

UTILIZATION OF POTASSIUM CYANIDE
AS A SPECTROPHOTOMETRIC REAGENT

With Particular Application To The
Determination Of Nickel

by

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TABLE OF CONTENTS

Introduction.	1
Previous Work in this Field.	4
The Problem.	5
Apparatus, Reagents and Solutions	5
Use of Potassium Cyanide in Determination of Nickel.	8
I. Normal Spectrophotometric	
Procedure.	8
Interference Studies	14
Individual Interferences	22
II. Spectrophotometric Titration Method.	39
III. Differential Colorimetry	47
Conclusion.	58
Bibliography.	60

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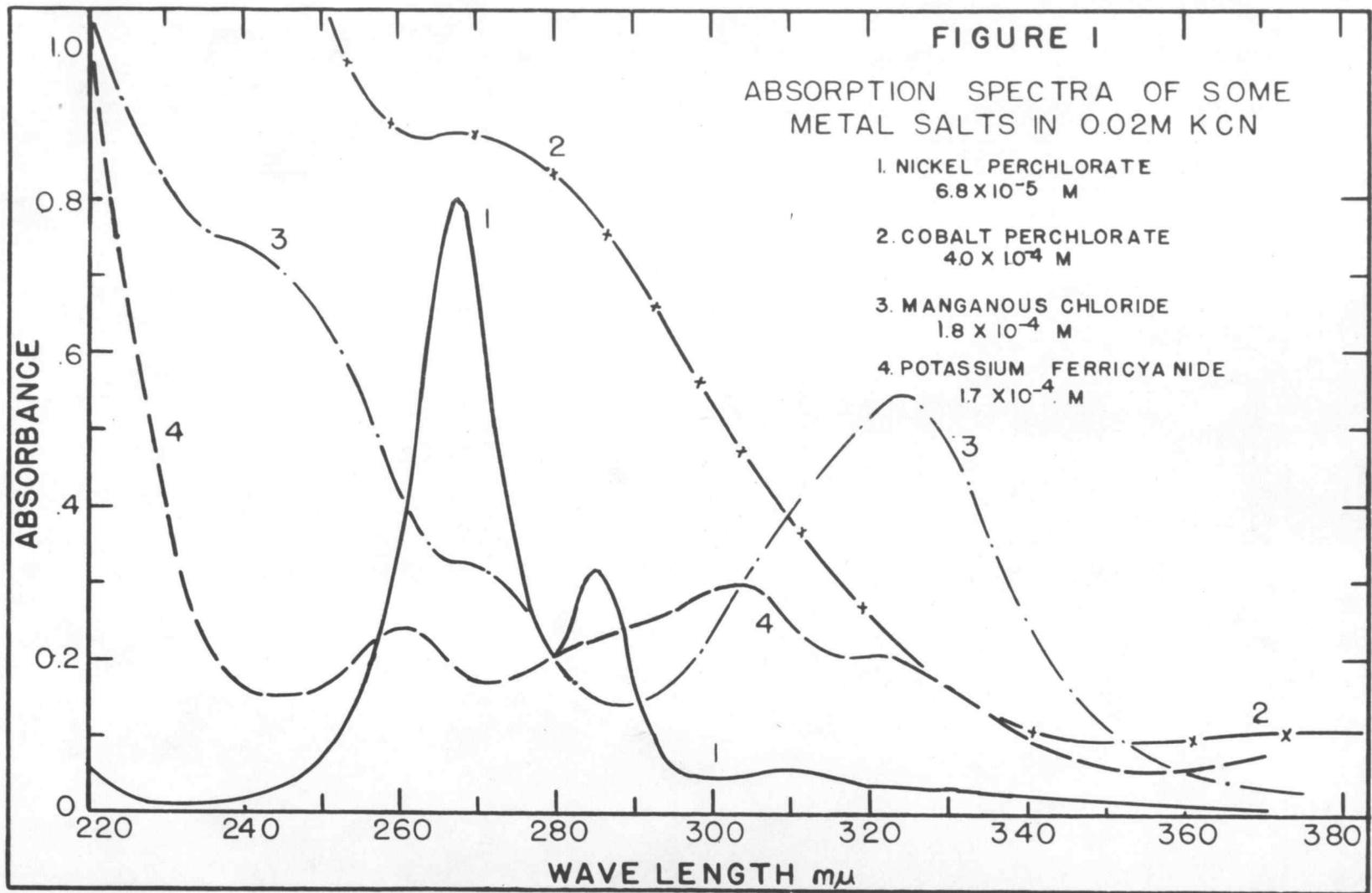
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INTRODUCTION

During the course of a spectrophotometric investigation of the stability constant of the tetra cyano nickel (II) complex, carried out in this laboratory, a characteristic absorption curve shown in Figure 1 was obtained for the complex. Since concentrations of nickel in the order of micrograms per milliliter gave highly absorbing solutions, it was thought that this complex could be utilized spectrophotometrically for the quantitative determination of nickel.

The research resolved itself into three sections. The first section covers the usual spectrophotometric method in which the absorbance of an unknown nickel solution is compared to those of standard nickel solutions. In the second section the spectrophotometric titration principle is explored. In this method the amount of nickel is determined by noting the increase in absorbance as the nickel complex is formed. This can be done directly by titrating the nickel with KCN or indirectly by titrating excess KCN with a standard nickel solution. The third section is devoted to the possibilities of

using a differential method for high levels of nickel. The advantages and disadvantages of each procedure are considered and discussed.



PREVIOUS WORK IN THIS FIELD

A literature survey revealed that while the cyanide titration is a standard volumetric method for the determination of nickel very little had been done in the way of a colorimetric method using cyanide. Major (19, pp.17-34) has presented characteristic absorption curves for several nickel salts. Included were curves obtained from 0.1M $\text{Ni}(\text{ClO}_4)_2$ in 1.1 molar KCN. Absorption maxima were obtained at 267 μ , 288 μ , 328 μ and 460 μ . With the exception of the slight discrepancy in the positions of the peaks, the shape of the curves compared favorably to the one shown in Figure 1. The peaks at 328 μ and 460 μ are not predominant at the concentration used in this work. Buck, Singhadeja and Rogers (7, pp.1240-1242) have presented absorption curves for aqueous solutions of several anions and cations. They compared the curve for the nickel cyanide complex with those of $\text{Fe}(\text{CN})_6^{=}$, $\text{Cd}(\text{CN})_4^{=}$, $\text{Co}(\text{CN})_6^{=}$, $\text{Cu}(\text{CN})_3^{=}$, and suggested that the use of cyanide has possibilities as an analytical reagent for nickel because of its sensitivity and few interferences.

Brummet and Hollweg (6, p.887) used an aqueous solution of KCN to dissolve the oxide film from nickel

and the subsequent formation of $\text{Ni}(\text{CN})_4^{2-}$ as the basis for the determination of nickel in the oxide film on nickel metal. With the exception that their main peaks were at 268 $\text{m}\mu$ and 286 $\text{m}\mu$, the characteristic curve obtained by them was identical with that obtained in this work. Their description of the method used was sketchy and lacked work with interferences.

PROBLEM

There are many areas that need to be investigated before a method of analysis can be accepted or discarded. Some of these are: concentration ranges, interferences, precision, and accuracy.

It is the purpose of this work to carry out the investigation necessary for the utilization of the tetracyano nickel ion for the spectrophotometric determination of nickel. The possibilities of determining other metals with this method will also be discussed. As a practical application of the method for low concentrations, the amount of nickel in some zircalloy samples will be determined. In the section on the differential method, a Watt's nickel plating bath will be used.

APPARATUS, REAGENTS AND SOLUTIONS

Apparatus. All absorbance measurements were made

with a Beckman model D.U. Spectrophotometer. A photo-multiplier attachment was used in the section employing the differential procedure. A hydrogen discharge lamp was used as the source of radiation for all measurements below 340 m μ . A tungsten lamp was used for any measurements above 340 m μ . The absorbance measurements for the first and third sections were made using matched 1.00 cm. silica cells. In the section on titrations, a cell similar to the one constructed by Goddu and Hume (11, pp. 1314-1317) was used. The part of the cell above the instrument was enclosed in a light tight box arrangement in order to limit the effect of changing light conditions. In the first and third sections a reagent blank was used and all absorbances are net values.

pH values were obtained with a Beckman Model H-2 line operated pH meter with glass electrode and calomel cell.

Reagents and Solutions. All chemicals used were reagent grade.

Standard Nickel Solutions. All nickel solutions were made by diluting a concentrated (0.05 M) nickel solution which was prepared by fuming Coleman and Bell C.P. NiCO₃ with perchloric acid. The solution was standardized both by the usual dimethylglyoxime method (27, p.385)

and by KCN titration (13, p.415).

Interference Solutions. The interference solutions used to study the effect of some cations, were prepared by fuming the following with perchloric acid: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, CaCO_3 , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, AgNO_3 , CrO_3 , MgO , CdCO_3 , $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$.

The following interference solutions were prepared by dissolving the respective salts in H_2O . $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{K}_3\text{Fe}(\text{CN})_6$, and Na_3VO_4 .

As a source of tungsten, WO_3 was fused with Na_2CO_3 and molybdenum was obtained from molybdic acid which was dissolved in H_2O and boiled to remove the NH_3 .

To study the effect of anions the following salts were dissolved in H_2O and used as such: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, NaNO_3 , and NaCl .

Perchloric acid solutions were used in most instances because most alloys are fumed with perchloric acid prior to the determination of silica and the perchlorate ion is noted as a poor complex former.

Potassium cyanide solutions were prepared by dissolving C.P. KCN in H_2O . The concentrated solution was standardized with the usual silver nitrate titration.

Silver nitrate was prepared by dissolving C.P. AgNO_3 in distilled H_2O and standardized by titrating weighed amounts of dried C.P. NaCl .

Borate buffers were used and prepared as described by Lange (18, p.2070).

Tartaric and citric acid solutions were prepared by dissolving the C.P. solids in distilled H_2O .

Sodium hydroxide was prepared by dissolving the pellets in distilled H_2O .

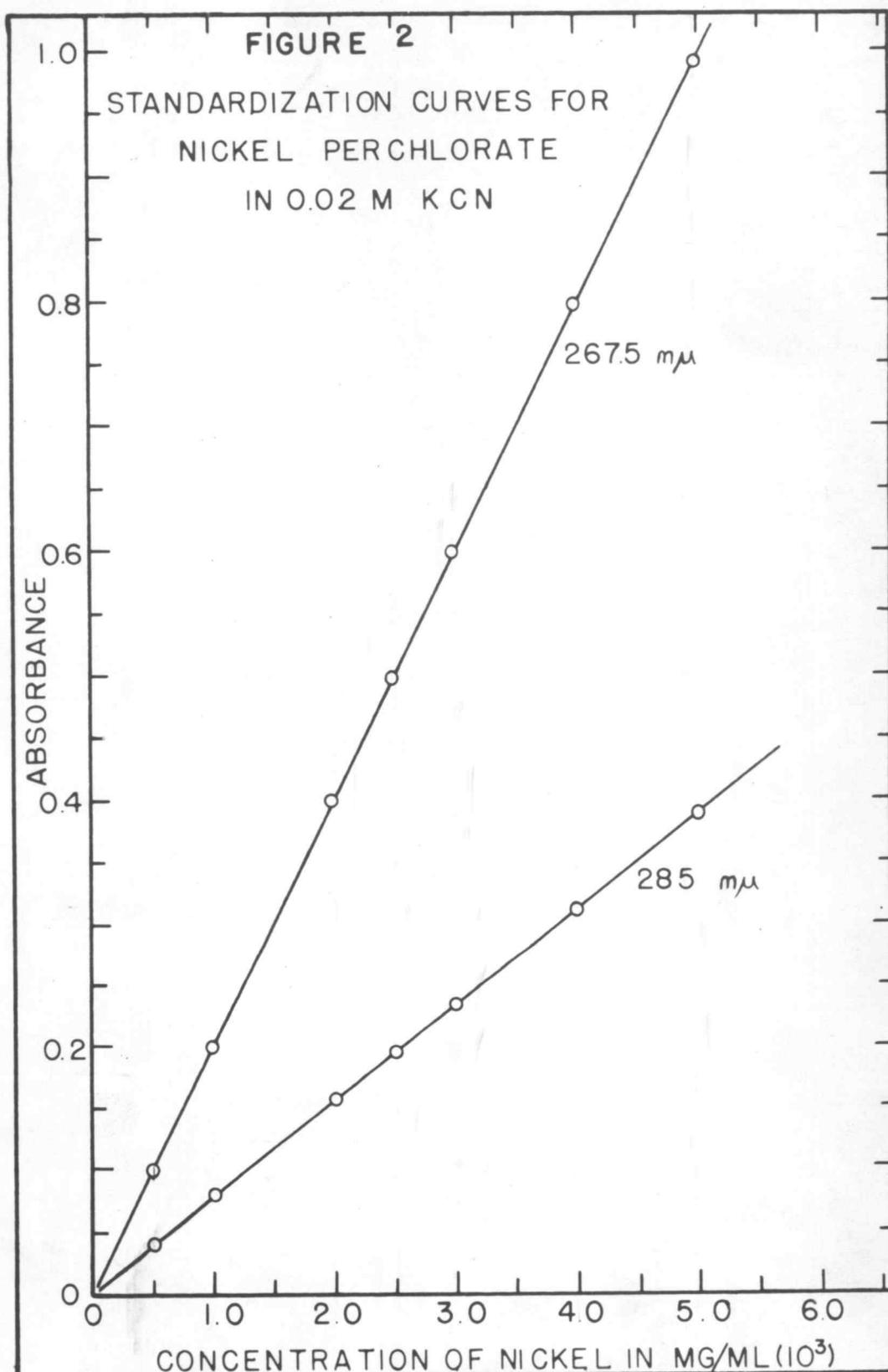
USE OF POTASSIUM CYANIDE IN DETERMINATION OF NICKEL

I. Normal Spectrophotometric Procedure. The usual spectrophotometric procedure for the determination of a metal or some other component utilizes the dependence of the absorbance of the solution on the concentration of the desired constituent. A set of standard solutions of varying known amounts of the component are prepared. The absorbance at a suitable wave length of each of these solutions is obtained on a suitable instrument. A standardization curve is then prepared by plotting absorbance vs total concentration of the desired material. If this absorbance follows Beer's Law a straight line will be obtained as in Figure 2. Deviation from Beer's

Law simply results in a curve which can be used in the same way as the straight line plot. The range of concentration that can be covered by this standardization curve is usually governed by the absorbance of the constituent. After this curve is prepared, and if there are no interferences, the concentration of the desired component is obtained from it.

When preparing the standardization curves for this procedure it is desirable to obtain two, one at 267.5 μ and the other at 285 μ . When an unknown solution is being analyzed the absorbance values of both 267.5 and 285 μ can be checked. Any interference should be detected for it is very doubtful that anything other than the nickel complex will have the proper absorbance at both wave lengths. As a further check a curve for 310 μ could also be prepared.

The optimum concentration range for this method was found by following the procedure outlined by Ayres (1, pp.652-657). Straight line plots, as described above, only show conformity to Beer's Law and do not show directly the concentration range for best accuracy. To find this optimum range, aliquots of a solution containing 5×10^{-2} mgs.Ni/ml. were added to 25ml. of 0.1M KCN in 100ml. volumetric flasks and diluted to the mark. By plotting percent absorptancy versus log concentration the



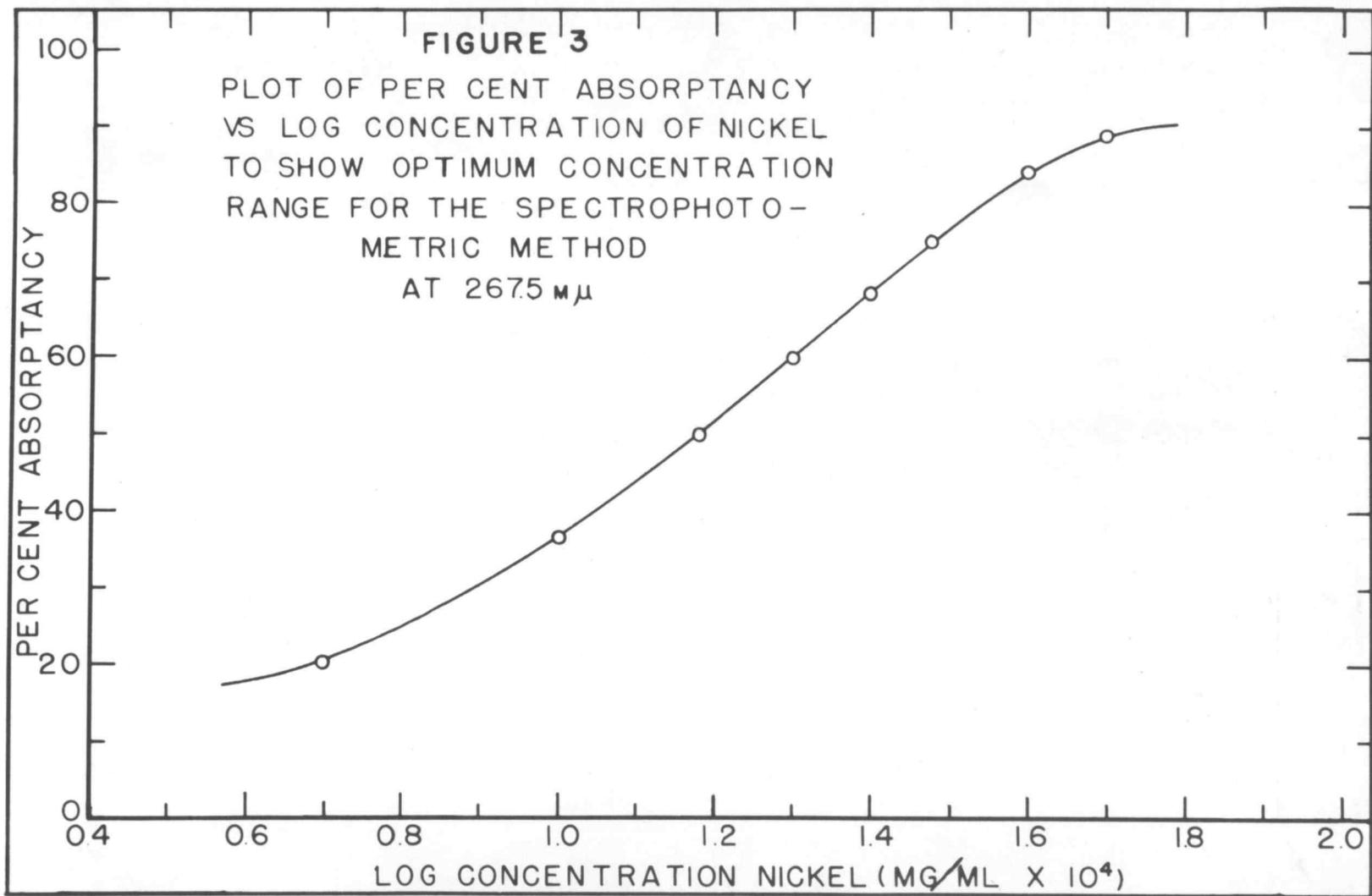
curve shown in Figure 3 was obtained. The concentration range of 1.0×10^{-3} mgs. Ni/ml. to 3.0×10^{-3} mgs. Ni/ml. appears to be optimum. The curve in Figure 3 was plotted from the data in Table 1. Percent absorptancy is defined by Ayres as 100 minus percent transmittancy. This correlates an increasing number with increasing concentration.

From the above curve a concentration of 2.0×10^{-3} mgs. Ni/ml. was used during this investigation. This gives an absorbance of about 0.400 which, as is shown by Hiskey (14, pp.1440-1446), is in the region where the absorbance can be obtained with the greatest accuracy when it follows Beer's Law.

TABLE 1

DATA OBTAINED USING AYRES METHOD FOR FINDING THE OPTIMUM CONCENTRATION RANGE

Concentration	A	%T	% Absorptancy	Log Conc. ($\times 10^{-4}$)
5×10^{-4} mg./ml.	.100	79.4	20.6	.699
10×10^{-4} mg./ml.	.200	63.2	36.8	1.0
15×10^{-4} mg./ml.	.298	50.2	49.8	1.176
20×10^{-4} mg./ml.	.398	40.0	60.0	1.301
25×10^{-4} mg./ml.	.497	31.9	68.1	1.398
30×10^{-4} mg./ml.	.598	25.3	74.7	1.477
40×10^{-4} mg./ml.	.793	16.1	83.9	1.602
50×10^{-4} mg./ml.	.991	10.2	89.8	1.699



The effect of varying amounts of KCN on the absorbance of the complex was investigated next. Solutions containing 20×10^{-4} mgs. Ni/ml with 5, 10, 20, and 25 ml. of 0.1M KCN were diluted to the mark in 100 ml. volumetric flasks. The absorbance obtained was essentially the same in all cases. No change was noted in any of the solutions after a 24 hour period. After 96 hours, all showed a slight decrease in absorbance. In order to insure an excess of KCN and still not use a superfluous amount, 20 ml. of 0.1M KCN/100 ml. of solution was decided upon.

Since cyanide is not present as CN^- in acid solution, it is necessary to neutralize the excess perchloric acid remaining after the fuming is completed. The first thought was to use ammonium hydroxide because several of the metals that interfere could be precipitated, and also concentrated solutions of ammonia are easier to keep than those of some of the other bases. Ammonium hydroxide was tried, but a change in its concentration effected the absorbance of the solutions. This was attributed to the competition between ammonia and cyanide for the nickel, and, to the different complexes between nickel and ammonia. Ammonia was discarded, and sodium hydroxide was tried. No trouble

was encountered, so it was used. It was kept in polyethylene bottles and measured with a 50 ml. burette.

The next question to be answered was the effect of pH on the absorbance of the complex. To determine this, several solutions were prepared containing 20×10^{-4} mg.Ni, 20ml. KCN and with pH varying between 8 and 10.5. The pH was maintained by means of NaOH - H_3BO_3 buffers. It was also determined that the presence of the buffers had no effect on the absorbance of the nickel complex. Increasing the pH above 9.5 had no apparent effect on the absorbance but below this value the absorbance decreased slightly with decreasing pH. Since 20 ml. of KCN provided a pH of about 10.5 if the nickel solution was nearly neutral prior to addition of the KCN, this pH will be used. It was found during the titrations, which will be discussed later, that the complex forms almost instantly if the pH of the solution prior to adding KCN is above 9.5. The time of formation lengthens as the pH decreases. This process is probably due to the fact that more free cyanide is available to be complexed by the nickel at the higher pH.

Interference Studies. Since the method for nickel will be used in the presence of other ions, mostly metal

or metal containing ions, their effect on the absorbance was studied next. These interferences fall into three categories: 1) Those ions that form complexes with cyanide, which according to Moeller (21, p.966) are Cu(I), Ag(I), Au(I), Ni(II), Cd(II), Hg(II), Pd(II), Pt(II), Mn(I), Mn(II), Fe(II), Co(II), Cu(II), Os(II), V(III), Cr(III), Mn(III), Fe(III), Co(III), Rh(III), Ir(III), Mo(IV) and W(IV). A very good discussion of most of these heavy metal cyanides is also presented by Callis (8, pp.150-156). 2.) Any ions not forming complexes with cyanide but by whose spectral characteristics cause absorption in the region of interest. 3.) Any ions that effect the solution chemically.

Since a pH of 10.5 will be used it will be necessary to first determine what should be done with the substances that will precipitate. It is common knowledge that the best procedure would be one in which no separations are required. So the first thought was to try to keep everything in solution. Complexing agents provide one of the best means of achieving this goal. Citric and tartaric acids seem to be the best for all around purposes. They were found to have many advantages. When using only nickel and cyanide in the sample, neither citric nor tartaric acid caused any change in

absorbance as long as the same amount was added to both blank and sample. Citric and tartaric acids have another advantage in that they are relatively transparent in the region of the spectrum used in this work. These two agents are also inexpensive and easy to obtain. Versene and oxalic acid were also tried. Versene was found to form too strong a complex with nickel and oxalic acid is too absorbant in the range of the spectrum used.

After making the above observations with nickel alone, citric and tartaric acids were tried with nickel plus each of the ions studied as interferences. When the citrate or tartrate complex of the metal absorbed in the region of the spectrum studied citric or tartaric acid were omitted and the metal was allowed to precipitate on increasing the pH. Each cation and anion that was studied in this work will be discussed individually later.

A convenient way to study the interferences is to set up a table showing the amounts of interfering substances that can be tolerated. These data are collected in Tables 2 and 3. To obtain the desired information for these tables, solutions containing foreign ions and nickel in the weight ratio of 1000 to 1 respectively were used. If any interference was encountered the

TABLE 2

EFFECT OF INTERFERENCES AT 267.5 μ

Interference	Nickel Taken	Nickel Found				
		Interference/Nickel (weight).				
		1/10	1/1	10/1	100/1	1000/1
Al(III) Citrate	0.199mg.	-	-	-	0.201	0.210
Cadmium(II)	0.199mg.	-	-	-	0.199	0.207
Chloride	0.199mg.	-	-	-	-	0.200
Chromium(III)	0.199mg.	-	0.205	∞	∞	∞
Cobalt(II)	0.199mg.	0.204	0.241	∞	∞	∞
Copper(II)	0.199mg.	-	0.205	0.270	∞	∞
Iron(II)	0.199mg.	0.204	0.241	∞	∞	∞
Iron(III)	0.199mg.	0.202	0.219	∞	∞	∞
Magnesium(II)	0.199mg.	-	-	-	0.200	0.208
Manganese(II)	0.199mg.	0.203	0.230	∞	∞	∞
Mn Citrate	0.199mg.	0.205	∞	∞	∞	∞
Molybdenum(VI)	0.199mg.	-	0.201	0.212	0.315	∞
Nitrate	0.199mg.	-	0.203	0.228	∞	∞
Silver(I)	0.199mg.	-	-	-	0.201	0.217
Sulfate	0.199mg.	-	-	-	-	0.199
Tungsten(VI)	0.199mg.	-	-	-	-	0.199
Uranium(IV)	0.199mg.	0.200	0.205	0.252	∞	∞
Vanadium(V)	0.199mg.	0.210	∞	∞	∞	∞
Zinc(II)	0.199mg.	-	-	-	0.199	0.206
Zr(II) (filtered)	0.199mg.	-	-	-	-	0.199
Zr Citrate	0.199mg.	-	-	0.198	0.205	0.253

TABLE 3

EFFECT OF INTERFERENCES AT 285 mu

Interference	Nickel Taken	Nickel Found				
		Interference/Nickel (weight).				
		1/10	1/1	10/1	100/1	1000/1
Al(III) Citrate	0.199mg.	-	-	-	0.202	0.217
Cadmium(II)	0.199mg.	-	-	-	0.199	0.202
Chloride	0.199mg.	-	-	-	-	0.198
Chromium(III)	0.199mg.	-	0.202	0.252	∞	∞
Cobalt(II)	0.199mg.	0.210	0.300	∞	∞	∞
Copper(II)	0.199mg.	-	0.201	0.256	∞	∞
Iron(II)	0.199mg.	0.202	0.250	∞	∞	∞
Iron(III)	0.199mg.	0.203	0.255	∞	∞	∞
Magnesium(II)	0.199mg.	-	-	-	0.199	0.202
Manganese(II)	0.199mg.	0.203	0.238	∞	∞	∞
Mn Citrate	0.199mg.	0.202	0.275	∞	∞	∞
Molybdenum(VI)	0.199mg.	-	-	-	0.200	0.210
Nitrate	0.199mg	-	0.218	∞	∞	∞
Silver(I)	0.199mg	-	-	-	0.198	0.201
Sulfate	0.199mg.	-	-	-	-	0.199
Tungsten(VI)	0.199mg.	-	-	-	-	0.200
Uranium(IV)	0.199mg.	0.201	0.206	0.261	∞	∞
Vanadium(V)	0.199mg.	0.216	∞	∞	∞	∞
Zinc(II)	0.199mg.	-	-	-	0.198	0.204
Zr(II) (filtered)	0.199mg.	-	-	-	-	0.199
Zr Citrate	0.199mg.	-	-	0.199	0.210	0.300

amount of foreign substance was reduced so as to obtain a ratio of 100 to 1 and so on until a 1 to 10 ratio was reached or until no interference was noted.

Setting a concentration of 20×10^{-4} mgs./ml. as an optimum working range for the nickel, the solutions were prepared in the following manner:

1. 100 ml. volumetric flasks were used in all cases.
2. 20×10^{-2} mgs. of nickel were mixed in one flask with the proper amount of interference to obtain a weight ratio of 1000 to 1. (interference over nickel).
3. When necessary, tartaric or citric acid was added.
4. In order to determine the quantity of NaOH needed, the same amount of nickel and interference as taken above was titrated to a phenolphthalein end point with 2M NaOH. This amount of NaOH plus that required to neutralize the citric or tartaric acid was then added to the flask containing the interference solution.
5. 20 mls. of 0.1M KCN were added.
6. The flasks were diluted to the mark with buffer (pH 10). If the pH prior to this step is

9.5 or greater, distilled water can be used instead of the buffer.

7. The absorbance of each solution was obtained on a Beckman D.U. Spectrophotometer at both 267.5 and 285 μ in order to compare the behavior at both wave lengths. The apparent amount of nickel was obtained from the standard curve and compared to the amount known to be present.
8. When a difference was noted between the amount of nickel found and the amount taken, the concentration of the interference was reduced by a factor of 10 as shown in Tables 2 and 3.
9. In each case where interference was encountered an attempt was made to remedy it.

A dimethylglyoxime separation of the nickel provides one of the best methods for eliminating interferences. In the cases where this is recommended, the procedure was as follows:

1. The nickel was precipitated with dimethylglyoxime in the usual way as outlined by Willard and Diehl (27, p.385). The precipitate was filtered and retained on fritted glass funnels.
2. The precipitate from number 1 was dissolved in as small an amount of HNO_3 as possible. It is

also soluble directly in KCN, but it required too much and the presence of the dimethylglyoxime increased the absorbance markedly.

3. After dissolving in HNO_3 the resulting solution was heated until almost dry.
4. About 20 mls. of 70% perchloric acid were added. This was then fumed for 5 to 10 minutes or until all of the NO_3^- was expelled. The resulting solution was diluted and boiled to remove any chlorine that remained from the decomposition of the perchloric acid.
5. The final solution was diluted to a definite volume depending on the amount of nickel present.
6. Aliquots of this solution were then added, with enough NaOH to neutralize the acid, to 100 ml. flasks. After adding 20 ml. of KCN, the solutions were diluted to the mark, mixed and allowed to reach equilibrium (15 - 20 minutes). Then the absorbance values were obtained and the amount of nickel present was found from the standardization curve.

This procedure is quicker and less tedious than drying and weighing, and in most cases the presence of any

interference that comes through with the precipitate could be discovered as described, using both 267.5 and 285 m μ . In many cases, the amount of this interference could be determined and the correction applied to the nickel. Table 4 illustrates the accuracy obtained with a dimethylglyoxime separation of the nickel prior to its determination with cyanide.

TABLE 4

DIMETHYLGLYOXIME SEPARATION OF NICKEL

Nickel Taken	Nickel Found
12.21 mgs.	12.23 mgs.
18.78 mgs.	18.80 mgs.

Individual Interferences. The following cations were investigated.

Aluminum. In concentrations of the order of 100 times that of nickel, the absorbance of the citrate or tartrate complex of aluminum is negligible.

A separation of aluminum was tried by precipitating the hydrous oxide by increasing the pH after adding cyanide to complex the nickel, but some of the nickel was removed from solution on filtering.

If the amount of aluminum exceeds that that can be handled by the tartrate without increasing the absorbance, the nickel can be separated with dimethylglyoxime.

Cadmium Although cadmium forms $\text{Cd}(\text{CN})_4^{2-}$ with KCN it causes only a slight increase in absorbance even at the 1000 to 1 ratio. The best way to handle cadmium was to allow it to precipitate on increasing the pH to about 10 and then dissolve the precipitate with excess KCN. Cyanide strips cadmium from tartrate or citrate so these will have no effect.

Calcium The best way to work with calcium was to leave it in solution. Calcium itself has very little absorbance, 0.007 at 267.5 μ , when the concentration is 1000 times that of nickel. When citric acid was added the absorbance at 267.5 and 285 μ is about doubled, so it is better if the acid can be omitted, at least when the concentration of the calcium is more than 100 times that of nickel.

Chromium Since this method is to be used after a perchloric acid fuming, chromium (VI) will be of principal interest. There is no evidence of any cyanide complexes with chromium (VI) so the main interference will arise from the absorbance of the yellow chromate ion which exists at the pH used (24, p.259). The characteristic curve for chromate is shown in Figure 6.

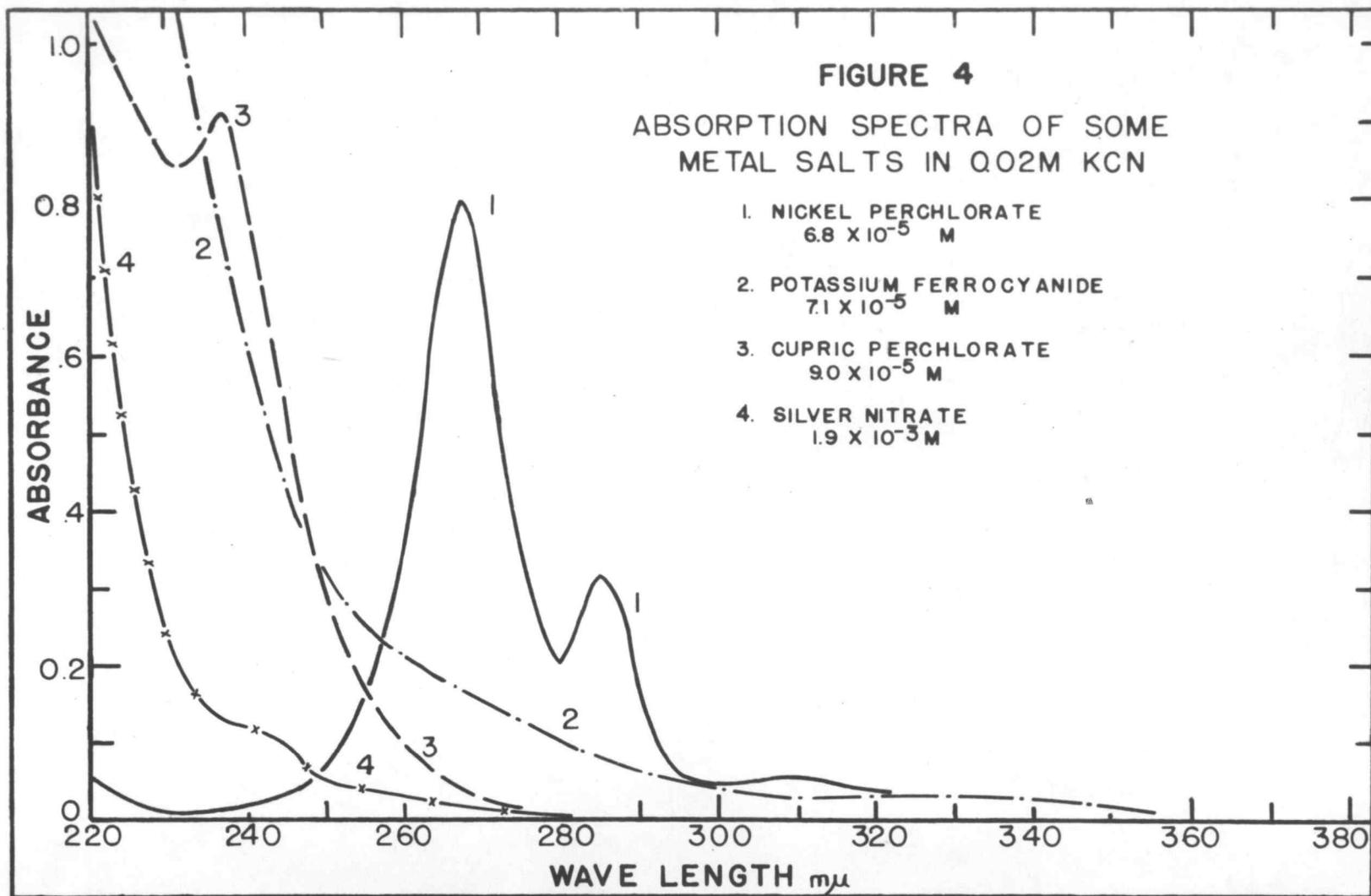
If the chromium is in excess of about 1×10^{-6} gms. per milliliter a separation from the nickel is necessary.

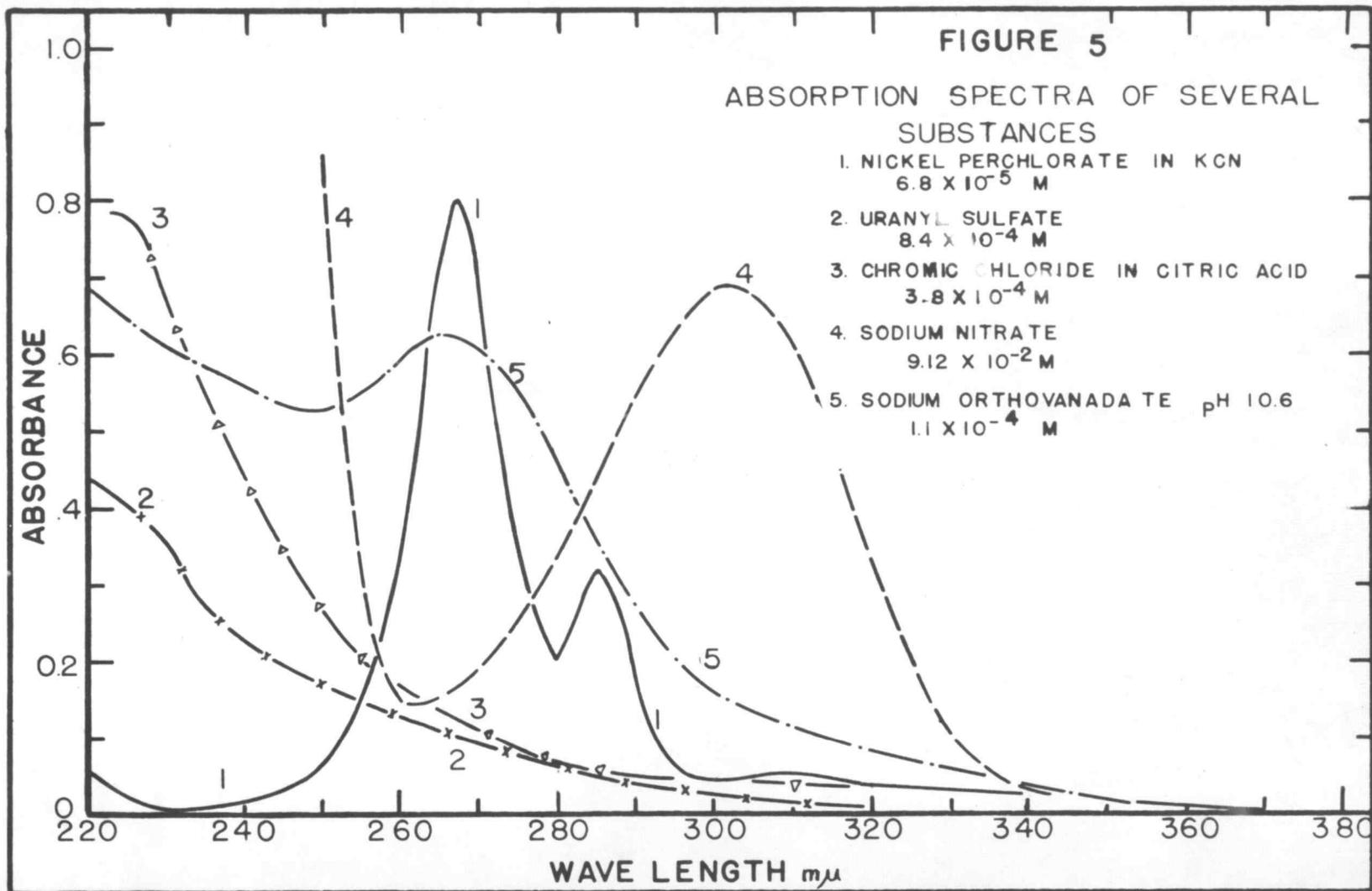
This is probably best done with a dimethylglyoxime separation.

When the concentration of the chromate is low enough so that its absorbance can be measured, it is apparent by comparing its characteristic curve with that of nickel cyanide, that a simultaneous determination of the two elements can be used. The calculations will be similar to those used in the discussion on copper.

There is a complex between chromium (III) and cyanide but according to Diehl and Smith (9, p.386) it is formed by the oxidation of the chromium (II) cyanide complex and not by the direct action of cyanide on chromium (III). This was confirmed in that a solution of chromium (III) plus cyanide gave the same absorption curve as that obtained from a chromium (III) solution. A chromium (III) solution is almost as absorbant as the chromate so nothing would be gained by reducing the chromium (VI). The chromium (III) solution is not as stable as chromium (VI) so this would make the reduction detrimental.

Citric acid was also tried with chromium (III) but again nothing seemed to be gained by this action. The absorption spectrum is shown in Figure 5.

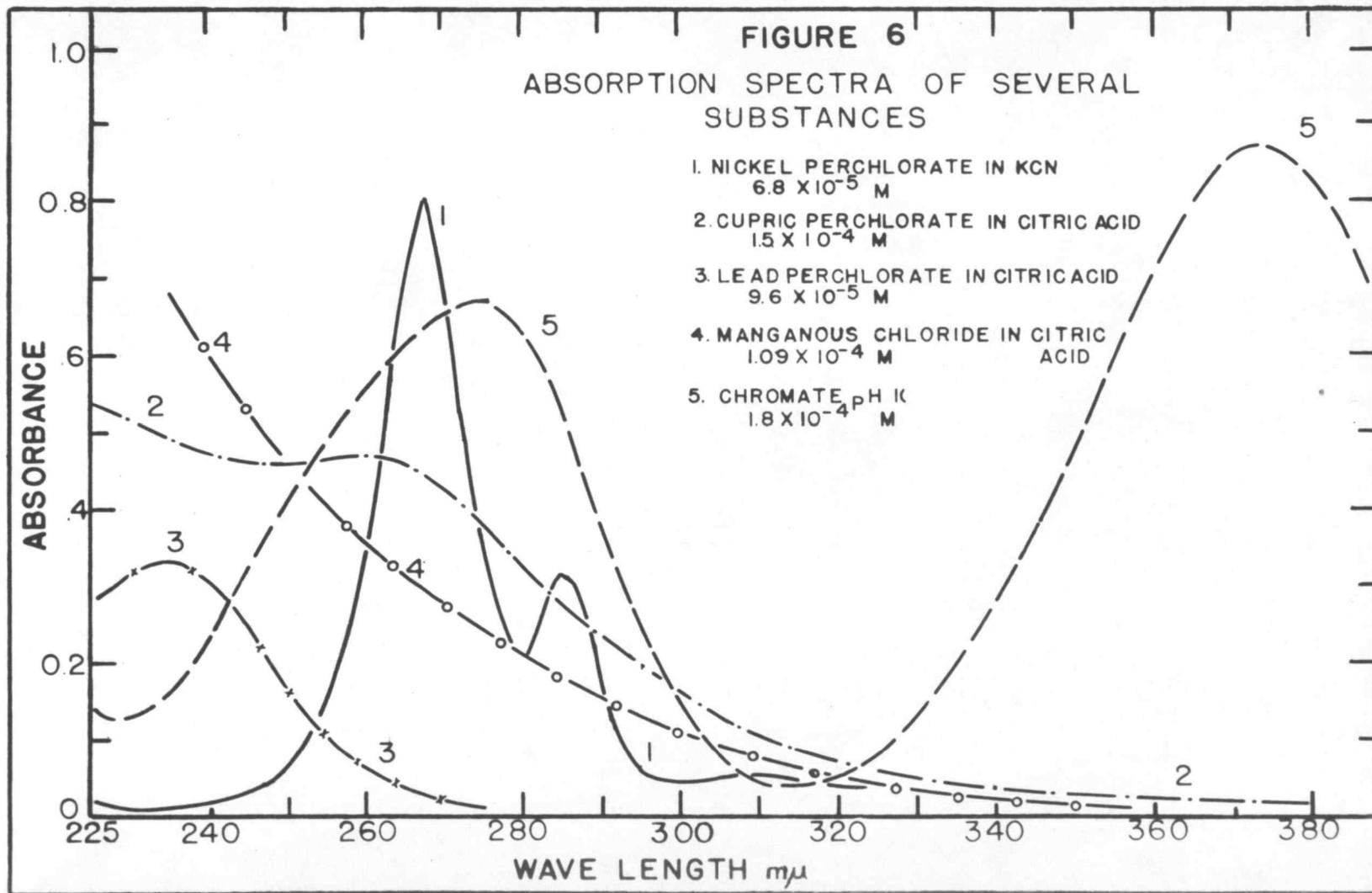




Cobalt Cobalt (II) reacts with cyanide to form $\text{Co}(\text{CN})_6^{-4}$ which is a powerful reducing agent. This rapidly reduces water with the formation of $\text{Co}(\text{CN})_6^{-3}$ (9, p.386). This probably helps to account for the fact that the absorbance of the solution containing cobalt and cyanide was still decreasing at the end of a 72 hour period. Since the maximum for the characteristic curve for the cobalt cyanide complex as shown in Figure 1, is in the same region as that for the nickel complex it would be almost impossible to use a simultaneous method. In cases where the weight of cobalt exceeds that of nickel it is best to separate the two with the dimethylglyoxime precipitation of the nickel.

Tartrate was added to the cobalt, nickel and cyanide solution without any apparent effect.

Copper (II) forms only an intermediate complex with CN^- . The stable complex $\text{Cu}(\text{CN})_3^-$ is formed by the reduction of copper with the formation of cyanogen (9, p.386). Evidence of this change was a decrease in absorbance with time and the formation of the same shaped curve as obtained with copper (I) and cyanide. The stable curve obtained using copper (II) as starting material is shown in Figure 4.



As is shown in Tables 2 and 3, copper in excess of the nickel causes considerable interference.

Concentrations of copper in excess of nickel would best be handled by a dimethylglyoxime precipitation of the nickel. When the concentration of copper is of the same order as the nickel, a simultaneous method can be used and thereby obtain the values for both the nickel and copper. An example of the procedure involved in the determination of copper and nickel would be as follows: Obtain absorbance vs concentration curves for pure copper and pure nickel cyanide solutions at each of the two maximum wave lengths (237.5 μ for copper and 267.5 μ for nickel).

The absorbance is then obtained at 237.5 and 267.5 μ on a solution containing both nickel and copper with cyanide. The amount of nickel and copper are then determined by solving the following simultaneous equations (15, pp.342-343).

$$\text{at } 237.5 \mu \text{ Absorbance} = a_{Ni} \times c_{Ni} + a_{Cu} \times c_{Cu}$$

$$\text{at } 267.5 \mu \text{ Absorbance} = a'_{Ni} \times c_{Ni} + a'_{Cu} \times c_{Cu}$$

a = slope of standardization curve for respective element at the respective wave length.
 c = concentration of the element which is to be determined.

These two equations develop from Beer's Law which

states that absorbance = $a \times c \times l$ (l is optical path). The same 1 cm. cells are used in all cases so the value for the optical path is 1 and therefore disregarded.

Cyanide strips the copper from the complexes that it forms with citrate or tartrate so that the presence of either one of these substances does not appear to have any effect on the absorbance of the copper cyanide complexes.

Iron forms two complexes with cyanide, $\text{Fe}(\text{CN})_6^{-4}$ and $\text{Fe}(\text{CN})_6^{-3}$, both of which are stable. It is evident from Tables 2 and 3 and Figures 1 and 4 that iron will cause considerable interference. A simultaneous method might be the answer when iron is of the same order of magnitude as the nickel. The best way to take care of large amounts of iron is to separate the nickel with a dimethylglyoxime precipitation. According to Willard and Diehl (27, p.135) nickel can be separated from iron by adding cyanide to the slightly acid solution of nickel and iron (III). The iron is then precipitated by increasing the pH. Cyanide will complex the nickel and prevent its precipitation. This was tried but it was found that the cyanide complexed with enough iron to interfere. When tartaric or citric acid was added to the iron, the complex formed was more absorbent than the

iron cyanide complex.

Lead is another metal that will precipitate as the hydrous oxide in the pH range used for this work. It was found that lead citrate or tartrate complexes were too highly absorbent as shown in Figure 6, to be of much value. Even when the ratio was as small as 10 to 1 considerable interferences resulted. Only when the ratio was reduced to 1 to 1 could it be present without any difficulty.

An attempt was made to separate the lead by precipitating it as the hydrous oxide but this proved unsuccessful because the nickel was partially removed from solution.

For high levels of lead the only apparent solution is to separate the nickel with a dimethylglyoxime precipitation.

Magnesium seems to be unique among the interferences studied. Magnesium perchlorate absorbs very little in the range studied. A solution of approximately 2 mgs. magnesium per ml. has an absorbance of 0.020 at 267.5 μ . The citrate complex has an absorbance of 0.068 at the same wave length. From this it is evident that the best way to work with magnesium present would be to omit

the citrate. But since it is hard to neutralize the solutions without precipitating the magnesium, an attempt was made to use citrate when magnesium was in the 100 to 1 and lower concentrations. It was found that when magnesium is present with citrate or tartrate, the formation of the nickel cyanide complex is slowed down considerably. Instead of being an instantaneous process it now takes hours for it to develop fully.

After allowing the solution to stand 24 hours, the nickel cyanide complex was formed completely and the absorbance of the solution did not change for at least another 24 hours. This slowness of formation was encountered even when the magnesium was only 10 times that of the nickel.

An attempt was made to precipitate the hydrous oxide and filter it, but this proved to be unsuccessful due to removal of the nickel. From this it is then concluded that the magnesium is best handled by not removing or complexing it. This can be done by carefully neutralizing the solution without precipitating the hydrous oxide and then adding the KCN. The pH maintained by the KCN seems to be just below that required for the precipitation of the magnesium.

Manganese Both manganese (II) and (III) form complexes with cyanide but like chromium the manganese (III) complex is formed only by oxidation of the manganese (II) complex and not by direct action of cyanide on manganese (III) (9, p.386). When excess cyanide was added to manganese (II) a complex was formed that gave the characteristic absorption curve as shown in Figure 1. It was not determined which of the two complexes this was. At the end of a 24 hour period the peak at 324 μ had not changed and the rest of the curve dropped very slightly in absorbance. Large quantities of manganese will have to be separated but when the concentration is low enough so that absorbance values can be obtained, a simultaneous method similar to the one already discussed could be used for both nickel and manganese.

Citric acid complexes with manganese (II) and gives a characteristic absorption curve as in Figure 6. The absorbance in the region between 267 and 285 μ is higher than that obtained with the cyanide complex for the same concentration of manganese so nothing is gained by adding citric acid. Cyanide will not strip manganese from citrate because the stability of both complexes is about the same.

As would be expected, manganese in the form of

permanganate causes considerable interference even when it is the same concentration as the nickel. Since the presence of any permanganate will be unlikely, nothing more was done with it.

Molybdenum It is molybdenum (IV) that forms complexes with cyanide (21, p.719). No change in the curve for molybdate was observed when cyanide was added to the solution. The presence of citrate also causes little change in the characteristic curve for molybdate.

If the molybdenum is in greater concentration than the nickel the best way to handle it would be to carry out a dimethylglyoxime precipitation. An attempt was made to remove the molybdenum as molybdic acid but the separation was not complete.

Silver forms a very stable complex with cyanide, $\text{Ag}(\text{CN})_2^-$. When silver is of the order of 1000 times that of nickel there is only a slight interference, so the proper way to handle it is to leave it in solution as the complex. The curve for this complex is shown in Figure 4. It was found that the complex forms best when the pH is increased to 10, precipitating the hydrous oxide and dissolving this with KCN. It is important to have sufficient KCN to complex with both the nickel and silver or low results will be obtained probably due to

the competition between silver and nickel for the cyanide.

The hydrous oxide of the silver cannot be filtered from the nickel without removing some of the nickel from solution and thereby getting low results.

Tin Some difficulty was encountered in an attempt to keep the tin in solution with citrate and tartrate. The complex was unstable and the tin usually came out of solution after a short period of time. At the higher concentration of tin the complex with citrate or tartrate was too absorbant to be of any use.

An attempt was made to separate the tin by precipitating the hydrous oxide but was unsuccessful due to removal of the nickel. For high levels of tin the dimethylglyoxime separation is the best procedure. Below the 100 to 1 region the tartrate complex can be tolerated at 285 m μ .

Tungsten was used in the form of tungstate by fusing tungstic oxide with sodium carbonate. Tungsten is like molybdenum in that it is tungsten (IV) that complexes with cyanide. This was partially confirmed, at least for tungsten (VI), because the curve obtained from a solution of tungstate and cyanide was the same as that for tungstate alone.

Tungstate alone does not interfere with the nickel, even in the region of 1000 to 1. The presence of citrate or tartrate increases the absorbance of tungstate by a factor of about 10. So these would have to be omitted with high levels of tungsten.

Using the above information it would be possible to determine the amount of nickel, if any, that was trapped when tungstic acid is separated in the usual procedure for determining tungsten.

Uranium Uranium(VI) caused considerable interference as low as the 10 to 1 region. This is due to the absorption of the uranyl ion UO_2^{++} as shown in Figure 5. The curve for the uranyl ion did not change when cyanide was added, but after standing for a few minutes the solution became cloudy. When citric acid was added to the uranium solution there was a slight change in the curve and it continued to change with time. The presence of the citric acid kept the solution clear.

Here again it is felt that for large concentrations of uranium the best solution would be a dimethylglyoxime separation of the nickel.

Vanadium According to Gottlieb (12, pp.7-16) vanadium in the basic region is present as ortho vanadate

$(VO_4)^{=}$, pyrovanadate $(V_2O_7)^{=}$ or meta vanadate $(VO_3)^{-}$ depending on the pH. Using a pH of 10.6 for our work we would have a mixture of pyrovanadate and ortho vanadate. The characteristic curves for the three ions are very similar, varying only slightly in height and slightly in wave length for the maximum peaks. In this work the mixture at pH 10.6 was used without trying to differentiate the species present.

Since the characteristic curve for the vanadate, as shown in Figure 5, is so similar to that for nickel there isn't much that can be done in the way of a simultaneous method for the two components. Also, if the determination of the vanadium were of interest, the pH would have to be critically controlled.

Even when the vanadium is present in as small a concentration as in the 1 to 1 ratio there is considerable interference presented. Adding citrate or tartrate only seems to increase the absorbance slightly. Therefore, the nickel must be separated from the vanadium with the dimethylglyoxime method.

Zinc was found to be very similar to cadmium except that neither citrate nor tartrate would hold it in solution when the pH was increased. Like cadmium, it is best handled by increasing the pH to about 10 and precipitating the hydrous oxide, then dissolving the oxide

with excess KCN to form $Zn(CN)_4^{2-}$ which causes very little interference even in the 1000 to 1 region.

Zirconium Since zirconium does not form any complexes with cyanide, any interference will be caused by the absorbance of the metal perchlorate. Since the metal will come out of solution as the hydrous oxide at the pH used, the first thought was to complex it with citric or tartaric acid. This was done but it was found that the complex had too high an absorbance value, at least in the 1000 to 1 region. The alloys that are of primary interest in this work are in the neighborhood of 95% zirconium, so the citrate or tartrate complex would offer considerable interference.

The next attempt at handling the zirconium was to allow it to precipitate on increasing the pH. This proved to be quite successful. The zirconium precipitate is easily filtered and if KCN is added before the precipitation is completed, none of the nickel is removed from the solution. The dimethylglyoxime precipitation would also work here, but if only zirconium is to be removed it is felt that the hydrous oxide precipitation method is sufficient.

The following anions were also studied:

Chloride The chloride ion offers no interference.

Nitrate The nitrate ion offers considerable interference because it is highly absorbant in the region studied as shown by the curve in Figure 5. It has a molar absorbance of 1.8 at 267.5 and 5.8 at 285 m μ . This interference is easily overcome by fuming with perchloric acid.

Phosphate The phosphate ion is relatively transparent in the region of the spectrum used but in its presence the formation of the nickel cyanide complex is greatly retarded. This is probably due to complexation between the phosphate and the nickel.

Sulfate The sulfate ion like the chloride offers no apparent interference.

II Spectrophotometric Titration Method

Osborn, Elliott and Martin (22, pp.642-646) discuss some of the principles upon which spectrophotometric titrations are based and give a very good bibliography of the work prior to 1943. Since the late 1940's and early 1950's more and more of this work has appeared in the literature. Some of the most important of these will be referred to.

The photometric detection of an end-point depends on the change in absorbance of a solution as increments

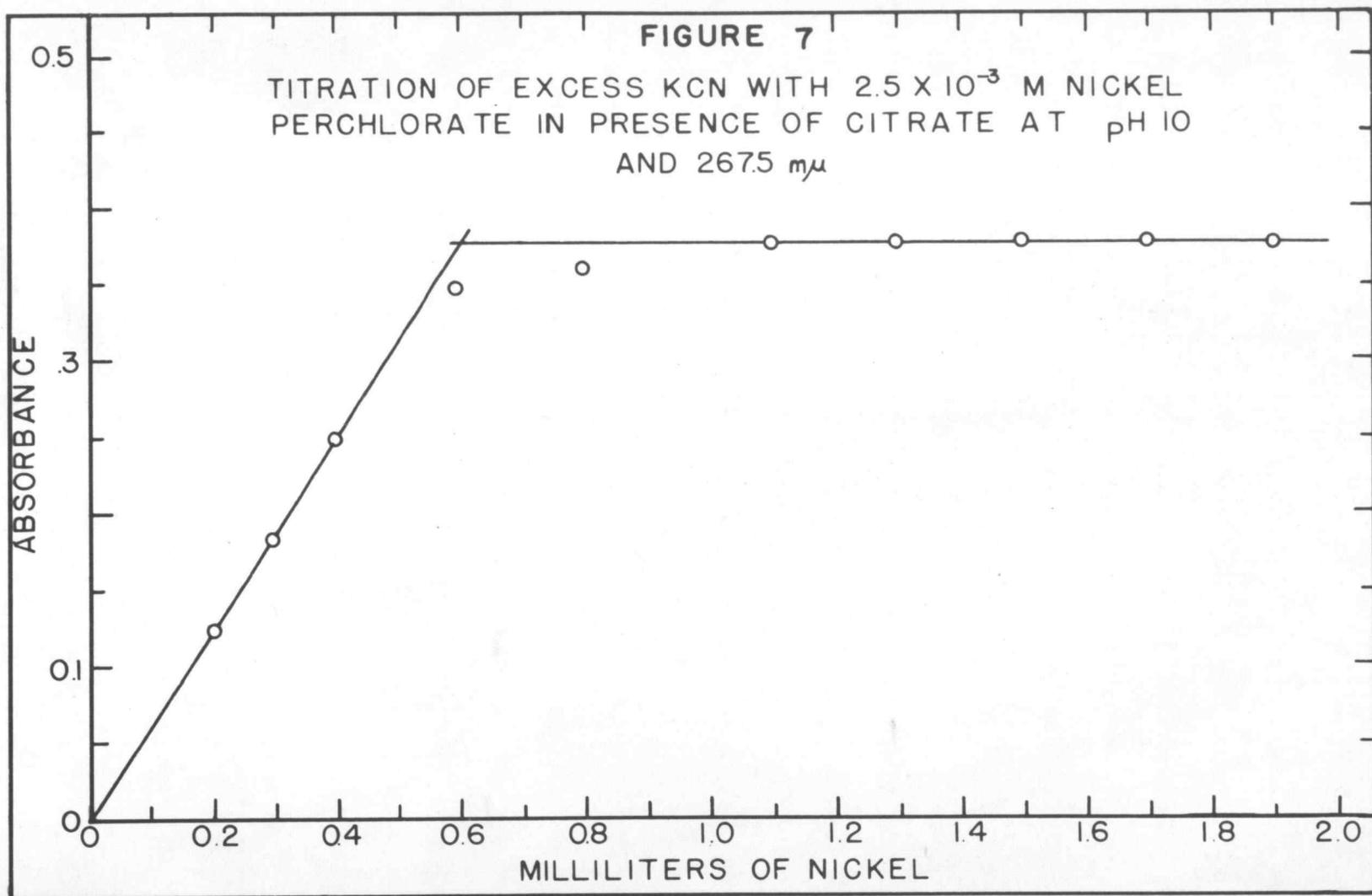
of a titrant are added. There are several ways that this can be done. Four of the most common are: 1.) by the formation of a species with a subsequent increase in absorbance (26, pp.1334-1336), 2.) by the change in absorbance as a complex or some other entity is eliminated or changed by the titrant (23, pp.1124-1126), 3.) by adding an indicator to follow some changing condition (22, pp.642-646), and 4.) by an indirect method. When a complex does not absorb light it is possible to locate the end-point by adding some substance that forms an absorbent complex with the titrant after the desired substance is fully complexed. The equivalence point of the first substance is located at the point where the absorbance starts to increase due to the formation of the second complex (25, pp.1910-1912).

The use of changing light conditions as a means of locating the end-point in a titration, while not being new, (The first evidence of its use appeared in 1926 (10, pp.445-450).) has not received much attention until recent years. This is probably due to two facts. The first of these is the development of better instruments for measuring light and the second is the utilization of the ultraviolet region of the spectrum. The importance of the first of these reasons is self explanatory. According to Bricker and Sweetser (5, pp.409-410) the

use of the ultraviolet region has several advantages over the visible. The molar extinction coefficients of many reagents have their maximum value in this region. The number of reagents that can be used is greater because more substances absorb in the ultraviolet.

Photometric detection of end-points has many advantages. Since the end-point is found by extrapolation on a graph, as shown in Figure 7, the tedious task of watching for a color change is eliminated also the use of extrapolation makes it unnecessary to obtain readings near the end-point as is done with potentiometric titrations. This is of great advantage when the reaction is slow to reach equilibrium near the end-point (23, pp.1124-1126).

This titration method of analysis has an advantage over the regular colorimetric method because all that is of interest is the change in absorbance as a titrant is added to the solution. This means that substances that do not react with the reagent but still absorb in the range used do not interfere. When a substance is not inert to the reagent added, if its stability constant is sufficiently different from that of the main constituent being analysed it may be possible to determine both constituents. When the titration curve is plotted for a two component system under the above conditions there will be



two changes in the slope corresponding to the two endpoints. An example of this is shown by Wilhite and Underwood (26, p.1335) in the determination of lead and bismuth by titrating with ethylenediaminetetraacetic acid.

As the increase in absorbance is being followed, the solution containing nickel will be placed in the titration cell and the instrument balanced at zero absorbance. After this is done no other instrumental changes are made except to adjust the absorbance scale to balance the meter needle after each addition of the titrant.

The first thing that was done was to find an optimum pH value for the titration. By varying the pH of the nickel solutions with the borate buffers and taking readings every 30 seconds for a period of three minutes after adding the KCN it was possible to follow the rate of attaining equilibrium. Following this procedure it was found that most of the complex was formed within the first 30 seconds when the pH was above 9.5. The rate of stirring was probably the limiting factor. With a fairly fast stirring rate equilibrium was reached between 1 and 2 minutes at a pH of 9.5 or above.

The alloy that is to be analyzed by this method contains zirconium 98%, nickel 0.05%, tin 1.2%, iron 0.25%

and chromium 0.10%. In order to study the effect of the interferences on the titration, solutions were prepared that corresponded as closely as possible to the actual solution of the alloy. The zirconium, tin, and chromium did not cause any interference because they are inert to the action of cyanide. Since the iron is complexed by cyanide, it will be necessary to either remove it or complex it so that it will not use cyanide. Tartaric acid was tried, and it was found to complex the iron sufficiently to keep it from using cyanide, at least during the time it took to perform the titration. Also, the complex between tartrate and nickel did not prevent the rapid formation of $\text{Ni}(\text{CN})_4^{2-}$. However, when tartaric acid was used, the yellow color of the chromium(VI) disappeared and low results were obtained for the nickel. This was attributed to the reduction of the chromium.

Citric acid was tried next. The chromium was no longer reduced, but the complex with nickel retarded the formation of the nickel cyanide complex. Since one of the advantages of a spectrophotometric titration is speed, this was a decided handicap. To overcome this time factor, excess KCN was added to the solution before placing the cell in the instrument. After the solution reached equilibrium, found by observing the absorbance

until it stopped increasing, the excess KCN was titrated with a standard nickel solution. This method has the disadvantage that two standard solutions are needed but it is believed that the shortening of the time required for the titration more than compensates for this.

Ethylenediaminetetraacetic acid was also tried but the complex that it formed with nickel was too stable to permit rapid formation of the nickel cyanide complex.

Table 5 contains the results obtained on synthetic samples using citric acid and the back titration method.

TABLE 5

DETERMINATION OF NICKEL IN SYNTHETIC SAMPLES USING SPECTROPHOTOMETRIC TITRATIONS

Metals Present	Nickel Taken	Nickel Found
Ni	0.0628 mgs.	0.0630 mgs.
Ni and Fe(III)	0.0628 mgs.	0.0629 mgs.
Ni and Cr(VI)	0.0628 mgs.	0.0630 mgs.
Ni and Cr(III)	0.0628 mgs.	0.031 mgs.

The zirconium samples were prepared and titrated in the following manner:

1. The alloy was dissolved with hydrofluoric acid in platinum crucibles.

2. The resulting solution was fumed almost to dryness with 4 mls. of 70% perchloric acid. Sulfuric acid was also tried but the results were always low. This was due to insufficient oxidation of the chromium.

3. The residue was taken up with distilled water and the solution boiled to remove any chlorine that had formed. After cooling, the solution was filtered into 100 ml. volumetric flasks. Seven milliliters of citric acid were added and the excess acid neutralized with NaOH. The solution was diluted to the mark with buffer of pH 10. Since the standard nickel solution is acid the buffer was used to keep the pH from falling below that at which the complex forms.

4. Forty milliliters of the solution were added with standard KCN to the titration cell.

5. After reaching equilibrium, the solution was titrated with a standard nickel solution. The concentrations of the standard nickel and cyanide solutions depend on the amount of nickel present and were chosen so that about 2 mls. of nickel solution would be used during the titration. This small amount keeps the dilution error to a minimum.

The nickel solution was standardized using the regular colorimetric cyanide method. The cyanide solution was standardized against nickel using the same procedure as was used to titrate the unknown solutions.

The amount of nickel in the sample was found by subtracting the KCN equivalent to the amount of standard nickel used, from the total KCN added. This gives the

amount of cyanide used by the nickel in the sample. From this, the amount of nickel was calculated.

Table 6 gives the results for the analysis of the alloy.

TABLE 6

DETERMINATION OF NICKEL IN ZIRCALLOY SAMPLES

Sample Number	Nickel Present*	Sample Fumed With HClO_4	Sample Fumed With H_2SO_4
1	0.05%	0.0495%	-----
2	0.05%	0.0535%	0.0454%
3	0.05%	0.0525%	0.0381%

* Alloys were made up to contain this much nickel and analyzed with dimethylglyoxime. A more accurate analysis is not known.

The analyses of two component systems were tried by titrating cobalt and nickel, iron and nickel, and copper and nickel. Unsatisfactory results were obtained in each case. This was probably due to the fact that the stability constants of each complex are not sufficiently different to allow one complex to form at a time.

III Differential Colorimetry

One of the hindrances to the advancement of colorimetric or spectrophotometric determinations of major constituents has been the limit of accuracy imposed

by the conventional methods. For the normal absolute methods of colorimetric analysis it can be shown that the precision of measuring the intensity of a given color does not increase indefinitely with increasing concentration of the color (2, pp.972-974). It has also been shown that with colors that obey Beer's Law, the maximum precision is obtained when the absorbance of a given colored solution is 0.434. This is due to the fact that up to this point the absorbance increases more rapidly than ΔA_s (the minimum difference in the absorbance of the sample that can be detected). As 0.434 is passed, ΔA_s increases more rapidly than the absorbance (3, pp.160-166).

It is the popular opinion of most authors that due to error in scale reading (0.2 divisions out of 100) and errors in the standard curve, that the average concentration error is about 1%. It is obvious that this error is too large for the determination of major constituents.

Some methods, such as adding a standard solution to the blank and using special apparatus to lessen this error, have been described as being too tedious or inconvenient (2, pp.972-974).

In the usual methods of measuring the extinction of a complex or ion, the solvent is used as the blank. This is satisfactory for small concentrations but when the

concentration is increased the instrument would go off scale. Differential methods of analysis are an attempt to overcome these difficulties.

Most of the principles of differential colorimetry are discussed by Bastian (2, pp.972-974), Bastian, Weberling and Palilla (3, pp.160-166) and Hiskey (14, pp.1440-1446). Bastian (2, p.973) has shown that if a known amount of the substance being analyzed is added to the solvent blank, the concentration of the samples can be increased with a subsequent potential increase in the accuracy with which the material can be determined.

In order to get the increase in light needed for these more concentrated solutions, a wider slit becomes necessary which naturally increases the band width. Increasing the band width will in most cases decrease the absorbance of the solution and also increase the effect of absorbent entities other than the one that is desired.

The next step involved is, therefore, to determine the concentration that should be used in the null cell in order to obtain maximum accuracy and still not have too wide a slit. To obtain this concentration the following procedure, outlined by Bastain (4, pp.580-586), was followed. Bastain (3, p.160) has shown that for a plot of absorbance against concentration the accuracy obtainable at a certain scale reading is directly proportional to the slope times the concentration at that

point and inversely proportional to the minimum difference in absorbance that can be detected at that point. Since the slope, S , is expressed as change in absorbance per change in weight and since the volume terms cancel out, the concentration can be expressed in grams of substance, G . The increasing slit aperture will cause the value of S to decrease if all dilutions are to the same volume, (in this case, 100 mls.) as the weight of the nickel in the null cell increases.

Assuming that the value of minimum difference in absorbance that can be detected is independent of the slit width, the accuracy is proportional to S times G for the differential zero standard. If it is further assumed that all plots are straight lines, the value of S will be constant for each range and can be determined by measurement of a single fairly distant point (4, p.582).

In order to obtain the data for calculating S and S times G a series of solutions was prepared in 100 ml. volumetric flasks. Each solution, in the series, contained: 0.25 mgs. of nickel more than the previous one, 25 mls. of 0.01M KCN, and 1 ml. of 2M NaOH. The series was started by obtaining the absorbance of the lowest concentrated nickel solution by comparing it to a solvent blank. This nickel solution was then used as the blank for the next solution and so on. At

the beginning, the sensitivity control on the photo-multiplier attachment was set on "full" and the sensitivity control on the spectrophotometer was set 3 turns from the extreme clockwise position. This still retains enough sensitivity for balancing the meter needle. From this point on these controls were not changed and the instrument was balanced at zero absorbance each time by adjusting the slit width. The absorbance values obtained as well as S and SxG are shown in Table 7.

TABLE 7

BASTIAN METHOD FOR FINDING OPTIMUM CONCENTRATION FOR THE NULL CELL IN THE DIFFERENTIAL METHOD AT 285 m μ .

Null Cell mg. Ni/100ml.	Sample Cell mg. Ni/100ml.	Slit mm	A	S	SxG
Blank	0.25	.142	.197	.788	--
0.25	0.50	.182	.188	.752	0.188
0.50	0.75	.230	.188	.748	0.374
0.75	1.00	.290	.193	.722	0.579
1.00	1.25	.365	.184	.736	0.736
1.25	1.50	.464	.189	.756	0.945
1.50	1.75	.575	.175	.700	1.050
1.75	2.00	.711	.166	.664	1.162
2.00	2.25	.850	.166	.664	1.328
2.25	2.50	1.08	.152	.608	1.368
2.50	2.75	1.18	.143	.572	1.430

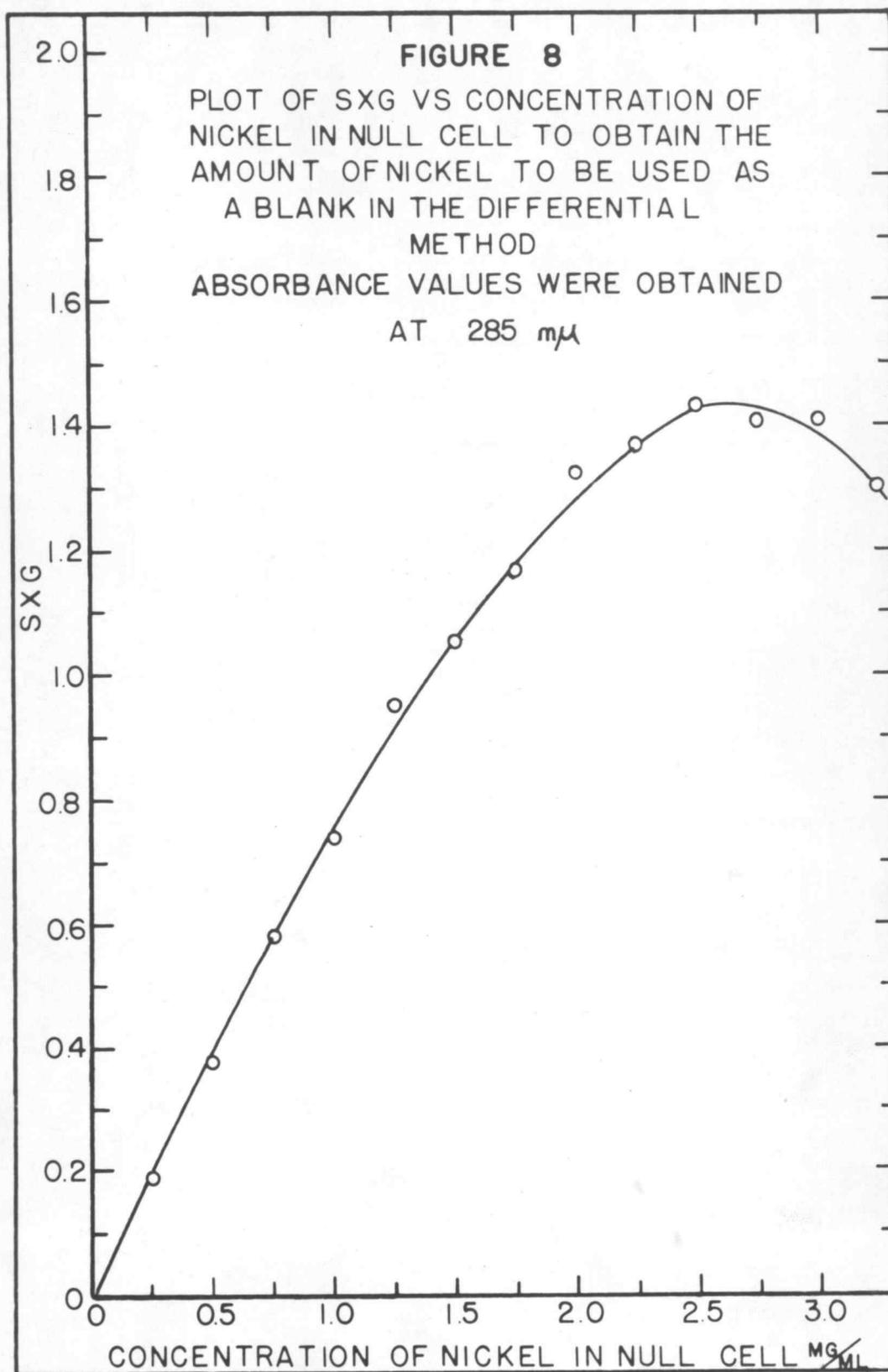
TABLE 7 (Continued)

Null Cell mg. Ni/100ml.	Sample mg. Ni/100ml.	Slit	A	S	SxG
2.75	3.00	1.34	.128	.512	1.408
3.00	3.25	1.50	.117	.468	1.404
3.25	3.50	1.66	.100	.400	1.300

It is evident from the characteristic curve for nickel that by working at 267.5 μ the maximum sensitivity will be obtained but that the concentration of the null or standard cell must be kept low in order to obtain enough light. 285 μ can be used without too much sacrifice as far as sensitivity is concerned and it will allow more concentrated solutions to be used. The use of 310 μ would allow more concentrated solutions but there would be a great loss in sensitivity. After considering these facts it was decided to use a wavelength of 285 μ .

When the values of S times G at 285 μ are plotted against the concentration in the null cell the curve shown in Figure 8 is obtained. From this curve a concentration of 2.00 mgs.Ni/100 mls. was chosen for the null cell. As is shown a concentration of about 2.50 mgs.Ni/100 mls. would give the theoretical maximum accuracy, but the wide slit necessary would probably overcome any advantage of using the higher concentration.

For optimum results with this differential method the absorbance of the unknown should be the same as that

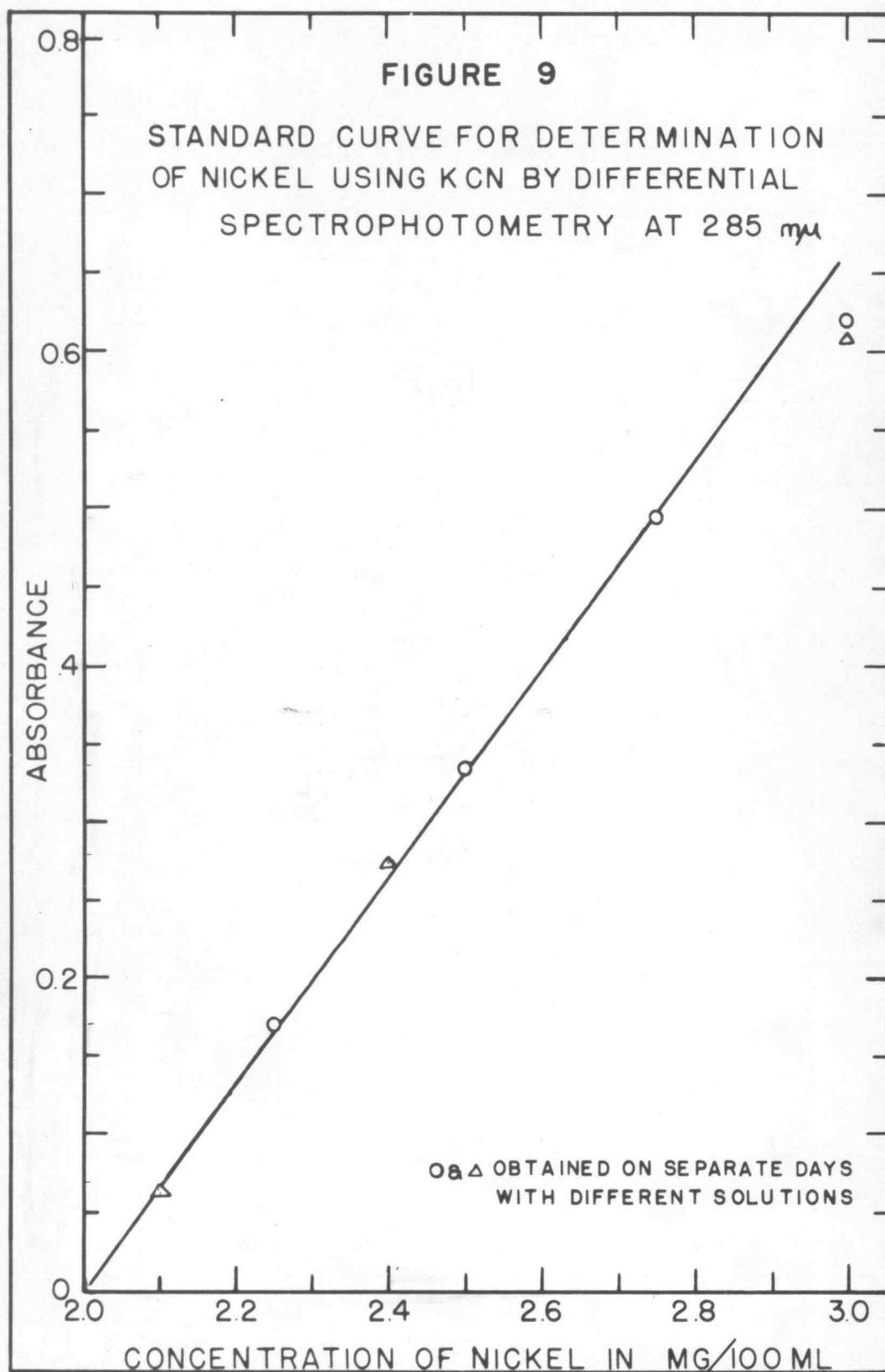


of the standard if the absorbance of the standard is 0.434 or greater (3, p.160). Excellent results can, however, be obtained when the absorbance of the unknown is different from that of the standard (3, p.160). Since the concentration of the nickel in the unknown may be only roughly known, the method used in this paper will cover as large a range in concentration as is practical.

Because of the potential increase in accuracy there are a few sources of error which may be relatively unimportant in ordinary colorimetric methods. In order to take full advantage of the accuracy available, these must be considered. The first and possibly the most important of these errors is any discrepancy in the volumetric equipment used. For optimum results the same flasks and pipettes that are used for preparation of the standardization curve should be used in preparing the unknown solutions to be analyzed. Any difference in the absorption cells will also be a source of error. They should be kept scrupulously clean and should be calibrated against each other always using the same one as the null or standard cell. Variations in room temperature can effect both the absorbance of the solutions and the volumetric equipment. It is believed that this source of error is best handled by obtaining the data for the standardization curve and for the unknown

at as nearly the same time as is possible. Heating of the solutions by the instrument must be kept to a minimum since the null solution is in the instrument longer than the individual samples and standards (4, p.586). It is probably best if the instrument and light source are allowed to warm up only long enough to reach stability and then the readings should be made as rapidly as possible. Also the concentration of the absorbing constituent in the null cell must be determined with the same amount of accuracy as is expected for the samples compared to it.

After choosing concentration of 2.00 mgs. Ni/100 ml. for the null cell, the standardization curve shown in Figure 9 was obtained by placing this amount of nickel in each of 5 - 100 ml. volumetric flasks. One flask was kept for the null solution and increasing amounts of nickel were added to the other flasks. The proper amount of NaOH needed to neutralize the acid and 25 mls. of KCN were added to the flasks which were then diluted to the mark with distilled water. The absorbance values of these 4 solutions were then obtained against the null solution and plotted as shown. The last point corresponding to a concentration of 3.00 mgs. Ni./100 ml. is beyond the range of the method. For best results the unknown solutions will have to lie between 2.00 and



about 2.75 mgs. Ni/100 ml. The absorbance values of these same solutions were obtained in the same manner the next day without any change. The points on the curve at 2.10, 2.40, and 3.00 mgs. Ni/100 ml were obtained on another day with all new solutions.

As shown in Table 8, the results obtained from this curve for the Watt's nickel solution and the results obtained from the dimethylglyoxime determination, differ by only 2 parts/1000. This is very good, especially considering that the overall time for the differential method was about 1/4 that of the dimethylglyoxime method. By working over smaller concentration ranges, the extent of this accuracy could be improved considerably.

TABLE 8

ANALYSIS OF WATT'S NICKEL BATH USING DIFFERENTIAL
COLORIMETRY AND DIMETHYLGLYOXIME

Dimethylglyoxime Method	Differential Method
46.95 mgs. Ni/ml.	47.10 mgs. Ni/ml.
46.95 mgs. Ni/ml.	46.92 mgs. Ni/ml.
	47.10 mgs. Ni/ml.
	47.10 mgs. Ni/ml.

Hiskey and Firestone (15, pp.342-347) give the principles involved in two-component and multi-component differential colorimetry. Nothing was done to apply these methods to the cyanides but there is no apparent reason

why they would not work.

CONCLUSION

Cyanide has been investigated as a spectrophotometric reagent for the determination of nickel and was found to have very good possibilities. The more important substances that might interfere were studied and a procedure for handling each one was discussed. Nothing extensive was done with mixtures other than nickel and one interfering ion, so there are possibilities that double complexes such as $\text{KCuFe}(\text{CN})_6$ (21, p.721) will offer special disadvantages or may even be advantageous.

The advantages of the spectrophotometric titration method were investigated and described. It is believed that the titration method can be very useful when numerous interferences are present. There are probably other complexing agents besides those described that can be used for specific cases to make the method even more valuable.

It was shown that the differential method will work very well for higher levels of nickel and is comparable in accuracy to and much easier to perform than the dimethylglyoxime method.

All three variations of the method offer the possibility of simultaneous determination of nickel and

other metals if the proper conditions can be found.

All in all it is believed that the use of cyanide has tremendous possibilities as a spectrophotometric reagent for the determination of nickel and several of the other metals.

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