


5-16-1941

# The Investigation of Different Variables in the Assaying of Silver Cyanide Solutions

Phillip L. Banfield

Follow this and additional works at: [http://digitalcommons.mtech.edu/bach\\_theses](http://digitalcommons.mtech.edu/bach_theses)

 Part of the [Ceramic Materials Commons](#), [Environmental Engineering Commons](#), [Geology Commons](#), [Geophysics and Seismology Commons](#), [Metallurgy Commons](#), [Other Engineering Commons](#), and the [Other Materials Science and Engineering Commons](#)

---

## Recommended Citation

Banfield, Phillip L., "The Investigation of Different Variables in the Assaying of Silver Cyanide Solutions" (1941). *Bachelors Theses and Reports, 1928 - 1970*. Paper 127.

This Bachelors Thesis is brought to you for free and open access by the Student Scholarship at Digital Commons @ Montana Tech. It has been accepted for inclusion in Bachelors Theses and Reports, 1928 - 1970 by an authorized administrator of Digital Commons @ Montana Tech. For more information, please contact [ccote@mtech.edu](mailto:ccote@mtech.edu).

*Banfield, P.*

The Investigation of Different Variables  
in the Assaying of Silver Cyanide Solutions

by

Phillip L. Banfield

Montana School of Mines

Butte, Montana

May 16, 1941



The Investigation of Different Variables  
in the Assaying of Silver Cyanide Solutions

by

Phillip L. Banfield

Submitted to the Department of Metallurgy  
as partial fulfillment of the requirements for the  
degree of Bachelor of Science in Metallurgical  
Engineering.

*14538*

Montana School of Mines

Butte, Montana

May 16, 1941



W11196-140175

ACKNOWLEDGMENT

I wish to acknowledge the assistance of  
Dr. Curtis L. Wilson  
and  
Prof. B. Cullity  
under whose guidance this work was performed.



## CONTENTS

	page
Introduction -----	1
Review of Methods -----	2
Chlorine Method	2
Volhard's Method	3
Evaporation Method.	4
Precipitation Method	4
Copper Sulphate Method	4
Sodium and Zinc Salts Method	5
Mercuric Chloride Method	5
American Cyanimid Co. Method	6
Argentio-auric-cyanide Method	6
Homestake Mining Co. Method	7
Hydroxylamine hydrochloride M.	7
Electrolytic Method	8
Preparation of Solutions -----	9
Lead Boat Method -----	12
Homestake Mining Co. Method -----	21
Chiddey Method -----	25

Copper Sulphate Method	-----	37
Hydroxylamine hydrochloride M.		44
Electrolytic Method	-----	48
Conclusions	-----	55

-----



## The Investigation of Different Variables in Assaying of Silver Cyanide Solutions

The cyanide method of extraction of gold and silver from their ores is extensively used in the United States and elsewhere and it is becoming increasingly more important in its use as the mining of lower grade deposits continues.

Consequently the latest methods of laboratory methods of extraction and subsequent assaying of solutions is becoming more important.

It is the object of this thesis to apply to the assaying of silver cyanide solutions various representative procedures used in both wet and fire assay analysis of solutions and to investigate the different variables in each of these methods.

This report is wholly confined to the assay of silver cyanide solutions but, although not discussed in this thesis, the methods reviewed here will work equally as well for gold solutions unless stated otherwise.



In beginning this discussion of the investigation of the variables of assaying silver cyanide solutions, let first be specified the word "variable" as it is applied in this report. It will devote its entirety to the investigation and discussion of those variants such as chemicals used and their relative amounts, the operations used and the techniques involved therein and the various apparatus used.

Many methods are recommended and employed in metallurgical procedure for silver analysis but due to the lack of time and necessary equipment, only a few of these proposed methods were investigated. Of the many methods enumerated below, some are applicable to assaying of cyanide solutions and some are not. The following will attempt to give a general review of the most popular methods used in the analysis of silver compounds.

Of those methods classified as gravimetric and volumetric, the best known are:

- 1 Chlorine Method

This method utilizes the reaction of silver and chlorine and the formation of an



insoluble compound, silver chloride. This is done either by titration of the solution with a normal salt solution or with hydrochloric acid, and computing the amount of silver chloride formed. As this method is only useful on compounds that are highly ionizable, it may be used only for acid solutions.

## 2 Volhard's Method of Standardizing silver nitrate Solutions

This method is based on the formation of a complex silver sulphocyanide compound in nitric acid solutions with potassium sulphocyanate, the finishing point being the development of a reddish brown colour produced by the action of excess potassium sulphocyanate on the indicator, ferric sulphate. This method too is inadvisable for cyanide liquors for the same reasons as stated above, but was used later on in the experiment for standardization of the master silver nitrate solution.

The following methods are commonly recognized as some of the correct means of assaying silver, and gold, cyanide solutions.



### 1 Evaporation Method

An old reliable method of determining the gold and silver contents of a solution is by the evaporation method. Solutions from the foot of an extractor box, carrying only a few grains of metal per ton of solution, usually require one thousand c.c. for an assay. The liquor is poured into an enameled dish and placed on a hot plate. A little litharge is sprinkled into the solution and allowed to boil to dryness. The residue is scraped out and mixed with argols, borax, etc., placed into a crucible which is put into a furnace and allowed to fuse for twenty minutes. The lead button formed is then cupelled, the gold and silver being found directly from the remaining bead.

### 2

Precipitation of silver and gold from acid cyanide solutions is also an effective method of analysis. The solution is placed under the hood and nitric acid is added to it. It is then boiled for several minutes and filtered. The residue is scraped out, fused and cupelled as usual.

### 3 Copper Sulphate Method



A large volume of solution is placed into a two liter flask and agitated for several minutes with a few grams of copper sulphate and ten to fifteen c.c. of hydrochloric acid. The precipitate formed is filtered and assayed either by the crucible or scorification method.

#### 4 Precipitation with sodium sulphide and chloride of zinc.

In this method the silver is precipitated with sodium sulphide. Filter off the remaining liquor, dry and wrap the residue in foil lead, cupel and assay for silver.

The remaining solution containing gold, is treated with chloride of zinc which precipitates the gold. This dried, is mixed with fine lead and cupelled.

#### 5 With Mercuric Chloride

Prepare a solution of mercuric chloride in water, one hundred grains per ounce. Keep in a glass stoppered bottle. Take eight or ten ounces of solution, accurately measured, and from a burette turn in mercuric chloride in excess, that is, until a drop of mercuric solution produces no further precipitate. The residue is fluxed, fused and



cupelled as usual, the gold and silver being calculated on the basis of the original amount of solution taken.

#### 6 American Cyanamid Company Method

To the liquor add five drops of saturated solution of potassium ferrocyanide and fifteen c.c. of precipitating solution, ( a saturated solution of copper sulphate with caustic soda); stir thouroughly and add twenty c.c. sulphuric acid. Filter off the precipitate and complete the fire assay on the residue in the ordinary manner.

#### 7 Argentic-auric-cyanide

Carefully measure eight or ten ounces of solution to be tested and add twenty drops of bichromate solution. If the deep red color appears it is evident that the cyanide is consumed and that the precipitation of gold and silver as argentic-auric-cyanide is complete. Add one hundred grams of zinc dust, mix thouroughly and add sufficient sulphuric acid to dissolve all excess zinc. The filtrate is washed, dried and fire assayed as usual.

#### 8 Lead Boat Method

This method is by far the most simple



method of all those enumerated in this report. It consists merely of evaporating a measured amount of liquor in a prepared lead boat and subsequent fire assay of the lead button formed.

9 In this procedure the gold and silver are precipitated with metallic lead by the reducing action of zinc dust on lead acetate solution which is added to the solution. The lead sponge formed is rolled in a strip of lead foil and cupelled directly for gold and silver.

#### 10 Homestake Mining Company Method

This method which is discussed at length later in the report is much like the Chiddey method. This entails the assay of larger volumes of solution, the lead sponge is filtered and consequently an extra fusion step is needed to destroy the filter paper.

#### 11 Method using hydroxylamine hydrochloride

This method which is also discussed later in this thesis is inapplicable for assay of silver cyanide solutions but it will work for gold bearing liquors. An amalgam formed by the reduction of mercuric chloride with zinc dust and hydroxylamine hydrochloride collects the silver



and gold. The amalgam then can be parted with nitric acid and the residue assayed for gold.

#### 12 Electrolytic Method

In this method the silver, dissolved in a basic cyanide solution, is electrolyzed with a small current over a period of several hours. A cathode of lead foil is used and the amount of silver deposited on the cathode is found by fire assaying.

The methods that were investigated for this thesis are:

- 1 Lead Boat Method
- 2 Homestake Mining Company Method
- 3 Chidley Method
- 4 Copper Sulphate Method
- 5 Hydroxylamine Hydrochloride Method
- 6 Electrolytic Method



## Preparation of Solutions

Before attempting to carry out the experiments it was necessary to prepare both the cyanide and silver nitrate solutions in such a way that a constant value per unit volume of each of these solutions could be kept throughout the series of experiments.

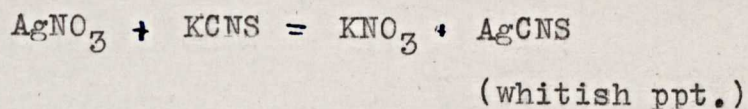
The sodium cyanide solution was made by dissolving hydrated sodium cyanide in water. This was made at a concentration of four pounds of sodium cyanide per ton of solution, that is, two grams of the salt were added per liter of solution.

The silver nitrate solution was made as accurately as possible and yet in such a volume so that it would be convenient to use for all of the methods involved. A carefully weighed amount of pure silver foil, (3.456 gm.), was dissolved in nitric acid this solution then being diluted to a larger volume so as to give a concentration of 0.01 gm. of silver per c.c., that is, the total volume of the solution equaled 345.6 c.c.

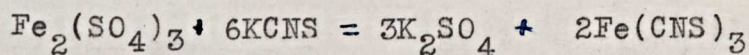
Throughout the experiments it was believed advisable to restandardize this solution from time to time. In the standardization of this master



silver nitrate solution it was decided to use Volhards method. In this method the silver is precipitated from nitric acid solutions with potassium sulphocyanate, the finishing point being the development of a reddish brown colour produced by the action of excess potassium sulphocyanate upon the ferric sulphate indicator.



The silver sulphocyanate precipitates rapidly and leaves the solution clear.



A persistent brown colouration indicates the end point of the titration.

The KCNS solution was made by dissolving 9.2 grams of the hydrated salt, 99.99 percent pure, in one liter of water.

The ferric sulphate indicator was produced by making a saturated solution of ferric sulphate or ferric ammonium sulphate in water. After the solution was saturated sufficient nitric acid was added to clear it up.



The titration consists of placing a known amount of silver nitrate solution in an Erlenmeyer flask, diluting it to about seventy-five c.c. with cold distilled water and adding sufficient sulphocyanate solution to precipitate the greater part of the silver. Then add five c.c. of ferric sulphate indicator to the solution and continue to titrate slowly until a reddish brown colour is permanently developed.

#### Results of Titrations

$\text{AgNO}_3$ Titrated (c.c.)	KCNS Added (c.c.)	Silver Present (gm.)
5	4.9	0.049
5	5.1	0.051
5	5.0	0.050

Average: 0.050 gm. Ag/ 5.0 c.c. or

0.010 gm. Ag/ 1.0 c.c. of solution.



### The Lead Boat Method

This method is, by far, the simplest for assaying small volumes of gold and silver bearing cyanide solutions. The procedure is as follows:

Introduce into a lead boat a measured volume of pregnant solution, evaporate to dryness, fold the boat into a tight ball, and cupel for the gold and silver.

Larger volumes of solution may be assayed, if necessary, by evaporating to dryness several boatfuls of the solution. The size of the boat used also determines the amount of solution that may be conveniently and accurately assayed, but as the size of the boat itself is regulated by the size of a convenient cupel button, the practice is to use as large a boat as possible and to evaporate its capacity to dryness as many times as is necessary to consume the desired volume of liquid.

The variables investigated in this phase of the experiment were:

1. The size of the lead boat (weight of the lead foil).
2. The weight of solution assayed.



### Assay Results

Weight of Lead Boat (gm)	Percent Recovery
29.17	92.0
20.6	93.4
14.6	94.5
10.3	94.0

Table 1

Weight of Solution ( A.T. )	Percent Recovery
2.0	98.3
1.4	95.5
1.0	96.0
0.7	98.1
0.3	94.3

Table 2



### Assay Results

Weight of Silver Added to Solution (mg)	Percent Recovery
100.00	87.25
50.00	89.56
25.00	94.80
12.50	96.00
6.13	98.00

Table 3

Concentration of Sodium Cyanide in Solution (pounds per ton)	Percent Recovery
4.0	89.5
2.8	98.0
1.5	97.0
1.0	97.4

Table 4



The following chart which is a condensed version of a similar chart printed in Fulton's "Manual of Fire Assaying", page 162.

Weight of Silver	Weight of Lead	Percent Loss
25 (mg)	5 (gm)	2.14
25	25	2.46
50	5	1.43
50	25	2.31
100	5	1.00
100	25	2.01
200	5	0.86
200	25	1.51

A curve showing silver losses in cupellation is also shown in this book.

## 2 The Effect of the Amount of Solution Assayed

In this phase of the work the weight of silver was held at ten milligrams.

From the results of Table 2 it can be ascertained that the amount of the solution assayed has little or no effect on the results of the assay. The only



effect that this variable has on these results is due to the tendency of the solution to splatter when the concentration of the silver salt in the reduced volume of solution becomes very high.

### 3. The Effect of the Concentration of Silver in Solution.

As accurately as possible, using a one to two dilution of the standardized silver nitrate, and measuring the volumes of the solution by a burette, it was attempted to add to one assay ton of sodium cyanide solution the following weights of silver: 100, 50, 25, 12.5, and 6.13 mg. These various concentrations of silver were used because it was felt that they would cover a wide enough range of concentrations.

It would seem from the results in Table 3 that this method is not as well suited to the concentrations of rich silver liquors as it is with the less concentrated ones. However it is shown below that this method compares favorably with the Chiddey method.

Method	Silver added to Solution (mg)	Percent Recovery
Chiddey	20.0	94.0
Lead Boat	25.0	94.8



4. The effect of the concentration of sodium cyanide.

As the standard solution that was used throughout this experiment is only four pounds per ton, the variations of this concentration should be, of necessity, less than four pounds.

From the results shown in Table 4., we can consider that the concentration of the cyanide solution has little effect upon the accuracy of the assay. However, the concentration of the cyanide should be kept high when cyaniding ores in order to be sure of complete solution of the silver and gold.



3. The concentration of silver in the solution.

4. The concentration of the sodium cyanide solution.

The standard weights and concentrations of the constituents used were:

Four pounds of sodium cyanide per ton of solution,

29.16 grams of lead

29,16 cubic centimeters of solution,

0.01 grams of silver, 1 c.c. silver nitrate.

1. The effect of varying the weight of the lead boat.

The following weights of lead foil were used:

6 1/2 inches	of lead foil	or	29.16	grams,			
4 2/3	"	"	"	"	20.6	"	,
3 1/4	"	"	"	"	14.6	"	,
2 1/3	"	"	"	"	10.3	"	.

In using the smallest boats a second evaporation was necessary in order to assay one assay ton of solution. In all cases ten milligrams of silver were added to the charge. In Table 1, it is noted that the higher recovery is noted when using the smaller lead boats.



### Summary

There are several advantages that this method presents that makes it superior in many respects to other methods used in assaying silver cyanide solutions. First, this method is simple in its procedure; second, it is as accurate as the other methods; next, it presents a fast method for assaying small samples of solutions of one or two assay tons; last, this method may be carried out with a minimum of equipment.

The disadvantages may be summed up as follows: it is not overly accurate for large volumes, the presence of impurities in the solution will effect the accuracy of the results and splattering of the solution in the final stages of evaporation will cause a large error in the assay results.

The best concentrations, volumes and weights of the reagents that can be used were those that were generally used in the experiment. It was found that this was true when considering the relative merits of convenience, adaptability and accuracy of each charge that was experimented with. While the small boat, for instance, may give a smaller cupellation loss its small capacity, its



tendency to allow splattering, etc., offsets this advantage. The same considerations may be applied to the other variables; a large volume of solution offers an accurate method of sampling the liquid, but the elements of time and conveniency of assaying may in some instances void this accuracy. The concentration of the silver in the solution allows relatively accurate answers when this concentration is low, however a glance at the chart\* which shows the cupellation losses for various amounts of silver per weight of lead button will show that this statement may be partially nullified by the fact that the higher the silver content of the button the less the percent of loss during cupellation.

\* See part 1 of this experiment.



## The Homestake Mining Method

This method is very similar to the Chiddey method in that the same reagents and so forth were used and the same procedure except a scorification step is not used in the Homestake mining method.

It was submitted by Allan J. Clark, of the Homestake Mining Company and was published in a book, "A Manual of Fire Assaying" written by Fulton and published in 1911.

The procedure is as follows: Place in a large evaporating dish or beaker ten to twenty assay tons of the solution which is to be assayed. Add ten to twenty cubic centimeters of lead acetate of about the same concentration as that used in the Chiddey method. Also add three or four grams of zinc dust and heat until nearly boiling. There has been formed a lead sponge, in the meantime, which contains the valuables of silver and gold. Add slowly twenty cubic centimeters of concentrated hydrochloric acid and allow it to stand, remaining hot, until effervescence stops or until all the zinc has been dissolved.

Filter the solution, retain the sponge in the filter, paper, scorify, and cupel.



The main reason for using this method was to find the effect of scorification on the accuracy of the results of the Chiddey Method. The procedure that was used in scorifying the sponges was to add sufficient test lead to the charge to obtain a good sized button, add three to five grams of borax glass, place in a scorification dish, and scorify at a temperature of about 750° C. for a few minutes. The variables being investigated were primarily those concerning the concentration of the silver in the solution and the volume of the solution. These two variables helped to correlate the effect of scorification on the similar experiments in the Chiddey method. Experimenting was done also with the scorification phase of the procedure by varying the amounts of test lead and of borax glass used and of the time of scorification.

#### Data and Results

The volume of the solution assayed.

The results here were lower than for the Chiddey method. The separate results for weights ranging from thirty to five assay tons of liquid were respectively the same as those received before.



The concentration of the silver.

The concentration of the silver was varied from two to twenty ounces per assay ton of the liquid. Here again the results were from one to two per cent lower than those received in the Chiddey analysis but were relatively of the same proportionate value.

The weight of the test lead.

The values received in this part bear out those results that were found in the Lead Boat assay; that the more lead in the button the greater percent of silver loss. It was found that the best weight of lead used was that amount that added to the weight of the sponge was equal to thirty to forty grams.

The amount of borax glass.

The best amount of borax glass to be used was found to be about three grams.

Time of scorification.

The time of scorification is not to be definitely set. It depends upon a number of conditions in the muffle itself, such as, the temperature of the muffle, the atmosphere and draft of the muffle, and other conditions. The best time was found to be at that moment when the borax glass slag has opened to a desired extent. The operator may use his own judgement with regard to this.



## Summary

This method closely resembles the Chiddey method. It is not as accurate, however, and because of this, it is not of any particular value. The losses are probably due to slag and vaporization. The entire experiment requires much more time than other methods of solution analysis.



## The Chiddey Method

This method of assaying silver cyanide liquors was proposed in a letter sent to the Engineering and Mining Journal in Feb. 10, 1903, by Alfred Chiddey and was printed in this journal on March 28, 1903.

The as proposed by Alfred Chiddey is as follows:

" I have been experimenting for some time in trying to find a more rapid method than those in ordinary use and have at last devised the following: Introduce into a porcelain dish four assay tons or more of the solution to be assayed, add ten c.c. of ten percent solution of acetate of lead, then four grams of zinc shavings, boil a minute, add twenty c.c. of hydrochloric acid. When the action has ceased, boil again; wash the sponge with distilled water, transfer it with a stirring rod to a piece of filter paper; squeeze it into a compact lump and place in a hot cupel. The mouth of the muffle should contain a piece of dry pine wood so that it is filled with flame at the moment of introducing the sponge lead.

The above process, which I believe is strictly



original, gives slightly higher results than the evaporation method as ordinarily conducted and is much more rapid, occupying only twenty-five minutes.

The proportion of silver to gold in our solutions here is about ten to one. In the case of very dilute nearly pure solutions of gold, I would suggested a known quantity of nitrate of silver dissolved in cyanide before adding the acetate of lead.

Alfred Chiddey  
Cyanide Manager,  
El Transito Mine  
Amapala, Honduras

The Chiddey method as was used here and as given in Bugbee's "Textbook of Fire Assaying", is nearly the same as given above with the following exceptions:

1 The solution is not boiled either before or after the addition of the zinc dust.

2 The zinc was added, ( for the most part), as a dust rather than as shavings.

3 Pine wood was not introduced into the mouth of the muffle.

4 The sponge was wrapped in lead foil before



cupelling.

5 As no gold was present in the solution, the assay was run purely for silver.

The variables investigated are as follows:

1 The concentration of silver per assay ton of solution.

2 The volumes of the solutions taken to be assayed.

3 The volume of lead acetate added per unit volume of solution.

4 The amount of zinc dust added.

5 The zinc added as zinc shavings.

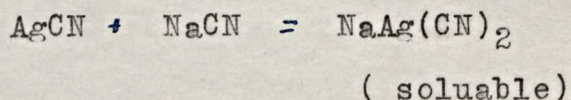
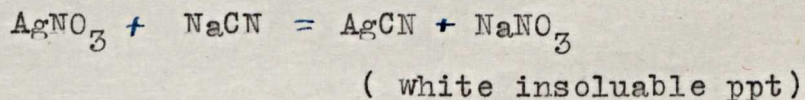
6 The zinc added as a zinc emulsion.

7 The volume of hydrochloric acid used.

8 The amount of zinc left in the sponge.

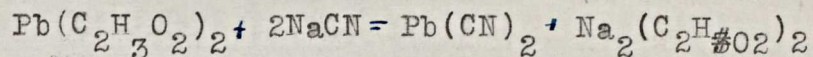
Before attempting to discuss the various results obtained in this experiment it would seem best to review the chemical reactions involved:

Upon adding silver nitrate to the sodium cyanide solution:





When Lead acetate is added:



Upon the introduction of zinc dust:



As the lead is reduced to the metallic state it takes the silver out of solution with it.

### Data and Results

#### 1 Varying Concentration of the Silver

During this part of the work it was attempted to hold all other factors at a constant value and to vary only the concentration of the silver in the solution. Using a standard volume of five assat tons of cyanide solution, silver nitrate was introduced in various volumes giving equivalent concentrations of silver in each of the solutions assayed.

From the results of the above procedure, ( see Table 1, next page), it can be concluded that the Chiddey method is more accurate on the less concentrated silver solutions; this is probably due partly to the fact that the loss of silver during cupellation varies with the amount of silver cupelled.



### Assay Results

Conc. of Silver (mg.)	Assay Value (mg.)	Percent Recovery
40.0	36.4	91.0
20.0	18.8	94.0
10.0	9.2	92.0
5.0	4.8	96.0
2.5	2.4	96.0
1.24	1.20	97.0
0.6	0.58	96.7
0.1	0.09 (plus)	--

Table 1

Weight of NaCN Solution (Assay Tons)	Percent Recovery
10.0	94.0
5.0	92.0
2.5	96.0
1.3	93.0
0.6	94.0

Table 2



## 2 The Effect of Varying the Volume of Solution Assayed

With all other variables held at a constant value, this phase of the experiment demanded variation of the volume of the sodium cyanide solution that was to be assayed.

For results see Table 2 , above.

It can be deduced from this data that the best solution volume need not be either large or small in size in order to give the most accurate results. Rather, however, the volume should be of such size that it will be first, a representative sample of the whole solution and secondly, that it is of such size that it will be easy to handle with ordinary equipment.

Assay	Results
Volume of Lead Acetate ( c.c.)	Character of Sponge ( approximate weight)
5	small ( 1/4 A.T.)
10	medium ( 1/2 A.T.)
15	medium ( 2/3 A.T.)
20	large ( 3/4 A.T.)

Table 3-a



### 3 The Effect of Varying the Concentration of the Lead Acetate

Four pairs of samples were run using different volumes of lead acetate, respectively, five, ten, fifteen, and twenty c.c. Ten milligrams of silver were added to each sample of about five assay tons of solution each.

The description of the sponges in Table 3-a, are mostly of qualitative value, the weights being hastily estimated.

#### Assay Results

Volume of Lead Acetate (C.c.)	Percent Recovery
5	94.0
10	94.0
15	92.0
20	88.0

Table 3-b

From the data in the above table, 3-b, one may note: the larger the sponge- the larger the larger the charge to cupel, therefore- the larger the silver losses in the charge.



#### 4 The Effect of Varying the Amount of Zinc Dust Added

Different weights of zinc dust; one, two and four grams, were added to otherwise similar solutions for the precipitation of the lead sponge. The size of the sponge precipitated was in direct proportion to the amount of zinc added. The efficiency of the recovery did not seem to vary in accordance to the size of the sponge.

Each solution contained five assay tons of solution and ten milligrams of silver.

#### Assay Results

Weight of Zinc Added	Percent Recovery
1 (gm.)	93.0
2	94
4	93

Table 4

#### 5 The Effect of Zinc Added as Shavings

This part of the experiment was carried out with but one sample run to determine the effect of adding coarse zinc as the reducing agent. As zinc, in the form of coarse shavings, was not



available, the same conditions as in part (4) were endeavored by adding three grams of -35 mesh, Anaconda pure zinc.

With the remainder of the charge the same as in part (4), except for an additional amount of acid added to be sure of complete solution of the zinc, the results received checked very closely with those of part (4); the percent recovery being ninety-three percent efficient.

The most disagreeable characteristic encountered when using coarse zinc is its ability to remain in the lead sponge and be carried over to the cupel. If this be the case a scorification of the bead may save the sample.

#### 6 The Effect of Adding Zinc as an Emulsion

The regular zinc emulsion is made by adding to a desired amount of zinc dust sufficient water to form a thick paste.

The results received in this phase of the experiment were not different than those attained in parts (4) and (5).

#### 7 and 8 The Effects of the Hcl added and the Zinc left in the Sponge

The more zinc that is added to the



solution the more hydrochloric that will have to be used to dissolve the zinc.

#### Assay Results

HCl Added (c.c.)	Zinc Added (gm.)	Character of Sponge	Percent Recovery
10	3	Sunk	91.3
20	3	Floats	92.2

Table 4-b

In special cases where it is probable that all of the zinc has not been removed from the sponge, it may be necessary to make a zinc analysis of the final silver bead. For this analysis it is suggested that the method recommended in Low's "Technical Methods of Ore Analysis", be used.

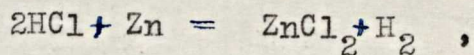
The ability of the sponge to float is important in that it is easy to handle and to remove from the solution and that it may indicate the amount of zinc left in the sponge; that is,

1 Presence of undissolved zinc in the sponge would necessarily make it more dense.

2 If the sponge floats then this is due in part to the bouyant effect of occluded hydrogen bubbles in the sponge caused by the



reaction:



which indicates favorable solution of the zinc.

#### Summary

The Chiddey method is fairly accurate for both high and low concentrations of silver. Although it is more accurate on lower concentrations it may be renovated to suit high silver liquors by increasing the amounts of lead acetate and zinc dust added.

It may be used successfully on any range of volumes of solution to be assayed. A combination of this method and the evaporation process can be used to reduce and analysis large volumes of dilute solutions to smaller more convenient volumes.

The amount of lead acetate used is determined by the size of the lead sponge desired. As the sponge should be small the volume of lead acetate will not exceed ten c.c.

Two to three grams of zinc should be added to get the best results. If the amount of zinc added is lower than this the complete reduction of the lead acetate is doubtful.



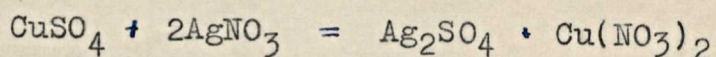
The form in which the zinc is added has little effect on the efficient recovery of silver. However, due to the convenience of adding zinc as dust, it is advised that this method of adding zinc be used.

Sufficient hydrochloric acid, approximately fifteen c.c., should be added in order to insure complete solution of excess zinc in the sponge.

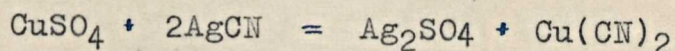


## The Copper Sulphate Method

This method utilizes the ability of  $\text{CuSO}_4$  to precipitate silver from acid or cyanide solutions.



or



This method is given as Miller's method in the Engineering and Mining Journal of July 23, 1904, page 977. The procedure is given as follows: Take 1000 c.c. of silver or gold bearing solution and put in a two liter flask. Add one or two grams of powdered copper sulphate and agitate for a few minutes to dissolve all the crystals. Add 10 to 15 c.c. concentrated hydrochloric acid and agitate again thoroughly. After the precipitate is settled, filter the solution. Do not wash the precipitate. Burn the filter paper, and assay the precipitate by the crucible or scorification method, preferably the former. The filter paper will furnish the necessary reducing agent.

In performing this experiment, it was noticed that the variables that effected the results were the weight of the solution, the concentration of the solution, the amount of hydrochloric acid added, and the amount of copper sulphate added. It was also noticed that the



crucible method of assaying was the more accurate because less silver was lost in the slag or by volatilization, and that, contrary to what was stated in the method, the filter paper did not furnish sufficient reducer for the litharge, and an extra two or three grams of argols was necessarily added.

#### The Effect of the Volume of the Solution

The volumes of solution chosen were so chosen as to include all convenient volumes within their ranges.

#### Data and Results:

The concentration of silver was kept at five ounces per assay ton. Two grams of copper sulphate were added to the solutions. Fifteen cubic centimeters of hydrochloric acid were added. The results are shown on the following page.



Weight of Solution (A.T.)	Character of Precipitate	Percent Recovery
37.3	(a) no precipitate formed	98.4
	(b) pure white flour* precipitate, clear solution	
15.0	(a) light, coagulate	98.8
	(b) creamy coagulate solution clear	
3.75	(a) same	99.0
	(b) same	

(a) Appearance of precipitate before addition of hydrochloric acid.

(b) Appearance of precipitate after addition of hydrochloric acid.

The conclusions reached as the results of the above data are that the volume of the solution has little effect on the accuracy of the answers if the concentrations of the copper sulphate and hydrochloric acid are held in the relative amounts.

#### The Effect of the Concentration of the Silver

In this section of the experiment it was attempted to vary the concentration of the silver while holding constant the other variables.

\* As no precipitate was formed as the result of adding copper sulphate, the precipitate that was formed was largely silver chloride.



The table for this section of the experiment follows:

Concentration of Silver (mg.)	Assay Results (mg.)	Per cent Recovery
3.00	2.9	96.7
6.00	5.92	98.7
12.00	111.91	99.2
25.00	24.89	99.5

The per cent of silver lost decreases as the concentration of the silver added to the solution increases. This is probably due, in part, to the fact that the per cent of silver lost during cupelation is lower for the higher concentrations of silver.

#### The Effect of the Amount of Copper Sulfate Added

As the amount of copper sulphate to be added depends upon the concentration of the silver in the solution, the amount of copper sulphate was varied with this in mind.

Copper Sulphate Added (g,ms.)	Concentration of Silver	Assay Results Per(cent Recovery
2	0.05 g. silver per 5 A.T. solution	99.2 (1)
4		96.6 (2)
8		97.6 (3)



### Character of the Precipitate\*

- (1) (a)  
No precipitate was formed, the solution was colorless.
- (b)  
The precipitate was light, the solution colorless.
- (2) (a)  
Light and coagulated precipitate, solution bluish .
- (b)  
The precipitate was the same; the solution blue.
- (3) (a)  
Same as (2a).
- (b)  
Same as (2b)
- \* (a) Before the addition of hydrochloric acid.  
(b) After the addition of hydrochloric acid.

In comparing the chart above with the chart of the first part, the effect of the volume of the solution, we discover that the amount of copper sulphate to be added does not only depend upon the amount of silver in the solution but also upon the volume of the solution.

It can be seen that for large volumes of liquors at least four grams of copper sulphate must be added since two or three grams were insufficient to complete the reaction. The equation is as follows:





When this reaction is complete the solution will be slightly bluish from excess copper sulphate or copper chloride, and a white precipitate of silver sulphate will have formed.

#### Summary

As the amount of hydrochloric acid added depends upon the amount of copper sulphate added to the solution it seemed that this variable did not need investigation. However, to completely coagulate the precipitate, a volume of 15 to 20 cubic centimeters of hydrochloric acid should be added. The volume of the solution should be kept at about 15 assay tons. This is equivalent to 800 to 900 cubic centimeters. This method is equally accurate on both high and low concentrations of silver. The copper sulphate salt should be added at three to five grams per charge.

In considering the method of fire assaying the precipitate, the crucible method was chosen in favor of the scorification method. The slag losses and volatilization losses were found to be smaller in the former method.

While this method is fairly accurate, it is with certain reservations that this method is recommended. There are too many places where the



experiment may go astray, and as fusion of the charge is necessary the time of performing the complete analysis may be too long to be of practical use in plant work.



### Hydroxylamine Method

A method using hydroxylamine chloride as proposed by R.V. Lundquist, Chemist, Idaho Bureau of Mines and Geology, Moscow, Idaho; appeared in the November, 1940 issue of the "Engineering and Mining Journal" and proposed a new method of assaying cyanide solutions. In this article it was particularly recommended for gold solutions. However as gold was not available it was attempted to alter the procedure slightly and apply to the assaying of silver cyanide solutions.

Following are excerpts from the article:

" To one assay ton of solution, or any other convenient volume, add 0.3 grams of zinc dust and agitate for one minute. Add 0.5 grams of mercuric chloride and warm on a hot plate to dissolve the salt. Add 0.5 grams of hydroxylamine hydrochloride and 3.0 c.c. of concentrated ammonium hydroxide, adding two or three c.c. in excess. Boil for a few minutes in order to give the hydroxylamine hydrochloride time to reduce the mercuric chloride to metallic mercury. A nearly clear solution results.

Remove from the hot plate and add five c.c. of concentrate hydrochloric acid. Boil until a nearly clear solution develops and most of the free zinc has been dissolved.



At this point fine drops of mercury should appear and settle, although some may float attached to air bubbles. A flocculent precipitate will appear which will also be difficult to settle. Destroy it by adding a few drops of phenothalien and making the solution basic with ammonium hydroxide. Add one-half gram of hydroxylamine hydrochloride and boil until a clear solution results. Allow to settle and decant most of the clear solution, being careful not to lose any of the amalgam. Add ten c.c. of hydrochloric acid and boil for a few minutes to clean the surface of the droplets so that they will coalesce. Dilute to fifty c.c. and continue boiling for another minute. Stir vigorously to detach gas from the droplets of amalgam and, using a stirring rod, collect the amalgam to one large globule. Wash this globule several times with hot water to remove the last traces of hydrochloric.

Transfer the globule to a porcelain cup and part with dilute nitric acid, one to four. More concentrated acid will react too violently and flour the gold. When completely parted, cool, decant the liquid and add one c.c. concentrated nitric acid. Repeat this procedure several times to remove the last traces of mercury and zinc.



Wash the residue with distilled water, anneal, and weigh as gold."

Because of the lack of gold to carry out the procedure as outlined above no remarks either pro or con concerning this method are forthcoming in this report.

It was attempted however, to apply this method to the assay of silver cyanide solutions by altering the procedure in several ways.

The first change made was to dissolve the silver added to the solution with concentrated sulfuric acid instead of nitric acid so as to prevent formation of aqua-regia late on in the experiment. Another alteration was to eliminate parting the mercury amalgam with nitric acid as this operation would also dissolve the silver present.

All attempts to obtain a correct assay by this method failed. The main reasons for their failure are: first, during sublimation of the final mercury amalgam splattering of the bead would occur do to the presence of zinc in the amalgam; second, the zinc could not be substituted or eliminated from the experiment because the presence of zinc was necessary to aid in the reduction of the mercuric chloride and to produce the amalgam.



The theory of the chemical reactions involved in this process can be summarized as follows:

Mercuric chloride dissolves in sodium cyanide forming mercuric cyanide; the mercuric cyanide is partially reduced with hydroxylamine hydrochloride to metallic mercury and mercurous cyanide. The latter, being unstable, decomposes into mercury and mercuric cyanide. This reaction is aided and the reduction completed by addition of metallic zinc.

This method, as far as is now known, is not applicable to the assay of silver cyanide solutions.



## The Electrolytic Method

The final method of assaying silver cyanide solutions that was investigated in this thesis is the method by which silver is extracted from the solution by electrolysis.

Two types of procedure are generally accepted for this method, one with a platinum cathode the other with a lead foil cathode. The first system of analysis runs as follows:

According to the strength of the silver bath ten or twenty c.c. are filtered into a tared two hundred c.c. platinum dish and according to the greater or smaller excess of cyanide present 0.1 to 1 gram of potassium cyanide solution is added. The electrolyte, diluted about to one-half inch from the edge of the dish is kept, by a flame underneath, at a temperature of sixty to sixty degrees Centigrade during the period of electrolysis at a current of 0.08 amperes.

Complete the precipitation, which requires about three and one-half hours. Without interruption of current, by use of a siphon, displacement of the electrolyte with water is accomplished.

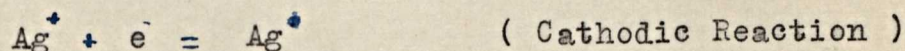
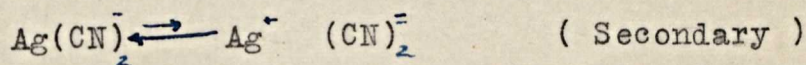
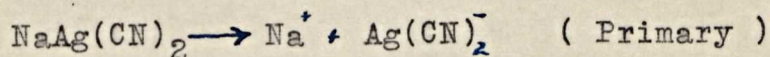
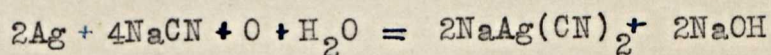


Wash the cathode with alcohol and either set aside to dry or wash with ether and dry immediately.

The second system proceeds in a similar manner. This method which uses a lead foil cathode has a definite advantage over the platinum cathode method. Although the rate of deposition is much faster using the latter and the weighing of the cathode speedier, the lead cathode yields more accurate analysis of impure solutions because of a final elimination of impurities through fire assay.

The current is held approximately at 0.2 amperes and the time of electrolysis should be from eight to ten hours.

The chemistry of the electrolysis of silver cyanide solutions may be stated thus:



The primary ionization of sodium argento-cyanide proceeds for the most part to the right of the equation. The secondary ionization proceeds much



slower and due to this low rate of ionization the electrodeposition of silver from cyanide solutions is very slow.

Three variables were investigated in this work and, as each variable was chosen with an eye to its effect upon the accuracy, speed of deposition and general convenience of assaying, the study of these variables afforded a comprehensive examination of this method.

#### 1 Accuracy of Assay vs. Type of Cathode

For results of this experiment see Table 1, below.

Assay Results		
Cathode	Silver Added	Percent Recovery
Platinum	0.0134 (gm)	100 (plus)
	0.2370	99
Lead	0.0128	94
	0.0230	96

Table 1

This table shows that higher results were received using the platinum cathode than were



received using the lead foil cathode. However it was noted that the high values received with the former were due, in part, to inclusion of particles of carbon which were mechanically entrapped in the deposit. Decomposition of the anode seriously effected the results when the current used was 0.2 amperes or over.

## 2 Rate of Deposition

Using a lead foil cathode, with a current of 0.3 amperes, this variable was investigated through varying the time of deposition from ten minutes to eight hours.

From the results of Table 2 it can be concluded that the rate of deposition varies inversely as the time of electrolysis. Also that the results are effected by losses in fire assaying making them uniformly low.

Deviations in the curve accompanying this table are probably due to mechanical losses caused by handling the cathode previous to fire assaying.



Assay Results		
Time (min.)	Silver Deposited (gm.)	Percent Recovery
8	0.0010	3.3
12	0.0016	5.3
45	0.0048	16.0
75	0.0102	34.0
135	0.0198	68.0
195	0.0262	87.5
255	0.0278	92.7
375	0.0288	96.0
480	0.0294	98.0

Table 2

3 The Effect of the Concentration of Sodium Cyanide

Concentration of Sodium Cyanide	Percent Recovery
4 (lb./ton)	98.5
2	98.3
1	98.4

Table 3



Using a lead foil cathode, a current of 0.2 amperes and a time of six hours, the concentration of sodium cyanide in the solution was varied.

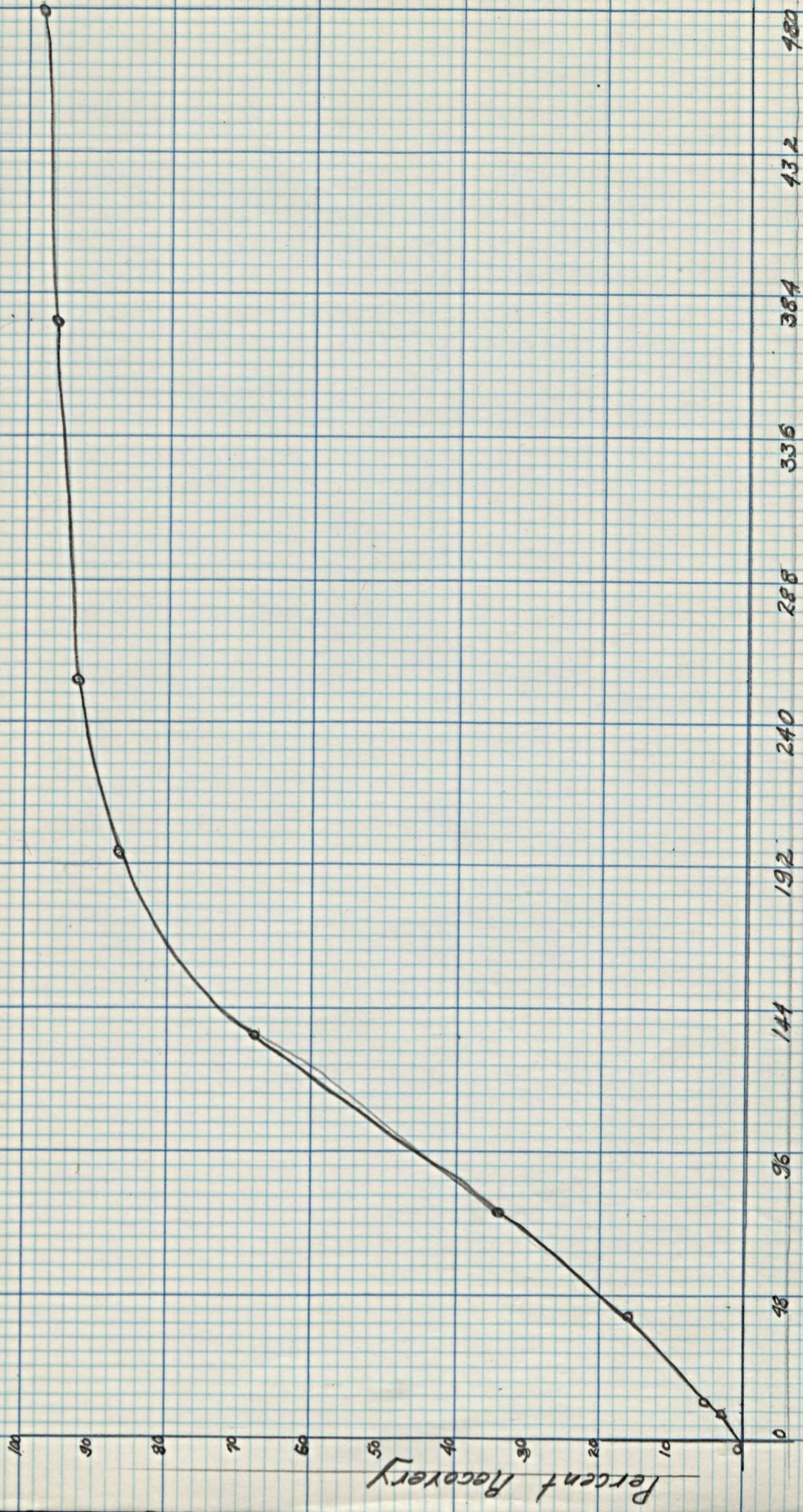
The results were not noticable in degree of variation caused by these concentrations. However, when using the lowest concentration of cyanide, the deposit was found to be coarse and brittle and would not stand rough handling.



### Summary

This method of assaying silver cyanide solutions is too slow to be used commercially. High volumes of solutions or high concentrations of silver in these solutions are not adaptable to this method and, unless lead cathodes are used, impurities in the electrolyte may be either electrolytically or mechanically deposited, thus effecting the accuracy of the results.





Time of Electrolysis (minutes)



## Conclusions

The experiments carried out and recorded in this thesis were so done with the view of finding the most convenient, the most accurate and the fastest method that can be applied in general practice to the assaying of silver cyanide solutions. Of the procedures tried it is believed, for the sake of these advantages, that the Lead Boat Method and the Chiddey Method are the best.

Other methods applicable to this sort of work would have been profitably investigated but neither available time or facilities allowed their study.

The method proposing recovery of silver from solution using hydroxylamine hydrochloride would be satisfactorily convenient if a means by which the silver could be assayed for in the amalgam could be found and thus eliminate a lengthy fire assay step in the analysis.

Further work concerning the Electrolytic Method is also advised such as using revolving cathodes, higher current densities, addition agents and purified solutions.



BIBLIOGRAPHY

- "A Manual of Fire Assaying" -- Fulton  
"Technical Methods of Metallurgical Analysis"  
--Scott  
"A Manual of Practical Assaying" Furman  
" Metallurgical Analysis" -- Lord  
" The Sampling and Assaying of the Precious  
Metals" -- Smith  
  
"Watt's Dictionary of Chemistry"  
" International Critical Tables"  
  
" Engineering and Mining Journal"  
Nov. 1940