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ELECTROLYTIC BOARD FOR THE DETERMINATION OF LEAD, AND
SOME COMMENTS ON THE PROCEDURE FOR LEAD IN LOW-GRADE
TAILINGS OF THE SOUTHEAST MISSOURI LEAD DISTRICT.

- By -

Oliver Wendell Holmes.

A

T H E S I S

submitted to the Faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in fulfillment of the work required for the
Degree of
CHEMICAL ENGINEER.

Rolla, Missouri,

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35705

Approved:

W. T. Schrenk
Professor of Chemistry.

TABLE OF CONTENTS.

	<u>P a g e</u>
Preface	ii
Acknowledgments	ii
Introduction	1
Apparatus	2
Method	4
General Discussion	5
Precautions	5
Accuracy	7
Copper	7
Cost and Upkeep	9
Summary	9
Conclusions	10
Bibliography	11
General Index	12

P R E F A C E.

This thesis is presented to the Faculty of the Missouri School of Mines and Metallurgy in fulfillment of the work required for the degree of Chemical Engineer.

The results reported herein are the direct outgrowth of experience obtained during the course of milling research on the lead ores of the Southeast Missouri Lead Belt for the last three years. This research has been carried on by the Mississippi Valley Experiment Station of the United States Bureau of Mines, working in cooperation with the Missouri School of Mines and Metallurgy, Rolla, Missouri.

ACKNOWLEDGMENTS.

Acknowledgments are due Mr. William Kahlbaum, formerly Assistant Metallurgist, U. S. Bureau of Mines for his assistance in the construction of the electrolytic board; to Mr. Will H. Coghill and J. B. Clemmer, Supervising Engineer and Junior Metallurgist of the Mississippi Valley Station of the Bureau of Mines, respectively, for their constructive criticism; to Mr. D. P. Morgan, Junior Chemist of the same station, and to Dr. W. T. Schrenk, Professor of Chemistry at the Missouri School of Mines and Metallurgy for their helpful suggestions and advice in the preparation of the manuscript.

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INTRODUCTION.

Recent improvements in the practice of milling lead ores of the Southeast Missouri Lead Mining District has resulted in the production of low-grade mill tailings. The tenor of the lead in the tailings is often between 0.05 and 0.25 per cent. In view of the fact that large tonnages are handled daily and that further improvements are under way, it is imperative that the lead content of these tailings be accurately determined.

For this purpose an electrolytic board, which speeds up the electrolytic determination of lead in low-grade mill tailings, has been devised at the Mississippi Valley Experiment Station of the United States Bureau of Mines, in cooperation with the Missouri School of Mines and Metallurgy, Rolla, Missouri.

The electrolytic board is the result of several years work in cooperation with large lead mining companies. The method employed in the determination of small amounts of lead has been included as well as certain precautionary measures.

APPARATUS.

The apparatus used is a modification of the Guess-Haultain cabinet, and is so arranged that 24 leads, or 24 coppers, or 12 leads and 12 coppers may be run simultaneously. A photograph of the cabinet is shown in Figure 1, the details of which are given in the appended drawing. It has two rows of 12 cells each, one above the other, and any cell may be removed from the circuit without disturbing the others. Stationary anodes and cathodes are used. The anode is made of sand-blasted corrugated sheet platinum. The dimensions of the corrugated anode are 6 by 3 centimeters. Each cell contains two platinum foil cathodes, 8.4 by 0.3 centimeters. The electrode holders are made of aluminum, and extend horizontally from the surface of the cabinet. When the electrodes are in place a 150 ml. beaker of regular form with lip, containing the electrolyte may be put in place and the moveable beaker-rest pulled out.

When it is desired to remove an anode while a series of determinations is being made, the removal is accomplished in the following manner:

The beaker support is slipped back into the cabinet, the knife switch corresponding to the cell is closed, and simultaneously, the beaker containing the electrolyte is lowered and removed. The anode may then be removed and treated in the usual manner.

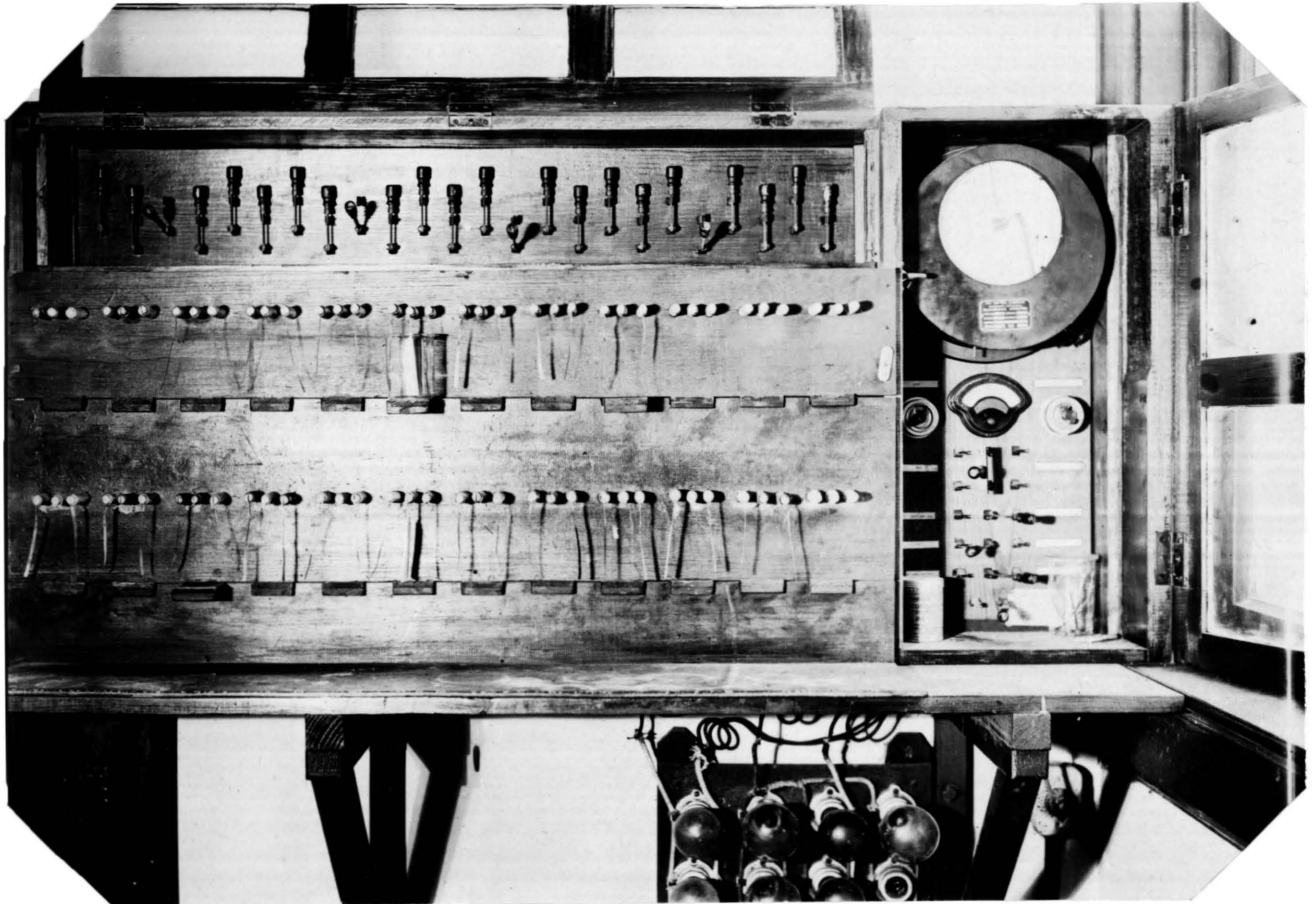


Figure 1. View of Electrolytic Board.

The cabinet contains as an integral part, a recording ammeter of 0 to 5 amperes capacity for overnight determinations of copper. Another small ammeter with a range of 0 to 6 amperes is incorporated in the apparatus for lead work.

By means of conveniently arranged switches a line current of 220 volts, D. C., may be thrown into any series of cells and the amperage recorded on the desired ammeter. The amperage may be adjusted by means of a variable resistance using either a rheostat or a bank of carbon lamps.

The aluminum electrode holders were originally $2\text{-}\frac{7}{8}$ inches by $3\frac{1}{8}$ inch at the base, tapering to $1\frac{1}{4}$ inch at the end. These were cast in a carbon block mould, and later the base machined to $1\frac{1}{4}$ inch. The electrode holders are riveted to aluminum plates for connection at the back of the cabinet face. They were cut lengthwise through the middle to a depth of $1\text{-}\frac{5}{8}$ inches and then cut from the side until one of the pieces fell away. When in service the pieces are held together by gum rubber tubing slipped over them they make a clamp that holds the electrodes firmly when inserted in the slit. The wires are protected from fumes by placing them behind the cabinet face.

The apparatus is a modification of those used in the Southeast Missouri Lead Belt. It incorporates new ideas and details, which simplify the manipulation.

METHOD.

The customary procedure is as follows:

In this method it is convenient to weigh one or more factor weights* of the sample, depending upon the lead content. When the lead content of the sample does not exceed two per cent, two or more factor weights are used; when it is from two to seven per cent, one factor weight is used. If the sample contains over seven per cent lead the molybdate method is to be recommended.

The theoretical factor for converting lead dioxide to lead is 0.866.

Weigh the amount of sample decided upon into a 150 ml. beaker. Add 25 ml. of nitric acid (d 1.4), heat until the evolution of brown fumes has ceased. Wash down the sides of the beaker with water and add 15 to 20 ml. of a solution of ammonium nitrate, made by dissolving one pound of the chemically pure salt in two liters of distilled water. Dilute the electrolyte to about 145 ml. Electrolyze for two hours at a temperature of 70 to 80° C., with a current density of two amperes and a potential of 3.5 volts.

GENERAL DISCUSSION.

When interfering elements are absent electrolysis may extend overnight at 0.2 amperes.

When the lead content of the electrolyte is less than ten milligrams, 25 ml. of a solution of lead nitrate, containing the equivalent of 0.00048 gram of lead dioxide per ml., should be added before electrolysis. The addition of the solution of lead nitrate is to increase the lead content to the point where maximum deposition is obtainable. Experiment has shown that the results are more satisfactory when the electrolyte contains the equivalent of 12 to 80 milligrams of lead dioxide. It is necessary to take certain precautions to insure best results.

PRECAUTIONS.

This method cannot be used with a high degree of accuracy when the electrolyte contains more than 0.03 gram of manganese. The quantity of manganese may be regulated by reducing the size of the sample. The detrimental effect of manganese will then be overcome by the presence of the given amount of free nitric acid in the electrolyte. In no case should the concentration of free nitric acid in the electrolyte exceed 15 per cent by volume. The presence of manganese in a sample prevents electrolysis at low current density for a long period of time. The manganese would deposit with the lead.

Copper, iron, and zinc do not interfere with the deposition of lead. Antimony and bismuth, when present, would likely have to be combatted in the same manner as manganese, that is, by reducing the size of the sample taken for analysis; no recent experience has been encountered with antimony and bismuth. Arsenic must be removed before electrolysis.

The acidity of the electrolyte has a very important effect upon the deposition of the lead dioxide. Experience has shown that 15 per cent by volume of nitric acid (d 1.4) is necessary for the best results. Erratic results are obtained when the acid concentration varies far from this value.

Before electrolysis the anodes are cleaned by immersing in a dilute solution of nitric and oxalic acids. They are then brushed with a camel hair brush, rinsed with distilled water, ignited to constant weight in the flame of a Fisher burner, cooled in a desiccator, and weighed.

After electrolysis is complete the anode is detached and immediately immersed in a beaker of distilled water. It is dipped consecutively into two beakers containing ethyl alcohol. The anode is removed from the beaker and the alcohol burned off, keeping the anode in motion to prevent the alteration of the deposit. Cool in a desiccator and weigh.

ACCURACY.

It has been found that this method of electrolytic recovery of the lead in mill tailings is the best for mill practice when the time element is standardized. But research has to be done to determine its accuracy.

Because of the simplified procedure and the small number of steps necessary, the electrolytic method is much to be desired over others. In fact it is possible to accomplish more determinations with a high degree of accuracy in less time than when any other method is employed.

A number of mill tailing samples were analyzed by the author and a chemist of the National Lead Company of St. Francois, Missouri. The results obtained by using this method are given in Table I.

COPPER.

The apparatus as given for lead determinations is also adapted to, and suitable for, the determination of copper.

The method employed is the standard procedure for electrolytic copper. The apparatus is not the type generally employed for such work, but highly accurate results are obtainable by overnight deposition.

Table I. Comparison of Results.

Sample Number	Assay Per cent Lead		Difference
	Results obtained by National Lead Company's Chemist	Results obtained by the author	
1	0.08	0.075	0.005
2	0.10	0.095	0.005
3	0.10	0.098	0.002
4	0.70	0.70	--
5	0.52	0.52	--
6	0.44	0.45	0.010
7	0.40	0.39	0.010
8	0.30	0.31	0.010
9	0.30	0.29	0.010
10	0.09	0.08	0.010
11	0.04	0.05	0.010
12	0.045	0.06	0.015
13	0.04	0.05	0.010

COST AND UPKEEP.

The first cost of such an apparatus is high, but thereafter the main expense is for the current consumed in operation. It needs but little care and will last indefinitely.

SUMMARY.

It is desirable to keep the following points in mind in order that the highest degree of accuracy may be obtained.

1. The size of the sample taken depends not only on the lead content of the ore but on the manganese content as well.
2. Maximum recovery is not possible when the lead content of the solution is below 12 milligrams PbO_2 .
3. Low results are obtained when the solution contains more than 70 milligrams of lead, because the deposit flakes off.
4. Manganese is deposited very readily from solutions when a low current density is employed.
5. Practically complete deposition of lead from pure solutions is obtained by using low current densities for long periods of time.

6. Current densities of 2 to 3 amperes for a period of two hours is sufficient for low-grade materials; electrolysis for two hours is a good standard.
7. The electrodes should be sand-blasted occasionally to facilitate the adherence of the deposit.

CONCLUSIONS.

In view of the fact that the electrolytic method for the determination of lead is rapid and accurate, it is to be preferred over gravimetric methods whenever it can be applied, or whenever a large number of determinations are to be made.

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GENERAL INDEX.

	<u>P a g e</u>
Accuracy	7
Acidity	5
Acknowledgments	ii
Ammeters	3
Ammonium nitrate solution	4
Anode cleaning	6
construction	2
weighing	6
Antimony	6
Arsenic	6
Bismuth	6
Blueprint	Appended
Cathode construction	2
Comparison of Analyses, Table I	8
Conclusions	10
Conditions of electrolysis	4
Copper	6
Cost and Upkeep	9
Determination of Copper	7
Electrode holders	3
Factor	4
Guess-Haultain Cabinet	2
Iron	6
Lead nitrate solution	4
Manganese	5
Method	4
Removal of anodes from circuit	2
Summary	9
Tenor of mill tailings	1
Zinc	6