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UNIVERSITY OF LOUISVILLE

THE POTENTIOMETRIC DETERMINATION OF ZINC
IN DOWMETAL ALLOYS

A DISSERTATION

SUBMITTED TO THE FACULTY

OF THE GRADUATE SCHOOL OF THE UNIVERSITY OF LOUISVILLE

IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

BY

JAMES S. GOODMAN

YEAR
1943

NAME OF STUDENT: James S. Goodman

TITLE OF THESIS: THE POTENTIOMETRIC DETERMINATION
OF ZINC IN DOWMETAL ALLOYS

**APPROVED BY READING COMMITTEE COMPOSED OF THE
FOLLOWING MEMBERS:**

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G. L. Corley

NAME OF DIRECTOR: G. L. Corley

DATE: 5/19/43

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INTRODUCTION

This research was begun because of a desire to find a quicker, easier, and more accurate means of routinely determining zinc in certain of the Dowmetal magnesium alloys.

The analytical procedure recommended by the Dow Chemical Company for the determination of zinc in their alloys is a volumetric method involving the titration of the zinc solution with potassium ferrocyanide using diphenylbenzidine as an internal indicator.(2) This method has been found to be very slow, and the exact end point of the analysis is not sufficiently sharp to permit good check analysis to be run on the same sample.

A few months previously I worked out a rapid potentiometric method for the analysis of Aluminum in Dowmetal alloys. In this research a Fisher Electrometric Titrimeter was employed which is a very compact vacuum tube voltmeter--potentiometer instrument using an electron ray tube to indicate the end point of the titration instead of the usual galvanometer.

The speed and accuracy of this method led to a belief that a potentiometric method might be worked out for the analysis of zinc in Dowmetal alloys using the same Fisher apparatus.

With this in mind the literature was searched to see just what had been done by others in applying a potentiometric method to the determination of zinc. Kolthoff and Furman (7) have discussed the direct titration of zinc with potassium ferrocyanide using a potentiometric system. Kolthoff found however that many factors entered into the accuracy of his method (time, temperature, addition of certain salts, ect.), and he leaves us with no positive conclusions drawn as to any certain method.

Sturges (13) has gone much further in solving the problem of time for equilibrium to be reached between the zinc and the ferrocyanide by adding an excess of ferrocyanide to the zinc samples and back titrating the excess with ceric sulfate using a Titrimeter and a platinum-tungsten electrode. But here again the investigation seemed to be of a preliminary nature, and furthermore was done on pure zinc samples rather than on alloys.

REDOX NONMETALLIC REDOX METALLIC AND QUANTITATIVE

HIGH LOW

QUALITY CONDUCTANCE

FISHER TITRIMETER
QUALITATIVE UNIT

GLASS ELECTRODE

OFF ON

EYE CONTROL

FISHER SCIENTIFIC CO.
PITTSBURGH, PA. U.S.A.

SERIAL NO. []

FISHER TITRIMETER
QUANTITATIVE UNIT

PUSH TO STANDARDIZE

STANDARDIZING CONTROL

100 VOLTS 100 OHMS
10 VOLTS 10,000 OHMS
1 VOLT 1,000,000 OHMS

BLANK ELECTRODE

FISHER SCIENTIFIC CO.
PITTSBURGH, PA. U.S.A.
EITHER & ARSINO
NEW YORK, N.Y. U.S.A.

SERIAL NO. []

EQUIPMENT

The apparatus essential to the success of this research consisted of an Ainsworth Chainomatic Analytical Balance, a set of analytical weights, class S, chromium plated, and a Fisher Electrometric Titrimeter, Senior Model, with glass, calomel, platinum-platinum, and platinum-tungsten electrodes.

The accuracy of the analytical weights and the special burettes supplied with the Titrimeter had been found in previous work to be of a very high degree, and it was not deemed necessary to take time from the problem by repeating the usual calibration work.

The Fisher Titrimeter, as shown in the photograph on the opposite page, consists of a stand housing the electron ray tube or "Electric Eye" which acts as a galvanometer in indicating the end point of a titration, the stirring motor, a burette clamp, and a support for the beaker during the titration. It further consists of a "Qualitative Unit" which is essentially a vacuum tube voltmeter amplifier, and a "Qualitative Unit" which introduces a wheatstone-bridge circuit for use in pH determinations with the glass-calomel electrode system. The electrode holders are

so designed as to make the interchange of the electrodes and electrode-stirrers a quick and easy matter. The stirring motor is connected with the stirrer by means of a spring belt.

The reagents used were of C.P. quality and were obtained from reputable manufacturers. They consisted of potassium ferrocyanide, ceric sulfate, o-phenanthroline ferrous complex indicator, ammonium sulfate, ammonium chloride, ammonium persulfate, sodium oxalate, pure zinc metal, potassium permanganate, hydrogen sulfide, diphenylbenzidine indicator, tartaric acid, hydrochloric acid, sulfuric acid, formic acid, and ammonium hydroxide.

The potassium ferrocyanide solution was made up by dissolving 18 g. of $K_4Fe(CN)_6$ in a liter of distilled water and allowing the solution to stand for three weeks in order for complete equilibrium to be reached. It was standardized against standard zinc solution immediately before use each time, the method depending upon the zinc method used as this was considered to give the utmost in accuracy.

Ceric sulfate was a relatively new reagent, and considerable time was spent in investigating its

properties. It forms two compounds, cerous in which it has a valence of 3 and is colorless, and ceric in which it has a valence of four and has an orange color. As compared with potassium permanganate it is fully as strong as an oxidizing agent, is very stable, can be used in the presence of hydrochloric acid, and has only one possible valence change. It was made up by dissolving 33.25 g. of anhydrous $\text{Ce}(\text{SO}_4)_2$ in 1 N. sulfuric acid and making the total volume to 1 liter with the same 1 N. sulfuric acid solution, its own color being used as an indicator. Three runs were as follows--

1. Wt. $\text{Na}_2\text{C}_2\text{O}_4$ ---0.1866 g. 2. Wt. $\text{Na}_2\text{C}_2\text{O}_4$ ---0.1260 g.

Ml. $\text{Ce}(\text{SO}_4)_2$ -- 24.95

Ml. $\text{Ce}(\text{SO}_4)_2$ -- 16.84

$$N = \frac{0.1866}{24.95 \times 0.067}$$

$$N = \frac{0.1260}{16.84 \times 0.067}$$

$$N = 0.1116$$

$$N = 0.1117$$

3. Wt. $\text{Na}_2\text{C}_2\text{O}_4$ ---0.1230 g.

Ml. $\text{Ce}(\text{SO}_4)_2$ -- 16.45

$$N = \frac{0.1230}{16.45 \times 0.067}$$

$$N = 1.1116$$

The agreement obtained on the three runs was considered

to be very good; in no case was there any doubt as to the end point of the titration. The temperature was kept just below the boiling point.

The o-phenanthroline ferrous complex indicator was obtained in the prepared form. It sometimes bears the trade name "Feroïn".

The ammonium sulfate and ammonium chloride were used in crystalline form, simply being added to the solutions for certain purposes. These will be discussed under the experiments in which they were used.

The tartaric acid solution was made up by dissolving 25 g. of tartaric acid in distilled water and making up to 500 ml.

The diphenylbenzidine indicator solution was made up by dissolving 0.5 g. of diphenylbenzidine in 50 ml. of sulfuric acid (sp. gr. 1.84).

The standard zinc solution was made up by weighing out very accurately 4 g. of pure zinc metal and dissolving in hydrochloric acid (1:4). This was then diluted to one liter with distilled water. The zinc content of this solution was 0.004 g. per ml.

A formate buffer solution was prepared by diluting 200 ml. of formic acid (sp. gr. 1.20) to 970 ml.

with distilled water and adding 30 ml. of ammonium hydroxide (sp. gr. 0.90).

The hydrogen sulfide used was obtained in small cylinders from the Fisher Scientific Co., and was of C.P. analytical quality.

The other reagents not mentioned specifically here will be discussed where used.

THEORY

A detailed description of the wiring diagram of the Fisher Electrometric Titrimeter is beyond the scope of this investigation, although the diagram is shown on the opposite page. The principle involved is that of the classical potentiometric method. (5, 8) While there is no known method which is reasonably reliable for measuring a single potential difference, it is possible to measure the potential of any given electrode by means of another electrode which has a constant potential. Such an electrode is known as a standard half-cell. In the following work the electrode having the constant known potential will be referred to as the reference electrode, and the electrode whose potential changes during the course of a titration as an indicator electrode.

The principle of the potentiometer method consists in balancing the potential difference that is to be measured against a known opposed potential difference. When such a balance is reached it is indicated by a null point on the galvanometer or by a steady slit in the electron ray tube of the Fisher instrument.

This principle is illustrated by the simple diagram at the top of the preceeding page. Let S be a battery having an E.M.F. greater than that of the unknown cell X, the E.M.F. of which we want to determine. SA and SB are of heavy copper so as to have a very small resistance. AB is a slide wire of uniform diameter throughout its entire length so as to have a uniform fall of potential from A to B. C is a contact sliding along the wire AB, and is so connected to the unknown X that the positive pole of X corresponds to the positive pole of the battery and that the negative pole of X is connected to the negative pole of the battery. Thus in the circuit CXGB there are two different electromotive forces, E_{cb} between C and B and that of X which is furnishing current in the opposite direction. C is now moved along AB until G

indicates that current is no longer flowing through CXBG. Since AB is of uniform cross section, the difference in potential between A and B is equal to $\frac{BC}{AB} \times E$, where E is the electromotive

force of the battery. $\frac{BC}{AB}$ is the ratio between the

resistances of BC and AB. In this case this ratio is equal to that of the lengths of AB and BC. If the total length of AB is 1000 mm., then the relation for e, the unknown E.M.F. of X we have

$$e = \frac{BC}{1000} E = \frac{a}{1000} E$$

where a is the value read on the slide wire. E in this case is unknown, but may be easily determined by switching X out of the circuit and throwing in its place a standard cell of known E.M.F. such as a Weston cadmium cell.

With this elementary discussion of the potentiometer, a study of electrometric titrations may now be discussed. Such a titration may be defined as a titration in which the end point of the reaction is detected by measuring the change in potential of a suitable electrode during the titration as referred to a standard reference electrode. In the course of this research a reversible electrode must of necessity be dealt with, and therefore the potential can be expressed

by the thermodynamic equation

$$E = E^{\circ} + \frac{RT}{F} \ln (a_1)^{1/n}$$

where a_1 is the activity of the ion in question and n is its valence. Furthermore an oxidation-reduction system is used in this investigation, and therefore the determining factor in the potential of the indicator electrode is the ratio of the activities or concentrations of the oxidized and reduced forms and the above equation becomes

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{a(\text{ous})}{a(\text{ic})}$$

This equation determines the shape of the titration curve and the value of E° obtained from the equilibrium constant will determine its position. In ordinary potentiometric titrations, such as would be run in routine work, it is only necessary to find the end point of the reaction, and the activities of the ions are not concerned. As the titration progresses the reagent is added gradually until the voltage changes rapidly with the addition of fractional parts of a milliliter of the reagent. At the end point the rate of change of this potential with a small change in concentration reaches a maximum value.

EXPERIMENTAL

This research is to find out if zinc can be titrated with reasonable ease, speed, and accuracy using a Fisher Electrometric Titrimeter.

A study of both the platinum-platinum and platinum-tungsten electrodes to determine which is best suited to the titration, will be made. On the basis of the work of other investigators (7,13) it is believed that an indirect titration using an excess of ferrocyanide and back titrating with an oxidizing agent is to be preferred over a direct titration with the ferrocyanide.

An investigation of the effect of time of titration, temperature, acidity, and the addition of certain salts will also be conducted.

The success or failure of the method will be measured by comparing the results obtained with several Dowmetal alloy standards furnished by the Dow Chemical Company. The same samples will be analyzed using the old volumetric procedure, and will also run the same samples spectrographically. It was furthermore to be determined if the sulfide separation of the impurity elements by suitable treatment of the sample could be avoided.

EXPERIMENT No.1

The sample used in this, as well as in the following experiments, was prepared by casting the alloy in half-inch square bars using iron molds. It has been determined that this procedure provides fast chilling of the metal with resulting fine grain structure and uniformity of composition. These bars are cut into thin slices using a power sample saw, and these slices are taken for analysis.

In this first experiment the only interest was in testing the instrument to see if suitable inflection points could be noted with the "electric eye" of the instrument. A sample was selected at random from the regular run of samples. A weight calculated to contain 0.05 to 0.1 g. of zinc was weighed out, dissolved in hydrochloric acid, the zinc separated as the sulfide, and the solution placed in the titration assembly using the platinum-tungsten electrodes. Titrating first with ferrocyanide solution a very sharp break took place after the addition of about 15 ml. This break was not permanent however, so another 10ml. of ferrocyanide was added and the solution back titrated with ceric sulfate solution. The end point of this back titration was quite sharp and the eye remained permanently in a closed position. The result of this experiment, though qualitative, served

to show that the instrument would indicate end points and that the research could be continued in a careful quantitative manner.

EXPERIMENT NO. 2

In this experiment duplicate samples were prepared from Downmetal standard No. N. This sample contained

Al--10.17%
Mn-- 0.18%
Zn-- 2.06%

The treatment of the sample was as follows: The weight of sample was calculated to contain 0.05 to 0.1 g. of zinc. The samples were dissolved in hydrochloric acid using 7.5 ml. per gram of sample and an excess of 10ml. When solution was complete they were diluted to 200 ml. and sulfided for 3 minutes and filtered. The filtrate was boiled to expel the H_2S , 50ml. of tartaric acid solution was added (to prevent the formation of aluminum hydroxide) and the samples neutralized to methyl red with ammonium hydroxide (1:1). 25 ml. of formate buffer were added, the solutions heated to boiling and sulfided for 15 minutes with a rapid stream of H_2S . The zinc sulfide was dissolved from the filter paper with hot HCl (1:4), boiled to expel H_2S , and made neutral to litmus with ammonium hydroxide. 10 g. of ammonium chloride and 15 ml. of sulfuric acid (1:4) were added, and the samples were ready to titrate.

The above procedure for the treatment of the sample is the same as that used for the volumetric titration as recommended by the Dow Chemical Company (2). It was thought that until the findings showed differently such a procedure might well be used for, if such treatment prior to titration is suitable for direct volumetric titration, it should also be suitable for a potentiometric titration. The data and results are as follows--

Sample No. I

Wt. sample -- 2.6423 g.

ml. $K_4Fe(CN)_6$ -- 30.00ml. $Ce(SO_4)_2$ -- 7.59

% Zn -- 2.07

Sample No. II

Wt. sample -- 2.8010g.

ml. $K_4Fe(CN)_6$ -- 30.00ml. $Ce(SO_4)_2$ -- 6.64

% Zn -- 2.08

The platinum-tungsten electrode system was used in both titrations and time allowed between the addition of the ferrocyanide and the back titration with ceric sulfate was 20 minutes. This wait was allowed to be sure that equilibrium was established in the zinc ferrocyanide precipitation.

A sample of standard zinc solution was run at the same times as the unknown to standardize the ferrocyanide.

A fairly good deflection of the electric eye was noted as the ferrocyanide was being added, and upon back titration with the ceric sulfate a very pronounced effect was noted, the change at the end point being from completely open to completely closed. The results are also in very close agreement with the theoretical value of 2.06 %.

The results obtained in this first experiment were much better than one would normally expect in the first quantitative run of a research determination, in fact, they would justify a claim for success if they could be proven to hold in all cases. However, this was not known, and many factors could possibly enter in.

EXPERIMENT No. 3

In order to determine if the same degree of accuracy might be obtained on a different sample of a slightly different alloy, two samples of Dowmetal Standard No. H were prepared in exactly the same way as in the previous experiment. A standard zinc sample was run at the same time as the unknown and received the same treatment in order to standardize the ferrocyanide. The time between the addition of the ferrocyanide and the back titration with ceric sulfate was again 20 minutes. The data and results are as follows--

1. Wt. Sample --- 3.0070 g.	2. Wt. Sample --- 2.7903g.
ml. $K_4Fe(CN)_6$ --- 35.00	ml. $K_4Fe(CN)_6$ --- 35.00
ml. $Ce(SO_4)_2$ --- 5.85	ml. $Ce(SO_4)_2$ --- 8.70
% Zn --- 2.57	% Zn --- 2.40

Average --- 2.49%

The theoretical composition of this sample was as follows--

Al - - 6.35 %
Mn - - 0.36 %
Zn - - 2.50 %
Si - - 0.28 %

In this case we did not obtain quite as good checks as in the previous run, but the accuracy is still considered quite good for potentiometric work

of a routine nature. Furthermore it was as good as had been found using the volumetric method. Again the eye gave a very definite indication of the ceric sulfate end point.

EXPERIMENT No. 4

In this experiment duplicate samples of Dowmetal standard No. H were prepared. The treatment was the same as in the previous experiments, but upon titration they were back titrated with 0.1 N. potassium permanganate instead of ceric sulfate. The results were disappointing. Instead of the quick definite closing of the electric eye at the end point of the titration as in the case of ceric sulfate, a gradual change took place which was difficult to see.

The data and results are as follows--

Sample No. 1	Sample No. 2
Wt. Sample --- 2.7670 g.	Wt. Sample --- 2.3454 g.
ml. $K_4Fe(CN)_6$ -- 30.00	ml. $K_4Fe(CN)_6$ -- 30.00
ml. $KMnO_4$ --- 6.75	ml. $KMnO_4$ --- 5.50
% Zn -- 2.18 (Theoretical - 2.50%)	% Zn -- 2.26

This leads to the conclusion that potassium permanganate is not as suitable for the back titration of excess ferrocyanide as the ceric sulfate.

EXPERIMENT No. 5

The previous experiments had all employed the platinum-tungsten electrode system. This experiment was made to determine the comparative sensitivity and accuracy of the platinum-platinum electrode system.

In order to have a basis of comparison, a fourth sample of the same Dowmetal standard H was prepared in the same way as previous samples. The only change was in the electrode system, ceric sulfate again being used for the back titration.

The results of this titration were uncertain. The electric eye would flutter at the addition of each increment of reagent, and no definite end point was ever reached. It must be concluded therefore that the platinum-platinum electrode system is totally unsuited to the potentiometric determination of zinc. The data, though meaningless, is given below--

Wt. Sample --- 3.5095 g.

ml. $K_4Fe(CN)_6$ -- 30.00

ml. $Ce(SO_4)_2$ -- 50.00 (End point not reached)

% Zn -- ?

EXPERIMENT No. 6

This experiment is to determine the effect of varying the acidity of the solution being titrated. Six samples of the Dowmetal Standard H were weighed out and prepared identically down to the addition of the 1:4 sulfuric acid. To samples Nos. 1 and 2 were added 10 ml. of acid; to samples Nos. 3 and 4 were added 20 ml. of acid; and to sample No. 5 and 6 were added 30 ml. of acid. They were then titrated in the same way using the platinum-tungsten electrode and ceric sulfate as the back titrant. The data and results are given below--

	Sample 1	Sample 2(10ml)	Sample 3
Wt. sample	2.3945 g.	2.4425 g.	2.3188 g.
ml. $K_4Fe(CN)_6$	30.00	30.00	30.00
ml. $Ce(SO_4)_2$	4.51	7.10	4.70
% Zinc	2.38	2.30	2.42

	Sample 4(20 ml)	Sample 5	Sample 6(30ml)
Wt. sample	2.5276 g.	2.2023 g.	2.5231 g.
ml. $K_4Fe(CN)_6$	30.00	30.00	30.00
ml. $Ce(SO_4)_2$	4.91	6.30	6.29
% Zn	2.53	2.35	2.33

The result agreeing most closely with the theoretical in the above series was obtained from sample 2 with 20 ml. of 1:4 sulfuric acid added. The results from both 1 and 3 are much lower indicating that there is an optimum acidity for this titration. This would seem to bear out the Dow specification of 15 ml. fairly closely. It was also noted that the sharpest end point was obtained with the No. 2 sample, and in the No. 3 sample, which was most strongly acid a tendency in the eye to flutter was noticed.

EXPERIMENT No. 7

This run was made to see if the temperature of the titration had any bearing on the results obtained. Three temperatures were arbitrarily chosen; room temperature of 21°C , 50°C , and 70°C . The upper limit was chosen because at temperatures above this hydrocyanic acid begins to form. The Dowmetal Standard N was chosen for the samples, which were prepared as in experiment No. 2. The platinum-tungsten electrode system was employed and the back titration was made with ceric sulfate. Sample Nos. 1 and 2 were titrated at 21° , sample Nos. 3 and 4 were titrated at 50° , and sample Nos. 5 and 6 were titrated at 70° . The data and results are given below.

	Sample 1	Sample 2	Sample 3
Wt. sample	2.4250 g.	2.5373 g.	2.3204 g.
ml. $\text{K}_4\text{Fe}(\text{CN})_6$	30.00	30.00	30.00
ml. $\text{Ce}(\text{SO}_4)_2$	5.80	5.80	6.20
% Zinc	2.09	2.02	2.11
	Sample 4	Sample 5	Sample 6
Wt. sample	2.4475 g.	2.3340 g.	2.3588 g.
ml. $\text{K}_4\text{Fe}(\text{CN})_6$	30.00	30.00	30.00
ml. $\text{Ce}(\text{SO}_4)_2$	5.95	7.70	2.05
% Zn	2.07	1.99	2.05

The results of all six analyses show very good agreement with the theoretical value of 2.06%, the conclusion being that temperature does not play a very important part in the titration. However the best agreement is shown by samples 1 and 2 titrated at room temperature, and this normal temperature is a decided advantage where many samples have to be determined in a routine manner.

EXPERIMENTS No. 8

Several investigators have noted that one cause of the difficulty in zinc titrations has been the slowness with which the titration must be made in order to avoid errors caused by lack of equilibrium in the zinc ferrocyanide formation. (7) This difficulty may be largely overcome by adding an excess of ferrocyanide, and after a time interval back titrate the excess with an oxidizing agent. This experiment is to determine if possible the effect of different times of standing of the solutions after adding the excess of ferrocyanide but before back titrating. Eight samples of Dowmetal Standard H were prepared as in the previous experiment. Nos. 1 and 2 back titrated immediately, Nos. 3 and 4 were allowed to stand for 10 minutes, Nos. 5 and 6 for 20 minutes, and Nos. 7 and 8 for 40 minutes. The data and results are given below.

	Sample 1	Sample 2	Sample 3
Wt. Sample	2.4576 g.	2.3772 g.	2.0679 g.
ml. $K_4Fe(CN)_6$	30.00	30.00	30.00
ml. $Ce(SO_4)_2$	4.85	5.59	6.20
% Zn	2.27	2.21	2.43

	Sample 4	Sample 5	Sample 6	Sample 7
Wt. sample	2.6438 g.	3.0534 g.	2.7609 g.	2.6686 g.
ml. $K_4Fe(CN)_6$	30.00	30.00	30.00	30.00
ml. $Ce(SO_4)_2$	4.38	5.88	3.86	4.52
% Zn	2.51	2.53	2.48	2.46

Sample 8

Wt. sample	2.5037 g.
ml. $K_4Fe(CN)_6$	30.00
ml. $Ce(SO_4)_2$	5.00
% Zn	2.54

The above results seem to indicate that an immediate back titration produces low results, but that after ten minutes little change is produced by further increasing the time of wait.

EXPERIMENT No. 9

This experiment was designed to determine the effect of ammonium chloride upon the zinc titration. Six samples were run with additions of 10 g., 20 g., and 30 g. respectively. These analyses were made upon Downmetal Standard N, and the samples were prepared as in the preceding experiment. Samples Nos. 1 and 2 contained 10 g of NH_4Cl , samples Nos. 3 and 4 contained 20 g of NH_4Cl , and samples Nos. 5 and 6 contained 30 g of NH_4Cl . The data and results are given below.

	Sample 1	Sample 2	Sample 3	Sample 4
Wt. sample	2.5764 g.	2.4773 g.	2.5068 g.	2.5530 g.
ml. $\text{K}_4\text{Fe}(\text{CN})_6$	25.00	30.00	25.00	30.00
ml. $\text{Ce}(\text{SO}_4)_2$	3.85	5.70	5.20	5.91
% Zn	2.11	2.09	1.98	1.99

	Sample 5	Sample 6
Wt. sample	2.5904 g.	2.7212 g.
ml. $\text{K}_4\text{Fe}(\text{CN})_6$	25.00	30.00
ml. $\text{Ce}(\text{SO}_4)_2$	4.90	5.44
% Zn	1.96	1.94

Samples 1, 2, 3, and 4 are not so far from the theoretical value of 2.06 %, but nos. 5 and 6 are a little on the low side. The tendency seems to be for the larger amounts of NH_4Cl to lower the results of the analysis. No effect could be noted in the reaction of the electrodes as measured by the activity of the electric eye at the end point. Since the theoretical value of 2.06 lies between the results on samples 1 and 2, and 5 and 6, and since 15 g. is between the 10 and 20 used in 1 and respectively, it seems justifiable to continue to use the addition of 15 g.

EXPERIMENT No. 10

This experiment was to determine if there was an appreciable difference in the end point as shown by the electric eye of the Titrimeter and that shown by an internal indicator in the solution.

For this experiment a sample was selected at random and prepared in the standard way. The ferrocyanide was added, and after a wait of 20 minutes 3 drops of o-phenanthroline ferrous complex indicator was added. The titration was continued with the ceric sulfate until the electric eye showed an end point by a rapid closing. A further addition of two drops of the reagent produced a distinct color change in the solution from red to blue.

The above results indicated that there is a very close agreement between the electrometric end point and the indicator end point when the solution is titrated as above.

EXPERIMENT No. 11

This experiment was run to get a comparison between an analysis of the alloy for zinc separated in the manner described in experiment 2, and an analysis run without any separation whatever. Accordingly one sample was weighed out and prepared in the same way as in previous experiments. A second sample was weighed out and treated in the same way except for the sulfide precipitations. The sulfied sample was marked No. 1 and the sample not separated marked No. 2. The data and results are as follows:

	Sample 1	Sample 2
Wt. sample	2.4576 g.	2.3685 g.
ml. $K_4Fe(CN)_6$	30.00	30.00
ml. $Ce(SO_4)_2$	6.28	5.50
% Zn	2.06	2.18

These results would seem to indicate that the failure to separate zinc as the sulfide and redissolving causes the analysis to give results that are too high, although the difference was much less than expected.

EXPERIMENT No. 12

The results of the previous experiment led us to wonder if possibly the presence of manganese in the solution might be causing the results to be high, because Kolthoff found that this element would interfere.(7) It was decided therefore to repeat the preceeding experiment using one sample prepared in the standard way as a reference, and preparing two other samples in which we precipitated the manganese as the dioxide with ammonium persulfate. Sample No. 1 was treated as in experiment 2; samples Nos. 2 and 3 were treated with the persulfate. The data and results are given below.

	Sample 1	Sample 2	Sample 3
Wt. Sample	2.3389 g.	2.3728 g.	2.4206 g.
ml. $K_4Fe(CN)_6$	30.00	30.00	30.00
ml. $Ce(SO_4)_2$	8.52	8.60	9.50
% Zinc	2.04	2.00	1.98

The results of these runs are in much better agreement with the theoretical value than the results in the preceeding experiment. In fact, even though

they are still on the low side, there is good indication that by this potentiometric method the zinc in magnesium alloys may be very quickly estimated in this way without any long sulfide precipitations whatever. The eye of the instrument further seemed unaffected by the change in procedure.

EXPERIMENT No. 13

In previous experiments it has been seen that the potentiometric titration of zinc using an excess of potassium ferrocyanide and back titrating the excess with ceric sulfate is a usable method, and have determined the effect of certain factors. In this last experiment of this research our findings on six samples will be tested, running them potentiometrically, volumetrically, and spectrographically.

For the potentiometric titrations the samples will be prepared as in experiment No. 2.

For the volumetric titration the samples will also be prepared as in experiment No. 2, but they will be directly titrated with potassium ferrocyanide to an end point using diphenylbenzidine as an indicator. This is in accordance with the procedure listed in the Dow Chemical Company Manual.(2)

For the spectrographic determination the samples were run on a Dietert grating spectrograph, using the internal standard method of Gerlach and Schweitzer.(4) The zinc line used was 3282 A. and

was referred to the internal standard line of magnesium at 3074 A.

The data and results are as follows:

Sample No.	Potentiometric % Zinc	Volumetric %Zinc	Spectrographic %Zinc
12H18E2	2.59	2.53	2.56
12C9E3	1.98	1.90	2.01
12H10A3	2.16	2.13	2.17
B123	1.92	1.86	1.91
D Stand.	2.77	2.73	2.79
12C22C6	2.17	2.11	2.17

The above results seem to clearly indicate that the potentiometric titration of zinc is a reliable method. We consider the spectrographic determination to be much more accurate and reproduceable than the volumetric analysis, and a glance at the above table shows that the potentiometric and the spectrographic results agree much more closely than the volumetric.

SUMMARY

This research has demonstrated that zinc can be determined by a potentiometric titration using a Fisher Electrometric Titrimeter employing an electron ray tube or "electric eye" as an indicator.

It was determined that the addition of an excess of ferrocyanide and the subsequent titration of the excess after equilibrium had been reached with ceric sulfate was more reliable and reproduceable than a direct titration.

Experiments showed that the use of potassium permanganate for titrating the excess of ferrocyanide was totally unsatisfactory, and that while the platinum-tungsten electrode was satisfactory, the platinum-platinum electrode would give no results whatever.

The effect of temperature, time, acidity, and electrolyte on the titration was studied. The temperature seemed to have little effect on the results. It was found that the solutions could not be immediately back titrated, but that after equilibrium had been reached time had no effect. In the case of acidity

and electrolyte concentration in the form of NH_4Cl it was found that low concentrations of both were desirable.

A comparison of the end points shown on the same sample by the electric eye and an internal indicator showed good agreement between the two.

Experiments run to determine the accuracy of the method if the other constituents were not separated from the zinc were run. The first runs gave high values for zinc, but the addition of ammonium persulfate to precipitate the manganese lessened the trouble considerably, and it is believed that fair accuracy can be obtained.

In conclusion, it is believed that this method is very desirable for the analysis of zinc in Dowmetal Magnesium Alloys. It was believed that the success of this investigation was fostered by having an excellent instrument with which to work.

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