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**A STUDY OF THE ELECTROLYTIC DETERMINATION OF LEAD**

by

**Philip Hall Delano**

**A**

**T H E S I S**

**Submitted to the Faculty of the**

**SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI**

**in partial fulfilment of the work required for the**

**Degree of**

**MASTER OF SCIENCE IN CHEMICAL ENGINEERING**

A handwritten signature in cursive script, reading "W. T. Schrenk". The signature is written in dark ink and is positioned to the right of the main text block.

**Rolla, Missouri**

**1930**

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## Foreword

The author wishes to thank Dr. Schrenk for his advice and suggestions during the preparation of this work. Also to thank Mr. W. T. Isobel for his suggestions and for the use of the equipment of the St. Joseph Lead Company at Bonne Terre, Missouri, in several of the experiments.

## The electrolytic Determination of Lead

### Introduction

The electrolytic determination of lead is one of the most used methods, particularly for control work and where large numbers of analyses have to be run each day. The method is adopted because of its simplicity and because of the small amount of the chemist's time required. It is particularly suited for the determination of small amounts of lead. However, it has been noted that deviations from certain conditions produce results which vary widely from the actual amount of lead present, though results which check with each other may be obtained. Certain elements interfere with the determination and must be absent or present only in small amounts.

The method depends upon the fact that lead electrolysed in acid solution is deposited upon the anode as  $PbO_2$ . Under proper conditions the lead is deposited quantitatively and from the weight of  $PbO_2$  obtained the weight of lead in the sample can be calculated.

This investigation was suggested by the fact that students in the laboratory, working by the accepted procedure, obtained such varying results that the determination

had to be abandoned. The writer, although he had run thousands of electrolytic leads in a commercial laboratory, had the same trouble and could not obtain correct results. This failure suggested an investigation to determine the reasons for the trouble and the correct conditions for the analysis.

### Historical

There has been a great deal of work done on the electrolytic determination of lead. The details of many of the experiments have been very briefly given and the investigators do not agree as to the best conditions.

Most of the experimenters who have published their work have used the Classen dish, a rotating anode, or some other device which would be impracticable for industrial work because of difficulty of manipulation or because of the large investment in apparatus which would be necessary. As the conditions for the analysis vary with the type of anode used and as this investigation is concerned with the determination when using paddles of corrugated sheet platinum, most of the references in the literature do not bear directly upon this investigation.

Becquerel (Ann. Chim. Phys. 43, 1830) was the first to separate lead from other metals by deposition as peroxide. He used an acetic acid solution.

Luckow (Dingl. Jour. 177, 396, 1865) first published a method for the quantitative determination of lead as peroxide. He used 10% free nitric acid and electrolysed for several hours.

May (Am. Jour. Sci. 237, 6, 265, 1873) used platinum foil  $2\frac{1}{2}$ " x 2" as the anode and strips  $\frac{1}{8}$ " wide as the cathodes.

Guess (Bull. Am. Inst. Mining Engrs. 1239, 1905) was the first to apply this method to industrial analysis. He used paddles of corrugated sheet platinum as anodes with narrow platinum strips as cathodes. These were held by contact pressure in slotted aluminum terminals.

Other chemists have done work which bears directly upon this determination but their experiments will be cited under the topics to which they apply.



### The Problem

The accuracy of the electrolytic determination of lead depends upon the following factors:

1. Type and condition of anodes.
2. Temperature.
3. Time of electrolysis.
4. Concentration of acid.
5. Current.
6. Amount of lead present.
7. Added reagents, as  $\text{NH}_4\text{NO}_3$ , etc.
8. Type of material analysed.

These factors may all be varied within wide limits, but at the same time the limit is well defined and passing this will surely result in a poor determination.

The purpose of this work is to study the effect of these factors upon the determination of lead, to find the best conditions for the analysis, and to determine the degree of accuracy which may be expected from the method.

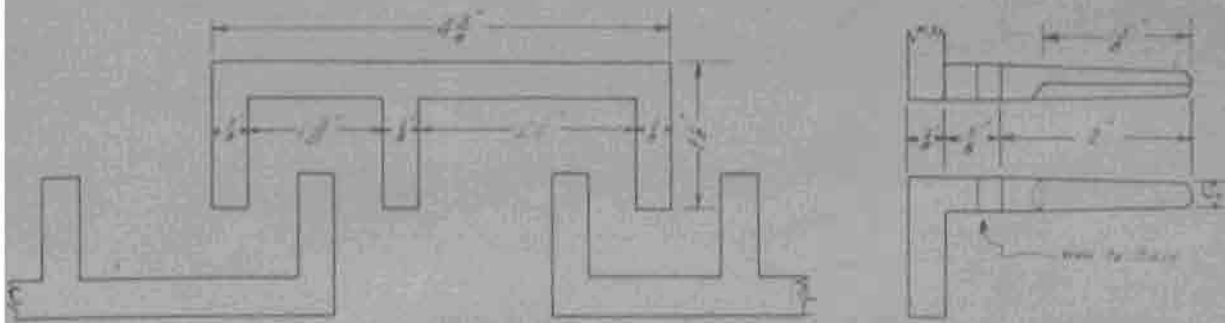
### Apparatus

In these experiments platinum anodes 3 x 6 cm. of .002 sand blasted corrugated sheet platinum were used with two narrow platinum strips as cathodes. They were held by contact pressure in slotted aluminum terminals. A modification of the Guess-Houltain cabinet was used and the board was so arranged that six samples could be run simultaneously.

Though this arrangement was satisfactory for this work a permanent set-up for industrial work should embody certain other features. The anodes should be heavier, .005 sheet platinum would do nicely. The terminals should be of rolled or hard drawn aluminum which resist the acid fumes to which they are exposed. Cast terminals must be renewed after about six months of daily service. There should also be a switching arrangement by which one or more samples as desired can be run and removed without disturbing other samples which may be on the board.

O. W. Holmes and D. P. Morgan (J. Ind. Eng. Chem., Anal. Ed. 1, 210, 1929) have described an apparatus which possesses considerable merit.

On the next page is given a diagram of the apparatus which seems to best satisfy the conditions desired. The resistance of an individual cell is just about one ohm,



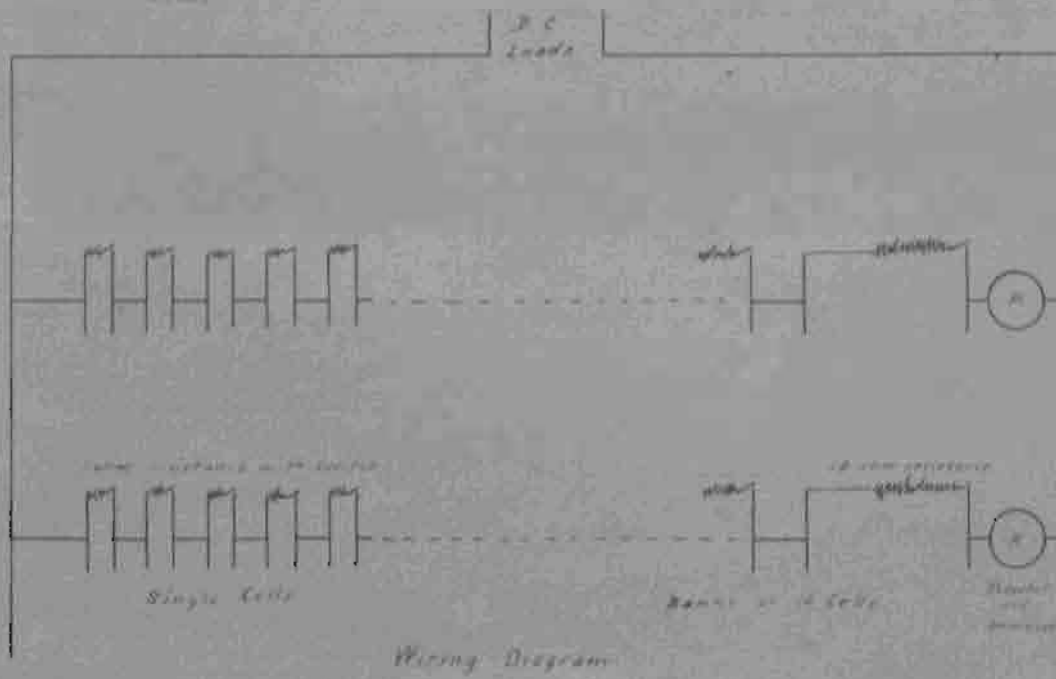
Terminal



A side



C side



Wiring Diagram

therefore to remove one sample from the board, the switch corresponding to the cell is closed and the beaker dropped. As the total resistance of the circuit is unchanged the main rheostat does not have to be readjusted and there is no sudden increase in the current as might occur if the samples were only shorted out. There is thus provision for ten single samples and as many banks of ten cells as desired may be put into the circuit to provide for larger numbers of samples. The drawn aluminum terminals insure against corrosion and the rubber sleeve will secure enough pressure to insure good contact and hold the anodes firmly. The cathodes which are very seldom disturbed may be held more firmly if a short sleeve of bakelite is placed on the end of the terminal. The welded joint insures against poor contacts between the terminal and base. The cathode is stiffer and lasts longer if crimped as shown. The base may be cast or machined as it is not exposed to acids.

To secure best results the anodes are sandblasted. This secures better adherence and prevents scaling. The writer has deposited as much as two grams of  $PbO_2$  on a properly sandblasted anode with no tendency to scale. Smooth anodes or old anodes will hold only a fraction of this amount.

The apparatus here described possesses the advantage of being simple and easy to manipulate and will give very

accurate results under proper conditions. It is especially convenient where large numbers of determinations must be run every day.

The apparatus is one of the most important factors and to variations in the type of apparatus used and to variations in its conditions may be attributed many of the conflicting results obtained by different experimenters.

Anodes must be cleaned and sandblasted again after a certain period of use. After a time they become smoother and all the lead does not deposit. The following results show the contrast between properly conditioned anodes and old anodes:

	PbO <sub>2</sub> Taken	PbO <sub>2</sub> Found			
Old	.0250	.0247	.0243	.0244	.0246
New	.0250	.0250	.0252	.0250	.0250

Lead nitrate was prepared by dissolving pure lead (99.99%) in nitric acid. The salt was then recrystallized by solution in hot water, filtration through a quartz filter, and precipitation with concentrated nitric acid. The recrystallization was repeated several times and the salt dried.

### Experimental

The experimental work was carried out by using the apparatus described on pages 8 to 11. In the preliminary experiments the conditions were selected which had been recommended by other workers and which we had been using in the laboratory. Then all factors were held constant save one which was varied and the effect of this variable was studied. The procedure as first used was to take a suitable weight of the sample and digest with 20 cc. of  $\text{HNO}_3$ . When brown fumes ceased to be evolved, 15 cc. of a saturated solution of  $\text{NH}_4\text{NO}_3$  was added and the solution boiled for approximately one minute. The sample was then diluted with cold water and electrolyzed for  $1\frac{1}{2}$  to 2 hours. If a pure lead solution was used instead of a standard sample, the procedure was approximately the same. In either case the sample was electrolyzed cold.

In order to secure a known amount of lead in the sample, solutions of known lead content were made up and portions measured out to obtain the desired quantity of lead. This especially purified lead nitrate was then weighed and dissolved in water to obtain solutions containing .01, .001, and .0001 grams  $\text{PbO}_2$  per cc. The concentration of lead in these solutions was then checked by the sulfate method.

The effect of time on the completeness of the deposition was first studied. It was found that quantitative deposition of lead in the cold could be secured only by electrolyzing for a period of eight or more hours. Electrolysis for a period of  $1\frac{1}{2}$  to 2 hours yielded only indifferent results. There was considerable trouble in this series of experiments due to the tendency toward deposition of metallic lead upon the cathodes. This metallic lead dissolved only very slowly.

After a considerable number of runs had been made in the cold, experiments were undertaken to determine the effect of temperature upon the electrolysis. This series of experiments brought out the fact that under the new conditions quantitative deposition of the lead could be obtained in a period of one and one half to two hours. An initial temperature of  $90^{\circ}$  to  $95^{\circ}$  seemed to give the best results. This temperature dropped during the analysis to about  $50^{\circ}$  at which temperature the last traces of Pb were plated out. If the temperature was maintained at  $90^{\circ}$  incomplete deposition resulted.



Table I. The Effect of Time and Temperature.

PbO <sub>2</sub> taken	.0288	
Average of 8 determinations (cold) 1½ hours		.0254
Maximum deviation from average		.0003
	Error	.0034
PbO <sub>2</sub> taken	.0250	
Average of 6 determinations (cold) 8 hours		.0249
Maximum deviation from average		.0002
	Error	.0001
PbO <sub>2</sub> taken	.0250	
Average of 22 determinations (hot) 1½ hours		.02501
Maximum deviation from average		.0002
	Error	.00001

These results indicate that the temperature is one of the most important factors in the electrolysis of a lead solution. Results in the cold are poor unless a long period of electrolysis is used, while results with a hot solution are very good in  $1\frac{1}{2}$  to 2 hours. The experiments also brought out the fact that checking results could be obtained under practically all conditions even though all of the lead was not deposited from the solution. This emphasizes the fact that checking results do not mean a quantitative result.

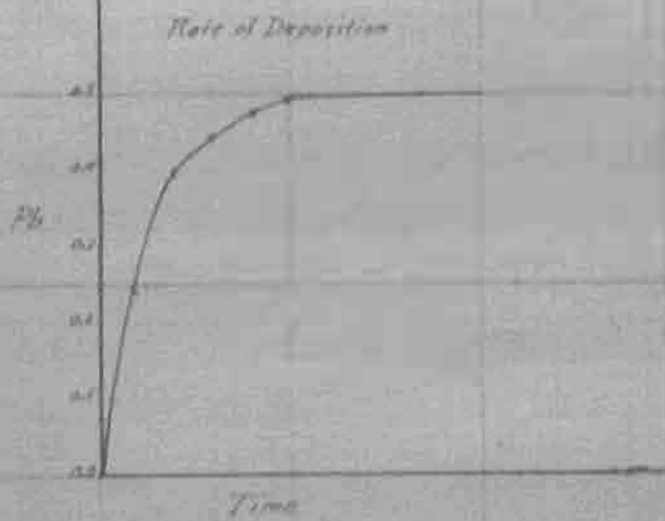
## Time

The time of electrolysis, an important factor in the determination, depends upon the current, temperature, acid concentration, and amount of lead present. Other experimenters have continued their electrolysis to complete deposition of the lead and then recorded the time required. In these experiments, comparative results were desired and so the electrolysis was discontinued at a predetermined time and the results obtained were compared with the true results and with those from other runs. Under proper conditions the deposition was practically complete in  $1\frac{1}{2}$  hours when the amount of lead present was between 5 and 150 milligrams. Larger amounts generally require more time so that two hours should be used to electrolyse samples of high lead content.

The time of electrolysis depends upon the current, and in general, the greater the current the shorter the time required. Sand, in his experiments with the rotating anode and high currents<sup>(45)</sup> secured good results in ten minutes. Part of this effect was due, however, to the stirring of the solution obtained by the rotating anode. His apparatus because of its cost and difficulty of manipulation is impractical for most laboratory and industrial work. Electrolysis for long periods with a small current has also been found to give good results. With the usual value for current of 3 to 3.5

amperes, and with the apparatus used in these experiments, one and a half hours will usually be sufficient if the temperature and acid concentration are high. Time decreases with increase of temperature. If electrolysis is carried out in the cold there is a marked tendency for metallic lead to deposit upon the cathodes. To prevent this, a small current must be used or the electrolysis must be continued for a long enough period to permit the lead to redissolve. In either case eight hours or more are usually required. With a hot solution, however, this deposition is prevented and good results are obtained. The acid concentration affects time principally as it prevents the deposition of metallic lead on the cathodes and so a high acid concentration should be best. The amount of lead present affects the electrolysis, for the greater the amount the longer the time required. This is only true within certain limits, however, for in every case most of the lead is deposited within the first few minutes and the remainder of the time is occupied in removing the last traces.

Benner (J. Ind. Eng. Chem., 2, 348, 1910) has studied this time relation and plotted his results which are shown on the next page.



*Benner - Ind. Eng. Chem. 2, 348, 1910.*

Table II. Effect of Nitric Acid Concentration.

Solution cold at start of electrolysis.

cc. HNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	1.	2.	3.
in 135 cc. Sol.		Lead taken	Lead taken	Lead taken
		Lead found	Lead found	Lead found
		.0025	.0250	.2887
10	--	.0011	.0173	.0972
15	--	.0011	.0183	.1774
20	--	.0012	.0197	.2319
25	--	.0008	.0208	.2485
30	--	.0000	.0222	.2567
35	--	.0000	.0208	.2535
10	15	.0008	.0171	.2167
15	15	.0008	.0203	.2327
20	15	.0012	.0214	.2535
25	15	.0010	.0193	.2398
30	15	.0002	.0212	.2629
35	15	.0000	.0199	.2472

Table III. Effect of Nitric Acid Concentration  
 Solution hot (90°) at beginning of electrolysis.

	Lead taken	Lead taken	Lead taken
cc. HNO <sub>3</sub>	.0025	.0250	.1156
in 135 cc. soln.	Lead found	Lead found	Lead found
10	.0009	.0096	----
15	.0014	.0188	.1125
20	.0016	.0238	.1146
25	.0017	.0249	.1147
30	.0014	.0250	.1148

These experiments indicate the importance of temperature and also that acid concentration depends to some extent upon temperature. In the cold a higher acid concentration is necessary to prevent deposition of lead upon the cathodes than if the solution is electrolysed hot. High acid concentration produces a more coherent firmer deposit but slows up the deposition to some extent. In any case from 20% to 30% free acid will give best results when a current of 3 to 3.5 amperes is used. If the solution is cold, complete deposition is not secured with any acid concentration unless a longer time is used (about eight hours).

A much smaller amount of acid can be used if a small current and a long time are used. Other experimenters<sup>(3,6,7)</sup> have determined the limiting concentration to be about 7% free  $\text{HNO}_3$ .



### Current

The usual value for current with the type of anodes used in this experiment is from 3 to 3.5 amperes. This seems to be the most economical value, securing good results in  $1\frac{1}{2}$  to 2 hours. Higher values of current may be used with the rotating anode with corresponding decrease of the time required. However, higher current in these experiments seems to have very little effect. Low current (.1 to .5 amperes) must be used when the solution is electrolysed in the cold as lead deposits on the cathode with higher current.

### Amount of Lead Present

The best results are secured when the lead is deposited from a solution containing from 5 to 150 mg. of lead. Less than 5 mg. of lead leads to incomplete deposition. If acid concentration is low complete deposition may be secured with a long period of electrolysis but the best procedure is to add about 25 mg. of lead to all low ores. When the amount of lead present is above 150 mg. scaling may take place unless the anodes are in good condition and other conditions are correct. Also, results when this amount of lead is present are usually low by 1 or 2 mgs. due to Pb remaining in the solution.

Although the writer has deposited two grams of  $PbO_2$ , this as a rule is not to be recommended. Furthermore, above .2 to .3 grams any variation in the composition of the  $PbO_2$  from that of the factor used may begin to affect the determination. Small amounts of  $PbO_2$  are always near the theoretical in composition but larger amounts occlude more foreign matter. Experimenters by analysing the deposit obtained have shown that the factor for the lead in lead dioxide varies from .850 to .866 according to the conditions under which the deposition takes place. According to this the tendency of the method should be toward high results but in these experiments high results were

never obtained unless some impurity such as Mn, Bi, or Sn were present. The factor, lead taken over  $\text{PbO}_2$  deposited, is always .8662 if the proper conditions are observed. A period of  $1\frac{1}{2}$  hours for the electrolysis is sufficient to secure accurate results when the sample is low in lead but a longer time, at least 2 hours, should be used if the sample runs high in lead.

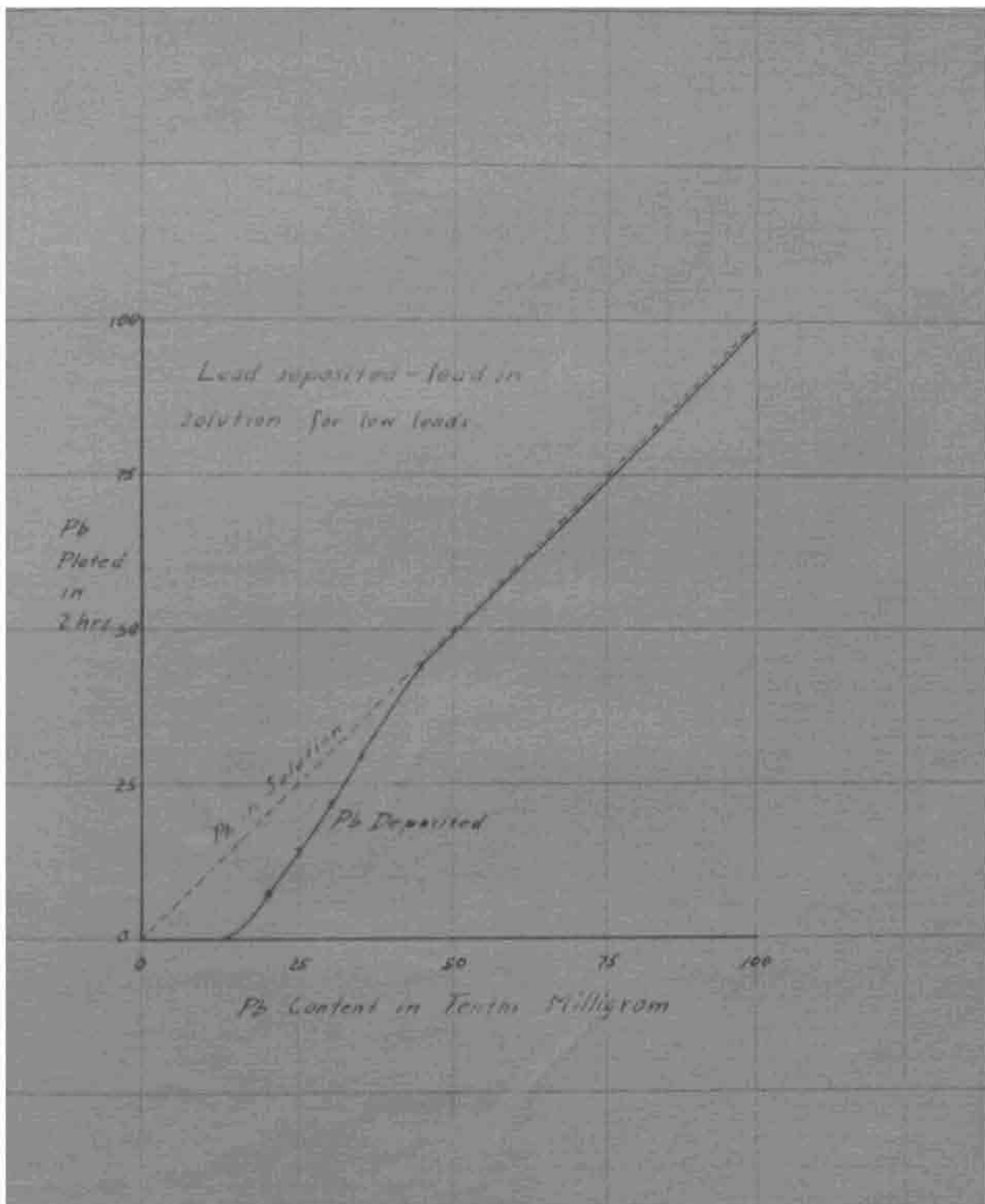
The variation in composition of  $\text{PbO}_2$  with the amount deposited has been studied by Fischer (Z. f. a. Ch. 50, 759, 1911). The writer has determined the factor  $\text{Pb}/\text{PbO}_2$  for some of his deposits with similar results.

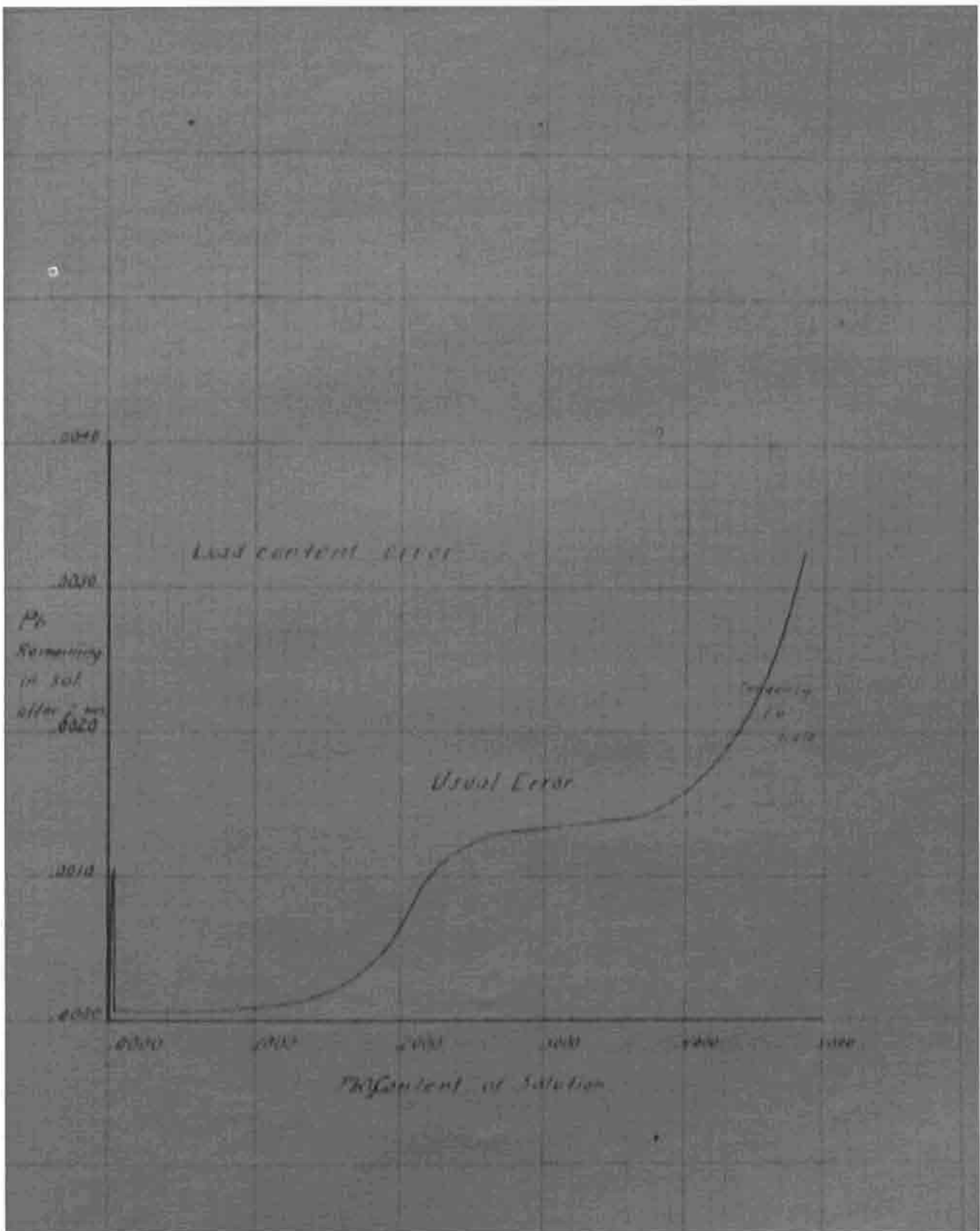
The deposited  $\text{PbO}_2$  adsorbs water which can only be expelled with great difficulty. Drying at a temperature high enough to expel the water results in decomposition of the  $\text{PbO}_2$ . The solution of the difficulty lies in the fact that electro-endosmosis keeps the deposit practically free of water during the electrolysis. Rapid washing and drying will prevent further adsorption of the water and secure a deposit near the theoretical in composition. Sand<sup>(45)</sup> has shown clearly the difficulty in obtaining a uniform composition of the deposited  $\text{PbO}_2$ .

The following curves show the relation between the amount of lead and the results to be expected.

Table IV.  
Relation of Amount of PbO<sub>2</sub> Deposited  
to the Factor Pb/PbO<sub>2</sub>.

PbO <sub>2</sub> Deposited	Fischer Factor	Delano Factor
to .1 g.	.866	.8660
.1 g.	.8658	.8657
.1 - .3 g.	.8652	-----
.5 g.	.8629	-----
1.0 g.	.8610	-----





Having established the effect of time, temperature, acid concentration, and current, a study of the effects of other substances was undertaken. In electrolyzing a solution of a pure lead salt, it was found that it is difficult to completely deposit the lead. If much lead is present, scaling is likely to take place. If some substance as  $\text{NH}_4\text{NO}_3$  is added to the solution, results are usually improved but  $\text{NH}_4\text{NO}_3$  has a tendency to increase scaling of large amounts of lead. Ammonium nitrate is usually added for the purpose of securing complete solution of the sample where  $\text{PbSO}_4$  or  $\text{Pb}(\text{CrO}_4)$  might be present. If solution can be obtained without the use of  $\text{NH}_4\text{NO}_3$  it is as well to leave it out.

When a few drops of  $\text{H}_2\text{SO}_4$  are present in the solution excellent results are obtained in  $1\frac{1}{2}$  to 2 hours. Sulfuric acid in hot solution gives a firmer more coherent deposit. The best effects are obtained if .25 to .50 cc. are present but an amount up to 2.50 cc. can be present without harming the results. More than 5 cc. (in 140 cc. of solution) will not give good results even when  $\text{NH}_4\text{NO}_3$  is present due to the precipitation of  $\text{PbSO}_4$ . If the solution is cold,  $\text{H}_2\text{SO}_4$  interferes for the same reason.

When the sample is high in lead it is practically impossible to get good results unless .25 to .50 cc. of  $\text{H}_2\text{SO}_4$  are added. Lead concentrates are now being run with the addition of  $\text{H}_2\text{SO}_4$  and excellent results obtained.

Table V. Effect of NH<sub>4</sub>NO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>

PbO <sub>2</sub> Taken	PbO <sub>2</sub> Found	NH <sub>4</sub> NO <sub>3</sub>	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	Remarks
.0188	.0182	--	30	--	
.0469	.0454	--	30	--	
.1407	.1351	--	30	--	
.0188	.0175	15	30	--	
.0469	.0452	15	30	--	
.1407	.1384	15	30	--	
.0188	.0187	--	30	8 drops	
.0469	.0470	--	30	"	
.1407	.1410	15	30	"	
.2887	.2864	--	30	--	Slight scaling
.2887	.2806	15	30	--	Scaling increased
.2887	.2876	--	30	8 drops	
.2887	.2878	15	30	"	
.1156	.1156	--	30	$\frac{1}{2}$ cc.	
.1156	.1156	--	30	$1\frac{1}{2}$ cc.	
.1156	.1154	15	30	$1\frac{1}{2}$ cc.	
.1156	.1155	15	30	$2\frac{1}{2}$ cc.	
.1156	.1156	--	30	$2\frac{1}{2}$ cc.	
.1156	.1080	15	30	5 cc.	Very low results.
.1156	----	15	30	30 cc.	No deposit.



The effects of  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{CaSO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{K}_2\text{Cr}_2\text{O}_7$  were next studied. A small amount of these substances aided the deposition of  $\text{PbO}_2$  from a solution of a pure lead salt. Increasing the amount did not have any effect, however, and no effect at all was observed when a little  $\text{H}_2\text{SO}_4$  was present or a sample of ore was used.

The effect of  $\text{HClO}_4$  was also studied and the only noticeable effect was that due to acid concentration.

Certain elements, however, do interfere with the determination. An investigation of the effects of Ag, Bi, As, Sb, Hg, Mn, Sn,  $\text{CrO}_4$  and  $\text{P}_2\text{O}_5$  was made and the results are shown in Table VII. From these experiments it can be seen that Ag, Bi, As, Sb, Sn, Hg, Mn,  $\text{CrO}_4$  and  $\text{P}_2\text{O}_5$  have a definitely harmful effect upon the determination. Some of these impurities deposit with the lead while others act to prevent the lead from depositing. Also, the impurity may cause scaling of the  $\text{PbO}_2$  deposit. In any case in which these elements are present in an amount large enough to cause trouble, a separation must be performed.

Traces of these impurities may be present without the production of any appreciable interference. For example: .03 g. of Mn may often be present without the production of any harmful effect. Colors may be produced in the deposit but the amount of Mn actually present is too small to produce an appreciable error.

The practical limit for most determinations is about .03 gms. of Mn and there should be twice this amount of lead in the solution.

Moltkenhansen (Electrochem. Ind. 1, 351, 1903) has investigated the effect of Mn with about the same results.

A small amount of  $\text{CrO}_4$  does not harm the determination so that it would be possible to precipitate lead from solution as  $\text{PbCrO}_4$ , redissolve, and deposit electrolytically as  $\text{PbO}_2$ .

Table VI. Effect of Certain Elements

PbO<sub>2</sub> taken .1156 g. 30 cc.HNO<sub>3</sub>, 1½ hrs. 3 amps. No H<sub>2</sub>SO<sub>4</sub>.

Pure Lead sol.	gms.	Ca(NO <sub>3</sub> ) <sub>2</sub>	gms.	NaNO <sub>3</sub>	gms.	Fe(NO <sub>3</sub> ) <sub>3</sub>
.1148		.1151		.1148		.1147
.1146	.25	.1151	.05	.1148	.25	.1148
.1149	1.00	.1151	.50	.1151	1.00	.1150
.1150	2.00	.1149	1.00	.1150	2.00	.1147
.1147	5.00	.1150	5.00	.1147	5.00	.1148
<u>.1148</u>	10.00	<u>.1140</u>	10.00	<u>.1121</u>	10.00	<u>.1127</u>
Avg. .1148		.1150		.1149		.1148

gms.	Na <sub>2</sub> SO <sub>4</sub>	gms.	KNO <sub>3</sub>	gms.	CaSO <sub>4</sub>	gms.	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>
	.1148		.1148		.1146		.1146
.05	.1139	.05	.1148	.05	.1145	.05	.1146
.50	.1140	.50	.1153	.50	.1143	.25	.1160
1.00	.1152	1.00	.1151	1.00	.1151	1.00	.1125
5.00	.1163	5.00	.1147	5.00	.1168	2.00	.1182
10.00	<u>.1119</u>	10.00	<u>.1090</u>	10.00	<u>.1115</u>	5.00	<u>.1122</u>

Table VI. (Cont.) Effect of Certain Elements

PbO<sub>2</sub> taken .1156 g. 30 cc. HNO<sub>3</sub>, 1½ hrs. 3 amps. No H<sub>2</sub>SO<sub>4</sub>.

	+ HClO <sub>4</sub>	+ H <sub>2</sub> SO <sub>4</sub>
5 cc.	.1148	.1153
	.1148	.1152
	.1147	.1161
	.1150	.1155
	.1149	.1161
	<u>.1151</u>	<u>.1155</u>
Avg.	.1149	.1156

Table VI. (Cont.) Effect of Certain Elements.

PbO<sub>2</sub> taken .1156 g. 30 cc. HNO<sub>3</sub> 1½ hrs. 3 amp. .25 cc. H<sub>2</sub>SO<sub>4</sub>

Pure Lead Sol.	gms.	Mg(NO <sub>3</sub> ) <sub>2</sub>	gms.	NaNO <sub>3</sub>
.1153		.1151		.1155
.1152	.25	.1154	.05	.1153
.1161	1.00	.1157	.50	.1157
.1155	2.00	.1155	1.00	.1153
.1161	5.00	.1156	5.00	.1152
<u>.1155</u>	10.00	<u>.1150</u>	10.00	<u>.1110</u>
<b>Avg. .1156</b>		<b>.1154</b>		

gms.	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	gms.	Na <sub>2</sub> HPO <sub>4</sub>
	.1159		.1156
.05	.1157	.05	.1147
.25	.1168	.50	.1100
1.00	.1186	1.00	.0980
2.00	.1206	5.00	.0326
5.00	<u>.1128</u>	10.00	<u>----</u>
<b>Avg.</b>			

Table VII. Effect of Interfering Elements

30 cc. HNO<sub>3</sub>, 1½ hrs. 3 amps. ¼ cc. H<sub>2</sub>SO<sub>4</sub>, 90°

Impurity	Amount	PbO <sub>2</sub> Taken	PbO <sub>2</sub> Found	Remarks
Present				
As <sub>2</sub> O <sub>3</sub>	.0050	.0100	.0064	As prevents
	.0100	.0500	.0416	deposition
MnO <sub>2</sub>	.0300	.0100	.0108	Deposits with
	.0200	.0500	.0504	PbO <sub>2</sub> and loosens
	Scaling with large amounts of Mn.			deposit
Cd(NO <sub>3</sub> ) <sub>2</sub>	.5000	.0500	.0498	No interference
	1.0000	.0500	.0502	
Bi <sub>2</sub> O <sub>3</sub> CO <sub>3</sub>	.0050	.0500	.0524	Deposits with
	.0100	.0500	.0550	PbO <sub>2</sub> and may
	.0500	.0500	Scaling	loosen deposit
Sn	.2500	.0500	.0552	Deposits with PbO <sub>2</sub> .
	.5000	.0500	.0590	
Sb <sub>2</sub> S <sub>5</sub>	.0100	.0500	.0520	Deposits with PbO <sub>2</sub> .
	.1000	.0500	.0494	May prevent deposition.
AgNO <sub>3</sub>	.0100	.0500	.0506	AgO <sub>2</sub> deposits
	.1000	.0500	.0510	with PbO <sub>2</sub>
Hg(NO <sub>3</sub> ) <sub>2</sub>	.0100	.0500	.0426	Hg on cathode
	.1000	.0500	.0422	holds Pb.
Cu	.2500	.0500	.0497	No effect
	1.0000	.0500	.0496	

Table VII. Effect of Interfering Elements (Cont.)

Impurity	Amount	PbO <sub>2</sub> Taken	PbO <sub>2</sub> Found	Remarks
H <sub>3</sub> PO <sub>4</sub>	1 cc.	.0500	very low	Prevents deposition
	5 cc.	.0500	no deposition	
Zn(NO <sub>3</sub> ) <sub>2</sub>	.2500	.0500	.0500	No effect
	2.0000	.0500	.0498	
Pine oil	.25 cc	.1156	.1150	Small amounts have
	5.00 cc	.1156	low	little effect.
Phospho cresylic acid	.25 cc	.1156	.1158	Small amounts have
	5.00 cc	.1156	low	little effect.
Xanthate	.25 g.	.1156	.1156	Small amounts have
	5.00 g.	.1156	.1170	little effect.

The precision of this method was determined by analyzing various ores and synthetic samples containing known amounts of lead and using the conditions established in the previous experiments. The results obtained indicate that an accuracy of from 0.1 to 0.01 per cent is obtainable depending upon the amount of lead in the samples. A variation of not more than two to four tenths of a milligram can be expected if the lead content is between 5 and 150 milligrams. The precision to be expected is shown by the curves on pages 26 and 27. Any error is practically always on the negative side.

The mesh to which the sample is ground also may affect the determination. Concentrates should be ground to pass at least a 150 mesh screen and preferably a 200 mesh screen in order to obtain checking results.

A sample of concentrate was submitted for analysis and the results obtained did not check. Upon regrinding to 200 mesh the results obtained were very good.



Original sample	Sample	Sample
100 mesh	150 mesh	200 mesh
51.76	53.88	53.92
53.76	53.68	53.92
53.96	53.60	54.04
53.92	53.76	# 53.88
54.46	53.88	# 53.84
53.72	54.08	# <u>53.84</u>
53.44		53.91% ± .05%
53.48		
54.46		
53.42		
53.90		
53.90		

It is usually best to take a  $\frac{1}{4}$  plumb sample for analysis if the sample is high in lead. A  $\frac{1}{2}$  plumb sample may be run but the chance for error is somewhat greater as can be seen from the curves on pages 26 and 27.

# Run by A. W. Holmes U. S. Bureau of Mines

### Procedures

The procedure as finally adopted and recommended for use when no harmful impurities are present or when they are present in such small amounts as not to interfere is as follows: A sample, the amount depending upon the per cent of lead, is weighed out into an ordinary 150 cc. electrolytic beaker. 35 cc.  $\text{HNO}_3$  is added and the beaker set on the stove to boil. The sample is boiled until brown fumes cease to be evolved. The sides of the beaker are washed down and .25 cc.  $\text{H}_2\text{SO}_4$  added. The solution is boiled again for one to two minutes, diluted to 140 cc. and heated to a temperature of  $85^\circ$  to  $95^\circ$ . It is then electrolyzed for  $1\frac{1}{2}$  to 2 hours at 3 to 3.5 amperes. The anodes are removed from the board, washed in water, in alcohol, and dried rapidly in an oven or on a hot plate, cooled, and weighed. The weight of  $\text{PbO}_2$  deposited is equal to the per cent of lead when a factor weight of the sample has been used.

If the lead content of the sample is low, it is recommended that a known amount of a standard lead solution (equivalent to about 25 mg.  $\text{PbO}_2$ ) be added to obtain a suitable lead content.

When running a sulfide ore there is always a little sulfate present either from the original ore or formed during the solution of the sample by the action of the nitric acid.

This sulfate present explains the excellent results usually obtained in the electrolytic analysis of sulfide ores.

The treatment of the ore depends upon the impurities present as certain elements interfere with the determination when present in very small amounts.. When these are present, it is necessary to perform a separation before electrolyzing.

In order to secure greater accuracy in ores and tailings which run as low as .1% it is often desired to take a larger sample. Because of the Mn usually present it is impossible to do this directly and a separation must be performed. A procedure which secures accurate results is as follows: Take the sample whose size depends upon the amount of lead present, and add 25 cc. HCl. Boil and dilute to 200 cc. Heat to boiling and pass in H<sub>2</sub>S. While passing in H<sub>2</sub>S add NH<sub>4</sub>OH drop by drop till the iron starts to come down. Continue the H<sub>2</sub>S for 10 minutes then filter and wash.. Return the paper and precipitate to the original beaker and add 10 cc. HNO<sub>3</sub> and 2 cc. H<sub>2</sub>SO<sub>4</sub>. Take to fumes adding HNO<sub>3</sub> as the charring proceeds until the residue is white. Cool, add 10 cc. HNO<sub>3</sub>, 15 cc. NH<sub>4</sub>NO<sub>3</sub> and boil. Filter and wash with hot water. Add 15 cc. HNO<sub>3</sub>, dilute and electrolyze as usual.

By this method a 20 gram sample in the case of low grade ores or a sample high in Mn can be analyzed with accurate results. If harmful impurities as Ag, Bi, As, Sb, Hg, Sn, P<sub>2</sub>O<sub>5</sub> or CrO<sub>4</sub> are present, this method can be adapted by including the usual methods of separation.

### Summary

The electrolytic determination of lead has been studied and the best results found to be obtained when the following conditions were observed: the sample should be electrolyzed for  $1\frac{1}{2}$  to 2 hours with a current of 3 to 3.5 amperes and placed on the board at a temperature of  $85^{\circ}$  to  $95^{\circ}$ . The anodes should be sand-blasted and clean and the amount of lead present between 5 and 150 milligrams. The solution should contain from 20% to 30% free nitric acid and about  $\frac{1}{4}$  cc. of sulfuric acid. Interfering elements should be absent.

The effects of interfering impurities were investigated and Ag, Bi, Mn, Sn, As, Hg,  $\text{CrO}_4$  and  $\text{P}_2\text{O}_5$  were found to cause poor results. If these elements are present in any great amount, a separation should be used before electrolysis. K, Na,  $\text{NH}_4$ , Ca, Mg, and Fe were found to have no interfering effect unless the solution was loaded with the salt.

The precision of the method was determined. It was found that the maximum variation obtained was only two to four tenths of a milligram when the lead content of the sample is between 5 and 150 mg. Samples of higher lead content can be run but the error is usually somewhat larger, about one milligram. The error is practically always negative.

The theoretical factor should always be used with this method in order to avoid low results.

### Bibliography

1. Becquerel            Ann. Chim. Phys., 43, 380 (1830)  
                          Z. Electrochem., 2, 232 (1895)
2. Despretz            Compt. rend., 45, 449 (1857)  
                          Phil. Mag. (4) 15, 78 (1858)
3. Luckow              Ding. J., 177, 296 (1865)  
                          Z. anal. Chem. 8, 24 (1869)  
  11, 9213 (1872)  
  19, 15 (1880)
4. May                  Am. Jour. Sci (3), 6, 255 (1873)
5. Herpin              Ding. J., 215, 440 (1875)  
                          Jahr. Ber., 28, 957 (1875)
6. Richie              Chem. News, 36, 96 (1877)  
                          Compt. rend., 85, 226 (1877)  
                          Jahr. Ber., 30, 1066 (1877)  
                          Z. anal. Chem., 17, 218 (1878)  
                          Ann. chim. phys. (5), 13, 508 (1878)
7. Schucht             Z. anal. Chem., 22, 487 (1883)
8. Classen and Reis    (Ber., 14, 1627 (1881))
9. Deros                Compt. rend., 97, 1068 (1883)
10. Tenny               Am. Chem. Jour., 5, 413 (1883)
11. Weiland            Ber., 17, 1611 (1884)
12. Cornelly and Walker    J. Chem. Soc., 53, 85 (1888)  
  Jahr. Ber., 41, 459 (1888)

13. Classen and Messinger Ber., 21, 368 (1888)
14. Kohn J. Soc. Chem. Ind., 10, 327 (1891)  
Chem. News, 68, 188 (1893)
15. Rudorff Z. angew. Chem., 5, 198 (1892)  
6, 453 (1893)
16. Smith and Salter J. anal. appl. Chem., 7, 128  
J. Soc. Chem. Ind., 12, 605 (1893)  
Jahr. Ber., 46, 2138 (1893)
17. Medicus Ber., 25, 2490 (1892)
18. Smith and Moyer J. anal. appl. Chem., 7, 252  
Chem. Zentr., 335 (1893)
19. Nissenson Z. angew. Chem., 6, 646 (1893)
20. Classen Ber., 27, 163 and 2060 (1894)  
Z. Electrochem., 1, 229 and 287 (1894)
21. Thomälsen Chem. Ztg., 18, 1355 (1894)  
Z. Electrochem., 1, 304 (1894)
22. Newman Chem. Ztg, 20, 381 (1896)  
Z. Electrochem., 2, 231, 252, 269 (1895)
23. Kreichgauer Ber., 27, 315 (1894)  
Z. anorg. Chem., 9, 89  
Jahr. Ber., 2867 (1895)  
Z. Angew. Chem., 8, 599 (1895)
24. Von Giese Z. Electrochem., 2, 586 and 598 (1896)
25. Steen Z. Angew. Chem., 8, 534 (1895)
26. Smith and Meyer Z. anorg. Chem., 4, 267

27. Heidenreich Ber., 29, 1585 (1896)
28. Winhart Pharm. Zentralhalle, 37, 759 (1896)  
Z. Electrochem., 4, 128 (1897)
29. Wolman Z. Electrochem., 3, 538 (1897)
30. Hollard Bull. soc. chim. (3), 19, 911  
Jahr. Ber., 759 (1898)
31. Kendrick Indiana Acad. Sci., 16, 109 (1900)
32. Marie Bull. Soc. chim., (3) 23, 563  
Cempt. rend., 130, 1032 (1900)
33. Geroult Ann. chim. anal., 5, 372  
Jahr. Ber., 469 (1900)
34. Moltkenhansen Chim. Ztg., 25, 393 (1901)  
Electrochem. Ind., 1, 371 (1903)
35. Nissenson and Danneel Z. Electrochem., 9, 760 (1903)
36. Fischer and Boddaert Z. Electrochem., 10, 949 (1904)
37. Hollard Cempt. rend., 136, 229 (1903)  
138, 142 (1904)  
Bull. soc. chim., (3) 31, 239 (1904)  
Chem. News, 88, 5 (1903)
38. Hollard and Bertaux Bull. soc. chim. (3), 31, 1124 (1904)  
J. Soc. Chem. Ind., 23, 1162 (1904)
39. Exner J. Am. Soc., 25, 904 (1903)
40. Guess Bull. Am. Inst. Mining Eng. 1239 (1905)  
J. Soc. Chem. Ind.

41. R. O. Smith J. Am. Chem. Soc., 27, 1287 (1905)
42. Vortmann Ann., 351, 283 (1907)
43. Gooch and Beyer Am. J. Sci., (4), 25, 249 (1908)  
(4), 27, 59 (1909)
44. Westercamp Arch. Pharm., 245, 132  
Jahr. Ber., 2244 (1905)
45. Sand Fr. Chem. Soc., 22, 43 (1906)  
23, 26 (1907)  
Trans. Chem. Soc., 91, 397 (1907)  
Z. Electrochem., 14, 7 (1908)  
Trans. Faraday Soc., 5, 159 to 209 (1909)  
Chem. News, 100, 269 (1910)
46. British Ass'n. Comm. on Electro-analysis Electrician, 63, 919 (1909)
47. Benner Min. Sci. Press, 101, 642 (1911)  
J. Ind. Eng., Chem., 2, 348 (1911)
48. Karr Metal. Ind., 8, 346 (1910)
49. Foerster Z. Electrochem., 16, 832 (1910)
50. Fairchild J. Ind. Eng. Chem., 3, 902 (1911)
51. Woiciechowski Met. Chem. Eng., 10, 108 (1912)
52. List Met. Chem. Eng., 10, 135 (1912)
53. E. F. Smith Electro-analysis, 1912 ed.
54. Hendrixson Am. Ch. Soc. Jour., 34, 389 (1912)
55. A. J. White Trans. Am. Electrochem. Soc., 24, (1914)
56. F. C. Mathers Trans. Am. Electrochem. Soc., 23, 178 (1913)



57. Fischer & Stecher Z. Electrochem., 17 & 18  
Farben Ztg., 18, 18 (1912)
58. Utz Arch. Chem. Mikros., 5, 309 (1912)
59. Bertiaux Ann. Chim. anal., 18, 217
60. Compagno, Rome Ann. Chim. applicata, 3, 164, (1915)
61. E. A. Lewis Metal Ind., 13, 463 (1915)
62. Mathers Trans. Am. Electrochem. Soc., 21, 313, (1912)  
27, 133, (1915)  
31, 271 (1917)
63. A. Czapski Z. f. anal. Ch., 57, 63 (1918)
64. B. P. Richardson Z. f. a. Ch., 56, 321 (1917)
65. F. B. Diana Chem. Analyst, 47, 6 (1926)
66. Hugo Beinhardt Z. f. a. Ch., 67, 97 (1926)
67. L. R. Raymond Chem. Analyst, 40, 3 (1923)
68. Maria Bleesen Z. f. a. Ch., 63, 225 (1923)
69. A. J. Engelenberg Z. f. a. Ch., 62, 273 (1923)
70. J. C. Bull Z. f. a. Ch., 41, 657 (1902)
71. H. Weber Z. f. a. Ch., 42, 628 (1903)
72. Holmes J. Ind. Eng. Chem., Anal. ed., 1, 210 (1929)
73. W. E. Hughes

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