1928

A means of making a segregate preparatory to chemical analysis of the sulphide minerals in a low-grade dolomitic ore-pulp containing lead, zinc, and copper

Julius Bruce Clemmer

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A MEANS OF MAKING A SEGREGATE PREPARATORY TO CHEMICAL ANALYSIS
OF THE SULPHIDE MINERALS IN A LOW-GRADE DOLOMITIC ORE-FUEL
CONTAINING LEAD, ZINC, AND COPPER.

- By -

Julius Bruce Clemmer.

-----O-----

A

THESIS

submitted to the Faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

DEGREE OF

MASTER OF SCIENCE.

Rolla, Missouri,

1928.

Approved: [Signature]

Supervising Engineer,
Mississippi Valley Experiment Station,
United States Bureau of Mines.
Thesis: A means of making a segregate preparatory to chemical analysis of the sulphide minerals in a low-grade dolomitic ore-pulp containing lead, zinc, and copper. Clemmer. 1928.
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PREFACE.

This thesis is presented to the Faculty of the Missouri School of Mines and Metallurgy of the University of Missouri in partial fulfillment of the work required for the degree of Master of Science.

The results of the investigation embodied in this thesis were obtained from work carried on at the Mississippi Valley Experiment Station of the United States Bureau of Mines, Department of Commerce, in cooperation with the Missouri School of Mines and Metallurgy of the University of Missouri at Rolla, Missouri.

ACKNOWLEDGMENTS.

Acknowledgments are due to Mr. Will H. Coghill, Supervising Engineer of the Mississippi Valley Experiment Station of the United States Bureau of Mines, for supervision of the investigation and his many helpful suggestions; to Messrs. F. D. DeVaney, R. G. O’Heara, and A. B. Campbell, all of the Bureau of Mines, with whom the writer was associated; Mr. O. W. Holmes, Chemist of the State Mining Experiment Station, who made the assays; and to Dr. W. T. Schrenk, Associate Professor of Chemistry, Missouri School of Mines and Metallurgy of the University of Missouri, for his helpful advice and suggestions.
A MEANS OF MAKING A SEGREGATE PREPARATORY TO CHEMICAL ANALYSIS
OF THE SULPHIDE MINERALS IN A LOW-GRADE DOLOMITE ORE-PULP
CONTAINING LEAD, ZINC, AND COPPER.

By
Julius Bruce Clemmer.

INTRODUCTION.

A study of the methods for the quantitative determination of lead, zinc, and copper in low-grade ore pulps is pertinent to the entire Southeast Missouri Lead District in that the operating companies desire to attain more accuracy in the assay of tailings.

Standard methods are employed by the chemists for the determination of lead, zinc, and copper but they concur in the belief that these methods are only accurate within certain limits, depending upon the type of material to be analyzed. In one case it was found that the determinations submitted by several chemists using the same method for lead, showed variations ranging from 0.03 to 0.07 per cent when assaying mill heads that contained about four per cent lead. These chemists, using the same method when determining the lead in tailings, showed variations of 0.02 to 0.04 per cent, the tailings assaying about 0.15 per cent lead. The variations obtained for the determination of zinc were considerably larger in every case, while those for copper agreed well with one another.
It is evident that the degree of accuracy for the determination of lead is satisfactory when the material is high grade, but if the mill is making a tailing with a tenor of 0.15 per cent lead, and the chemist, while staying within his former limits, reports 0.11 per cent lead on one day and 0.19 per cent on the next, it is apparent that the mill crew cannot use the chemist's results as a guide to curtail losses. For this reason it is desirable to have analyses on low-grade material that are accurate to within 0.01 per cent. That this problem of lead determination is pertinent to the entire Southeast Missouri Lead District can be seen when it is considered that the mills of this district are treating an average of 15,000 tons of ore per day, and when 0.01 per cent lead is lost in the tailings it means a loss of 3,000 pounds of lead. This amount of lead at five cents a pound results in a loss of $150.00 per day. Considered in this light the problem assumes its true position.

The determinations for zinc, though less accurate than those for lead, is of lesser importance because the amount of zinc is so small that its recovery is not stressed. However, improvements in zinc determinations are needed as well as for lead. Copper occupies a minor position in the district at the present time, but must be considered in view of possible developments in the future.
OBJECT OF INVESTIGATION.

The object of this investigation was to find a means of obtaining from a low-grade dolomitic ore pulp a segregate of the sulphide minerals of lead, zinc, and copper preliminary to chemical analysis so that the chemist's error of 0.03 per cent would be divided by the ratio of the segregate to the entire pulp, and hence be reduced.

Two methods of obtaining the segregate were investigated: (1) By float-and-sink tests, and (2) by selective dissolution of the dolomite, which is the main gangue constituent of the ore.

MATERIALS TESTED.

The samples tested in this investigation were typical low-grade tailings from the mills in the Southeast Missouri Lead District. These samples were selected so as to give variations in lead, zinc, and copper content—the same as would be encountered in actual practice.

METHODS OF TESTING.

Sink-and-Float.

Sink-and-float testing consists of a method based solely on specific gravity for separating the constituents of an ore. An ore is a more or less complex aggregate of mineral components, each of which has a definite specific gravity. If the ore were crushed fine enough the components would be completely liberated. When a sample of the finely divided ore is placed in a liquid of definite
specific gravity, minerals of lower specific gravity will float and those of higher specific gravity will sink in the separating medium.

These separating mediums are called "heavy liquids" or "heavy solutions," and may be any liquid that has the desired specific gravity, has a low vapor pressure, is non-corrosive to the sample, wets the solid, and is not decomposed by atmospheric agents. Detailed information regarding the care and use of heavy liquids may be obtained by reference to Sullivan's¹ paper on the subject.


In this investigation samples of low-grade tailings and classifier products were treated in acetylene tetrabromide, specific gravity 2.95, as the separating medium. This gravity was selected to float dolomite, specific gravity 2.8 to 2.9, and allow all of the sulphide minerals and heavy aggregates to sink. By the removal of the float a segregate remains, that is, the minerals to be assayed are concentrated into a smaller bulk which appears as a sink, whereas the float is expected to be barren.

Procedure: Samples of unsized table tailings and classifier products from several mills in the Southeast Missouri Lead District were treated in acetylene tetrabromide, specific gravity 2.95, and the float and the sink products removed. These products were washed thoroughly with benzene to remove the acetylene tetrabromide,
then dried and weighed. The original pulp and the float product were assayed for lead by the electrolytic method. The content of lead in the sink had to be calculated because of its small amount. The assays of the original pulp were deemed sufficiently accurate for the preliminary investigation. If the assay of the float revealed the presence of lead, then it would be evident that this method of segregation is unsatisfactory.

In case the sample contained a large amount of fine material it was sized on a 48 mesh screen. The material coarser than 48 mesh was subjected to a sink-and-float test in the usual manner by using a beaker filled with acetylene tetrabromide. Small additions of the sample were made at a time, the float being removed in each case before another addition of sample. The sink was allowed to accumulate in the beaker until the entire sample had been treated, and was then removed. The material finer than 48 mesh was treated by using acetylene tetrabromide in a separatory funnel. The fine material was added to the heavy liquid in the funnel and shook for a few minutes; after allowing to stand for a few minutes a complete separation of float-and-sink products was obtained. The sink was removed, the funnel again agitated and allowed to stand until all of the sink had definitely been removed from the float. In some cases this required three or four treatments. The clean float product was then removed and drained of excess acetylene tetrabromide. The floats and sinks from the treatments of the minus 48 mesh product and the plus 48 mesh product were combined.
before washing with benzene, then dried and weighed.

Some of the results obtained in these tests are given in Table I following:

Table I: Sink-and-Float Tests on Unsized Table Tailings and Classifier Products.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Product</th>
<th>Weight</th>
<th>Assay Per cent of Lead</th>
<th>Per cent of total lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Float on 2.95 sp.gr.</td>
<td>99.04</td>
<td>0.055</td>
<td>49.52</td>
</tr>
<tr>
<td></td>
<td>Sink in 2.95 sp.gr.</td>
<td>.95</td>
<td>5.73</td>
<td>50.48</td>
</tr>
<tr>
<td></td>
<td>Composite</td>
<td>100.00</td>
<td>0.11</td>
<td>100.00</td>
</tr>
<tr>
<td>2</td>
<td>Float on 2.95 sp.gr.</td>
<td>98.68</td>
<td>0.055</td>
<td>56.18</td>
</tr>
<tr>
<td></td>
<td>Sink in 2.95 sp.gr.</td>
<td>1.32</td>
<td>7.25</td>
<td>43.82</td>
</tr>
<tr>
<td></td>
<td>Composite</td>
<td>100.00</td>
<td>0.115</td>
<td>100.00</td>
</tr>
<tr>
<td>3</td>
<td>Float on 2.95 sp.gr.</td>
<td>99.47</td>
<td>0.052</td>
<td>33.03</td>
</tr>
<tr>
<td></td>
<td>Sink in 2.95 sp.gr.</td>
<td>1.53</td>
<td>6.78</td>
<td>66.97</td>
</tr>
<tr>
<td></td>
<td>Composite</td>
<td>100.00</td>
<td>0.155</td>
<td>100.00</td>
</tr>
<tr>
<td>4</td>
<td>Float on 2.95 sp.gr.</td>
<td>97.06</td>
<td>0.07</td>
<td>18.45</td>
</tr>
<tr>
<td></td>
<td>Sink in 2.95 sp.gr.</td>
<td>12.94</td>
<td>2.09</td>
<td>81.55</td>
</tr>
<tr>
<td></td>
<td>Composite</td>
<td>100.00</td>
<td>0.33</td>
<td>100.00</td>
</tr>
<tr>
<td>5</td>
<td>Float on 2.95 sp.gr.</td>
<td>95.53</td>
<td>0.04</td>
<td>16.61</td>
</tr>
<tr>
<td></td>
<td>Sink in 2.95 sp.gr.</td>
<td>4.47</td>
<td>4.22</td>
<td>83.39</td>
</tr>
<tr>
<td></td>
<td>Composite</td>
<td>100.00</td>
<td>0.23</td>
<td>100.00</td>
</tr>
<tr>
<td>6</td>
<td>Float on 2.95 sp.gr.</td>
<td>95.95</td>
<td>0.01</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Sink in 2.95 sp.gr.</td>
<td>4.05</td>
<td>32.60</td>
<td>99.28</td>
</tr>
<tr>
<td></td>
<td>Composite</td>
<td>100.00</td>
<td>1.33</td>
<td>100.00</td>
</tr>
<tr>
<td>7</td>
<td>Float on 2.95 sp.gr.</td>
<td>91.47</td>
<td>0.045</td>
<td>2.83</td>
</tr>
<tr>
<td></td>
<td>Sink in 2.95 sp.gr.</td>
<td>8.53</td>
<td>16.57</td>
<td>97.17</td>
</tr>
<tr>
<td></td>
<td>Composite</td>
<td>100.00</td>
<td>1.455</td>
<td>100.00</td>
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</table>
Discussion of Results: From the results obtained it is evident that sink-and-float tests cannot be used to make a segregate for assay. The belief that this method could be employed was justified, however, in that since the sulphide minerals are so much heavier than the liquid medium they should form a sink product. The discrepancy is probably due to the fact that very small particles of the sulphide minerals are held within the dolomite, forming chat or locked grains. The gravity of some of the chat grains is insufficient to cause them to go into the sink. This condition causes losses sufficient to justify the rejection of this method for producing a segregate.

In these sink-and-float tests a considerable amount of material was present with a gravity about the same as that of the heavy liquid. It was held in suspension in the liquid and did not form a true sink or a float. Whether or not this material should go into the sink or the float depends upon the object in making the test. If a clean sink is desired, then the suspended material should be taken as float, but if a clean float is desired, then this material should be considered as sink. In Samples 4, 5, 6, and 7 a clean float was attempted and the intermediate material was taken as sink. In Samples 1, 2, and 3 a clean sink was undertaken and this intermediate material was considered as float. If this material is considered as float, then the amount of lead in the float is increased.
No difficulty was encountered in these tests due to the presence of very fine material because the samples taken had been well deslimed, but to adapt this method for use with ore pulps it would be necessary to observe the action of finely ground mineral in heavy solutions. In order to observe this effect, finely ground galena—through 100 mesh—was placed in acetylene tetrabromide, specific gravity 2.90. The fine galena formed a scum on the surface of the liquid and was found to be held in suspension throughout the liquid, forming no appreciable sink even after standing twenty-four hours. This is probably due to the fact that when galena is ground to pass a 100 mesh screen a large proportion of it is much finer than this. This fine galena resists the wetting action of the heavy liquid and consequently remains as a scum on the surface, or is held in suspension in the liquid. Entrapped air bubbles also assist in keeping the galena in the liquid. From this, however, it should not be inferred that sink-and-float methods will not work successfully on finely ground material. It has been found by tests carried on elsewhere that non-sulphide material finer than 100 mesh may be successfully treated by sink-and-float methods if it is sized preliminary to the treatment. Obviously, preliminary sizing of ore pulps is not feasible in the problem at hand because of the extra amount of work required.
Dissolution Tests.

The main gangue constituent of the ore from the Southeast Missouri Lead District consists of a dolomitic limestone. This dolomite is fairly soluble in certain reagents, while the sulphide minerals are relatively insoluble. This offered the possibility of selective dissolution by leaving the sulphides in the residue. The solvents were solutions of certain salts and acids of known concentrations.

Salts.

There are several salts which have the ability of dissolving dolomite in preference to the sulphide minerals of lead, zinc, and copper. The most important of these salts are ammonium chloride, ammonium nitrate, and ammonium acetate. Others show the tendency to dissolve the sulphide minerals to a greater extent.

In these tests a known weight, ten grams, of a standard ore pulp was treated in boiling salt solutions of known concentration for given periods of time. The residue, after filtration and washing, was dried, weighed, and assayed for lead by a standard method of analysis. The results obtained in these tests are given in Table II following.
Table II: Dissolution Tests Using Salt Solutions as Solvents.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Concentration: Grams per Liter</th>
<th>Time</th>
<th>Per cent of Lead in Pulp</th>
<th>Per cent of pulp Dissolved</th>
<th>Per cent of total lead Residue</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄Cl</td>
<td>29.4</td>
<td>1 hour</td>
<td>0.14</td>
<td>19.59</td>
<td>59.25</td>
<td>40.75</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>29.4</td>
<td>30 minutes</td>
<td>0.20</td>
<td>5.16</td>
<td>99.83</td>
<td>0.17</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>118</td>
<td>1 hour</td>
<td>0.22</td>
<td>20.38</td>
<td>92.20</td>
<td>7.80</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>118</td>
<td>30 minutes</td>
<td>0.20</td>
<td>5.00</td>
<td>100.00</td>
<td>0.0</td>
</tr>
<tr>
<td>NH₄Ac</td>
<td>148</td>
<td>30 minutes</td>
<td>0.18</td>
<td>9.19</td>
<td>56.12</td>
<td>43.88</td>
</tr>
</tbody>
</table>

Discussion of Results: From the results obtained it is evident that all the salts gave low degrees of segregation and there was a tendency of the lead minerals to be dissolved with the dolomite. If the ratio of concentration—the ratio of the weight of the pulp to the weight of the residue—is not greater than two, then there is little gained by the treatment as the original error is only decreased by half. If the sulphide minerals are dissolved with the dolomite when the ratio of concentration is large, the error introduced becomes magnified to such an extent that the process is less accurate than when the assay is made directly upon the pulp.
The amount of material dissolved is dependent upon the concentration of the salt solution and upon the time or period of the dissolution test. The greater the salt concentration and the longer the solution period, the greater the amount of material dissolved. The velocity of the solution rate should be such that a maximum amount of the dolomite and a minimum of the sulphide minerals is dissolved in the least amount of time. The amount of material that is dissolved also depends upon the type of salt used in the test. The solubility of dolomite in various salts as given by Comey should be taken with reservation as these values are given for pure dolomite. The presence of certain other substances renders wide variations in the solubility of dolomite.

Conclusions: From the tests made it is evident that the degree of segregation is low when salts are used for solvents of dolomite.

In all cases when there is a large amount of dolomite dissolved there is also a considerable amount of the sulphide minerals dissolved.

The solvent action of salts are dependent upon the concentration of the salt solution, upon the period of dissolution, and upon the characteristics of the salt used in the test.
Acids.

The low degrees of segregation obtained when using salts as solvents indicated that stronger solvents for dolomite were necessary. This lead to the investigation of the use of acids for solvents.

The use of acids for solvents must be carried on with care, for the concentration of the acid must be so regulated that the dolomite is dissolved in preference to the sulphide minerals. Theoretically, when just a sufficient quantity of acid is added to dissolve the dolomite, the sulphide minerals should not be dissolved, as the dolomite is more readily soluble in dilute acids than the sulphide minerals.

The acids used in this investigation were limited to acetic, citric, boric, tartaric, oxalic, and hydrochloric. Other acids were not used because it seemed probable that similar results would have been obtained.

Procedure: In these tests 20-gram samples of standard ore pulp, which was ground to pass a 100 mesh screen, were treated with hot acid solutions of known concentration for various lengths of time. The residues were filtered out of the solution, dried, and weighed. The filtrates were rejected. These residues were then assayed. The results obtained are shown in Tables III and IV below.
Table III: Dissolution Test Using Acetic Acid as the Solvent.

<table>
<thead>
<tr>
<th>Concentration: Per cent by Volume</th>
<th>Time</th>
<th>Per cent of Lead in Pulp</th>
<th>Per cent of Pulp Dissolved</th>
<th>Per cent of total lead in Residue Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1 hour</td>
<td>0.17</td>
<td>13.40</td>
<td>77.46</td>
</tr>
<tr>
<td></td>
<td>2 hours</td>
<td>0.20</td>
<td>16.72</td>
<td>87.66</td>
</tr>
<tr>
<td></td>
<td>3 hours</td>
<td>0.20</td>
<td>23.99</td>
<td>80.01</td>
</tr>
<tr>
<td>10</td>
<td>1 hour</td>
<td>0.15</td>
<td>22.92</td>
<td>60.85</td>
</tr>
<tr>
<td>15</td>
<td>1 hour</td>
<td>0.13</td>
<td>27.02</td>
<td>49.93</td>
</tr>
<tr>
<td>20</td>
<td>1 hour</td>
<td>0.17</td>
<td>29.77</td>
<td>62.33</td>
</tr>
</tbody>
</table>

Table IV: Dissolution Test Using Hydrochloric Acid as the Solvent.

<table>
<thead>
<tr>
<th>Concentration: Per cent by Volume</th>
<th>Time</th>
<th>Per cent of Lead in Pulp</th>
<th>Per cent of Pulp Dissolved</th>
<th>Per cent of total lead in Residue Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1 hour</td>
<td>0.20</td>
<td>14.77</td>
<td>89.71</td>
</tr>
<tr>
<td>2-1/2</td>
<td>2 hours</td>
<td>0.24</td>
<td>13.07</td>
<td>97.17</td>
</tr>
<tr>
<td>2-1/2</td>
<td>3 hours</td>
<td>0.23</td>
<td>13.89</td>
<td>92.13</td>
</tr>
<tr>
<td>4</td>
<td>1 hour</td>
<td>0.24</td>
<td>24.59</td>
<td>95.25</td>
</tr>
</tbody>
</table>
Discussion of Results: From the results obtained it is evident that with the use of dilute acids the degree of segregation is low in comparison with the results which, theoretically, should be obtained. This is probably due to the fact that the salts formed in the solution of the ore retards the solution rate of the dolomite.

The amount of galena dissolved was much larger than would be expected under the conditions of the test, as only sufficient acid was added to theoretically dissolve the dolomite. That such a quantity of the lead was dissolved suggests the possibility that some of the lead was in the oxidized form. If such is the case, then it is entirely possible that good degrees of segregation could be obtained on ore pulps if the oxidized lead were absent. Since lead sulphide oxidizes very readily, practically every sample of ore pulp will contain some oxide.

The results show that acetic acid is prone to attack the galena in preference to the dolomite more so than does the hydrochloric acid. This is evidently due to the fact that the acetates of lead are the most soluble of any of the lead salts.

The tests indicate that the amount of the total lead dissolved decreases with an increase in hydrochloric acid concentration. This can be readily explained in that the lead which is dissolved is partially precipitated as the chloride and remains in the unwashed residue. The solubility of the chlorides of lead decreases
with an increase in the concentration of the chloride ions present. That is, the higher the acid concentration the greater the amount of galena that is dissolved, but the more complete the precipitation of the lead as the chloride. These two tendencies oppose each other and give lower degrees of apparent solubility to the galena than actually exists.

Tartaric, oxalic, boric, and citric acids failed to give good degrees of segregation. Small amounts of lead were dissolved in all cases.

Conclusions: This series of tests, using acids for solvents of the dolomite in preference to the sulphide minerals of lead, zinc, and copper, indicates that only fairly good degrees of segregation can be obtained. The amount of minerals dissolved is large, probably due to their presence in the oxidized forms.

Hydrochloric acid gives the most desirable results of any acid tested, in that it exerts a stronger solvent action upon the dolomite and less action on the galena. Although the lead which is dissolved is partially precipitated in the form of the chloride, considerable loss of lead still persists in the solution.
Dissolution Tests on Pure Galena.

The fact that galena was dissolved in dilute acids, even in the presence of considerable amounts of the more readily soluble dolomite, lead to the investigation of the solubility of pure galena in acid solutions of various concentrations.

Some pure galena from the Tri-State Zinc District was crushed by hand and sized on standard Tyler screens. This galena was then treated with dilute hydrochloric acid to remove any oxide coating, filtered, washed, and dried. Ten-gram samples of this galena were treated with hydrochloric acid of known concentration for one hour on the hot plate. Samples were agitated continuously to prevent selective action. The galena was then filtered and washed thoroughly with hot water to dissolve any lead chloride precipitated. The filtrates were assayed for lead by the Guess Modified Dichromate method. The results obtained are shown in Table V.

Table V. The Solubility of Galena in Hydrochloric Acid with the Acid Concentration as Shown in Terms of Normality.

<table>
<thead>
<tr>
<th>Mesh Size</th>
<th>Per cent of total lead dissolved in 100 cc. of HCl of normality.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.12N .24N .30N .48N .6N .72N .96N 1.2N</td>
</tr>
<tr>
<td>- 24 + 32</td>
<td>.132 .476 .689 1.60 2.04 2.80 3.98 5.42</td>
</tr>
<tr>
<td>- 42 + 60</td>
<td>.135 .675 .918 1.78 2.06 3.59 5.32 5.44</td>
</tr>
<tr>
<td>- 80 + 115</td>
<td>.132 .511 .740 1.55 1.71 3.38 4.19 4.46</td>
</tr>
</tbody>
</table>
Discussion of Results: From the results obtained it is evident that
the percentage of the total lead in the sample which is dissolved
increases with an increase in the acid concentration, size of parti­
cles remaining the same.

The size of the particles has a definite effect upon the
solubility of the galena particles. It was expected that the finer
the material, the more surface exposed to solvent action, the more
soluble would be the particles of galena. From this test it is evi­
dent that such is not the case. If the area of the surface of the
24 to 32 mesh galena is considered as unity, then the 42 to 60 mesh
material will exhibit four times this amount of surface area for
solvent attack, and the 60 to 115 mesh material will exhibit sixteen
times this amount of area for solvent attack. With other con­
tions remaining the same, if the solubility of galena is in a direct pro­
portion to the amount of area exposed to solvent attack, we should
expect the acid to dissolve four times the amount of lead from the
42 to 60 mesh galena as it would from the 24 to 32 mesh material,
and similarly sixteen times as much from the 60 to 115 mesh material
as from the 24 to 32 mesh material.

In order to observe the method of attack of hydrochloric acid
upon galena several cubical crystals of various sizes were etched in
a boiling solution of the acid. These cubes were examined under
the microscope and the structure revealed that the various particles
were attacked in a definite manner, depending upon the size of the
particles. The larger particles were attacked along certain planes
parallel to the cube faces, accentuating the cleavage of the galena, and large etching pits were noticed on the faces. With the smaller particles the etching pits apparently disappeared, the etch merely accentuating the cubic cleavage.

If such is the case this differential etching of particles of the various sizes offers a possible explanation for the fact that the solution velocity of galena in hydrochloric acid does not increase in a direct proportion to the amount of surface exposed to solvent attack.

The fact that lead sulphide, galena, can be dissolved in, or precipitated out of acid solutions of less than 0.3 normal can be readily explained as follows: The reaction occurring can be given as follows:

\[ \text{PbS} + 2 \text{HCl} \leftrightarrow \text{PbCl}_2 + \text{H}_2\text{S} \]

If the hydrogen sulphide is allowed to escape, then the equilibrium of the reaction is upset and the reaction proceeds to the right.

If the hydrogen sulphide is introduced into the acid solution containing the lead chloride, then the reverse is true, the reaction proceeds to the left and lead sulphide is thrown out of solution until it is completely removed or until the reaction again comes to an equilibrium condition.

Conclusions: The results of this test show that galena is appreciably soluble even in dilute acids, and that the amount dissolved is directly proportional to the strength of the acid and the time of solution, size of particles remaining the same. The solubility
does not increase in direct proportion to the amount of free surface exposed to solvent attack as would be expected.

The Production of a Zinc Segregate.

Since the production of a lead segregate by the dissolution tests failed in that considerable amounts of the lead were dissolved, probably due to its presence in the oxidized form, it was thought advisable to attempt the production of a zinc segregate using similar methods. Since the zinc in these ores is less liable to oxidation the method employed for lead should give suitable segregates of the zinc minerals.

Procedure: Samples of unsized table tailings of low zinc content were treated with hydrochloric acid, a small portion was added at a time and allowed to be consumed before another addition was made. After the major portion of the dolomite had been dissolved, the residue was filtered, washed, dried, and weighed. This segregate was then assayed for zinc by the standard ferrocyanide method. Some of the results obtained in these tests are given in Table VI.

From these tests it is evident that the amount of zinc is too high to allow this method to be used for the production of zinc segregates.
Table VI: Dissolution Tests on Unsized Table Tailings When Using Hydrochloric Acid as the Solvent.

<table>
<thead>
<tr>
<th>Product</th>
<th>Weight Per cent</th>
<th>Per cent of Total Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved</td>
<td>80.90</td>
<td>68.68</td>
</tr>
<tr>
<td>Segregate</td>
<td>19.10</td>
<td>31.32</td>
</tr>
<tr>
<td>Sample</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Dissolved</td>
<td>80.16</td>
<td>65.88</td>
</tr>
<tr>
<td>Segregate</td>
<td>19.84</td>
<td>34.12</td>
</tr>
<tr>
<td>Sample</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Dissolved</td>
<td>80.04</td>
<td>67.27</td>
</tr>
<tr>
<td>Segregate</td>
<td>19.96</td>
<td>32.73</td>
</tr>
<tr>
<td>Sample</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Another series of tests were made upon a standard ore pulp ground to pass a 100 mesh screen. The procedure used was the same as before. Some of the results obtained are given in Table VII.

Table VII: Dissolution Tests on Standard Ore Pulp When Using Hydrochloric Acid as the Solvent.

<table>
<thead>
<tr>
<th>Product</th>
<th>Weight Per cent</th>
<th>Per cent of Total Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved</td>
<td>93.68</td>
<td>42.61</td>
</tr>
<tr>
<td>Segregate</td>
<td>6.32</td>
<td>57.39</td>
</tr>
<tr>
<td>Sample</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Dissolved</td>
<td>82.90</td>
<td>37.98</td>
</tr>
<tr>
<td>Segregate</td>
<td>17.10</td>
<td>62.02</td>
</tr>
<tr>
<td>Sample</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Discussion of Results:

In all of these tests the amount of zinc dissolved was large due to the strong solvent action of hydrochloric acid upon the sulphide minerals of zinc. Several other acids were used in place of hydrochloric acid; slightly better results were obtained. One of the tests using acetic acid as the solvent gave the following results:

<table>
<thead>
<tr>
<th>Product</th>
<th>Weight Per cent</th>
<th>Per cent Per cent of Total Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved</td>
<td>33.60</td>
<td>21.30</td>
</tr>
<tr>
<td>Segregate</td>
<td>66.46</td>
<td>0.70</td>
</tr>
<tr>
<td>Sample</td>
<td>100.00</td>
<td>0.59</td>
</tr>
</tbody>
</table>

It is evident that acetic acid exerts a strong solvent action upon the zinc sulphide present, causing too high losses through solution. The other acids, boric, citric, and tartaric failed to give high degrees of segregation and the products obtained were not assayed.

These tests clearly show that the preferential attack or solvent action of acids upon dolomite and the sulphide minerals of zinc is not as great as would be expected, otherwise the dolomite would be completely dissolved before the sulphide minerals were attacked. In order to increase this preferential action it was thought that by adding a foreign sulphide to the ore pulp, which was more readily attacked than the zinc sulphide, that it would be possible to dissolve the major portion of the dolomite and leave the zinc sulphide in the residue unattacked. The sulphide to be attacked would be the one most readily soluble. Per-
rous sulphide was selected for this purpose since it is soluble even in very dilute acids. The results obtained by some of the tests are given in Table VIII. The standard ore pulp contained 0.59 per cent zinc.

Table VIII. Segregates from Dissolution Tests Made Upon a Standard Ore Pulp Containing a Small Amount of Added Ferrous Sulphide.

<table>
<thead>
<tr>
<th>Residue</th>
<th>Solvent</th>
<th>Percent to Total Weight</th>
<th>Percent of Zinc</th>
<th>Percent of Total Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HCl</td>
<td>19.70</td>
<td>2.04</td>
<td>68.16</td>
</tr>
<tr>
<td>2</td>
<td>HCl</td>
<td>29.75</td>
<td>1.23</td>
<td>62.02</td>
</tr>
<tr>
<td>3</td>
<td>HCl</td>
<td>20.21</td>
<td>1.86</td>
<td>66.82</td>
</tr>
<tr>
<td>4</td>
<td>HAc</td>
<td>65.45</td>
<td>0.73</td>
<td>77.90</td>
</tr>
<tr>
<td>5</td>
<td>HAc</td>
<td>64.83</td>
<td>0.81</td>
<td>76.92</td>
</tr>
</tbody>
</table>

These tests indicate that the amount of zinc sulphide dissolved is decreased by the addition of a small amount of ferrous sulphide. The ferrous sulphide caused no difficulty in the assay for zinc due to its presence, as the particles were large enough to be removed before the residue was assayed. Although the addition of ferrous sulphide to the ore pulp increases the differential attack of acids upon dolomite and the zinc sulphide, the amount of zinc dissolved is still large enough to cause the rejection of this method for producing a zinc segregate.
Dissolution and Segregation Tests.

Since the results of the solution tests on pure galena shows that galena is slightly soluble in dilute acid, it becomes necessary, if a segregate is to be made from a dolomitic ore pulp, that the lead dissolved be precipitated out of the solvent solution and taken with the residue to form a segregate. This also applies to zinc and copper.

With this in mind it was thought advisable to treat the low-grade ore pulp with a sufficient quantity of strong acid to dissolve the major portion of the dolomite and then by the use of certain precipitants to obtain the lead, zinc, and copper in a residue suitable for assay.

L e a d.

The preliminary dissolution tests upon the low-grade dolomitic ore pulp shows that as high as fifty per cent of the lead was dissolved with the dolomite. Since a method for obtaining this lead was not attempted, the segregation tests failed. Later tests indicated that galena was slightly soluble in dilute acids. For this reason it is necessary to precipitate the dissolved lead out of solution in a form suitable for assay. The form in which it will be precipitated depends upon the presence of impurities in the solution and upon the completeness of the precipitating reaction.

- 23 -
In chemical determination of lead in dolomitic ore pulps, where the lead is to be separated from other elements, the usual method is to precipitate the lead as the sulphide, the sulphate, the chromate, or as the molybdate and this segregate is then assayed for lead by a standard method of analysis. In making a segregate it is desirable to eliminate as many of the interfering elements as is possible in order to shorten the manipulation required to obtain a pure precipitate for assay. The method selected for making a segregate should be rapid, simple in manipulation, and accurate, otherwise it cannot be adapted to the commercial testing laboratory for routine work.

Size of Sample: The question as to the size of sample which is to be selected for the dissolution test is of importance and should be considered. In ordinary methods for chemical analysis the size of the sample selected for assay depends upon the grade of the material. On medium and high grade materials the samples are usually from .5 to 2 grams, but in the case of low-grade material a larger sample must be taken in order to insure against large errors entering into the determination due to the small amount of the valuable constituent present.

The size of sample which can be economically handled when dealing with low-grade material depends to a great extent upon the procedure used and upon the difficulties involved in manipulation. The sample is usually limited to five grams of material.
In the dissolution tests a sample of 10, 20, or in some cases as high as 40 grams can be taken without involving long and difficult manipulations. The size of the segregate produced from such a sample depends upon the procedure adapted to the material, but rarely exceeds 5 to 10 grams. If a sample of 20 grams of low-grade material is segregated to 5 grams, then the chemist's error is reduced to one-fourth, other conditions remaining the same. The larger the sample of ore taken the more accurate the results obtained. The time element enters here also, but in most cases it takes but slightly longer to treat a 20-gram sample than it does for a 10-gram sample.

Separation as the Chromate: Several tests were made using chromate precipitation methods, but in these tests the amount of lead in the segregate was low, indicating that the lead was not completely precipitated from the hydrochloric acid solution by the use of potassium di-chromate. The procedure used may be given as follows:

Ten-gram samples of the standard low-grade ore pulp were treated in enough hydrochloric acid to theoretically dissolve all of the dolomite. After solution of the dolomite, 10 cc. of a saturated solution of potassium dichromate was added and the solution boiled for several minutes. The segregate after filtration was washed thoroughly, dried, weighed, and then assayed for lead by a standard method for lead analysis. The results of one of the tests are as follows:
It is evident that the dichromate failed to precipitate all of the lead dissolved. The chlorides present probably reacted to dissolve the chromate precipitate and caused the lead in the segregate.

In order to remove the effect of the hydrochloric acid upon the chromate precipitate, a number of tests were made using hydrochloric acid as the solvent for the sample, then neutralizing the solution with ammonium hydroxide to remove the free acid. The solution was then made acid with acetic acid and 10 cc. of a saturated solution of potassium dichromate added as before. The segregate produced contained nearly all of the lead, but the other chromates that were precipitated increased the weight of the segregate to such an extent that the degree of segregation was low. The results of the tests are as follows:

<table>
<thead>
<tr>
<th>Product</th>
<th>Weight</th>
<th>Weight Per cent</th>
<th>Assay Per cent Lead</th>
<th>Per cent of Total Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved</td>
<td>3.0431</td>
<td>30.43</td>
<td>0.06</td>
<td>8.88</td>
</tr>
<tr>
<td>Segregate</td>
<td>6.2568</td>
<td>62.57</td>
<td>0.27</td>
<td>91.12</td>
</tr>
<tr>
<td>Sample</td>
<td>10.0000</td>
<td>100.00</td>
<td>0.205</td>
<td>100.00</td>
</tr>
</tbody>
</table>

It is evident that the dichromate failed to precipitate all of the lead dissolved. The chlorides present probably reacted to dissolve the chromate precipitate and caused the lead in the segregate.

In order to remove the effect of the hydrochloric acid upon the chromate precipitate, a number of tests were made using hydrochloric acid as the solvent for the sample, then neutralizing the solution with ammonium hydroxide to remove the free acid. The solution was then made acid with acetic acid and 10 cc. of a saturated solution of potassium dichromate added as before. The segregate produced contained nearly all of the lead, but the other chromates that were precipitated increased the weight of the segregate to such an extent that the degree of segregation was low. The results of the tests are as follows:
Separation as the Sulphide: Lead can be readily precipitated in slightly acid solutions by hydrogen sulphide. This method of separation is often employed for obtaining lead from solutions containing iron and zinc.

In order to successfully precipitate lead as the sulphide by hydrogen sulphide the acid concentration of the solution should not be over 0.3 normal and must be free of oxidizing agents, such as nitric acid. The precipitation is preferably carried out in a hydrochloric or sulphuric acid solution. If copper, cadmium, bismuth, mercury, arsenic, antimony, or tin are present they will precipitate with the lead. This method does not precipitate aluminum, zinc, chromium, manganese, iron, cobalt, or nickel, unless these elements are present in the solution in large amounts and the acid concentration is not correctly maintained.

After a series of extensive tests using hydrogen sulphide as the precipitant, the following procedure was adopted which gave very good results.

A convenient sized sample, 20 to 50 grams, of the low-grade ore was taken for analysis, the size depending upon the lead content of the ore. The sample of ore was placed in a tall 800 cc. beaker and enough water added to just cover it. Concentrated hydrochloric acid was added slowly from a burette, keeping the beaker in constant agitation and allowing each addition of the acid to completely react with the dolomite before adding more. This treatment was continued until all the dolomite was dissolved;
this may be noted when the acid addition fails to give effervesence.

This method of titration, either in hot or cold solutions, seems to give less dissolved lead than when the acid is added in large quantities. The chances of loss through effervescence is less when the acid is added in small amounts. If the solution is heated to boiling to expel all the carbonic acid formed, and methyl orange indicator is added it should indicate that the solution is slightly acid. If the solution is not acid, then additions of more acid are necessary as the reaction is not complete.

The residue can be filtered out of solution at the discretion of the operator. Filtering is to be recommended as the residue masks the color change when the solution is neutralized. With practice the end point can be observed even in the presence of the residue. If the residue is filtered through a Gooch crucible under suction very little time is consumed in the operation and better results can be obtained.

The filtrate, if of large, volume, should be concentrated by boiling down to 150 cc. Add a few drops of methyl orange, then ammonium hydroxide drop by drop to the cold solution until the pink color just disappears and a slight precipitate begins to form. Add enough acid to bring the solution back to acidity, and then a few drops in excess. The acid concentration should not exceed 30 milli-equivalents if hydrochloric acid is used or 50 milli-equivalents if sulphuric acid is used.
Pass a rapid stream of hydrogen sulphide gas into the cold solution for 15 to 20 minutes. The precipitate should settle rapidly. Allow the gased solution to stand for as long a time as possible; then filter through the same Gooch crucible as was used for the filtering of the residue. Wash the precipitate thoroughly with cold water.

The clear filtrate should be tested for acidity after boiling to remove the hydrogen sulphide. In case the acid concentration is high, it is advisable to repeat the above operation again to insure complete precipitation of the lead.

The segregate can then be dissolved in nitric acid and the lead determined by any standard method of analysis. Some of the results obtained by this method are given in Table IX.

Table IX: Comparison of the Lead Analysis Obtained by Usual Method and that Calculated from the Analysis Made on a Segregate from a Large Sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Per cent Lead by Direct Electrolytic Method on a 3.452 gram sample</th>
<th>Per cent Lead by Electrolysis of Segregate From a 20 gram sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.115</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>4</td>
<td>0.12</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The segregates were not weighed, except in one case when a 20-gram sample gave a segregate weighing 4.452 grams. The ratio or degree of segregation was 4.5 in this case.
Discussion: This method gives very satisfactory results when care is used in keeping the acid concentration within certain limits. The ratio of segregation is higher than that given by other methods.

The fact that the assays for lead are higher when made upon the segregates than when made upon smaller samples by direct electrolysis can be expected. The assays from the segregates are probably more nearly the correct value for the ore.

This method offers a possible solution to the difficulty encountered in direct electrolysis due to the presence of manganese. The manganese being present in the ore—usually in the soluble form—dissolves in the acid and is not precipitated with the lead as the sulphide from acid solutions. The lead deposits obtained by the electrolysis of solutions from segregates were clean and free of manganese interference.

In some cases it is advisable to add a little ammonium acetate to the solution before passing in the hydrogen sulphide in order to keep the acid concentration from becoming too high.

Conclusions: This method of segregation can be used upon low-grade dolomitic ore pulps with very good results if care is used in maintaining the acid concentration during precipitation.
The segregation tests as made for zinc minerals consisted in dissolving the dolomite and then precipitating the dissolved zinc as the sulphide in neutral or slightly alkaline solutions.

Considerable difficulty was encountered in attempting to precipitate the zinc as the sulphide, for the acid concentration must be held within very rigid limits or the precipitation is not complete.

In attempting to neutralize a solution containing iron, zinc, and aluminum, preliminary to precipitating the zinc as the sulphide, the iron and aluminum precipitate by hydrolysis even though the solution indicates that it is strongly acid. The reactions may be given as follows:

\[
\begin{align*}
FeCl_3 + 3 \text{H}_2\text{O} & \rightarrow Fe(\text{OH})_3 + 3 \text{HCl} \\
AlCl_3 + 3 \text{H}_2\text{O} & \rightarrow Al(\text{OH})_3 + 3 \text{HCl} \\
3 \text{HCl} + 3 \text{NH}_3\text{OH} & \rightarrow 3 \text{NH}_4\text{Cl} + 3 \text{H}_2\text{O} \\
\text{HCl} + \text{Na C}_2\text{H}_3\text{O}_2 & \rightarrow \text{HC}_2\text{H}_3\text{O}_2 + \text{NaCl}
\end{align*}
\]

The iron and aluminum, when precipitating as the hydroxides, liberate an equivalent quantity of hydrochloric acid. If this hydrochloric acid is neutralized with ammonium hydroxide the reaction proceeds to the right rapidly and continues until all of the iron and aluminum are precipitated before the solution becomes basic. The addition of any salt which unites with the acid to form another acid, which is ionized to a lesser extent, also permits this reaction to take place. Sodium acetate, since it reacts with the hydro-
chloric acid to produce acetic acid which is ionized to a smaller extent than the hydrochloric acid, allows this reaction to occur.

From this it is evident that the regulation of acid concentration is very difficult when considerable amounts of iron and aluminum are present in the solution.

A series of tests were made using the Waring modified method for zinc. These tests gave low results and considerable difficulty was encountered in the manipulation. The use of aluminum for the reduction of iron and the precipitation of the copper-group elements merely added more aluminum to the solution, and upon subsequent neutralization the aluminum hydrolyzed, producing a large bulky precipitate of aluminum hydroxide. This method was employed, using both formic acid and ammonium sulphocyanate, but under the conditions neither gave good results. The sulphocyanate assists in salting-out the zinc sulphide formed. The reaction for the precipitation can be given as follows:

\[
\begin{align*}
\text{ZnCl}_2 + 4 \text{NH}_4\text{CNS} & = \text{Zn(CNS)}_2 \cdot 2 \text{NH}_4\text{(CNS)}_2 + 2 \text{NH}_4\text{Cl} \\
\text{Zn (CNS)}_2 \cdot 2\text{NH}_4\text{(CNS)}_2 & \rightleftharpoons \text{Zn(CNS)}_2 + 2 \text{NH}_4\text{(CNS)}_2 \\
\text{Zn (CNS)}_2 + \text{H}_2\text{S} & = \text{ZnS} + 2 \text{HCNS}
\end{align*}
\]

The zinc sulphocyanate is converted into the insoluble sulphide and precipitates, the equilibrium of the reaction having been disturbed the reaction continues until all of the zinc is precipitated.
In precipitating zinc as the sulphide from an acid solution the zinc sulphide is produced in both the hydrogel and hydrosol form. The hydrosol form does not precipitate, therefore, in order to have complete precipitation of the zinc the hydrosol must be converted to the hydrogel form. This can be accomplished by the presence of some salt which represses the hydrogen ion concentration and so allows the reaction to go to completion. The reactions may be given as follows:

\[
\text{Zn Cl}_2 + 2 \text{HSH} = \text{Zn} \left( \begin{array}{c}
\text{SH} \\
\text{SH}
\end{array} \right) + 2 \text{HCl}
\]

In order to allow the zinc sulphide to precipitate, the hydrochloric acid concentration must be decreased in order to decrease the hydrogen ion concentration, as hydrochloric acid is highly ionized. This can be accomplished by adding a salt that produces an acid that is ionized to a lesser extent than the hydrochloric acid. Sodium acetate reacts in this manner.

\[
\text{HCl} = \text{H} + \text{Cl} \\
\text{NaC}_2\text{H}_4\text{O}_2 = \text{Na} + \left( \text{C}_2\text{H}_4\text{O}_4^- \right) \\
\text{H} + \left( \text{C}_2\text{H}_4\text{O}_4^- \right) \iff \text{HC}_2\text{H}_4\text{O}_2 \\
\text{HCl} + \text{NaC}_2\text{H}_4\text{O}_2 = \text{HC}_2\text{H}_4\text{O}_2^- + \text{NaCl}
\]

In decreasing the hydrogen ion concentration, (H), the following reaction can take place readily:

\[
\text{Zn} \left( \begin{array}{c}
\text{SH} \\
\text{SH}
\end{array} \right) = \text{ZnS} + \text{H}_2\text{S}
\]
The presence of sodium acetate causes the zinc sulphide to be salted out of solution, although reacting in a different manner than the ammonium sulphocyanate. The presence of sodium acetate reduces the hydrogen ion concentration through the formation of a weakly dissociated acid, allowing the iron and aluminium to precipitate by hydrolysis.

From the foregoing it can be seen that the precipitation of zinc as the sulphide in the presence of considerable amounts of iron and aluminum is difficult. This is due to the fact that the hydrogen ion concentration, which is necessary to allow zinc to precipitate as the sulphide, is of such a low value that the solubility product of aluminium and iron hydroxides are exceeded. They then precipitate as the hydroxides in preference to the precipitation of the zinc.

Zinc can be precipitated as the sulphide from sulphuric acid solutions having a hydrogen ion concentration great enough to prevent the precipitation of iron and aluminum as the hydroxides, but considerable difficulty is encountered in the presence of large amounts of calcium. For this reason, in order to remove the effect of calcium, the metals were precipitated as the sulphides from an alkaline solution. All of the iron, zinc, copper, and lead were precipitated completely.

The sulphide precipitate was dissolved in nitric acid, then treated with sulphuric acid to convert all of the nitrates to the sulphates. The lead sulphate was filtered out of the solu-
tion, washed, and used for the lead determination. The filtrate, containing all of the iron, copper, and zinc was made almost neutral with ammonium hydroxide and then made slightly basic with sodium bi-carbonate. The solution was then made acid with sulphuric acid and gased with hydrogen sulphide. The copper precipitated as the sulphide and was filtered out of the solution. The filtrate was boiled to remove all of the hydrogen, made just neutral as before, then just slightly acid by adding a few drops of sulphuric acid. A few grams of ammonium sulphocyanate was added to the solution. The solution was heated to boiling and a rapid stream of hydrogen sulphide gas passed into the solution for 15 to 20 minutes. After allowing the solution to stand for as long a time as possible it was filtered. The zinc sulphide precipitate was washed thoroughly, then dissolved and the zinc determination made by the standard ferrocyanide method. The iron remained in the solution for the hydrogen ion concentration was great enough to permit its precipitation.

This method can be used for the determination of lead, zinc, and copper on the same sample, although it is advisable to run copper on a separate sample. The method is quite long but gives very good results when care is used in maintaining the acid concentration within the allowable limits. One of the tests gave the following results:
Table X: Comparison of Analyses Made on Segregates and Pulp by
Standard Methods.

<table>
<thead>
<tr>
<th>Standard Pulp</th>
<th>Zinc Segregate Per cent</th>
<th>Lead Segregate Per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>0.19</td>
<td>---</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.24</td>
<td>0.25</td>
</tr>
<tr>
<td>Copper</td>
<td>0.005</td>
<td>---</td>
</tr>
<tr>
<td>Iron</td>
<td>3.30</td>
<td>Trace</td>
</tr>
<tr>
<td>Manganese</td>
<td>---</td>
<td>Trace</td>
</tr>
</tbody>
</table>

Conclusions: The method devised for making a segregate of zinc is quite long, but gives results comparable to the standard ferrocyanide method for zinc, when care is exercised in the control of the acid concentration.

This method is merely an adaptation of a chemical method to a large size sample of pulp.

Copper.

Since the electrolytic and iodide methods for the determination of copper are very accurate, the producing of a segregate of copper minerals is not of such importance as for lead and zinc.

Copper can be easily and completely precipitated as the sulphide from acid solutions by hydrogen sulphide. Lead, if present in the solution, will be precipitated with the copper, but as the copper is usually determined by the electrolytic method the lead causes no interference. In case the ore contains arsenic,
antimony, or bismuth the sulphide precipitation of copper is not feasible as these elements precipitate with the copper and must be removed if copper is to be determined by the electrolytic method.

With ores free of arsenic, antimony, or bismuth the sulphide segregation method works well. The procedure used is as follows:

The sample of ore, 20 to 50 grams, is titrated with hydrochloric acid as in the case of lead. The residue is filtered out of solution and treated with concentrated nitric and hydrochloric acids to insure complete solution of the copper minerals. The washed residue from this treatment is discarded. The filtrate is taken to dryness and baked to remove all free nitric acid. Redissolve in hydrochloric acid and combine this solution with the first obtained filtrate.

The filtrate is neutralized with ammonium hydroxide and sodium bi-carbonate, then made slightly acid; total acidity not to exceed 30 milli-equivalents of the acid. A rapid stream of hydrogen sulphide gas is passed into the solution for 15 to 20 minutes. The copper and lead sulphide precipitate is filtered out of the solution after standing for an hour or so. This precipitate is dissolved in nitric acid, boiled to expel all of the hydrogen sulphide, and the copper determined electrolytically, or by some other standard method for copper. The results of one of the tests are given in Table XI.
Table XI: Comparison of Results Obtained From Electrolytic Analysis of Standard Pulp Sample and Sulphide Segregate.

<table>
<thead>
<tr>
<th>Per cent Copper</th>
<th>Per cent Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight Electrolytic on a 5-gram sample</td>
<td>Electrolytic on Sulphide Segregate from a 20-gram sample</td>
</tr>
<tr>
<td>0.038</td>
<td>0.0395</td>
</tr>
<tr>
<td>0.164</td>
<td>0.162</td>
</tr>
<tr>
<td>0.060</td>
<td>0.055</td>
</tr>
</tbody>
</table>

Conclusions: From the results obtained it is evident that a segregate can be made of the copper minerals in a low-grade ore pulp by using sulphide segregation methods. The results compare closely to those obtained by the straight electrolytic method.
CONCLUSIONS.

From the tests made it is evident that segregates can be made of the lead, zinc, and copper in low-grade dolomitic ore pulps. The sulphide segregation methods gave the best results, although slightly longer than other methods.

Lead can be segregated with ease by the sulphide method. Good results were obtained when using this method in conjunction with the electrolytic method for the determination of lead. This method was slightly more accurate than the electrolytic method for lead determinations.

Zinc can be segregated, but the procedure is long and the results obtained will not warrant the additional time spent in the procedure over that required for the standard ferrocyanide method for zinc determinations.

Copper can be segregated in much the same manner as lead. The results obtained were comparable to the straight electrolytic method for copper determinations. It is doubtful that the slight increase in accuracy will justify the additional time required for this method.
METHODS OF CHEMICAL ANALYSIS.

Introduction.

In the foregoing it has been shown that reliable segregates cannot be made by float-and-sink methods. Selective dissolution was then undertaken. From the results obtained by the selective dissolution tests on a low-grade dolomitic ore pulp it seemed necessary to consider some of the methods that are being used at the present time for the determination of lead, zinc, and copper. Each method of determination is specifically adapted to a certain type of ore, that is, certain methods work well on one kind of material but are of little value on others. Speed and accuracy are essential in any method of determination to be used in the commercial laboratory. Many methods for the determination of lead, zinc, and copper are given which are so involved in manipulation that the chemist engaged in routine testing work finds it impossible to utilize them successfully. Other methods in common use give results consistently too high or too low, but a proper consideration of the fundamental principles of chemistry involved in these methods, can in many cases, convert a poor method into a good method without undue length of procedure.

Methods for the Determination of Lead.

Many methods have been proposed for the determination of lead in ores. Lead may be determined gravimetrically in the following form:

The oxide (PbO), the sulphate (PbSO₄), the peroxide (PbO₂), the chromate (PbCrO₄), the molybdate (PbMoO₄), and in a few cases as the chloride (PbCl₂).
Many methods have been proposed for the volumetric analysis of lead, the most important of these are the ferrocyanide method, the permanganate method, the chromate-iodide method, the chromate-ferrous iron method, and many modifications of the above named methods.

It is obvious that all of the above mentioned methods cannot be studied in detail. However, the methods for the determination of lead will be considered as to their applicability to ores containing a high lime content, as the Southeast Missouri lead ores.

**GRAVIMETRIC METHODS.**

**The Sulphate Method.**

The gravimetric determination of lead as the sulphate is a standard method for the analysis of lead ores. It is the most accurate method and can be used for materials containing either high or low percentages of lead. Briefly stated the procedure may be given as follows:

The weighed sample of the ore, depending upon the lead content, is dissolved in hydrochloric and nitric acid. The lead is precipitated as the sulphate by addition of sulphuric acid and taking to fumes. The solution is cooled, diluted, heated to boiling to dissolve all soluble sulphates, and then filtered. The precipitate is washed with water containing about ten per cent of sulphuric acid until free of soluble impurities. If the precipitate is known to be free of impurities, such as the insoluble sulphates of calcium or barium, and silica, it may be dried, then ignited at a dull red heat.
to constant weight, cooled, and weighed as the sulphate.

In the analysis of ores it is advisable to purify the precipitate due to the presence of calcium and barium sulphates. This is usually accomplished by washing the precipitate with a hot saturated solution of ammonium acetate containing about two per cent of free sulphuric acid. This solution dissolves the lead as the acetate, leaving the calcium and barium sulphates as a residue. The filtrate containing the lead is then treated with sulphuric acid and the lead precipitated as the sulphate, filtered, washed, dried, ignited, and weighed as the sulphate.

The reactions involved in the procedure may be given as follows:

\[
PbS + 2 \text{HCl} = PbCl_2 + H_2S
\]

\[
3 PbS + 8 \text{HNO}_3 = 3 Pb \left(\text{NO}_3\right)_2 + 4 H_2O + 2 \text{NO} + 3 S
\]

\[
PbCl_2 + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + 2 \text{HCl}
\]

\[
Pb\left(\text{NO}_3\right)_2 + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + 2 \text{HNO}_3
\]

\[
CaCO_3 + 2 \text{HCl} = Ca\text{Cl}_2 + H_2\text{CO}_3
\]

\[
Ca\text{Cl}_2 + \text{H}_2\text{SO}_4 = Ca\text{SO}_4 + 2 \text{HCl}
\]

\[
Ba\text{Cl}_2 + \text{H}_2\text{SO}_4 = Ba\text{SO}_4 + 2 \text{HCl}
\]

\[
Pb\text{SO}_4 + 2 \text{NH}_4\text{C}_2\text{H}_2\text{O}_2 = \text{Pb}\left(\text{C}_2\text{H}_2\text{O}_2\right)_2 + \left(\text{NH}_4\right)\text{SO}_4
\]

\[
Ca\text{SO}_4 + 2 \text{BaSO}_4 = Ca\text{SO}_4 + \text{BaSO}_4
\]

\[
Pb\left(\text{C}_2\text{H}_2\text{O}_2\right)_2 + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + 2 \text{H}_2\text{C}_2\text{O}_4
\]
When this method is used on a low-grade dolomitic ore pulp considerable trouble is experienced in obtaining the correct amount of lead due to the interference of calcium sulphate. Special precautions in dissolving out the lead sulphate will obviate all difficulties with calcium sulphate. The trouble due to the interference of barium sulphate is eliminated by use of a small amount of sulphuric acid in the extraction solution. The presence of the sulphuric acid prevents the barium sulphate from dissolving.

In high lime ores considerable trouble is usually experienced in fuming with sulphuric acid to precipitate the sulphates. This is due to the large amount of calcium present which must be converted and precipitated as the sulphate before the lead will be precipitated completely. Ores that contain large amounts of calcium and barium may best be treated by precipitating the metals out of a slightly acid solution with hydrogen sulphide, and then to take this washed precipitate and treat it with sulphuric acid for the production of the lead sulphate. This procedure eliminates all difficulty due to the interference of calcium and barium as the sulphates.

Chromate Method.

This method is applicable to a large class of materials and is of special importance in the precipitation of lead from acetic acid solutions, the method depending upon the insolubility of lead chromate in acetic acid.¹ This method is usually used in connection

with the sulphate method on ores containing a high lime content.

The sulphate precipitate, as obtained by the sulphuric acid treatment, containing the lead, calcium, and barium is treated with a saturated solution of ammonium acetate containing acetic acid to dissolve the lead sulphate. Often this requires boiling the sulphate precipitate with the extraction solution when the lead content is low and the calcium content is high. To the acetate solution an excess of a saturated solution of potassium dichromate is added and the solution boiled until the yellow precipitate turns to an orange color. Allow to settle, then filter the lead chromate through a weighed Gooch crucible. Wash the precipitate well with water containing a little ammonium acetate. Dry in an oven at 110° C., cool and weigh. The weight of lead chromate when multiplied by 0.641 gives the weight of the lead.

The reactions involved in this procedure may be given as follows:

\[ \text{PbS} + 2 \text{HCl} = \text{PbCl}_2 + \text{H}_2 \text{S} \]

\[ 3 \text{PbS} + 8 \text{HNO}_3 = 3 \text{Pb(NO}_3)_2 + 4 \text{H}_2 \text{O} + 2 \text{NO} + 3 \text{S} \]

\[ \text{PbCl}_2 + \text{H}_2 \text{SO}_4 = \text{PbSO}_4 + 2 \text{HCl} \]

\[ \text{Pb(NO}_3)_2 + 2 \text{NH}_4 \text{C}_2 \text{H}_3 \text{O}_2 = \text{Pb(C}_2 \text{H}_3 \text{O}_2)_2 + (\text{NH}_4)_2 \text{SO}_4 \]

\[ 2 \text{Pb(C}_2 \text{H}_3 \text{O}_2)_2 + \text{K}_2 \text{Cr}_2 \text{O}_7 + 3 \text{H}_2 \text{O} = 2 \text{PbCrO}_4 + \text{K}_2 \text{H}_2 \text{C}_2 + 2 \text{H}_2 \text{C}_2 \text{H}_3 \text{O}_2 \]
The impurities in the acetate solution which seriously interfere with the precipitation are iron, copper, cadmium, and zinc. They should have been removed by washing the sulphate precipitate with dilute sulphuric acid before dissolving the lead as the acetate. If any barium is present in the solution it will be precipitated with the lead and give high results.

Molybdate Method.

The determination of lead as the molybdate is rapid and has the following advantages:

1. The sulphation of lead is avoided.
2. The acetate extraction is eliminated.
3. The precipitate can be ignited.
4. The ratio of lead to its molybdate compound is greater than either lead to the sulphate or to the chromate, hence lessening the chances of error due to weighing.

The procedure may be given briefly as follows:

The sample is decomposed with nitric acid or with aqua regia as the case may require. Dehydrate to remove silica and take up in nitric acid and filter. To the filtrate add several grams of ammonium chloride and sufficient ammonium acetate to destroy the excess free nitric acid; this requires approximately two grams per cc. of free acid present. Add 40 cc. of the molybdate solution, containing four grams of ammonium molybdate per liter and 10 cc. of acetic acid,
for each 0.1 gram of lead present. Stir the mixture well during the addition. Boil for several minutes, allow the precipitate to settle, then filter and wash the precipitate well with hot water. Ignite, cool, and weigh the residue. The weight of the lead molybdate multiplied by 0.5642 gives the amount of lead present.

The reactions involved in the procedure may be given as follows:

\[
\begin{align*}
3 \text{ PbS} + 8 \text{ HNO}_3 &= 3 \text{ Pb(NO}_3)_2 + 4 \text{ H}_2\text{O} + 2 \text{ NO} + 3 \text{ S} \\
\text{Pb(NO}_3)_2 + (\text{NH}_4)_2\text{MoO}_4 &= \text{PbMoO}_4 + 2 \text{ NH}_4\text{NO}_3 \\
\text{Ca(NO}_3)_2 + (\text{NH}_4)_2\text{MoO}_4 &= \text{CaMoO}_4 + 2 \text{ NH}_4\text{NO}_3 \\
\text{CaMoO}_4 + 2 \text{ NH}_4\text{C}_2\text{H}_3\text{O}_2 &= 2 (\text{NH}_4)_2\text{MoO}_4 + \text{Ca(C}_2\text{H}_3\text{O}_2)_2 \\
\text{Fe(NO}_3)_2 + (\text{NH}_4)_2\text{MoO}_4 &= \text{FeMoO}_4 + 2 \text{ NH}_4\text{NO}_3
\end{align*}
\]

This method for the determination of lead, although rapid, has several disadvantages in that the calcium present in solution from a dolomitic ore pulp interferes even in the presence of considerable amounts of ammonium acetate. The iron present reacts with the molybdate solution to form an insoluble precipitate.

**Electrolytic Method.**

The electrolytic method in which the lead is determined as the peroxide is one of the most rapid methods for lead determination. It can be used upon many types of ores with wide variations in lead content.

Briefly stated the electrolytic method may be given as follows:

- 46 -
The sample is dissolved in nitric acid, a sufficient quantity being added to have about 25 or 30 cc. of excess concentrated acid. The sample is diluted to 150 cc. and electrolyzed cold for two hours with a current of two amperes, or for one and one-half hours with a current of three amperes. The lead is deposited upon the anode as the peroxide (PbO₃). When the deposition of PbO₃ is complete the anodes are removed without breaking the current. They are immediately washed in water, then alcohol, dried, and weighed. From the weight of the peroxide obtained the amount of lead can be calculated by multiplying by the factor 0.866. It has been found that by using the factor 0.863 that more concordant results can be obtained. This is probably due to the excess of oxygen held within the peroxide deposit. Some prefer to gently ignite the anode to convert the PbO₃ to the oxide, PbO₂, and then weigh the oxide deposit. It is claimed to give better results.


The reactions involved in this procedure may be given as follows:

\[
3 \text{PbS} + 8 \text{HNO}_3 = 3 \text{Pb(NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO} + 3 \text{S}
\]

\[
\text{Pb(NO}_3)_2 \xrightarrow{++} \text{Pb} + 2 \text{NO}_3
\]

\[
\text{H}_2\text{O} \xrightarrow{+} \text{H} + \text{OH}
\]

\[
\text{Pb} + 4 \text{OH} = \text{PbO}_2 + 2 \text{H}_2\text{O}
\]

\[
\text{PbO}_2 + 2 \text{e} = \text{PbO}_2\text{ (anode)}.
\]
In the electrolytic method the size of the sample used should be such that there are at least ten milligrams of lead in the solution to be deposited, otherwise complete deposition of the lead is impossible. If the solution contains much more than 70 milligrams of lead the deposited peroxide is liable to fall from the anode causing low results. If the best results are to be obtained the size of the sample should be so selected as to keep the lead content between 10 and 70 milligrams.

Samples weighed out for electrolytic lead determinations are usually done so in accordance to some whole multiple of the gravimetric factor for conversion of PbO₂ to Pb, that is, if 0.863 grams of ore is taken, or some multiple of this amount. For the sample, then, the weight of the lead peroxide obtained may be taken as the amount of lead in per cent directly by multiplying by 100. This weight of the sample, 0.863 grams, is usually termed a "plumb." The number of "plumbs" taken for assay depends upon the lead content of the ore, usually four or six "plumbs" are used when the material is low-grade.

Manganese is the most likely element to interfere with electrolytic lead determinations because it is deposited simultaneously with the lead when the concentration of the acid is low, or when the period of deposition is long. The interference of manganese in the lead deposit can be overcome if an excess of 25 cc.
concentrated nitric acid is maintained in the solution. If the manganese content of the ore is low, then the acid concentration can be reduced without causing any of the manganese to be deposited. The deposition of manganese along with the lead may be detected by the appearance of the deposit in that the manganese causes an uneven brown deposit. The statement has been made by other writers that the presence of small amounts of manganese is beneficial in helping to throw the lead out of solution and give a better deposit. According to O. W. Holmes, Chemist of the State Mining Experiment Station, Rolla, Missouri, such is not the case as he noticed no beneficial effects due to the presence of manganese in electrolyzing solutions of lead nitrate which contained manganese nitrate.

Other impurities which affect the determination are bismuth and antimony. They are partly deposited with the lead. If selenium, tellurium, or arsenic are present in the ore they must be removed, as their presence will partly, or wholly, prevent the deposition of the peroxide. It should be noted that the solution to be electrolyzed must be chloride free, as the chlorine evolved would attack the platinum electrode.

The electrolytic method works well in the hands of the experienced analyst; but with the inexperienced the results obtained should be held in question. Many factors affect the type of deposit obtained, the principal ones being the current density, the time and rate of deposition, the presence of manganese and other impurities.
Mr. O. H. Holmes, who has already been referred to, made a series of tests upon the electrolytic method for the determination of lead. From the results of his work the following conclusions may be drawn.

1. The size of sample to be taken for analysis depends upon, not only the lead content of the ore, but also upon the manganese content of the ore.
2. In every case where the lead content of the solution falls below 10 milligrams complete deposition of the lead is impossible. When the lead content of the solution exceeded 70 milligrams lead was lost due to the failure of the peroxide to adhere to the anode.
3. The tendency of the manganese to deposit was retarded as the concentration of free nitric acid in the solution was increased.
4. That a long period of deposition with a low current density increased the tendency of the manganese to deposit.
5. That complete deposition of the lead from pure solutions was obtained when using low current densities for long periods of time.
6. That current densities of 1.5 and 2 amperes for a period of 2 or 3 hours were sufficient for low-grade materials.
7. That the surface condition of the anode is important. The peroxide fails to adhere to a smooth surface and is lost, causing low results. The electrode should be sand-blasted occasionally to facilitate the electrode to take the deposit.

8. Rotating electrodes are to be preferred to stationary ones as the deposit obtained is more uniform and more strongly adherent.

CONCLUSIONS.

The gravimetric methods as given are the ones in most common use. The electrolytic method in the hands of the experienced analyst gives very good results. The sulphate method is the most accurate of any given and is used as a check for other methods. The dichromate method gives results comparable to the sulphate method when care is used in the precipitation. The molybdate method is valuable on certain types of ores, but is of little use on high-lime ores.
VOLUMETRIC METHODS.

The volumetric methods for the determination of lead are not as accurate as the gravimetric methods, but they can at times be used to advantage. In general the volumetric methods consist of taking a precipitate, dissolving, and then titrating with a solution of known strength. This procedure with the precipitate increases the chance of error through manipulation, titration, and observing the true end-point. These would be eliminated if the washed precipitate were ignited and weighed, making the procedure a gravimetric one. The most important volumetric methods may be given as follows:

The Dichromate Method.

This method for lead depends upon the precipitation of lead chromate from an acetic acid solution. The precipitate is dissolved in hydrochloric acid, potassium iodide is added, and the liberated iodine is titrated with a standard solution of thiosulphate. This method is rather long but gives good results when used by an experienced analyst. Briefly considered the procedure may be given as follows:

The sample is dissolved in hydrochloric and nitric acids, then taken to fumes with sulphuric acid. The precipitate is filtered out of solution and washed free of all soluble sulphates. The lead sulphate is extracted from the precipitate by treating with a boiling saturated solution of sodium acetate containing some acetic acid. The filtrate is heated to boiling and the lead is precipitated by adding an excess of a saturated solution of potassium dichro-
mate. The precipitate is filtered off and washed free of soluble chromates. The lead chromate is dissolved in a saturated solution of sodium chloride containing free hydrochloric acid. Several grams of potassium iodide are added to the filtrate and the liberated iodine is titrated immediately with a standard solution of thiosulphate until the brown coloration fades to a yellow color. A couple of cc. of starch solution are then added and the titration completed. The end-point is a sharp color change from blue to a light green.

The reactions involved in the procedure may be given as follows:

\[
PbS + 2 \text{HCl} = PbCl}_2 + H_2S
\]

\[
3 \text{PbS} + 8 \text{HNO}_3 = 3 \text{Pb(NO}_3)_2 + 4 \text{H}_2O + 2 \text{NO} + 3 \text{S}
\]

\[
PbCl}_2 + 2 \text{H}_2\text{SO}_4 = 2 \text{PbSO}_4 + \text{2 HCL}
\]

\[
Pb(\text{NO}_3)_2 + 2 \text{HNO}_3 = 2 \text{Pb(NO}_3)_2 + 2 \text{H}_2O
\]

\[
\text{PbSO}_4 + 2 \text{Na}_2\text{C}_2\text{H}_3\text{O}_7 = \text{Pb(C}_2\text{H}_3\text{O}_7)_2 + \text{Na}_2\text{SO}_4
\]

\[
2 \text{Pb(C}_2\text{H}_3\text{O}_7)_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2O = 2 \text{PbCrO}_4 + 2 \text{K}_2\text{C}_2\text{H}_3\text{O}_7 + 2 \text{H}_2\text{C}_2\text{H}_3\text{O}_7
\]

\[
\text{PbCrO}_4 + 2 \text{HCL} = \text{PbCl}_2 + \text{H}_2\text{CrO}_4
\]

\[
\text{H}_2\text{CrO}_4 + 6 \text{KI} + 12 \text{HCL} = 6 \text{KCl} + 2 \text{CrCl}_3 + 8 \text{H}_2\text{O} + 3 \text{I}_2
\]

\[
2 \text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = 2 \text{NaI} + \text{Na}_2\text{S}_4\text{O}_6
\]
Considerable difficulty is encountered when using this method for high calcium ores. This is due to the small amount of lead sulphate in a large amount of calcium sulphate. The lead sulphate is difficult to remove from this large precipitate of calcium sulphate by mere washing with the extraction solution. In many cases it is best to boil the precipitate with the extraction solution and re-filter. If there is barium present the residue from the acetate extraction may contain lead, even if the precipitate has been given the boiling treatment. In this case it is recommended that the residue be treated with a small amount of concentrated hydrochloric acid, taken to dryness, then giving the acetate extraction treatment. Bismuth, if present in small amounts, does not interfere with the determination.

Some trouble is experienced in observing the true end-point in these titrations. In many cases the color change indicating that the end-point has been reached is observed, but upon allowing to stand for a minute or so a change occurs in which a precipitate is formed and the solution turns blue again. The addition of a few drops of thiosulphate again produces the green color. Analysts at times experience difficulty in checking their own end-point within several tenths of a cc.

A shorter method has been devised by H. A. Guess for the determination of lead by the chromate method in which the sulphation of the lead is omitted. Guess' modification is given as follows:

---

The ore sample is treated with hydrochloric and nitric acids. The solution is then neutralized with ammonium hydroxide until a slight precipitate is formed. Acetic acid, 80 per cent strength, is added until the solution is decidedly acid. A little ammonium acetate is added to insure complete solution of the lead salts. An excess of a saturated solution of potassium dichromate is then added and the solution boiled for a few minutes. The precipitate is filtered off and washed free of all soluble chromates by a dilute solution of acetic acid. The precipitate is then dissolved with hydrochloric acid and sodium chloride extraction solution. A few grams of potassium iodide is added to the solution and the liberated iodine titrated with a standard solution of sodium thiosulphate as in the standard dichromate method.

The reactions occurring in this determination may be given as follows:

\[ 3 \text{PbS} + 8 \text{HNO}_3 = \text{Pb(NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO} + 2 \text{NaNO}_3 \]

\[ \text{Pb(NO}_3)_2 + 2 \text{NaC}_2\text{H}_3\text{O}_2 = \text{Pb(C}_2\text{H}_3\text{O}_2)_2 + 2 \text{NaNO}_3 \]

\[ 2 \text{Pb(C}_2\text{H}_3\text{O}_2)_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} = 2 \text{PbCrO}_4 + \text{K}_2\text{C}_2\text{H}_3\text{O}_2 + 2 \text{HC}_2\text{H}_3\text{O}_2 \]

\[ \text{PbCrO}_4 + 2 \text{HCl} = \text{PbCl}_2 + \text{H}_2\text{CrO}_4 \]

\[ \text{H}_2\text{CrO}_4 + 6 \text{KI} + 12 \text{HCl} = 6 \text{KCl} + 2 \text{CrCl}_3 + 3 \text{H}_2\text{O} + 6 \text{I} \]

\[ 2 \text{I} + 2 \text{Na}_2\text{S}_2\text{O}_3 = 2 \text{NaI} + \text{Na}_2\text{S}_4\text{O}_6 \]
This method, though shorter than the regular dichromate method, is less accurate in the presence of certain impurities such as antimony, bismuth, or silver. Guess found that no interference was caused by the presence of aluminum, arsenic, calcium, magnesium, copper, cadmium, or zinc. Manganese does not cause trouble when the solution of the ore is such that it goes into the form of the chloride. Barium and silver form chromates which if present in solution cause high results. Bismuth if present interferes in that it forms a hydrate when the ammonia is added. This hydrate does not dissolve completely in acetic acid.

Care must be used with the washing of the soluble chromates from the chromate precipitate obtained. The washings must be thorough or the results obtained are high, due to the presence of foreign chromates. The presence of large amounts of iron and aluminum cause difficulty due to hydrolysis when the ammonia is added. They are precipitated as the hydroxides and liberate a corresponding amount of acid. When the iron and aluminum content is high it is advisable to complete the neutralization with sodium carbonate, using methyl orange as the indicator. This neutralization should be carried out in the cold or large amounts of iron and aluminum will be precipitated by hydrolysis.

Concordant results can be obtained by this method on ores with a wide range in lead content. The method works well on ores containing over half of a per cent lead. On ores containing less than this amount of lead a large sample of the ore must be taken for analysis.
in order to eliminate errors as much as is possible.

Other modifications of the chromate method for lead are being used. The best of these is probably Wilder's modification in which


The reactions may be given as follows:

\[
\begin{align*}
K_2Cr_2O_7 + 6 KI + 7 H_2SO_4 & = 4 K_2SO_4 + Cr_2(SO_4)_3 + 6 I + 7 H_2O \\
2 I + 2 Na_2S_2O_3 & = 2 NaI + Na_2S_2O_5.
\end{align*}
\]

Calcium and iron interfere with the titration and must be removed before the titration can be made.

The Molybdate Method.

This method is rapid but is not as accurate as the chromate methods. The determination depends upon the fact that lead is precipitated from an acetic acid solution by a standard solution of ammonium molybdate. The termination of the reaction being recognized by the yellow color produced by the excess of reagent when a drop of the mixture comes in contact with a drop of tannic acid solution used as an outside indicator.

The procedure may be given as follows:

The sample is decomposed with hydrochloric and nitric acids. Sulphuric acid is added and the solution taken to strong fumes. Filter off the sulphates and wash well with a 10 per cent sulphuric acid solution to remove all soluble sulphates. The lead sulphate is dissolved
by means of an acetate extraction solution as in the chromate determinations. The lead solution is then titrated with a standard molybdate solution using tannic acid as the indicator.

The reactions involved in the determination may be given as follows:

\[ 3 \text{PbS} + 6 \text{HNO}_3 = 3 \text{Pb(NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO} + 3 \text{S} \]

\[ \text{PbCl}_2 + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + 2 \text{HCl} \]

\[ \text{Pb(NO}_3)_2 + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + 2 \text{HNO}_3 \]

\[ \text{PbSO}_4 + 2 \text{NaC}_2\text{H}_3\text{O}_2 = \text{Pb(C}_2\text{H}_3\text{O}_2)_2 + \text{Na}_2\text{SO}_4 \]

\[ \text{Pb(C}_2\text{H}_3\text{O}_2)_2 + (\text{NH}_4)_2\text{MoO}_4 = \text{PbMoO}_4 + 2 \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \]

\[ \text{Fe(NO}_3)_2 + (\text{NH}_4)_2\text{MoO}_4 = \text{FeMoO}_4 + 2 \text{NH}_4\text{NO}_3 \]

Many modifications of the volumetric molybdate method are in use. In general these modifications were developed to facilitate the removal of interfering elements such as calcium, strontium, barium, bismuth, antimony, and iron. These methods will not be discussed as they have a limited range of applicability and the procedure becomes lengthy and requires more time than the results obtained will warrant. For high calcium ores from the Southeast Missouri Lead District this method is of little value. The results obtained by use of this method should be held in suspicion as there is a tendency for the results to be high.
The Permanganate Method.

This method for the determination of lead is very satisfactory in most cases in that the ordinary constituents of lead ores, with the exception of calcium, do not interfere with the determination.\footnote{Op. cit., p. 277.}

It depends upon the separation of lead as the sulphate, conversion of the sulphate to the carbonate, dissolution of the carbonate in acetic acid and precipitation of the lead as the oxalate. The lead oxalate is decomposed in sulphuric acid and the separated oxalic acid is titrated with standard permanganate.

The reactions involved in the determination may be given as follows:

\[
PbS + 2 \text{HCl} = PbCl_2 + H_2S
\]

\[
3 \text{PbS} + 8 \text{HNO}_3 = 3 \text{Pb(NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO} + 3 \text{S}
\]

\[
PbCl_2 + H_2\text{SO}_4 = Pb\text{SO}_4 + 2 \text{HCl}
\]

\[
Pb\text{(NO}_3)_2 + 2 \text{HNO}_3 = Pb\text{(NO}_3)_4 + 2 \text{H}_2\text{O}
\]

\[
Pb\text{SO}_4 + (\text{NH}_4)_2\text{CO}_3 = Pb\text{CO}_3 + (\text{NH}_4)_4\text{SO}_4
\]

\[
Pb\text{CO}_3 + H_2\text{C}_2\text{O}_4 = Pb\text{C}_2\text{O}_4 + H_2\text{CO}_3
\]

\[
Pb\text{C}_2\text{O}_4 + H_2\text{SO}_4 = Pb\text{SO}_4 + H_2\text{C}_2\text{O}_4
\]

\[
2 \text{KMnO}_4 + 5 H_2\text{C}_2\text{O}_4 + 3 H_2\text{SO}_4 = K_2\text{SO}_4 + 2 \text{MnSO}_4 + 8 H_2\text{O} + 10 \text{CO}_2
\]
The permanganate method may be used with alkaline solutions, but according to Ballenbach\textsuperscript{a} the titration by permanganate in alkaline solution does not give concordant results. If the alkaline solution of lead is poured into an excess of the permanganate and the residual permanganate determined by titration with a standard lead nitrate solution, concordant and satisfactory results can be obtained.

The reaction may be given as follows:

\[
2 \text{KMnO}_4 + 6 \text{Pb(NO}_3)_2 + 12 \text{KOH} = 2 \text{MnO}_4^- + 3 \text{Pb}_3\text{O}_8 + 2 \text{KOH} + 12 \text{KNO}_3 + 5 \text{H}_2\text{O}
\]

The presence of calcium interferes in the permanganate determinations and must be removed if true results are to be obtained. Iron present in the ferrous state also consumed permanganate and causes high results. Permanganate methods cannot be recommended for use on high calcium ores from the Southeast Missouri Lead District, due to the long procedure and the inaccurate results usually obtained.

Various modifications of the permanganate method have been worked out by several investigators, but in every case the results obtained were inaccurate and the procedures were too long for commercial application.

The Ferrocyanide Method.

The ferrocyanide method has been pronounced by Bull to be "Bull. I. C., Chemical News, Vol. 87, pp. 2253-55, 1903."

the best of the common volumetric procedures, claiming: "The results obtained are very accurate."

The procedure may be given as follows:

The lead is precipitated as the sulphate, as in the previous methods, and is converted to the carbonate. The carbonate is dissolved in acetic acid and the resulting solution is titrated with standard potassium ferrocyanide when using uranyl acetate as an outside indicator.

The reactions involved in the determination may be given as follows:

\[
PbSO_4 + (NH_4)_2CO_3 \rightarrow PbCO_3 + (NH_4)_2SO_4
\]

\[
PbCO_3 + 2 HC_2H_3O_2 = Pb(C_2H_3O_2)_2 + H_2CO_3
\]

\[
2 Pb(C_2H_3O_2)_2 + K_4Fe(CN)_6 \rightarrow Pb_2[Fe(CN)_6] + 4 KC_2H_3O_2
\]

In this method iron is the interfering element which causes most of the trouble. Antimony, bismuth, strontium, and calcium cause little trouble and the error due to their presence is negligible. Free ammonia must be absent as it reacts with the uranium indicator, giving a false end-point. In the presence of material amounts of chlorides or hydrochloric acid the results obtained are erroneous.\textsuperscript{10}

\textsuperscript{10} Leyher and Melocke, Chemical News; Vol. 107, p. 162.

In order to obtain the best results with this method the conditions should be the same as when the standard solution was standardized. Blanks should be run upon all reagents.
Discussion of Volumetric Methods.

The volumetric methods for the determination of lead, though less accurate than the gravimetric methods, find favor with many chemists. Of the volumetric methods given Guess' modified dichromate method is the most rapid and also the least accurate when working with ores containing high calcium and iron. The ferrocyanide method is accurate in the absence of iron and calcium. The molybdate method is fairly accurate in the absence of iron. The permanganate method is long and the results obtained are accurate only when iron and calcium are absent.

The observation of the true end-point is probably one of the largest sources of error in volumetric analysis. The color change selected by the chemist for the end-point should be definite. An off colored end-point should be sufficient to hold the determination in question.

Discussion of the Methods for the Determination of Lead.

Of the methods given the gravimetric are more accurate than the volumetric. The sulphate and chromate gravimetric methods are the most accurate of any of these given. The electrolytic method gives very good results in the hands of the experienced analyst.

The sulphation of the sample is probably the most difficult of any part of the procedure. This is due to the large amounts of calcium present that must be precipitated as the sulphate before the lead will be precipitated completely. A high temperature and a large excess of concentrated sulphuric acid is necessary in order to pre-
cipitate the sulphates and to destroy the nitric acid. When the sulphate precipitate is obtained it must be washed thoroughly in order to insure that all of the soluble sulphates are dissolved.

The small amounts of lead in the ore makes it advisable to use large samples of the ore in order to insure the presence of enough lead to form a precipitate of such a size that the errors due to manipulation are correspondingly reduced.

Comparison of Methods.

A series of tests were made by Bull\textsuperscript{11} at Columbia University using several methods for the determination of lead in ores in the presence of certain impurities. The following table shows the results which he obtained:

Table XII: Comparison of Results Obtained by Various Methods for the Determination of Lead. Figures are for Assay Per cent Lead (After Bull).

\begin{table}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Coe & Sulphate & Chromate & Electrolytic & Dichromate & Ferrocyanide & Molybdate \\
\hline
1 & 78.68 & 78.71 & 78.73 & 78.75 & 78.67 & 75.74 \\
 & 78.63 & 78.68 & 78.73 & 78.73 & 78.55 & 78.82 \\
2 & 37.20 & 37.28 & 37.35 & 37.31 & 37.31 & 37.41 \\
 & 37.26 & 37.30 & 37.35 & 37.37 & 37.39 & 37.41 \\
3 & 10.74 & 10.77 & 10.80 & 10.80 & 10.80 & 10.80 \\
 & 10.76 & 10.77 & 10.80 & 10.80 & 10.90 & 10.80 \\
4 & 18.40 & 18.45 & 18.50 & 18.34 & 18.44 & 18.47 \\
 & 18.43 & 18.40 & 18.45 & 18.45 & 18.48 & 18.51 \\
5 & 27.25 & 27.23 & 27.32 & 27.25 & 27.25 & 27.44 \\
 & 27.21 & 27.20 & 27.32 & 27.32 & 27.19 & 27.35 \\
6 & 38.50 & 38.47 & 38.60 & 38.57 & 38.65 & 38.66 \\
 & 38.54 & 38.50 & 38.60 & 38.50 & 38.58 & 38.58 \\
\hline
\end{tabular}
\end{table}
From the above table it is evident that the dichromate method is the more liable to be inaccurate than the others, unless a great deal of time is spent in washing out the foreign chromates, which are in many cases sparingly soluble. The ferrocyanide and molybdate methods give fairly good results even in the presence of considerable amounts of impurities, iron being absent. The results obtained by the electrolytic method are higher than the sulphate or chromate gravimetric methods, and this is probably due to the presence of oxygen in the peroxide deposit. The chromate and sulphate methods are probably the most accurate of any of the methods given. It would seem that Mr. Bull exercised extreme care in obtaining pure precipitates for analyses as the results agree with one another very closely. In commercial testing work the element of time would prohibit such a refinement of manipulation necessary to obtain these results.
METHODS FOR THE DETERMINATION OF ZINC.

A great variety of methods have been proposed for the determination of zinc in ores. Some of these methods are fairly accurate, while others are practically worthless in the presence of certain interfering elements. Some of the methods in use are inherently weak and give inaccurate results regardless of the care expended in manipulation.

The methods in general use for the determination of zinc are less accurate than those for the determination of lead and copper. The degree of accuracy which can be obtained by any one method depends upon the type of ore, the presence of impurities, and the chances of error through faulty manipulation. For this reason the checking limits for zinc are greater than for lead and copper.

A single determination on high-grade material, necessitating that a small sample be taken for analysis, may be in error as much as one-half per cent; whereas, if several chemists assayed the same sample using the same method, they should be able, with due care in manipulation, to check within several tenths of a per cent. When material of low or medium grade, containing small amounts of impurities, is assayed the results obtained should agree within a tenth of a per cent.

The methods in use for the determination of zinc may be classified into three groups: (1) The gravimetric methods, (2) The electrolytic methods, and (3) The volumetric methods. The most important of these methods will be considered briefly in respect to their applicability to high lime ores containing some iron and copper. The detailed account of any of the methods may be found in a good textbook on analytical chemistry or by reference to the periodicals.
GRAVIMETRIC METHODS.

The Oxide Method.

Zinc may be determined gravimetrically as the oxide by gently igniting the carbonate, nitrate, acetate, oxalate, or sulphate precipitate that is obtained by the procedure best adapted to the ore.\(^2\)


The sulphate can be transformed to the oxide form but the procedure is difficult and hard to accomplish with any degree of success. The chloride can be converted to the oxide by ignition with mercuric oxide, the mercuric chloride formed through the double decomposition is readily volatilized leaving pure zinc oxide as the residue.\(^3\) The difficulty that is encountered in this method for the determination of zinc is the obtaining of a pure precipitate. The method is rapid and accurate when the precipitate is obtained from a material free of interfering elements, but it is of little use on impure ores, such as those from the Southeast Missouri Lead District. Other methods give greater accuracy and are better adapted to the type of ores from this district.

Of the procedures given, the method in which the zinc is precipitated as the sulphide from a neutral solution by hydrogen sulphide with subsequent ignition to the oxide is probably the best and most rapid. A discussion of the precipitation of zinc as the sulphide from acid and ammonical solutions has been previously considered.
Sulphate Method.

Zinc may be determined as the sulphate by taking the sulphide precipitate and dissolving in sulphuric acid and evaporation to dryness in a weighed crucible. The excess acid is driven off and the residue ignited at a dull red heat. This method, more accurate than the determination as the oxide, has many defects and cannot be recommended for use with ores. The presence of other elements will cause high results to be obtained, the removal of these impurities makes the procedure so long that the additional time spent in manipulation is not warranted by the results obtained. Many other methods can be used that give more accurate results in a shorter time. This method is given in detail by Scott.1

1 op. cit., page 599.

Phosphate Method.

The determination of zinc as the pyrophosphate is the most accurate gravimetric method for the determination of zinc. Briefly, it consists in taking the sulphide precipitate and dissolving in hydrochloric acid.2 The solution is neutralized very carefully with ammonium hydroxide and a drop or so added in excess. To the cold dilute acid solution a large excess of ammonium sodium hydrogen phosphate is added with constant stirring. Warm gently until the flocculent precipitate of zinc ammonium phosphate has settled as a dense

crystalline powder. Filter and wash well. The precipitate can be
dried and weighed as zinc ammonium phosphate or it can be ignited and
weighed as the pyrophosphate. It is recommended that the zinc be de­
termined as the pyrophosphate as this method eliminates the long wash­
ing that is required to remove the ammonium salts when the zinc is to
be determined as the ammonium phosphate. When the precipitate is
weighed as the pyrophosphate the ammonium salts are volatilized in the
ignition and so it is not necessary to remove them by washing.

If a precipitate is formed when the solution is neutralized
with ammonium hydroxide, it is necessary at this point to remove all
of the iron by precipitation as the hydroxide in the presence of am­
monium chloride. The precipitate obtained is filtered and washed
thoroughly. If a large bulky precipitate is obtained it should be
dissolved and re-precipitated in order to completely remove the zinc.
The filtrates are combined with the original and the procedure follow­
ed as before.

In this method of determination it is necessary that the zinc
sulphide precipitate obtained be washed free of calcium and magne­
sium salts. If there are any magnesium salts present in the solution
when the sodium ammonium hydrogen phosphate is added, then a preci­
pitate of magnesium hydrogen phosphate is thrown down with the zinc
ammonium phosphate.

The following reaction takes place:

\[
\text{NaH}_{2}\text{PO}_4 + \text{MgCl}_2 + \text{NH}_4\text{OH} = \text{NaCl} + \text{NH}_4\text{Cl} + \text{MgNH}_4\text{PO}_4 + \text{H}_2\text{O}
\]
The reactions involved in this method may be given as follows:

\[
\begin{align*}
ZnS + 2 \text{HCl} &= ZnCl_2 + H_2S \\
ZnCl_2 + H_2S &= ZnS + 2 \text{HCl} \\
ZnS + 2 \text{HCl} &= ZnCl_2 + H_2S \\
ZnCl_2 + \text{NaNH}_4\text{PO}_4 + \text{NH}_3\text{OH} &= \underline{\text{ZnNH}_4\text{PO}_4 \cdot H_2O + \text{NaCl + NH}_4\text{Cl}} \\
\text{ZnNH}_4\text{PO}_4 \cdot H_2O + (\text{heat}) &= \text{ZnNH}_4\text{PO}_4 + H_2O \\
2 \text{ZnNH}_4\text{PO}_4 + (\text{heat}) &= \text{Zn}_2\text{P}_2\text{O}_7 + 2 \text{NH}_3 + \text{H}_2\text{O}
\end{align*}
\]

In this determination care must be exercised when the zinc is precipitated, as the zinc ammonium phosphate is soluble in both acids and ammonia.

Of the gravimetric methods given the determination as the phosphate is the most accurate and nearly as rapid as any other. The interfering elements are iron and lead and must be removed for accurate determination of the zinc.

**Electrolytic Determination of Zinc.**

The electrolytic method for the determination of zinc may be carried out in either acid or alkaline solutions. The determination is best made from an alkaline electrolyte or one slightly acid with acetic acid containing considerable amounts of sodium acetate.  

---

Electrolysis in Alkaline Solutions: The electrolytic method as carried out in an alkaline solution may be given as follows:

The sample is digested in hydrochloric and nitric acids. The zinc precipitated as the sulphide from a neutral solution. The sulphide precipitate is dissolved in nitric acid and then transformed to the sulphate by treating with sulphuric acid. The solution of the zinc sulphate, chlorides and nitrates absent, is treated with sodium hydroxide until a permanent coloration is obtained when using phenolphthalein as the indicator. Then add 20 to 25 cc. of a normal caustic soda solution. The solution is diluted to 150 cc. and electrolyzed with a current of one ampere at a potential of three to four volts. The time required for electrolysis varies with the zinc content, but with a content of zinc not greater than 0.5 gram about three hours are sufficient. The electrodes are removed from the bath before breaking the current. The cathode is washed with water, then alcohol, dried above a flame, cooled in a desiccator, and weighed. To make sure that all of the zinc has been deposited the electrodes are cleaned and the solution electrolyzed for thirty minutes longer. A slight increase in weight will be obtained in every case for the anode is slightly attacked by the alkaline solution and the cathode slowly gains in weight due to the deposited platinum. If at the end of thirty minutes the gain in weight is not over 0.3 milligram, then it may be considered that the deposition of the zinc was complete.

The reaction involved in the procedure may be given as follows:
3 \( \text{ZnS} + 8 \text{NH}_4 \) = 3 \( \text{Zn(NO}_3)_2 \) + 4 \( \text{H}_2\text{O} \) + 2 \( \text{NO} \) + 3 \( \text{S} \)

\( \text{Zn(NO}_3)_2 \) + \( \text{H}_2\text{SO}_4 \) = \( \text{ZnSO}_4 \) + 2 \( \text{NH}_4 \)

\( \text{ZnSO}_4 \) \( \xrightarrow{++} \) \( \text{Zn} + \text{SO}_4 \)

\( \text{NaOH} \) \( \xrightarrow{+} \) \( \text{Na} + \text{OH} \)

Upon electrolysis:

\( ++ \)

\( \text{Zn} + 2 \Theta \) = \( \text{Zn} \) (cathode)

\( + \)

\( 2 \text{Na} + \text{SO}_4 \) = \( \text{Na}_2\text{SO}_4 \)

\( + \)

\( \text{H} + \text{OH} \) = \( \text{H}_2\text{O} \)

In this determination ammonia must be absent. If ammonium salts are present in the solution, the solution must be boiled with caustic soda until all ammonia has been expelled.

Many elements interfere with this determination in that cobalt, nickel and copper deposit along with the zinc from alkaline solutions. They must be removed if accurate results are to be obtained. Lead does not interfere as it is removed when the sulphide precipitate is given the sulphate treatment. If it is not removed as the sulphate then it deposits along with the zinc. Iron, if present in the solution, causes high results. The results obtained by this method are always a little high due to the presence of zinc oxide or hydroxide in the deposit.  

Electrolysis in Acid Solutions: The procedure for the electrolysis in acid solutions is usually carried out as follows:

The zinc is separated from the other elements by precipitating as the sulphide from dilute sulphuric acid solutions by hydrogen sulphide. The precipitate is dissolved in nitric acid and then transformed to the sulphate by treatment with sulphuric acid. The sulphate solution is then treated with sodium hydroxide until slightly alkaline. The solution is then acidified with acetic acid and several grams of sodium acetate added. The solution is diluted up to 125 cc. and electrolyzed. A current of 0.5 ampere at a potential of five volts is usually used, the period of deposition depends upon the zinc content of the solution. The electrodes are removed before stopping the current, the cathode is washed in water, then alcohol, dried, cooled, and weighed. The solution should be tested for zinc again before it is assumed that deposition is complete.

This method is better than the method for electrolysis in alkaline solutions as the difficulty with the increase in weight of the deposit due to the hydroxide is eliminated. The precipitate obtained is pure if the electrolyzing solutions are pure. Other metals if present tend to deposit with the zinc causing high results to be obtained.

The reactions involved in this method of determination are very similar to those for the electrolysis in alkaline solutions; they are:
\[ 3 \text{ZnS} + 8\text{HNO}_3 = 3 \text{Zn(NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO} + 3 \text{S} \]
\[ \text{Zn(NO}_3)_2 + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + 2 \text{H}_2\text{O} \]
\[ \text{ZnSO}_4 + 4 \text{NaOH} = \text{Na}_2\text{ZnO}_4 + \text{Na}_2\text{SO}_4 + 2 \text{H}_2\text{O} \]
\[ \text{Na}_2\text{ZnO}_4 + 4 \text{HC}_2\text{H}_3\text{O}_2 = 2 \text{NaC}_2\text{H}_3\text{O}_2 + \text{Zn(C}_2\text{H}_3\text{O}_2)_2 + 2 \text{H}_2\text{O} \]

\[ \text{Zn(C}_2\text{H}_3\text{O}_2)_2 \rightleftharpoons \text{Zn} + 2 \{\text{C}_2\text{H}_3\text{O}_2\} \]

\[ \text{Zn} + 2 \overset{\text{C}}{\text{C}} = \text{Zn} (\text{cathode}) \]

\[ 2 \{\text{C}_2\text{H}_3\text{O}_2\} + 2 \overset{\text{C}}{\text{C}} = 2 \text{HC}_2\text{H}_3\text{O}_2 (\text{anode}) \]

Due to the long procedure necessary for the elimination of impurities and the care necessary to obtain accurate results, the electrolytic methods for zinc are less desirable than the gravimetric or ferrocyanide methods. A very good and complete discussion of electrolytic methods for the determination of zinc may be found in Smith's book on Electro-Analysis.\(^7\)

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VOLUMETRIC METHODS.

The volumetric methods for the determination of zinc are widely used in that they are rapid and as accurate as the other methods in common use. There are at the present time many volumetric methods given for the determination of zinc, but they are all similar in that the zinc is determined by titration with a standard solution of potassium ferro-cyanide either in an acid or alkaline solution. Many modified methods are in use for the elimination of certain interfering elements, such as lead, iron, or copper. A few of the best methods will be considered briefly.

Titration in Acid Solution.

Standard Method.

This method for the determination of zinc is of almost universal application in that the zinc is precipitated as the sulphide out of a slightly acidified sulphuric acid solution. It is somewhat longer than other methods, but can be used on all classes of zinciferous materials. It is especially adapted to impure ores containing iron, lead, copper, and cadmium.

The procedure may be given as follows:

The sample of material, depending upon the zinc content, is dissolved in hydrochloric and nitric acids. The solution is treated with sulphuric acid to convert all the chlorides and nitrates to the sulphates. After fuming the solution is cooled, then diluted to about 50 cc. and a gram or so of 20 mesh shot aluminum added. The solu-
tion is boiled until it is water white. This will reduce all of the iron and precipitate all of the copper group metals with the exception of cadmium. Cadmium is partially precipitated but re-dissolves. The silica and precipitated metals are filtered off and washed.

If cadmium is present add 5 cc. of 1:1 sulphuric acid to the filtrate. Dilute to a volume of 100 cc. and pass a rapid stream of hydrogen sulphide gas into the solution for 15 or 30 minutes. Add dilute ammonium hydroxide, a drop at a time, until yellow cadmium sulphide precipitates. Heat the solution to nearly boiling and continue to pass in hydrogen sulphide for a few minutes. Filter out the precipitate and wash well with a 10 per cent sulphuric acid solution. If cadmium is absent this step can be omitted.

The filtrate is boiled to remove the hydrogen sulphide, cooled, neutralized with potassium hydroxide and finally with potassium carbonate when using methyl orange as the indicator. Add 2 to 4 cc. of a 5 per cent sulphuric acid solution per 100 cc. of solution. Cool the solution and pass a rapid stream of hydrogen sulphide through the solution for 30 minutes. Allow the precipitate to settle, then filter, and wash well with cold water. Dissolve the precipitate in hydrochloric acid and boil to expell all of the hydrogen sulphide. Add 15 cc. of ammonium hydroxide, then neutralize with hydrochloric acid and add 3 cc. in excess. Dilute the solution to 200 cc. Add a small amount—0.04 milligrams—of ferrous iron in the form of ferrous sulphate to the solution. Titrate with standard ferrocyanide solution. The end-point is delicate and is obtained when the color fades from a blue to a sharp pea-green.
The reactions involved in the determination may be given as follows:

\[
\begin{align*}
\text{ZnCl}_2 + H_2SO_4 & = \text{ZnSO}_4 + 2 \text{HCl} \\
\text{Zn(NO}_3)_2 + 2 \text{HNO}_3 & = \text{ZnSO}_4 + 2 \text{HNO}_3
\end{align*}
\]

\[
\begin{align*}
\text{Fe}_2(SO}_4)_3 + 3 \text{Al} + H_2SO_4 & = 2 \text{Fe(SO}_4)_3 + 3 \text{Al}_2(SO}_4)_3 + H_2 \\
3 \text{Cu(SO}_4)_2 + 4 \text{Al} & = 3 \text{Cu} + 2 \text{Al}_2(SO}_4)_3 \\
3 \text{CdSO}_4 + H_2S + H_2SO_4 & = \text{CdS} + 2 H_2SO_4 \\
\text{ZnSO}_4 + H_2S & = \text{ZnS} + H_2SO_4 \\
\text{ZnS} + 2 \text{HCl} & = \text{ZnCl}_2 + H_2S \\
3 \text{ZnCl}_2 + 2 \text{K}_2\text{Fe}_3(\text{CN})_6 & = \text{Zn}_3\text{K}_2\text{Fe}_3(\text{CN})_6 + 6 \text{KCl}
\end{align*}
\]

This method for the determination of zinc is not as rapid as other methods which will be given, but in the hands of the experienced analyst gives excellent results that are comparable to the gravimetric phosphate method.

It must be borne in mind that in all zinc determinations in which the zinc is to be brought down as the sulphide, preliminary to subsequent treatment, that the acid concentration must be rigidly maintained in order to completely precipitate the zinc and to insure the removal of interfering elements. The precipitation of the zinc as the sulphide liberates an equivalent quantity of acid. The reaction may be give as follows:

\[
\text{ZnSO}_4 + H_2S \rightleftharpoons \text{ZnS} + H_2SO_4
\]
The reaction, since it is reversible, can only be made to go to the right by the addition of a large excess of hydrogen sulphide and by keeping the concentration of the sulphuric acid below such a value that tends to bring the reaction to an equilibrium. It is obvious if the sulphuric acid concentration becomes great enough, the zinc sulphide will fail to precipitate completely or will dissolve if it is precipitated.

The use of aluminum for the reduction of iron and the precipitation of other metals causes difficulty if a large quantity of the aluminum is dissolved, for upon neutralizing the aluminum hydrolyzes and precipitates as the hydroxide. This can be eliminated if care is used in keeping the sulphuric acid concentration down to a low figure when using aluminum as a precipitate.

The color change occurring at the end-point can be explained as follows: The ferrocyanide, having stood for several weeks has oxidized slightly to ferricyanide. The few milligrams of ferrous iron added to the solution reacts with the ferricyanide giving the ferro-ferricyanide blue color as long as the ferrocyanide is not in excess. Upon titration the blue color of the ferro-ferricyanide changes to the colorless ferro-ferrocyanide when sufficient ferrocyanide has been added to precipitate all of the zinc as the complex ferrocyanide. In all of the ferrocyanide titrations it is important that the conditions be the same as when standardizing the solution. The standardizations should be repeated as often as is necessary in order to keep the strength of the solution known.
This method does not work well on ores containing large amounts of iron, copper, or cadmium. The use of ferrous salts as indicators would not be recommended, it is more accurate to use uranyl acetate or ammonium molybdate as an indicator.

Rapid Ferrocyanide Method.

This method is especially adapted to material low in such impurities as iron, aluminum, manganese, copper, and cadmium. When the operator gains experience in manipulation, it is possible to obtain good results on samples higher in these impurities. When the copper or cadmium content of the ore is high it is better to use the standard method for analysis.3


The procedure may be given as follows:

A sample, the size depending upon the zinc content, of the material is dissolved in hydrochloric and nitric acids and taken almost to dryness. Add a small quantity of nitric acid to dissolve the residue. Add a small amount of potassium chlorate to the solution. Carefully take to dryness. To the residue add about 50 cc. of an extraction solution, made up by dissolving 200 grams of ammonium chloride and 500 cc. of concentrated ammonium hydroxide in 750 cc. of water. Heat to boiling and add about 25 cc. of bromine water. Boil for a few minutes and then filter. Wash the precipitate well with a solution made by dissolving ammonium chloride in ammonium hydroxide. Make the filtrate just acid with hydrochloric acid and then add about
3 cc. in excess. If copper is present add about 50 cc. of hydrogen sulphide water. Heat the solution to nearly boiling and titrate hot with a standard potassium ferrocyanide solution, using uranyl acetate as the indicator.

The reactions involved in this determination may be given as follows:

\[
\begin{align*}
\text{ZnS} + 2 \text{HCl} &= \text{ZnCl}_2 + \text{H}_2\text{S} \\
3 \text{ZnS} + 8 \text{HNO}_3 &= 3 \text{Zn(NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO} + 3 \text{S} \\
\text{Fe(NO}_3)_2 + 3 \text{NH}_4\text{OH} &= \text{Fe(OH)}_3 + 3 \text{NH}_4\text{NO}_3 \\
\text{Al(NO}_3)_2 + 3 \text{NH}_4\text{OH} &= \text{Al(OH)}_3 + 3 \text{NH}_4\text{NO}_3 \\
\text{Mn(NO}_3)_2 + \text{HClO}_3 &= \text{MnO}_2 + 2 \text{ClO}_2 + 2 \text{HNO}_3 \\
\text{Zn(NO}_3)_2 + 4 \text{NH}_4\text{OH} &= \text{Zn(NH}_4)_4(\text{NO}_3)_2 + 4 \text{H}_2\text{O} \\
\text{Zn(NH}_4)_4(\text{NO}_3)_2 + 4 \text{HCl} &= \text{ZnCl}_2 + 2 \text{NH}_4\text{NO}_3 + 2 \text{NH}_4\text{Cl} \\
2 \text{ZnCl}_2 + \text{K}_2\text{Fe(Cu)}_4 &= \text{Zn}_2\text{Fe(Cu)}_4 + 4 \text{HCl}
\end{align*}
\]

This method of determination is based upon the fact that iron, aluminum, and manganese can be precipitated free of zinc when a large excess of ammonium salts are present. These precipitates ordinarily occlude large amounts of zinc, but the presence of the ammonium ions causes the formation of a complex salt of zinc which is very soluble. This method of determination cannot be used on highly impure ores due to the trouble experienced with iron and manganese. The manganese is completely precipitated from an acid solution by hydrochloric acid or by bromine in an alkaline solution.
The use of hydrogen sulphide to precipitate out the copper works very well in case the copper content of the ore is low. When large amounts of copper are present, then the black copper sulphide precipitate masks the end-point. If the copper content is high it is best to use other methods.

This method for the determination of zinc in ores is rapid and can be used on fairly pure ores with accurate results being obtained. On the impure ores the determination must be guarded against errors due to faulty manipulation.

Other Methods.

The two methods given were for the ferrocyanide titration in acid solution. Many other methods have been devised, but they are all fundamentally the same in that the purified solution is titrated with ferrocyanide. The modifications are a difference in procedure devised to remove the interfering elements. A few of these modifications will be considered.

The modified Von Schultz and Low method is similar to the rapid ferrocyanide method as given, with the exception that the iron and alumina are precipitated by hydrolysis out of a solution made neutral with potassium hydroxide and ammonium carbonate. The zinc and copper dissolve in the ammonium carbonate and are kept in solution. The manganese is precipitated out of an acid solution by potassium chlorate. The copper is removed by passing a strong current of hydrogen sulphide gas into the strong acid solution, and so comes down free of zinc. The titration is completed in a hot acid solution.
In the Von Schultz and Low method\textsuperscript{14} the sample is dissolved in nitric acid and potassium chlorate. To make sure that the manganese is completely precipitated, the solution is treated with bromine water. The iron and aluminum are removed by precipitation with ammonium hydroxide in the presence of ammonium chloric. The copper is removed by treating the acidified solution with granulated lead. The acid solution is heated and titrated as before.

In Scott\textsuperscript{9} a method is given for the determination of zinc by titrating in acid solution, after removing iron, aluminum, and manganese with ammonia and bromine. The zinc is removed from the precipitate by re-precipitating as many times as it is necessary. This method is rather long when dealing with an impure ore and does not make any provision for the removal of large amounts of copper or cadmium.

Of the methods given the modified Waring method for zinc is probably the most reliable under certain conditions. This method is accurate and especially valuable when there are large amounts of manganese present. It depends upon the separation of lead, copper, and cadmium from zinc by means of metallic aluminum, from manganese, iron, nickel and cobalt by means of hydrogen sulphide in a solution very slightly acidified with formic acid. The manganese, iron, nickel and cobalt are kept in solution, whereas the zinc precipitates as the sulphide.
Briefly the procedure may be given as follows:

The sample of ore is dissolved in hydrochloric and nitric acids. The sample is then taken to fumes with sulphuric acid. The solution is then diluted with about 50 cc. of water, heated to boiling and filtered. The precipitate should be washed thoroughly with water containing a little ammonium chloride. Sulphuric acid is added to the filtrate to bring the amount of free acid up to about 10 per cent. A piece of heavy sheet aluminum is placed in the solution and boiled until water white. This reduces the iron and precipitates lead, copper, and cadmium out of solution. The solution is filtered and the precipitate washed. The filtrate is cooled and several drops of methyl orange indicator added. The solution is neutralized with sodium bicarbonate to a light straw color. Add, drop by drop, a 20 per cent formic acid solution until the pink color is just restored, then a few drops more. Dilute and add several grams of ammonium thiocyanate, heat to boiling and saturate with hydrogen sulphide. The zinc should separate as a white sulphide precipitate free of lead and copper. Allow the solution to stand several hours, or longer if possible, then filter and wash the precipitate well. The precipitate can be dissolved in hydrochloric acid and the zinc determined by the ferrocyaneid titration, or the zinc can be determined gravimetrically as the phosphate.

This procedure is rather long but gives good results on moderately pure ores. With low-grade, high calcium ores, results obtained by this method are liable to be low due to the failure of washing the large calcium sulphate precipitate free of occluded zinc.
The use of aluminum for the precipitation of copper and cadmium from the solution works well when the acid concentration is maintained within certain limits. If the acid concentration is high the cadmium partially re-dissolves and fails to precipitate in solutions of higher acid concentration. The use of granulated lead in place of aluminum has been recommended by many investigators. The lead causes less interference upon neutralizing the solution, as it does not hydrolyze as does aluminum.

The use of hydrochloric acid and ammonium thiocyanate in place of formic acid has been used with success. Tartaric and citric acids can also be used for this purpose of keeping the iron and aluminum in solution.

In the precipitation of the zinc sulphide the acid concentration must be kept within close limits. One of the main difficulties in this procedure is to obtain a neutral solution preliminary to the sulphide precipitation. This is probably due to the ferrous salts acting upon the indicator in such a manner that the color change is masked and a definite end-point cannot be obtained.

In the ferrocyanide titration methods the presence of many impurities or salts exert a solvent action upon the indicator and cause erratic results to be obtained. A series of tests made by Miller and Hall shows the effect of certain salts upon the ferrocyanide titration of zinc. They found that if aluminum was used for the pre-
cipitation of copper that the aluminum sulphate formed interferes with the end-point color change, giving irregular results.

Discussion of Methods.

The methods for the determination of zinc are many and varied. Of the methods considered it is probable that the determination of the zinc as the phosphate is the most accurate. The electrolytic method cannot be recommended for commercial laboratory use as the results obtained are erratic. Of the volumetric methods considered the standard ferrocyanide method is the best with fairly pure ores. With pure ores the rapid ferrocyanide method gives very good results. The ferrocyanide methods are liable to large errors unless extreme care is used in manipulation.

It should be borne in mind that every method of chemical analysis has its limitations, each is especially suited for analyzing certain types of material, and when so used gives very good results. With other types of material, although the method may work with a fair degree of success, the manipulation may become so lengthy and involved that it fails to give results comparable with those obtained by other methods better suited to the type of material.
METHODS FOR THE DETERMINATION OF COPPER.

Many methods have been devised for the determination of copper in ores. Each method is particularly adapted to a certain type of ore and gives very good results when care is used in manipulation. All of the methods given are not adapted to the ores from the Southeast Missouri Lead District, and accordingly only a few of the most important methods of determination will be considered. More complete information may be found by reference to the textbooks on analytical chemistry or to the periodicals.

GRAVIMETRIC METHODS.

Copper can be determined gravimetrically as the sulphide, the oxide, the sulphocyanate, or as metallic copper by the electrolytic method. The electrolytic method has replaced the other gravimetric methods to a large extent. Various methods are employed for the express purpose of obtaining a suitable precipitate that can be subsequently treated by the electrolytic method for the determination of the copper.

Sulphocyanate Method.

Isolation of copper from solutions containing iron, nickel, cobalt, zinc, cadmium, arsenic, antimony, and tin can be accomplished by this method. The elements, lead, mercury, tellurium, and selenium, if present, will contaminate the precipitate. This method forms the basis for a number of other methods for the determination of copper. The procedure in use varies with the object in view, but in general
can be given as follows:

**Op. cit., page 181.**

The sample is dissolved in hydrochloric and nitric acids. Then taken to fumes with sulphuric acid to expel all of the hydrochloric and nitric acids in excess and to convert all salts to the sulphates. In treating high calcium ores the large precipitate of sulphates should be filtered off and washed thoroughly. The filtrate should be partially neutralized; the solution should be just slightly acid. To the cold, concentrated, and slightly acid solution of the copper sample add a solution of an alkali bisulphite in excess of that amount theoretically required to reduce all of the copper and ferric iron present. A solution of an alkali thiocyanate—sulphocyanate—of about normal strength is added with constant stirring until precipitation ceases. The precipitate is allowed to settle, then filtered by the aid of suction and washed thoroughly with cold water. The precipitate can then be dried and ignited and the copper determined gravimetrically, or the precipitate can be dissolved in nitric acid and the copper determined by the electrolytic or volumetric method, as desired.

The reactions may be given as follows:

\[ 3 \text{CuS} + 3 \text{HNO}_3 = 3 \text{Cu(NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO} + 3 \text{S} \]

\[ \text{Cu(NO}_3)_2 + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + 2 \text{HNO}_3 \]

\[ 2 \text{CuSO}_4 + 2 \text{KCN} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} = 2 \text{CuKCN} + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \]

The precipitate is pure if the lead has been removed by the sulphuric acid treatment. If lead is not removed it is precipitated as the sulphite along with the copper sulphocyanate. Silver, if present, also precipitates as the sulphocyanate.
Metallic Copper.

In many cases the copper is precipitated out of solution in the metallic state by a more positive metal, the copper is then dissolved in hot dilute nitric acid, evaporated to a small volume and determined by the procedure preferred. In general the procedure used to obtain the copper precipitate may be given as follows:

The ore is dissolved in the regular manner and then treated with sulphuric acid to remove the nitric and hydrochloric acids. The sulphate precipitate is filtered off and washed thoroughly. The filtrates are combined and neutralized to a point where there is about 10 per cent free sulphuric acid present. A piece of sheet aluminum or granulated aluminum is added to the solution. Boil until water white. A small quantity of saturated hydrogen sulphide water may be added to precipitate traces of copper in the solution. The solution is filtered while hot and washed several times. The copper is removed from the precipitating metal by using dilute nitric acid. The copper is determined in the solution by electrolysis or by a volumetric method.

The reactions may be given as follows:

\[ 3 \text{CuS} + 8 \text{HNO}_3 \rightarrow 3 \text{Cu(NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO} + 3 \text{S} \]
\[ \text{Cu(NO}_3)_2 + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + 2 \text{HNO}_3 \]
\[ \text{Ca(NO}_3)_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2 \text{HNO}_3 \]
\[ \text{Pb(NO}_3)_2 + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + 2 \text{HNO}_3 \]
\[ 3 \text{Cu(SO}_4)_2 + 2 \text{Al} = 5 \text{Cu} + \text{Al}_2(\text{SO}_4)_3 \]
Many metals may be used in place of aluminum if so desired.

This procedure works well and is fairly accurate and rapid. The use of hydrogen sulphide water to insure complete precipitation of the copper is to be recommended. Cadmium, if present, partially precipitates along with the copper.

**Sulphide Method.**

Copper can be separated from certain other metals like iron, zinc, manganese, cobalt, and nickel by precipitation as the sulphide in an acid solution. If lead, bismuth, arsenic, antimony, or tin are present they are precipitated with the copper, but as the precipitate is usually dissolved in nitric acid and the copper determined by the electrolytic method these elements cause little or no interference.

**Electrolytic Method.**

The electrolytic method for the determination of copper is the most accurate of the gravimetric methods. This method can be used for the determination of copper from solutions containing free nitric or sulphuric acids, or from alkaline solutions. The solutions electrolyzed should in every case be free of chlorides as they produce a spongy deposit of copper and exert solvent action upon the anode.

Many conditions affect the character of the deposit obtained. The important ones are the quantity and concentration of the copper, size and shape of the electrodes, the distribution of the current over the electrodes, the temperature and rate of circulation.
of the electrolyte, the volume of the solution, the current density and period of deposition, and the presence of impurities or oxidizing agents in the solution.\footnote{Op. cit., p. 186.}

This method can be used on a large variety of copper bearing materials with very accurate results. If the material contains such interfering elements as silver, bismuth, arsenic, antimony, selenium, or tellurium the results obtained are high due to their deposition with the copper. These elements must be removed subsequent to electrolysis, in many cases the volumetric methods may give the more accurate results. When the rapid method is used there is a tendency for the results to be high, probably due to the occlusion of gases in the deposit.

The most accurate results are obtained in the electrolytic method by using a low current density and a long period of deposition. This is called the "slow method." In commercial practice the period of deposition is usually reduced to several hours with a consequent increase in current density. This is called the "rapid method." The current density cannot be increased too high as a high current density promotes the formation of a spongy deposit of copper contaminated with impurities.

The use of the revolving cathode is recommended as the deposit obtained is more uniform and adheres more strongly to the cathode. A higher current density can be employed with the revolving cathode and consequently the period of deposition can be reduced without endangering the accuracy of the method.
The electrolytic copper methods are so well known that they will only be considered briefly.

Electrolysis from Acid Solutions: The electrolytic method for the determination of copper from acid solutions may be made in solutions containing either free sulphuric or nitric acids. The method employing the use of free sulphuric acid is to be recommended in preference to the nitric acid. The solution must be free of all chlorides, if hydrochloric acid is used for the solution of the sample it must be removed by a treatment with sulphuric acid preliminary to electrolysis.

In general the procedure used for ores free of arsenic, antimony, or bismuth may be given as follows:

The sample is dissolved in hydrochloric and nitric acids, then treated with sulphuric acid to remove all the hydrochloric and nitric acids. If a large precipitate is formed it should be filtered out of solution and washed thoroughly. If the precipitate is small and settles well, it need not be removed by filtration. The filtrate is then ready for electrolysis. Warm the solution and electrolyze with a current of one ampere at a potential of 2. to 2.5 volts for several hours. The current density and period of deposition can be best determined for each type of ore treated experimentally, as definite information cannot be given that will fit all cases. When the deposition is complete the electrodes are removed from the solution before breaking the current, washed with distilled water, then with alcohol, dried above a flame, cooled, and weighed.
The reactions may be given as follows:

\[ 3 \text{CuS} + 8 \text{HNO}_3 = 3 \text{Cu(NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO} + 3 \text{S} \]

\[ \text{Cu(NO}_3)_2 + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + 2 \text{HNO}_3 \]

\[ \text{CuSO}_4 \rightarrow \text{Cu} + \text{SO}_4 \]

In case the ore contains arsenic, antimony, or bismuth, the copper should be separated as the sulphocyanate and this precipitate treated in the following manner: Dissolve the precipitate in nitric acid and boil till all nitrogen is expelled. Add sulphuric acid and take to fumes. The solution is then diluted, a little nitric acid is added, and the solution electrolyzed as before. The reactions involved may be given as follows:

\[ \text{CuCNS} + 2 \text{HNO}_3 = \text{Cu(NO}_3)_2 + \text{HCNS} \]

\[ \text{Cu(NO}_3)_2 + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + 2 \text{HNO}_3 \]

\[ \text{CuSO}_4 \rightarrow \text{Cu} + \text{SO}_4 \]

If the copper is precipitated as the sulphide and the copper then determined by the electrolytic method, the following procedure should be followed. The sulphide precipitate is dissolved in dilute nitric acid and boiled to expel all hydrogen sulphide. Dilute to a volume of about 125 cc. The free acid content should not be over 3 cc. A few drops of sulphuric acid is added and the solution electrolyzed as before. The lead does not interfere with the determination if it is less than the ratio of 1 to 4 with the copper. A suitable
method has been devised whereby simultaneous determinations of copper and lead can be made in the same solution.\footnote{White, Arthur, J., Chem. & Met., Vol. 11, No. 10, page 530.}

Electrolysis in Alkaline Solutions: This method of determination cannot be carried out if lead, bismuth, mercury, cadmium, zinc, or nickel are present in solution. The method of solution of the sample is the same as in the cases given before. Ammonium hydroxide is added to the solution containing the copper until the precipitate first formed dissolves. Three or four grams of ammonium nitrate are added and the solution electrolyzed as before. After deposition the electrodes are removed without breaking the current, washed, dried, cooled, and weighed.

This method has no distinct advantages over the electrolysis in acid solution, but either can be used with very good results.
VOLUMETRIC METHODS.

The volumetric methods for the determination of copper are widely used at the present time in that they are more rapid and nearly as accurate as the electrolytic method. The copper is separated, usually as metallic copper or as the sulphocyanate, from the other metals and determined in this segregate by either the iodide, cyanide, or permanganate methods.

The Iodide Method.

The procedure depends upon the fact that cupric salt when treated with potassium iodide liberates iodine, the cuprous iodide formed being insoluble in dilute acetic acid. The liberated iodine is titrated with standard sodium thiosulphate.

The procedure used depends upon whether the copper has been separated as the metallic copper or as the sulphocyanate. Each will be considered separately.

Methods for Metallic Copper: The sample of metallic copper is dissolved in a small quantity of nitric acid and a few cc. of bromine water added. The solution is boiled until all the bromine is expelled and the volume of the solution is about 25 cc. The solution is made slightly ammonical with ammonium hydroxide. Boil to expel the excess of ammonia, and then make acid with acetic acid. Add to the solution about 5 or 6 cc. of a potassium iodide solution. Titrate with standard sodium thiosulphate until the brown coloration fades to a yellow color. Add several cc. of a starch solution and complete the titration. The color changes from a blue to a light green.
The reactions may be given as follows:

\[
3 \text{Cu} + 8 \text{HNO}_3 = 3 \text{Cu(NO}_3)_2 + 4 \text{H}_2\text{O} + 2 \text{NO}
\]

\[
3 \text{Cu(NO}_3)_2 + 4 \text{NH}_4\text{OH} = \text{Cu(NH}_3)_4(\text{NO}_3)_2 + \text{H}_2\text{O}
\]

\[
3 \text{Cu(NH}_3)_4(\text{NO}_3)_2 + 4 \text{HCO}_2\text{H}_2\text{O} = \text{Cu(C}_2\text{H}_3\text{O}_2)_2 + 2 \text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)_2 + 2 \text{NH}_4\text{NO}_3
\]

\[
2 \text{Cu(C}_2\text{H}_3\text{O}_2)_2 + 4 \text{KI} = \text{Cu}_2\text{I}_3 + 4 \text{HCO}_2\text{H}_2\text{O} + \text{I}_2
\]

\[
2 \text{Na}_2\text{S}_2\text{O}_3 + 2 \text{I} = \text{Na}_2\text{S}_4\text{O}_6 + 2 \text{NaI}
\]

Bromine water is added to insure that all salts present are in their state of highest oxidation, otherwise they would be oxidized by the liberated iodine and hence would give high results for copper.

If the procedure is properly carried out the solution should be free of iron, zinc, arsenic, antimony, etc. Silver, even though present, does not interfere with the assay. Lead or bismuth merely causes trouble due to the fact that they form iodides which mask the end-point; they do not cause a liberation of iodine.

In place of adding iodide and titrating the liberated iodine with sodium thiosulphate, the nitric acid solution of the copper can be treated with ammonium hydroxide until the precipitate first formed re-dissolves, and then titrating this solution with a standard potassium cyanide solution.

In the cyanide method it is advisable to have the copper in solution as the sulphate. The addition of ammonium hydroxide to the solution causes the formation of a complex of copper and ammonia, which is blue. The titration with the cyanide converts the copper into a cyanide which is colorless. The end-point is reached when the blue color of the solution disappears.
The reactions upon which this procedure is based may be given as follows:

\[
2 \text{Cu(NH}_3)_4\text{(SCN) H}_2\text{O} + 7 \text{KCN} = \text{K}_4\text{NH}_4\text{Cu}_4\text{(CN)}_6 \cdot \text{NH}_4\text{CNO} + 2 \text{K}_3\text{SCN} + 6 \text{NH}_3 + \text{H}_2\text{O}
\]

Methods for Sulphocyanate: The volumetric methods used for the determination of copper after precipitating as the sulphocyanate may be classified as iodide\(^3\) and permanganate\(^3\) methods. These methods, though fairly accurate, are not as rapid nor as accurate as the iodide method when employed on metallic copper precipitates. It is recommended that sulphocyanate precipitates be run by the electrolytic method rather than by volumetric methods.

The Iodide Method.

The sulphocyanate precipitate is placed in a 250 cc. glass-stoppered bottle, 5 cc. of chloroform, 20 cc. of water, and 30 cc. of strong hydrochloric acid added. Standard potassium iodate solution is added from a burette until the violet color first appearing in the chloroform layer disappears. The disappearance of color is the end point. The reaction in the completed form upon which this method is based may be given as follows:

\[
4 \text{CuCNS} + 7 \text{KIO}_3 + 14 \text{HCl} = 4 \text{CuSO}_4 + 7 \text{KCl} + 7 \text{ICl} + 4 \text{HCl} + 5 \text{H}_2\text{O}
\]
The Permanganate Method.

The procedure used with the permanganate method may be given briefly as follows:

The sulphocyanate precipitate is decomposed on the filter with a boiling solution of sodium hydroxide. The filtrate is then made acid with dilute sulphuric acid and titrated with a standard potassium permanganate solution.

The basic reactions of this method may be given as follows:

\[
\begin{align*}
\text{CuCNS} + \text{NaOH} & = \text{Cu(OH)} + \text{NaCNS} \\
2 \text{NaCNS} + H_2\text{SO}_4 & = \text{Na}_2\text{SO}_4 + 2 \text{HCNS} \\
5 \text{HCNS} + 6 \text{KMnO}_4 + 4 H_2\text{SO}_4 & = 3 K_2\text{SO}_4 + 6 \text{MnSO}_4 + 5 \text{HCN} + 4 H_2O
\end{align*}
\]

This method is liable to be in error due to the incomplete solution of the copper and by the possible incompleteness of oxidation. This necessitates the use of an empirical factor for the permanganate conversion value.

In some cases this method is modified in the following manner:

The sulphocyanate precipitate is titrated with an excess of sodium hydroxide solution of lower strength, and the cuprous hydroxide is filtered off. The excess of sodium hydroxide is titrated with a standard hydrochloric acid solution.
Discussion of Methods.

Of the various methods given it is evident that when accuracy is more essential than speed, the "slow" electrolytic method gives the best results. The "rapid" electrolytic method gives results which agree with one another quite closely and are well within the checking limits usually employed in commercial laboratories. The iodide method when employed on metallic copper precipitates gives very accurate results. If the copper is separated as the sulphocyanate it is recommended that the electrolytic process be used for the volumetric methods fail to give accurate results.
GENERAL SUMMARY.

This investigation brings out the following facts, which may be stated briefly:

The use of heavy liquids for producing segregates failed in that small amounts of the fine sulphides remained in the float by film suspension.

The dissolution tests made with salt solutions as the solvents gave low degrees of segregation and small amounts of the mineral were dissolved along with the dolomite. Tests made with acids as solvents gave higher degrees of segregation, but larger amounts of the mineral were dissolved.

Dissolution and segregation tests made when using hydrochloric acid as the solvent and with subsequent precipitation of the dissolved metals by hydrogen sulphide gave good degrees of segregation. These segregates when assayed for lead, zinc or copper gave results but slightly better than those in use at the present time. It is doubted that the increase in accuracy will compensate for the time spent when using these segregation methods.

An investigation of the attack of galena by acids revealed that the galena was attacked by very weak acids. The amount dissolved increases in a direct proportion to the acid concentration and the time of solution, size of particles remaining the same. The amount dissolved does not increase in direct proportion with the amount of free surface exposed to solvent attack, acid concentration and time of solution remaining the same.
The chemical methods of analyses in use at the present time for the determination of lead, zinc, and copper were studied and the following conclusions drawn:

(1) Lead is usually determined by the electrolytic method. This method when used by an experienced analyst gives accurate results. The chromate and sulphate methods give the most accurate results for lead, but cannot be adapted to high calcium ores in that the manipulation becomes lengthy.

(2) Zinc can be determined most accurately by the phosphate method. The ferrocyanide method gives good results when pure precipitates are assayed.

(3) Copper is usually determined by the electrolytic method, which is as accurate and nearly as rapid as the other gravimetric or volumetric methods. The method in use is sufficiently accurate for all commercial testing work.
APPENDIX.

The chemists of the Southeast Missouri Lead District have improved their methods for the electrolytic determination of lead in low-grade ore pulps since the work on this problem was undertaken. This improvement is due to the chemists having learned how to handle these low-grade pulps through experience, and are exercising more care in manipulation than was formerly thought necessary. This improvement has resulted in determinations that are well within the allowable checking limits. This problem, which was mainly concerned with the determination of lead present in low-grade ore pulps, loses much of its importance in view of these recent developments.

A few of the results which show the degree of accuracy that may be obtained on these low-grade pulps are given in Table XIII. The original determinations were made by a mill chemist in the Southeast Missouri Lead District and were checked by O. W. Holmes, Chemist of the State Mining Experiment Station, Rolla, Missouri. Both chemists made their determinations on the same ore pulp.

These results show a remarkable agreement with one another and serve to illustrate the fact that two chemists using the same methods for determination of lead can check one another very closely if care is exercised in manipulation.

A similar series of assays made by these chemists on fractions from a hydrotator test on flotation tailings are given in Table XIV.
Table XIII: Comparison of Results Obtained When Assaying Low-Grade Table Tailings for Lead by the Electrolytic Method.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Assay Per cent Lead</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mill Chemist</td>
<td>Rolla Chemist</td>
</tr>
<tr>
<td>1</td>
<td>0.08</td>
<td>0.075</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.095</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>0.096</td>
</tr>
</tbody>
</table>

Table XIV: Comparison of Results Obtained When Assaying Fractions From Hydrotator Test on Flotation Tailings for Lead by Electrolytic Method.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Assay Per cent Lead</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mill Chemist</td>
<td>Rolla Chemist</td>
</tr>
<tr>
<td>1</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>2</td>
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<tr>
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<tr>
<td>4</td>
<td>0.40</td>
<td>0.39</td>
</tr>
<tr>
<td>5</td>
<td>0.30</td>
<td>0.31</td>
</tr>
<tr>
<td>6</td>
<td>0.30</td>
<td>0.29</td>
</tr>
<tr>
<td>7</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>8</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>9</td>
<td>0.045</td>
<td>0.06</td>
</tr>
<tr>
<td>10</td>
<td>0.04</td>
<td>0.05</td>
</tr>
</tbody>
</table>
These results agree very well with one another throughout the range of lead content.

The improvement in lead determinations is mainly due to the added experience the chemists are having in handling these low-grade ore pulps. In cases it is known that certain chemists assay their low-grade pulps using the same size, or but slightly larger samples, the same current density, and period of deposition as they use for their medium or higher grade pulps. Obviously good results cannot be obtained if this procedure is followed. Low-grade pulps must be assayed separately if good results are to be expected. Dr. Holmes noted in one case that in his determination for lead in a low-grade pulp he obtained only a trace of lead when using a one "plumb" sample, whereas by using a four "plumb" sample he obtained 0.10 per cent lead. This shows that the size of the sample which is to be used is of great importance.

Several chemists in the district are adding a known amount of a standard lead solution to the solution to be electrolyzed in case the sample contains less than 10 milligrams of lead. (It has been stated previously that in the electrolysis of solutions containing less than 10 milligrams of lead, the lead fails to completely deposit). Whether or not this innovation will increase the accuracy of the determination for lead cannot be stated definitely at this time. Further research work along this line will prove its value in this respect.
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