SECRET
SECURITY INFORMATION

ORNL-1430

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360628 4

MODIFICATIONS OF THE DIMETHYLGLYOXIME METHOD FOR THE COLORIMETRIC DETERMINATION OF NICKEL BASED ON THE USE OF POTASSIUM PERSULFATE AS THE OXIDANT

By

M. L. Druschel
O. Menis
R. Rowan, Jr.

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

LIBRARY LOAN COPY

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
OAK RIDGE, TENNESSEE

RESTRICTED DATA
This document contains restricted data as defined in the Atomic Energy Act of 1946. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

SECRET
SECURITY INFORMATION

[redacted]

Index No. ORNL-1430
This document contains 44 pages.
This is copy 72 of 162, Series A.

Subject Category: Chemistry General

MODIFICATIONS OF THE DIMETHYLGLYOXIME METHOD FOR THE COLORIMETRIC DETERMINATION OF NICKEL BASED ON THE USE OF POTASSIUM PERSULFATE AS THE OXIDANT

M. L. Druschel
O. Menis
R. Rowan, Jr.

DECLASSIFIED Per Letter Instructions Of AEC 11-23-53
12/14/53 for W. C. Brown M. T. Brown SUPERVISOR CENTRAL FILES ORNL

November 3, 1952

ANALYTICAL CHEMISTRY DIVISION

M. T. Kelley, Director
C. D. Susano, Associate Director

[redacted]

OAK RIDGE NATIONAL LABORATORY
Operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
Oak Ridge, Tennessee

Contract No. W-7405-eng-26

[redacted]

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360628 4

[redacted]

ABSTRACT

Potassium persulfate [redacted] was used as the oxidizing reagent in the dimethylglyoxime method for the colorimetric determination of nickel.

The optimum conditions, including pH, wavelength, temperature, quantity of reagents, tolerance for interfering ions, and time factors have been determined.

The preferred procedures for two ranges of nickel concentration, 0.2 to 1.5 and 1.5 to 8.0 micrograms per ml, as well as a modified procedure suitable for the entire range, are given.

The standard deviation of the method, under the best conditions, is less than two per cent.

[redacted]

[redacted]

CONTENTS

	Page
INTRODUCTION	6
OXIDATION OF NICKEL WITH AMMONIUM PERSULFATE	10
OXIDATION OF NICKEL WITH POTASSIUM PERSULFATE	12
Stability	12
Quantity Required for Oxidation of Nickel	12
Stability of the Nickel-Dimethylglyoxime Complex	15
Wavelength	15
Optimum pH for Oxidation	19
Nickel - 1.5 to 8 micrograms per ml	19
Nickel - 0.2 to 1.5 micrograms per ml	19
Optimum Temperature for Oxidation	23
Composition of the Reference Solution	25
Quantity of Dimethylglyoxime	25
Order of Addition of Reagents	25
Interference of Foreign Ions	29
Interference of Iron	29
Interference of Uranium	29
Ammonium Citrate Concentration	38
Optimum Conditions for the Method	41
REFERENCES	43

[redacted]

[redacted]

MODIFICATIONS OF THE DIMETHYLGLYOXIME METHOD FOR THE COLORIMETRIC DETERMINATION OF NICKEL BASED ON THE USE OF POTASSIUM PERSULFATE AS THE OXIDANT

INTRODUCTION

The object of this investigation has been to make available a colorimetric method for the determination of nickel, [redacted] having the maximum possible precision. The sensitivity of the method must be equal to or higher than that of existing methods, but sensitivity is secondary in importance to precision.

Perhaps the most widely used colorimetric method for the determination of nickel makes use of dimethylglyoxime. After oxidation of the nickel-dimethylglyoxime complex, a red soluble complex is formed in an alkaline solution and can be readily determined spectrophotometrically. Because of the high degree of specificity of the reagent, it has been possible to apply the method to a wide variety of materials with a minimum of separations. Since the dimethylglyoxime method is the one for which the greatest background of experience is available, it was decided to make a critical study of this method in an effort to establish conditions yielding improved precision.

In this report the sensitivity of the method is judged by the relative value of the colorimetric factor, F:

$$F = \frac{C}{A}$$

where:

C = concentration in micrograms per ml

A = absorbancy = $\log \frac{1}{T}$

An increase is indicated in the sensitivity as the colorimetric factor

[redacted]

decreases. The precision of the method is stated in terms of the standard deviation of the factor obtained from a number of determinations on standard solutions.

The initial work involving the use of dimethylglyoxime as a colorimetric reagent for nickel was done by Rollet[17] in 1926. Since his publication, a number of papers have been published which describe modifications of the method involving variations in the oxidizing reagent, quantity of alkali required, complexing reagents for the interfering ions, and wavelength to be used for the absorbancy measurements. Some of the conditions as described in several of these articles are listed in Table I.

The most frequently used oxidant for nickel has been bromine water, but Cooper[4] and Babko[1] claim better precision with iodine. Babko[1] recommends iodine, stating that a mild oxidizing reagent leads to the best results. Rodden and Petretic[16] introduced persulfate as a substitute for bromine water or other oxidants. According to these authors, it is claimed that the color stability of the nickel-dimethylglyoxime complex is greatest when ammonium persulfate is used as the oxidant. Furman and McDuffie[6] have reported some stability studies, using potassium persulfate as the oxidant in solutions adjusted to pH 12 with sodium hydroxide.

In studies of substances which interfere with this method, the presence of iron in the ferrous state has been found to be the most serious of the interfering ions. (Sandell.)[18] Citrate, in the form of a solution of either ammonium citrate or citric acid, has been used to the greatest extent for complexing iron, although tartaric acid was used by Makepeace[9] with equal success.

The wavelengths at which various investigators have measured the absorbancy of the nickel-dimethylglyoxime complex have varied considerably,

Table I

Summary of Current Literature Survey

Oxidant	Reference	Quantity of Alkali	Wavelength mμ	Sensitivity and Precision	Color Stability Minutes
Bromine Water	(2)	Conc. NH_4OH until Br_2 color disappears + 5 ml excess	540	No statement	15 - 180
	(3)	Conc NH_4OH until Br_2 color disappears + 1 drop excess	525	Std. dev. 0 1 per cent. Factor 9.0	15
	(5)	5 ml conc. NH_4OH	Fischer "Electro-photometer" green light filter	No statement	---
	(6)	pH 9 5 ammonium ion conc 0 5 to 2 0 M	530	No statement	30 (maximum)
	(7)	NH_4OH to pH 8	530	No statement	---
	(9)	10 ml of conc. NH_4OH + 10 ml 6 N NaOH	530 or 470	Approx. 2 per cent std. dev. Accuracy only about 40 per cent	5
	(13)	5 ml 1 1 NH_4OH	530	Std dev. 0 4 to 6 per cent	10
	(14)	Final volume to be 0 33 N in respect to NH_4OH	535 or 442 5	No statement	60 (minimum)
Iodine	(1)	0 5 mg NH_4OH	500	No statement	---
	(4)	10 ml of 1 1 NH_4OH	540	Std. dev 0 25-0 5 per cent Factor 9 61	---
Persulfate	(6)	pH 12 with solid NaOH	530	No statement	Several hours
	(15)	5 ml of 1 1 NH_4OH	520	No statement	---

but, in general, the range between 520 and 540 mμ has been used in order to avoid the interference of ferric citrate. Apparently, very little work has been done at the wavelength of maximum absorbancy, which is about 450 mμ. Makepeace[9] has noted that there is a shift in the maximum if sodium hydroxide is introduced into the solution.

There is a scarcity of information in the literature concerning sensitivity, precision, and ranges of concentration of nickel being investigated. The best precision was reported by Cooper[4] who stated that for ten determinations, the standard deviation ranged from 0.25 to 0.5 per cent for a range of concentration varying from 0.2 to 6 μg of nickel per ml, while Murray[13] reported a precision in some cases of not better than five per cent. The other authors give very little information concerning the precision they obtained. Some reports were based only on three to five determinations.

Such values of the sensitivity of the method as are given in these reports appear to be in the same range. If expressed as concentration of nickel (μg/ml) per absorbancy unit, the average colorimetric factor is 9.5.

From this literature review it appears that a mild oxidant is to be preferred for this reaction. The use of a strong oxidizing reagent yields low results, which Babko[1] believes is caused by the destruction of the dimethylglyoxime complexing group by the strong oxidant. In the initial portion of this study, ammonium persulfate, a mild oxidant, was employed. Since ammonium persulfate was found to be too unstable, potassium persulfate was substituted for the ammonium salt, and variables such as the the quantity of reagent required, pH, oxidation temperature, interference

of uranium and other ions, and wavelength, were studied. This report presents the results of both studies and includes recommended procedures based on the use of potassium persulfate as the oxidizing reagent.

OXIDATION OF NICKEL WITH AMMONIUM PERSULFATE

On the basis of the findings of Rodden and Petretic[16] that the oxidation with ammonium persulfate yields the most stable complex, the initial studies were carried out with this reagent being used as the oxidizing reagent. Over a period of time, this procedure yielded erratic results. This is illustrated in Table II, where it will be observed that in 16 separate tests over a period of 23 days, absorbancy values varied over a range of 22 per cent. Further study revealed several possible sources of error. For example, it has been found that the chemical stability of this salt is poor. An empirical test was performed in which 5 grams each of several lots of reagent grade ammonium persulfate, designated by different batch numbers, was dissolved in 25 ml of water. The pH of these solutions ranged from 2.1 to 3.5. The use of the reagent solutions having pH values in the lower part of this range result in precipitation of the nickel-dimethylglyoxime complex. A proposed explanation for this reaction is the formation, at a low pH, of hydrogen peroxide as a decomposition product of Peroxydisulfuric acid formed in the ammonium persulfate. (Lattimer and Hillebrand.)[8] Hydrogen peroxide, a strong oxidizing agent in alkaline solution, causes the precipitation of the dimethylglyoxime oxidation product. To test this hypothesis, varying amounts of H_2O_2 were added in the ammonium persulfate procedure, and at higher H_2O_2 concentrations, precipitation occurred. Another objection to the use of ammonium

Table II

Reproducibility of Absorbancy with Ammonium Persulfate as the Oxidant in the Colorimetric Determination of Nickel

Results of two separate series of tests made at various intervals of time using the same bottle of reagent.

Wavelength: 530 mμ
Uranium present: none

Time, Days	Absorbancy 1.93 μg Ni per ml	Deviation from Average Per Cent	Absorbancy 3.86 μg Ni per ml	Deviation from Average Per Cent
1	0.219	+14.1	0.431	+14.3
3	0.245	+ 3.9	0.484	+ 3.8
3	0.258	- 1.2	0.518	- 3.0
6	0.278	- 9.0	0.542	- 7.8
7	0.279	- 9.4	0.539	- 7.2
8	0.265	- 3.9	0.540	- 7.4
21	0.259	+ 1.6	0.492	+ 2.2
23	0.234	+ 8.2	0.475	+ 5.6
Average	0.255		0.503	

persulfate is the slowness with which the maximum color intensity is developed and the continuous change in the color intensity with time, as shown in Figure 1. For these reasons the subsequent studies were carried out with potassium persulfate instead of the ammonium salt.

OXIDATION OF NICKEL WITH POTASSIUM PERSULFATE

A number of variables were studied in connection with the use of potassium persulfate as the oxidant in this method, including the chemical stability of the salt, the quantity of salt required, pH, oxidation temperature, stability of the nickel-dimethylglyoxime color, wavelength, and the interferences of iron and uranium. These variables will be discussed individually in the following paragraphs.

Stability of Potassium Persulfate

Willard[20] suggested the use of potassium persulfate instead of ammonium persulfate because of its greater chemical stability. It was demonstrated by laboratory tests that there was no variation in the absorbancy of the Ni-dimethylglyoxime complex over a period of at least 16 hours when a saturated solution of potassium persulfate (approximately five per cent w/v solution), kept at 35 °C, was used as the oxidant. Mellor[11] states that an aqueous solution of $K_2S_2O_8$ decomposes gradually in the course of a few months at ordinary temperatures to form the acid sulfate, with decomposition occurring at a faster rate at elevated temperatures.

Quantity of Potassium Persulfate Required for Oxidation of Nickel

As shown in Table III, the amount of potassium persulfate required

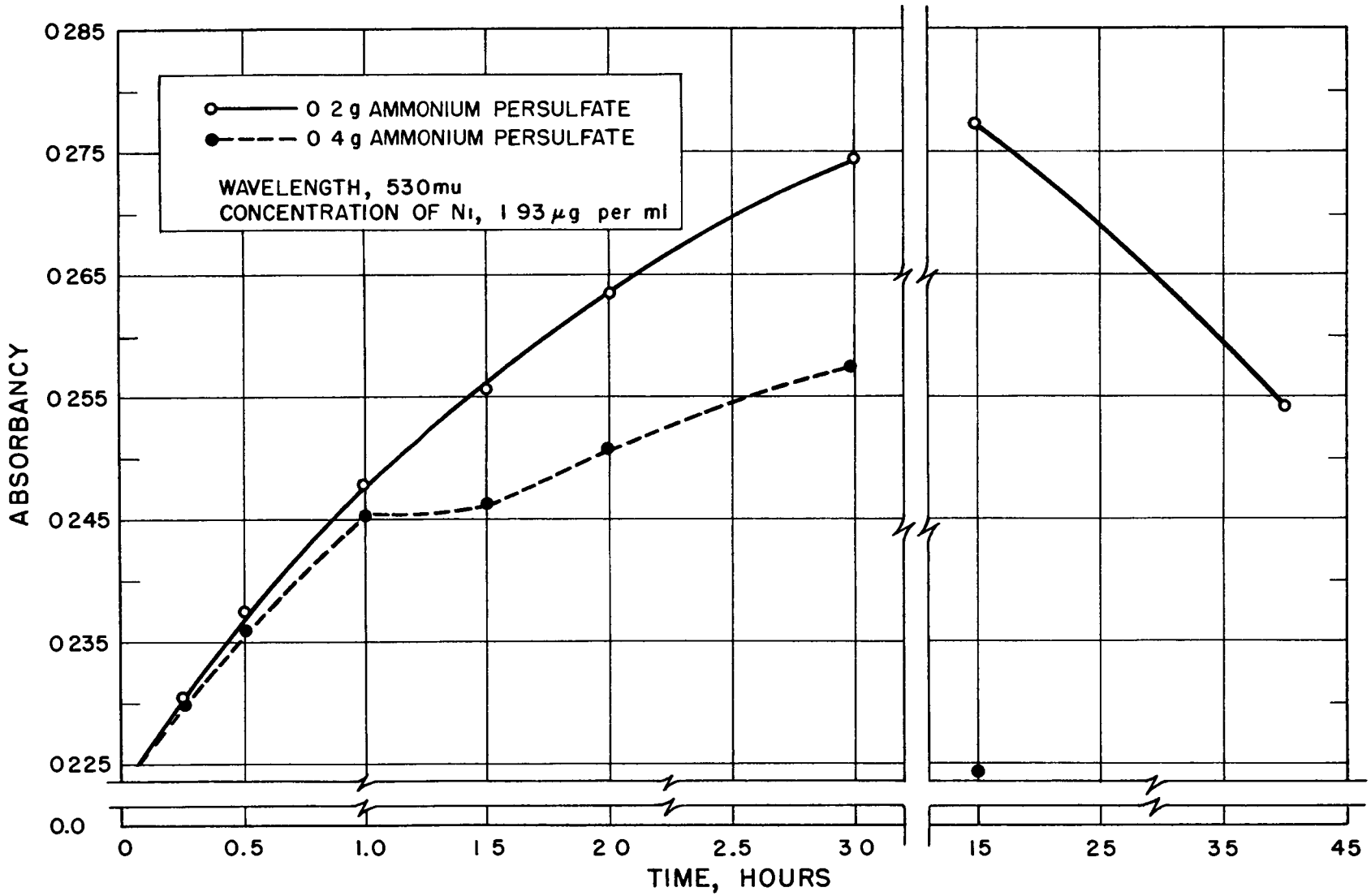

Fig 1 Stability of Nickel Dimethylglyoxime Complex, Ammonium Persulfate as Oxidant

Table III

Effect of Quantity of Potassium Persulfate on Absorbancy of the Nickel-Dimethylglyoxime Complex

Range of nickel concentration: 0.6 to 4 μg per ml
Uranium: none

		Wavelength			
		530 mμ		446 mμ	
$K_2S_2O_8$ Grams	No. Detns.	F Factor	Std.Dev. Per Cent	F Factor	Std.Dev. Per Cent
0.1(1)	6	7.83	4.2	4.21	3.6
0.2	10	8.00	3.2	4.03	1.5
0.3	10	8.09	3.0	4.02	1.5
0.4	10	8.17	2.1	4.01	2.0
0.7	10	8.20	1.3	4.02	2.0

(1) Precipitation occurred in the case of nickel concentration above 3 μg per ml

can be varied between 0.3 and 0.7 g per 50 ml of final volume with good retention of sensitivity and precision, particularly at 446 mμ, where the maximum absorbancy of the nickel-dimethylglyoxime complex occurs (as shown in Figure 2). Since the solution of potassium persulfate is relatively stable, a saturated solution, approximately 5 per cent, was used throughout the investigation.

Stability of the Nickel-Dimethylglyoxime Complex

Several experiments were made to determine the stability of the colored complex, so that the optimum time for the absorbancy measurements could be defined. The data presented in Table IV and Figure 3 demonstrate that the complex is stable from 15 to 120 minutes. Generally, throughout the course of this investigation, absorbancy measurements were made one-half hour after the addition of the reagents, although it would be permissible to allow as long as one and a half hours to elapse before the measurements in a given series are completed. The stability of the color, as shown in Table IV, is good when the solution has a pH in the range 9.2 through 10.5, although Sandell[18] reports that the stability is best in the more basic solutions.

Wavelength

Various authors differ in their preferences as to the most suitable wavelength to be used for the absorbancy measurement (see Table I). A wavelength at which absorbancy measurements are frequently made is 530 mμ. The absorption of uranyl ion is negligible at this wavelength, and this element therefore does not interfere. Sandell[18] mentions the possible use of three wavelengths: around 540 mμ where a minimum occurs in the Ni-dimethylglyoxime absorption spectrum; 560 mμ, where the absorbancy

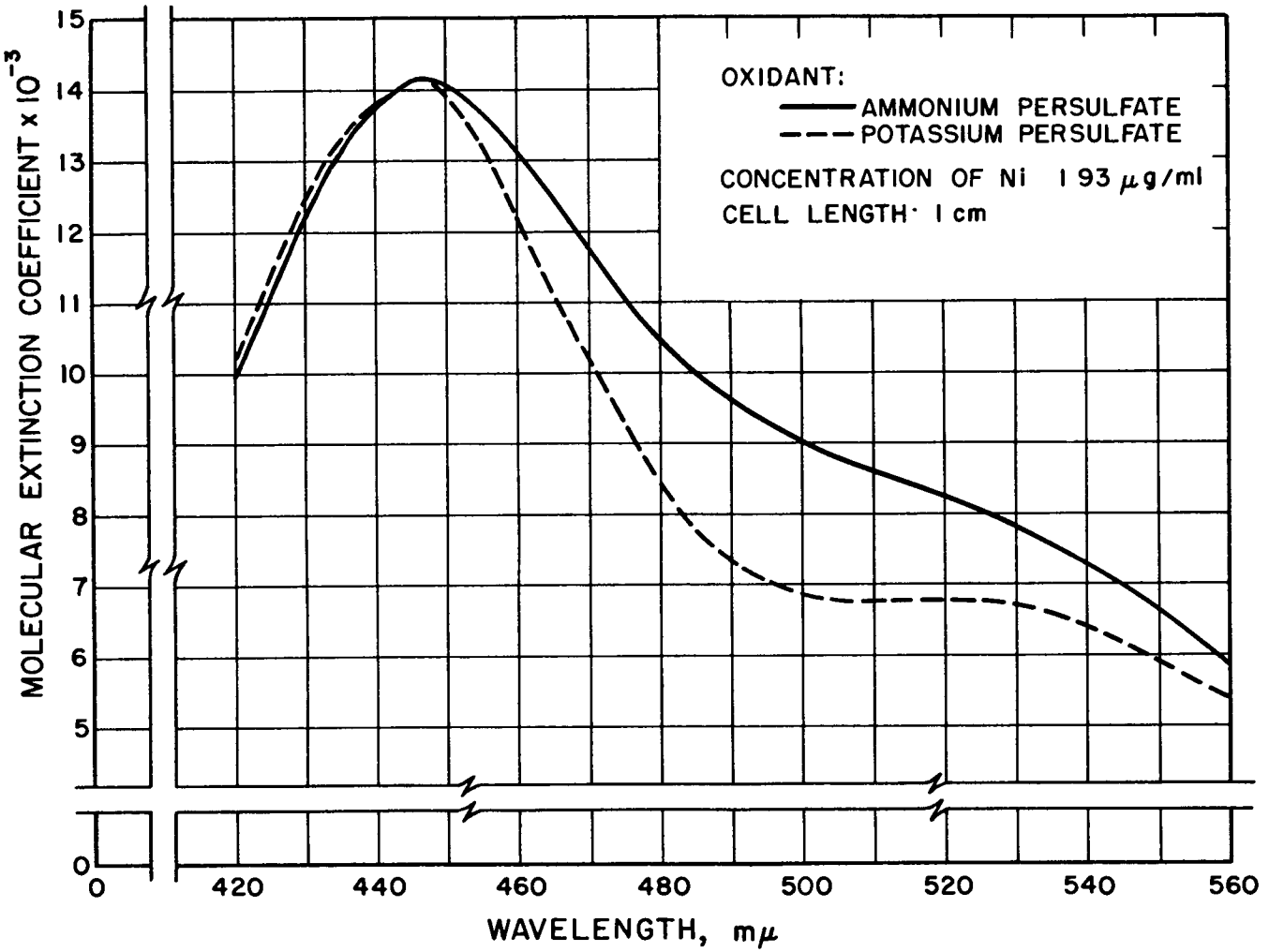

Fig 2 Absorption Spectra of Nickel Dimethylglyoxime Complex

Table IV

Stability of the Nickel-Dimethylglyoxime Complex

Oxidant: Potassium persulfate
Wavelength: 446 mμ

Nickel μg per ml	pH	Absorbancy After: 15 min.	30 min.	60 min.	90 min.	120 min.	180 min.
0.58	9.4	0.131	0.127	0.124	0.125	0.122	---
0.96	9.4	0.226	0.224	0.220	0.220	0.216	---
1.34	9.4	0.316	0.315	0.313	0.309	0.306	---
1.93	10.3	---	0.478	---	0.472	---	0.460
3.86	10.3	---	0.985	---	0.982	---	0.953

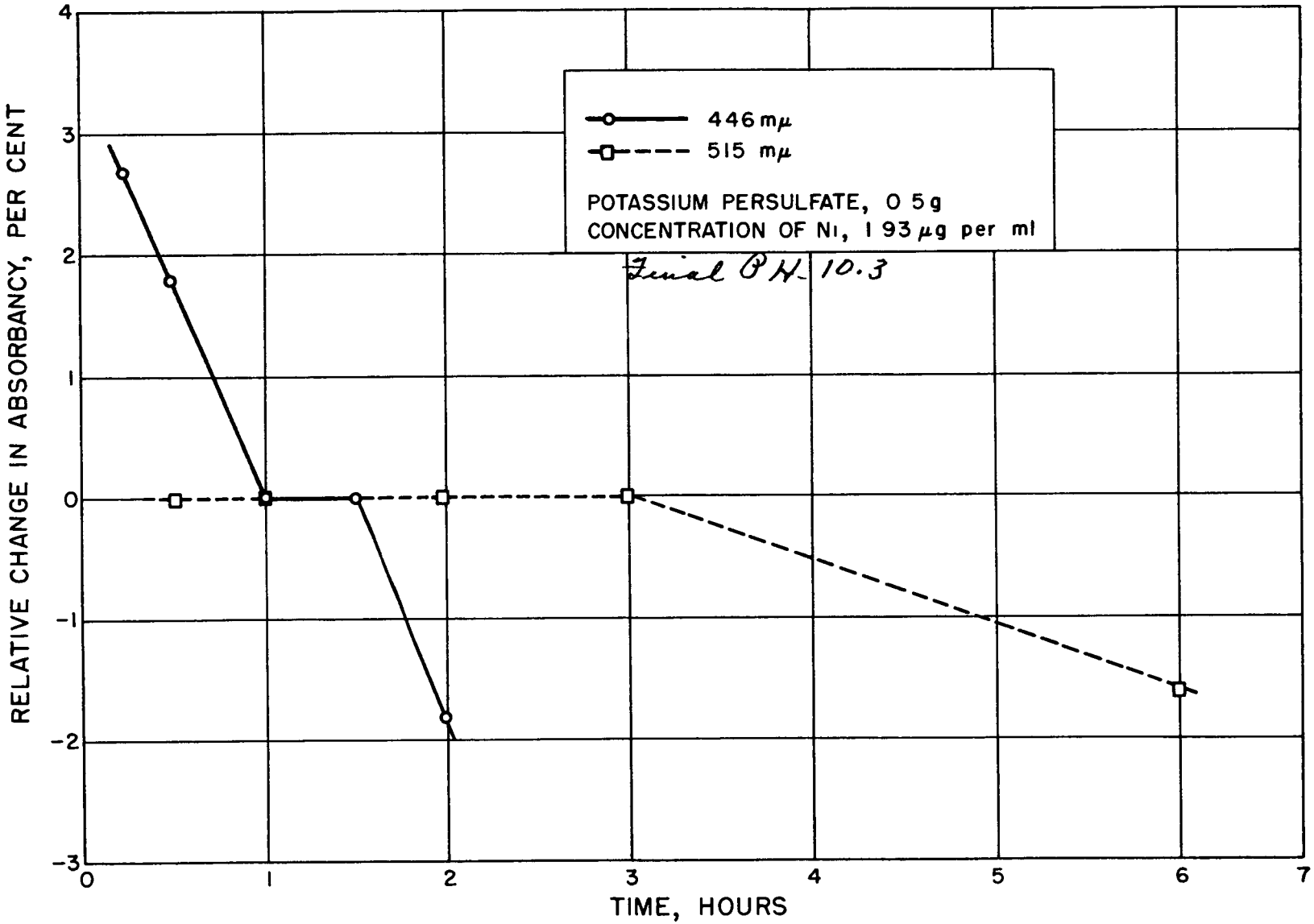

Fig 3 Stability of Nickel Dimethylglyoxime Complex, Potassium Persulfate as Oxidant

of the nickel complex changes less rapidly with time; or 450 mμ, at which the greatest sensitivity is achieved.

Measurements in this laboratory have indicated that there is a difference in the shape of the absorption curve of the nickel-dimethylglyoxime complex (see Figure 2) depending upon whether ammonium or potassium persulfate is used as the oxidant. Makepeace[9] obtained a shift in absorbancy maximum to 470 mμ upon the addition of sodium hydroxide to the ammoniacal solutions. White[19] confirms this shift. In Figure 2 it will be observed that, when $K_2S_2O_8$ is substituted for $(NH_4)_2S_2O_8$ as the oxidant, there is no shift in the absorption maximum at 446 mμ, but there is a definite plateau in the curve in the region of 520 to 510 mμ. If absorbancy measurements are made at 515 mμ, in the center of this plateau, [illegible] greater precision can be attained.

Optimum pH for Oxidation

In a study of the effect of pH, it was found that the optimum pH for oxidation of nickel varies with the wavelength being used for the absorbancy measurements and also with the concentration of nickel in the final solution.

Nickel - 1.5 to 8 Micrograms per ml. The variability of sensitivity and precision with pH at the two wavelengths for nickel concentrations ranging from 1.5 - 8.0 micrograms is shown in Figures 4 and 5 and in Table V. At 515 mμ, the optimum pH is 9.25 $\pm$ 0.05, but at 446 mμ, the best precision and sensitivity are obtained in a pH range of 10.0 to 10.5.

Nickel - 0.2 to 1.5 Micrograms per ml. As is shown in Table V and

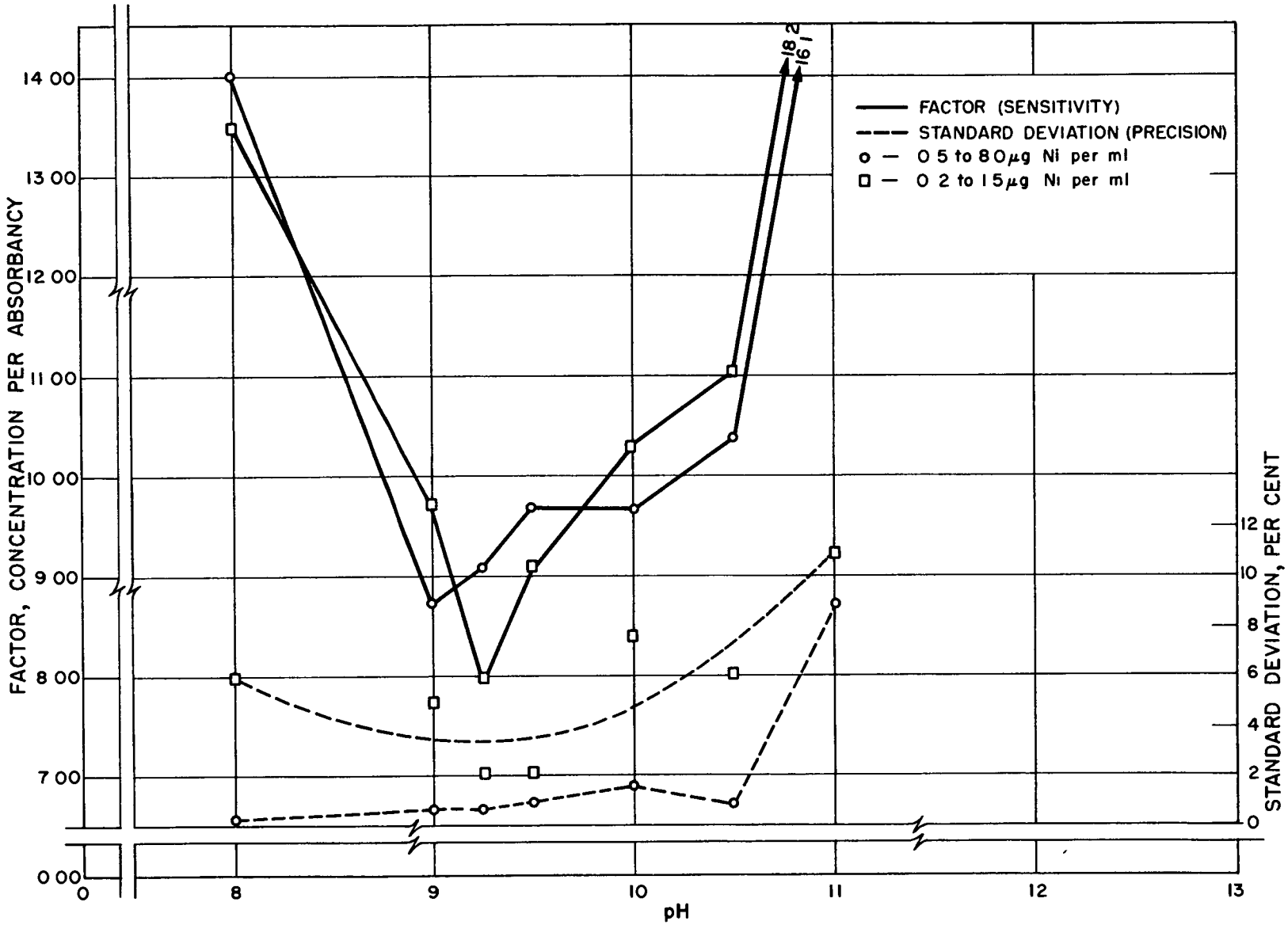

Fig 4 Effect of pH on Precision and Sensitivity in the Determination of Nickel-Measurement at 515 mμ

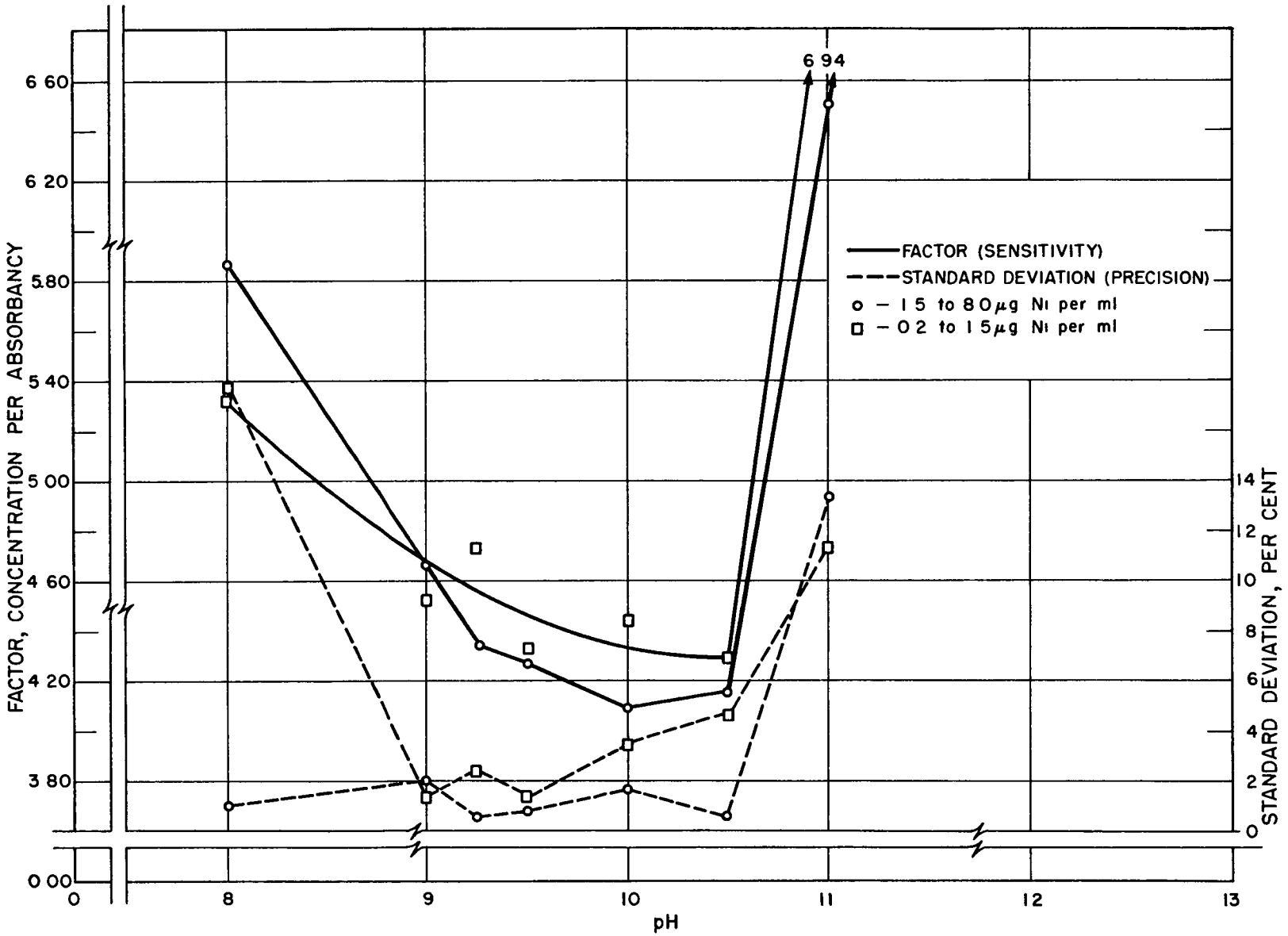

Fig 5 Effect of pH on Precision and Sensitivity in the Determination of Nickel-Measurement at 446 mμ

Table V

Effect of pH on Sensitivity and Precision in the Colorimetric Determination of Nickel

pH	Ni μg/ml	No. Detns.	Wavelength 446 mμ F Factor	446 mμ Std.Dev. Per Cent	515 mμ F Factor	515 mμ Std.Dev. Per Cent
8.0	0.2 to 1.5	4	5.34	17.8	13.5	6.1
9.0	0.2 to 1.5	4	4.53	1.5	9.75	5.1
9.25	0.2 to 1.5	8	4.74	2.5	8.01	2.2
9.5	0.2 to 1.5	4	4.32	1.4	9.11	2.3
10.0	0.2 to 1.5	4	4.46	3.6	10.3	7.7
10.5	0.2 to 1.5	4	4.30	4.6	11.1	6.2
11.0	0.2 to 1.5	4	6.94	11.5	18.2	11.1
8.0	1.5 to 8	6	5.86(1)	1.0	14.0(1)	0.4
9.0	1.5 to 8	6	4.67(1)	2.0	8.75(1)	0.8
9.25	1.5 to 8	6	4.34	0.7	9.12	0.8
9.5	1.5 to 8	6	4.26	0.9	9.71	1.0
10.0	1.5 to 8	6	4.10	1.7	9.60	1.8
10.5	1.5 to 8	6	4.14	0.7	10.4	1.1
11.0	1.5 to 8	6	6.50	13.4	16.1	9.1

(1) Precipitation occurred in case of nickel concentration above 3 μ g per ml

Figures 4 and 5, for the low concentrations of nickel (0.2 to 1.5 μg Ni per ml) a pH of 9.25 $\pm$ 0.05 should be used for the absorbancy measurements at 515 mμ in order to attain maximum sensitivity and precision. A pH of 9.5 $\pm$ 0.1 yields the best results where the measurements are made at 446 mμ.

In order to simplify the analytical procedure, a compromise pH of 10.0 $\pm$ 0.1 is recommended for the entire range of concentration, with absorbancy measurements being made at either wavelength. This choice results in only a moderate loss of sensitivity when the absorbancy is measured at 515 mμ. The precision at this pH at either wavelength for the whole range is not significantly reduced.

Optimum Temperature for Oxidation

Sandell[18] points out that the formation of the nickel-dimethylglyoxime complex should be carried out at a temperature of 30° C or lower. The results obtained in this study support this conclusion.

Tests were made in which the solutions, during the oxidation step, were kept at constant temperatures of 25 $\pm$ 0.5, 30 $\pm$ 0.5, and 35 $\pm$ 0.5° C. A test was also made at approximately 5° C with the aid of an ice-water bath. As can be observed (Table VI), good sensitivity and precision were obtained at temperatures of 25 and 30° C. At 35° C, however, although in one test the precision was good, in two other tests it was poor. The variation in the values of the colorimetric factor was also excessive. The color development at 5° C, as maintained with an ice-water bath, was very slow, and even after four hours the absorbancy of the complex was below that of the complex formed at normal room temperature.

Table VI

Effect of Temperature on Sensitivity and Precision in the Colorimetric Determination of Nickel

Number of determinations: 8 for each factor
Uranium concentration: 2 mg per ml
Oxidant: Potassium persulfate
pH: 9.5
Wavelength: 446 mμ

Temperature, °C	F Factor	Standard Deviation Per Cent
Ice Water Bath	4.74	4.7
25	4.19	0.7
	4.21	1.4
	4.15	1.2
	4.14	1.5
30	4.18	1.0
	4.16	1.2
35	4.23	1.2
	4.15	3.4
	4.45	4.0

Composition of the Reference Solution

An investigation, the results of which are shown in Table VII and in Figure 6, revealed that if dimethylglyoxime is added to the reference solution, this solution is unstable and must be changed in the cuvette just prior to each absorbancy measurement. However, on the omission of the dimethylglyoxime reagent, the reference solution is stable in the cuvette and the same solution can be used as a reference standard throughout a series of tests. One of the explanations which can be postulated is based on Babko's[1] observation that the complex is a combination of nickel ions with some unstable oxidation product of the dimethylglyoxime. In the absence of nickel, the dimethylglyoxime oxidation product decomposes, causing a change in the absorbancy of the reference solution with time.

Quantity of Dimethylglyoxime

The effect of variation in the quantity of dimethylglyoxime was studied. The results are listed in Table VIII. From 2 to 20 mg of the reagent, in the form of an alcoholic solution (generally one ml), was used, and the absorbancy values of the final solutions were determined at both 446 and 515 mμ. It is clear that two mg of the reagent is insufficient. Ten mg of dimethylglyoxime appears to be a good choice, although there was no great variation in sensitivity or precision at either wavelength when quantities of from ten to twenty mg were used.

Order of Addition of Reagents

The procedure, as commonly followed, is to make the solution ammoniacal and then add the oxidizing reagent, complexing agents, and finally the dimethylglyoxime, with the absorbancy measurements being

Table VII

The Colorimetric Stability of the Reference Solution in the Determination of Nickel

Total time for series of absorbancy measurements: 35 minutes

Nickel μg per ml	Absorbancy at 446 mμ Reference Solutions 1	2	3
0.77	0.151	0.153	0.154
1.15	0.219	0.254	0.243
1.54	0.262	0.326	0.318
1.93	0.382	0.452	0.457
2.69	0.523	0.596	---
3.86	0.813	0.898	0.890
5.87	1.257	1.342	1.370

1. Aqueous solution, containing all reagents, not changed in cuvette during the series of measurements.

2. Aqueous solution, containing all reagents, changed in cuvette just prior to each measurement.

3. Aqueous solution, containing all reagents except dimethylglyoxime, not changed in cuvette during the series of measurements.

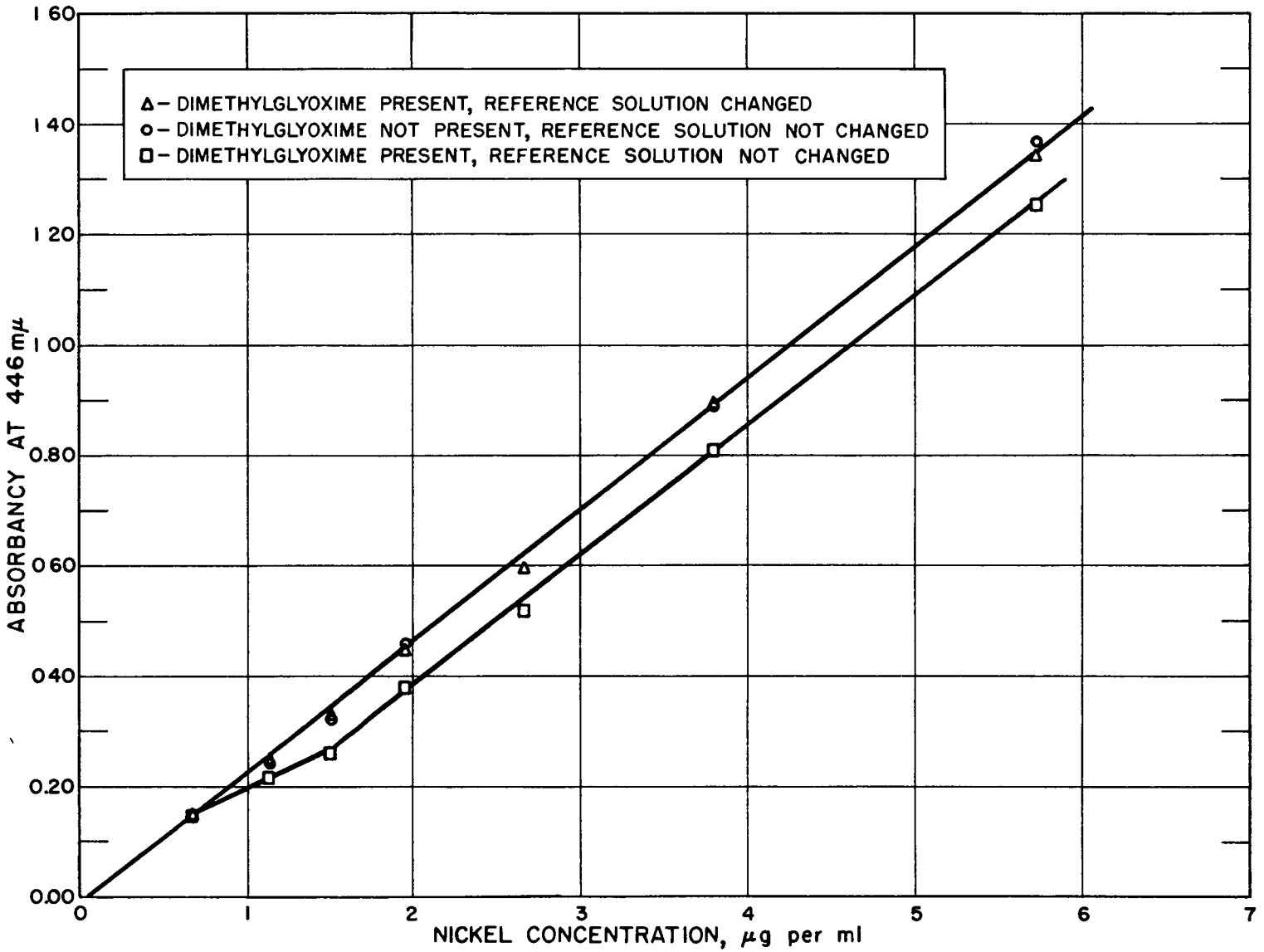

Fig 6 The Effect of Dimethylglyoxime Reagent in the Reference Solution in the Colorimetric Determination of Nickel

Table VIII

Effect of Variation in the Quantity of Dimethylglyoxime in the Colorimetric Determination of Nickel

Conditions:

Uranium concentration: 2 mg per ml
Nickel concentration: 2 to 6 μg per ml
pH: 9.5 $\pm$ 0.05
Final volume: 50 ml

Number of determinations in all cases was 6

Dimethylglyoxime Concentration Per Cent	446 mμ F Factor	446 mμ Std.Dev. Per Cent	515 mμ F Factor	515 mμ Std.Dev. Per Cent
0.004	5.16	8.1	12.9	8.5
0.010	4.24	0.7	10.0	1.5
0.020	4.04	1.2	9.33	2.9
0.030	4.22	1.2	8.79	5.1
0.040	4.14	1.7	8.85	4.1

made five to thirty minutes later.

The reverse process of addition of reagents in which the solution is adjusted in the final step of the procedure to a pH of ~~9.0~~ 10.0 with ammonia has been adopted because of greater ease of control of pH. Results shown in Table IX show that the change in order of addition does not lead to any difference in results.

Interference of Foreign Ions

According to Sandell[18] there are relatively few ions that interfere in the dimethylglyoxime method. The effect of ferric, ferrous and uranyl ions was of special interest and was investigated in this study.

Interference of Iron. Of the ions which interfere in the dimethylglyoxime method, Sandell[18] reports that Fe(II) has the greatest effect. A study was carried out in which various quantities of Fe(II) and Fe(III) were added prior to the determination of nickel in standard solutions. The data which are shown in Table X indicate that as much as 1 mg of Fe(III) per ml of final solution does not interfere. Concentrations of Fe(II) up to 20 μg per ml of final solution do not interfere, while as much as 1 mg per ml of final solution increases the absorbancy at 446 mμ by approximately 2 per cent.

Interference of Uranium. If, to obtain the maximum sensitivity, the 446 mμ wavelength is to be used, the limitations imposed by the considerable absorption of uranium at 446 mμ reported by Menis and Rowan[12] must be recognized. The reference solution must have the same concentration of uranyl ions as the sample. The results shown in Table XI emphasize the importance of matching the uranium concentration of the

Table IX

The Effect of Order of Addition of Reagents in the Colorimetric Determination of Nickel

Number of determinations in all cases was 6

Nickel µg per ml	pH	Wavelength mµ	Ammoniacal Oxidation F Factor	Ammoniacal Oxidation Std.Dev. Per Cent	Acid Oxidation F Factor	Acid Oxidation Std.Dev. Per Cent
2 - 6	10.3	446	4.14	1.4	4.15	1.2
2 - 6	10.3	515	9.65	1.8	9.64	1.7
0.2 - 1(1)	9.2	515	1.69	1.2	1.68	1.2

(1) Cells of 5-cm path length were used

Table X

Effect of the Ferrous and Ferric Ions on the Colorimetric Determination of Nickel

Uranium - 2 mg per ml

Final volume - 50 ml

	Nickel µg per ml	Iron µg per ml	No. Detns.	Wavelength 446 mµ F Factor	Wavelength 446 mµ Std.Dev. Per Cent	Wavelength 515 mµ F Factor	Wavelength 515 mµ Std.Dev. Per Cent
Fe(II)	1.93	0.5 to 2.0	6	4.19	0.7	8.60	0.8
	1.93	1000	2	3.80	---	8.88	---
	5.79	0.5 to 2.0	6	4.11	1.2	9.38	1.0
	5.79	1000	2	3.97	---	9.35	---
Fe(III)	1.93	0.5 to 20.0	8	4.17	1.0	8.56	1.9
	1.93	1000	2	4.03	---	9.24	---
	5.79	0.5 to 20.0	8	4.17	1.0	9.55	1.5
	5.79	1000	2	4.03	---	9.73	---

Table XI

The Effect of Variation of Uranium Concentration in Sample and Reference Solutions

Nickel concentration: 1.93 μg per ml

Difference in Uranium Between Reference and Sample Solutions[1] mg per ml	Difference Per Cent	Absorbancy At 446 mμ	Error in, Per Cent[2]	At 515 mμ	Error in, Per Cent[2]
-0.20	-10.0	0.530	+14.5	0.216	-2.3
-0.15	- 7.5	0.515	+11.2	0.218	-1.4
-0.10	- 5.0	0.494	+ 6.7	0.218	-1.4
-0.05	- 2.5	0.482	+ 4.1	0.219	-0.9
0.000	0	0.463	0	0.221	0
+0.05	+ 2.5	0.451	- 2.6	0.222	+0.5
+0.10	+ 5.0	0.429	- 7.3	0.222	+0.5
+0.15	+ 7.5	0.422	- 8.9	0.223	+0.9
+0.20	+10.0	0.406	-12.3	0.227	+2.7

(1) Uranium concentration: 2 mg per ml

(2) The relative difference between the observed value of absorbancy and the value when equivalent amounts of uranium are present in both solutions:

$\frac{M' - M}{M} \times 100$, where M = absorbancy with equivalent amounts of uranium,
M' = absorbancy observed for unmatched solutions.
This is the same percentagewise, as the error in the determination of nickel.

reference solution with that of the sample. These data indicate, for example, that a change of five per cent in the uranium concentration of the reference solution will introduce an error of seven per cent in the final absorbancy measurement.

There is also a limitation as to the maximum tolerable concentration of uranium in the solution. As the uranium content of the reference solution increases, the slit width of the Beckman DU spectrophotometer must be increased in order to balance electronic circuit of the instrument, until finally the transmitted spectral band becomes wider than the nickel-dimethylglyoxime absorption band. This will then cause a decrease in the absorbancy values with subsequent loss of sensitivity and precision, and, finally, at sufficiently high uranium concentrations, lead to serious deviations in Beer's Absorption Law.

In the method used to compensate for interference of the uranyl ion, with the reference solution in position, the spectrophotometer was brought into balance by opening the slit. It will be observed (Table XII) that, for one particular Beckman DU spectrophotometer, an increase in slit width of from 0.027 mm to 0.156 mm, corresponding to uranium concentrations of 0 and 4 mg per ml, respectively, produces little change in the colorimetric factor. The slit width range of 0.20 mm to 0.425 mm, corresponding to 5 to 7 mg of uranium per ml, yields a second series of factors which are slightly higher, indicating a slight decrease in sensitivity under these conditions. Beyond a slit width of 0.425 mm, Beer's law is no longer obeyed, and all determinations in the presence of higher uranium concentrations, requiring a slit larger than 0.425 mm, should be made at 515 mμ.

Table XII

The Effect of Uranium Concentration on Precision and Sensitivity

Uranium(1) mg per ml	Slit Width(2) mm	F Factor	Std.Dev., Per Cent
0	0.027	4.12	0.7
1	0.041	4.18	0.7
2	0.060	4.20	0.5
3	0.082	4.21	0.2
4	0.156	4.25	1.2
5	0.209	4.50	1.3
6	0.310	4.47	1.3
7	0.425	4.51	1.8
8	0.575	4.81	6.0
9	0.755	5.20	4.8

(1) U(VI) present as uranyl sulfate

(2) Beckman Spectrophotometer, Model DU

Although a Beckman Model DU spectrophotometer was used for almost all of the absorbancy measurements made in connection with this study, a brief study was made with the Beckman Model B spectrophotometer for the purpose of comparing the precision and sensitivity obtainable with the two instruments. The absorbancy measurements were made at 445 mμ and 515 mμ on four series of samples, each series containing a different quantity of uranium. In order to facilitate the setting of the wavelength scale of the Beckman Model B spectrophotometer, 445 mμ was used instead of 446 mμ, which is the wavelength of maximum absorption. As is shown in Table XIII, about equal precision and sensitivity are obtained for concentrations of uranium up to 2 mg per ml with either instrument at 445 mμ. For uranium concentrations above 2 mg per ml, however, both the sensitivity and precision rapidly decreased when the Model B is used at 445 mμ. Equal precision and about equal sensitivity were obtained for both instruments at 515 mμ. Different spectrophotometers may require different slit widths to achieve a state of balance for a given uranium concentration, and a table of factors similar to Table XII must be prepared for each instrument. Furthermore, since the sensitivity of the spectrophotometer may change, the slit width corresponding to a given uranium concentration may also change and should be checked from time to time. For the particular instrument used in the study, originally a solution containing 5 mg of uranium per ml required a slit width of 0.175 mm for balance, but when Table XII was prepared, the slit width had increased to 0.205 mm.

The data listed in Table XII and plotted in Figure 7 illustrate the variations in sensitivity, precision and slit width as a function

Table XIII

Comparison of Beckman Spectrophotometers
Models B and DU for the Determination of Nickel

Range of Nickel concentration: 2 to 6 μg per ml

pH: 9.5 ± 0.05

Wavelength mμ	Uranium mg per ml	No. Detns.	Model B F Factor	Model B Std.Dev. Per Cent	Model DU F Factor	Model DU Std.Dev. Per Cent
445	0	6	4.18	1.4	4.12	1.7
	2	12	4.19	1.7	4.06	1.5
	4	6	4.42	3.2	4.08	1.0
	6	12	5.20	3.1	4.29	0.7
515	0	6	9.68	2.0	9.22	4.3
	2	12	9.37	2.8	9.25	2.9
	4	6	9.40	1.8	9.21	2.7
	6	12	9.36	3.2	9.10	3.5

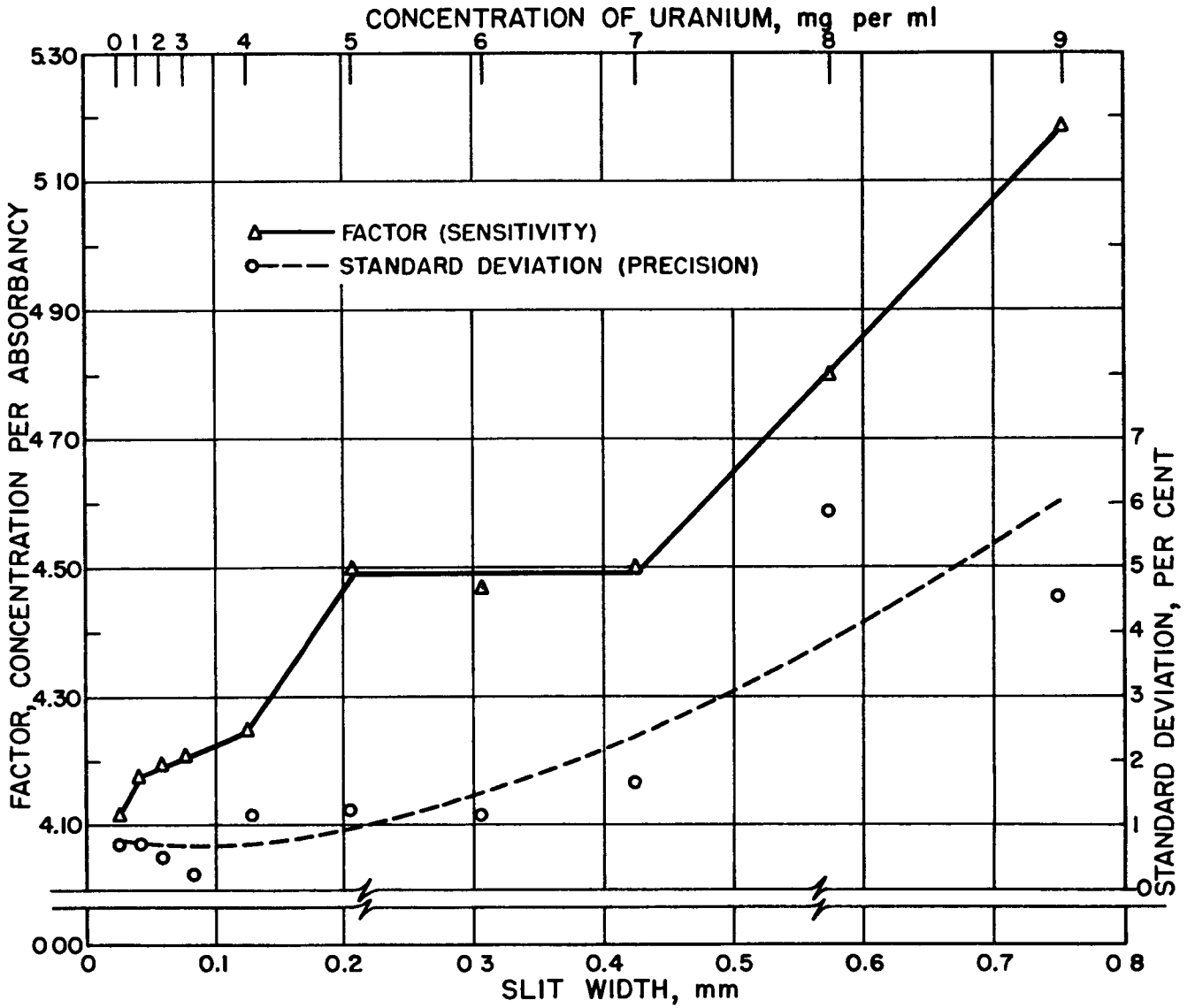

Fig. 7 Effect of Slit Width of the Beckman Spectrophotometer, a Function of Uranium Concentration, in the Determination of Nickel

of uranium concentration.

At 515 mμ, the absorbancy of the uranyl ion is negligible. At this wavelength the composition of the reference solution, which is critical when the 446 mμ wavelength is used, is of minor importance. At 515 mμ, also, much larger concentrations of uranium can be tolerated. However, any advantage gained by the use of the 515 mμ wavelength must be accompanied by a sacrifice of sensitivity and a slight decrease in precision, as is shown in Table XIV. In taking advantage of the greater sensitivity and precision at the lower wavelength, the effect of uranyl ions, up to a certain limit, can be easily corrected for by taking equal aliquots of the original sample for use in the nickel determination and in the reference solution.

Ammonium Citrate Concentration

In the determination of nickel in the presence of uranium, Rodden[15] recommends the use of 10 ml of a 20 per cent solution of ammonium citrate per final volume of 50 ml to complex the uranium and prevent it from precipitating in an ammonical solution. In the present experiments, however, for concentrations of uranium of 2 mg per ml and higher, a collodial precipitate of uranium was produced when the above recommendations were followed. The data in Table XV show that an increase in precision was obtained when the ammonium citrate solution was increased to 10 ml of a 30 per cent solution. However, too much ammonium citrate also reduced the precision and the sensitivity. Later work has shown that good precision is obtained for solutions having concentrations of uranium up to 7 mg per ml. The uranium concentration of the final solution must be

Table XIV

Sensitivity and Precision of the Colorimetric Determination of Nickel Using Potassium Persulfate as Oxidant, Controlled pH, and Temperature at 25° C

Uranium concentration: 2 mg per ml

		446 mμ			515 mμ		
pH	Nickel μg per ml	No. Detns.	F Factor	Std.Dev. Per Cent	No. Detns.	F Factor	Std.Dev. Per Cent
10.3	1.5 to 8	22	4.17	0.9	8	9.64	1.6
9.25	0.2 to 1.5(1)	14	1.03	3.9	18	1.65	2.4
9.5	0.2 to 1.5(1)	12	0.865	2.0	12	1.82	2.2
9.5	1.5 to 8	6	4.26	1.2	6	9.88	2.0

(1) Cells of 5-centimeter path length used

Table XV

The Effect of Ammonium Citrate in the Determination of Nickel

Uranium concentration: 4 mg/ml
pH: 10.3 ± 0.1
Wavelength: 446 mμ

Nickel μg per ml	Ammonium Citrate w/v Per Cent	Absorbancy
1.93	4	0.468
	4	0.430
	6	0.474
	6	0.469
	9	0.420
	9	0.408
2.89	4	0.698
	4	0.658
	6	0.693
	6	0.686
	9	0.668
	9	0.652

kept below this figure, or, alternately, the citrate content of the solution must be increased.

Optimum Conditions for the Method

The optimum conditions for the determination of nickel depend upon the range of concentration of nickel, the principal variation being in the pH of the final solution. These conditions have been discussed in a previous section of the report. A set of conditions which is suitable for the analysis of solutions in either concentration range, however, has been selected, and these are summarized in Table XVI.

Table XVI

Summary of Conditions for the Modified Method for the Determination of Nickel

(1) Wavelength: 446 mμ or 515 mμ.

(2) Temperature: 25 - 30° C.

(3) pH: ~~9.5~~ 10.0 ± 0.05, adjusted with NH_4OH.

(4) Oxidant: (0.5 g) 10 ml of saturated solution of potassium persulfate.

(5) Complexing agent: 10 ml of 30 per cent solution of ammonium citrate.

(6) Colorimetric reagent: 1 ml of 1 per cent dimethylglyoxime (w/v) in ethanol.

(7) Final volume: 50 ml.

(8) Oxidation time: 1/2 hour.

(9) Stability of complex: (a) 446 mμ 1.5 hours.
(b) 515 mμ 3 hours.

(10) Reference solution: (a) Match uranium concentration of unknown within one per cent.
(b) Omit dimethylglyoxime reagent.

(11) Uranium concentration. Establish analytical factor with known concentrations of uranium when using 446 mμ wavelength.

REFERENCES

1. Babko, A. K., Reaction of the Nickel Ion With Dimethylglyoxime in the Presence of Oxidizers, Zhur. Anal. Khim., 3, 284-9 (1948).

2. Beaumont, R. H., Jr., and G. J. Petretic, The Determination of Nickel in Zirconium With Dimethylglyoxime, NYO-2011, Aug. 15, 1950.

3. Bergstresser, K. S., Determination of Cobalt, Nickel and Copper in the Presence of Plutonium, LA-1063, Feb. 13, 1950.

4. Cooper, M. D., Spectrophotometric Determination of Nickel in Steel, Anal. Chem., 23, 875-80 (1951).

5. Dobratz, I. W., Determination of Nickel, M-2979, April 30, 1943.

6. Furman, N. H., and Bruce McDuffie, Studies of the Colorimetric Process for the Estimation of Nickel With Dimethylglyoxime, M-4234, Dec., 1947.

7. Haight, G. P., Jr., Semi-Monthly Information Report for Period of May 16 to May 31, 1944, A-1033, May 31, 1944.

8. Lattimer, W. M., and J. H. Hillebrand, Reference Book of Inorganic Chemistry, p. 255, MacMillan Co., N. Y. (1940).

9. Makepeace, G. R., and C. H. Craft, Colorimetric Determination of Nickel in Steel, Ind. Eng. Chem., Anal. Ed., 16, 375-7 (1944).

10. Martens, R. I., Colorimetric Determination of Nickel in Uranium Metal or Oxides, AECD-3125 (no date given)(Decl. March 26, 1951).

11. Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 10, p. 477, Longmans, Green and Co., New York (1930).

12. Menis, O., and R. Rowan, Jr., Absorption Spectrum of Uranyl Sulfate Solution, ORNL-1351, July 30, 1952.

13. Murray, W. M., Jr., and S. E. Q. Ashley, Determination of Manganese, Nickel and Phosphorus in Iron and Steel, Ind. Eng. Chem., Anal. Ed., 10, 1-5 (1938).

14. Overston, T. C. J., and C. A. Parker, Spectrophotometric Determination of Cobalt and Nickel in the Microgram Range, Anal. Chim. Acta, 4, 142-52 (1950)(in English).

15. Rodden, C. J., Analytical Chemistry of the Manhattan Project, Div. VIII, Vol. 1, p. 433-436, McGraw-Hill Book Co., New York (1950).

16. Rodden, C. J., and G. J. Petretic, A-1032, May 15, 1944, Sec. 2C.

17. Rollet, A. P., A New Colorimetric Method for Determining Nickel, Comp. rend., 183, 212-3 (1926).

18. Sandell, E. B., Colorimetric Determination of Traces of Metals, p. 470-4, Interscience Publishers, Inc., New York (1950).

19. White, J. C., private communication, Feb. 11, 1952.

20. Willard, H. H., private communication, April, 1952.