SPECTROPHOTOMETRIC DETERMINATION OF COBALT AS THE TRIOXALATOCOBALTATE (III)

by

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TO MY WIFE

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INTRODUCTION

The most widely used methods for the determination of cobalt are gravimetric, electrolytic, or titrimetric in nature. In recent years, however, it has become possible, through the use of the spectrophotometer to apply colorimetric procedures to quantitative analysis with an accuracy previously found impossible. Investigations made by Yoe and Barton (19, pp.405-9) and by Moeller (14, p.348) on cobalt determinations have shown this to be the case. Other workers (5, pp.616-18; 15, p.529) have employed colorimetric analyses for cobalt on plant, soils, paints, etc., and have obtained excellent results.

The emerald-green complex which is formed by the coordination of three oxalate ions to one ion of trivalent cobalt has been known to chemists for many years and has received much attention in the past. Because it has a dl-form and two optically active derivatives, Recoder (16, pp.31-4) has studied the optical properties of the complex to determine the positions of coordination. Also, spectrophotometric studies have been made by several workers (6, pp.335-69; 18, pp.1-15) to ascertain the structure of the complex ion. Solubility and conductivity measurements have been made by Scholder, Gadenne, and Niemann (17, pp.1510-25) to determine the configuration.

But, it was not until 1941 that the complex ion was used to determine cobalt quantitatively by a colorimetric method. Cartledge and Nichols (2, pp.20-1) employed visual means to determine cobalt as the trioxalatocobaltate (III).

The purpose of the present work was to develop a spectrophotometric method for the determination of macro quantities of cobalt by employing the trioxalatocobaltate (III) color reaction. Special emphasis was placed on a study of the effect of diverse ions and on the stability of the color system. Results were obtained using the specific extinction coefficient of Beer's law.

THEORETICAL CONSIDERATIONS

When a ray of monochromatic light enters an absorbing medium, its intensity decreases exponentially in accordance with the equation of Lambert which is expressed as

$$I = I_o e^{-\mu l}$$

where μ is a constant for any given wave length, l is the thickness of the absorbing medium, and I_o and I refer to the original and transmitted light intensities, respectively, at a given wave length.

If the absorbing medium is a solution, the foregoing still applies, but the concentration of the colored solute must also be taken into account. The absorptive capacity shown by a given thickness of solution is dependent on the number of colored molecules traversed by the ray of light. Since the number of colored molecules traversed is dependent on the concentration of solute and since the transmitted intensity varies logarithmically with the thickness of the column of liquid, Lambert's law may be expressed as

$$I = I_o \times 10^{-kcl}$$

where c is the concentration of colored solute in grams per liter. The constant k is known as the specific extinction coefficient, and refers to the absorption due to a single molecule which is constant for any given wave length. This equation is usually referred to as the Beer-Lambert law.

The intensity of absorption of the monochromatic light is

utilized in making quantitative determinations of a desired constituent, but in order to provide a logical basis for measuring the absorption, it is necessary to allow for losses caused by scattering and reflection at the boundaries of the cell containing the solution and also for the small losses caused by scatter within the liquid itself. This 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. This ratio I/I_o, is termed the transmittance of the solution. Thus, modifying the Beer-Lambert equation, we get

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

Only this ratio is significant. The actual values of the intensities are not required. The logarithm of the ratio I_o/I is termed extinction.

For single colored constituents there are two general procedures that may be followed to convert spectrophotometric data into terms of concentration of desired constituent.

One may work from a calibration curve coordinating concentration and transmission determined for a series of solutions of known concentrations. After determining the transmittance for an unknown solution, its concentration may be read from the calibration curve. This technique may be used in all cases, but is confined largely to those systems which do not conform to the Beer-Lambert law. Manganese by permanganate (8, pp.27-9) and nickel by ammonia

(7, pp.4-7) are examples where this technique has been applied.

If the color system does obey the Beer-Lambert law, it is possible to use this equation for calculation of the concentration of the desired constituent, after the specific extinction coefficient has been determined by use of solutions of known concentrations. Copper by ammonia (9, pp.387-9) and triethanolamine (11, pp.52-5) and iron by salicylic acid (10, pp.162-3), thioglycolic acid (12, pp.8-14), and 2,2'-dipyridyl (13, pp.52-5) have been determined in this manner.

Ideally, the Beer-Lambert law should apply in all cases where no alteration of the solute molecules has occurred. If the solute molecules dissociate, ionize, or associate, the law does not necessarily hold. Due to discrepancies in instrument construction, however, a system that obeys Beer's law with one instrument may not with another. For that 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.

EXPERIMENTAL

APPARATUS AND SOLUTIONS

Beckman Model B Spectrophotometer. All spectrophotometric measurements were made with a Beckman Model B spectrophotometer. The identical cells used were one centimeter in length. The same cells were used throughout; one reserved only for the "blank" solution, the other only for the colored solution.

Beckman Model H2 pH Meter. All pH measurements were made with a Beckman Model H2 pH meter.

Glacial Acetic Acid. A commercial 99.5 per cent solution.

Ammonium Acetate. A 20 per cent solution was prepared by dissolving 200 grams of the solid in distilled water and diluting to one liter.

Potassium Oxalate. A 1M solution containing 184 grams of the monohydrate per liter.

Hydrogen Peroxide. A commercial 3 per cent solution.

Standard Sodium Thiosulfate. A 0.1N solution was prepared in the usual manner and standardized against pure potassium dichromate.

Standard Cobalt Solution. A standard solution was made by dissolving 4.7723 grams of 99.95 per cent cobaltous sulfate heptahydrate

in distilled water and diluting to one liter. Each milliliter of the resulting solution contained 1.0 milligram of cobalt.

Diverse Ion Solution. Solutions of the diverse ions were prepared from the chloride, nitrate, and sulfate of the cations and from the sodium, potassium and ammonium salts of the anions. Distilled water was used in all cases. Each milliliter contained 10 milligrams of the ion in question.

THE COLOR REACTION

The soluble colored complex that is formed when cobaltous ion is oxidized in a weakly acid solution by lead peroxide in the presence of excess oxalate ions has, according to Cartledge and Nichols (2, p.20), the following formula:

$$Co(C_2O_4)_3^{---}$$

The potassium salt of this coordination complex gives an emerald-green hue in an aqueous solution.

To produce the color system the volume of standard cobalt solution necessary to yield the desired concentration of cobalt was measured into a 100-ml. volumetric flask. Two milliliters of glacial acetic acid were added, followed by 5 ml. of a 20 per cent ammonium acetate solution to obtain the desired acidity. Ten milliliters of 1M potassium oxalate solution and approximately one gram of solid lead peroxide were then introduced. The solution was then set away from bright light with occasional shaking and after a period of nine minutes was diluted to the mark, shaken thoroughly, and immediately filtered to remove excess of lead peroxide.

The study of the color system included the determination of (a) the wave length of maximum absorption, (b) factors affecting the color reaction and its development, and (c) the specific and molecular extinction coefficient for the system.

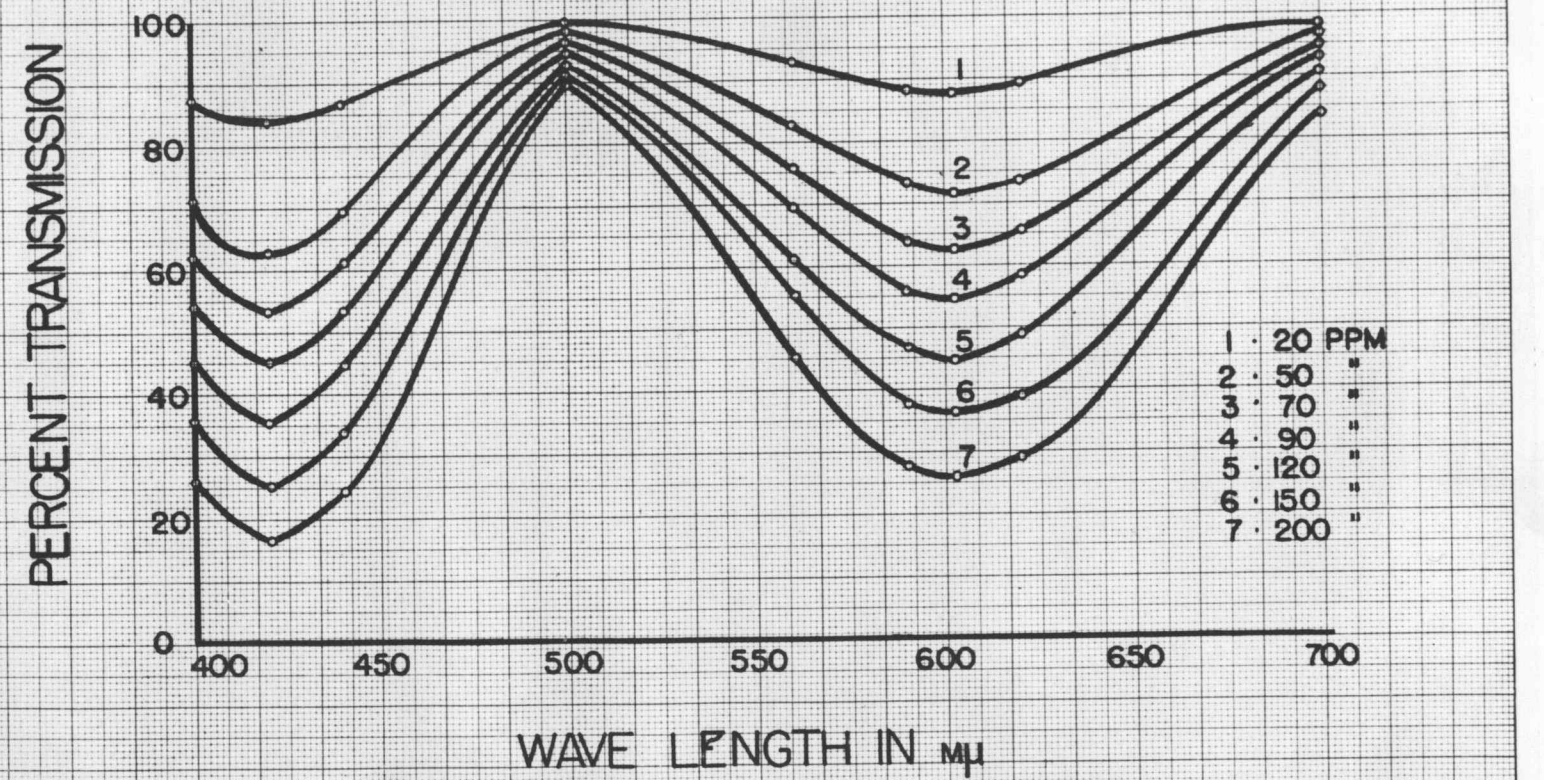
Wave Length of Maximum Absorption. The point of maximum absorption for the system was determined by employing eight solutions with

concentrations of 10, 20, 50, 70, 90, 120, 150, and 200 parts per million of cobalt. The color was produced exactly as described on the preceding page; in this case, the filtrate was caught directly in the absorption cell with the first portion of the filtrate being discarded. A "blank" solution was made by mixing 2 ml. of glacial acetic acid, 5 ml. of the ammonium acetate solution, and 10 ml. of the potassium oxalate solution and diluting to 100 ml. Transmission measurements were then made over a range of wave lengths varying from 400 to 700 mμ employing the spectrophotometer. The spectral transmission curves are shown in Fig. 1. Since maximum absorption occurred at 605 mμ, this value was used in making all further experimental measurements.

Factors Effecting the Color System. The effect of the pH value on the intensity of absorption by the colored complex was studied using solutions of the same cobalt content, but varying hydrogen-ion concentrations. Hydrochloric acid-biphthalate, sodium hydroxide-biphthalate, and acetic acid-ammonium acetate buffers were used to regulate the pH value. Readings were taken at intervals of 0.5 of a pH unit over the range of from 1 to 7. Above 7, no color formation occurred, since the oxidation of cobalt can not be affected in a basic solution. It was found that optimum color formation occurred between the values of 3.0 to 4.5. Within this range there is but slight variation of transmittance and the acidity is easily obtained and maintained with an acetic acid-ammonium acetate

FIG. 1

SPECTRAL ADSORPTION CURVES FOR TRIOXALATOCOBALTATE (III) COLOR SYSTEM



buffer. The system has an emerald-green hue in this pH range.

Studies were made to determine the stability of the complex with respect to time. The criterion set was the ability to duplicate transmittancy measurements after suitable time intervals. The complex was found to be light sensitive. When placed in direct sunlight, the color faded completely within one hour, but when kept in diffuse light readings were duplicated for a period of slightly over 24 hours.

The effect of the oxidizing agent on the system was also studied. Cartledge and Nichols (2, p.20) found that complete oxidation of the cobalt by lead peroxide required from five to ten minutes, and that the complex began to decompose if the excess of lead peroxide was not removed immediately. Readings were taken at one-minute intervals beginning at five minutes after the lead peroxide had been introduced. It was found that complete oxidation had not occurred until at least eight minutes had elapsed. Therefore, by allowing nine minutes for the oxidation to take place, and thus allowing one minute for dilution and removal of excess lead peroxide by filtration, excellent agreement resulted over the entire cobalt concentration range. It was also found that a large excess of lead peroxide was required. Small amounts produced incomplete oxidation, even though an excess was present. A large excess of oxalate ions was also found to be necessary to produce optimum color.

The order of addition of reagents was also found to be a

critical factor in obtaining reproducible results. The oxidation of the cobalt must take place in a weakly acid solution and in the presence of oxalate ions to produce the colored complex. Therefore, the acetic acid, ammonium acetate, and potassium oxalate solutions must be added prior to the lead peroxide.

Specific and Molecular Extinction Coefficients. In order to determine if the color system conformed to Beer's law, transmittancies for eight solutions containing from 10 to 200 parts per million of cobalt were measured. The color was developed and the transmittancy measurements were made at 605 mμ as was done in determining the point of maximum absorption.

When the extinction values for the eight standard solutions were plotted against their respective concentrations, a straight line resulted, as shown in Fig. 2. This indicates that Beer's law is obeyed for these concentrations. It was then possible to calculate the specific and molecular extinction coefficients for the system.

The calculation was made in the following manner:

The Beer-Lambert equation solved for k gives

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

Since $\log (I_o/I)$ is defined as the extinction, and $l = 1.00$, the equation may be written as

$$k = E/c.$$

The average value obtained for k was 2.913.

The molecular extinction may be defined as the product of the atomic weight of the element in question and the specific extinction coefficient,

$$e = Mk.$$

The average value obtained for e was 171.6. See Table I.

FIG. 2

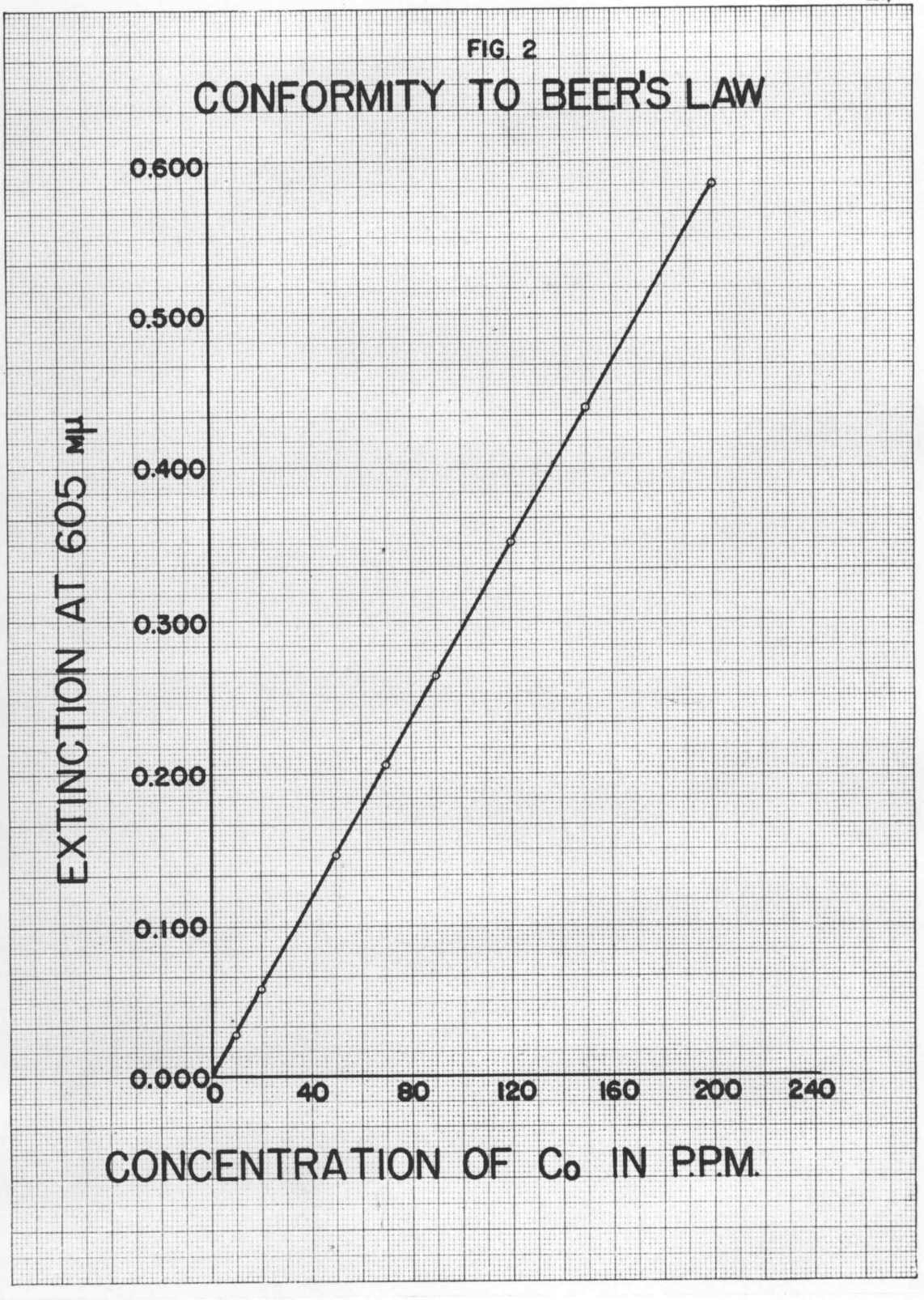

CONFORMITY TO BEER'S LAW
EXTINCTION AT 605 mμ
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
40
80
120
160
200
240
CONCENTRATION OF Co IN P.P.M.

TABLE I

Values of Specific & Molecular Extinction Coefficients Obtained

Concn. of Cobalt p.p.m.	Specific Extinction Coefficient	Molecular Extinction Coefficient
10	2.800	165.0
20	2.900	170.9
50	2.920	172.1
70	2.886	170.1
90	2.911	171.6
120	2.918	172.0
150	2.933	172.9
200	2.920	172.1
Average	2.913	171.6

DETERMINATION OF COBALT

An amount of sample was taken such that the cobalt content was between the limits of 0.5 and 1.5 grams. Upon solution of the sample in about 10 ml. of 6M hydrochloric acid, any insoluble matter was filtered off, and the filtrate was caught in a 100-ml. volumetric flask. The solution was then diluted with distilled water to the mark and shaken thoroughly. A large portion of this resulting solution was reserved for the determination of cobalt by the iodide method (1, pp.841-2). An aliquot of from 1 to 5 ml., depending upon the cobalt concentration, was accurately measured with a pipette into another 100-ml. volumetric flask. A solution of 6M sodium hydroxide was added drop by drop until a permanent precipitate of cobaltous hydroxide was formed. Two milliliters of glacial acetic acid were then added, followed by 5 ml. of a 20 per cent solution of ammonium acetate to buffer the solution at a pH of about 4.0 and 10 ml. of 1M potassium oxalate solution. The mixture at this point assumed a pink to deep violet color due to the formation of the trioxalatocobaltate (II) complex ion. One gram of solid, manganese-free lead peroxide was then added, the solution was shaken, and placed away from bright light with occasional shaking for a period of nine minutes.

A "blank" solution was then prepared during the interim by mixing 2 ml. of glacial acetic acid, 5 ml. of the ammonium acetate

solution, 10 ml. of the potassium oxalate solution, and finally diluting the mixture to 100 ml.

The cobalt solution was diluted to the mark with distilled water after the nine-minute wait, thoroughly shaken, and immediately filtered to remove the excess lead peroxide. The filtrate was caught directly in the absorption cell, following rejection of the first portion. The processes of dilution and filtration must be performed within one minute to prevent decomposition of the complex ion. The extinction was found in exactly the same manner as was used in determining the specific extinction coefficient. The percentage of cobalt in a particular sample was very readily calculated by use of the previously determined specific extinction coefficient.

The following example illustrates the method of calculation.

Experimental Data:

Weight of sample----2.9700 grams; 1.00 ml. aliquot taken; extinction for the colored solution----0.421 at 605 mμ; cell length----1.00 cm.; k----2.913.

The Beer-Lambert equation solved for concentration gives

$$c = \frac{\log (I_o/I)}{k \times l} \text{ grams of cobalt/liter.}$$

Therefore, since the final solution contained 0.01 of the original sample in 100 ml. of solution,

$$\% \text{ Co} = \frac{0.421 \times 10 \times 100}{2.913 \times 1.00 \times 2.9700} = 48.59\%$$

RESULTS

The method was tested by applying it to the determination of cobalt in various samples which were analyzed for cobalt by the Arny-Taub modification (1, p.841) of the Engle and Gustavson (3, pp.901-2) iodide method. These workers have shown that this method is as accurate as the electrolytic method.

The results obtained for eleven samples of cobalt salts are shown in Table II along with the values obtained by the iodide method. In no case was the difference between the two methods greater than ±0.4 per cent and the average difference was -0.04 per cent. The percentage error ranged from -2.045 to +0.542 per cent with an average of -0.145 per cent. Since the percentage transmittance scale of the spectrophotometer can be read only to 0.1 scale unit, corresponding to about 0.25 per cent cobalt in a sample containing 50 per cent cobalt, the average of several readings was taken for the transmission. Although the precision was not high, the average value of the results of at least two or more determinations for a given sample checked closely with the iodide method. Only those results which agreed to within at least 0.5 per cent of each other were used in calculating average values.

TABLE II

Comparison of Results Obtained

Sample No.	Cobalt by Iodide Method	Cobalt by Trioxalatocobaltate Method	Deviation	Percentage Error
	%	%	%	%
1	19.58	19.18	-0.40	-2.045
2	25.21	25.17	-0.03	-0.119
3	20.91	20.90	-0.01	-0.048
4	48.36	48.59	+0.23	+0.476
5	23.30	23.42	+0.12	+0.516
6	71.68	71.84	+0.16	+0.224
7	11.25	11.22	-0.03	-0.267
8	6.260	6.157	-0.103	-1.421
9	1.473	1.481	+0.008	+0.542
10	15.75	15.71	-0.04	-0.254
11	3.241	3.207	-0.034	-1.049

EFFECT OF DIVERSE IONS

Certain ions which are commonly encountered with cobalt were investigated to determine the effect of each on the color system. Measurements were made on solutions containing 50 parts per million of cobalt, and with varying concentrations of the ion in question up to a maximum of 300 parts per million. This maximum concentration was assumed to be sufficient to test for any possible interference. The solution of the diverse ion was added to the cobalt solution and the colored complex ion was formed and the solution made up to 100 ml. as in all previous work. Transmission measurements were made at 605 mμ.

The effect of the various ions studied upon the color developed at this wave length is indicated in Table III. When the difference between the transmittance of the two solutions amounted to 0.1 scale unit or less it was assumed that the ion in question caused no interference.

In general, it was found that the interference was of three types: (a) ions that interfere by producing a color, either of their own or by formation of a complex with the reagents, (b) ions which are strong reducing agents, and (c) ions which form a precipitate with the reagents.

Ions such as chromic, cupric, permanganate, etc., must be absent because of their characteristic color. Manganous ion must also be absent because of formation of the trioxalatomanganate (IV)

ion which is very unstable and induces the immediate decomposition of the trioxalatocobaltate (III) ion thereby producing no color (2, p.21).

Iodide, sulfite and nitrite interfere because of their reducing action on the trivalent cobalt. This type of interference is not serious, however, since it can be eliminated by preliminary oxidation. In many cases, this oxidation can be carried out by use of the lead peroxide reagent, thus accomplishing a two-fold purpose.

Calcium was the only ion encountered which formed a precipitate with the reagents. Thus, the presence of this ion removes oxalate ions and tends to prevent the colored complex from forming.

TABLE III

Effect of Diverse Ions

Ion	Added As	Concn. p.p.m.	Interference	Approx. Limiting Concn. p.p.m.
Acetate	$NaC_2H_3O_2$	300	Negligible	---
Aluminum	$AlCl_3$	300	"	---
Ammonium	NH_4Cl	300	"	---
Calcium	$CaCl_2$	300	Ppt. Formed	0
Cadmium	$CdCl_2$	300	Negligible	---
Chloride	NaCl	300	"	---
Chromic	$Cr(NO_3)_3$	300	Interferes	15
Cupric	$CuSO_4$	300	"	15
Dichromate	$K_2Cr_2O_7$	300	Negligible	300
Ferric	$Fe_2(SO_4)_3$	300	Interferes	10
Lead	$Pb(NO_3)_2$	300	Negligible	---
Magnesium	$MgSO_4$	300	"	---
Manganous	$MnSO_4$	300	Interferes	0
Nickelous	$NiSO_4$	300	"	80
Nitrate	$NaNO_3$	300	Negligible	---
Phosphate	Na_3PO_4	300	"	---
Potassium	KCl	300	"	---
Sodium	NaCl	300	"	---
Sulfate	Na_2SO_4	300	"	---

DISCUSSION

The results of the analysis of eleven cobalt samples show that the spectrophotometric method is sensitive over a very large range of percentages of the desired constituent. They also show that the method is as accurate as the iodide titration method.

The spectrophotometric method for cobalt as the trioxalatocobaltate (III) has an advantage over the visual colorimetric method in that it does not require a series of color standards which are time-consuming in preparation, and eliminates entirely matching color shades by eye.

Its advantage over the photoelectric colorimetric method consists in not requiring the use of a light filter or color screen.

Its advantage over existing titrimetric and gravimetric methods is the rapidity with which a determination can be performed.

Advantages of the spectrophotometric method in general include (a) the color forms immediately and is stable for at least 24 hours, (b) the system conforms to Beer's law, (c) pH value is not critical, (d) the method is rapid and involves few steps, (e) the reagents are not only inexpensive, but only very little amounts are required, (f) the color is independent of excess reagent, (g) interference by diverse ions is limited.

SUMMARY

A spectrophotometric method has been developed for the quantitative determination of cobalt. It depends upon the measurement of the light transmittancy at 605 mμ of the colored solution produced by the oxidation of the divalent cobalt ion to the trivalent state with lead peroxide in a weakly acid solution in the presence of potassium oxalate. This transmittancy is quantitatively related to the cobalt concentration, which may be calculated by use of the specific extinction coefficient for the system.

Results obtained by this method agree very closely with those obtained by the iodide titrimetric method.

The method is easily and rapidly carried out and requires much less time than the usual electrolytic and gravimetric methods. It also possesses several advantages over existing colorimetric methods for cobalt.

The range of concentration over which the quantitative determination of cobalt may be made has been ascertained, giving further proof that macro quantities can be satisfactorily determined spectrophotometrically.

The effect of diverse ions upon the color system has been determined.

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