THE DETERMINATION OF SMALL AMOUNTS OF

ZINC IN ORES

by

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A Thesis Submitted in Partial·Fulfilment of

the Requirements for the Degree of

MASTER OF ARTS

in the Department

of

CHEMISTRY

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1949

ABSTRACT

The determination of zinc by the back
titration of excess potassium ferrocyanide is
investigated and found very accurate and simple to
perform. The use of the external indicator method
is shown to be inaccurate and unreliable. A new
indicator giving excellent results is developed for
the titration of ferrocyanides with potassium
permanganate.

DEDICATION

The work in this thesis is dedicated

to

J. ALLEN HARRIS, PROFESSOR

for his continuous encouragement and assistance

during the course of this research.

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THE DETERMINATION OF SMALL AMOUNTS OF
ZINC IN ORES

INTRODUCTION

The accurate quantitative determination of zinc has been a difficult problem for a long time. One of the most satisfactory and yet inconsistent methods in use, since the beginning of the twentieth century, has been the ferrocyanide method.

In 1904 W. G. Waring[1] published a comprehensive article on the ferrocyanide method, indicating the many ways in which errors could be made in the determination of zinc in ores. According to Waring the precipitation of zinc by ferrocyanide proceedes in two stages.

$$4ZnCl_2 + 2K_4Fe(CN)_6 \longrightarrow 2Zn_2Fe(CN)_6 + 8KCl \qquad (1)$$

$$6Zn_2Fe(CN)_6 + 2K_4Fe(CN)_6 \longrightarrow 4K_2Zn_3\left[Fe(CN)_6\right]_2 \qquad (2)$$
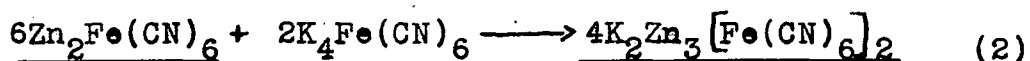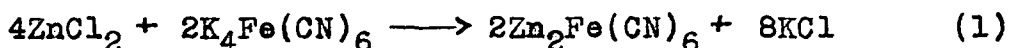
In 1907 W. H. Seaman[2] showed the great variety of results that could be obtained by varying the acidity, the temperature of the titration, and the concentration of the zinc and proposed optimum values at which to work. In the same year Wm. H. Keen[3] outlined a method for purification of a standard zinc solution with which he tested the accuracy of the ferrocyanide method.

Since the time of the above work many other quantitative methods of analysis for zinc have been

proposed using a great variety of reagents such as the pyrophosphate gravimetric method suggested by Stone[4], the mercuric zinc thiocyanate method suggested by Sarudi[5], and many reactions involving organic reagents for both colorimetric and gravimetric determinations. In this thesis, however, I shall be chiefly concerned with the improvement of the ferrocyanide method.

THE FERROCYANIDE METHOD

The External Indicator and the Effect of Ammonium Chloride.

It was early decided that the number of variables affecting the accurate ferrocyanide titration of a sample containing zinc were so numerous that a systematic method for investigation must be used. The variables are listed below with the treatment given them.

Acidity. The acid used was hydrochloric, the optimum concentration for the determination being between 0.3 to 0.5 moles per liter according to the work of Waring[6] and Seaman[7]. The concentration used was 0.4 moles per liter in the final volume of the titration solution.

Temperature. The temperature was held constant between (68 - 72)$^{\circ}$C. by means of a steam bath, optimum temperature conditions being in this range[8].

Indicator. A saturated solution of the standard external indicator, uranyl acetate, was used. In later work

ferrous ammonium sulfate was used.

Zinc Solution. A solution of 0.005184 grams per liter was used. Since no high grade purity zinc was available at the time, a combination of Waring's[9] and Keen's[10] method for purifying the C. P. grade zinc for use as a standard was carried out. Essentially the process was the following. The metallic zinc was washed with NH_4Cl and NH_3 (6N), rinsed three times with distilled water and five times with redistilled alcohol and carefully dried. Approximately ten grams was then accurately weighed, dissolved in dilute hydrochloric acid, treated with excess bromine which was then expelled, and then made basic with excess NH_4OH and NH_4Cl. The resulting small precipitate of $Fe(OH)_3$ impurity was washed carefully, redissolved and reprecipitated three times, and each time the filtrate was added to the main zinc solution. The precipitate of $Fe(OH)_3$ was then burned and determined as Fe_2O_3 and silica and this was deducted from the original weight of zinc. Later a solution requiring the presence of no NH_4Cl was made up from slab zinc spelters from the U. S. Bureau of Standards of a special high grade, with an analysis of 99.995 per cent purity. Both of the above solutions were checked for content of zinc by first, the formation of $ZnNH_4PO_4$ and second, the formation of $Zn_2P_2O_7$.

Potassium ferrocyanide. A solution 0.2096N (combining normality) was made up from crystals from the U. S. Bureau

of Standards with a purity of 99.97 per cent.

Time.   The time allowed for complete reaction was held constant at five minutes, the minimum required time for formation of a stable precipitate being three minutes.[11]

The time of addition of $K_4Fe(CN)_6$ solution was held constant at sixty seconds. Faster addition formed an unbreakable colloidal solution with consequent high absorption of $K_4Fe(CN)_6$.

Stirring.   Mechanical stirring was used as being the most efficient and satisfactory.

Dilution.   The volume of the solution was adjusted so that the final volume would always be 200 $\pm$ 2 milliliters.

Electrolyte.   The electrolyte used was recrystallized ammonium chloride in varying concentrations from 0.00 to 1.500 moles per liter.

Other factors.   The possibility of factors as yet unknown that would affect the accuracy of titration with ferro-cyanide are to be seriously considered.

The first investigation consisted in holding all of the above listed conditions constant except the concentration of ammonium chloride, and observing the variations from accuracy.

The volume of $K_4Fe(CN)_6$ added was found to steadily decrease as the concentration of NH_4Cl increased, finally reaching a minimum optimum value. Greater

concentrations of NH_4Cl then gradually increased the volume of ferrocyanide required to give an end point. With insufficient electrolyte in solution the formation of the colloidal $Zn_2Fe(CN)_6$ is favored and consequently large amounts of absorbed potassium ferrocyanide are occluded with the colloid. With too large concentrations of NH_4Cl it is impossible to prevent it from crystallizing out around the edges of the hot solution and so possibly crystallizing also, small amounts of $K_4Fe(CN)_6$ at the edges before it has a chance to be stirred completely into the solution. This is an objection to the mechanical method of stirring.

During the course of the titrations it was observed that the time required for development of the brown uranyl ferrocyanide precipitate, $(UO_2)_2Fe(CN)_6$, in the spot plate, varied tremendously for the actual titration and for the blank; the blank being ten to fifteen times slower in developing the color. The blank was of course the free blank, the solution reagents alone.

I considered that the most obvious reason for the slower reaction was, that without the presence of the zinc ferrocyanide precipitate, the brown uranyl ferrocyanide precipitated very slowly and finely, making early detection difficult. That is, the potassium zinc ferrocyanide precipitate would affect the end point determination in two ways: first, the excess $K_4Fe(CN)_6$ adsorbed on the

surface of the colloidal zinc precipitate, and thus presented more surface for the uranyl acetate to act; and second, the brown uranyl ferrocyanide formed, adsorbed on the surface of the zinc precipitate and thus the brown color developed and settled much more rapidly. The difference in the color development time varied the blank "end point" by as much as 0.05 to 0.20 milliliters, an error of one per cent, since the end point in the external indicator is determined on a set time basis (one minute after addition of the drop of test solution). On the basis of this reasoning then, I thought it advisable to re-run all the determinations, each time filtering the zinc precipitate, washing it thoroughly with hot water containing NH_4Cl, and then transferring it to the blank solution. The two tables of results below represent at least two and in some cases (where results seem to be inconsistent) as many as six titrations. The results tabulated are the averages.

TABLE I

Volume Variation of $K_4Fe(CN)_6$

with Different Concentrations of NH_4Cl

Concentration of NH_4Cl (m/1)	Corrected Volume of Titration (m/1)	Per Cent Error in Titrations
0.000	20.71	3.03
0.0467	20.42	1.60
0.0934	20.35	1.25
0.140	20.30	1.00
0.187	20.24	0.70
0.234	**20.20**	**0.50**
0.280	20.31	1.05
0.327	20.34	1.20
0.374	20.34	1.20
0.420	20.33	1.15
0.560	20.35	1.25
0.934	20.38	1.40
1.401	20.42	1.60

(Theoretical Volume of $K_4Fe(CN)_6$ Required = 20.10 ml.)

TABLE II

Volume Variation in Blank Determination

Conc. of NH_4Cl (m/1)	Vol. of Blank (No ppt)	Vol. of Blank (In pres. of ppt)	Per Cent Error in Blank	Per Cent Error In Det'n Due to Blank
0.000	0.70	0.75	7.0	0.25
0.0467	0.57	0.70	19.0	0.70
0.0934	0.58	0.69	16.0	0.60
0.140	0.55	0.62	11.0	0.40
0.187	0.50	0.59	15.0	0.50
0.234	0.53	0.61	13.0	0.40
0.280	0.51	0.61	16.0	0.50
0.327	0.59	0.68	13.0	0.50
0.374	0.56	0.66	15.0	0.50
0.420	0.57	0.67	15.5	0.50
0.560	0.43	0.49	12.0	0.30
0.934	0.40	0.50	20.0	0.50
1.401	0.42	0.64	34.0	1.05

Figure I, Curve (1) and Curve (2) show nicely

the effect of the NH_4Cl on the blank determination. The

Curve (1): No ppt. present in the Blank.

Curve (2): Zinc Ferrocyanide ppt. present in the Blank.

Curve (3): Actual titration of Zinc. (Ordinate 20.00)

CURVE (2)

CURVE (1)

CURVE (3)

FIGURE I

TITRATION CURVE USING $K_4Fe(CN)_6$ IN THE PRESENCE OF

AMMONIUM CHLORIDE

Volume of $K_4Fe(CN)_6$ (ml)

Concentration of NH_4Cl (M/L)

0.60

0.40

0.20

0.00   0.20   0.40   0.60   0.80

FIGURE II

CURVE SHOWING PER CENT ERROR AGAINST

CONCENTRATION OF AMMONIUM CHLORIDE

Point of minimum error (0.23 M/L)

Per Cent Error in Titration

Concentration of NH₄Cl (M/L)

minimum points of Curve (1) and Curve (2) for the blanks
correspond nicely, also, with the minimum point for
Curve (3), the actual titration of the zinc. The distance
of Curve (2) from Curve (1) shows also the constant amount
of absorption of ferrocyanide on the zinc precipitate.
This data would then indicate the possibility, also, of
internal absorption of $K_4Fe(CN)_6$ in the precipitate as it
formed. Internal absorption could not be removed by
washing and therefore would lower the actual reading of
the blank below its proper value, even in the presence of
the precipitate. Therefore in the light of these readings
it would be necessary to run a true blank in the following
manner. With each titration for an unknown quantity of
zinc, a duplicate would have to be run on a similar
concentration of zinc of known value, and the theoretical
volume of ferrocyanide subtracted from the actual
calculated volume required and this volume subtracted as
the true blank.

During the early course of titrations it was
observed that another source of error in the blank deter-
mination was in the size of the drop of uranyl acetate used
in the spot plate. This error was easily eliminated by
using the same eye dropper held at the same angle each
time.

Determinations using ferrous ammonium sulfate
external indicator gave a set of results analogous to

those for uranyl acetate, the maximum error in the
presence of the precipitate being 0.5 per cent at optimum
concentration of ammonium chloride.

In the light of data set down above, it is
conclusively evident that high accuracy cannot be obtained
by the use of the external indicator. It is impossible
to obtain results of greater certain accuracy than 0.5 to
1.0 per cent. Unless optimum acidity, concentration of
zinc solution, amount of uranyl acetate used for indicator,
time of development of indicator color, concentration of
electrolyte, presence of the precipitate in the blank,
and other factors already mentioned are strictly adhered
to, errors as high as 5.0 percent will be encountered
since the effects are additive. Of special significance
is the concentration of the electrolyte. Table I and
Table II show the critical value of the concentration of
ammonium chloride in obtaining correct results. Figure II
shows the very steep drop and the steep rise again in the
per cent error with increasing concentration. This phase
of the work on external indicators was then considered
concluded in so far as gaining greater accuracy.
Comparison will be made later with other methods developed.

THE BACK TITRATION METHOD

The Back Titration of Excess Ferrocyanide with Potassium Permanganate.

In 1941 an article appeared by Z. S. Mukhina and M. L. Mironenko[12] stating that zinc could be determined by precipitation with potassium ferrocyanide and potassium ferricyanide and then back titrated with potassium permanganate using indigo carmine as an indicator. Since the original reference was not available, I first had to run checks on the back titration accuracy by running blank determinations on the potassium ferrocyanide solution using potassium permanganate. Conditions of the titration in the presence of zinc were simulated. The ferrocyanide was pipetted into a solution 0.5 molar in hydrochloric acid containing also 0.23 moles per liter of ammonium chloride. The solution, hot at (60 - 65)°C. was then titrated with $KMnO_4$. It was found for this titration that no indicator was necessary, since the light yellow green color of the ferricyanide at this dilution (200 ml) does not hinder the detection of the end point.

In the first titrations that were run on the above method a considerable error (0.5 - 2.0 per cent) was found to occur and was attributed to the formation of a fine gelatinous precipitate which interfered

somewhat with the determination of the true end point.
The precipitate was determined to be $Mn_2Fe(CN)_6$ and
formed only in the presence of an ammonium salt.#

In view of the discrepancy mentioned
above, I considered it necessary to make a thorough
investigation of the ferrocyanide - permanganate titra-
tion. The following method was used. Exactly 40 milli-
liters of potassium ferrocyanide were pipetted into 400
milliliter beakers and the solutions made up to 190
milliliters with sulfuric acid and water, to contain at
the end point, concentrations of acid from 0.00 to 2.00
moles per liter. A series of titrations were made varying
the concentration of acid and then varying the concentra-
tion of first, ammonium chloride; second, ammonium sulfate;
and third, sodium sulfate; with a given concentration of
acid. Blanks were run on the water and sulfuric acid and
in no case, even in the presence of the salts, was there
found a greater titration value for the blank than 0.02
milliliters. Tables III, IV, V, and VI, show the results
of these experiments.

Note: The complete identification of this precipitate
         is given in detail in the appendix.

TABLE III

Variation in Volume of $KMnO_4$ With Different

Concentrations of Hydrogen Ion

Volume of $K_4Fe(CN)_6$	Conc. H (m/l)	Volume of $KMnO_4$	Difference	% Error
39.96 ml	0.00	(End Point Obscured)-----		
	0.10	16.51	0.01	0.06
	0.50	16.48	0.04	0.24
	1.00	16.50	0.02	0.12
	1.50	16.46	0.06	0.24
	2.00	16.43	0.09	0.54

(Theoretical Volume of $KMnO_4$ Required = 16.52 ml)

TABLE IV

Variation in Volume of $KMnO_4$ With NH_4Cl

Concentration

Volume of $K_4Fe(CN)_6$	Conc. H (m/l)	Conc. of NH_4Cl	Volume of $KMnO_4$	Diff.	%Error
39.96	0.10	0.000	16.52	0.00	0.00
	0.10	0.047	16.45	0.07	0.42
	0.10	0.140	16.43	0.09	0.54
	0.10	0.187	16.40	0.12	0.73
	0.30	0.093	16.40	0.12	0.73
	0.30	0.140	16.38	0.14	0.85
	0.30	0.187	(End Point Obscured)--		

(Theoretical Volume of $KMnO_4$ Required = 16.52 ml)

TABLE V

Variation in Volume of $KMnO_4$ With $(NH_4)_2SO_4$

Volume of $K_4Fe(CN)_6$	Conc.H (m/l)	Conc. of $(NH_4)_2SO_4$	Volume of $KMnO_4$	Diff.	% Error
19.98	0.10	0.010	8.28	0.02	0.24
	0.10	0.019	8.27	0.01	0.12
	0.10	0.028	8.20	0.06	0.73
	0.10	0.038	8.37	0.11	1.30
	0.30	0.010	8.25	0.01	0.10
	0.30	0.019	8.28	0.02	0.24
	0.30	0.028	8.30	0.04	0.48
	0.30	0.038	8.13	0.13	1.60

(Theoretical Volume of $KMnO_4$ Required = 8.26 ml)

TABLE VI

Variation in Volume of $KMnO_4$ With Na_2SO_4

Volume of $K_4Fe(CN)_6$	Conc.H (m/l)	Conc. of Na_2SO_4	Volume of $KMnO_4$	Diff.	% Error
39.96	0.45	0.017	17.25	0.05	0.29
		0.035	17.27	0.03	0.17
		0.052	17.33	0.03	0.17
		0.070	17.34	0.04	0.23
		0.087	17.37	0.07	0.40
		0.105	17.38	0.08	0.46

(Theoretical Volume of $KMnO_4$ Required = 17.30)

Table III shows a definite change in
accuracy with a varying concentration of acid. The safe
range of acid for accurate titration appears to be from
about (0.3 - 1.5) moles per liter. Table IV and Table V
indicate the increasing inaccuracy involved in the ferro-
cyanide - permanganate titration in the presence of
increasing concentration of ammonium ion. In the case of
using ammonium chloride as the electrolyte (Table IV),
no really accurate titration was made, even in the pres-
ence of as little as 0.05 moles per liter. Furthermore,
increasing acid concentration seems to increase the
error. In the case of the ammonium sulfate, however,
(Table V) increasing acid concentration does materially
aid the accuracy of the titration. This is more satis-
factory, since an acid concentration of at least 0.3
moles per liter is desired for the zinc precipitation.
Table VI shows that at 0.45 moles per liter of acid,
any concentration of sodium sulfate from 0.00 to 0.10
or larger is satisfactory. Thus we can see that ammonium
chloride cannot be used as the electrolyte in the precip-
itation of potassium zinc ferrocyanide when using potassium
permanganate for the back titration reagent. The safe
range for ammonium sulfate appears to be from (00.00 -
0.03) moles per liter in an acid concentration 0.30 moles
per liter or greater. The use of such small concentrations
of ammonium sulfate should be satisfactory, since the

FIGURE IV

$K_4Fe(CN)_6$ - $KMnO_4$ POTENTIOMETRIC TITRATION

(In the Presence of Na_2SO_4)

Potentiometric Reading (Millivolts)

Volume of $KMnO_4$ Added (Milliliters)
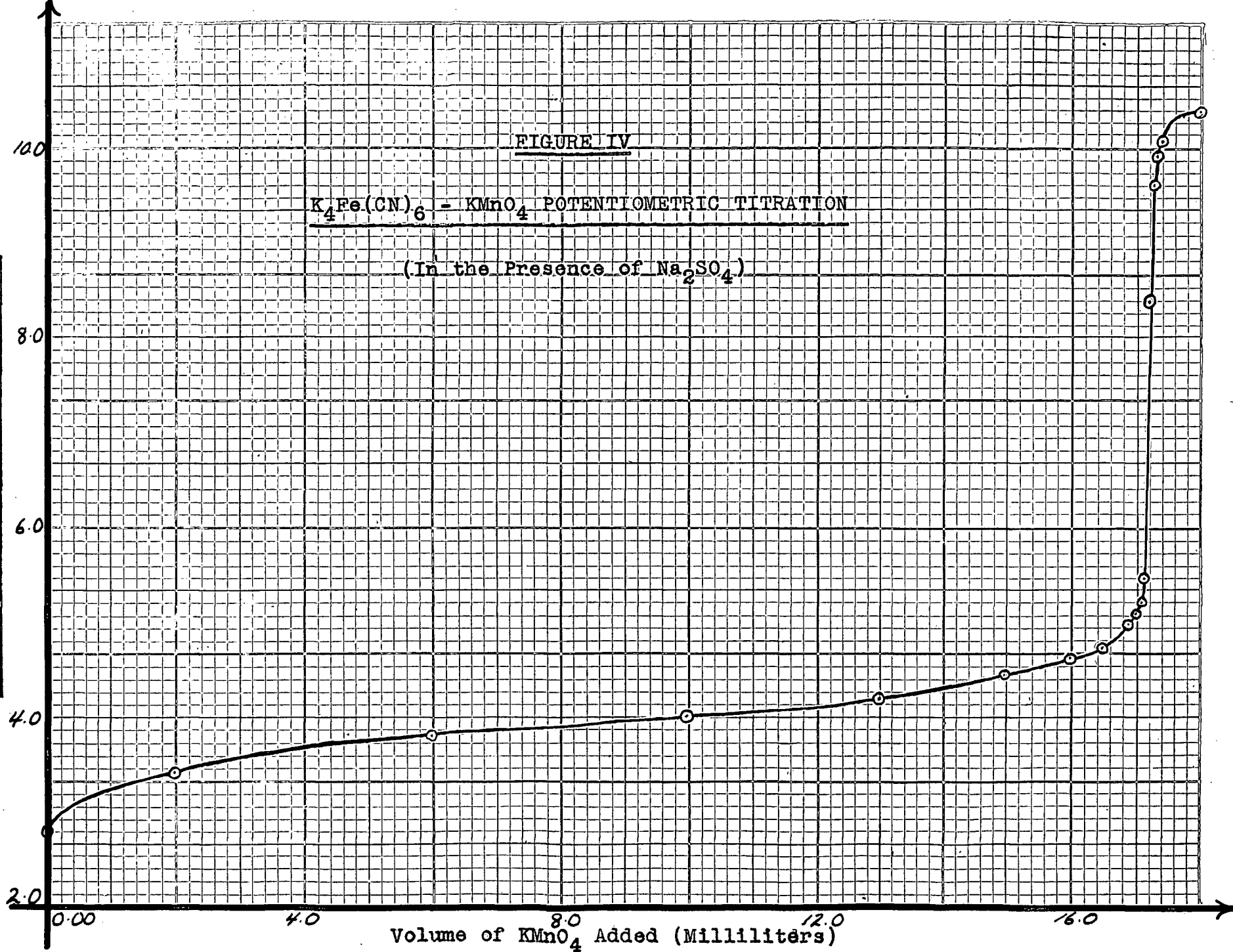
FIGURE III

$K_4Fe(CN)_6$ - $KMnO_4$ POTENTIOMETRIC TITRATION

(In the Presence of NH_4Cl)

End Point 8.12ml.

End Point 8.22ml.

Tit'n at 35°C.

Tit'n at 20°C.

Potentiometric Reading (Millivolts)

Volume of $KMnO_4$ Added (Milliliters)
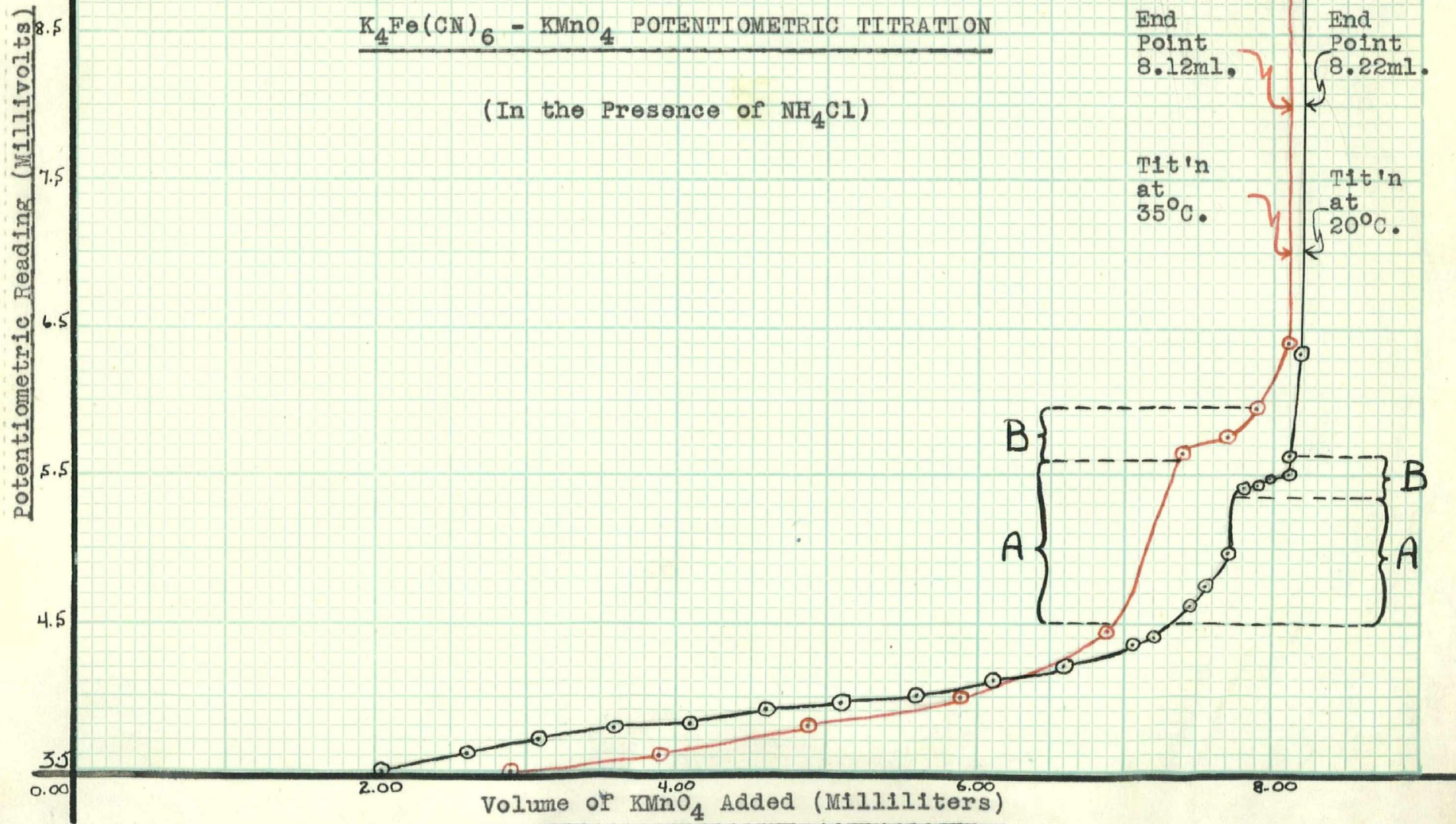
theory and experiment suggest that ammonium sulfate is
a much stronger agent for coagulation than is ammonium
chloride, being of the order 250 to 1 for some inorganic
sols [13]and of the order 16 to 32 times better for other
sols.

The difference in effect of an ammonium
salt and a non-ammonium salt on the ferrocyanide - per-
manganate titration is well illustrated by the two
graphs. (Figures III and IV). Note that the region (A)
bracketed in Figure III is a region of sharp increase
in potential but in region (B) instead of the potential
continuing to increase sharply it levels off and then
gives the final large jump. The region (A) is accounted
for by the fact that manganese ferrocyanide has precip-
itated and thus effectively removed some of the ferro-
cyanide, giving a premature end point. At the point of
sudden leveling, however, the concentration of ferro-
cyanide has been lowered (by its oxidation) below the
concentration required to keep the precipitate out of
solution and so the precipitate dissolves. The solution
of the precipitate then keeps the potential almost
constant until the precipitate has completely dissolved.
At complete solution of the precipitate the potential
again begins to rise rapidly. Figure IV shows the smooth,
normal oxidation curve and gradual rise of the potential
until the true end point, that is, the titration is a

normal one and so should be, and is, more accurate than
that titration in the presence of ammonium ion.

Since the use of an ammonium salt for an
electrolyte does involve a slightly larger error than the
use of sodium sulfate, I thought it would be interesting
to attempt using only sodium sulfate as the electrolyte.
In order to obtain the best results involving the optimum
conditions for the precipitation of a stable, constant
composition precipitate of zinc, and to obtain maximum
accuracy of the back titration, the following method was
finally developed.

Exactly 19.98 milliliters of standard
zinc solution, 13.5 milliliters of 6N sulfuric acid,
137.5 milliliters of water and 2.00 grams of sodium
sulfate were mixed together, heated to 70°C, and exactly
19.98 milliliters of standard ferrocyanide run in at the
rate of 60 drops per minute. After the last drop of
ferrocyanide had been added, the solution was stirred at
a constant speed for exactly three minutes. The mixture
was cooled for five minutes to (15 - 20)°C. in a water
bath and then the second 19.98 milliliters added rapidly
with stirring. Now 90 per cent of the required standard
potassium permanganate was run in in the cold. The
mixture was then heated for three minutes to 65°C. over
a Bunsen flame and the titration completed at this temp-
erature to the end point. The end point of all these
titrations was determined by means of a research model

Beckman pH Meter converted to potentiometric readings.
A high temperature platinum electrode (#1281-X11), and
a high temperature calomel electrode (#8970-T) for refer-
ence, were used. The use of the Beckman for the deter-
mination of the back titration end point became a
necessity, for the following reason. The normal color
change using potassium permanganate as its own indicator,
when titrating potassium ferrocyanide, was from green
(color of the ferricyanide) to yellow to orange. The
appearance of the first faint orange color is the end
point, not the pink[15]. In the presence of the zinc
potassium ferrocyanide precipitate, however, the color
change was almost completely obscured and when this method
of identification of the end point was used, errors as
high as 15 per cent were incurred. The use of the
potentiometric method, then, was devised and it was by
this method that Table VII below, was compiled. The last
four readings of Table VII were determined by an internal
indicator, orthophenanthroline ferrous complex. The
last two of the readings were determined in the presence of
nitrobenzene.

TABLE VII

Determination of Zinc by Back Titration.

Variation With Na_2SO_4.

Vol. of $ZnSO_4$ Std.	Vol. of $K_4Fe(CN)_6$ Added	Conc. of Na_2SO_4	Conc. of H	Back Tit'n With $KMnO_4$	Equiv. Vol. of $K_4Fe(CN)_6$	Vol. of $K_4Fe(CN)_6$ Req'd by Zinc	Calc. Wt. of Zinc	Theoret. Wt. of Zinc	% Error
19.98	39.96	0.035	0.45	9.02	20.84	19.12	0.0978	0.0999	2.10
		0.070		8.99	20.77	19.19	0.0982		1.70
		0.105		8.95	20.68	19.28	0.0986		1.30
		0.210		8.88	20.51	19.45	0.0995		0.40
15.00		0.035		11.06	25.55	14.41	0.0737	0.0750	1.73
		0.070		11.02	25.46	14.50	0.0742		1.06
		0.105		11.02	25.46	14.50	0.0742		1.06
		0.210		10.98	25.37	14.59	0.0746		0.53
10.00		0.035		13.03	30.10	9.86	0.0504	0.0500	0.80
		0.070		13.18	30.45	9.51	0.0487		2.60
		0.105		13.13	30.33	9.63	0.0493		1.40
		0.210		13.07	30.19	9.77	0.0500		0.00
3.00	22.98	0.105		8.70	20.10	2.88	0.01473	0.0150	1.80
		0.210		8.67	20.03	2.95	0.01540		2.60
		0.210		8.68	20.05	2.93	0.01498		0.13
		0.210		8.68	20.05	2.93	0.01498		0.13

Considerable technique was required in applying the Beckman to the recognition of the true end point. The potassium permanganate gives a good potential jump, as in most other straight forward oxidation reactions, but in five to eight seconds after the large potential rise at the end point, the potential begins to fall off again very rapidly. In approximately one to three minutes, depending on how far past the end point the titration has been run, the potential remains constant at about 0.75 to 1.5 millivolts above the potential where the first rise began. On addition of each extra drop of potassium permanganate to the solution the negative potential surges up from approximately (6.5 - 10) millivolts, remains constant at this reading for five to eight seconds and then steadily drops back again. Since the actual peak of the potential lasts for such a short time, it was necessary to be sure that the oxidation was complete, that is, that the fall was not due to a slow reaction of the permanganate on the ferrocyanide. This consideration is taken care of by carrying out the titration at 65°C. At this temperature the reaction of permanganate and ferrocyanide is very rapid. A graph showing the variation of potential with time for one drop of potassium permanganate is shown in Figure V. This curve shows that the end point has really been reached, since even after three minutes the potential is still well

FIGURE V

VARIATION OF POTENTIAL WITH TIME

AT THE END POINT.

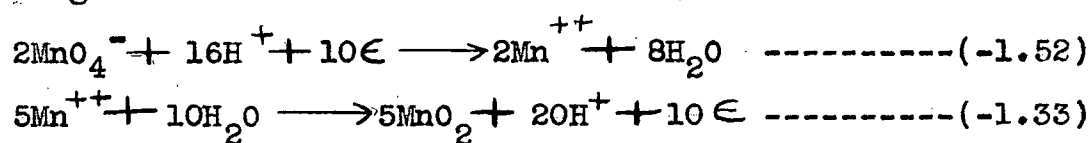(0.06 ml. KMnO$_4$ Added)

Potential
Plateau

Potentiometric Reading (Millivolts)
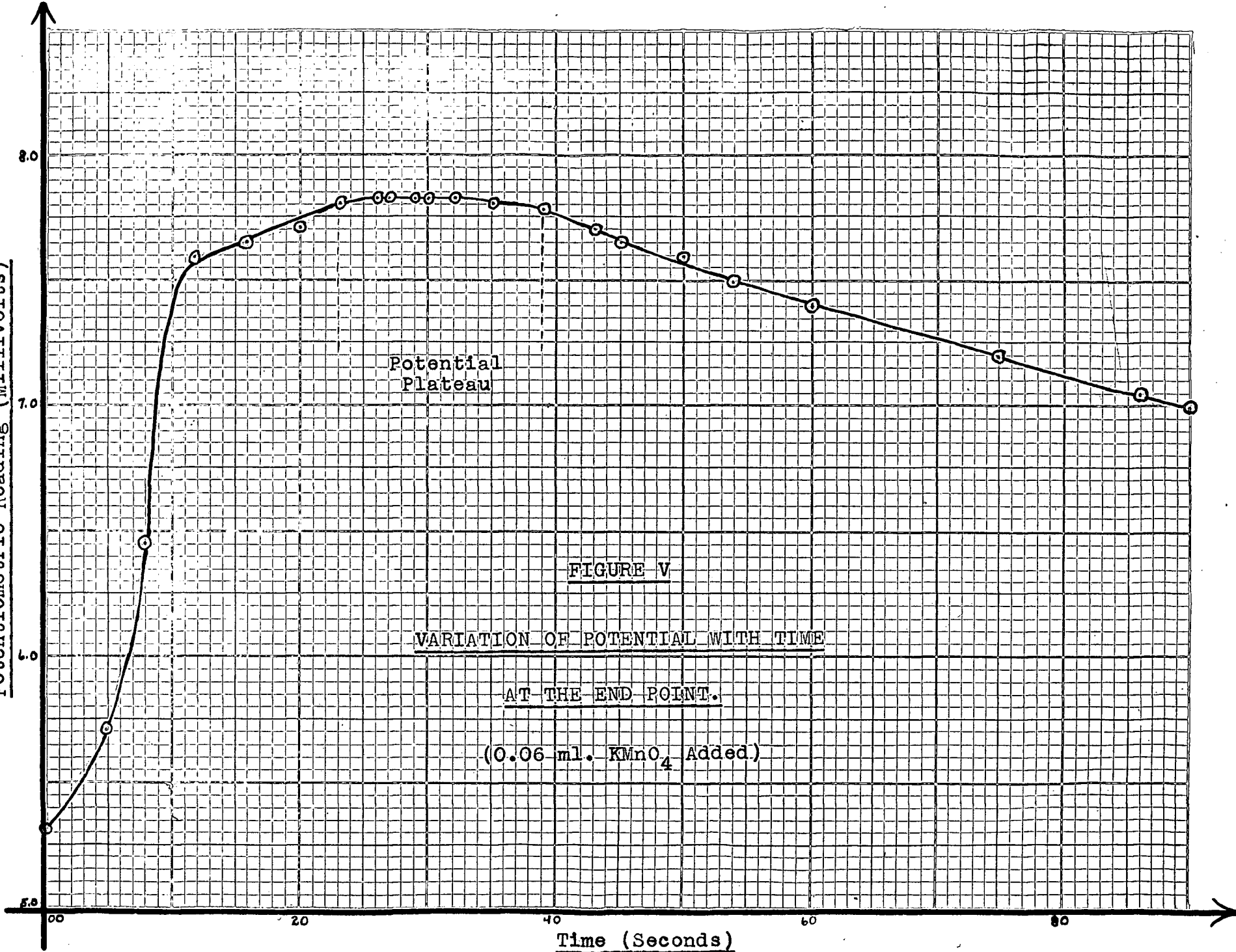
Time (Seconds)

above the starting point of the potential rise. The curve, Figure V, was obtained by carrying the titration to just one drop (0.06 ml.) from the true end point. The drop was then added and zero time taken as that time when the drop just touched the surface of the solution. Readings of time in seconds and potential were then taken over a period of three minutes from the time the drop touched the solution.

The gradual falling off of the potential after the potential plateau was reached was due to the fact that secondary reactions catalysed by the precipitate of zinc, began to set in. In these reactions the permanganate is gradually reduced with the subsequent production of manganese dioxide.

$$2MnO_4^- + 16H^+ + 10\epsilon \longrightarrow 2Mn^{++} + 8H_2O \quad ----------(-1.52)$$

$$5Mn^{++} + 10H_2O \longrightarrow 5MnO_2 + 20H^+ + 10\epsilon \quad ----------(-1.33)$$

Displacement of air by nitrogen, over the solution to be titrated did not increase the plateau period by any appreciable time.

Since the potentiometric method is somewhat more difficult than is to be desired, I thought that the use of an internal indicator would perhaps increase the sensitivity of the determination. The indicator finally decided on was orthophenanthroline ferrous complex[#]. As

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[#] Note. This indicator is manufactured by the G. Frederick Smith Company and is sold under the name of "Ferroin".

was to be expected the color change at the end point was not permanent. The change, however, from the reduced form to the oxidized and back again to the reduced form was so rapid that the determination of the end point was extremely difficult. It was necessary then to find something to inhibit the effect of the precipitate of zinc. Nitrobenzene was found to slow down the rapid indicator change. The following method using orthophenanthroline ferrous complex as indicator was developed and found satisfactory.

The required volume of zinc depending upon the concentration of the solution, was pipetted[#] into 15 milliliters of 6N sulfuric acid, and 6 grams of anhydrous sodium sulfate. Enough distilled water was then added so that the final volume of solution at the end of the titration would be approximately 200 milliliters. The acid solution was then heated over a Bunsen for four minutes to 70°C. and the required volume of ferrocyanide added drop by drop to give just a slight excess. The solution was stirred for exactly three minutes and then placed in a water bath and cooled to (15 - 20)°C. for five minutes. Three milliliters of pure nitrobenzene were now added with vigorous stirring and then the second portion of ferrocyanide for the back titration added. Approximately

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Note. The precipitate of zinc should not contain more than 0.10 grams of zinc.

90 per cent of the required potassium permanganate was now run in and the solution heated to $(60 - 65)^\circ C$. To the hot solution were added two drops of 0.05M Ferroin and then the titration was completed by the addition of permanganate to the end point. The color change at the end point is from orange to a clear green color which lasts from five to ten seconds before gradually taking on the orange tint again. A white base and good back ground lighting are essential.

The use of Ferroin as an indicator applies either in the presence of zinc or out of the presence of zinc. The use of this indicator in the straight forward titration of ferrocyanide is almost ideal and is far more satisfactory for the identification of the permanganate - ferrocyanide end point than the use of the permanganate itself as previously suggested. All those determinations in Table III and Table VI which were made previously can be made even more accurately in the presence of Ferroin.

COMPARISON OF THE PERMANGANATE METHOD

A comparison of the final methods developed for the analysis of zinc was considered necessary for a final examination of the permanganate method. Since this was to be a comparison the analysis was done on four different ore samples. These ores were treated to extract the zinc and then this extracted zinc was analysed by the

external indicator method, and by the back titration method using both the internal indicator and potentiometric determination. The methods and their various results are tabulated in Table VIII. The four ores were treated by the following extensive method.

The ore samples were dried at $100^{\circ}C$. for one hour. Approximately four gram samples were taken and weighed accurately, placed in an erlenmeyer, and 40 milliliters of concentrated hydrochloric acid added with warming until effervescence ceased. The solution was then evaporated to 20 milliliters and 20 milliliters of concentrated nitric acid added and the whole mixture then boiled to near dryness. The solution was then cooled and 40 milliliters of concentrated sulfuric acid added. This mixture was heated over an open flame to fumes of sulfur trioxide. Since in the permanganate back titration method it is imperative that no nitrate be present, the above sulfuric acid solution was heated almost to dryness[#], exactly 100 milliliters of water was added to the cooled mixture and then 20 milliliters more of concentrated sulfuric acid. Pellets of pure aluminum were added and the mixture boiled for 10 minutes and filtered into a beaker through paper containing pellets of aluminum.

Note. It has been the experience of this worker that HNO_3 is not completely driven off with the first few minutes of sulfur trioxide fuming. It was found necessary to evaporate the sulfuric acid mixtures almost to dryness before obtaining complete expulsion of nitric acid.

The filtered solution was evaporated to 125 milliliters and 6N ammonium hydroxide added until the precipitate of zinc hydroxide just failed to redissolve. Then 100 milliliters of 1M citric acid[16] were added and made neutral to methyl orange by adding 6M ammonium hydroxide. An excess of citric acid, 100 milliliters of 1M solution, was now added and also 100 milliliters of a 20 per cent solution of ammonium sulfate. Since no cobalt was present the use of ammonium thiocyanate for this ore was not necessary. The volume was then adjusted to 800 milliliters, the solution heated to 60°C., and air replaced with hydrogen sulfide. The mixture was then heated to 95°C. and the exit tube closed. It was allowed to cool and become saturated with hydrogen sulfide under the pressure of the generator, and was shaked frequently for 40 minutes, allowed to settle, separated by filtration, and washed with a 0.1M solution of citric acid saturated with hydrogen sulfide.

When the washings were complete the filter paper and residue (ZnS) were dropped into a beaker and boiled with 40 milliliters of 6N sulfuric until no more hydrogen sulfide remained in the solution. The filter paper was filtered out while hot and washed repeatedly with small portions of 200 milliliters of boiling hot water. The filtrate containing the zinc was then made up to exactly 250 milliliters in a volumetric flask.

Aliquots of this solution were analysed for zinc by the methods tabulated in Table VIII.

TABLE VIII

Comparison of Methods
for the Determination of Zinc.

Ore Number	Sample Number	Sample Weight (gms.)	Back Tit'n Method Potentio-metric (gms.)	Internal Indic. (gms.)	Ext. Indic. Method (gms.)
1	A	4.7058	0.6369	0.6349	0.6482
	B	4.1090	0.5525	0.5520	0.5673
4	A	4.1006	0.6369	0.6337	0.6439
	B	4.2711	0.6627	0.6632	0.6650
6	A	4.1853	0.6925	0.6905	0.7052
	B	4.0532	0.6680	0.6695	0.6811
8	A	4.2769	0.7789	0.7764	0.7890
	B	4.1222	0.7840	0.7471	0.7520

Ore Number	Sample Number	Thorn Smith Analysis (%)	(%)	(%)	(%)
1	A	13.54	13.54	13.49	13.77
	B		13.45	13.44	13.81
4	A	15.49	15.53	15.45	15.70
	B		15.52	15.53	15.57
6	A	16.91	16.55	16.50	16.85
	B		16.48	16.38	17.05
8	A	18.17	18.21	18.15	18.45
	B		18.15	18.12	18.24

An examination of Table VIII shows that of the two methods of determination, potentiometric or internal indicator, the most relyable appears to be the potentiometric. The table illustrates also the extremely

consistent results obtained by either method. Ignoring
Ore #6, the largest single deviation from the values
reported by Thorn Smith is 0.10 per cent, and the largest
mean deviation for any one ore is 0.06 per cent. The
discrepancy in Ore #6 is accounted for by the presence of
a slight amount of reducing substance in the extracted
solution due to an error in technique, thus increasing
slightly the required volume in potassium permanganate
and consequently reducing the amount of reported zinc.
As shown previously in Table II the external indicator
method gives consistently high results.

CONCLUSIONS AND TREATMENT OF MATERIAL

1. The external indicator method while
it gives consistent results, will not give accuracy of
greater certain value than 98.5 per cent.

2. In the precipitation of zinc as
potassium zinc ferrocyanide, an electrolyte is not only
necessary but its concentration for maximum accuracy
is critical. This applies to all determinations
involving this zinc precipitate.

3. The titration of ferrocyanide with
permanganate can be made extremely accurately by any one
of the following three methods, provided that ammonium
ion is not present in the solution in greater concentration

than 0.05M.

     (a) By observation of the end point by means of a potentiometer.

     (b) By using potassium permanganate as its own indicator.

     (c) By the use of orthophenanthroline ferrous complex.

Of these three methods the last named is by far the fastest, the easiest to handle, and the most satisfactory.

     4. The determination of zinc in a solution by the back titration with potassium permanganate will give excellant accuracy if care is taken with the procedure developed and caution is used when determining the end point by either the internal indicator or the potentiometer.

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15. cf. Snell and Biffen, Commercial Methods of Analysis,
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APPENDIX

Identification of the $Mn_2Fe(CN)_6$ Precipitate.

Since the precipitate appeared each time upon the addition of $KMnO_4$ to the $K_4Fe(CN)_6$ solution, it was considered to be manganese dioxide, manganese ferrocyanide, or manganese ferricyanide.

Since the turbidity produced was not dark and was soluble in hot dilute H_2SO_4, then the formation of both MnO_2 and $Mn_3\left[Fe(CN)_6\right]_2$ are eliminated. Furthermore MnO_2 should not form in an acid solution. Since the turbidity seemed to appear more rapidly on allowing the $KMnO_4$ to layer, then it was thought perhaps that it was due to a high concentration of Mn^{++}. Later work however, showed that the precipitate which formed was due to an uncommon ion effect in the presence of the ammonium ion. A considerable number of salts then were used, for example K_2SO_4, Na_2SO_4, NH_4Cl, $(NH_4)_2SO_4$, and others, and in each case the precipitate was found to form only when an ammonium salt was used.

The precipitate on filtration appeared a faint grey blue to mauve color when wet and this is the characteristic color of $Mn_2Fe(CN)_6$. The precipitate was then washed thoroughly with 50 per cent ethyl alcohol and dissolved in hot very dilute sulfuric acid. On evaporating the solution it takes on the beautiful light blue color

that is characteristic of the decomposition of ferro-cyanide, that is, the formation of $Fe_4[Fe(CN)_6]_3$. The evaporated solution plus nitric acid and sodium bis-muthate gave the distinct rose color for MnO_4^- ion, thus proving qualitatively the positive presence of manganese in the precipitate. Further evidence that it must be the ferrocyanide of manganese is the fact that each time the solution cleared up just before the end point. Thus the oxidation of the ferrocyanide to ferricyanide reduced the concentration of $Fe(CN)_6^{-4}$ ion below the solubility product of the precipitate at the concentration of the manganese ion present in the final solution.

On the basis of the qualitative tests carried out above, I considered it expedient to test the precipitate quantitatively for its composition. The tests applied to the weighed precipitate were first, the exact amount of ferrocyanide present; second, the determination of the exact amount of manganese in the precipitate; and third, the exact amount of ammonium present. The precipitate for analysis was prepared in the following rigorous manner.

Pure standard potassium ferrocyanide solution (50 ml.) was diluted to 180 ml., 20 ml. of 6N H_2SO_4 and two grams of $(NH_4)_2SO_4$ added, and 18 ml.

of standard $KMnO_4$ titrated in. This solution was then
stirred gently and heated over a burner to (50 - 55)°C.
to help coagulate the precipitate which formed. The
solution was then allowed to stand covered with a watch
glass for one half hour to allow the precipitate to settle.
The mixture was filtered through a carefully prepared
Gooch crucible under a pressure of exactly eight pounds.
The precipitate was then washed three times with cold
distilled water and three times with cold very dilute
sulfuric acid (10 ml. 6N H_2SO_4 to 190 ml. H_2O). Each time
the washing was sucked completely dry. The Gooch crucible
was then dried in a constant temperature oven at exactly
105°C., desiccated for exactly 30 minutes, and weighed
immediately. The precipitate was then dissolved with
boiling dilute sulfuric acid (20 ml. 6N H_2SO_4 to 180 ml.
H_2O) by means of pouring small portions of it repeatedly
through the crucible. The filtrate was then titrated with
standard $KMnO_4$ for the available ferrocyanide. The Gooch
crucibles were again dried, desiccated and weighed under
exactly the same conditions as before. The difference in
weight was the weight of the precipitate dissolved. This
method was used in preference to the method of filtering
the precipitate through a weighed Gooch crucible, drying,
desiccating and weighing the precipitate and then dis-
solving and titrating for available ferrocyanide; since
it was found that very slight impurities catalysed the

formation of ferric ferrocyanide with a consequent error in the weight of the precipitate. With the method used, however, ferric ferrocyanide is not soluble in the boiling dilute sulfuric acid, and therefore does not enter into the weight of the precipitate obtained.

The titrated available ferrocyanide was calculated in grams of $Fe(CN)_6^{-4}$ and this weight was used to calculate the total weight of various, most probable, forms of the precipitate. These weights on comparison show quite plainly the most closely related forms by weight. A table of results below (Table I) indicate the value of these comparisons.

TABLE I (a)

Sample number....	1	2	3
A Wt. of Actual ppts.	0.0203	0.0570	0.0664
B Wt. of $Fe(CN)_6^{-4}$ by titration	0.01298	0.0369	0.0434

TABLE I (b)

Calculated Weights from B for the
Following Forms.

Sample Number	1	2	3
$Mn_2Fe(CN)_6$	0.0197	0.0561	0.0659
$Mn(NH_4)_2Fe(CN)_6$	0.0185	0.0528	0.0621
$Mn_3(NH_4)_2[Fe(CN)_6]_2$	0.0191	0.0544	0.0640
$Mn(NH_4)_6[Fe(CN)_6]_2$	0.0179	0.0512	0.0601
$MnK_2Fe(CN)_6$	0.0211	0.0601	0.0707
$Mn_3K_2[Fe(CN)_6]_2$	0.0204	0.0581	0.0683
$Mn K_6[Fe(CN)_6]_2$	0.0218	0.0621	0.0731

TABLE I (c)

Deviation from the Observed Weights <u>A</u>
for the Following Forms.

Sample Number	<u>1</u>	<u>2</u>	<u>3</u>
$Mn_2Fe(CN)_6$	-0.0003	-0.0009	-0.0005
$Mn(NH_4)_2Fe(CN)_6$	-0.0015	-0.0052	-0.0043
$Mn_3(NH_4)_2[Fe(CN)_6]_2$	-0.0009	-0.0026	-0.0024
$Mn(NH_4)_6[Fe(CN)_6]_2$	-0.0021	-0.0058	-0.0063
$MnK_2Fe(CN)_6$	0.0011	0.0031	0.0043
$Mn_3K_2[Fe(CN)_6]_2$	0.0004	0.0011	0.0019
$MnK_6[Fe(CN)_6]_2$	0.0018	0.0051	0.0067

An examination of Table I (c) shows that
the closest formula by weight is the form $Mn_2Fe(CN)_6$.
Two other formulae, namely $Mn_3K_2[Fe(CN)_6]_2$ and
$Mn_3(NH_4)_2[Fe(CN)_6]_2$, are too close by weight comparisons,
to make a definite decision regarding actual formula of
the precipitate. For this reason two further tests were
made on the precipitate; one a qualitative test for
potassium and the other a quantitative test for ammonium.

The ferrocyanide precipitate was prepared
in exactly the same manner as described previously[#].
The filtrate was evaporated almost to dryness, 10 ml.
of concentrated HCl added and then the solution again
evaporated to a paste. The residue was taken up in 10 ml.
of hot water and the ferric ferrocyanide precipitate
filtered out and kept aside for further tests. To 10 ml.
of the filtrate was added 5 ml. of sodium cobaltinitrite

See APPENDIX Pp. ii and iii

solution $[Na_3Co(NO_2)_6]$. The solution was then buffered with 3 ml. of sodium acetate. The mixture was shaken and allowed to stand for one hour. Since no precipitate formed, it was assumed that no appreciable amount of potassium was present. This is logical, since the precipitate used, weighed 0.0532 grams, and if the form is $K_2Mn_3[Fe(CN)_6]_2$ then there would be 6.3 milligrams of potassium present. The cobaltinitrite test is sensitive for 0.2 - 0.3 milligrams [#]. Since there was a chance that the potassium had been filtered out in the ferric ferrocyanide precipitate it was examined spectroscopically for the presence of potassium. The solution was also examined spectroscopically. In neither substance was there found even a trace of potassium. The formula $Mn_3K_2[Fe(CN)_6]_2$ can thus be eliminated as a possibility.

The quantitative test for ammonium proved to be one of the most difficult tests undertaken. Of ten determinations that were made first, some appeared to correspond to a definite form of the original precipitate, some however, did not correspond to any definite compound and others were high beyond all reason. After a considerable amount of time was lost, the difficulty was found to be a physical carry over of the sodium hydroxide in the distillation of the ammonia. The difficulty was remedied by simply placing a long dry condenser vertically in the neck of the flask and from the top of this, the steam was led through a trap and

Noyes and Swift, Qual. Chem. Anal., Macmillan, Pg. 298.

condensed in a short cold condenser into 50 ml. 0.2N
H_2SO_4 standard solution. Of four runs using this set up,
the maximum weight of NH_4 found was 0.0005 grams on a
precipitate containing 0.0309 grams of $Fe(CN)_6^{-4}$. This
maximum figure, however, does not correspond to any
possible formula for the precipitate under investigation.
The results of this work show that the formula cannot be
$Mn_3(NH_4)_2\left[Fe(CN)_6\right]_2$.

The composition of the ferrocyanide of
manganese must be then the one originally assumed [#],
namely $Mn_2Fe(CN)_6$. This conclusion is further established
by the table below (Table II) assuming the above compos-
ition of the precipitate.

<div align="center">TABLE II</div>

Weight of ppt	Total wt of Mn found	Wt Mn added (Tit'n)	Difference (Wt Mn in ppt)	Calculated wt Mn from ppt	Deviation
0.0450	0.0154	0.0015	0.0139	0.0154	-0.0015
0.0570	0.0210	0.0019	0.0191	0.0195	-0.0004
0.0664	0.0240	0.0023	0.0217	0.0227	-0.0010

The manganese was determined by the
bismuthate method on the titrated precipitate. The ferro-
cyanide precipitate which had been titrated with a known
volume of standard $KMnO_4$ was placed in a conical flask
and 50 ml. of dilute nitric acid (1 : 3) added, then 0.5
grams of sodium bismuthate added. The solution was
boiled for five minutes and the pink color of the per-
manganate formed was removed by the dropwise addition of

[#] M. D. Francis, Unpublished Thesis, "The Det'n of Small
Amounts of Zinc in Ores"

freshly prepared sodium sulfite. The oxides of nitrogen
were then removed by vigorous boiling. The solution was
cooled with running water to (10 - 15)°C., 0.5 grams of
sodium bismuthate added, and a further 0.5 gram sample
of sodium bismuthate added to give an excess. The
mixture was stirred for three minutes. To this solution
was added 50 ml. of oxide free, three per cent nitric
acid, and the whole solution filtered through a freshly
ignited Gooch crucible. The filtrate to which were added
the three per cent nitric acid washings was over titrated
with ferrous ammonium sulfate solution and the excess
back titrated with standard potassium permanganate. The
manganese added in the ferrocyanide titration was then
subtracted from the total manganese determined above.
The difference was the manganese present in the precipitate.

Upon reviewing the evidence from both
qualitative and quantitative tests presented in the
argument, it is evident that the precipitate must be of
the composition $Mn_2Fe(CN)_6$. This is the conclusion of
the evidence for composition.

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