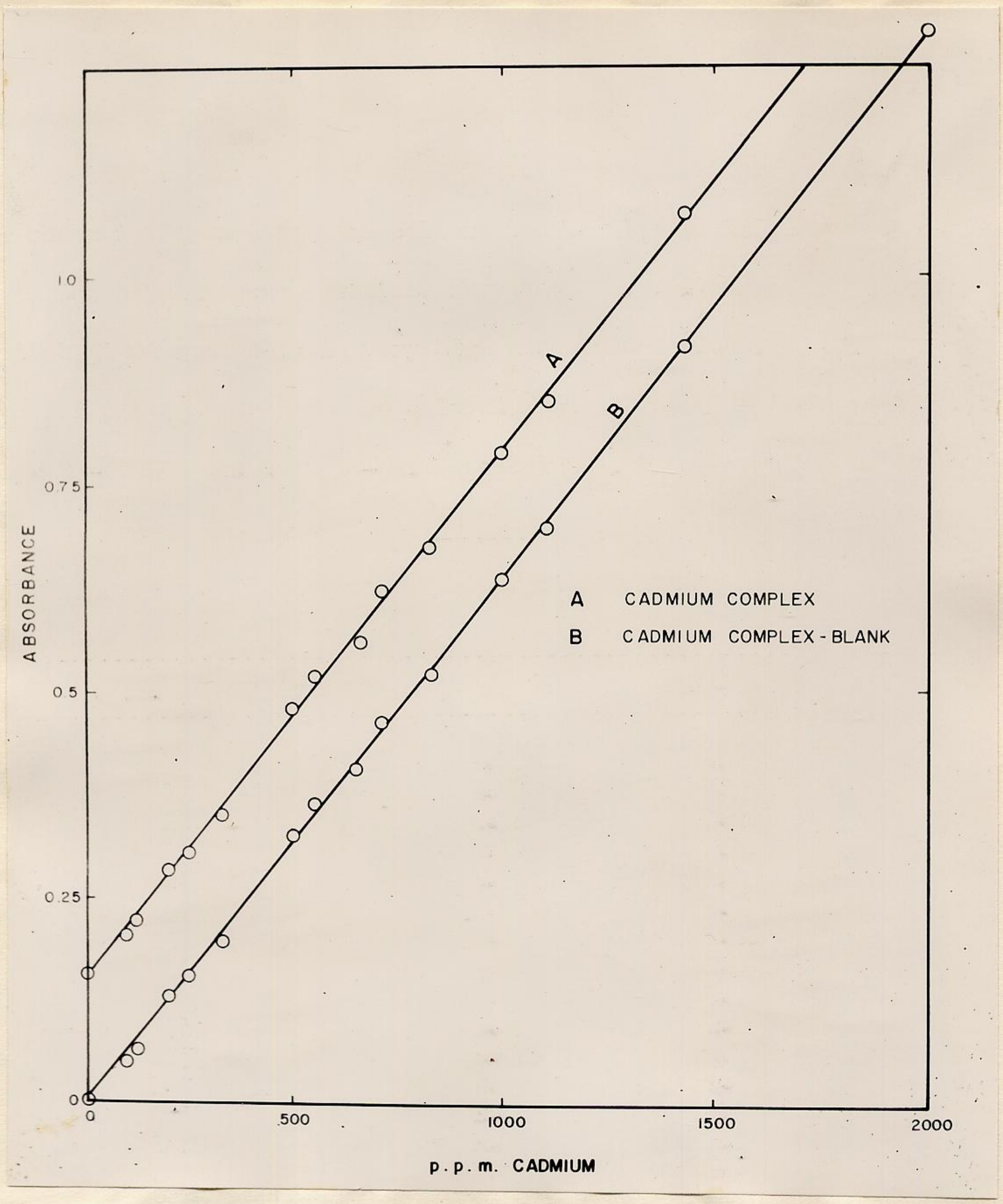


Figure 4 - Calibration for Cadmium (Absence of Foreign ions Method)

The results of the analysis of a series of synthetic samples containing cadmium by the above procedure are shown in Table 5.

Table 5

Analysis of Synthetic Samples

Cd(II) in p.p.m.		
Added	Absorbance - Blank	Found from Figure 4
200	0.130	205
500	0.330	515
714	0.470	735
1000	0.640	1005
2000	1.290	1993

These results show that the maximum deviation in cadmium determination is 3%, this deviation drops to 0.5% for 1000 p.p.m. of Cd(II) and to 0.35% for 2000 p.p.m. Cd(II).

2. Procedure for the determination of cadmium in presence of intefering ions.

In the presence of interfering ions such as Fe(III), Co(II), Ni(II), Mn(II), Ca(II), Cu(II) a modified procedure has to be used. It was observed that addition of NaOH and Na_2HPO_4 eliminated the interference of these ions. The NaOH-Na_2HPO_4 buffer maintained the solution at a pH of 13.7. It was prepared by adding 25 mls of saturated $Na_2HPO_4.12H_2O$

solution to 25 mls of 10% NaOH solution. The following procedure was finally adopted.

To 0.05 ml of the cadmium sample solution transferred into a centrifuged tube by a microsyringe, 0.6 ml of NaOH-Na_2HPO_4 mixture was added. The solution was shaken well and 0.2 ml of the reagent solution was added. After stoppering the centrifuge tube with a cork, it was inverted 30 times and centrifuged at 3000 r.p.m. for 5 minutes. The lower chloroform layer was transferred into another centrifuge tube, and centrifuged at 3000 r.p.m. for 5 more minutes. The clear chloroform extract was then transferred into a cell and the absorbance read at 460 mμ. Concentrations following best Beer's law were taken, that is between 500 - 1000 p.p.m. The same procedure was carried out for the reagent blank.

Maximum absorbance for the cadmium complex by this procedure was again at 460 mu, and readings were taken 25 minutes after the addition of the NaOH-Na_2HPO_4 mixture. Results are shown in Table 6 and plotted in Figure 5.

Table 6

Absorbance Calibration Values

p.p.m. of Cadmium	Absorbance	Absrobance -Blank
blank	0.170	0.000
500	0.670	0.500
555	0.728	0.558
666	0.845	0.680
714	0.910	0.740
833	1.035	0.865
1000	1.190	1.020

The color system obeys Beer's law over the concentration range investigated, that is between 500 - 1000 p.p.m. of Cd(II).

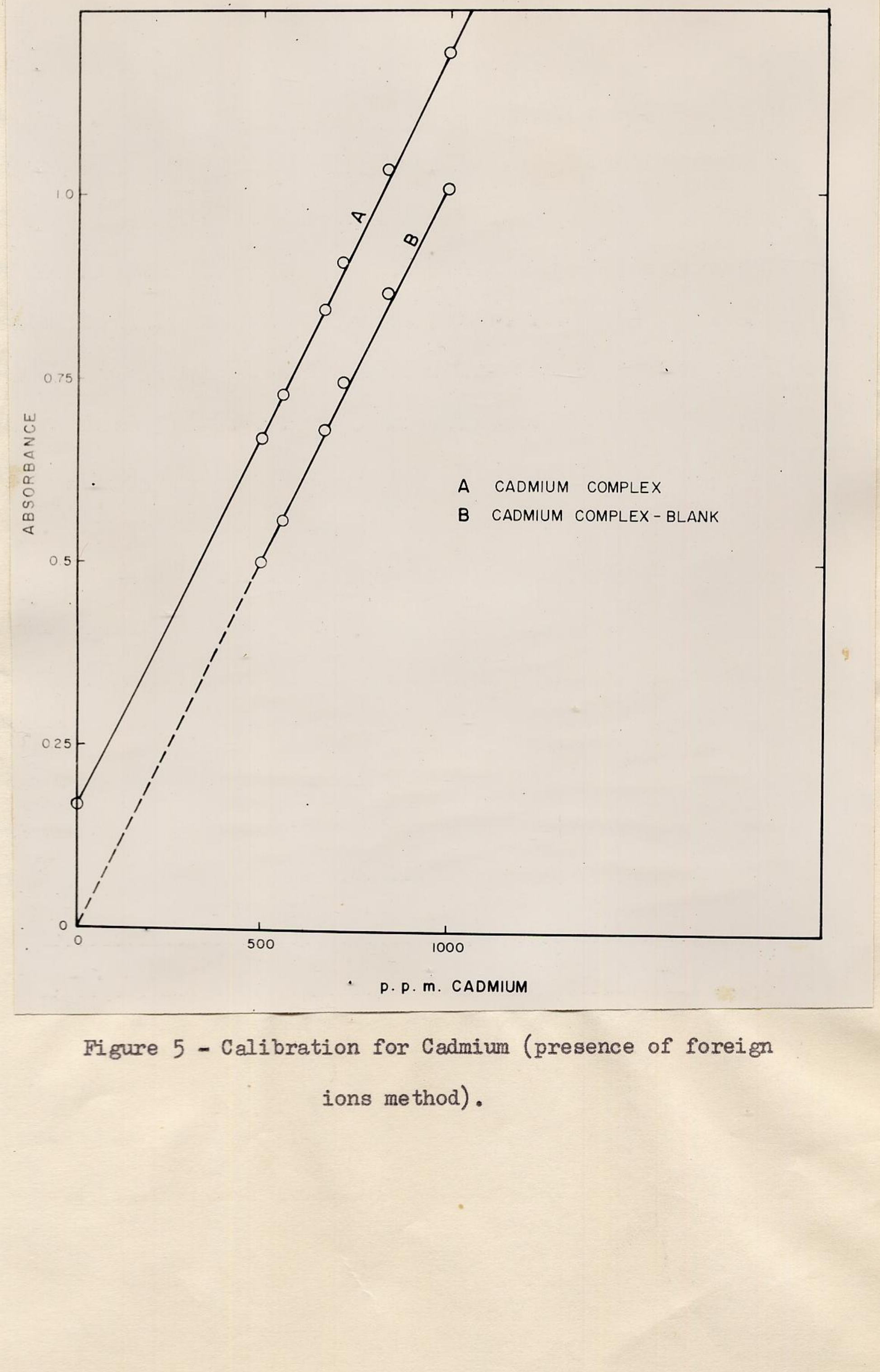


Figure 5 - Calibration for Cadmium (presence of foreign ions method).

Determination of cadmium in the presence of foreign ions.

The determination of cadmium was repeated in the presence of the following interfering ions: Fe(III), Co(II), Ni(II), Mn(II), Ca(II), Cu(II). The procedure was identical to the procedure described above, with the exception of Ca(II) and Cu(II). When Ca(II) or Cu(II) were present it was necessary to heat the test tube in a water bath for 25 seconds for Ca(II) and 30 seconds for Cu(II), after addition of the $NaOH-Na_2HPO_4$ mixture. Cadmium at concentrations above 500 p.p.m. with equal or smaller concentrations of Ca(II) and Cu(II) did not need heating in a water bath. When the other interfering ions were present in concentrations smaller than that of cadmium, they did not interfere.

The results obtained with various foreign ions are shown in table 7. Therefore cadmium could be determined in presence of the same concentration of Mn(II), Ni(II), Co(II), Fe(III), Ca(II), Cu(II) (500 p.p.m. Cd(II)- 500 p.p.m. of interfering ions) with a maximum deviation of 1.6%. With larger concentrations of cadmium and foreign ions (1000 p.p.m. Cd(II)- 1000 p.p.m. interfering ions) the maximum deviation in the cadmium determination is 2%.

Table 7

Analysis of Synthetic Samples of Cadmium and Foreign Ions.

p.p.m. of Cd(II) and foreign ions	Absorbance -Reag. Blank	p.p.m. of Cd(II) found from Fig.5
500 ppm Cd(II)+500 ppm Mn(II)	0.500	500
500 ppm Cd(II)+500 ppm Ni(II)	0.500	500
500 ppm Cd(II)+500 ppm Co(II)	0.505	502
500 ppm Cd(II)+500 ppm Fe(III)	0.508	508
500 ppm Cd(II)+500 ppm Ca(II)	0.495	493
500 ppm Cd(II)+500 ppm Cu(II)	0.500	500
1000 ppm Cd(II)+1000 ppm Mn(II)	1.020	1000
1000 ppm Cd(II)+1000 ppm Ni(II)	1.020	1000
1000 ppm Cd(II)+1000 ppm Co(II)	1.010	1008
1000 ppm Cd(II)+1000 ppm Fe(III)	1.010	1008
1000 ppm Cd(II)+1000 ppm Ca(II)	1.040	1020
1000 ppm Cd(II)+1000 ppm Cu(II)	1.025	1005

When the concentrations of interfering ions were less than those indicated above, the absorbances of the complex were in agreement with the absorbances of the cadmium alone.

B. Spectrophotometric Determination of Manganese

Apparatus

Spectrophotometric determinations were made with the Unicam SP 600 spectrophotometer using glass cells of 1 cm thickness.

A Hamilton Co. Inc., microsyringe was used for smaller than 0.1 ml volume measurements.

pH measurements were made with a Radiometer pH meter type PHM 4C.

An M.S.E. centrifuge was used for centrifugation.

Reagents

Reagent solution

The reagent used was 2,6 dimethylpyridinediimine N,N'-bis (o-hydroxy phenyl). The reagent solution was prepared daily by dissolving 2.5 mg of the solid reagent in 5 ml of ethyl alcohol and was kept in a dark brown glass bottle.

Masking solutions

A 5% KCN solution and a 0.2% $(NH_4)_2CO_3$ solution were prepared.

Standard manganese solutions

A 1% manganese solution was prepared by dissolving 3.7908 gr of $MnCl_2.4H_2O$ in 100 ml of water. The 1% solution was diluted to 0.1%.

Stock solutions of manganese containing 100, 200, 250, 333, 500, 666, 714, 833 p.p.m. were prepared by adding to 1 ml portions of the 0.1% manganese solution 9, 4, 3, 2, 1, 0.5, 0.4, 0.2 ml of water respectively.

Stock solutions of manganese containing 1250, 2000, 2500, 5000 p.p.m. were also prepared by adding to 1 ml portions of the 1% manganese solution 7, 4, 3, 1 ml of water respectively.

Solutions of foreign ions

A 1% solution of each of the following ions was prepared: Cu(II), Ca(II), Ni(II), Co(II), Cd(II), Fe(III), Mg(II) by dissolving 3.9098 gr of $CuSO_4.5H_2O$, 5.9261 gr of $Ca(NO_3)_2.4H_2O$, 4.3896 gr of $NiCl_2.6H_2O$, 4.9792 gr of $Co(NO_3)_2.6H_2O$, 1.7700 gr of $CdCl_2$, 7.2290 gr of $Fe(NO_3)_3.9H_2O$, and 10.5300 gr of $Mg(NO_3)_2.6H_2O$ respectively in 100 ml of water.

1. Procedure for the determination of manganese in the presence of foreign ions.

In the presence of interfering ions such as Fe(III), Co(II), Ni(II), Cd(II), Ca(II), Cu(II), it was necessary to add a mixture of KCN and $(NH_4)_2CO_3$ to eliminate the interference of these ions. The following procedure was finally adopted.

To 0.1 ml of the manganese sample solution transferred to a centrifuge tube by a microsyringe, 0.3 ml of 5% KCN solution was first added. The mixture was shaken well and 1.5 ml of 0.2% $(NH_4)_2CO_3$ and 0.3 ml of the reagent solution were then added in that order. The pH of the solution was 10.1. 5 ml of chloroform was added and the centrifuge tube stoppered with a cork and shaken well by inverting it 30 times. The mixture was centrifuged for 5 minutes at 3000 r.p.m., and the lower chloroform extract transferred into another centrifuge tube. Centrifugation for another 3 minutes was repeated at 3000 r.p.m. and the chloroform extract transferred into a cell. The absorbance was read by the spectrophotometer against a standard of pure chloroform. The same procedure was carried for a reagent blank containing 0.1 ml of water instead of the sample solution.

It was found that the absorbance varied with time; in order to obtain reproducible results it was necessary to fix the time at which the reading

was taken. A preliminary investigation showed that maximum absorbance was around 375 mμ. In Table 8 are shown the values for absorbance taken at one minute intervals from the time the reagent is added. These values are plotted in Figure 6.

Table 8

Variation of Manganese Complex Absorbance With Time After Addition of 0.3 ml of the Reagent

Time in minutes	Absorbance at 375 mμ.
13	0.450
14	0.445
15	0.420
16	0.438
17	0.435
18	0.440
19	0.440
20	0.440
21	0.440
22	0.440
23	0.440
24	0.440
25	0.440
26	0.440
27	0.440
28	0.440
29	0.440
30	0.440

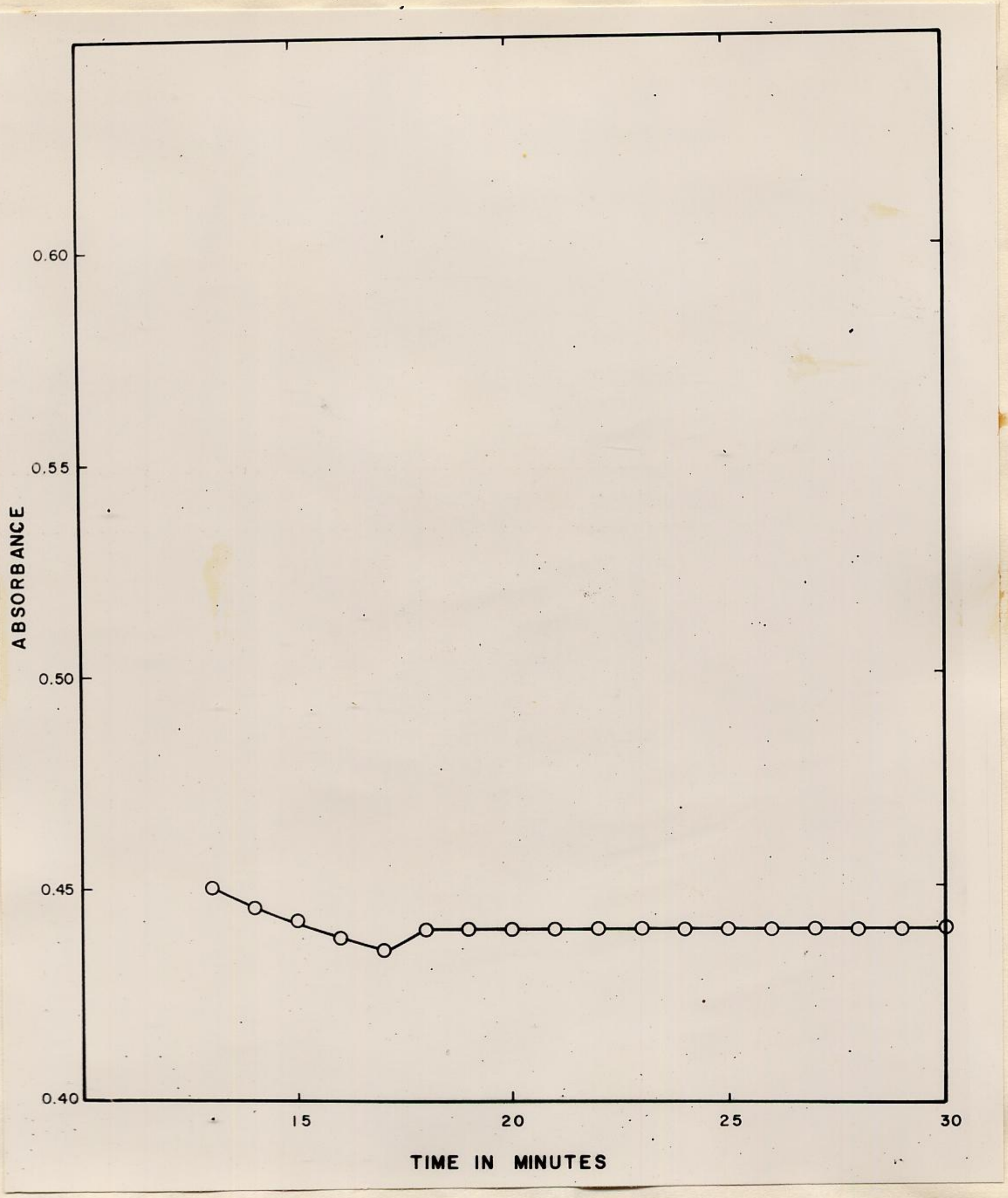


Figure 6 - Variation of Manganese Complex

Absorbance with Time

Absorbance values at different wavelengths for the blank and manganese complex are shown in Table 9. The procedure described above was followed and the time for taking the reading was 20 minutes after the addition of the reagent solution. The values are plotted in Figure 7.

Table 9

Absorbance Values for Manganese Complex and Reagent Blank

λ in mμ.	Absorbance	
	Reagent Blank	Manganese Complex
360	0.115	0.619
362		0.629
364	0.125	0.640
366		0.651
368		0.658
370	0.130	0.668
372		0.671
374		0.669
375		0.669
376	0.135	0.671
377		0.669
378		0.665
379		0.664
380	0.130	0.661
385		0.639
386	0.125	
390	0.115	0.600
400	0.095	0.480
410	0.075	0.355
420	0.050	0.248
430	0.036	0.200
440	0.030	0.198
450	0.025	0.206
460	0.022	0.215
470	0.020	0.225
480	0.018	0.235
490	0.016	0.240
500	0.014	0.246
510	0.014	0.246
525	0.014	0.244
550	0.010	0.225
580	0.007	0.175
600	0.005	0.145
625		0.115
650	0.008	0.085
675		0.074

Table 9 - Continued

λ in mμ.	Absorbance	
	Reagent Blank	Manganese Complex
700	0.010	0.093
725		0.135
750	0.015	0.174
775		0.198
800	0.017	

Therefore maximum absorbance for the manganese complex is at 376 mμ. At this wavelength the reagent blank has an absorbance of 0.135.

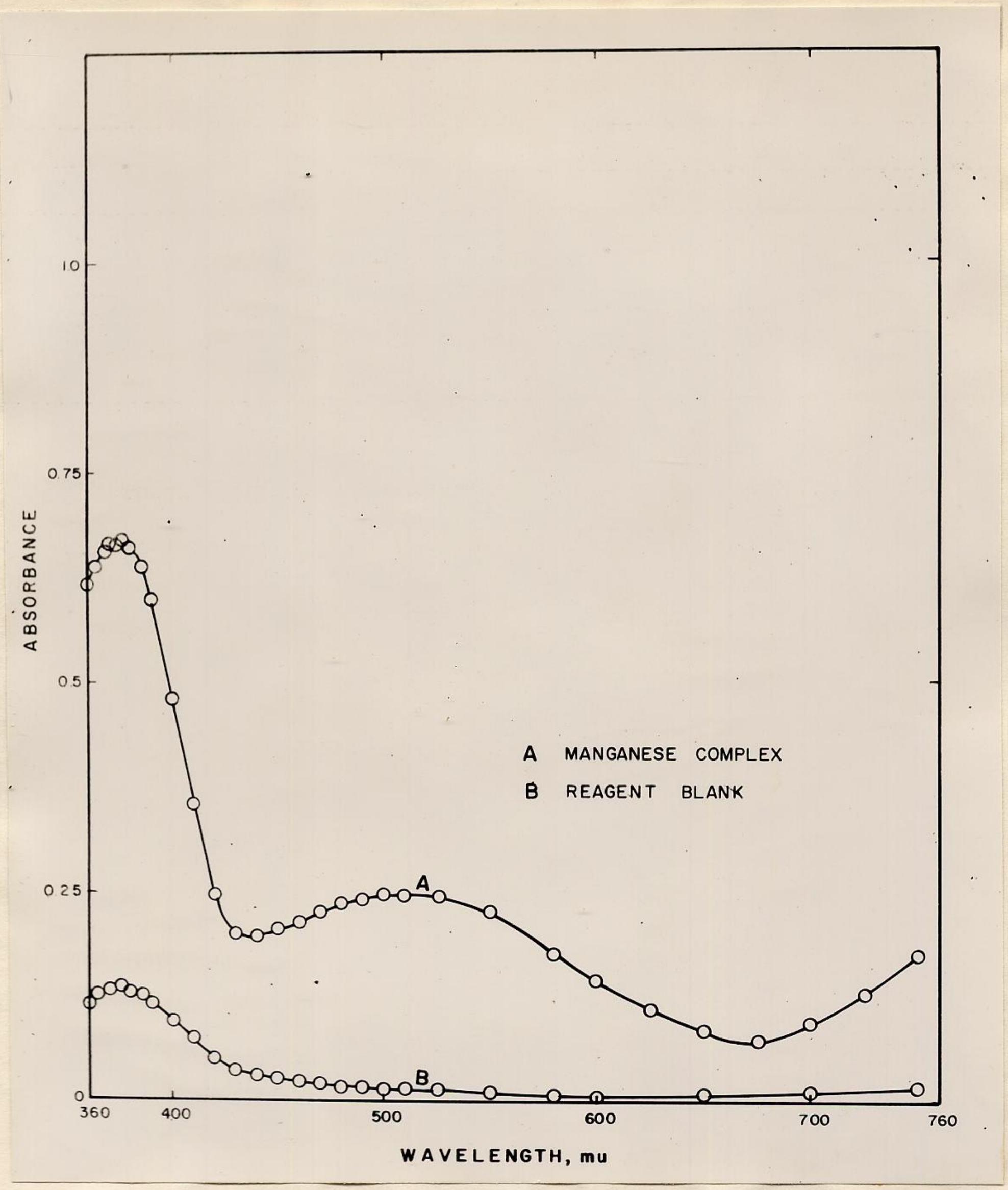


Figure 7 - Absorbance Curve for Manganese Complex and Reagent Blank.

Absorbances were obtained for the different stock solutions of manganese by following the procedure described for manganese. Values for the absorbance are shown in Table 10 and the calibration is plotted in Figure 8.

For manganese concentrations above 2500 p.p.m. turbid solutions were obtained. It is recommended under all conditions to add the KCN solution before the $(NH_4)_2CO_3$. Figure 8 shows that the color system obeys Beer's law over the range 0 - 2000 p.p.m. or 0 - 0.2% of manganese.

Table 10

Absorbance Calibration Values

p.p.m. of Manganese	Absorbance	Absorbance - Blank
blank	0.135	0.000
100	0.195	0.060
200	0.240	0.105
250	0.280	0.145
333	0.310	0.175
500	0.400	0.265
666	0.475	0.340
833	0.580	0.445
1000	0.660	0.525
1250	0.795	0.650
2000	1.190	0.955
2500	1.440	1.305
5000	>1.5	--

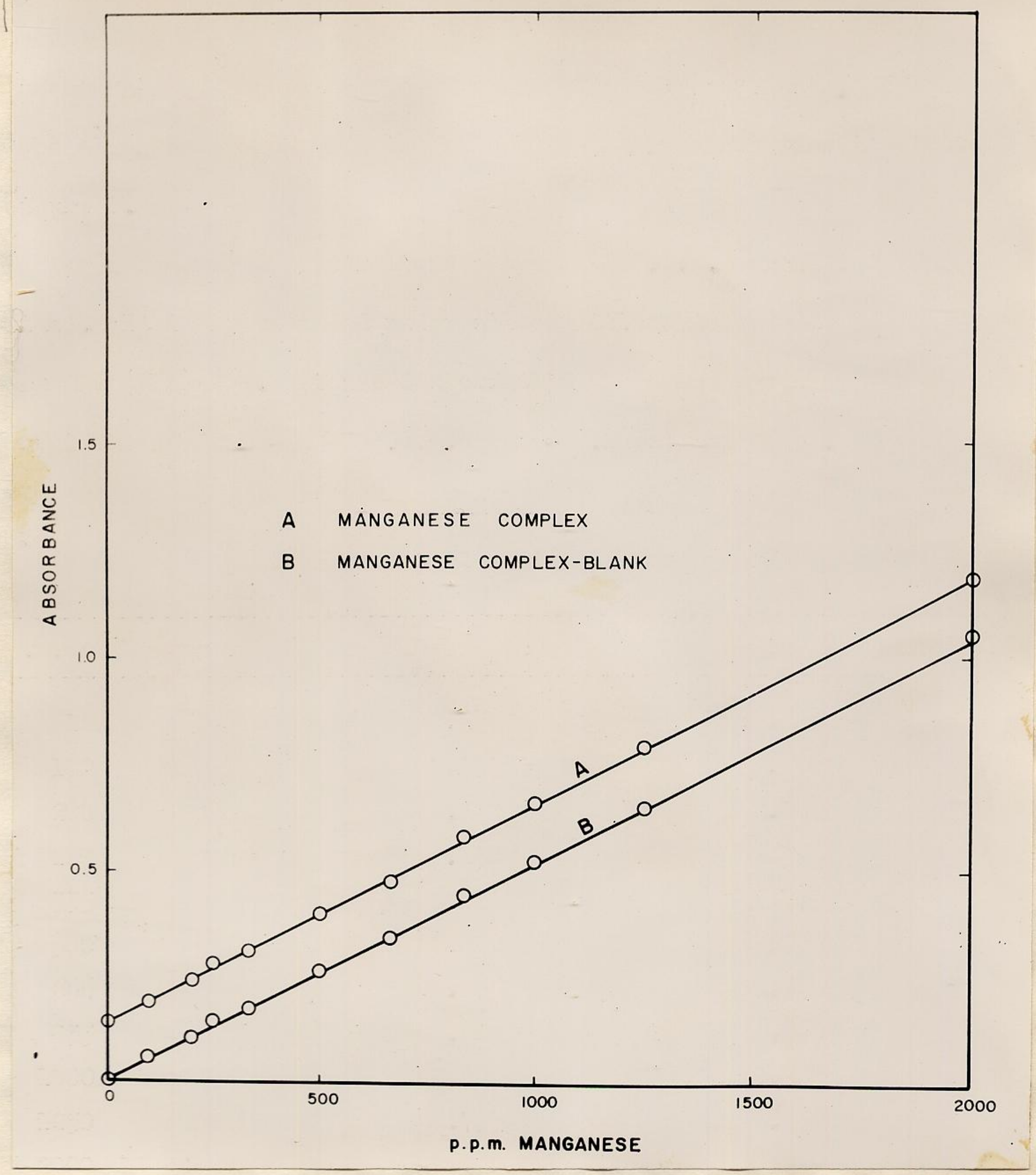


Figure 8 - Calibration for Manganese

Determination of manganese in the presence of foreign ions.

The determination of manganese was repeated in the presence of the following interfering ions: Fe(III), Co(II), Ni(II), Cd(II), Ca(II), Cu(II), Mg(II). The procedure was identical to the procedure used for manganese alone with the exception of Ca(II) and Fe(III). When Ca(II) or Fe(III) are present, it is necessary to heat the test tube in a water bath for 2 minutes after addition of $(NH_4)_2CO_3$. Fe(III) at concentrations above 1000 p.p.m. interferes and imparts a pink coloration to the solution. Results obtained with various foreign ions are shown in Table 11.

When the interfering ions are present in a concentration smaller to that of manganese they do not interfere. In fact manganese can be detected in presence of ten times its concentration of Ni(II), Cu(II), Co(II), Cd(II), Ca(II) (200 p.p.m. of Mn(II) - 2000 p.p.m. of other ions) with maximum deviation of 2.5%, and five times its concentration of Fe(III) (1000 p.p.m. of Fe(III)) with a deviation of 2.5%. Excellent results are obtained when 500 p.p.m. of Mn(II) are present with 40 times its concentration (20000 p.p.m.) of Ni(II) and Cd(II), and good results with 20 times its concentration (10000 p.p.m.) of Cu(II) and Co(II). Mg(II) however, proved to be a serious interfering ion at concentrations as low as 500 p.p.m.

Table 11

Analysis of Synthetic Samples of Manganese and Foreign Ions

p.p.m. of Mn(II) and Intefering Ions	Absorbance - Blank	p.p.m. of Mn(II) found from Figure 8
200 ppm Mn(II)+2000 ppm Ni(II)	0.105	200
200 ppm Mn(II)+2000 ppm Cu(II)	0.107	202
200 ppm Mn(II)+2000 ppm Co(II)	0.105	200
200 ppm Mn(II)+2000 ppm Cd(II)	0.105	200
200 ppm Mn(II)+2000 ppm Ca(II)	0.110	205
200 ppm Mn(II)+2000 ppm Mg(II)	0.330	640
1000 ppm Mn(II)+2000 ppm Ni(II)	0.525	1000
1000 ppm Mn(II)+2000 ppm Cu(II)	0.530	1020
1000 ppm Mn(II)+2000 ppm Co(II)	0.529	1018
1000 ppm Mn(II)+2000 ppm Cd(II)	0.525	1000
1000 ppm Mn(II)+2000 ppm Ca(II)	0.525	1000
1000 ppm Mn(II)+2000 ppm Mg(II)	0.700	1360
2000 ppm Mn(II)+2000 ppm Ni(II)	1.055	2000
2000 ppm Mn(II)+2000 ppm Cu(II)	1.055	2000
2000 ppm Mn(II)+2000 ppm Co(II)	1.045	1992
2000 ppm Mn(II)+2000 ppm Cd(II)	1.055	2000
2000 ppm Mn(II)+2000 ppm Ca(II)	1.050	1998
2000 ppm Mn(II)+2000 ppm Mg(II)	1.210	2040
200 ppm Mn(II)+1000 ppm Fe(III)	0.110	205
1000 ppm Mn(II)+1000 ppm Fe(III)	0.533	1025
500 ppm Mn(II)+20000 ppm Ni(II)	0.265	500
500 ppm Mn(II)+20000 ppm Cd(II)	0.265	500
500 ppm Mn(II)+10000 ppm Co(II)	0.270	518
500 ppm Mn(II)+10000 ppm Cu(II)	0.275	525

2. Manganese determination in various samples

The method was applied to determine the manganese content of sea water, blood serum and brass. Results obtained are shown in Table 12.

Samples of sea water were obtained in Beirut, a sample being collected from the shore, another 5 meters away from the shore.

Blood serum was first used but because of its high turbidity was replaced by clear protein free blood serum dilution 1:10.

Analyzed brass samples supplied by British Chemical Standards were used. All values for manganese determined by this method were too high. This was probably due to the presence of foreign ions in large concentrations. Attempts were made to reduce their interference by heating the sample to be analyzed in a water bath for 2 minutes after addition of $(NH_4)_2CO_3$.

With sea water the results obtained were too high compared to values given in the literature, but they were reproducible. With brass and blood serum the results were not reproducible and high. In sea water the high magnesium content could be responsible for the high values obtained for manganese, for it was found that magnesium interferes at as low concentrations as 500 p.p.m. Table 11 shows that 2000 p.p.m. of magnesium in presence of 200 p.p.m. manganese gives completely erroneous results.

The brass used contains 58.8% copper, 0.93% iron and 1.03% manganese. Table 11 shows that the method is valid in presence of 2000 p.p.m. Cu(II) whereas the maximum tolerated Fe(III) concentration is 1000 p.p.m. It is therefore to be expected that copper and to a certain extent iron should interfere in this case.

The results obtained with blood serum indicate that interfering ions are responsible for the high values obtained although the non-reproducibility which is observed could be due to turbidity of the solutions.

Table 12

Determination of Manganese in Various Samples

Samples taken	Absorbance - Reag. Found	p.p.m. of Mn(II) found from Fig.8	Values given in Lit.
Sea water from shore	0.420	545*	$2x10^{-5}$-$2x10^{-4}$ gr ion/l [30]
Sea water from 5 meters away from shore	0.415	535**	$2x10^{-5}$-$2x10^{-4}$ gr ion/l [30]
Brass sample I	0.195	105	103 ppm
Brass sample II	0.395	500	206 ppm
Blood Serum	0.257	230	--
1:10 dilution of blood serum filtrate	0.205	130	--
1:1 dilution of above	0.160	40	--

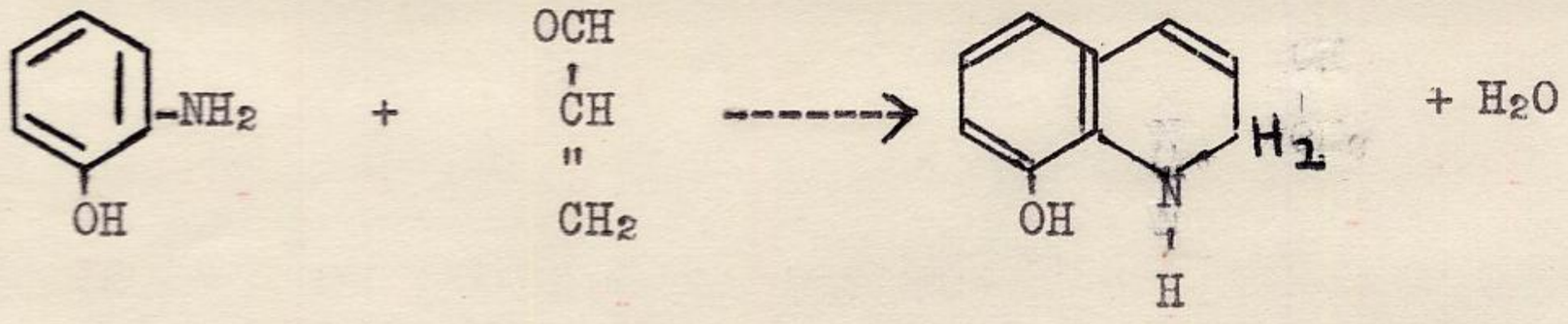
*545 ppm of Mn(II) corresponds to $99x10^{-4}$ gr ion/l.

**535 ppm of Mn(II) corresponds to $97x10^{-4}$ gr ion/l.

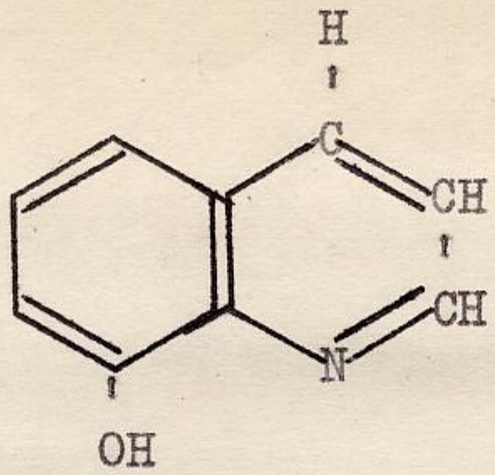
PART TWO: A NEW METHOD FOR THE DETECTION AND DIFFERENTIATION OF THE ISOMERS OF AMINO PHENOL

I. INTRODUCTION AND HISTORICAL

In general ortho, meta and para aminophenols are identified by converting them to the corresponding acetyl, benzoyl, benzenesulfonyl, toluene p-sulfonyl, phenyl urea derivatives and determining their melting points.[31] These methods are tedious and often involve many operations. Differentiation can also be obtained by converting the 3 isomers to the hydrochloride, thus the hydrochloride of the o-amino-phenol gives a brown precipitate with $FeCl_3$ and a yellow brown color slowly in the cold, rapidly on warming with $AgNO_3$. The hydrochloride of meta aminophenol gives no characteristic color with $FeCl_3$ in the cold, while the para aminophenol gives purple color in the cold with $FeCl_3$ and $AgNO_3$.[31] F. Feigl and W.A. Mannheimer[32] have developed a very sensitive method for the detection of ortho aminophenol based on its condensation with acrolein to give through ring closure 8-hydroxy-1,2-dihydroquinoline.



The latter is then oxidized to 8-hydroxyquinoline (oxine).

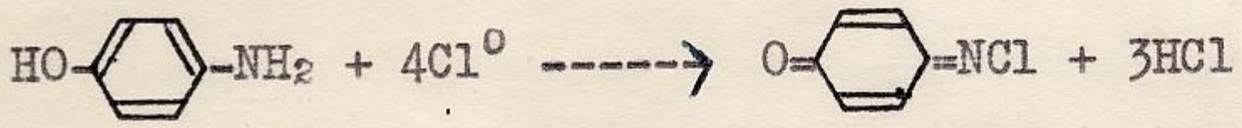


Oxine reacts under suitable conditions, with many metal ions to form water insoluble inner complex salts. The oxinates of colorless metal ions, either as solids or dissolved in organic liquids, exhibit an intense fluorescence, which is yellow green in most instances. Even at high dilutions, magnesium salts in ammoniacal solution precipitate magnesium oxinate. This test requires a number of operations and takes at least 20 minutes to perform.

L.M. Kul'berg and Z.V. Ivanova[33] distinguish between o-amino-phenol and p-aminophenol through their reactions with copper. A grain of the unknown is dissolved in 1 - 2 drops of alcohol and a drop of a 10% solution of $CuSO_4$ added. In presence of o-aminophenol a purple red color appears while with p-aminophenol the color of the solution remains faint blue. Feigl and Goldstein[34] describe a spot test for o-aminophenol alone. The colorless Schiff base, glyoxal bis-(2-hydroxy anil), produced by the condensation of o-aminophenol and glyoxal affords a sensitive and specific test for cadmium ions, with which it forms a red inner complex salt. This test is the basis of a test for either glyoxal or ortho aminophenol, para aminophenol does not respond to this test.

E. Jungreis[35] has developed a method for the identification of p-aminophenol through oxidation to p-quinone-4-chloroimine.

Excellent yields of p-quinone-4-chloroimine are obtained by the action, under cooling, of chloride of lime or alkali hypochlorite on hydrochloric acid solutions of p-aminophenol. The active agent is the chlorine liberated from the hypochlorite and hydrochloric acid:



p-quinone-4-chloroimine condenses with phenol in the presence of ammonia to give the blue ammonium salts of an indophenol dye. Feigl[36] improved the method and by using chloramine T as chlorine donor was able to develop a selective spot test for p-aminophenol.

It was realized in the course of this work that the procedure used to test for cadmium could be reversed and applied to the detection of o-aminophenol. The method consists in forming a Schiff base with the pyridine 2,6-dialdehyde and the aminophenol and adding cadmium ions.

When cadmium ions are added to the Schiff base obtained from pyridine 2,6-dialdehyde and o-aminophenol and the solution made basic with NaOH an intense red color is obtained which is completely extractable in chloroform. Successive dilutions of the o-aminophenol has shown that the test is sensitive at 5 γ of the aminophenol per drop. If cadmium ions are added to the Schiff base obtained with the pyridine dialdehyde and m-aminophenol no color is formed while cadmium ions added to the Schiff base obtained with the pyridine dialdehyde and p-aminophenol gives an intense red color which is not extractable in chloroform. The test gave a positive reaction at 5 γ of p-aminophenol per drop.

It is thus possible by using the same procedure and the same

reagent, pyridine 2,6-dialdehyde to differentiate between the isomeric forms of aminophenols in a matter of 3 minutes. It is also possible to detect a mixture of the o- and p-isomers.

The method could be developed for the quantitative determination of the o- and p-isomers, although the extractibility of the complex formed with the o-aminophenol would no doubt make it a superior method.

II. EXPERIMENTAL

Reagents

1% solutions of ortho, meta and para aminophenol were prepared by dissolving 1 gr of freshly sublimed portions of each in 100 ml of water.

A 0.63% solution of 2,6 pyridine dialdehyde was prepared by dissolving 0.63 gr in 100 ml of water.

A 10% NaOH solution was prepared by dissolving 10 gr of pure NaOH pellets in 100 ml of water.

A 1% Cd(II) solution was prepared by dissolving 1.7700 gr of $CdCl_2$ in 100 ml of water.

All other reagents were of analytical grade and were used without further purification.

Procedure

To one drop of a 1% solution of ortho, meta and para aminophenol each in a test tube, a drop of 0.63% 2,6 pyridine dialdehyde was added. The mixtures were heated in a water bath for 2 minutes. Upon cooling a yellow precipitate of the Schiff base was formed in each test tube.

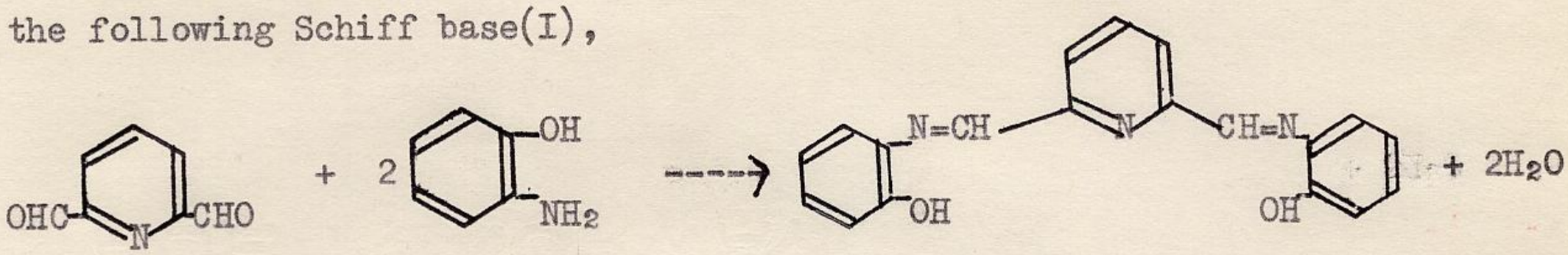
A drop of 1% Cd(II) solution followed by one drop of 10% NaOH solution were added to each tube. An intense red color was obtained with ortho and para aminophenol, and no color was obtained with meta aminophenol. Chloroform was added to the two red solutions and the test tubes shaken vigorously. The red color formed with ortho aminophenol was extracted in chloroform, whereas the chloroform layer of the para aminophenol remained colorless.

The 1% solution of ortho and para aminophenol was then diluted ten times to 0.1%. The test was repeated for ortho and para aminophenol and the colors obtained compared with a blank which contained all the reagents but Cd(II). A definitely detectable difference was observed between the blank and the solutions. If the 0.1% solutions were diluted again ten times to 0.01% and the test repeated for each, a very faint difference of colors could be observed between the blank and the test solutions. The 0.01% solutions were diluted again to 0.005% and the test repeated. There was no detectable difference between the blank and the test solutions.

Thus, the test is sensitive to 5γ/drop of ortho or para aminophenol.

DISCUSSION

The condensation of pyridine 2,6-dialdehyde with o-aminophenol forms the following Schiff base(I),



(I)

Analysis of the structure and of atomic models of the Schiff base show that it is planar. Figure 9 is a photograph of a Dreiding model of the molecule.

In the absence of a study of the nature of the complex formed in solution with metal ions and its empirical formula it is difficult to postulate a definite structure for the complex. By analogy to similar cases, the possibility of formation of salt like inner complex should be considered. This is supported by the fact that complex formation takes place in alkaline conditions where one or two hydrogen ions may be lost from the phenolic groups. Such behavior would produce a tetradentate or a pentadentate ligand. It is doubtful that a rigorously flat polydentate ligand can satisfy the stereochemical requirements of such a variety of metals as Cu(II), Ni(II), Mn(II), Zn(II), Pb(II), Cd(II), Tl(I), Mg(II), Co(II), Fe(III), Cr(III) and Th(IV) all of which form red complexes with the reagent.

On the other hand there is evidence that the $|\overline{O}|^-$ is not acting as a center of coordination. Thus when pyridine 2,6-dialdehyde is condensed with p-aminophenol a Schiff base is obtained in which the OH

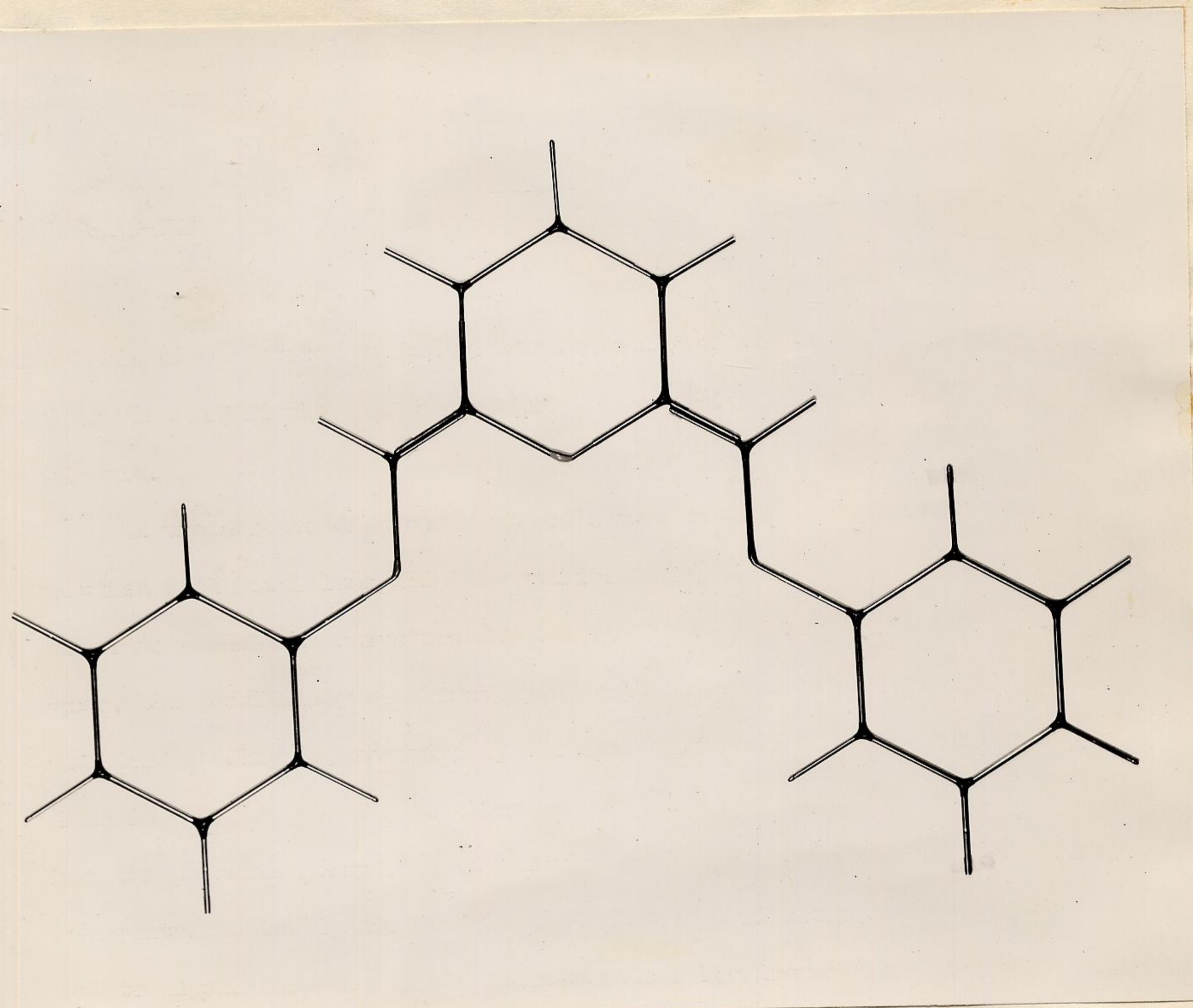
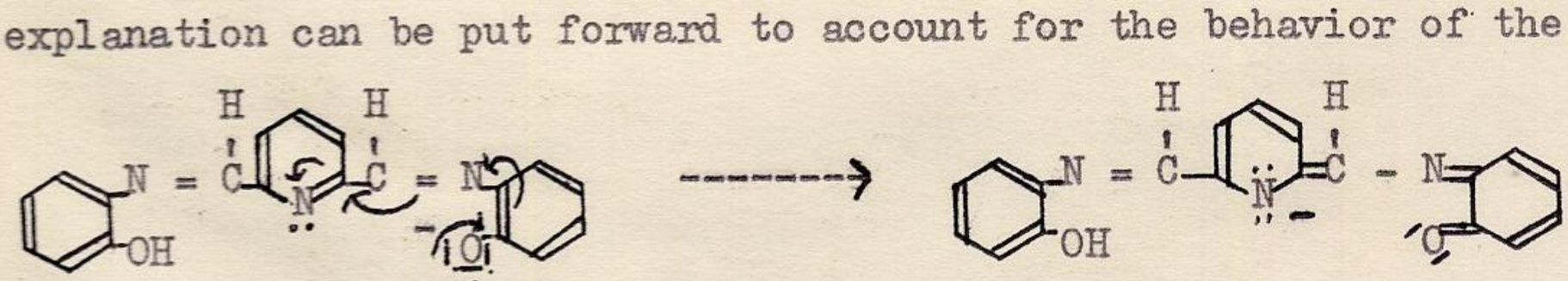


Figure 9 - Photograph of the Reagent Model

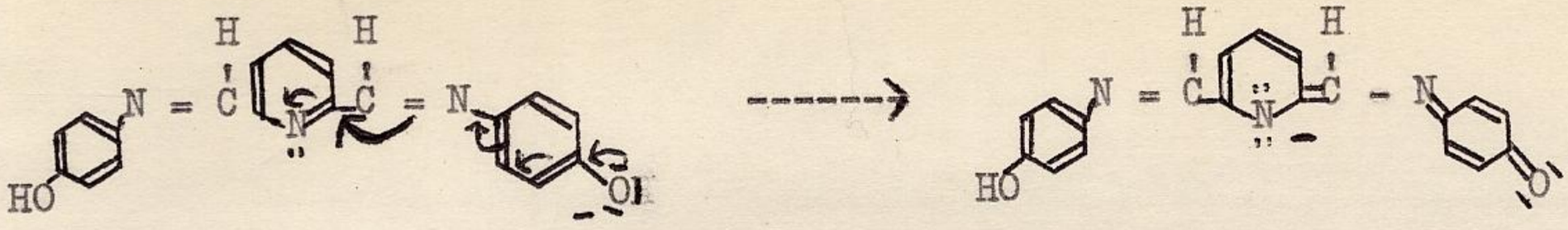
is in a most unfavorable position to coordinate with the metal ions. The fact that the Schiff base obtained with p-aminophenol forms complexes which are similar to those formed with o-aminophenol suggests that coordination is taking place through the three nitrogens. Any position around the metal not occupied by the chelating agent could be filled by a solvent molecule.

The presence of three nitrogens which are free to coordinate is not however sufficient to form colored complexes with metal ions. Thus when pyridine 2,6-dialdehyde is condensed with aniline a Schiff base is obtained which forms no colored complexes with the same metal ions. It would therefore seem that the donating properties of the pyridine nitrogen have to be enhanced. Further, the red color which is obtained with the different metals suggests that it can not be due to nitrogen atoms directly bonded to the metal and implies that the color is due to resonance arising through conjugation.

This approach is substantiated by the fact that both Schiff bases obtained with ortho and para aminophenols form red complexes while the base obtained with meta aminophenol does not give red complexes. If one remembers that both ortho and para aminophenols are capable of resonating as in II and III while the meta aminophenol can not resonate, a possible explanation can be put forward to account for the behavior of the reagent.



(II)



(III)

The quinoid structure and the conjugate system obtained with the ortho and para aminophenols could thus be responsible for the red color formed with these isomers. This would explain the experimental results obtained in the second part of the work, namely the differentiation between o, m and p-aminophenols. According to this argument the Schiff base obtained with m-aminophenol should not give colored complexes which is in agreement with the experimental results.

Further, resonance will increase the negative character of the pyridine nitrogen and complexes which were not obtained with aniline condensing with pyridine 2,6-dialdehyde are now formed. The double bond character which is acquired by the bonds because of rsonance will decrease the flexibility of the molecule and will force it into a flat configuration.

On the other hand three nitrogen atoms do not seem to be a necessary requirement for complex formation. Thus when pyridine 2 aldehyde is condensed with o-aminophenol a Schiff base is obtained which forms complexes with metal ions very similar to those obtained with pyridine 2,6-dialdehyde and o-aminophenol. This would suggest that two nitrogen atoms acting as donors are sufficient to form the red complex. The pyridine 2-aldehyde was not however used because its reaction with o-aminophenol yielded a gum which could not be crystallized.

The reagent 2,6-dimethylpyridinediimine N,N'-bis-(o-hydroxyphenyl) could thus act as a tridentate or bidentate depending on whether three

nitrogens or two nitrogen atoms act as donors.

On the basis of a flat tridentate chelating agent the configuration of complexes can be visualized. With metals forming planar complexes the three nitrogens will occupy three positions in one plane, the fourth one being occupied by a solvent molecule. With metals forming tetrahedral complexes the chelating agent will satisfy the three positions lying on one plane. With metals forming octahedral complexes two molecules of the chelating agent will be required. One will satisfy three positions in one plane, while the other will be perpendicular to it and will chelate the three other positions. On the basis of a bidentate flat chelating agent the requirements of metals having coordination number four and six could be satisfied with two or three molecules of the reagent respectively.

There is need for further investigation on the nature and composition of the complexes formed. It would also be desirable to investigate the effect of pH on complex formation; if the above approach is correct then an increase in pH would favor the formation of complexes.

The determination of Zn(II) qualitatively and quantitatively still presents certain difficulties; the Schiff base used in this work could possibly be developed into a reagent for zinc.

BIBLIOGRAPHY

1. Feigl, F., Thabet, S., Goldstein, D., Unpublished results.

2. Vogel, V.A., "Quantitative Inorganic Analysis, 2nd ed., Longmans, Green, London, pp. 428-429 (1951).

3. Wenger, P., Masset, E., Helv. chim. acta., 23, 34 (1940).

4. Souchay, P., Bull. soc. chim. France, 7, 797 (1940).

5. Miller, ., Page, R.T., Z. anorg. chem., 28, 233 (1901).

6. Austin, M., Am. J. Sci. 4 , 14, 156 (1902).

7. Weiser, H.B., Durham, E.J., J. Phys. Chem., 32, 1061 (1928).

8. Charlot, G., Bezier, D., Quantitative Inorganic Analysis, 3rd ed. Buttler and Tanner, London, p. 363, (1957).

9. Shennan, R.J., Smith, E.F., Ward, A.M., Analyst, 61, 395 (1936).

10. Spacu, G., Kuras, M., Z. anal. chem., 99, 26 (1934).

11. Saltzman, B.E., Anal. Chem., 25, 493 (1953).

12. Lomakina, G.G., Tolmachev, V.N., Izvest. Vysshikh Ucheb. Zavedeniy Khim. i Khim. Tekhnol, 3, 819-22 (1960).

13. Nobuichi, Oi., Bunseki Kagaku, 9, 770-3 (1960).

14. Shibata, S., Anal. Chim. Acta., 25, 348-59 (1961).

15. Lazarev, A.I., Lazarena, V.I., Zavodskaya Lab., 25, 783-6 (1959).

16. Hannay, J.B., J. Chem. Soc., 33, 269 (1878).

17. Hillebrand, W.F., Lundell, G.E.F., Applied Inorganic Analysis, John Wiley & Sons, Inc., New York, p. 340 (1929).

18. Blum, W., J. Am. Chem. Soc., 34, 1382 (1912).

19. Gibbs, W., Am. J. Sci. II , 44, 216 (1867).

20. Blair, A.A., J. Am. Chem. Soc. 26, 793 (1904).

21. Blum, W., J. Am. Chem. Soc., 34, 1395 (1912).

22. Scott, W.W., Furman, N.H., Standard Methods of Chemical Analysis, Vol. I, 5th ed., Van Nostrand, New York, 561 (1939).

23. Vogel, V.A., Quantitative Inorganic Analysis, 2nd ed., Longmans, Green, London, p. 713 (1951).

24. Park, B., Ind. Eng. Chem., Anal. ed., 7, 327 (1935).

25. Bankovekis, J., Ievins, A., Luksa, E., Zhur. Anal. Khim., 14, 222-6 (1959).

26. Lukin, A.M., Osterova, E.D., Trudy Vsesoyuz, Nauch. Issledovatel. Inst. Khim. Reaktivov, No. 21, 3-9 (1956).

27. Dutta, R.L., J. Indian Chem. Soc., 37, 167-70 (1960).

28. Hartkamp, H., Angew Chem., 72, 349 (1960).

29. Shibata, S., Anal. Chim. Acta., 25, 348-59 (1961).

30. Sverdrup, H.U., Johnson, M.W., Fleming, R.H., The Oceans, Prentice-Hall, Inc., New York, p. 184 (1942).

31. Mann, F.G., Saunders, B.C., Practical Organic Chemistry, 4th ed., Longmans, England, p. 549 (1960).

32. Feigl, F., Spot Tests in Organic Applications, 4th ed., Elsevier, Amsterdam, p. 284 (1954).

33. Kul'berg, L.M., Ivanova, Z.V., Zhur. Anal. Khim., 2, 198 (1947).

34. Feigl, F., Goldstein, D., Z. Anal. Chem., 163, 30 (1958).

35. Jungreis, E., Unpublished results.

36. Feigl, F., Spot Tests in Organic Analysis, 6th ed., Elsevier, Amsterdam, p. 413 (1960).