

SPECTROPHOTOMETRIC DETERMINATION OF
NICKEL IN STEEL WITH POTASSIUM
DITHIO-OXALATE

by

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ADVANCE BOND



TO MY WIFE

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INTRODUCTION

Nickel is commonly determined by means of methods which are gravimetric or titrimetric in nature. More recently, due to the development and wide distribution of the spectrophotometer, it has been possible to apply colorimetric procedures to quantitative analysis with an accuracy comparable to that of the more common methods. Thus absorption spectroscopy has been applied very successfully to the determination of nickel as well as many other substances.

Jones and Tasker (4, pp.1904-1909) in studying the characteristic reactions of various metal salts with potassium dithio-oxalate, reported that this substance was a very sensitive reagent for nickel. They also suggested that the complex formed was potassium nickelo-dithio-oxalate. Potassium dithio-oxalate was later employed by Fairhall (2, pp.528-533) to determine nickel colorimetrically in biological materials.

Yoe and Wirsing (18, pp.1866-1876) have made a critical study of the potassium nickelo-dithio-oxalate color system with reference to its use in the colorimetric determination of nickel. The sensitivity of the reaction, appli-

cation of Beer's law, effect of various ions, and different experimental conditions were studied.

The purpose of the work described herein was to develop a spectrophotometric method for the determination of nickel in steel. The nickel was first separated from interfering ions by precipitation with dimethylglyoxime, the filtered precipitate was dissolved in nitric acid, the resulting dimethylglyoxime destroyed with nitric acid, and the nickel determined by the measurement of the light transmitted by the potassium nickelo-dithio-oxalate color system at a wave length of 500 m μ . Results were calculated using the specific extinction coefficient of the Beer-Lambert law.

THEORETICAL CONSIDERATIONS

A relationship of much importance in chemical colorimetry is the Beer-Lambert law, which is expressed in its most convenient form as

$$\log_{10}(I_0/I) = kcl$$

where I represents the intensity of light of a given wave length transmitted by a color system; I_0 is the intensity of the light entering the system; k is the specific extinction coefficient, which refers to the absorption due to a single molecule; l is the length in centimeters of the absorbing medium through which the light passes; and c is the concentration of colored solute in grams per liter. The logarithm of the ratio I_0/I is termed extinction. This same ratio is also known as absorbancy and as optical density to many.

To measure the absorption of light it is necessary to allow for losses by reflection and scattering at the boundaries of the cell containing the medium and also for the small losses caused by scattering within the liquid itself. Such a correction is made by comparing the intensity of the ray that has passed through the colored solution with the intensity of the ray which has passed through the colorless solution of similar refractive index contained in an

identical cell. The actual values of the intensities are not required in absorption spectroscopy; only the ratio is significant. The ratio $I/I_0 \times 100$ is termed the per cent transmittancy of the sample.

There are two general methods used in determining the concentration of single colored constituents from transmittancy data.

Working with a series of solutions of known concentrations, one may construct a reference curve coordinating concentration and transmittancy at a given wave length. It is possible to convert the transmittancy of an unknown solution to concentration by use of this curve. This procedure may be used in all cases, but is generally used for those systems which fail to conform to the Beer-Lambert law. This procedure has been applied to the determination of nickel in steel by ammonia (6, pp.4-7), manganese in steel by permanganate (7, pp.27-29), and iron in ores by kojic acid (13, pp.642-643).

The technique used for color systems conforming to the Beer-Lambert law is much less cumbersome. It is possible, for any given constituent to use the equation of Beer and Lambert for converting transmission data into concentration, having first obtained a value for the specific extinction coefficient by the use of solutions of known concentrations. The above procedure has been used in

determining iron by thioglycolic acid (11, pp.8-14), salicylic acid (8, pp.162-163), and 2,2'-bipyridyl (12, pp.52-55), and copper by ammonia (9, pp.387-389) and by triethanolamine (10, pp.52-55).

Mellon (14, pp.97-98) summarizes the chemical causes for deviation from the Beer-Lambert law as follows:

1. Change in refractive index with concentration.
2. Displacement of equilibria involving the absorbing entities, such as ions.
3. Reciprocal interaction of the absorbing entities, either (a) among themselves, or (b) with the solvent or foreign substances.

A system that obeys the Beer-Lambert law with one instrument may fail to do so with another instrument due to instrument discrepancies. For this reason, it is necessary to determine the specific extinction coefficient for a given system on the instrument to be used rather than to rely upon a published value for this constant.

The problem of primary interest in quantitative analysis is to determine concentration with a minimum percentage error. The percentage error will vary, depending upon the transmittancy of the solution. The optimum transmittancy range is commonly given as from 20 to 60 per cent transmittancy for photoelectric spectrophotometers (1,p.652)

and (3, pp.124-125). The transmittancy may be brought into this optimum range by:

1. Adjustment of concentration.
2. Use of absorption cells of different thickness.
3. Adjustment of the specific absorption coefficient by operating at a different wave length.
4. Measurement against a solution of known concentration.

EXPERIMENTAL

APPARATUS AND SOLUTIONS

Beckman Model B Spectrophotometer. All transmission measurements were made with a Beckman Model B spectrophotometer. The same corex cells were used throughout; one was used only for the "blank" solution, the other only for the colored solution. In all transmission measurements, the intensity of the incident beam of light was regulated by means of the slit width so that the galvanometer pointer read 100 when the "blank" solution was in position. The cell containing the colored solution was then put into the light beam, and the resulting galvanometer reading represented per cent transmittancy directly.

Hydrochloric Acid. The concentrated hydrochloric acid was the commercial 12M solution. The dilute 6M acid was prepared from the concentrated acid by suitable dilution.

Nitric Acid. A commercial 16M solution.

Ammonium Hydroxide. The concentrated solution was a commercial 15M solution. The 6M ammonium hydroxide solution was prepared by suitable dilution of the 15M solution.

Ammonium Chloride. A 1M aqueous solution containing 54 grams per liter.

Tartaric Acid. An aqueous solution containing 333 grams per liter.

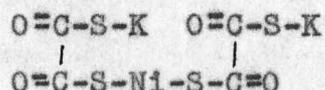
Dimethylglyoxime. A filtered solution of 10 grams in 1 liter of 95 per cent ethanol.

Potassium Dithio-oxalate. A 0.1 per cent aqueous solution containing 20 milligrams in 20 ml. Only enough of this reagent was prepared to last for an hour since a yellow turbidity developed if the solution stood much longer. The solid reagent was stable for only a few months after which time it darkened and produced a turbidity immediately upon being dissolved in water.

Standard Nickel Solution. A standard stock solution of cobalt-free nickelous nitrate hexahydrate was made by dissolving 49.6388 grams of salt in water, adding about 2 milliliters of dilute hydrochloric acid to prevent hydrolysis, and diluting to 2 liters. This solution was standardized by weighing the nickel dimethylglyoxime precipitate obtained from a known volume. Each milliliter contained 5.039 milligrams of nickel. By means of micro-burette, an aliquot of 9.92 ml. of this solution was transferred to a liter volumetric flask and diluted to volume with distilled water. Each milliliter of this solution contained 0.05 mg. of nickel. This was a convenient concentration for the standard solution since 1 ml. diluted to a final volume of 50 ml. gave a concentration of 1 mg. of nickel per liter (1 p.p.m.).

THE COLOR REACTION

Yoe and Wirsing (18, p.1875) gave the complex formed between nickel and potassium dithio-oxalate the following structural formula:



The color of the potassium nickelo-dithio-oxalate is magenta.

To produce the color system, the volume of the standard nickel solution necessary to give the desired concentration of nickel was measured into a 50-ml. volumetric flask from a micro-burette. About 3 ml. of 0.1 per cent potassium dithio-oxalate solution was added followed by approximately 0.04 ml. of dilute hydrochloric acid. The solution was then diluted to volume and thoroughly mixed.

The study of the color system consisted of determining (a) the wave length of maximum absorption, (b) factors influencing the color reaction, and (c) the specific extinction coefficient of the system at the wave length of maximum absorption.

Wave Length of Maximum Absorption. The wave length of maximum absorption for the color system was found by using seven solutions with concentrations of 1, 2, 3, 4, 5, 6, and 7 p.p.m. of nickel. Transmission curves were produced for

each solution over a range of wave lengths varying from 400 to 700 μ at intervals of 10 μ . The colored solution was produced in the same manner as described above. A "blank" solution was prepared by adding to a 50-ml. volumetric flask approximately 3 ml. of potassium dithio-oxalate solution followed by about 0.04 ml. of dilute hydrochloric acid and diluting up to the mark and thoroughly mixing. The spectral transmission curves are shown in Fig. I. Since the maximum absorption was found to occur at 500 μ , all further transmission measurements were made at this wave length. The point of maximum absorption was selected as the point to take further measurements because the percentage transmission is most reproducible when measured at a low point on the transmission curve where the slope is not rapidly changing with wave length.

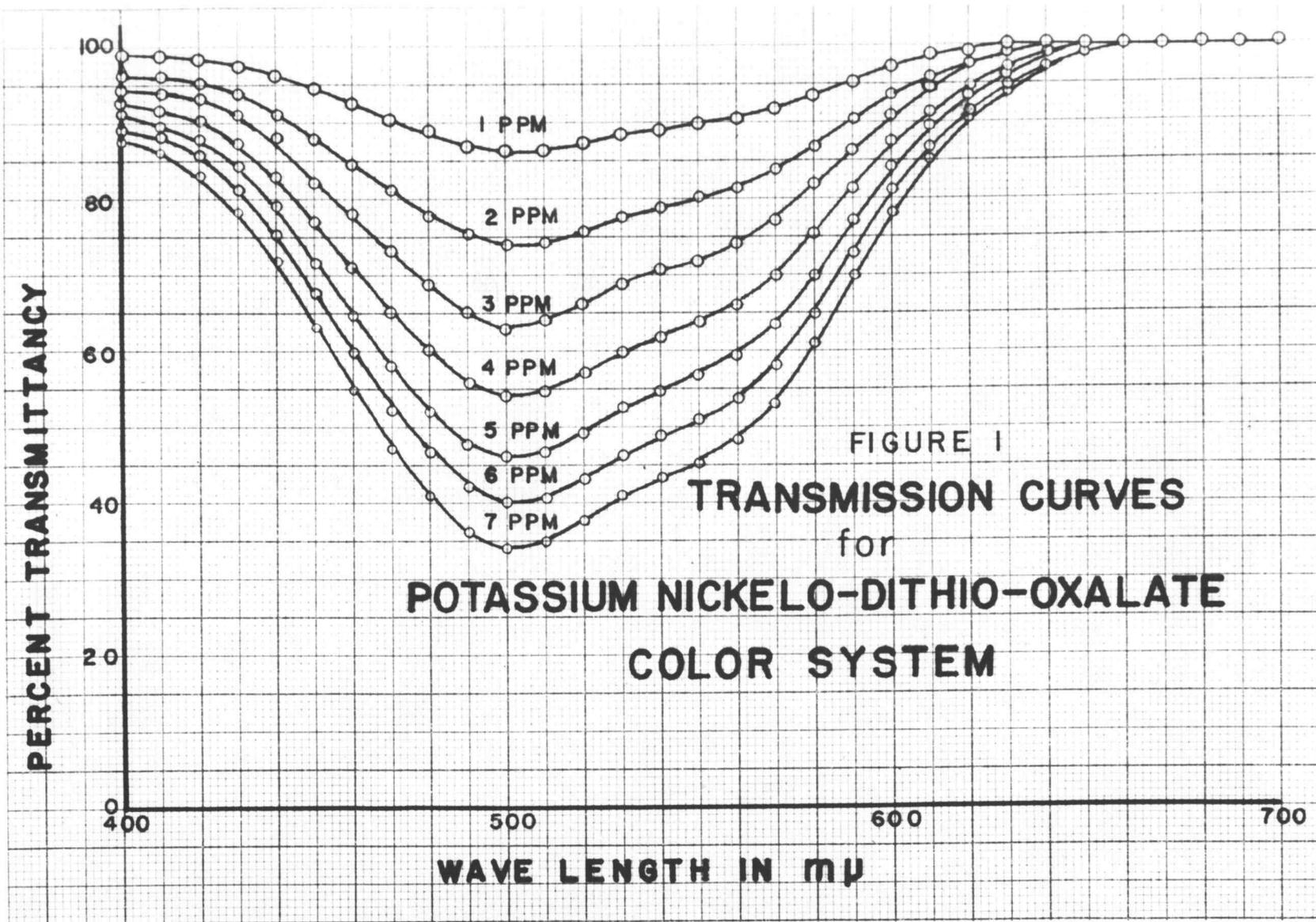
Factors Influencing the Color System. The effect of varying amounts of acidity on the intensity of absorption by the colored complex was studied using solutions containing the same concentration of potassium dithio-oxalate and nickel, and varying the hydrogen-ion concentrations with hydrochloric acid. Readings were taken over a range of solutions from neutral to 1M. Over this entire range there was found to be no immediate variance in transmittancy. It was found, however, that the color of the system faded in a shorter time and turbidity developed in the colored

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solutions faster as the acidity was increased. The above phenomenon was especially noticeable in solutions from 0.2M to 1M in hydrochloric acid.

The effect that excess aqueous potassium dithio-oxalate had on the color system was also studied. The nickel concentration and acidity were held constant while the amount of aqueous potassium dithio-oxalate was varied up to 4 ml. in excess. It was found that over the range covered an excess of this reagent did not alter transmission readings. As the amount of excess aqueous potassium dithio-oxalate increased, the time necessary for the development of turbidity in the color system decreased.

Studies were also made to determine the stability of the color system with respect to time using 0.04 ml. of dilute hydrochloric acid and 3 ml. of potassium dithio-oxalate solution with the right concentration of nickel to produce the color. The criterion set was the ability to duplicate transmittancy measurements after suitable time intervals. The color system was found to be stable for two hours. Instability of solutions containing from 1 to 3 p.p.m. of nickel was due to the development of turbidity in the color system, while instability of solutions containing from 4 to 7 p.p.m. of nickel resulted from a fading of the color.



Specific Extinction Coefficients. To determine if the potassium nickelo-dithio-oxalate color system obeyed the Beer-Lambert law or not, the extinctions of eight standard nickel solutions (representing nickel concentrations from 1 to 8 p.p.m.) were determined at a wave length of 500 m μ . A straight line, shown in Fig. 2, was obtained when the concentrations for the solutions representing nickel concentrations ranging from 1 to 7 p.p.m. were plotted against their respective extinctions. This indicated that the color system conformed to the Beer-Lambert law up to a nickel concentration of 7 p.p.m. The specific extinction coefficient for the system could then be calculated.

The constant can be obtained in the following manner:

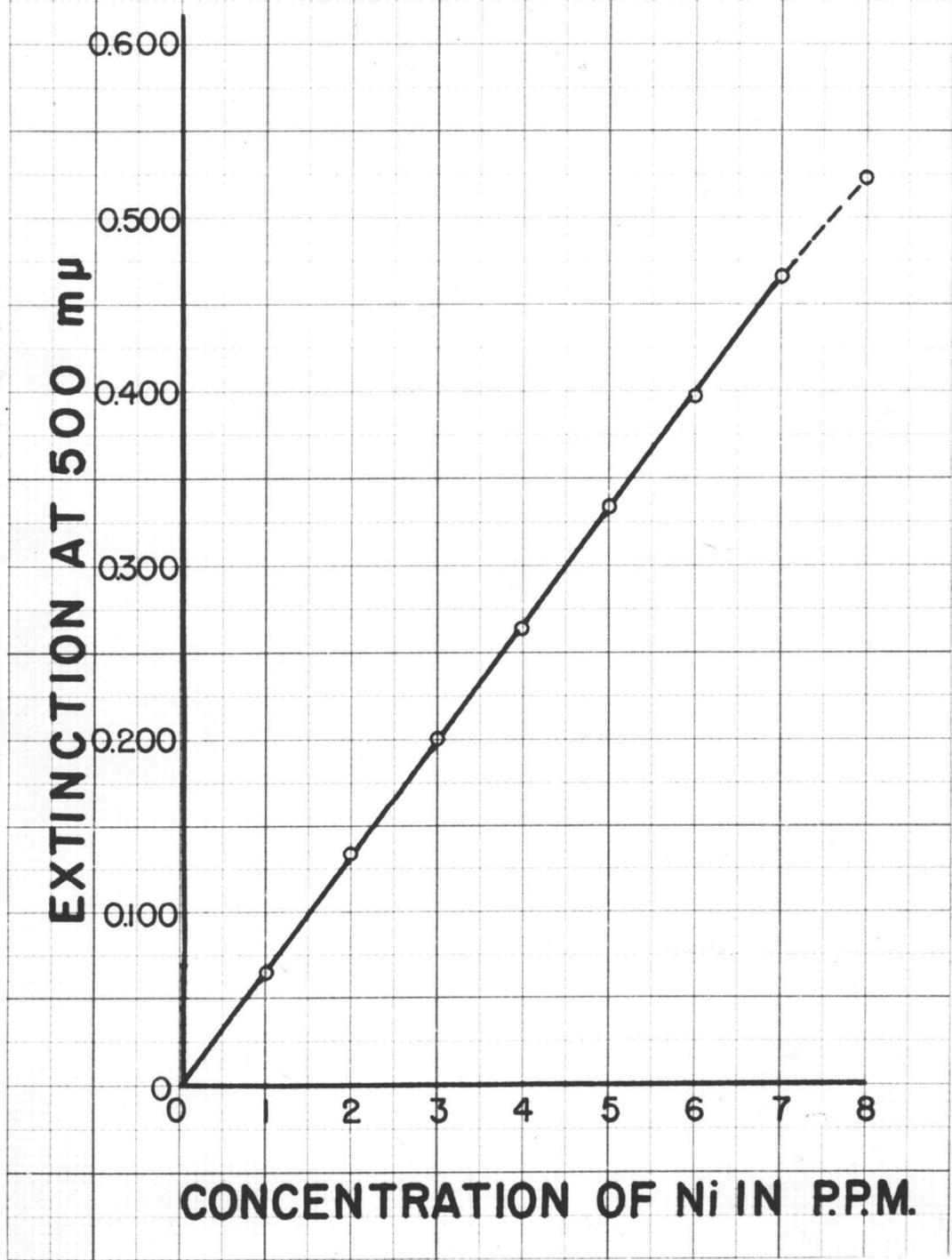
Solving the Beer-Lambert law for k gives

$$k = \frac{\log(I_0/I)}{cl}$$

Since $l = 1.00$, c is a known concentration, and I/I_0 , which is obtained from the galvanometer reading of the spectrophotometer, can be converted into the ratio I_0/I ; k can readily be calculated. The average value obtained for k was 66.56. See Table I.

FIGURE 2

CONFORMITY TO THE BEER-LAMBERT LAW



CONCENTRATION OF Ni IN P.P.M.

TABLE I.

Values of Specific Extinction
Coefficients Obtained

Concn. of Nickel p.p.m.	Specific Extinction Coefficient
1	65.00
2	66.86
3	66.89
4	66.70
5	67.26
6	66.31
7	66.93
Average	66.56

DETERMINATION OF NICKEL IN STEEL

The sample of steel was weighed and treated according to the method of Lundell, Hoffman, and Bright (5, p.281) for the precipitation and separation of nickel dimethylglyoxime. Three grams of steel were taken if the nickel content was less than 1 per cent, 1 gram if 1 per cent to 3 per cent nickel was present, 0.5 gram if nickel was between 3 per cent and 6 per cent, and 0.25 gram if the sample had more than 6 per cent nickel. The sample was then dissolved in 6M hydrochloric acid and heated until decomposition was complete. Ten milliliters of 1:1 nitric acid were added and the solution boiled until the iron and carbides were oxidized. The solution was boiled ten minutes longer to expel nitrogen oxides. The mixture was diluted up to 200 ml. with water if 1 gram or less of sample was used (or to 160 ml. if 3 grams of sample were used). Twenty milliliters of tartaric acid solution were added for each gram of sample used, the solution was neutralized with 15M ammonium hydroxide until the base was slightly in excess, and all insoluble matter was filtered off, washing the residue with hot water containing a little ammonium hydroxide and ammonium chloride. The filtrate was slightly acidified with concentrated hydrochloric acid, heated to a temperature of from 60° to 80° C., and 20 ml. of 1 per cent dimethylglyoxime

solution were added. After the solution had been made slightly alkaline with dilute ammonium hydroxide, the precipitate was filtered through a Gooch crucible. If the percent of nickel was less than one, the solution was allowed to stand an hour before filtering. This precipitate was then dissolved by pouring concentrated nitric acid through the Gooch crucible, using suction and catching the solution in an 8-inch test tube placed inside the filter flask. The asbestos mat was thoroughly washed with hot water. The contents of the test tube were transferred to a casserole and evaporated to a volume of a few drops. Two milliliters of concentrated nitric acid were added and the solution again evaporated almost to dryness to insure destruction of the dimethylglyoxime. Almost all of the nitric acid was removed by the addition of a few milliliters of distilled water and evaporating the solution to a few drops; this latter step was repeated to insure the complete removal of the nitric acid. A few milliliters of water were added and the solution was transferred to a 100-ml. volumetric flask and diluted up to the mark with distilled water.

By means of a micro-burette, an aliquot of from 1 to 10 ml. of the above solution, depending upon the nickel concentration, was transferred to a 50-ml. volumetric flask. Such an aliquot of the solution was taken that the percentage transmittancy of the color system later developed would

lie between 34 and 63 per cent. About three milliliters of potassium dithio-oxalate solution and about 0.04 ml. of 6M hydrochloric acid were added, and the solution diluted up to the mark with distilled water and shaken thoroughly. A "blank" was prepared containing the same concentrations of all reagents except the nickel. Transmittancy measurements of this solution in a 1-cm. cell were made at 500 m μ .

The following example illustrates the method of calculation.

Experimental Data:

Weight of sample---3.0050 grams; 10 ml. aliquot taken; percentage transmission for the colored solution---47.8 per cent at 500 m μ ; cell length---1.00 cm.; k---66.56.

The percentage transmission can be converted into extinction as follows:

$$I/I_0 = 0.478$$

$$I_0/I = 1/0.478$$

$$\log(I_0/I) = \log(1/0.478) = 0.3206$$

The Beer-Lambert equation solved for concentration gives:

$$c = \frac{\log(I_0/I)}{k \times l} = \frac{0.3206}{66.56 \times 100} = 0.004816 \text{ grams of Ni/liter.}$$

Therefore, since in 50 ml. of the above solution there is 0.0002408 grams, which represents 10 ml. of the original 100 ml. of solution,

$$\% \text{ Ni} = \frac{0.0002408 \times 10 \times 100}{3.0050} = 0.080\%$$

RESULTS

The method was tested by applying it to the determination of nickel in twelve steel samples. Table II shows the results that were obtained along with the values obtained by using the dimethylglyoxime gravimetric method of Lundell, Hoffman, and Bright (5, p.281). The percentage error of the spectrophotometric method varied from +1.35 to -3.33 per cent with an average of -1.24 per cent. Since the spectrophotometer used gives percentage transmittancy readings reproducible to 0.3 scale unit, corresponding to about 0.003 per cent nickel in a sample containing 0.281 per cent nickel, the average of several readings was taken for the transmittancy. Although the precision was not consistently high, the average of the results of two determinations for a given sample checked closely with the gravimetric results.

TABLE II.

Results Obtained by the Spectrophotometric Method

Sample No.	Nickel by Gravimetric Method	Nickel by Spectrophotometric Method	Deviation	Percentage Error
	%	%	%	%
1	0.227	0.228	+0.001	+0.44
2	0.080	0.078	-0.002	-2.50
3	0.540	0.522	-0.018	-3.33
4	0.282	0.283	+0.001	+0.35
5	0.154	0.151	-0.003	-1.95
6	3.49	3.47	-0.02	-0.57
7	9.04	8.93	-0.11	-1.22
8	0.196	0.192	-0.004	-2.04
9	0.074	0.075	+0.001	+1.35
10	0.062	0.061	-0.001	-1.61
11	1.70	1.68	-0.02	-1.13
12	1.17	1.14	-0.03	-2.56

DISCUSSION

The results obtained from analyzing twelve steel samples show that the spectrophotometric method can be applied successfully over a very large range of percentages of nickel. They also show that the method compares well in accuracy with the dimethylglyoxime gravimetric method which is the most common one for determining nickel in steel. The spectrophotometric method is faster than the gravimetric method, but it has the disadvantage of requiring the constant attention of the analyst during the latter part of the first evaporation of the nickel solution after nitric acid has been added to destroy the dimethylglyoxime. Also close attention is needed in the subsequent evaporations. Results of the analysis also compare favorably with the spectrophotometric method of determining nickel in steel by ammonia (6, pp.4-7) and the spectrophotometric method of determining nickel in steel with dimethylglyoxime (15, pp.2-3).

The spectrophotometric method for nickel in steel as potassium nickelo-dithio-oxalate has an advantage over the visual colorimetric method in that it eliminates matching color shades by eye, and does not require a series of color standards which are time-consuming in preparation. In the

commonly used colorimetric methods for nickel (16, pp.313-320), the percentage error varies from 1 to 5 per cent.

According to Snell and Snell (16, p.317) quite a number of ions interfere with the potassium nickelo-dithio-oxalate color system. Manganese affects the color of the system when present in excess of 15 mg. in 50 ml. Iron gives a deep purple with potassium dithio-oxalate. Other ions which give color are antimony, bismuth, cadmium, cobalt, copper, mercury, silver, tin, palladium, platinum, zinc, gold, thallium, titanium and vanadium. The precipitation of nickel with dimethylglyoxime in the presence of tartaric acid separates nickel from all the above interfering ions commonly occurring in steel except when excess copper is present and when iron and cobalt are both present in excess (17, pp.383-384). According to Willard and Diehl (17, p.384) nickel is separated best from copper by first reducing the copper to the univalent state by a sulfite, and the precipitation of nickel then made by the addition of tartrate, dimethylglyoxime, and acetate. They also state that interference from iron and cobalt may be avoided by reducing the iron with sulfur dioxide prior to the precipitation of the nickel (17, p.384).

The spectrophotometric method possesses the following advantages in general: (a) the system conforms to Beer's law, (b) the pH value is not critical, (c) the color is

stable for at least 2 hours, and (d) the color is independent of excess reagent.

Disadvantages of the method result from the relative instability of both the solid and aqueous potassium dithiooxalate. The fact that the above reagent is very uncommon to the ordinary laboratory may be listed as a disadvantage also. The reagent is obtainable commercially.

SUMMARY

A spectrophotometric method has been developed for the determination of nickel in steel, depending upon measuring the light transmittancy of the potassium nickelodithio-oxalate color system at a wave length of 500 mu. The nickel is first separated from ions interfering with the color system by precipitating as nickel dimethylglyoxime followed by solution of the precipitate and destruction of the resulting dimethylglyoxime by nitric acid. The concentration of nickel is related quantitatively to the transmittancy of the above color system, and may be calculated by use of the specific extinction coefficient for the system.

Results obtained by this method agree closely with those obtained by the dimethylglyoxime gravimetric method. The method also compares favorably with other recent spectrophotometric methods for nickel in steel.

Diverse ions commonly occurring in steel which interfere with the color system are removed in the course of the procedure.

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