A FERROCYANIDE-CERIOMETRIC METHOD
FOR THE DETERMINATION OF ZINC IN ORES

by

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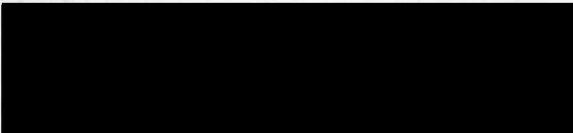
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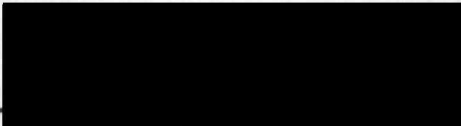the requirements for the
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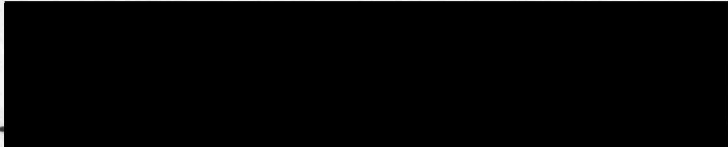
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INTRODUCTION

Gravimetric methods have heretofore been the only completely reliable means for the determination of zinc in ores. The most widely used titrimetric method for zinc at present is the Waring titration using a solution of potassium ferrocyanide. This method has long been the subject of controversy in regard to the experimental conditions and the accuracy of the determination, especially as it is applied to zinc ores. Although the rapidity with which this titration may be carried out and the ease in observing the end point have been greatly facilitated by the introduction of diphenylamine and diphenylbenzidine as internal indicators by Cone and Cady (3) in place of the old external indicators of uranyl nitrate or acetate, the determination at best is good only for routine analysis even when uniform conditions are maintained. Thus there has been a real need for the introduction of new titrimetric methods for zinc.

The present study was undertaken in an attempt to utilize the insolubility in acid solution of the white

precipitate, $K_2Zn_3[Fe(CN)_6]_2$, and to make use of the fact that the precipitant, as a reducing agent, may be titrated quantitatively with some standard oxidant. Since potassium ferrocyanide is readily titrated with standard ceric sulfate solution, either potentiometrically [1,7,17] or with indicators [2,7,21] such as o-phenanthroline ferrous complex and diphenylamine, it seemed desirable to use this oxidant, especially in view of its many advantages, including extreme stability in solution, simplicity of chemical change, and use in hydrochloric acid solution.

The purpose of the present work, therefore, was to develop a simple method for the determination of zinc in ores by making use of potassium ferrocyanide and ceric sulfate. The method consists in the final precipitation of the zinc in acid solution as potassium zinc ferrocyanide with excess standard potassium ferrocyanide solution, removal of the zinc precipitate by filtration, and titration of the excess ferrocyanide in the filtrate with standard ceric sulfate solution.

EXPERIMENTAL

Preparation of Solutions

Potassium Ferrocyanide, approximately 0.1 $\underline{M}$ solution. The crystalline salt, $K_4Fe(CN)_6 \cdot 3H_2O$, of 99.99 per cent purity was used. This solution was standardized by the ferrocyanide-ceriometric method (to be described) against a sphalerite ore (#379), for which the percentage of zinc had been determined gravimetrically as described below. One milliliter of this solution was found to be equivalent to 0.009961 gram of zinc. The average deviation of the separate standardizations was only 0.3 parts per thousand.

Ceric Sulfate. An approximately 0.1 $\underline{M}$ solution was prepared by dissolving 80 grams of ceric ammonium sulfate in 500 ml. of 2 $\underline{N}$ sulfuric acid and diluting to one liter. This solution was standardized against the standard potassium ferrocyanide solution by measuring about 20 ml. of the latter from a burette into a 250-ml. Erlenmeyer flask, adding 0.5 ml. of 6 $\underline{N}$ hydrochloric acid and 50 ml. of water, and titrating with the ceric sulfate solution using 4 drops of sodium diphenylamine sulfonate indicator. Each milliliter of the ceric sulfate solution was equivalent to 0.9108 ml. of standard potas-

sium ferrocyanide solution. The average deviation of these standardizations was 0.7 parts per thousand.

Sodium Diphenylamine Sulfonate. A 0.01 M solution was made by dissolving 0.32 gram of the pure barium salt in 100 ml. of water and adding 0.5 gram of sodium sulfate. The precipitate of barium sulfate was filtered off, and the filtrate was used as the indicator solution.

Diphenylamine. One gram of the pure solid (Merck) was dissolved in 100 ml. of concentrated sulfuric acid.

Diphenylbenzidine. One gram of the solid (Eastman) was dissolved in 100 ml. of concentrated sulfuric acid.

Diammonium Acid Phosphate. A 10 per cent solution was prepared by dissolving the salt in cold water and making barely basic to phenolphthalein by adding dilute ammonium hydroxide dropwise in order to convert any mono-ammonium salt that may be present into the diammonium salt.

Gravimetric Determination of Zinc in Sphalerite Ores (12)

The ores used were found by preliminary qualitative analysis to contain no cadmium or copper and only small amounts of iron. 1 gram samples of the ore were weighed out and dissolved in a casserole with 15 ml. each of concentrated hydrochloric and nitric acids. The casser-

ole was covered and warmed to assist solution of the sample. When action had ceased, the mixture was evaporated by boiling to a syrupy consistency, cooled, and transferred to a 250-ml. beaker. Then the mixture was diluted to 100 ml. and heated to near boiling. Ammonium hydroxide was added in excess of that required for complete precipitation of ferric hydroxide. After the residue of ferric hydroxide, silica, and sulfur had settled, it was filtered through #42 Whatman paper, retaining as much of it in the beaker as possible. This residue was washed by decantation with five 15-ml. portions of hot water, and the filter paper was washed well with hot water.

Then the clear filtrate was carefully neutralized with dilute hydrochloric acid until the white, gelatinous precipitate of zinc hydroxide, which formed first, redissolved. One milliliter of 10 per cent acetic acid was added, and the volume of the solution was adjusted at 150 to 200 ml. The solution was heated to boiling, and 25 ml. of 10 per cent diammonium acid phosphate solution were added dropwise with vigorous stirring. The mixture was kept at near boiling on a hot plate for 30 minutes with occasional stirring in order to convert the amorphous zinc ammonium phosphate to the crystalline modification.

After standing one to two hours, the mixture was filtered through a Gooch filter that had been dried at 105° C for one hour and weighed. A wash solution of 1 per cent diammonium acid phosphate was used to transfer the precipitate and to wash it, using three 15-ml. portions. Then the precipitate was washed 4 times with 15-ml. portions of 50 per cent methanol, dried to constant weight in an oven at 105° C, and weighed as $ZnNH_4PO_4$.

Ferrocyanide-Ceriometric Determination
of Zinc in Ores

One gram samples of the ore were weighed out and dissolved, the iron removed, and the filtrate was carefully neutralized with dilute hydrochloric acid as described in the gravimetric method above. To the solution were added 15 ml. of 6 $\underline{N}$ sulfuric acid, and the volume was adjusted at 100 to 150 ml. Then about 30 ml. of standard potassium ferrocyanide solution were added from a burette dropwise with stirring to the cold solution. The white precipitate of potassium zinc ferrocyanide was allowed to settle for 15 minutes and was then filtered off on a Gooch filter with an asbestos mat of 4- to 6-mm. thickness, using 0.3 $\underline{N}$ hydrochloric acid solution for transferring. The precipitate was washed with four 15-ml. portions of this wash solution.

The filtrate in the suction flask was titrated with standard ceric sulfate solution using 8 drops of sodium diphenylamine sulfonate indicator. At the end point the color changed sharply from a light green to a deep wine color.

Modified Waring Titration
(Ferrocyanide Method) (11)

To the neutral zinc solution were added 15 ml. of 6 $\underline{N}$ sulfuric acid, 10 grams of ammonium chloride, and a crystal of potassium ferricyanide. The solution was titrated with potassium ferrocyanide solution at room temperature using 2 to 4 drops of diphenylamine or diphenylbenzidine indicator solution. The color changed from purple to light green .

Data and Observations

The results obtained on the sphalerite ores by the gravimetric method are given in Table I. Synthetic methanol was substituted for 95 per cent ethanol in the final washing solution because a similar substitution in the gravimetric determination of magnesium as $MgNH_4PO_4$. $6H_2O$ in this laboratory has been successful (13).

Table I.

Gravimetric Determination of Zinc in Ores

Sample no.	Zinc Found %	% Zinc (mean value)	Average Deviation (parts per 1000)
378	14.38 14.29	14.34	3.1
379	15.40 15.42 15.41	15.41	0.4
380	16.60 16.58 16.61	16.60	0.6
381	18.30 18.27 18.31	18.29	0.9
382	19.82 19.85 19.76	19.81	1.7

Table II shows the results obtained on the same ores by the ferrocyanide-ceriometric method.

Table II.

Ferrocyanide-Ceriometric Determination of Zinc in Ores

Sample no.	Zinc Found %	% Zinc (mean value)	Average Deviation (parts per 1000)
378	14.36 14.32	14.34	1.4
380	16.58 16.55	16.57	0.9
381	18.30 18.27 18.27	18.28	0.7

Table II (continued)

Sample no.	Zinc Found %	% Zinc (mean value)	Average Deviation (parts per 1000)
382	19.88	19.81	3.9
	19.86		
	19.70		

A comparison of the data obtained for the sphalerite ores by the gravimetric method and by the ferrocyanide-ceriometric method is given in Table III.

Table III.

Comparison of Results of Gravimetric and Ferrocyanide-Ceriometric Determinations

Sample no.	% Zinc (mean value) Gravimetric	Titrimetric	Difference %
378	14.34	14.34	0.00
380	16.60	16.57	-0.03
381	18.29	18.28	-0.01
382	19.81	19.81	0.00

Average = -0.01

The results show a very close agreement between the gravimetric and the ferrocyanide-ceriometric determinations.

The potassium ferrocyanide solution was also standardized indirectly against pure Mohr's salt through the ceric sulfate solution. The normality factor thus obtained was 0.09821 $\underline{N}$ with respect to oxidation-reduction.

Since the composition of the zinc precipitate is $K_2Zn_3[Fe(CN)_6]_2$ according to DeKoninck and Prost (4), one potassium ferrocyanide should be equivalent to $\frac{3}{2}$ Zn, and the calculated zinc equivalence of the ferrocyanide solution is 0.009631 gram as compared to 0.009961 gram, the zinc equivalence actually obtained experimentally.

Thus it seems that the relation between zinc and ferrocyanide is an empirical one. However, that the composition of the zinc precipitate is constant, is shown by the low average deviation of the results of the ferrocyanide-ceriometric determinations and the excellent agreement of these results with those of the gravimetric determinations.

During the course of the investigations on the ferrocyanide-ceriometric method, an attempt was made to titrate the excess potassium ferrocyanide with ceric sulfate without previous removal of the zinc precipitate by filtration. However, it was found that the precipitate is too easily oxidized, and consequently a drifting end point was obtained.

According to Waring (19) and DeKoninck and Prost (4) the formation of the potassium zinc ferrocyanide precipitate occurs much more rapidly on heating than in the cold. Kolthoff and Pearson (10) recommend a temper-

ature of 50° C for the regular ferrocyanide titration,
but they state that its purpose is merely to facilitate
the color change at the end point. The precipitation of
zinc in the ferrocyanide-ceriometric determination was
at first carried out in hot solution followed by diges-
tion on a hot plate. This resulted in the formation of
a dark blue precipitate, the amount of which seemed to
be proportional to the length of time of the digestion.
This phenomenon was also observed, although to a much
less extent, when precipitation was made in a hot solu-
tion which was then allowed to cool.

It is concluded that the dark blue precipitate was
ferric ferrocyanide formed by the decomposition of po-
tassium ferrocyanide or traces of potassium ferricyanide
on heating. Consequently, the precipitation was carried
out at room temperature as already described. Although
the formation of the zinc precipitate is slower at such
a temperature, it is facilitated by the presence of am-
monium salts from neutralization of the solution, by
acid, and by the presence of excess potassium ferrocya-
nide according to the observations of Seaman (16) and of
DeKoninck and Prost (4).

An attempt was made to utilize sintered glass fil-
ters in removing the zinc precipitate before final ti-
tration. The finest filter of this kind available to

the writer was a 1-G4, but it failed to retain the precipitate. Thereafter a Gooch asbestos filter of at least 4-mm. thickness was found to be quite satisfactory.

In getting the ore samples in solution for analysis in both the gravimetric and titrimetric methods, the iron was removed by precipitation with ammonium hydroxide before the siliceous matter had been filtered off. According to Waring (19) such a procedure invariably results in a combination of zinc with silica. In view of the consistency of the results obtained, however, it seems likely that either this action is negligible, or else the resulting error is constant.

Another factor must be considered in removing the iron. It has been found (19) that iron precipitated by ammonium hydroxide is capable of holding tenaciously one fifth of its weight in zinc. Therefore, it would be advisable to dissolve the ferric hydroxide and reprecipitate it to recover the occluded zinc if the sample contains much iron. However, the ores used in the present work were found to contain so little iron as to make such a precaution unecessary.

In preliminary titrations of potassium ferrocyanide against ceric sulfate, a 0.5 $\underline{M}$ solution of ferric chloride was used as the indicator as suggested by Dernbach

and Mehlig (5). Three drops of this solution were added near the end point, giving green colloidal ferric ferrocyanide. This green color changed to the brownish-yellow color of ferric ferricyanide at the end point. However, this color change was not always easily discerned, and it was found that a much more satisfactory end point could be obtained using 3 or 4 drops of 0.01 $\underline{M}$ sodium diphenylamine sulfonate solution as the indicator. With this indicator the color changes sharply from light green to a deep wine color.

In the first part of the work, an attempt was made to use pure $ZnSO_4 \cdot 7H_2O$ as a primary standard. The results of several analyses by the ferrocyanide-ceriometric method are given in Table IV. They show that the salt was gradually taking up moisture from the air. This hygroscopicity was observed even during the weighing of a 5-gram sample of the salt.

At first it was thought that this change might be due to instability of the potassium ferrocyanide solution. Concerning the stability of ferrocyanide solutions the literature seems to be in some disagreement. Keen states (8) that the strength of a potassium ferrocyanide solution remains constant almost indefinitely. However, Kolthoff and Pearson (9) have found that photo-

chemical decomposition of aqueous potassium ferrocyanide
solutions occurs even in the absence of atmospheric oxy-
gen, but when kept in the dark the solutions are stable
for three months or more. These investigators recommend
the addition of 0.2 per cent sodium carbonate, which
makes ferrocyanide solutions stable for long periods.

Table IV.

Effect of Absorption of Moisture
on Composition of $ZnSO_4 \cdot 7H_2O$

Time (days)	Zinc Found %	Difference %
0	25.49	
		-0.41
2	25.08	
		-0.31
4	24.77	
		-0.30
16	24.47	
		-0.27
21	24.20	
		-0.15
47	24.05	

In order to test the stability of the potassium
ferrocyanide solution used in the ferrocyanide-ceriomet-
ric determinations, the solution was titrated at various
intervals against the ceric sulfate solution as des-
cribed above in the standardization of the latter. The
results, which are given in Table V, indicate that there
was no significant change in the strength of the ferro-

cyanide solution during its period of use. The ceric sulfate solution itself may be considered stable according to Furman (6) and Willard and Young (20), who observed that 0.1 $\underline{N}$ solutions were stable for 40 weeks.

Table V.

Stability of 0.1 $\underline{N}$ $K_4Fe(CN)_6$ Solution
as Shown by Titration vs. $Ce(SO_4)_2$ Solution

Time (weeks)	Normality of $K_4Fe(CN)_6$	Deviation from Initial Value (parts per 1000)
0	0.09821	----
4	0.09819	-0.2
17	0.09854	+3.4

Both the potassium ferrocyanide and the ceric sulfate solutions used in this work were kept in the dark when not in actual use.

Study of the Modified Waring Method

A brief study of the Waring ferrocyanide titration was carried out using the modified method described above. A solution of zinc sulfate was used instead of zinc ores. Diphenylbenzidine was found to be fully as satisfactory as diphenylamine as an indicator, and according to Cone and Cady (3) it has the advantage over the latter in that the amount used does not affect the

titration. Titrations carried out with sodium diphenyl-
amine sulfonate as the indicator confirmed the observa-
tions of Oesper (14) that this indicator exhibits slug-
gish response and, therefore, is not suitable for this
titration.

The total acidity was found to affect the sharpness
of the color change at the end point when the concentra-
tion of hydrochloric acid was as much as 10 ml. of ex-
cess concentrated hydrochloric acid in 150 ml. of solu-
tion. Similar observations have been made by Waring
(19) and by Seaman (16), who found that too much hydro-
chloric acid gives high results. The latter investiga-
tor found 5 ml. of excess hydrochloric acid in 150 ml.
of solution to be the optimum concentration.

The average deviation in the results of these ti-
trations was 8.4 parts in a thousand. This compares fa-
vorably with the degree of accuracy obtained by Cone and
Cady (3), whose data shows deviations ranging from 2 to
13 parts per thousand, with an average of 6 parts per
thousand. These investigators have found the ferrocya-
nide titration to be much more satisfactory when either
diphenylamine or diphenylbenzidine internal indicator is
used in place of the uranyl nitrate external indicator,
but even so, they state that this method is suitable on-

ly for routine analysis.

Waring and Stone (18) place no such limitations on the accuracy of the method provided that all conditions of the determination, including preliminary treatment of the sample, are rigidly adhered to. However, no other investigators have reported such success with the method. In fact, Oesper reported (14) that deviations from the known quantity of zinc as determined by potentiometric titrations ranged from -1.1 to -1.3 % in ferrocyanide titrations with internal indicators which were carried out under strictly uniform conditions.

The procedure for carrying out the Waring titration as given by Mahin (11) states that the standard potassium ferrocyanide solution should be made with an equivalence of about 0.005 gram of zinc. Since the Waring titrations already described in this study had been made with a ferrocyanide solution of about twice this strength, it was hoped that by using a more dilute solution more consistent results could be obtained. However, this did not prove to be the case, for the average deviation was 11.8 parts in a thousand.

Interference

Obviously the same elements which interfere in the Waring ferrocyanide titration will also be objectionable in the ferrocyanide-ceriometric determination. The most important of these are iron, cadmium, and copper, and their complete removal must be made before precipitation of the zinc. Waring (19) also includes under interference antimony, manganese, aluminum, and organic acids.

If hydrogen sulfide is used to separate interfering elements in an ore and is, therefore, present during the precipitation of the zinc, it must also be present in the standardization of the potassium ferrocyanide solution according to Park (16), because it reduces potassium ferricyanide which is invariably present in small amounts in the potassium ferrocyanide solution.

Advantages and Disadvantages

The results of the ferrocyanide-ceriometric determinations of zinc in sphalerite ores compare very favorably with the results of the gravimetric determinations, the greatest difference being only -0.03 per cent zinc. The deviations varied from 0.7 to 3.9 parts per thousand as compared with 0.4 to 3.1 parts per thousand for the gravimetric method. This new method has the advantage

over the modified Waring method of not only giving
greater accuracy, but also of having a color change at
the end point which is very readily seen.

The disadvantages of the method are that two stan-
dard solutions are required instead of only one, and
that the additional operation of filtering off the zinc
precipitate is necessary. Furthermore, the potassium
ferrocyanide solution must be standardized against a
zinc salt or ore of known zinc content since the rela-
tion between potassium ferrocyanide and zinc appears to
be an empirical one.

SUMMARY

A new titrimetric method has been developed for the determination of zinc in ores using excess standard potassium ferrocyanide solution to precipitate the zinc in acid solution as potassium zinc ferrocyanide, the excess precipitant being determined by titration with standard ceric sulfate solution after removal of the zinc precipitate by filtration. This method gives results which check within 0.03 per cent of the values obtained by the zinc ammonium phosphate gravimetric method (12).

A study of the modified Waring method as outlined by Mahin (11) confirms the observations of Cone and Cady (3) and of Oesper (14) in regard to the limited degree of accuracy of the method.

The results of the ferrocyanide-ceriometric method are reproducible within 0.6 to 3.9 parts in a thousand as compared to 8.4 to 11.8 parts per thousand for the modified Waring method.

The advantages of the new method over the Waring method, as well as its disadvantages, have been indicated.

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