THE USE OF DITHIZONE AS AN INDICATOR IN THE TITRIMETRIC DETERMINATION OF ZINC WITH FERROCYANIDE

by

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Theoretical Considerations</td>
<td>3</td>
</tr>
<tr>
<td>Solutions and Apparatus</td>
<td>6</td>
</tr>
<tr>
<td>Dithizone Indicator Solution</td>
<td>6</td>
</tr>
<tr>
<td>Potassium Acid Phthalate Solution</td>
<td>6</td>
</tr>
<tr>
<td>Potassium Ferrocyanide Solution</td>
<td>6</td>
</tr>
<tr>
<td>pH Meter</td>
<td>7</td>
</tr>
<tr>
<td>Experimental Procedures</td>
<td>8</td>
</tr>
<tr>
<td>Experimental Results and Sample Calculations</td>
<td>12</td>
</tr>
<tr>
<td>Table I. Comparative Results for Methods of Determining Zinc</td>
<td>12</td>
</tr>
<tr>
<td>Experimental Results</td>
<td>13</td>
</tr>
<tr>
<td>Sample Calculations</td>
<td>13</td>
</tr>
<tr>
<td>Determination of Zinc</td>
<td>14</td>
</tr>
<tr>
<td>Preparation of Samples</td>
<td>14</td>
</tr>
<tr>
<td>Precipitation and Filtration</td>
<td>14</td>
</tr>
<tr>
<td>Titration</td>
<td>15</td>
</tr>
<tr>
<td>Description of End Point</td>
<td>16</td>
</tr>
<tr>
<td>Interfering Ions</td>
<td>17</td>
</tr>
<tr>
<td>Discussion</td>
<td>18</td>
</tr>
<tr>
<td>Summary</td>
<td>19</td>
</tr>
<tr>
<td>Literature Cited</td>
<td>20</td>
</tr>
</tbody>
</table>
THE USE OF DITHIZONE AS AN INDICATOR IN THE TITRIMETRIC DETERMINATION OF ZINC WITH FERROCYANIDE

Introduction

The organic compound diphenylthiocarbazone, commonly called dithizone (7, p. 1), has already found wide acceptance as an analytical reagent for the quantitative determination of zinc through the intense coloration of its metallic derivatives and its extractive powers. The coloration of its metallic derivatives is used for the colorimetric (2, pp. 127-131) or spectrophotometric determination (1, pp. 145-149) of the concentration of metallic ions in solutions, while its extractive powers are the basis for titrimetric methods (6, pp. 35-36).

In each of these methods the dithizone serves as a standardized reagent; a role for which it is not well adapted because of certain of its physical and chemical properties which will be reviewed in the theoretical considerations of the method proposed in this thesis. At the same time, potassium ferrocyanide has been used as a reagent for the quantitative precipitation of zinc in titrimetric determinations (3, pp. 268-271). These existing methods have inherent defects which cause them to be rather tedious or require the preparation of more than one standard solution.

The object of the present work was to develop a method for the determination of zinc which embodied the desirable
qualities of each of these reagents. This could be developed if the dithizone was used merely to indicate the presence of the zinc ions in solutions, while the ferrocyanide ion was used as a means of removing zinc ions from solution as the insoluble zinc potassium ferrocyanide. The research conducted was to determine whether conditions demanded by each of these reagents could be met in a manner that would afford the greatest degree of accuracy with the least possible manipulation of the sample.

As a result of this research a method is presented which allows for direct and accurate determination of the concentration of zinc ions in solution by a titrimetric method. It involves the use of only one standardized solution and requires minimum handling of samples and solutions.
Theoretical Considerations

The distinguishing feature of the proposed method for the determination of zinc is that the end point of the reaction is detected by an indicator which owes its action solely to the presence of an excess of the ion being determined. This eliminates the need of using more than one standard solution as is often the case in titrimetric determinations of metallic ions. Another unusual but very important aspect in favor of this indicator is that it is contained in a tiny droplet of an organic solvent which is immiscible with water. This localization of the indicator allows for greater color contrast at the end point than is possible when the indicator is dispersed throughout the entire volume of the reactants.

This indicator, diphenylthiocarbazone, or dithizone as it is more commonly referred to in literature, has the following composition and forms metallic complexes (7, p.1) as indicated below:

\[
\begin{align*}
N: & :N: \text{C}_6\text{H}_5 \\
S: & :C \\
N: & :N: \text{C}_6\text{H}_5 \\
\text{H}: & \text{H}
\end{align*}
\]

\[
\begin{align*}
N: & :N: \text{C}_6\text{H}_5 \\
\text{H}: & \text{S}: C \\
N: & :N: \text{C}_6\text{H}_5 \\
\text{H}: & \text{H}
\end{align*}
\]
These metallic complexes are stable, but will form only in a limited pH range (5, p. 67). For zinc this range is wide; the reaction of the dithizone with zinc takes place slowly at pH 3.5 and more rapidly as pH 5.0 is approached or exceeded. The speed of reaction of dithizone with the zinc ion sets the lower limit of the pH range for this method at pH 3.5, while the stability of the zinc-ferrocyanide precipitate seems to limit the upper range at pH 5.0. Within these limits the dithizone, normally a bright emerald green, rapidly turns pink due to formation of the metallic complexes shown above if a slight quantity of zinc ion is free in the media surrounding the indicator droplet. This indicator and its metallic derivatives are very soluble in chlorinated solvents such as carbon tetrachloride, but are practically insoluble in water. It is
this property which allows the localization of the color and intensifies the contrast when the end point is reached.

The above property along with the chemical property of being easily oxidized are the properties which make the preparation and storage of a standardized solution of dithizone difficult. The volatility of the solvent causes rapid variations of the concentration of the standard solution while the effect of oxidation (5, p. 67) causes a continual decrease in concentration of standard solutions. In the case of spectrophotometric determinations these oxidation products also interfere (7, p. 4) as their absorption bands do not coincide with the absorption bands of either the dithizone or its metallic complexes. The variations caused by these properties do not in any way affect the value of the dithizone as an indicator.

Since the dithizone indicator is capable of reacting with zinc in this slightly acid solution and the standard precipitant, potassium ferrocyanide, is specific for zinc under these conditions, the use of these reagents is well suited for the intended purpose. The bulk of the experimental work, therefore, consisted of determining the best method for preparing solutions of the sample to conform to these requirements, and the determination of permissible variations in the order of addition of reagents and indicator to furnish the most accurate and consistent results.
Solutions and Apparatus

**Dithizone Indicator Solution.** This solution was prepared by dissolving 0.007 gram of pure dithizone crystals in 100 ml. of carbon tetrachloride. The concentration of this solution should be adjusted so that one drop of the zinc solution to be analyzed in 50 ml. of buffer solution (pH 4) will cause the indicator to turn pink in less than 30 seconds.

**Potassium Acid Phthalate Solution.** A ten per cent solution was prepared by dissolving 100 grams of pure potassium acid phthalate in one liter of distilled water.

**Potassium Ferrocyanide Solution.** The standard solution was prepared by dissolving 1.7 grams of the trihydrate in one liter of water. This solution should be extracted with dithizone solution to remove any possible interfering metallic ions. The extraction should be repeated until the dithizone retains its original color after it has been in intimate contact with the reagent solution for at least ten minutes. After the dithizone extraction the solution was standardized against a sphalerite ore the zinc content of which had been previously determined gravimetrically by weighing zinc ammonium phosphate and titrimetrically by the ferrocyanide-cerimetric method (4, p. 52). The standardization was performed according to the procedure for titration recommended in this work.
**pH Meter.** The instrument used to determine the pH values of the various solutions was a Beckman model H2 pH meter.
Experimental Procedures

This research was based on facts from literature concerning both the indicator, dithizone, and the standard precipitant. It has been shown by previous investigators that dithizone is capable of extracting zinc ions from aqueous solutions between pH 3 and pH 6 (5, p. 69) and that ferrocyanide precipitates zinc quantitatively in slightly acid solutions (3, p. 269). In view of these facts a series of tests was carried out to determine whether the zinc ferrocyanide precipitate was insoluble enough in the imposed pH range to lower the zinc ion concentration below the minimum concentration detectable by the sensitive reagent dithizone.

Aliquots of a solution containing zinc ions were prepared and to each was added an increment of ferrocyanide solution. Since the relationship is empirical the increment was varied to provide solutions with an excess of ferrocyanide and with an excess of zinc ions, while between the extremes the excesses decreased at regular intervals. One drop of dithizone solution was added to each and the time required for the color change of the droplet was noted. The time required for the color change varied only slightly and if no change was apparent in one minute, no change occurred thereafter. Since all the solutions
which changed color were below a certain minimum amount of ferrocyanide it was apparent that the ferrocyanide could reduce the zinc ion concentration to a point where the dithizone could not detect it and, therefore, would be suitable as a precipitant.

Investigation was conducted to determine approximately the effect of pH. A series of solutions, identical to the two solutions from the first series which indicated the least excess of zinc and ferrocyanide, respectively, was prepared and buffered to pH values of 3.0, 3.5, 4.0, 4.5, and 5.0. All pH values were measured with a Beckman model H2 pH meter. To each of these solutions one drop of dithizone indicator was added and the time required for the color change was noted. In all cases where an excess of zinc was present the color of the indicator changed to pink, but the solution buffered to pH 3.0 took excessive time to change. In the case of the solutions containing excess ferrocyanide a color change of the indicator was noted only in the solution buffered to pH 5.0. This indicated that precipitation was not complete at this pH value. From these tests it was decided that the titrations should be performed at a pH value near 4.0 since pH 3.0 caused slow action of the indicator and pH 5.0 did not give complete precipitation.
The reproducibility of the end point was established by performing a series of titrations. An attempt was made to titrate the standard zinc solution with the standard ferrocyanide solution using the results of the first investigations as a guide. The first titration showed that the ferrocyanide, even in excess, was not capable of discharging the pink color of the indicator in a reasonable length of time. When the titration was carried out in reverse order a point was reached where the indicator retained its normal green color, but on addition of a single drop of the zinc solution the indicator would rapidly turn pink, thereby indicating an excess of zinc ions. This effect could be repeated with these quantities of zinc and ferrocyanide solutions or equivalent fractions thereof.

The ferrocyanide solution was then standardized and from this standardization the zinc content of a second ore was determined. Two zinc solutions were prepared from ores of known zinc content. One was used to standardize the ferrocyanide solution and the other was used to check the standardization. Each of these solutions was buffered with potassium acid phthalate to pH value 4.0. This was done to avoid any possibility of error from this source. The ferrocyanide solution was titrated and the equivalence of this solution in grams of zinc per milliliter was calculated by the formula given in the experimental results. The second
solution was then titrated by the recommended procedure and the per cent content of zinc was calculated. A tabulated summary of the results for the four ores assayed is presented in the section dealing with experimental results.
## Experimental Results and Sample Calculations

### Table I

**Comparative Results for Methods of Determining Zinc**

<table>
<thead>
<tr>
<th>Sample no. 1 - pH 4.0</th>
<th>Sample no. 2 - pH 4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate method -</td>
<td>Phosphate method -</td>
</tr>
<tr>
<td>16.60 per cent zinc</td>
<td>18.29 per cent zinc</td>
</tr>
<tr>
<td>Dithizone method -</td>
<td>Dithizone method -</td>
</tr>
<tr>
<td>Zinc (per cent)</td>
<td>Zinc (per cent)</td>
</tr>
<tr>
<td>Deviation (per cent)</td>
<td>Deviation (per cent)</td>
</tr>
<tr>
<td>16.64 + 0.04</td>
<td>18.25 - 0.04</td>
</tr>
<tr>
<td>16.60 0.00</td>
<td>18.29 0.00</td>
</tr>
<tr>
<td>16.62 + 0.02</td>
<td>18.27 - 0.02</td>
</tr>
<tr>
<td>16.57 - 0.03</td>
<td>18.31 + 0.02</td>
</tr>
<tr>
<td>16.61 + 0.01</td>
<td>18.28 - 0.01</td>
</tr>
</tbody>
</table>

**Sample no. 3 - pH 4.0**

<table>
<thead>
<tr>
<th>Phosphate method -</th>
<th>Dithizone method -</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.81 per cent zinc</td>
<td></td>
</tr>
<tr>
<td>Zinc (per cent)</td>
<td>Zinc (per cent)</td>
</tr>
<tr>
<td>Deviation (per cent)</td>
<td>Deviation (per cent)</td>
</tr>
<tr>
<td>19.82 + 0.01</td>
<td>15.45 + 0.04</td>
</tr>
<tr>
<td>19.80 - 0.01</td>
<td>15.45 + 0.04</td>
</tr>
<tr>
<td>19.78 - 0.03</td>
<td>15.43 + 0.02</td>
</tr>
<tr>
<td>19.79 - 0.02</td>
<td>15.44 + 0.03</td>
</tr>
<tr>
<td>19.80 - 0.01</td>
<td>15.44 + 0.03</td>
</tr>
</tbody>
</table>

**Sample no. 4 - pH 3.5**

<table>
<thead>
<tr>
<th>Phosphate method -</th>
<th>Dithizone method -</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.41 per cent zinc</td>
<td></td>
</tr>
<tr>
<td>Zinc (per cent)</td>
<td>Zinc (per cent)</td>
</tr>
<tr>
<td>Deviation (per cent)</td>
<td>Deviation (per cent)</td>
</tr>
<tr>
<td>15.32 - 0.09</td>
<td>15.32 - 0.09</td>
</tr>
<tr>
<td>15.32 - 0.09</td>
<td>15.30 - 0.11</td>
</tr>
<tr>
<td>15.31 - 0.10</td>
<td>15.31 - 0.10</td>
</tr>
<tr>
<td></td>
<td>Average</td>
</tr>
</tbody>
</table>
Experimental Results. The results for the determination of zinc in four sphalerite ores by the proposed method of using dithizone as the indicator are shown in Table I. The values obtained by the phosphate gravimetric method (3, p. 524) are also included for comparison.

The ferrocyanide was standardized at pH 4.0 against a sample of known zinc content. All samples were titrated at this same pH value with the exception of sample number 4 which was also titrated at pH 3.5 to show any error caused by variations in the pH value.

Sample Calculations. All calculations of zinc content were made from the following basic formula:

\[
\text{Per cent Zn} = \frac{(\text{Vol. made up})(\text{Ml. Std. Fe(CN)}_4^-)(\text{Eq. of std.})(100)}{\text{(Aliquot)} \times \text{(Sample wt.)}} \\
= \frac{(500 \text{ ml.})(20.00 \text{ ml.})(0.0003042 \text{ gm.})(100)}{1.0000 \text{ gm.}(18.89 \text{ ml.})} = 15.45 \text{ (ml.)}
\]

The equivalence of the standard was calculated by rearranging this formula and substituting the known and experimental values:

\[
\text{Eq. of std.} = \frac{\left(\frac{\% \text{ Zn in ore}}{(\text{Aliquot})(\text{Sample wt.})} \right)(\text{Vol. made up})(\text{Ml. of std.})(100)}{\left(\text{(Vol. made up)(Ml. of std.)}(500 \text{ ml.})(15.20 \text{ ml.})(100)\right)} \\
= \frac{(14.34)(31.45 \text{ ml.})(0.5058 \text{ gm.})}{(500 \text{ ml.})(15.20 \text{ ml.})(100)} = 0.0003042 \text{ gm. of Zn per ml. of ferrocyanide.}
\]
Determination of Zinc

Preparation of Samples. A 0.5-gram sample of ore was warmed in a covered 400-ml. pyrex glass beaker with a mixture of 10 ml. each of concentrated nitric and hydrochloric acids. When the action had ceased the mixture was evaporated to sirupy consistency for the removal of excess acids.

Precipitation and Filtration. The above mixture was diluted to 100 ml. and nearly neutralized with 6 M. sodium hydroxide solution and an excess of 6 M. ammonium hydroxide was added to precipitate any iron. The solution was heated almost to boiling and the supernatant liquid filtered directly into a 500-ml. volumetric flask. The residue in the beaker was washed three times with hot water and the washings were added to the solution in the flask. It was found desirable to reprecipitate the ferric hydroxide, adding all of the solution thus obtained to the volumetric flask. The solution in the flask, after dilution to approximately 300 ml., was neutralized with 6 M. hydrochloric acid until the precipitate of zinc hydroxide just dissolved and was buffered to a pH value of about 4 by adding 30 ml. of a 10 per cent solution of potassium biphthalate. The solution was made up to volume at 20° C. with distilled water after which it was allowed to stand until it had reached room temperature.
Titration. A 20-ml aliquot of the potassium ferrocyanide was allowed to run into a 250-ml Erlenmeyer flask and one drop of dithizone indicator solution was introduced. The zinc solution was added slowly with constant agitation to the ferrocyanide solution until the drop of dithizone turned pink. This run was used only to estimate the amount of zinc solution necessary to react with the aliquot of the ferrocyanide solution.

On the following runs the addition of the dithizone was deferred until shortly before the end point was due as indicated by the first run. After the addition of the indicator, titration was performed drop-wise with a 15-second delay after each drop to allow for development of color in the indicator. The practice of withholding the indicator until near the end point was adopted to allow more rapid addition of the zinc solution without building up a temporary excess of zinc ions and possibly obtaining a false end point. This means of shortening the length of time required for a titration was found to be advantageous because the titration could be carried out at a speed which allowed the zinc ferrocyanide compound to remain in a semicolloidal state and not obscure the color of the drop by its turbidity. Should the solution become turbid before the end point, the indicator can be viewed
through the bottom of the flask and the turbidity furnishes an excellent background for noting the color.

The vessels for each run were set to one side while the next run was made because false end points obtained by too rapid addition of the zinc solution fail to develop the full pink color, or the color may even return to the original green. Back titration can be accomplished, if the end point is passed, by removing the indicator drop with a capillary eyedropper and adding more ferrocyanide solution. A new drop of indicator is then introduced and the titration performed in the normal way. The error thus introduced is very small if care is taken to remove only the indicator drop. The indicator is much more sensitive if the one drop present is broken into many small droplets by vigorous shaking of the flask.

**Description of the End Point.** If the single drop of indicator present in the reaction flask is broken into many droplets the sharpness of the end point is enhanced. False end points caused by too rapid an addition of the zinc solution may be avoided as only a few of the droplets will be affected. The indicator solution itself is a clear emerald green and turns to a bright pink in the presence of zinc ions. This color reaction is not instantaneous, but proceeds rapidly through off shades of green and purple to the final pink color. The time required for this change
is a function of the concentration of the unknown zinc solution. For this reason it is advisable to test the indicator solution by adding one drop of the zinc solution to 50 ml. of a buffer solution, pH value 4, and placing one drop of the indicator in the flask and noting the time required to turn from green to pink. If the time required is more than 30 seconds, it is advisable to use a more dilute solution of the indicator or to prepare a more concentrated solution of the unknown sample.

**Interfering Ions.** The dithizone metals are potential interferences. Since the proposed method differs from current methods only in the means of actual determination of the ion, it is suggested that any method for separation of the zinc ion for a particular ore should be retained. The method of titration recommended is applicable to any solution containing only the zinc ions, ions of the alkali metals, or ammonium ions.

Anion interferences are avoided by the treatment given the ore to bring it to solution and it is unnecessary to introduce these ions in any form after the dissolution of the ore. Any strong oxidizing agents should be removed or reduced in the most feasible manner because dithizone is easily oxidized to an inactive compound which gives a yellow coloration in carbon tetrachloride.
Discussion

The method developed for determining zinc is capable of giving results which compare favorably with those given by the phosphate-gravimetric (3, p. 524) and the ferrocyanide-ferrogravimetric (4, p. 53) methods. It involves no extra filtrations, outside indicators, or other standard solutions. It is, therefore, more convenient and less expensive than these methods. In addition, the color change of the indicator in a droplet of carbon tetrachloride enhances the color contrast at the end point and allows for back titration if necessary.

There are possibilities of error, but they can be avoided by careful work necessary in analytical procedures. The pH factor must be controlled and care must be taken to attain the same pH value, in solutions to be analyzed, as was attained in the standardization of the reagent. This is accomplished by following a set procedure in the neutralization of the solution and dissolution of the zinc hydroxide formed at this time. If the pH value of the solutions is properly controlled the results are consistent and accurate.

The average precision of the method proposed is about ± 0.02 per cent and the average percentage error is about ± 0.089 per cent.
Summary

A ferrocyanide method for the titrimetric determination of zinc has been developed wherein the end point is indicated by dithizone in carbon tetrachloride. The method depends on the formation of insoluble zinc ferrocyanide upon the addition of a zinc solution to standard ferrocyanide solution. When the first excess of zinc ions is reached the dithizone changes from its normal emerald green color to a bright pink; thus giving a distinct indication of the end point. The results obtained using this indicator are as good or superior to those obtained by the usual methods and the time consumed for each determination is greatly decreased.

It has been shown that dithizone is a suitable indicator for the titrimetric determination of metals in ores if certain limitations are met. The important requirement is to convert the metallic ion to a form, by precipitating the ion or possibly by forming a stable complex ion (5, p. 69) which does not react with dithizone in the proper pH range.

It is thought by the author that similar procedures can be worked out for many of the dithizone metals, although the present research was confined to zinc alone.
Literature Cited


