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FACTORS AFFECTING THE ELECTROLYTIC DEPOSITION OF SMALL AMOUNTS OF  
LEAD AS LEAD DIOXIDE AND THE COMPOSITION OF THE DEPOSIT

BY  
THOMAS GORDON DAY

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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 IN CHEMISTRY

Rolla, Mo.

1932

Approved by.....*W.T. Schrenk*.....  
Professor of Chemistry

## FOREWORD

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The author wishes to express his appreciation to Dr. W. T. Schrenk for his advice and suggestions during the course of this investigation. Also to thank Mr. P. H. Delano for acquainting the author with his method for the analysis of lead at the beginning of this investigation.

CONTENTS

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Foreword - - - - - I  
Illustrations - - - - - III  
Introduction - - - - - 1  
Historical - - - - - 3  
The Problem - - - - - 6  
Standard Lead Solutions - - - - - 7  
The Determination of Lead in Samples Containing less  
than Five Milligrams of Lead - - - - - 9  
The Effect of Large Amounts of Zinc on the Electrolytic  
Determination of Lead - - - - - 11  
The Effect of Large Amounts of Copper on the Electro-  
lytic Determination of Lead - - - - - 16  
The Effect of Temperature During the Electrolysis on the  
Nature of the Deposit - - - - - 18  
The Effect of Various Drying conditions on the depos-  
ited  $PbO_2$  - - - - - 20  
The Composition of the Deposited  $PbO_2$  - - - - - 24  
Summary - - - - - 30  
Bibliography - - - - - 31  
Index - - - - - 38

ILLUSTRATIONS

---

<u>Table</u>		<u>Page</u>
I	Standardization of Lead Solution - - - - -	8
II	The Effect of the Acid Concentration on the Determination of Lead - - - - -	10
III	The Effect of Zinc in the Electrolytic Deposition of Lead - - - - -	12
IV	The Separation of Lead from large amounts of Zinc-	15
V	Comparison of Separation of Lead to the Addition of a Blank - - - - -	15
VI	The Effect of Copper on the Electrolytic Deposition of Lead - - - - -	17
VII	The Effect of the Initial Temperature on the Nature of the Deposit - - - - -	19
VIII	The PbO <sub>2</sub> Content of Electrodes dried in a 400 cc. beaker - - - - -	21
IX	The PbO <sub>2</sub> Content of Electrodes dried in a closed oven - - - - -	22
X	The PbO <sub>2</sub> Content of Electrodes dried on the hot plate - - - - -	22
XI	The Effect of over heating the bottom Anode when on the hot plate - - - - -	23
XII	The PbO <sub>2</sub> Content of Anodes dried at 150° C. - - -	27
XIII	The PbO <sub>2</sub> Content of Anodes dried at 110° C. - - -	27

XIV & XV The  $\text{PbO}_2$  Content of Anodes that were not  
dried - - - - - 28

XVI The  $\text{PbO}_2$  Content of Anodes dried in a Desiccator . - 29

## INTRODUCTION

The electrolytic determination of lead as lead dioxide is perhaps the most preferred method for the determination of lead due to its simplicity and because of the small part of the chemists' time that it commands. It is applicable especially to the determination of small amounts of lead although certain elements interfere with the accuracy of the determination. The method depends on the fact that in an acid solution the lead is deposited on the anode as lead dioxide and is weighed as such. The amount of lead is calculated from the lead dioxide deposited.

In a previous paper, by W. T. Schrenk and Mr. P. H. Delano, (Ind. & Eng. Chem., Anal. Ed., 3, 1931) an electrolytic method was described for the determination of lead in samples containing from 5 to 150 milligrams of lead. The size of the sample was limited by the amount of interfering elements which might be present, so that for ores, four factor weights is usually the maximum permissible. From this it is seen that the ordinary method is limited to samples containing 0.15 percent of lead and greater. As this is above the percentage of lead found in many substances that must be analyzed for their lead content a method for the determination of lead in substances of lower lead content is desired.

Conflicting statements have also been made regarding the nature of the lead dioxide deposited electrolytically. Because of this fact a study of the deposit under the conditions outlined was undertaken.



## HISTORICAL

There has been a great deal of work done on the electrolytic determination of lead as lead dioxide. Some of this work is given briefly below. Most of the work on this subject found in the literature was accomplished with anodes that differed greatly from the corrugated paddles that were used by Schrenk and Delano, whose apparatus and procedure were used as a basis for this investigation, and thus has no connection with this investigation.

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

Luckow (Dingl. Jour. 177, 395, 1865) first published a method for the quantitative determination of lead as the dioxide. He accomplished this in a nitric acid solution by electrolyzing for several hours.

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

Schrenk and Delano (Ind. & Eng. Chem., Anal. Ed., 3, 1931) used an apparatus similar to that of Guess. As this

method is used in this investigation some of the points of their work are presented. The electrolytic method for the determination of lead was studied and the best results were 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 amperes and placed on the electrolytic board at a temperature between 90 and 95° C. The anodes should be sand blasted and clean, and the amount of lead present between 5 and 150 milligrams. The solution should contain 20 to 30 percent free nitric acid and about 0.25 cc. of sulphuric acid. Interfering elements should be absent. The effect of various impurities were studied. In this method the theoretical factor  $Pb/PbO_2$  should always be used.

This last fact would indicate that  $PbO_2$  was the composition of the deposit. However  $PbO_2$  is reported by several authors to decompose at temperatures below that at which the deposit is dried in this method.

Reinders and Handburg (J. W. Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VII, Longmans Green and Co.) prepared a compound of  $PbO_2$  which was 99 to 100 percent pure. They report that there is a perceptible decomposition at 100° C., at 141° C. oxygen was detected, and at 200° C. the decomposition was marked. The

temperature of drying in this case was  $150^{\circ}$  C. This is considerably below the temperature of decomposition reported by other authors as ranging from 250 to  $550^{\circ}$  C.

Fresenius, Gooch, Mahin and others recommend drying at  $200^{\circ}$  C. This is considerably above the decomposition point reported by Reinders and Hanburg.

Factors other than the theoretical for the calculation of lead from the weight of the  $PbO_2$  have also been recommended by many authors.

## THE PROBLEM

The purpose of this investigation is to determine the best conditions for the quantitative deposition of lead when the content of this element is below 5 milligrams and to study the composition of the deposited  $\text{PbO}_2$ .

The following conditions were studied during the course of the investigation.

1. The maximum amounts of copper and zinc permissible for the quantitative determination of lead.
2. Methods of separating lead from zinc when the latter element is present in amounts greater than are permitted in the determination of the lead.
3. The separation of lead from copper when this element is in greater amounts than are permissible in the determination of the lead.
4. The effect of the temperature on the deposit during electrolysis.
5. The effect of various solvents, the method of drying, and the temperature of drying on the deposited lead dioxide.
6. The amount of lead in solution after electrolysis.
7. Variations in the method of solution of the ore, and treatment before electrolysis.

## STANDARD LEAD SOLUTIONS

Standard lead nitrate solutions were made by using lead nitrate which was prepared by treating 99.99 percent pure lead with nitric acid and recrystallizing the lead nitrate thus formed several times using nitric acid as a precipitating agent. The salt was dried and this product was used for preparing the solutions. The solution was made up to contain lead equivalent to 0.01 grams of  $PbO_2$  per cc. of solution. A solution containing 0.001 grams of  $PbO_2$  was made by diluting this solution. In all tables given the lead content of the solutions is expressed as equivalent  $PbO_2$ . The solutions were standardized by the sulphate method and also by the electrolytic method. The results of the standardization are given in table 1.

Table I

## Standardization of Lead Solutions

## SULPHATE METHOD

No. of cc. taken	Weight of $\text{PbSO}_4$	Weight of $\text{PbO}_2$ / cc.
15	.1901	.009996
15	.1909	.010048
15	.1917	.010080

## ELECTROLYTIC METHOD

No. of cc. taken	Weight of $\text{PbO}_2$	Weight of $\text{PbO}_2$ / cc.
20	.2000	.010000
20	.2003	.010015
20	.1999	.009995
20	.2001	.010005
20	.2000	.010000
20	.1999	.009995

THE DETERMINATION OF LEAD IN SAMPLES CONTAINING LESS THAN  
FIVE MILLIGRAMS OF LEAD

From previous observations it was thought that by decreasing the nitric acid concentration of the solutions to be electrolyzed that samples containing less than 5 milligrams of lead could be run for their lead content. A series of determinations were made to test this theory. A known amount of lead was treated with various amounts of nitric acid keeping the other conditions constant.

The following conditions were maintained during the deposition of the lead dioxide; 0.25 cc. of sulphuric acid, 140 cc. of solution, a temperature of 90° C., and electrolysis at 3 amperes for two hours. The amounts of concentrated nitric acid ranged between 5 and 35 cc. The anodes were washed in water, alcohol, and dried at 150° C. on a hot plate.

It was found that lowering the acid concentration made it possible to determine as small a quantity as 2.5 milligrams of lead dioxide, or 2.0 milligrams of lead. The best results for the deposition of lead dioxide in amounts less than 5 milligrams, were obtained with 25 cc. of free nitric acid in the 140 cc. of solution. A concentration of 15 to 20 percent free nitric acid is workable. The results are tabulated in table II.

Table II

The Effect of the Acid Concentration on the Determination of  
Lead

No. of determin- ations	Amount of PbO <sub>2</sub> used (milligrams)	Amount HNO <sub>3</sub> present	Average PbO <sub>2</sub> Deposited	Maximum deviation (milligrams)
5	10	35	10.02	0.1
5	10	30	10.06	0.1
5	10	25	9.96	0.3
6	10	20	9.85	0.3
6	10	15	10.10	0.3
5	10	10	9.74	1.1
6	10	5	8.11	2.5
6	5	35	4.90	0.2
6	5	30	4.91	0.2
4	5	25	4.97	0.1
5	5	20	5.04	0.8
6	5	15	4.73	0.8
6	5	10	4.31	1.2
6	5	5	4.00	1.5
6	3	35	2.40	1.0
5	3	30	2.22	1.0
5	3	25	2.92	0.2
6	3	20	2.01	1.2
6	3	15	2.20	1.1
6	3	10	2.06	1.4
5	2.5	30	2.44	0.3
5	2.5	25	2.50	0.1
6	2.5	20	1.36	1.3
6	2	30	1.50	0.7
6	2	25	1.41	0.8
6	2	20	1.66	0.8
6	1	35	0.61	0.9
6	1	30	0.31	0.9
6	1	25	0.25	1.0
6	1	20	0.13	1.0
6	1	15	0.06	1.0



THE EFFECT OF LARGE AMOUNTS OF ZINC ON THE ELECTROLYTIC  
DETERMINATION OF LEAD

It is often necessary to determine the lead content of metallic zinc and zinc salts in which the lead content is very low. Large samples of the metal or salt are often used and the lead is determined directly without a previous chemical separation of the lead from the zinc. To determine the extent to which zinc may be present without interfering with the deposition of the lead, determinations were made in which different amounts of zinc were present. Table III gives the results.

The zinc was added to the solutions to be electrolyzed in the form of the nitrate. This was secured from two sources from C. P. zinc nitrate, and C. P. zinc oxide. Blanks were run on each of these solutions. No lead was present in the zinc oxide. However it occurred in the zinc nitrate and where this solution was used the amount present in the original salt was subtracted from that found in the solution.

The data shows that when 10 milligrams of  $PbO_2$  is present 15 grams of zinc will not interfere with the deposition of the lead. The results were erratic when 15 to 20 grams of zinc were added. More than 20 grams produced exceedingly meager deposits. When 5 milligrams of  $PbO_2$  were used the effect of the same amounts of zinc was even greater.

Table III

The Effect of Zinc on the Electrolytic Deposition of Lead

No. of determinations	Grams of Zinc present	Amount PbO <sub>2</sub> present (milligrams)	Average PbO <sub>2</sub> Deposited	Maximum deviation (milligrams)
1	5	10	9.9	0.2
2	10	10	10.	0.3
2	15	10	10.	0.3
1	18	10	8.8	1.2
1	19	10	5.6	4.4
15	20	10	7.1	9.0
2	21	10	6.9	5.6
2	22	10	5.1	10.0
1	23	10	6.0	4.0
1	25	10	7.2	2.6
2	30	10	0.1	10.0
1	5	5	5.0	
1	10	5	5.1	
1	15	5	4.4	
1	18	5	1.0	
1	20	5	0.1	
1	21	5	0.0	
1	22	5	0.0	

Modification of the process before electrolysis is essential in cases where the zinc contains so little lead that 15 grams as a sample is insufficient. Two modifications of the usual procedure were studied.

In the first of these the lead was chemically separated from the zinc. This required the use of a sample containing a minimum of 10 milligrams of lead dioxide.

The separation of lead from large amounts of zinc was accomplished by adding an excess of ammonia to the solution obtained by dissolving the zinc sample in nitric acid. The complex salt,  $Zn(NO_3)_2 \cdot 4 NH_3 \cdot H_2O$ , is formed. All the lead was precipitated by adding ammonium sulphide. The addition of ammonium sulphide was continued until the white zinc sulphide formed. The precipitate was filtered off, dissolved in nitric acid, and the lead determined electrolytically following the usual procedure. This method gave quite satisfactory results. Data obtained by this method are given in table IV. No success attended the precipitation of lead by hydrogen sulphide from acid solutions containing an excess of ammonium chloride.

The second of these methods consisted of adding a known amount of lead to the zinc sample so that 10 milligrams of lead was present when a 15 gram sample of the zinc was taken. Electrolytic zinc served for this determination. A 15 gram sample was dissolved in nitric acid, a known amount of lead as

lead nitrate added to the solution which was then electrolyzed. Subtraction of the amount of lead added to the solution from the total lead deposited gave the amount of lead present in the electrolytic zinc. The result was checked by using the first described modification. The figures are shown in table V.

Table IV

The separation of lead from large amounts of zinc

No. of determinations	PbO <sub>2</sub> present (milligrams)	Average PbO <sub>2</sub> found after separation (mg.)
2	25	24.9
2	10	10.1

Table V

Comparison of separation of lead to the addition of a blank

SEPARATION		
Grams of zinc	PbO <sub>2</sub> (milligrams)	lead percent
30	7.5	.0219
30	7.0	<u>.0202</u>
		.0210 average
ADDITION OF 10 MILLIGRAMS PbO <sub>2</sub>		
15	13.8 - 10	.0219
15	13.4 - 10	<u>.0196</u>
		.0207 average

THE EFFECT OF LARGE AMOUNTS OF COPPER ON THE ELECTROLYTIC  
DEPOSITION OF LEAD

As lead is often determined in the presence of large amounts of copper the effect of the latter on the electrolytic deposition of lead dioxide was next studied. It was found that copper had a greater effect on the deposition of the lead than that of zinc. The effect of 5 grams caused an appreciable difference in the amount of lead deposited. Larger amounts of copper caused increasingly lower results. Because of these facts a method is desired for separating lead from large amounts of copper preliminary to the electrolytic deposition of the lead. The results of these studied may be seen in table VI.

The following methods of separating lead from copper were studied. Chromate in acetic acid solution, sulphide in ammoniacal solution, and chloride in alcoholic solution, but satisfactory results were not obtained in either case when large amounts of copper were present.

Table VI

The Effect of Copper on the Electrolytic Deposition of Lead

Grams of copper	PbO <sub>2</sub> taken (milligrams)	PbO <sub>2</sub> deposited (milligrams)
5	10	9.5
5	10	9.6
10	10	9.1
10	10	9.4
15	10	8.2
15	10	8.3
20	10	5.4
20	10	5.2
20	10	1.1
20	10	0.6

THE EFFECT OF THE TEMPERATURE DURING ELECTROLYSIS ON THE  
NATURE OF THE DEPOSIT

In the paper by Schrenk and Delano a temperature of between 90 and 95° C. was recommended for the lead solutions when placing them on the electrolytic board. During the determination of low leads in this investigation it was noticed that some of the deposits turned brown and even yellow rather than the black of the good deposit. It was found that in these cases the solutions had an initial temperature of about 95° C. Those that were black had an initial temperature of approximately 90° C. The difference in the deposits was quite noticeable. The good deposit was black in color, adhered firmly to the anode and was hard to remove by rubbing. It was crystalline under the microscope. The poor deposit was dark brown in larger samples and brown to yellow in the smaller samples, rubbed off easily, and under the microscope it did not show the crystalline structure of the good deposit. An initial temperature of 85 to 90° C. is recommended instead of 90 to 95° C. in order to secure a more firmly adhering deposit. Table VII summarizes the results obtained.



Table VII

The Effect of the Initial Temperature on the Nature of the  
Deposited Lead Dioxide

---

Placed on the electrolytic board at 95° C. 15 milligrams PbO<sub>2</sub>

No.	1	2	3	4	5	6
PbO <sub>2</sub> deposited	14.8	14.5	14.3	14.5	14.8	14.4

(Poor deposits, easily rubbed off, color brown,  
low results)

---

Placed on the electrolytic board at 90° C. 15 milligrams PbO<sub>2</sub>

No.	1	2	3	4	5	6
PbO <sub>2</sub> Deposited	14.9	15.2	14.9	14.8	15.2	15.1

(Good deposits, firmly attached, color black,  
good results)

---

THE EFFECT OF VARIOUS DRYING CONDITIONS ON THE DEPOSITED  
LEAD DIOXIDE.

In determining small amounts of lead it was found that there was a considerable difference in the color of the deposit dried in an electric oven at 150° C. compared to that dried on the hot plate at 150° C. The weight in the former case tended to be low and on opening the oven aldehyde could be detected by its odor. In all probability the lead dioxide oxidized the alcohol in the presence of the platinum and in the absence of excess air. To determine whether this was so, several electrodes containing lead dioxide were dried in a 400 cc. beaker thus exaggerating the effect of the oven. The oxidizing power of those dried in the beaker showed 84 to 86 percent PbO<sub>2</sub>, those dried in the oven 88 to 90 percent PbO<sub>2</sub>, and those dried on the hot plate 90 to 91 percent PbO<sub>2</sub>. This would indicate a decomposition of the lead dioxide with consequent oxidation of the alcohol in the closed oven. The data is shown in tables VIII, IX, and X.

The method of drying on the hot plate gave very good results. It was noticed however that one electrode in each set dried in this manner tended to be low in weight. Investigation showed that this was always the bottom electrode.

The one resting directly on the hot plate. This condition was easily corrected by turning over the stack of electrodes after a few seconds of heating and reversing after another short time. This allows the alcohol to be driven off at a low temperature. Whereas if the electrode is left in contact with the hot plate the temperature rises quickly resulting in decomposition, probably oxidation of the alcohol as is the case of the closed oven. A glass triangle placed under the electrodes also tends to aid in remedying this trouble.

Table VIII

Electrodes dried in a 400 cc. beaker

Weight of deposit	cc. of $KMnO_4$ equivalent to $PbO_2$	Normality of $KMnO_4$	Percent $PbO_2$
.0855	8.75	.06922	84.73
.0866	9.00	.06922	86.04

Table IX  
Electrodes Dried in a Closed Oven

Weight of deposit	cc. of $\text{KMnO}_4$ equal to $\text{PbO}_2$	Normality of $\text{KMnO}_4$	$\text{PbO}_2$ Percent
.1997	14.83	.1004	89.23
.1998	14.98	"	90.19
.1999	14.85	"	88.89
.2001	14.83	"	88.50
.1961	14.83	"	90.87

Table X  
Electrodes dried on hot plate

Weight of deposit	cc. of $\text{KMnO}_4$ equal to $\text{PbO}_2$	Normality of $\text{KMnO}_4$	$\text{PbO}_2$ Percent
.2000	15.04	.1003	90.20
.2003	15.33	"	91.40
.1999	15.39	"	91.20
.2001	15.04	"	90.20
.2002	14.99	"	89.90

Table XI

The Effect of Over Heating the Bottom Anode on the Hot Plate

1	2	3	4	5	6
<del>.0142</del>	.0142	.0142	.0141	.0142	<u>.0132</u>
<u>.0229</u>	.0249	.0249	.0250	.0250	.0248
<u>.0225</u>	.0249	.0249	.0250	.0250	.0249

## THE COMPOSITION OF THE DEPOSITED LEAD DIOXIDE

The composition of the deposit with regard to the  $\text{PbO}_2$  content has already been briefly mentioned in that section dealing with the drying of the anodes. The oxidizing power of the  $\text{PbO}_2$  was measured in the following manner: Exactly 50 cc. of a ferrous perchlorate solution - sufficient to cover the anode - was measured into a large beaker. The anode is immersed in the solution. The  $\text{PbO}_2$  is reduced by the ferrous salt. The anode is removed when all of the  $\text{PbO}_2$  has reacted, 15 cc. of preventative solution is added and the excess of ferrous iron is titrated with standard potassium permanganate solution. The reducing power of the ferrous perchlorate was estimated with each series of determinations. The ferrous perchlorate solution was made by dissolving iron wire in an excess of dilute perchloric acid. The permanganate solution was standardized by Bureau of Standards' sodium oxalate.

The  $\text{PbO}_2$  content of the anodes dried in various ways have been mentioned:

Those washed in alcohol and water, dried in a beaker had a  $\text{PbO}_2$  content of 84 to 86 percent.

Those washed in alcohol and water, dried in an oven had a  $\text{PbO}_2$  content of 89 to 90 percent.

Those washed in alcohol and water, dried on the hot plate had a  $\text{PbO}_2$  content of 90 to 91 percent.

Further investigation demonstrated that deposits washed in water alone, instead of water and alcohol, contained a higher percentage of  $\text{PbO}_2$ . Those washed in hot and cold water and then dried on the hot plate at  $150^\circ \text{C}$ . showed a  $\text{PbO}_2$  content of 94 to 95 percent. Those dried at  $110^\circ \text{C}$ . had a  $\text{PbO}_2$  content of 97 to 98 percent. This led to the belief that drying partially decomposed the  $\text{PbO}_2$ . Two sets of determinations were run without drying the deposit. In one case the deposit was washed in cold and then in hot water, in this case the  $\text{PbO}_2$  content was 98.5 percent. In the other case the deposit was washed twice in cold water and the  $\text{PbO}_2$  content was the same. These results may be seen in tables XII, XIII, XIV, XV. In another experiment the deposit was washed in water and dried in a desiccator for several days. The  $\text{PbO}_2$  content varied from 90 to 95 percent. The results by weight were either satisfactory or slightly high.

These data tend to substantiate the work of Reinders and Hanburg (J. W. Mellor, A comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VII, Longmans Green and Co.) on the decomposition of  $\text{PbO}_2$ , thus placing it at a temperature below that reported by other authors.

It must also be concluded from these data that the deposit is not 100 percent  $\text{PbO}_2$ . Even when all the lead is deposited from the solution and when the deposit is not pure  $\text{PbO}_2$ , the theoretical factor  $\text{Pb}/\text{PbO}_2$  gives the true lead content.



Table XII

Anodes dried at 150° C. washed with cold and hot water

Weight of deposit	cc. of $\text{KMnO}_4$ equal to $\text{PbO}_2$	Normality of $\text{KMnO}_4$	$\text{PbO}_2$ Percent
.2004	22.92	.06922	94.73
.2003	22.93	.06922	94.78

Table XIII

Anodes dried at 110° C. washed with cold and hot water

*Weight of deposit	cc. of $\text{KMnO}_4$ equal to $\text{PbO}_2$	Normality of $\text{KMnO}_4$	$\text{PbO}_2$ Percent
.1010	11.78	.06922	97.57
.1012	11.79	"	97.65
.1010	11.79	"	97.65
.1012	11.77	"	97.49
.1010	11.76	"	97.41
.1015	11.76	"	97.41

\* The weight of the deposit is high due to the lower temperature of drying. The percentage is figured from the amount of  $\text{PbO}_2$  taken, .1000 gram.

Table XIV

Anodes washed in cold and hot water and titrated without  
drying

Weight of PbO <sub>2</sub> taken	cc. of KMnO <sub>4</sub> equal to PbO <sub>2</sub>	Normality of KMnO <sub>4</sub>	PbO <sub>2</sub> Percent
.1000	11.84	.06922	98.07
.1000	11.90	"	98.57
.1000	11.89	"	98.48
.1000	11.84	"	98.07
.1000	11.90	"	98.57
.1000	11.83	"	98.53

Table XV

Anodes washed in cold water and titrated without drying

Weight of PbO <sub>2</sub> taken	cc. of KMnO <sub>4</sub> equal to PbO <sub>2</sub>	Normality of KMnO <sub>4</sub>	PbO <sub>2</sub> Percent
.1000	10.69	.07692	98.38
.1000	10.69	"	98.38
.1000	10.68	"	98.30
.1000	10.68	"	98.30
.1000	10.67	"	98.21
.1000	10.72	"	98.67

Table XVI

Anodes washed in cold and hot water and dried in a desiccator

Weight of deposit	cc. of $\text{KMnO}_4$ equal to $\text{PbO}_2$	Normality of $\text{KMnO}_4$	$\text{PbO}_2$ Percent
.0961	9.80	.07692	90.20
.1000	10.10	"	92.96
.0992	10.28	"	94.62
.1012	10.36	"	95.36

## SUMMARY

- I. The electrolytic method for the determination of lead has been extended to the determination of as small a quantity as 2 milligrams of lead. This has been accomplished by lowering the acid concentration.
- II. The amount of zinc which may be present without interfering with the deposition of  $\text{PbO}_2$  has been determined. A satisfactory method for the separation of lead from large amounts of zinc is described.
- III. The effect of large amounts of copper on the deposition of  $\text{PbO}_2$  has been determined.
- IV. The temperature of electrolysis should not be over  $90^\circ \text{C}$ .
- V. Tests indicate that there is no residual lead in the electrolyzed solution.
- VI. Variations in the method of solution of ores does not effect the determination provided that the solution is not above  $90^\circ \text{C}$ . when placed on the electrolytic board.
- VII. The deposit on the anode is not 100 percent  $\text{PbO}_2$ . This is shown by the oxidizing power of the deposit. However all the lead is removed from solution and the theoretical factor must be used.

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INDEX

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Acid concentration, effect of, on low leads - - - - -	9
Bibliography - - - - -	31
Contents - - - - -	II
Copper, effect on the deposition of lead - - - - -	16
Copper, separation of large amounts from lead - - - - -	16
Composition of the deposited $PbO_2$ - - - - -	24
Delano and Schrenk, Method of - - - - -	3
Drying, The effect of, on the deposit - - - - -	20
Drying, The effect of, on the hot plate at $150^\circ C.$ - - -	20
Drying, The effect of, in an oven at $150^\circ C.$ - - - - -	20
Effect of, zinc on the deposit - - - - -	11
Effect of copper on the deposit - - - - -	16
Effect of Temperature during electrolysis on the deposit-	18
Effect of drying the deposit at different temperatures -	20
Factors for calculating the lead from the weight of the deposit - - - - -	5
Foreword - - - - -	I
Guess' Method - - - - -	3
Historical - - - - -	3
Illustrations - - - - -	-III
Introduction - - - - -	1
Lead Dioxide content of the deposit - - - - -	24

Lead, separation from large amounts of zinc - - - - -	13
Lead, separation from large amounts of copper - - - - -	16
Low Lead, Determinations of - - - - -	9
Modification of the method for low lead in the presence of zinc - - - - -	13
Oxidizing power, Method of determining, in PbO <sub>2</sub> - - - - -	24
Problem - - - - -	6
Standard Lead Solutions - - - - -	7
Summary - - - - -	30
Temperature, Effect of, during electrolysis on the nature of the deposit - - - - -	18
Variations in the method of solution of ores - - - - -	30
Zinc, effect on the determination of lead - - - - -	11
Zinc solutions - - - - -	11
Zinc, Separation of large amounts of, from small amounts of lead - - - - -	13