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Titrations involving cobalt in ethylenediamine solution

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TITRATIONS INVOLVING COBALT IN

ETHYLENEDIAMINE SOLUTION

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I. INTRODUCTION

The literature of analytical chemistry is replete with methods for the determination of cobalt. The interest with which this element has been studied is out of all proportion to its economic importance, and stems rather from the large number of compounds which are known to contain cobalt. This member of the first transition series is used as an alloying constituent in metallurgical products, it forms a large number of coordination complexes with organic and inorganic ligands, and is of proven value in the nutrition of mammals. The variety of forms in which this element occurs presents a challenge for the analytical chemist. Recent work with vitamin B_{12} serves to illustrate the complex aspects of the chemistry of cobalt-containing compounds (1).

Of the many papers dealing with the determination of cobalt, the greatest number has been concerned with either volumetric or colorimetric methods of analysis. Quite a few gravimetric methods for cobalt have been reported, but in general these are lacking in specificity and the conditions of precipitation and ignition are critical. The work by Mandas (2) gives a thorough review of the ammonium phosphate precipitation of cobalt. Precipitation reactions have been commonly used to separate cobalt from cations which would interfere in subsequent volumetric determinations. This will be discussed at greater length in the sections to follow.

The colorimetric determination of cobalt has been widely applied to trace analysis in soils and agricultural products. The most commonly used method involves the formation of a soluble, brown compound of cobalt with

nitroso-R-salt. Without prior separations colorimetric procedures are not generally applicable when large amounts of other cations are present.

II. REVIEW OF LITERATURE

The various volumetric methods for the determination of cobalt can be broken down into five classes: 1) indirect methods involving gravimetric separations, 2) oxidation of cobalt to the trivalent state and titration with a reducing agent, 3) cyanometric titrations, 4) miscellaneous complexometric methods, and 5) titrations with ferricyanide in ammoniacal solution.

The first of these classes is characterized by the diversity of precipitant and of the titrant used to conclude the determination. Three papers have discussed the precipitation of cobalt from a solution containing pyridine by the addition of excess thiocyanate, and in each case the excess thiocyanate is determined by back titration with silver nitrate (3, 4, 5). Nickel interferes in these determinations. Two papers deal with the separation of cobalt as cobaltinitrite and subsequent determination of the combined nitrite (6, 7). Portnov (8) has reported the precipitation of cobalt with $p-AcNHC_6H_4AsO_3H_2$; this author concludes the determination by bromometric titration of the arsonate. Nickel is not precipitated, but other cations interfere. Cavicchi (9) claims good accuracy for a method involving precipitation of cobalt with $\propto,\propto'$-bipyridyl, back titration of excess bipyridyl with silver nitrate, and finally titration of silver with thiocyanate.

Funk and Ditt (10) precipitated cobalt with anthranilic acid, filtered and dissolved the precipitate, and titrated the liberated anthranilic acid with bromate-bromide. Another interesting method is that due to Ledrut and Hauss (11), who precipitated cobalt as the oxalate and titrated the combined

oxalic acid with permanganate. Nitrates interfere in this method, as do

most metal ions. Valentin (12) suggests separating cobalt as the insoluble

arsenate, dissolving the precipitate in dilute acid, and titrating the

arsenic acid iodometrically. Here again the method lacks specificity. A

paper by Treadwell and Chervet (13) mentions the electrometric titration of

cobalt using lithium ferrocyanide as the titrant, but few data are given.

Schoeller and Powell (14) recommend the precipitation of cobalt ammonium

phosphate and subsequent titration of the precipitate with dilute acid

using cochineal as an indicator. Most common metals interfere. Coetzie

(15) precipitated cobalt as the bivalent hydroxide and titrated the precipi-

tate acidimetrically using cresol red as an indicator.

The second general class of volumetric methods for the determination

of cobalt is based on the oxidation of the metal to the trivalent state and

titration of cobaltic hydroxide with a reducing agent. Three papers have

proposed the oxidation of cobalt with hydrogen peroxide in basic solution;

in these methods the excess peroxide is destroyed by boiling, the cobaltic

oxide is dissolved in a slightly acid solution of potassium iodide, and the

method is concluded by titration with thiosulfate (16, 17, 18). Any ele-

ment forming peroxy compounds under these conditions would interfere, and

the method cannot be used in the presence of iron, copper, or nickel.

Several papers have advocated the oxidation of cobalt using perborate

in acid solution (19, 20, 21). The excess perborate is destroyed by boil-

ing with dilute alkali, and the amount of trivalent cobalt is determined

iodometrically or by titration with ferrous sulfate. The review by Sarver

(21) states that manganese, sexavalent chromium, and pentavalent vanadium

4

interfere, as does nitrate. One advantage lies in the noninterference of nickel. However, for accurate results conditions must be controlled within close limits, and the method has not been widely used.

Barbieri (22) proposed an unusual method in which cobalt is precipitated as the cobaltinitrite salt, the precipitate treated with bicarbonate, and the resultant solution titrated with an acid permanganate solution. Apparently nitrite is oxidized to nitrate and cobalt reduced from the tri- to the bivalent state in the process. The procedure is slow and of little general application.

A number of cyanometric methods have been proposed for the determination of cobalt. The first direct determination of cobalt by titration with potassium cyanide is that of Rupp and Pfennig (23), who determined the end point by the appearance of a permanent turbidity. Muller and Schluttig (24) used the same titrant, but the end point was determined by impressing a low voltage between two silver electrodes and noting the null point for the galvanometer deflection. Glasstone and Speakman (25) give a review of the cyanometric methods, and these authors advocate potentiometric determination of the end point. In all these methods nickel is titrated with cobalt.

Five papers have dealt with the analysis for cobalt by addition of excess potassium cyanide and back titration of cyanide with silver nitrate using ammonia and potassium iodide (26, 27, 28, 29, 30). Nickel interferes and should be determined separately. The method has been applied to the analysis of cobalt in steel, but tungsten must be removed and iron precipitates under the conditions of the titration.

An interesting method proposed by Burriel (31) in 1950 involves precipitation of potassium cobalticyanide using excess cyanide. Mercuric oxide is then added and potassium hydroxide formed is titrated with standard acid. Nickel, copper, and iron interfere.

Four papers comprise the fourth general class of volumetric methods for the determination of cobalt (32, 33, 34, 35). The first of these complexometric schemes is that due to Pribil and Malicky (32) who titrated cobalt potentiometrically with ceric sulfate using ethylenediaminetetraacetic acid as a complexing agent. The method is somewhat less than ideal since these authors recommend a two-minute wait between addition of cerate and reading of the galvanometer. The series of papers by Schwarzenbach and Biedermann (33, 34, 35) discusses the use of nitrilotriacetic, uramildiacetic, and ethylenediaminetetraacetic acids as complexing agents for bivalent cobalt. The metal-containing solution is titrated with one of the above complexing agents and the end point is determined by plotting the change in pH. Most other common metals are also titrated, although at different pH's, and the methods are at best selective.

All of the volumetric procedures discussed thus far have involved the isolation of cobalt from one or another interfering elements before the cobalt content could be ascertained. Several schemes have been reported in which cobalt may be determined by difference when in the presence of nickel, but in general these are unsatisfactory.

The problem of determining cobalt in steel without prior separations was solved almost simultaneously by Dickens and Maassen (36) and Tomicek and Freiberger (37) in 1935. In an ammoniacal solution cobaltous salts are

oxidized quantitatively by potassium ferricyanide and the reaction can be followed potentiometrically. The break in potential at the equivalence point is about 0.2 volt. Ammonium salts have a beneficial effect on the titration, and the recommended procedure calls for addition of an excess of ferricyanide and back titration with cobalt nitrate. Citrate or tartrate is added to prevent the precipitation of various other metal hydroxides. The titration can be run in the presence of iron, nickel, and copper. Manganese interferes seriously.

Several further papers have appeared dealing with this titration (38-46). In general, it has proved far superior to the volumetric methods for cobalt discussed above, and it has been adopted as a routine method of analysis in steel plant laboratories. The principal advantage lies in the fact that of the common metals only manganese interferes, and prior separation of this element may be effected by precipitation as the dioxide.

Several drawbacks to the ferricyanide titration have arisen in the course of further study. The completeness of the reaction has been disputed (43, 46) and the quantitative aspects of the reaction of manganese with ferricyanide under the conditions of the titration appear unsettled. Some disagreement appears in the literature concerning the interference of chromium, whether in the tri- or sexavalent state. In any case, the potential break for the cobalt titration is not as great as might be desired and becomes even smaller with increasing amounts of cobalt (43).

III. CONSIDERATION OF THE PROBLEM. OBJECTIVES.

The ferricyanide titration of cobalt in ammoniacal solution is the best of the volumetric methods proposed to date, but it is not without shortcomings. As pointed out above, the two principal drawbacks to the method are the small potential break at the equivalence point and the interference of manganese. The latter is especially important since cobalt alloys very frequently contain manganese in varying amount.

The method of approach to the problem was to find a complexing agent for trivalent cobalt other than ammonia which would effectively lower the reduction potential of the cobaltous-cobaltic couple. By so doing, the potential break at the equivalence point would be augmented, and perhaps the interference of manganese could be obviated.

A number of diamines such as ethylenediamine and propylenediamine are known to form complex compounds with cobalt, and the initial phases of this work were concerned with the choice of diamine which would give the best titration characteristics. Subsequent phases of the present work included the establishment of optimum conditions for the determination of cobalt in steels and non-ferrous alloys. The analysis of metallurgical products was undertaken in the belief that the method should be applicable under diverse and unfavorable conditions.

The second main subject of the present investigation was to study the possible use of cobalt-amine systems as standard reducing agents for the volumetric determination of other elements. Very few reducing agents are known which can be used in basic solution, and the stability of these is critically dependent on the conditions of storage. Cobalt sulfate would

have the advantage that it would have reducing properties only in the presence of a suitable complexing agent. Hence, a solution of cobalt sulfate could be stored indefinitely without change, and only on addition to a solution containing a diamine would it become a reducing agent.

IV. EXPERIMENTAL WORK, PART ONE. THE DETERMINATION OF COBALT.

A. Selection of Diamine

A number of amines were studied as possible replacements for ammonia in the ferricyanide titration of cobalt. Among these were triethylenetetramine, propylenediamine, diethylenetriamine, trimethylenediamine, ethylenediamine, and tetraethylenepentamine. In Figure 1 are shown representative curves for the potentiometric titration of cobalt with ferricyanide in the presence of four of these amines. All proved of value in their complexing action with trivalent cobalt, and of them ethylenediamine gave the best titration. With the others some drifting of the potential was observed during the titration, and in some cases equilibrium conditions were reached slowly.

The advantages of using ethylenediamine in place of ammonia in the ferricyanide titration were readily apparent. The cobaltous-ethylenediamine complex is a stronger reducing agent by some 0.5 volt than the corresponding ammonia-cobalt system; the potential break at the equivalence point in the titration is thus augmented by a similar amount. The determination can be carried out as a direct titration in most cases. A further advantage in using ethylenediamine is that if a suitable complexing agent is used cobalt may be determined in the presence of manganese.

The cobaltous-ethylenediamine compound is a powerful reducing agent, the reduction potential approaching that of the chromous-chromic system. Accordingly, oxygen must be removed from the solution prior to the addition of ethylenediamine. This is conveniently accomplished by passing oxygen-free

Fig. 1   Titration of Cobalt Sulfate with 0.01 N Potassium
Ferricyanide.   Effect of Amine on Titration Curve.
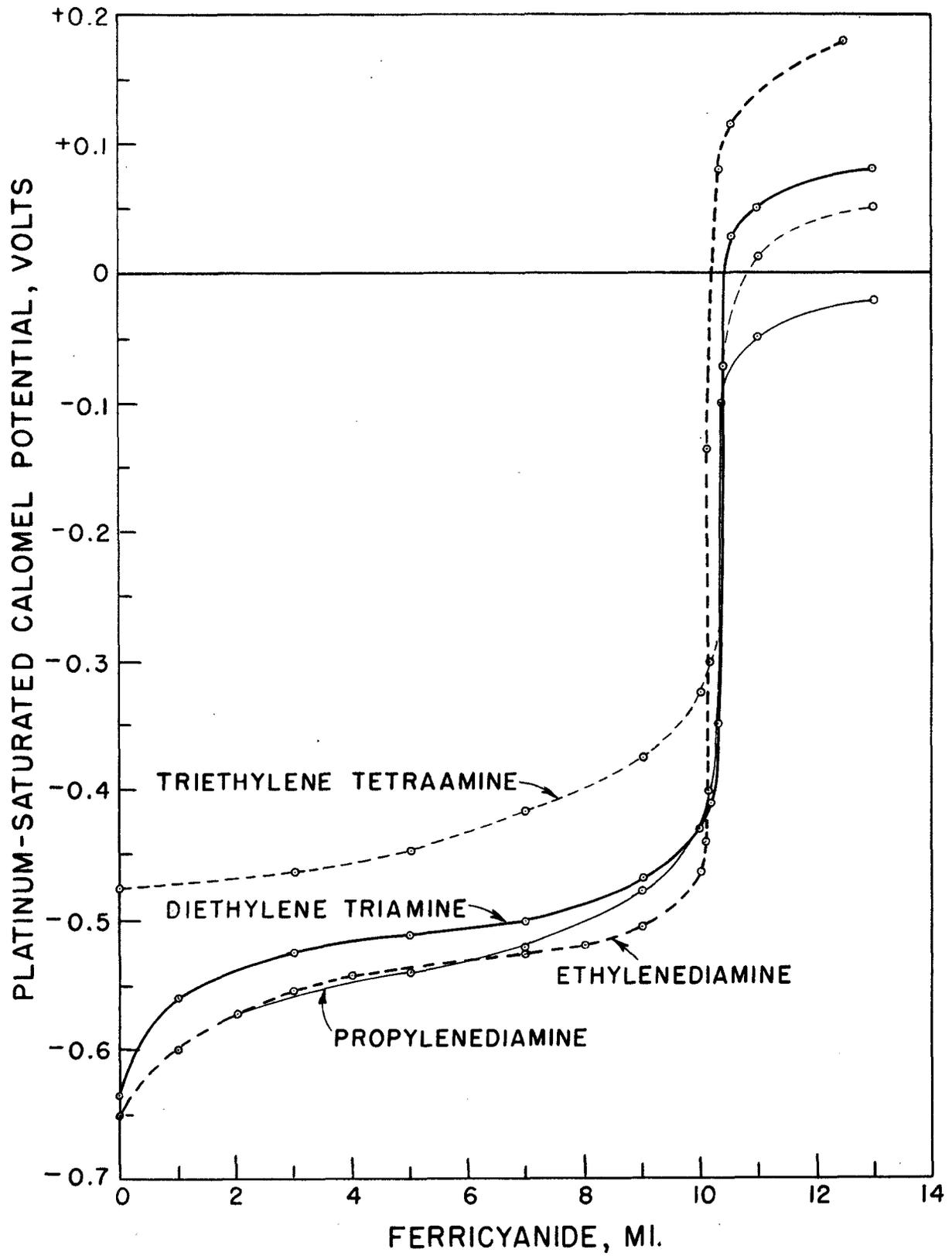
nitrogen through the solution to be titrated. Air must also be excluded during the actual titration.

As in the titration using ammonia, the presence of the salt as well as the free amine is essential. If ethylenediamine alone is present the potential drifts seriously; when both free diamine and its salt are present the potential rapidly reaches a steady state. The ethylenediammonium salt is conveniently formed in situ by neutralizing the acid remaining after dissolution of the sample.

B. Reagents and Apparatus

1. Ethylenediamine.

Commercial ethylenediamine was distilled over sodium hydroxide. The fraction boiling between $115\text{-}116^\circ$ was collected.

2. Standard potassium ferricyanide.

Approximately 0.01 N potassium ferricyanide solution was prepared by dissolving 6.6 g. of the reagent grade chemical in two liters of water. The solution was placed in a Machlett buret and was freed of oxygen by passing nitrogen through it for four hours. It was then standardized against cobalt sulfate.

3. Cobalt sulfate.

The reference standard, anhydrous cobalt sulfate, was prepared from reagent grade material in the following manner. Cobalt sulfate was first converted to hexamminocobalti oxalate (47). The luteo oxalate was then

ignited at a dull red heat to cobaltic oxide. The oxide was dissolved in sulfuric acid and the solution filtered and concentrated. The cobalt sulfate was finally heated to 555° (48).

Reagent grade acids and chemicals were used throughout this work unless otherwise specified.

All solutions used in the actual titrations were freed of dissolved oxygen by passing nitrogen through them for one hour.

4. Apparatus.

A Beckman Model G pH meter was used as a potentiometer. Bright platinum and saturated calomel electrodes were used. The titrations were performed in the three-necked vessel shown in Figure 2. A Beckman Model B spectrophotometer was used for the colorimetric determination of permanganate.

5. Nitrogen.

Commercial nitrogen gas was passed through a vanadous sulfate absorption train to remove trace amounts of oxygen (49). The terminal absorption bottle contained water so as to saturate the gas with water vapor at room temperature.

All titrations were performed at room temperature unless otherwise noted.
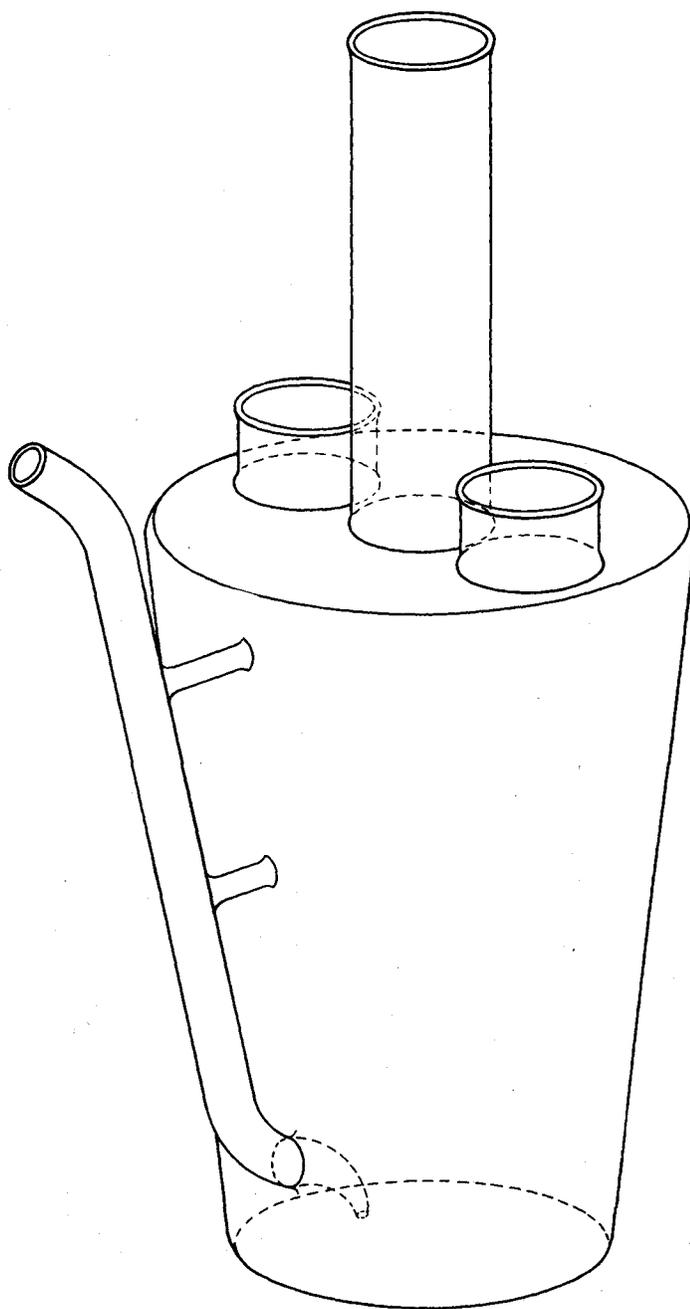
Fig. 2   Titration Vessel

C. Stability of Potassium Ferricyanide Solutions

Solutions of potassium ferricyanide decomposed slowly on standing; for a one-hundredth normal solution a decrease in normality of 12 per cent was observed after 46 days storage without exposure to air. Tenth normal solutions decomposed at a somewhat faster rate, although exclusion of light tended to improve the stability. Decomposition of ferricyanide solutions was accelerated by addition of acid, and a precipitate was observed in one case after three days storage at a pH of 4. Accordingly, approximately 0.01 N ferricyanide solutions were made up by dissolving the potassium salt in water; these solutions were standardized against cobalt sulfate just prior to use.

1. Standardization of ferricyanide solution.

An aliquot of a standard solution of cobalt sulfate containing 20 to 30 mg. of cobalt was pipetted into the titration cell. A volume of two ml. of dilute sulfuric acid (1:1) was added and the solution diluted to about 35 ml. Nitrogen was bubbled through the solution for ten minutes. A volume of 2.0 ml. of ethylenediamine was then added and the solution ti- trated potentiometrically with 0.01 N potassium ferricyanide solution. A representative titration curve so obtained is shown in Figure 3.

D. Effect of Other Metals

The determination of cobalt was carried out using the same procedure given for the standardization of ferricyanide. The cobalt was determined by direct titration as above or when necessary an excess of standard

PLATINUM-SATURATED CALOMEL POTENTIAL, VOLTS

FERRICYANIDE, MI.

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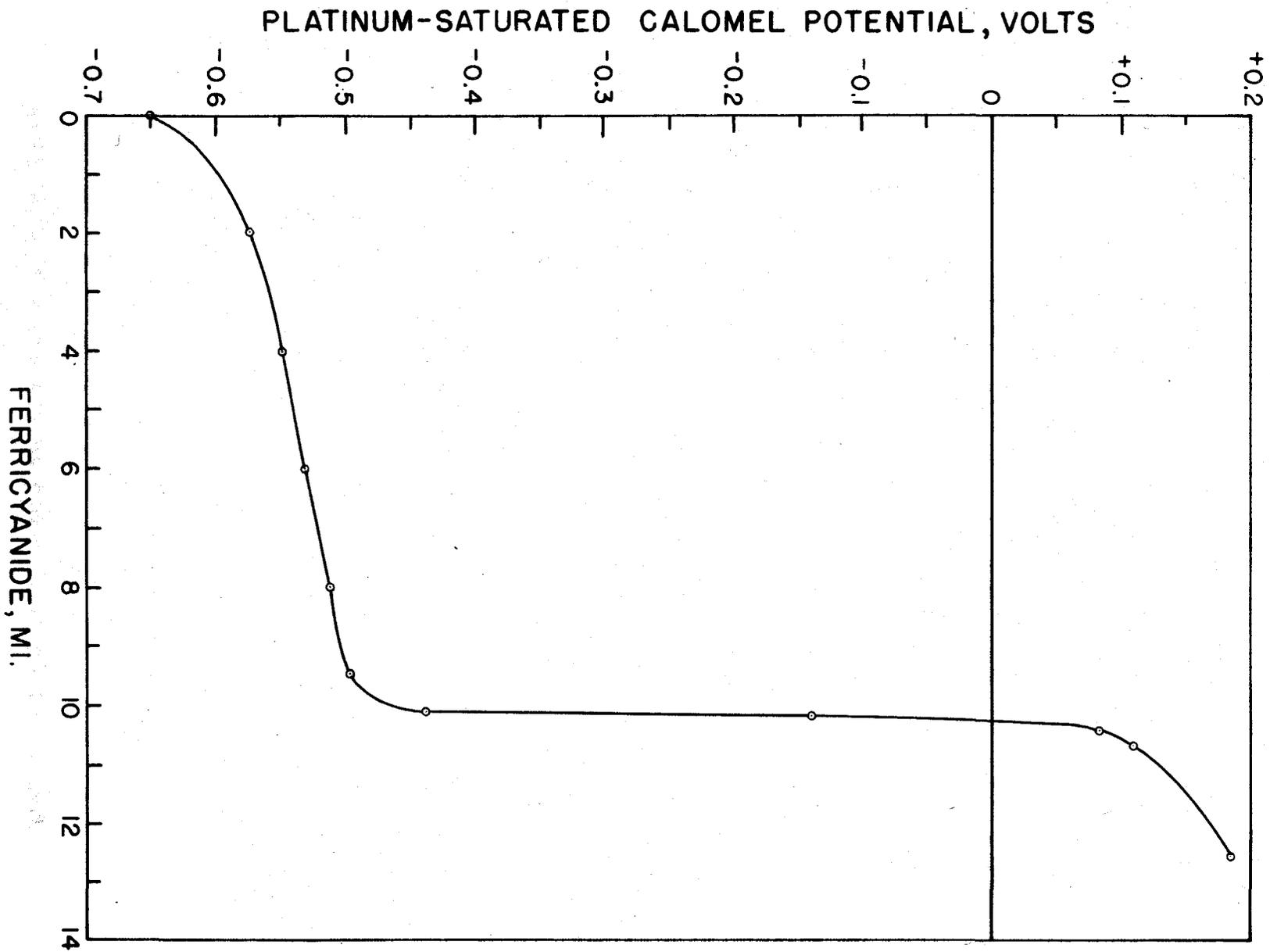
ferricyanide was added and the excess back titrated with cobalt sulfate. In either method the potential break was large and the system reached equilibrium rapidly. The direct titration was the more convenient and is recommended except for those cases in which cobalt is to be determined in the presence of silver or chromium-molybdenum-vanadium (or tungsten) as noted subsequently. The back titration must be used in these cases.

1. Iron.

When cobalt is to be determined in the presence of macro amounts of iron it is necessary to add a complexing agent to prevent the precipitation of ferric hydroxide from alkaline solution. Use of citrate, tartrate, pyrophosphate, fluoride, sulfosalicylate, and mannitol have been reported in this connection. Citrate, tartrate, and sulfosalicylate worked very well in the presence of ethylenediamine as inhibitors for the precipitation of ferric hydroxide, and these reagents of themselves did not interfere in the determination of cobalt. Fluoride, pyrophosphate, and mannitol were unsatisfactory owing to either the formation of a precipitate or to inter- ference in the titration with ferricyanide.

The presence of ferric iron changed the potential at the start of the titration, shifting the single electrode potential of the platinum, indica- tor electrode in the positive direction (reduction potential basis) by an amount depending on the amount of iron present. In the case of steel samples in which as much as 0.5 g. of iron was present, the potential was shifted from -0.6 v. to -0.2 v. toward the saturated calomel electrode. It is apparent that ferric iron equivalent to the cobalt was reduced and that

the subsequent titration was actually the titration of a ferrous iron complex. That this was the case was confirmed by the titration of a weighed quantity of ferrous ethylenediammonium sulfate under the same conditions as prevailed in the steel analysis, but in the absence of cobalt. The titration was quantitative and the potential break was approximately 0.6 v. or about the same size as that for the cobaltous-ethylenediamine titration with ferricyanide.

In the presence of ethylenediamine and citrate, tartrate, or sulfosalicylate the ferrous ion compares in strength as a reducing agent to the cobaltous-ethylenediamine system. Accordingly, oxidation of ferrous iron and cobalt would be expected to occur concurrently, and such was the case in practice. The large positive shift of the potential of the indicator electrode may be seen in Figure 4, which shows a typical titration curve for the determination of cobalt in stainless steel.

The use of sulfosalicylic acid as a complexing agent for ferric iron presented no advantage over the use of citrate except when manganese was present. This problem will be discussed subsequently. The sulfosalicylate complex with iron formed at a measurable rate, and several minutes were allowed for this reaction to occur before the titration was begun.

2. **Nickel and copper.**

In the presence of citrate or sulfosalicylate, neither nickel or copper interfere with the titration.
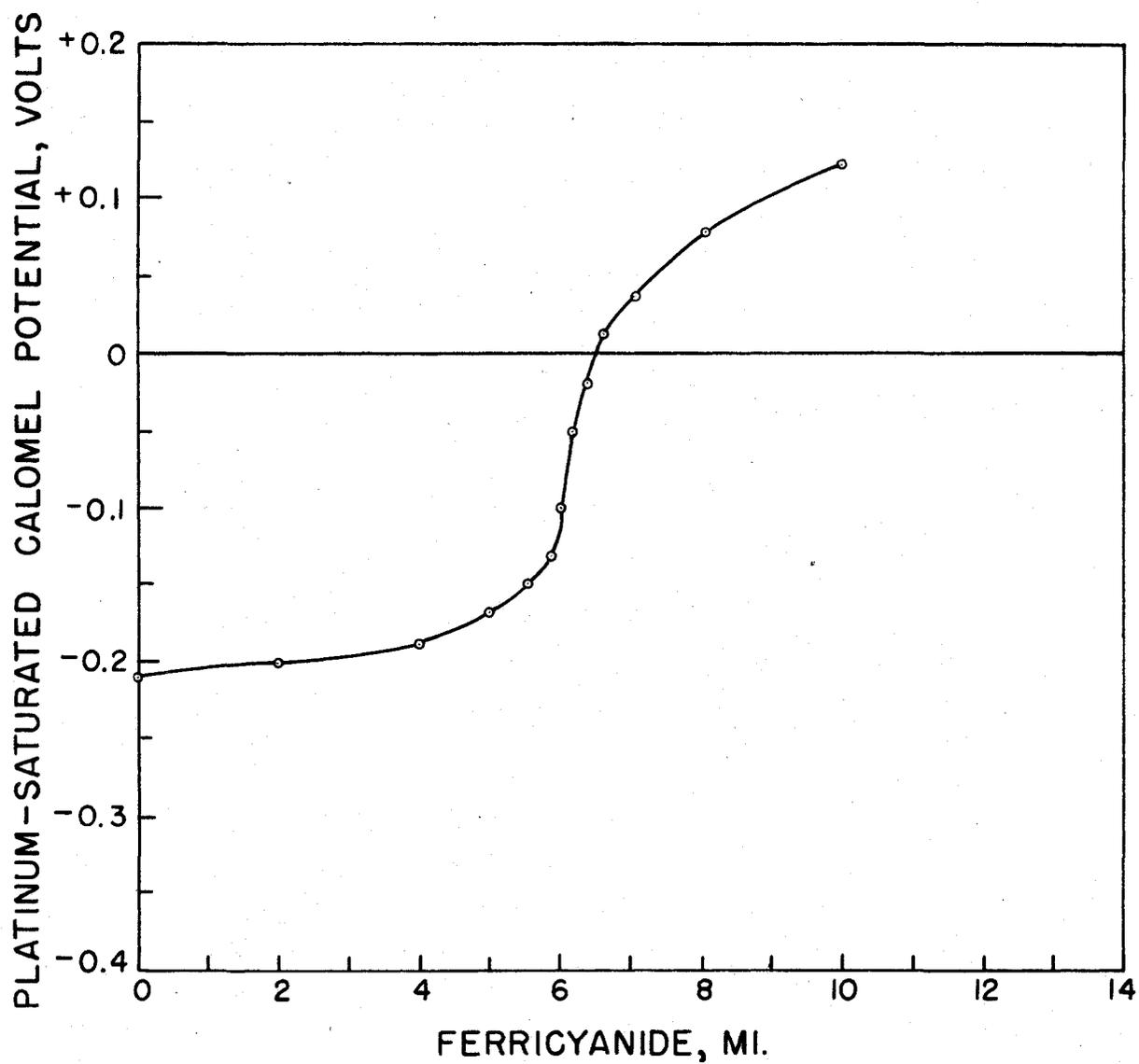
Fig. 4   Titration of Cobalt in Stainless Steel.   Direct Titration

Procedure in the Presence of Ethylenediamine and Sulfosalicylate.

Table 1. Effect of Other Metal Ions on the Direct Titration

of Cobalt with Ferricyanide in Ethylenediamine Solution.

Cobalt Taken, mg.	Cobalt Found, mg.	Other Metal Ion Present, mg.	Complexing Agent
11.94	11.94	Ni, 19.05	Citrate
11.94	11.90	Ni, 19.05	Sulfosalicylate
11.94	12.02	Cu, 20.3	Citrate
11.94	11.98	Cu, 20.3	Sulfosalicylate
11.94	11.94	Fe(III), 10.3	Citrate
11.94	11.87	Fe(III), 10.3	Sulfosalicylate
11.94	17.0	Mn(II), 17.7	Citrate
11.94	11.92	Mn(II), 17.7	Sulfosalicylate
5.97	5.91	Mn(II), 208	Sulfosalicylate

3. Manganese.

In an ethylenediamine solution, manganese was oxidized by ferricyanide to manganese dioxide. When cobalt and manganese were both present in the solution the titration went in two stages; first, the cobalt was oxidized and then the manganous salt was oxidized to the dioxide. However, the oxidation of manganese took place slowly as the equivalence point was approached, and the exact position of the end point depended on the rate of addition of ferricyanide. The slowness of the system to reach equilibrium appeared to be a measure of the rate of formation of manganese dioxide.

Manganese was partially oxidized to the trivalent state in an ethylene-diamine solution containing citrate. The oxidation of manganese was

incomplete and the potential of the manganous-manganic couple present was
such that the titration curve overlapped that of cobalt. Tartrate behaved
similarly in that it did not interfere with the simple cobalt titration,
but in the presence of manganese some manganous-tartrate was oxidized con-
comitantly with the cobalt and results were not stoichiometric for either
cobalt or manganese. The titrations were not exactly reproducible, but
Figure 5 shows a titration curve for a synthetic mixture of cobaltous and
manganous sulfates.

Pyrophosphate, fluoride, and mannitol were even poorer complexing
agents for the successive titration of cobalt and manganese. The potential
drifted extensively during the titration. Neither osmium tetroxide nor
potassium iodide catalyzed these reactions.

Use of the back titration procedure failed to improve the titration of
cobalt in the presence of manganese using citrate or tartrate as complexing
agents. Serious drifting of the potential was observed and reduction of
the excess ferricyanide and of the manganese-citrate or manganese-tartrate
complex took place at the same time.

The interference of manganese in the cobalt titration can be obviated
by the use of sulfosalicylic acid. In the presence of this complexing
agent, both cobalt and manganese were oxidized by ferricyanide in ethylene-
diamine solution. Quantitative oxidation of cobalt took place first, and
then manganese was oxidized to the trivalent state. The cobalt end point
was excellent; that for manganese was less sharp, Figure 6. The cobalt
titration was satisfactory for ratios of manganese to cobalt of up to
forty to one. The successive titration of cobalt and manganese failed,

Fig. 5 Titration of Cobalt and Manganese in the Presence of Tartrate and Ethylenediamine. Direct Titration with 0.01 N Ferricyanide.
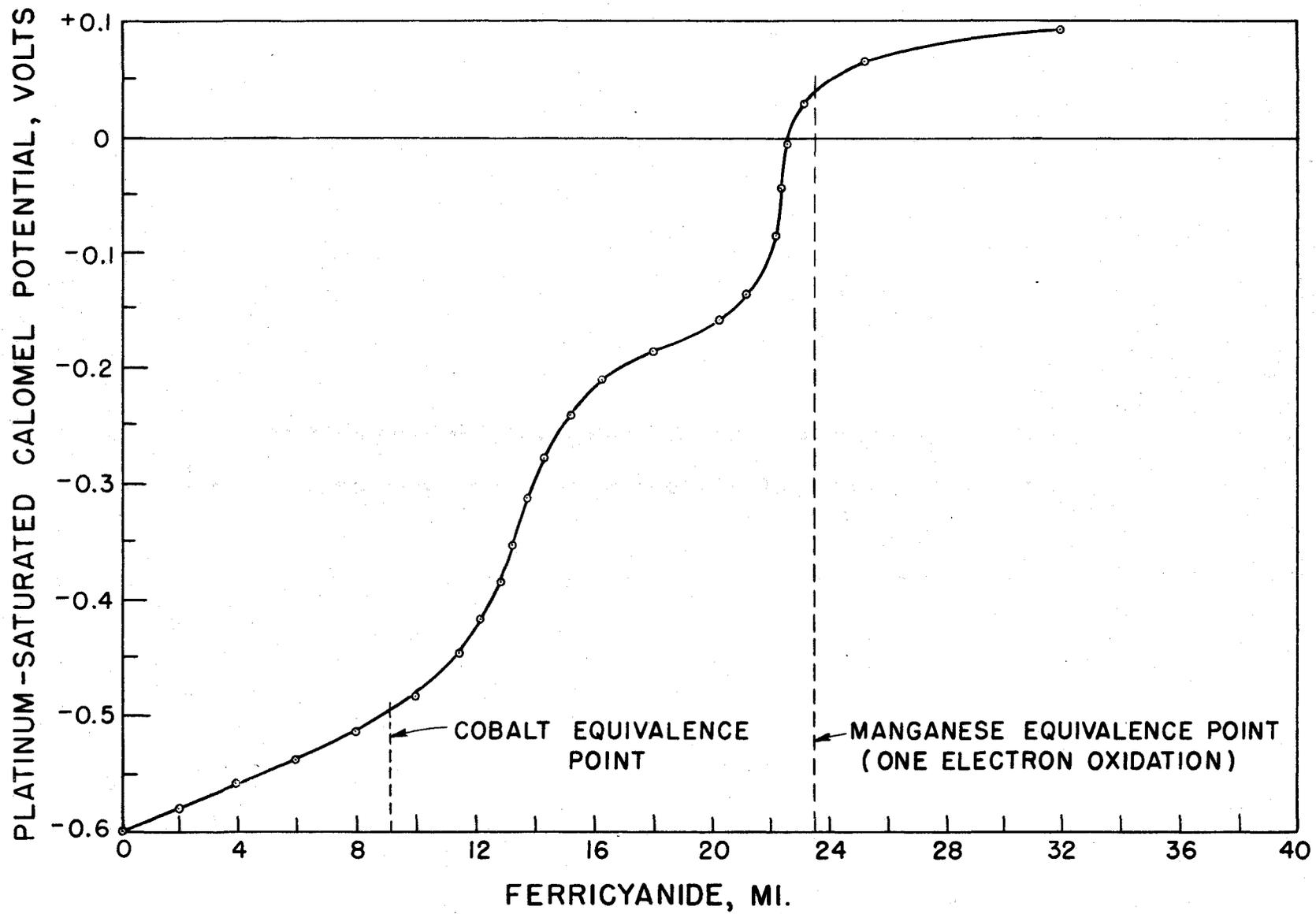
Fig. 6   Titration of Cobalt and Manganese in the Presence of Sulfosalicylate and Ethylenediamine.   Direct Titration with 0.01 N Ferricyanide.
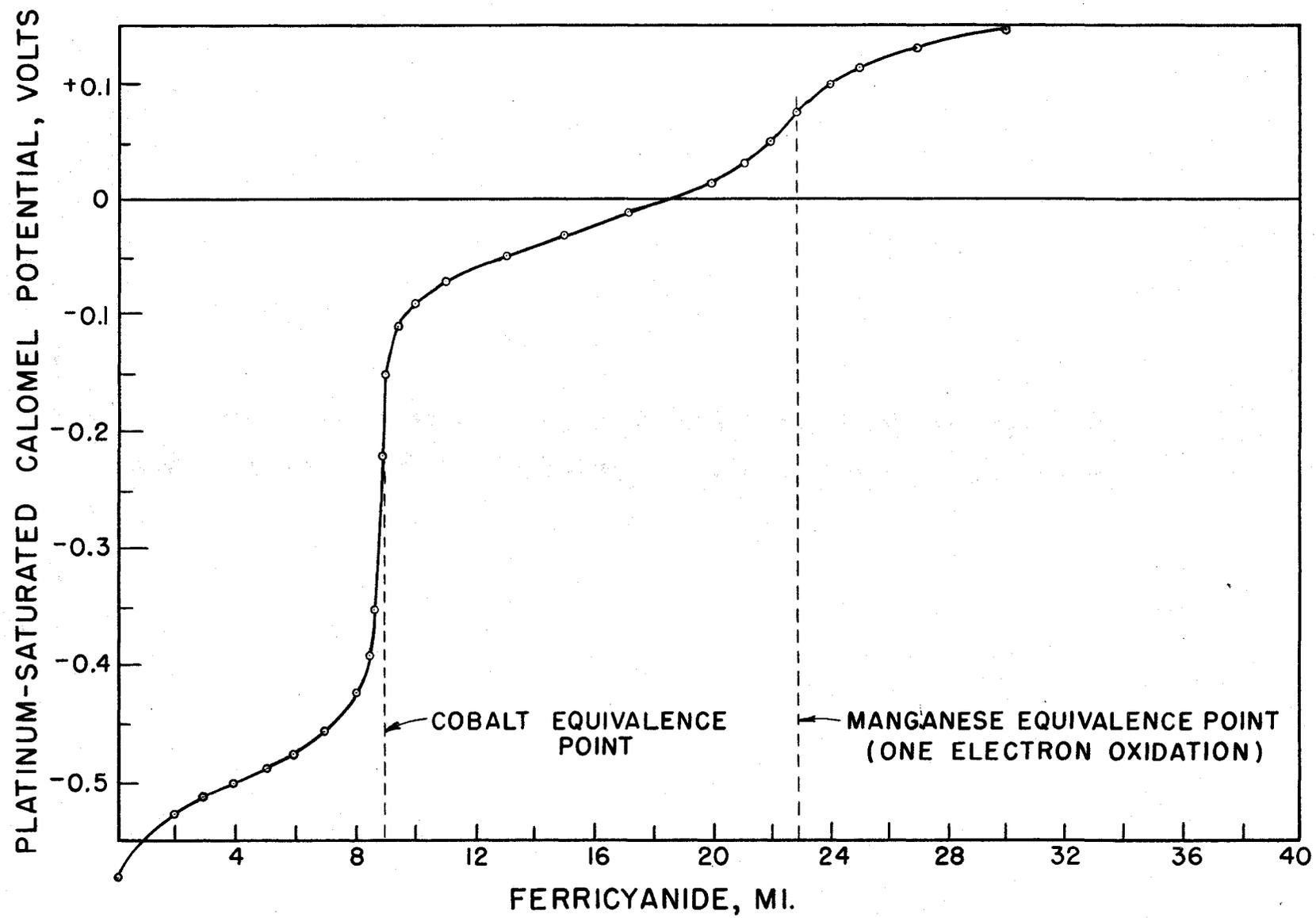
however, in the presence of large amounts of iron. Major amounts of ferric iron shifted the initial potential in the positive direction to such an extent that the break at the manganese end point disappeared, Figure 7. Amounts of iron up to four or five times that of manganese could be tolerated.

4. Chromium, molybdenum, vanadium, and tungsten.

(a) Direct titration. Sexavalent chromium, molybdenum, and tungsten, and pentavalent vanadium interfered in the direct titration of cobalt with ferricyanide in an ethylenediamine-citrate solution. The cobaltous-ethylenediamine system initially present reduced the higher valent forms of these elements to lower valent forms; reoxidation by the ferricyanide proceeded slowly and was not complete.

The interference of chromate in the direct titration of cobalt was obviated by reducing the chromate to chromic ion which did not interfere. Strong reducing agents were avoided since it was desired to reduce only the chromate. This reduction was conveniently effected by adding hydrogen peroxide to an acid solution of the chromate and then boiling to destroy the excess peroxide. The peroxide reduction could not be used if tungsten or molybdenum were present owing to the formation of stable peroxyacids of these elements which interfered with the subsequent titration. When these elements were present it was necessary to use the back titration method.

(b) Back titration. In the back titration procedure, chromate, tungstate, molybdate, and vanadate did not interfere in the determination of cobalt either when present singly or when present in pairs. However,

Fig. 7 Effect of Fe(III) on the Direct Titration of Zn(II) with

0.01 Ferricyanide. Ethylenediamine and Sulfosalicylate Present.

FERRICYANIDE, MI.

PLATINUM-SATURATED CALOMEL POTENTIAL, VOLTS

{ 8.85 mg. Mn(II)
501.6 mg. Fe(III)

{ 8.85 mg. Mn(II)
51.4 mg. Fe(III)

{ 8.85 mg. Mn(II)
20.7 mg. Fe(III)

8.85 mg. Mn(II)

MANGANESE EQUIVALENCE POINT
(ONE ELECTRON OXIDATION)
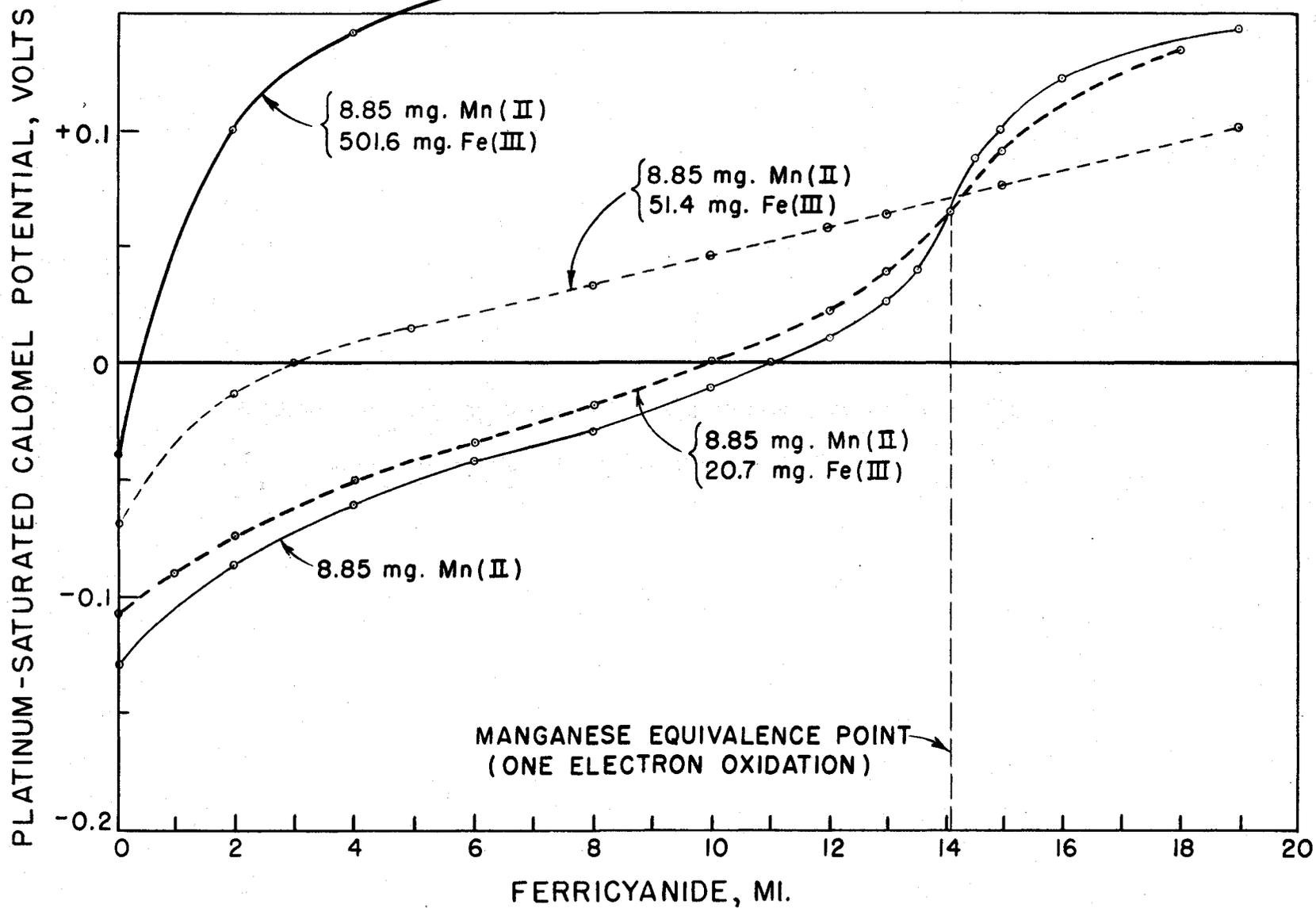
when a three-component mixture, chromate-molybdate-vanadate, chromate-tungstate-vanadate, or chromate-molybdate-tungstate, was present (as in Bureau of Standards 153 steel), the back titration scheme also failed unless the acidity of the solution was adjusted prior to the addition of citrate. Even with this precaution the precision of the method left something to be desired. The three-component system, tungstate-molybdate-vanadate, did not interfere in the back titration.

The reduction potentials of chromate, molybdate, tungstate, and vanadate are greatly pH dependent. The effect is so marked that at pH 10 ferricyanide is the strongest oxidizing agent of the above-mentioned systems. That only the three-component mixtures previously enumerated caused trouble in the back titration method implied that a heteropoly acid was present which was a fairly powerful oxidizing agent, sufficient to oxidize citric acid at low pH.

5. <u>Silver.</u>

Cobalt could not be determined by direct titration with ferricyanide in the presence of silver. The cobaltous-ethylenediamine complex reduced silver to the metal and the metallic silver redissolved slowly during the titration with ferricyanide. No attempt was made to filter off this precipitate of metallic silver because of the difficulties of filtering without allowing the solution to come in contact with air. Spurious results for cobalt were obtained when a precipitate of silver was present in the solution.

The back titration of excess ferricyanide with cobalt sulfate was successful in the presence of silver. It was necessary to add the

Table 2. Effect of Other Metal Ions on the Back Titration of

Ferricyanide with Cobalt Sulfate in Ethylenediamine

Solution. Hundredth Normal Solutions Used.

Cobalt Equivalent of Ferricyanide Taken, mg.	Cobalt Required for Back Titration, mg.	Other Metal Ion Present, mg.	Complexing Agent
13.25	13.20	Cr(VI), 2.84	Citrate
13.25	13.42	Cr(VI), 2.84	Sulfosalicylate
13.25	13.13	V(V), 19.7	Citrate
13.25	13.42	V(V), 19.7	Sulfosalicylate
13.25	13.25	Mo(VI), 32.9	Citrate
13.25	13.25	Mo(VI), 32.9	Sulfosalicylate
13.25	12.42	Ag, 22.3	Citrate
13.25	12.84	Ag, 22.3	Sulfosalicylate
13.25	13.40	W(VI), 85.8	Citrate
13.25	13.25	W(VI), 85.8	Sulfosalicylate
13.30	13.24	V(V), 19.7 Cr(VI), 2.84	Citrate
13.30	13.24	V(V), 19.7 W(VI), 85.8	"
13.30	13.20	V(V), 19.7 Mo(VI), 65.8	"
13.30	13.37	W(VI), 85.8 Mo(VI), 65.8	"
13.30	13.24	Cr(VI), 2.84 W(VI), 85.8	"
13.30	13.34	Cr(VI), 2.84 Mo(VI), 65.8	"
13.30	13.20	Cr(VI), 2.84 Mo(VI), 65.8 V(V), 19.7	"

Table 2 (cont.)

Cobalt Equivalent of Ferricyanide Taken, mg.	Cobalt Required for Back Titration, mg.	Other Metal Ion Present, mg.	Complexing Agent
13.30	13.09	$Cr(VI)$, 2.84 $W(VI)$, 85.8 $V(V)$, 19.7	Citrate
13.30	13.27	$Cr(VI)$, 2.84 $W(VI)$, 85.8 $Mo(VI)$, 65.6	"
13.30	13.20	$V(V)$, 19.7 $W(VI)$, 85.8 $Mo(VI)$, 65.8	"
13.30	13.27	$V(V)$, 19.7 $Cr(VI)$, 2.84 $Mo(VI)$, 65.8 $W(VI)$, 85.8	"

ferrioyanide just before adding the ethylenediamine; oxidizing conditions thus prevailed at the start of the titration. The reduction of the excess ferrioyanide took place before that of the silver ion, the titration curve showing two breaks. However, the reduction of silver was sluggish, and the second portion of the titration curve was of little use as an analytical method for silver. In Figure 8 is shown a titration curve for the determination of cobalt in the presence of silver.

E. Application to Metallurgical Materials

The present method was applied to a number of metallurgical products: beryllium-cobalt bronze (silver absent), beryllium-cobalt bronze containing silver, stainless steel, and a chrome-vanadium-molybdenum-cobalt steel (National Bureau of Standards 153 steel). NBS 153 steel presented a number of problems due to the complexity of the alloy. A discussion of these and related problems will be given subsequently.

In general the direct titration was applicable, the exceptions being ferrous alloys containing at once chromium, vanadium, and either tungsten or molybdenum and silver-bearing cobalt bronze. In these cases it was necessary to use the back titration procedure.

The alloys chosen for analysis were those in which cobalt was present in minor amount and in which there was a possibility of interference due to one or more constituents of the sample. Tables 3, 4, and 5 give the results for consecutive analyses on the various alloys studied. The recommended procedures should be followed carefully. The method can be applied to almost any cobalt-containing material; in the case of organic compounds it would only be necessary to destroy the organic matter with perchloric

Fig. 8   Determination of Cobalt in Silver-bearing Bronze.   Back Titration of Excess

Ferricyanide with 0.01 N Cobalt Sulfate in Ethylenediamine Solution.

PLATINUM-SATURATED CALOMEL POTENTIAL, VOLTS

COBALT SULFATE, Ml.

37a
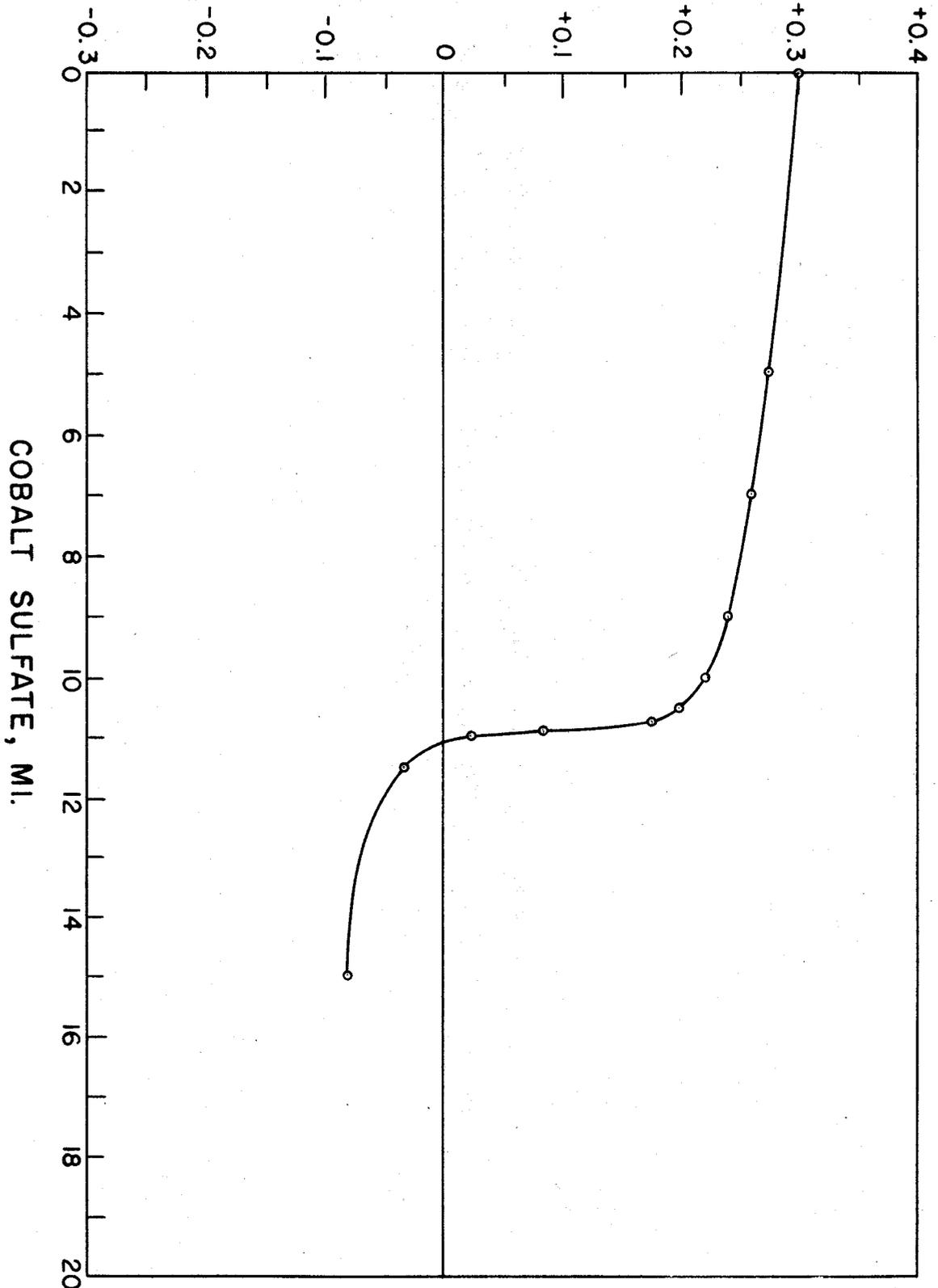
Table 3. Determination of Cobalt in Bronze (Silver Absent).*

Alloy and Reported Analysis	Weight of Sample, g.	Standard $K_3Fe(CN)_6$ Used, ml.	Cobalt Found Per Cent
Be-Cu-Co Alloy A**	1.0847	6.45	0.43
(cobalt 0.53 per	1.1124	6.50	0.43
cent as determined	1.0449	6.30	0.44
spectrographically)	1.0868	6.51	0.44
	1.1985	7.48	0.45
Be-Cu-Co Alloy B**	1.2409	4.6	0.27
(cobalt 0.27 per	1.1378	4.0	0.26
cent as determined	1.0667	4.2	0.29
spectrographically)	0.9667	3.6	0.27
	1.2041	4.7	0.29
Be-Cu-Co Alloy C**	0.9761	4.8	0.36
(cobalt 0.33 per	1.2502	6.3	0.37
cent as determined	0.9702	4.6	0.35
spectrographically)	1.1519	5.7	0.37
	1.0803	5.3	0.36
Ampco #91 Bronze	0.3409	14.35	2.92
(cobalt 2.897 per	0.3868	16.5	2.97
cent)	0.3361	13.7	2.83
	0.1992	8.35	2.91
	0.4180	17.62	2.93

*Results given are for consecutive analyses on each sample.

**Spectrographic analysis of Be-Cu-Co alloys showed the presence of the
  following: Be, 1.0-2.25 per cent; Sn, 0.05-0.40 per cent; and small
  amounts of Fe, Si, Al, Pb, Zn, and Ni.

Table 4. Determination of Cobalt in Silver-bearing Bronze.

Back Titration of Excess Ferricyanide with Cobalt Sulfate.*

Weight of Sample, g.	Standard $K_3Fe(CN)_6$ Added, ml.	Standard $CoSO_4$ Used, ml.	Cobalt Found Per cent
0.4978	25	13.6	1.73
0.5941	25	10.4	1.77
0.7020	25	7.80	1.73
0.4568	25	14.2	1.79
0.6228	25	9.90	1.75
		Average	1.75

*Analysis of Be-Cu-Co Alloy D: Co, 1.71 per cent; Be, 0.25-0.50; Ag, 0.90-1.10. Also small amounts of Fe, Si, Al, Sn, Pb, Zn, and Ni.

Table 5.   Determination of Cobalt in Armco

Stainless Steel #29.   Direct Titration.*

Weight of Sample, g.	Standard $K_3Fe(CN)$ Used, ml.	Cobalt Found Per Cent
0.6603	6.5	0.64
0.8017	7.3	0.60
0.7273	6.6	0.59
0.7429	7.1	0.63
0.6653	6.4	0.63
	Average	0.62

*Reported Analysis: Cr, 18 per cent; Ni, 10; Mn, 1.20-1.35; Co, 0.60-0.65.   Cb also present in undetermined amounts.

acid. There would seem to be no reason why the method could not be applied on the micro scale as well as for macro volumetric analysis.

1. Analysis for cobalt in NBS 153 steel. Problems.

A number of unusual problems were encountered in the determination of the cobalt content of NBS 153 steel. Besides macro amounts of chromium, vanadium, molybdenum, and tungsten, the Bureau of Standards Certificate of Analysis reports 8.45 per cent cobalt and 0.419 per cent manganese. Since three-component systems containing chromium, vanadium, molybdenum, and/or tungsten were known to interfere with the direct titration of cobalt using ferricyanide, it was necessary to resort to the back titration procedure. Even this expedient was not without complications, however. The nature of the problems encountered in the course of this study may be seen in the following breakdown: 1) method of dissolving the sample, 2) possible in-homogeneity of the sample, 3) necessity of prior separations, 4) necessity and means of reducing chromate, 5) choice of complexing agent for ferric iron, 6) adjustment of pH prior to the titration, and 7) effect of oxygen on the determination of cobalt.

The most efficacious means of dissolving the sample was that using equal volumes of nitric and hydrochloric acids. The steel dissolved on gentle heating and excess nitric acid was expelled by evaporation to strong fumes of perchloric acid. This treatment ensured oxidation of most constit-uents to their highest normal oxidation state except in the case of manga-nese which was known to remain in the bivalent state following this treatment.

Inhomogeneity of the sample was suspected when it was found that reproducible results were not readily obtained. NBS 153 steel samples were received in the form of rather coarse particles and the average particle weighed approximately five milligrams. No further division of the sample was attempted since crushing would undoubtedly have introduced impurities. Since the average sample size for use in this study consisted of not more than 40 particles of the steel, any inhomogeneity of the sample would cause a relatively large error in the titration. To exclude this possibility, samples of approximately seven grams were weighed out, dissolved, and the resultant solution diluted to a known volume. Aliquots of this master solution were then withdrawn for titration.

The necessity for effecting prior separations was also studied in the course of the analysis of this steel sample. It was believed that if chromate were removed it would be possible to titrate cobalt directly with ferricyanide. Volatilization of chromium as chromyl chloride from a solution of boiling perchloric acid seemed to effect this removal quantitatively. The subsequent titrations of cobalt gave spurious results, however.

The next step in the separation study was to precipitate tungsten with cinchonine and molybdenum with ∝-benzoinoxime. Again these were successful for the purpose, but the subsequent titration with ferricyanide failed to give reproducible results. In all cases the excess precipitant was destroyed by evaporation to strong fumes of perchloric acid. Since the method of Dickens and Maassen (36) (titration of cobalt in the presence of ammonia) does not require any preliminary separations for the analysis of this steel, it was not deemed advisable to pursue this phase of the study further.

Reduction of chromate was next investigated. The problem here was to reduce chromium and only chromium to the trivalent state in the hope that the direct titration scheme would then be applicable. Use of peroxide was ruled out by the presence of tungsten and molybdenum, both of which form very stable peroxyacids upon treatment with hydrogen peroxide. A number of other reducing agents were tried in an effort to reduce chromate; these included formaldehyde, oxalate, thiosulfate, nitrite, azide, ferrous sulfate, formic acid, and hydroxylamine. All of these effected the reduction of chromate, but the subsequent titration of cobalt with ferricyanide gave poor results. This is believed due to one or more of the following causes: 1) reduction of one or more of the other constituents of the sample, 2) failure to completely destroy excess reducing agent, and 3) interference in the titration by one of the reaction products. In any case, reduction of sexavalent chromium failed to improve the reproducibility of the cobalt titration.

Choice of complexing agent for ferric iron was the next phase studied. Citrate and tartrate proved to be the best complexing agents for this purpose; fluoride, pyrophosphate, and mannitol were unsatisfactory. Use of sulfosalicylic acid was not permissible since it behaved as a reducing agent insofar as reaction with chromate was concerned. The reduction products rendered the determination of cobalt impossible, whether by the direct or back titration procedures.

Citrate and tartrate are also weak reducing agents, and it was observed that some reaction took place between these reagents and chromate in acid solution. The oxidation of citrate, whether by a single component or by a

heteropoly acid, could be minimized by raising the pH of the solution prior to the addition of citrate. It was found that when the pH of the solution was adjusted to between 2.0 and 2.6, fairly concordant results for cobalt could be obtained. Raising the pH further gave poor results.

The final aspect of this study was concerned with the interference of oxygen in the determination of cobalt. The cobaltous-ethylenediamine system was known to be sensitive to oxygen, and lack of reproducibility might well be attributed to diffusion of air into the solution either before or during the titration. The problem was not studied quantitatively, but every precaution was taken to ensure removal of oxygen from all solutions used during the study. A further advantage to the back titration procedure lay in the fact that ethylenediamine was the last reagent to be added, and hence oxidizing conditions prevailed during all except the last stages of the titration.

Attempts to analyse NBS 153 steel for cobalt were thus not entirely satisfactory. Under certain conditions triplicate analyses were obtained which agreed well with the Bureau's Certificate of Analysis. Subsequent successive titrations yielded values differing by as much as four-tenths of a per cent from the accepted value. These discrepancies could not be explained completely, but one source of the error was thought to be the behaviour of the manganese in the sample. Use of citrate as a complexing agent was known to interfere with the cobalt titration in the presence of major amounts of manganese. Since sulfosalicylic acid could not be used in the analysis of this particular steel, recourse was made to the use of citrate.

Since this steel is probably as complex an alloy as is likely to be met in practice, the failure of the present method was not totally unexpected. The back titration method can be used to approximate the cobalt content of such a chromium-molybdenum-vanadium steel, and a detailed procedure is given for this reason.

F. Recommended Procedures

1. Cobalt in bronze (silver absent).

Weigh accurately a sample of no more than 1 g. and of such size as to contain 5 to 30 mg. cobalt. Dissolve the sample in the minimum amount of nitric acid; 4 ml. are adequate for a 0.3 g. sample. Add 5 ml. of perchloric acid and evaporate the solution to strong fumes over a burner. Cool the mixture, dilute to 30 ml., and boil for five minutes. Cool again and transfer to the titration vessel. Bubble oxygen-free nitrogen through the solution for ten minutes. Add ethylenediamine, 2.5 ml. for a 0.3 g. sample, 5.0 ml. for a 1 g. sample. Titrate the sample with 0.01 N ferricyanide and follow the titration potentiometrically using a platinum-saturated calomel electrode system.

2. Cobalt in bronze (silver present).

Weigh accurately a sample of 0.5 g. or of such size as to contain 5 to 30 mg. cobalt. Dissolve the sample in a mixture of 5 ml. of nitric acid and 5 ml. of perchloric acid, and evaporate the solution to strong fumes of perchloric acid. Cool the mixture and dilute to 30 ml. Boil the clear solution for ten minutes; if a precipitate of silver chloride appears at

this stage the sample must be discarded. After cooling, transfer the solution to the titration vessel and bubble oxygen-free nitrogen through the solution for ten minutes. Add concentrated sodium hydroxide dropwise to the point of incipient precipitation, and then add 5 g. of sodium citrate. In rapid succession add an excess of standard ferricyanide and 2 ml. of ethylenediamine. Titrate the solution with standard cobalt sulfate, following the titration potentiometrically. The ferricyanide should be standardized against cobalt sulfate under the same conditions.

3. Stainless steel.

Weigh accurately a sample of less than 1 g. and of such size as to contain 5 to 30 mg. cobalt. Dissolve the sample in a mixture of 10 ml. of nitric and 10 ml. of hydrochloric acids, using gentle heat as necessary. Add 6 ml. of perchloric acid and evaporate the solution to strong fumes of perchloric acid. Cool the mixture and dilute to 30 ml. with water. Add 4 ml. of 15 per cent hydrogen peroxide and boil the solution for ten minutes to reduce the volume and to destroy the excess peroxide. Transfer the resultant blue solution to the titration vessel, and add 3 g. of sulfo-salicylic acid. Bubble nitrogen through the solution for 15 minutes to ensure the removal of oxygen. Add 5 ml. of ethylenediamine and titrate the sample with 0.01 N ferricyanide, determining the end point potentiometrically.

4. Chrome-vanadium-molybdenum steel (e.g. NBS 153).

Weigh accurately a sample of 0.1-0.2 g. and dissolve in a mixture of 5 ml. of nitric and 5 ml. of hydrochloric acids. Add 5 ml. of perchloric

acid and evaporate over a burner to heavy fumes of perchloric acid. Cool

the mixture, dilute to 30 ml., and boil for ten minutes. Cool again and

transfer the solution to the titration vessel. Add concentrated sodium

hydroxide dropwise to the solution until a pH of 2.0-2.5 is reached.

Bubble nitrogen through the solution for ten minutes. Then add in rapid

succession 5 ml. of saturated sodium citrate solution, an excess of

ferricyanide (25 ml. in the case of NBS 153 steel samples), and 2.5 ml. of

ethylenediamine. Titrate the solution with standard cobalt sulfate,

following the titration potentiometrically.

V. EXPERIMENTAL WORK, PART TWO. USE OF COBALT SULFATE
AS A STANDARD REDUCING AGENT.

A. Preliminary Considerations

Preliminary work had shown that cobalt sulfate is a fairly powerful reducing agent in ethylenediamine solution, the reduction potential of the cobaltous-ethylenediamine system being approximately -0.25 v. The cobaltous-ethylenediamine system is sensitive to oxygen, but difficulty from this direction was obviated by use of a standard solution of cobalt sulfate. The ethylenediamine was added to the solution being titrated. The reducing agent was thus formed in situ upon the addition of cobalt sulfate. A standard solution of cobalt sulfate could be made up by weight and stored indefinitely without loss of titre.

Aside from the advantages of stability on storage and ease of preparation, it was expected that use of this reagent in alkaline solution would enable selective reduction of organic and inorganic compounds. By choice of diamine it was thought possible to vary the strength of reductant and hence enable even more selective reductions.

Initially, however, it was deemed advisable to study the use of the cobaltous-ethylenediamine system as a reducing agent for inorganic compounds. This cobalt complex has the lowest reduction potential of any of the cobalt-diamine systems studied; the diamine was readily purified, and equilibrium potentials were established rapidly in most cases.

It was thought advisable to investigate the reduction of such compounds as permanganate, dichromate, and arsenate which were known to be effective oxidizing agents in acid solution. The second group of elements

to be studied were those such as copper and mercury which formed complexes with ethylenediamine and which were reducible to a lower valence state. The final phase of this study was concerned with heavy metals, such as silver and mercury, which could be easily reduced to the free metal.

Insofar as organic compounds were concerned, the reduction of aromatic nitro compounds was studied. It was thought possible that the cobaltous-ethylenediamine system would reduce nitro groups to amines or possibly to intermediate reduction states. The expected solubility of organic compounds in ethylenediamine solution would enhance the practicality of these reductions. Here again by choice of diamine it might be possible to selectively reduce the nitro group to a nitroso or related group.

B. Reduction of Group VIA Anions

The first group of cations to be studied for their oxidizing power in alkaline solution were the metals of group VIA. Chromate, molybdate, tungstate, and uranate are all fairly easily reduced in acid solution, and it was expected that while this behaviour was pH dependent some reduction would take place in alkaline solution. A calculation indicated that the reduction potential for the chromate-chromous couple would be about -0.1 v. at a pH of 10, and hence reaction with the cobaltous-ethylenediamine complex would be expected to occur. The other group VI metals are less powerful oxidizing agents, but at the same time their reduction potentials are less pH dependent.

1. Reduction of dichromate.

The attempt to titrate dichromate with cobalt sulfate in ethylene-diamine solution met with failure. The initial Pt/S.C.E. potential of -0.26 v. reached -0.49 v. (essentially that of the cobaltous-ethylenediamine system) after the addition of one ml. of cobalt sulfate, whereas, complete reduction of the dichromate would have required more than 20 ml. of the cobalt solution. Apparently no reaction occurred between dichromate and the cobaltous-ethylenediamine complex at room temperature and at pH 10.

Attempts to facilitate the above reaction by complexation of the chromous ion failed. Also ineffective was the direct titration of di-chromate with cobalt sulfate in the presence of ethylenediamine and any one of the following: tartrate, citrate, thiocyanate, and sulfosalicylate. The potential drifted somewhat when citrate or tartrate were present, indi-cating a chemical reaction. However, the reaction could not be followed potentiometrically and was too slow to be of use as an analytical method. Dichromate was found to react with sulfosalicylic acid at low pH and hence this complexing agent could not be used.

The failure of the above complexing agents to improve the titration of dichromate may be explained on the basis of the slowness with which chromous complexes form. According to Taube (50), chromous complexes with such ligands as thiocyanate and tartrate form at a slow, measurable rate. Also chromousamine complexes are known to be of the inert type, and hence the failure of the cobaltous-ethylenediamine ion to reduce dichromate under alkaline conditions is probably due to kinetic phenomena.

2. **Reduction of molybdate.**

The reduction of molybdate in alkaline solution using the cobaltous-ethylenediamine system as a reducing agent failed to take place. The direct titration of molybdate with cobalt sulfate behaved as if molybdate was absent; no color change was observed and the Pt/S.C.E. potential reached -0.515 v. after the addition of 2 ml. of titrant. Addition of citrate, tartrate, and sulfosalicylate did not improve the titration and results were negative using the above complexing agents. Here again kinetic considerations may enter the picture, but the net result was that no reaction occurred under the conditions of the titration.

3. **Reduction of uranate.**

The next anion to be studied was that of the uranyl ion. Several grams of pure uranium were dissolved in nitric acid and diluted to a known volume. Aliquots of this solution were taken and attempts were made to titrate uranyl nitrate with cobalt sulfate in ethylenediamine solution. These attempts were unsuccessful for the apparent reason that the oxidizing power of the uranyl ion is decreased to such an extent in alkaline solution that it is not reduced by the cobaltous-ethylenediamine complex. No attempt was made to raise the temperature in hope of promoting the rate of reaction since the problem of oxygen diffusion into the solution is greater at boiling temperatures.

Several attempts were made to displace the reaction of uranate with cobaltous-ethylenediamine sulfate by complexing quadrivalent uranium with oxalic acid, ethylenediaminetetraacetic acid, and sulfosalicylic acid. Of

these only versene had any noticeable effect, and in this case the effect was deleterious. In the presence of versene and ethylenediamine, cobaltous salts do not exhibit reducing properties. A competitive complexation between these two ligands is thought to occur, and the chelation of the cobaltous ion with versene negates the corresponding effect of ethylenediamine with the cobaltic ion.

C. Reduction of Other Anions

1. Titration of stannate.

A number of other metal-containing anions were studied insofar as their reduction by cobaltous salts in ethylenediamine solution was concerned. A solution of sodium stannate was made up and aliquots withdrawn for titration. No reaction between the stannic ion and cobaltous-ethylenediamine sulfate was observed. Tartrate and oxalate failed to improve the titration of stannic ion.

2. Reduction of arsenate.

A solution of sodium arsenate was made up by weight and aliquots withdrawn for titration. At pH 10 no reaction was observed between pentavalent arsenic and the cobaltous-ethylenediamine complex. Here again the reduction potential was depressed to such an extent in basic solution that reaction did not occur. Tartrate and thiosulfate had no beneficial effect on the titration.

3. Titration of vanadate.

The attempted titration of pentavalent vanadium with cobalt sulfate in ethylenediamine solution was also unsuccessful. The potential of the platinum indicator electrode reached a value of -0.40 v. vs. the saturated calomel electrode after the addition of only 2 ml. of titrant. This was the same behaviour as found with a blank determination. Apparently no reaction occurred. The addition of citrate, tartrate, and sulfosalicylate had no effect on the titration.

D. Titration of Permanganate

The determination of permanganate by titration with cobalt sulfate in ethylenediamine solution presented a number of rather unique problems. Potassium permanganate solutions are known to be excellent oxidizing agents in alkaline solution, and the usual reduction product is hydrated manganese dioxide. The fact that a precipitate was involved during the titration proved to be a stumbling block insofar as the potentiometric method was concerned.

The first step in a systematic study of the permanganate titration was to add a dilute solution of potassium permanganate to an ethylenediamine solution and titrate with cobalt sulfate. Immediately upon adding the permanganate to the ethylenediamine, the solution was discolored indicating oxidation of organic material. Further titration with cobalt sulfate met with failure owing to precipitation of manganese dioxide and concomitant drifting of the potential.

It was postulated that if permanganate were added to an excess of cobalt sulfate in ethylenediamine solution and the excess back titrated with ferricyanide, that 1) permanganate would be reduced to the bivalent form and 2) oxidation of organic material would be minimized. Since manganous salts are oxidized to manganese dioxide by ferricyanide in alkaline solution, sulfosalicylate was added to complex trivalent manganese. Accordingly, an aliquot of 0.01 N potassium permanganate was slowly added to a solution of cobalt sulfate in ethylenediamine solution. Sulfosalicylic acid was then added and the resulting solution back titrated with 0.01 N potassium ferricyanide. The titration was followed potentiometrically and in Figure 9 is shown the titration curve so obtained. The first break in the titration curve was the end point for the back titration of excess cobalt sulfate; the result agreed closely with the theoretical amount based on the reduction of permanganate to bivalent manganese. The second portion of the titration curve was that showing the end point for the oxidation of bivalent manganese to the complex of trivalent manganese with sulfosalicylate.

For this latter oxidation results were high and not exactly reproducible. This was believed due to the presence of bivalent manganese salts in the permanganate, which had been standardized by titration against sodium oxalate. Accordingly, an aliquot of the permanganate was boiled with periodic acid and compared spectrophotometrically with permanganate solutions of known concentration. A Beckman Model B spectrophotometer was used for this purpose and readings were taken at 525 m . Results on two different aliquots showed that there was no detectable amount of bivalent manganese present in the permanganate solution.

Fig. 9   Back Titration of Excess Cobalt Sulfate with 0.01 N Ferricyanide following Addition of Permanganate.   Ethylenediamine and Sulfosalicylate Present.
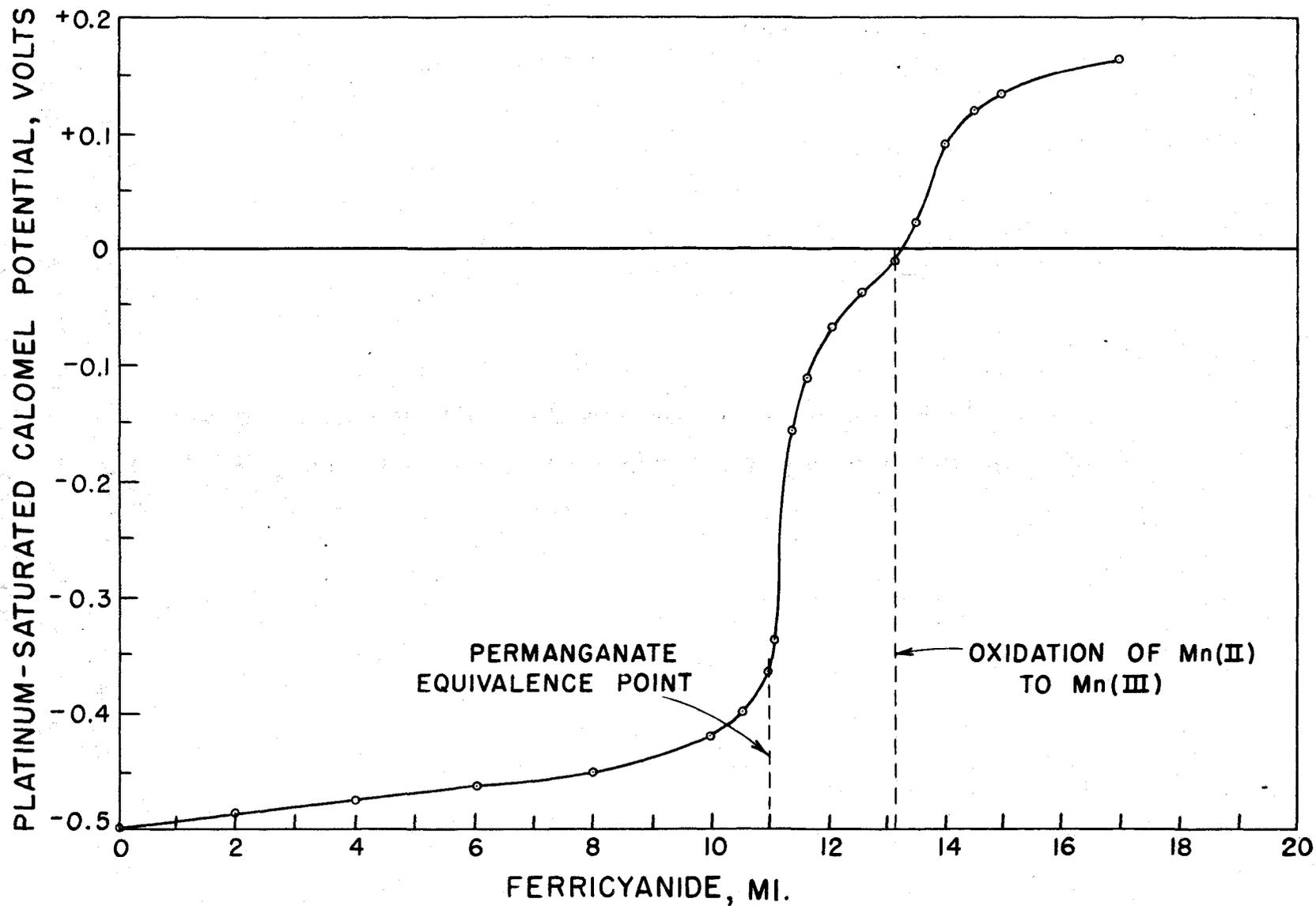
It was found that the rate of addition and the concentration of the permanganate added to the cobaltous-ethylenediamine system affected the position of the second end point in the titration with ferricyanide. This indicated that some permanganate had reacted with the ethylenediamine, possibly yielding an amine oxide. Amines are readily oxidized in alkaline solution, and this effect would be expected for ethylenediamine. However, since results based on the second portion of the titration curve were neither stoichiometric nor exactly reproducible, an alternative means of reducing permanganate was necessary.

The apparent solution to this problem would have to involve the reduction of permanganate in the absence of ethylenediamine, since oxidation of the latter is variable. But this would rule out the use of cobalt sulfate as a reducing agent, and this was to be the basis for the method. The way out of this dilemma was to add permanganate to a neutral or weakly acid solution of potassium ferrocyanide; the permanganate was reduced to the bivalent state and an equivalent amount of ferricyanide was formed. Ethylenediamine was then added and the ferricyanide back titrated with cobalt sulfate. Sulfosalicylic acid was added to inhibit the formation of manganese dioxide. The following reactions are the basis for the method:

$$KMnO_4 + 5K_4Fe(CN)_6 + 4H_2SO_4 \longrightarrow MnSO_4 + 5K_3Fe(CN)_6 + 3K_2SO_4 + 4H_2O$$

$$MnSO_4 + K_3Fe(CN)_6 \xrightarrow[HSS]{OH^-} Mn^{+3}(HSS)_n + K_4Fe(CN)_6$$

$$K_3Fe(CN)_6 + Co(en)_n^{++} \longrightarrow Co(en)_n^{+3} + K_4Fe(CN)_6$$

$$Mn(HSS)_n^{+3} + Co(en)_n^{++} \longrightarrow Co(en)_n^{+3} + Mn(HSS)^{++}$$
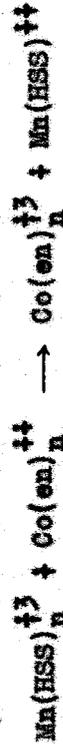
where en = ethylenediamine

HSS = sulfosalicylic acid.

In Figure 10 is shown a typical titration curve for the determination of permanganate by the above method.

Two distinct breaks in the titration curve were observed, and it seemed possible to determine permanganate and bivalent manganese with one titration. The permanganate could be determined by titrating the ferricyanide produced upon reaction with excess ferrocyanide. The second break in the curve should require one-fifth as many equivalents of reductant since a one-electron change is involved. If bivalent manganese salts were present the second end point should be displaced by an equivalent amount. The successive determination of permanganate and manganous ion by titration with cobalt sulfate was confirmed experimentally, but the results were not as precise as desired. In Table 6 are given a series of results for the analysis of synthetic mixtures of permanganate and manganous ion. Removal of oxygen from all solutions prior to the titrations improved the precision somewhat, but the results were not entirely satisfactory. Apparently the reoxidation of bivalent manganese with ferricyanide does not occur in a reproducible manner.

The next approach to the problem of determining permanganate using ferrocyanide was to add phosphate instead of sulfosalicylic acid in the theory that this reagent would precipitate bivalent manganese in alkaline solution; oxidation to the trivalent state with ferricyanide would thus be obviated. The following method was used to determine permanganate: a solution containing potassium dihydrogen phosphate and excess potassium ferrocyanide was freed of dissolved oxygen by flushing with nitrogen. Several drops of 1:1 sulfuric acid were added and then an aliquot of 0.01 N

Fig. 10   Titration with 0.01 N Cobalt Sulfate of the Ferricyanide Produced
by Treatment of Excess Ferrocyanide with Permanganate in Acid
Solution. Ethylenediamine and Sulfosalicylate Present.
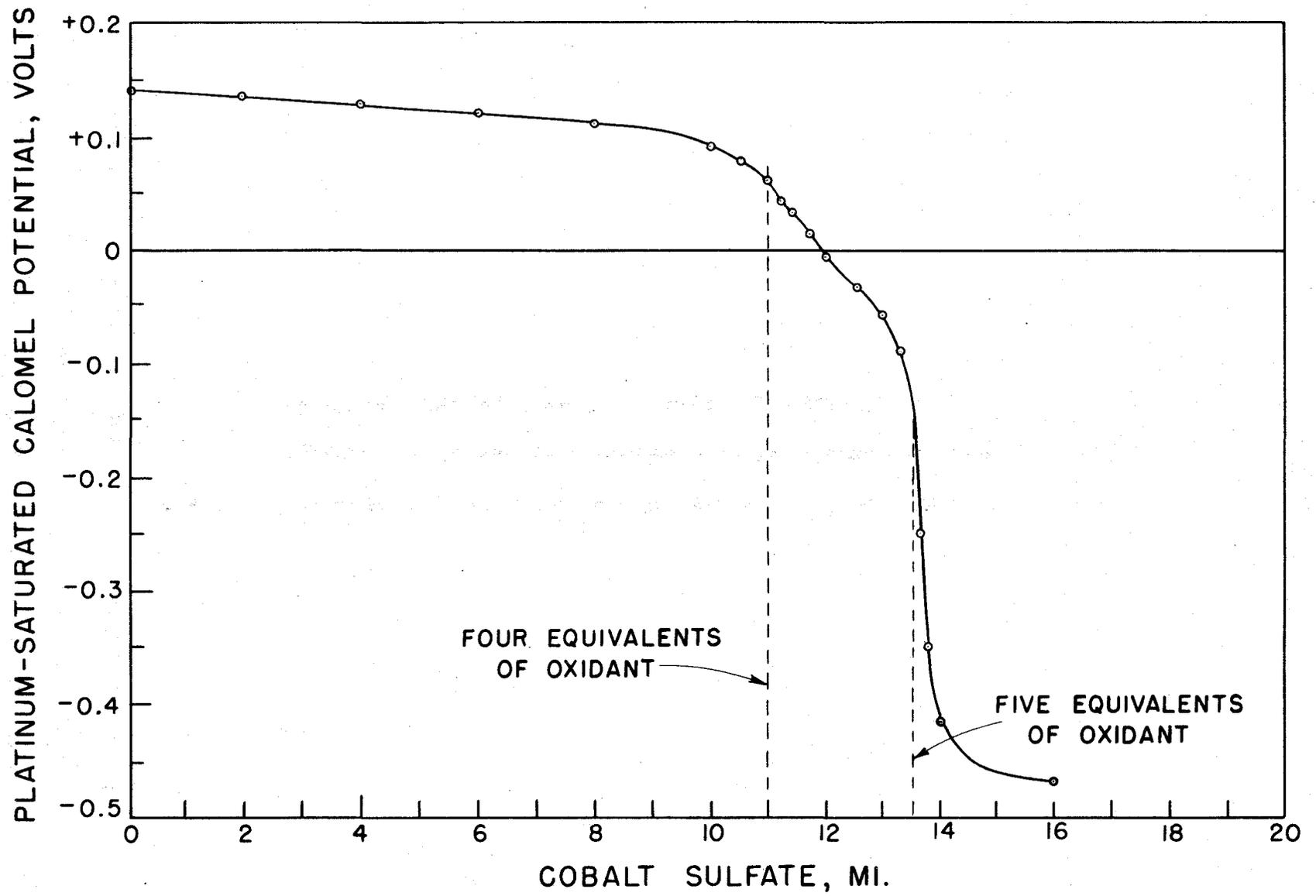
Table 6. The Determination of Permanganate and Manganous Ion by

Reaction with Ferrocyanide and Beck Titration of Ferricyanide

with Cobalt Sulfate in Ethylenediamine Solution.

| Mn(II) Taken, mg.	Cobalt Sulfate Required for Beck Titration, ml.	Mn(II) Found, mg.	Mn(VII) Taken, mg.	Cobalt Sulfate Required for Beck Titration, ml.	Mn(VII) Found, mg.
3.06	5.60	3.08	1.39	12.9	1.44
3.06	6.20	3.42	1.39	13.3	1.48
3.06	6.10	3.35	1.39	13.2	1.47
3.55	7.10	3.91	1.39	13.4	1.49

potassium permanganate was pipetted into the titration vessel. Ethylenediamine was then added and the solution titrated with cobalt sulfate. In Figure 11 is shown the potentiometric titration curve so obtained. Only one break in the titration curve was observed. Three titrations gave identical results and all were slightly high: taken, 1.39 mg. manganese; found, 1.45 mg. manganese. The method is clean-cut and highly reproducible; for accurate results the cobalt sulfate should be standardized against permanganate of known normality by the method described above.

In the course of the above work it was found necessary to determine the ferricyanide content of the potassium ferrocyanide used in the titration studies. Titration with cobalt sulfate in ethylenediamine solution is an excellent means of analysis for ferricyanide, since large amounts of ferrocyanide do not interfere in the titration.

E. Titration of Metal-Amine Complexes

A number of metals are known to form ammine complexes in alkaline solution. The work of Bjerrum (51) was instrumental in establishing the stability constants of many metal-amine systems, and the recent book of Martell and Calvin (52) contains an appendix listing chelate stability constants. Much data remain to be gathered, but a thorough groundwork has been laid for further systematic study in this field.

Fig. 11 Titration with 0.01 N Cobalt Sulfate of the Ferricyanide Produced

by the Reaction of Permanganate with Excess Ferrocyanide.

Ethylenediamine and Phosphate Present.
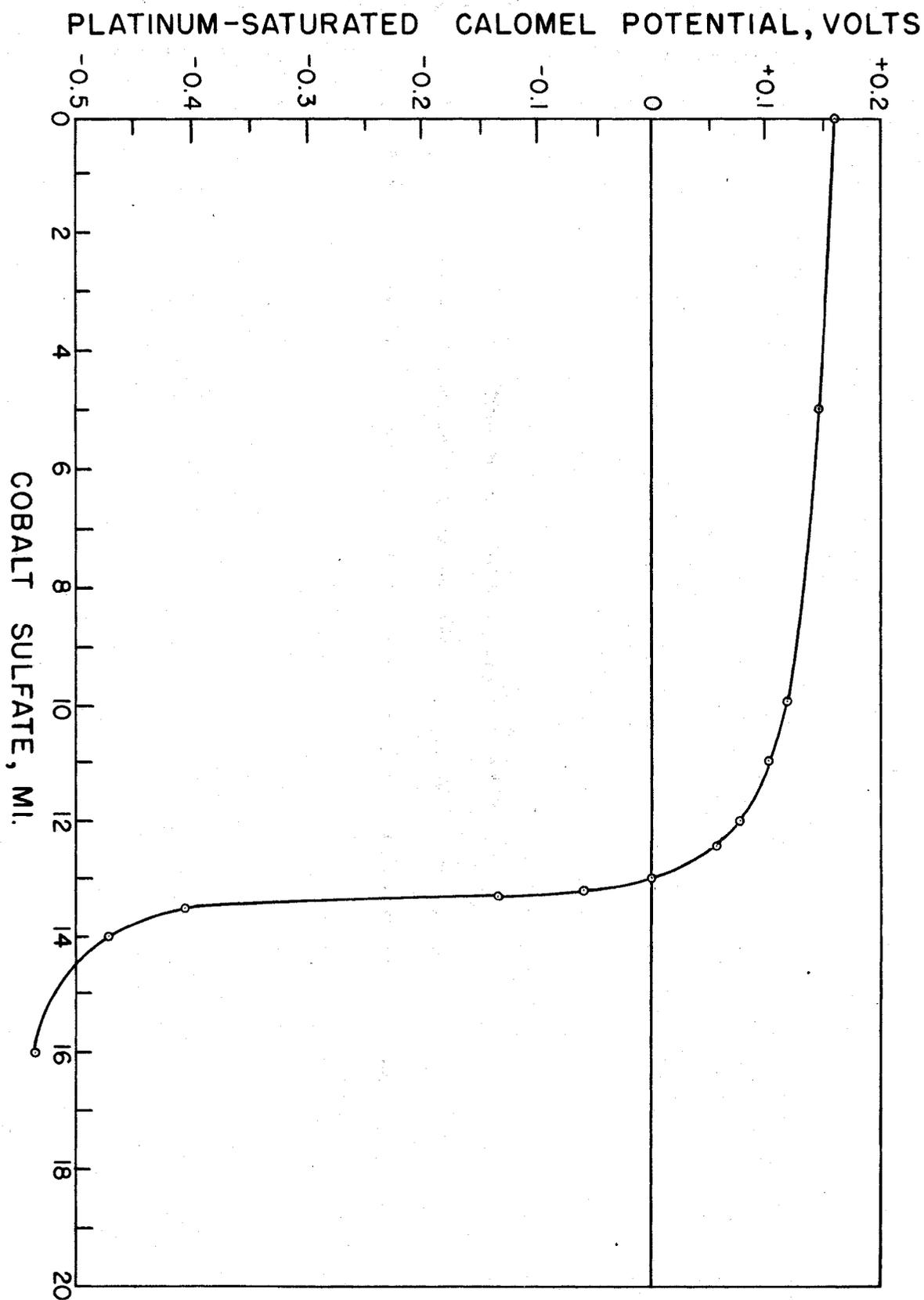
1. **Titration of copper.**

Monovalent and bivalent copper ions form a number of amine complexes of varying stability. The intense blue-colored cupric ammonia complex is well known in analytical chemistry, and the corresponding cuprous ammonia system has been used as an absorbent for oxygen. The oxidation-reduction characteristics of these species have been calculated, and a method for the separation of silver from copper is based on these properties (53).

Ethylenediamine forms a deep purple complex with bivalent copper. The cuprous complex with this ligand is colorless and somewhat less stable. By analogy with the ammonia complexes, it was believed possible to reduce the cupric to the cuprous ion in ethylenediamine solution using cobalt sulfate as the reducing agent. Accordingly, an aliquot of a copper sulfate solution was pipetted into the titration vessel, ethylenediamine added, and the solution titrated with cobalt sulfate following removal of oxygen from the solution. No color change was observed during the titration, and the potential of the platinum indicator electrode reached -0.47 v. vs. the calomel electrode after the addition of one ml. of titrant. Apparently the cuprous-ethylenediamine complex is at least as powerful a reducing agent as is the cobaltous-ethylenediamine system.

This conclusion was confirmed by the titration of cobalt sulfate with ferricyanide in ethylenediamine solution and in the presence of copper sulfate. Only one break in the titration curve was observed, and this agreed with the equivalence point for cobalt alone.

2. Titration of mercury.

In the case of mercury, the log equilibrium formation constant for the mercuric-ethylenediamine complex is given as 12.09 (54). The mercurous complex with this chelating agent would be expected to be considerably less stable, and the log equilibrium formation constant has not been reported. It was thought worthwhile, however, to attempt the reduction of the mercuric to the mercurous ion using cobalt sulfate in ethylenediamine solution. An aliquot of a mercuric chloride solution was pipetted into the titration vessel and the solution freed of dissolved oxygen. Five drops of 1:1 sulfuric acid were added and then 2 ml. of ethylenediamine. Titration with cobalt sulfate gave evidence of an equilibrium process, but some reaction did take place. It appeared that an excess of cobalt sulfate was necessary to reduce the mercuric-ethylenediamine complex to the corresponding mercurous chelate compound.

The next step was to add mercuric chloride to an excess of cobalt sulfate in ethylenediamine solution and back titrate the cobaltous complex with ferricyanide. This was done and the solution warmed to 60° to promote the reaction between the mercuric- and the cobaltous-ethylenediamine complexes. Back titration with ferricyanide gave a value which coincided with the equivalence point based on the amount of cobalt taken. The failure of reduction in this case is believed due to the instability of the mercurous-ethylenediamine system.

Another experiment was run in which sodium chloride was added to the mercuric chloride solution in the hope that by the formation of calomel the reaction with cobaltous-ethylenediamine sulfate would be favored. This

expedient failed to displace the reaction, and reduction with cobalt sulfate in ethylenediamine solution was ineffective.

F. Chemical Reduction of Heavy Metals

The final aspect of inorganic reduction using cobalt sulfate to be studied was that of reduction of heavy metals to the free state. In the case of silver-bearing cobalt bronze, it was found necessary to use the back titration procedure because of the interference of free silver formed in the course of the titration with cobalt sulfate. Further study revealed that the reduction of silver-containing solutions with cobaltous-ethylenediamine sulfate proceeded at such a rate as to render the titration useless as an analytical method.

Addition of excess cobalt sulfate to a solution of silver nitrate and back titration of the cobalt with ferricyanide was ineffective in that some silver was reoxidized during the course of the titration. No attempt was made to filter off the precipitated metal since this would involve exposure to air. In some cases silver deposited as a mirror on the walls of the titration vessel, and it was found that this freshly deposited metal reacted with ferricyanide during the titration.

In the case of mercury, reduction of the metal did not occur using the cobaltous-ethylenediamine complex as a reducing agent. Addition of excess cobalt sulfate and warming the solution to 60° failed to displace the reaction. Apparently the reduction of mercuric ion to the free metal in ethylenediamine requires a more powerful reducing agent than the cobalt-ethylenediamine system. No doubt the stability of the mercurio-ethylenediamine complex lowers the reduction potential of the mercuric-mercurous

couple considerably; this would tend to inhibit chemical reduction to the metal.

G. Reduction of Organic Nitro Compounds

The failure of ethylenediamine solutions of cobalt sulfate to reduce inorganic compounds was believed to be due to the dependence of the reduction potentials on pH and to the stabilizing effects of chelation with ethylenediamine.

In acid solution organic nitro compounds are reduced to amines by treatment with titanous chloride. The reaction is quantitative and is the basis for an analytical method (55). Since the reduction potential of the cobaltic-cobaltous couple in ethylenediamine solution compares favorably with that of titanous chloride in acid solution, use of the former reagent was believed possible for the reduction of organic nitro compounds. A further consideration would be the increased solubility of organic compounds in ethylenediamine solution.

A dilute solution of p-nitrophenol was made up and an aliquot withdrawn for titration. Ethylenediamine was added and the solution titrated with cobalt sulfate. The titration curve was superimposable on that of the blank, and no apparent reduction occurred at room temperature.

The attempted reduction of p-nitrophenol was repeated only using an excess of cobalt sulfate and back titrating with ferricyanide. Here again no reduction of the nitro compound was observed. Refluxing for five minutes gave no improvement in the attempted titration of the nitro group.

A sample of picric acid was weighed out and dissolved in water. An aliquot of this solution was pipetted into the titration vessel and an excess of cobalt sulfate added. Ethylenediamine was then added and the solution refluxed for five minutes under an atmosphere of nitrogen. Back titration with ferricyanide gave results identical with that of the blank. The failure of any reduction to occur in the case of picric acid would seem conclusive evidence that aromatic nitro compounds cannot be reduced by cobalt sulfate in ethylenediamine solution. Further study of the reduction of other organic compounds was not made since the same type of pH dependence would be expected.

VI. SUMMARY

1. A literature survey of the existing volumetric methods for the determination of cobalt has been presented. A critical analysis has been made of the ferricyanide titration of cobalt in ammoniacal solution.

2. An improved ferricyanide titration has been described in which ammonia is replaced by ethylenediamine as the complexing agent for the cobaltic ion. The cobaltous-ethylenediamine complex is a stronger reducing agent by some 0.5 v. than the corresponding ammonia-cobalt system, and the potential break at the end point is augmented by a similar amount.

3. Optimal conditions for the determination of cobalt have been established. Care must be taken to avoid the untoward effects of air. The determination can be carried out as a direct titration in most instances.

4. The effect of other metals on the ferricyanide titration of cobalt in ethylenediamine solution has been studied. The presence of iron was found to shift the potential at the start of the titration by as much as 0.4 v. The use of citrate, tartrate, fluoride, pyrophosphate, mannitol, and sulfosalicylate was studied in connection with the complexation of ferric iron. Nickel and copper were found not to interfere in the direct titration of cobalt with ferricyanide in ethylenediamine solution. The interference of manganese in the cobalt determination was studied in detail. It was found that citrate could not be used as a complexing agent when manganese was present; the manganese-citrate complex was oxidized by ferricyanide concomitantly with the cobaltous-ethylenediamine complex. Results for both cobalt and manganese were in error. Using sulfosalicylic acid, however, the successive titration of cobalt and manganese was possible in

ethylenediamine solution using ferricyanide as the oxidizing agent.

The back titration of excess ferricyanide with cobalt sulfate was found necessary when silver or a three-component mixture of tungsten (or molybdenum), chromium, and vanadium was present. Using this procedure the interference of these elements was obviated.

5. The application of the present method to the determination of cobalt in ferrous and non-ferrous alloys has been made. The following alloys have been analysed for cobalt with excellent results (all figures are percentages): 1) Armco stainless steel #29 containing 18 chromium, 10 nickel, 0.60-0.65 cobalt, 1.20-1.35 manganese, and niobium in unreported amount; 2) Ampcoloy beryllium bronze #91 containing 96.49 copper, 0.602 beryllium, and 2.897 cobalt; 3) beryllium bronze Alloy A containing 2.00-2.25 beryllium, 0.53 cobalt, and lesser amounts of iron, silicon, aluminum, tin, lead, zinc, and nickel; 4) beryllium bronze Alloy B containing 1.85-2.00 beryllium, 0.27 cobalt, and small amounts of iron, silicon, aluminum, tin, lead, zinc, and nickel; 5) beryllium bronze Alloy C containing 1.00-1.25 beryllium, 0.33 cobalt, 1.50-2.25 zinc, 0.35 iron, and small amounts of silicon, aluminum, tin, lead, and nickel; and 6) silver-bearing beryllium bronze Alloy D containing 0.25-0.50 beryllium, 0.90-1.10 silver, 1.71 cobalt, and lesser percentages of iron, silicon, aluminum, tin, lead, zinc, and nickel. The experimental conditions for carrying out these determinations have been described.

6. The analysis for cobalt in National Bureau of Standards 153 steel has been studied in detail. This steel contained macro amounts of chromium, vanadium, molybdenum, tungsten, and cobalt and smaller amounts of manganese

and phosphorus. The peroxide reduction of chromium could not be used due to the formation of stable peroxyacids of tungsten and molybdenum which interfered in the titration. Use of sulfosalicylate was ruled out since this reagent reacted with dichromate in acid solution. Furthermore, the direct titration procedure was inapplicable owing to the presence of tungsten, vanadium, and chromium.

The best solution to the problem of determining cobalt in this steel was to use citrate as the complexing agent with cobalt sulfate. Fair precision was obtained using this method. No separations were necessary prior to the titration and the method was rapid. The complex nature of the steel would account for the failure to obtain better precision; results ranging from 8.18-8.51 per cent cobalt were obtained, while the accepted value was given as 8.45 per cent.

7. The stability of potassium ferricyanide solutions has been qualitatively studied in the course of this research. Hundredth normal solutions of this reagent were found to be considerably more stable on storage than were tenth normal solutions.

8. The use of ethylenediamine solutions of cobalt sulfate as reducing agents has been studied. The formal reduction potential of the cobaltous-cobaltic couple in ethylenediamine solution was found to be approximately -0.25 v.

9. The attempted reduction of a number of anions using cobalt sulfate in ethylenediamine solution has been described. The failure of this reagent to reduce chromate, molybdate, vanadate, arsenate, uranate, and stannate was attributed to kinetic phenomena and the dependence on pH of

the reduction potentials of these anions.

10. The determination of permanganate by reaction with cobalt sulfate in ethylenediamine solution has been studied in detail. Permanganate was found to react with ethylenediamine itself, and erratic results were attributed to the variable oxidation of organic matter. A solution to this problem was found by adding permanganate to an acid solution of potassium ferrocyanide and back titrating the ferricyanide so produced. Phosphate was added to prevent the reoxidation of manganous ion by ferricyanide in alkaline solution.

11. The reduction of metal-amine complexes using cobalt sulfate in ethylenediamine solution as a reducing agent has been attempted. No reaction was observed between copper or mercury and cobalt sulfate in ethylenediamine solution. Apparently the bivalent complexes of these metals with ethylenediamine were not reduced to the corresponding monovalent complexes.

12. The reduction of heavy metals such as silver and mercury by ethylenediamine solutions of cobalt sulfate has been studied. Reduction of mercury to the free metal by treatment with cobalt sulfate in ethylenediamine solution was ineffective. Silver was reduced to the metal, but the reaction was so slow as to be useless as an analytical method.

13. The attempted reduction of organic nitro compounds using cobalt sulfate in ethylenediamine solution has been made. Picric acid and p-nitrophenol failed to react with this reagent at reflux temperatures. The cause of this was attributed to the dependence of organic reductions on conditions of acidity.

VII. REFERENCES CITED

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VIII. ACKNOWLEDGMENTS