with the result that the platinum was not attacked, but the cadmium was not completely precipitated even after allowing the current to pass for thirty-five minutes. This incomplete precipitation was observed in the previous experiments.

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THE RAPID DETERMINATION OF LEAD IN THE ELECTROLYTIC WAY.[1]

BY RALPH O. SMITH.

IN MAKING this study it was not proposed to determine the lead as metal but as dioxide, adopting, however, the course pursued by Exner.[2]

At the very beginning care was taken to use perfectly pure lead nitrate, that there might be no question as to its metal content.

After the solution of the salt had been made, definite portions of it were removed and evaporated to dryness with sulphuric acid, and after carefully heating, the residue was weighed as lead sulphate.

Thus, 25 cc. of the stock solution of the lead nitrate gave 0.3635 gram of lead sulphate, equivalent to 0.2438 gram of metallic lead, or 0.2867 gram of lead dioxide.

To 25 cc. of this solution 20 cc. of nitric acid (sp. gr. 1.4) were added and then diluted with water to 115 cc. The solution was heated to 70° before the current was allowed to pass.

These were the conditions in each of the following experiments. The rotating electrode, which in this case was the cathode, performed about 450 revolutions a minute.

TABLE I.

Experiment.	Time. Minutes.	PbO_2 found.	Pb calculated.	Pb present.	Volts.	N.D $_{100}$ amperes.
1	3	0.2478	0.2146	0.2483	3.7	11.6–11.0
2	6	0.2679	0.2320	0.2483	3.9–3.8	10 –10.8
3	9	0.2807	0.2431	0.2483	3.8	11
4	12	0.2858	0.2475	0.2483	3.7–3.8	10.8–11
5	15	0.2873	0.2488	0.2483	3.7–3.8	11
6	18	0.2873	0.2488	0.2483	3.9	11.2–11
7	15	0.2874	0.2489	0.2483	4.0	13

[1] From the author's thesis for the Ph.D. degree.
[2] This Journal, **25**, 896.

The solutions from these experiments were siphoned off from the deposits. They were combined with the wash-water and evaporated to dryness. The residue was taken up with a little dilute acetic acid and a few drops of a potassium bichromate solution were introduced. After some hours, precipitates were observed in all the cases excepting in Expts. 5, 6 and 7. These precipitates were yellow in color and dissolved in sodium hydroxide, indicating therefore that the lead had not been completely precipitated.

A slight deposit of metallic lead was observed upon the cathode in these cases, even when 20 cc. of nitric acid were present. It is true that no perceptible increase in the weight of the cathode could be noticed, but when it was treated with a little dilute acetic acid and tested, as above indicated, traces of lead chromate were noticed. It has frequently been observed in the electrolysis of acid solutions of lead salts, that metal is precipitated upon the cathode and that it gradually dissolves as the decomposition proceeds and is deposited upon the anode as dioxide. To hasten the solution of any metal which found its way to the cathode, the current was interrupted for a short time—five seconds—about the middle of the experiment and again for a brief period before the precipitation was completed.

At the end of each determination the acid liquid, as previously mentioned, was siphoned off without interrupting the current, fresh water being introduced to keep the level above the deposit until the ammeter stood at zero. The current was then interrupted, the dish removed, and its contents washed with absolute alcohol and with absolute ether. It was dried to constant weight at 230° C. and allowed to cool in a desiccator for fifteen minutes, when it was weighed. The deposit did not alter in weight after standing in the balance for two hours. It was removed from the dish with a mixture of oxalic and nitric acids.

In the next series of experiments the conditions were the same as those which prevailed in the first series with the exception that 50 cc. of the lead nitrate solution, equivalent to 0.4996 gram of lead, were used. The results were as follows:

TABLE II.

Experiment.	Time. Minutes.	PbO$_2$ found.	Pb found.	Pb present.	Volts.	N.D$_{100}$ amperes.
8	5	0.4940	0.4279	0.4996	4	11
9	10	0.5708	0.4944	0.4996	4 -3.9	11
10	15	0.5747	0.4978	0.4996	3.9–3.8	11 -10.9
11	20	0.5770	0.4997	0.4996	4 -3.6	11.1–11
12	25	0.5787	0.5012	0.4996	3.8–3.5	11.2–11
13	30	0.5789	0.5014	0.4996	3.6–3.7	11.2–10.8

The time-curve exhibited in the plate was constructed from the results presented in these two series. The residual liquids from the deposits were, with the exception of those in Expts. 12 and 13, found to contain traces of lead.
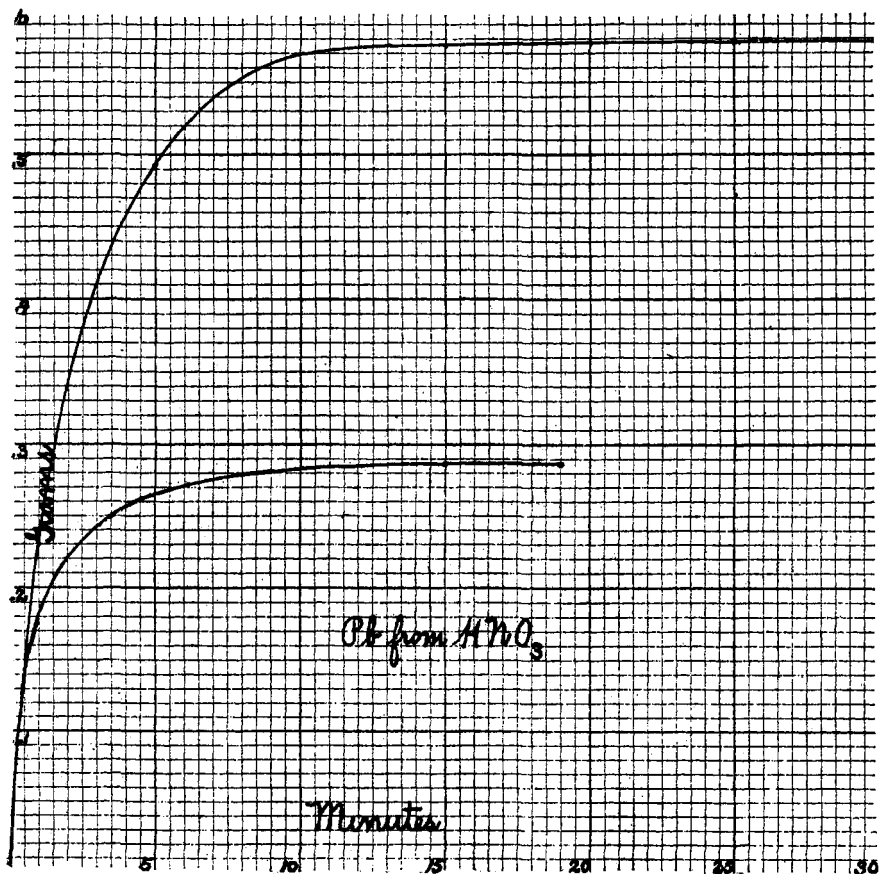
Rate of deposition of lead dioxide.

It will be seen from the series just presented that the maximum time period for a quarter of a gram of metal is fifteen minutes, and the maximum time for half a gram of metal is twenty-five minutes. It will be further noticed that the amount of lead calculated from the deposits is too large by 0.005 gram in the former case, and 0.0016 to 0.0018 gram in the latter.

To make sure that the preceding deductions were correct and to learn how far the method was accurate, a third series of experiments was conducted, different weights of material being used. Again the amount of lead in the nitrate was first determined as sulphate. The electrolyte and the conditions of electrolysis were the same as in the preceding experiments. The results of this third series were as follows:

TABLE III.

Experiment.	Time. Minutes.	PbO$_2$ found.	Pb calculated.	Pb present.	Error. Mg.	Error. Per cent.	Volts.	N.D$_{100}$ amperes.
12	25	0.5787	0.5021	0.4996	+1.6	+0.32	3.8–3.5	11.2–11
13	30	0.5789	0.5014	0.4996	+1.8	+0.36	3.6–3.7	11.2–10.8
14	25	0.5781	0.5007	0.4992	+1.5	+0.30	4 –3.6	11.3–11.2
15	30	0.5780	0.5006	0.4992	+1.4	+0.28	3.6	11
5	15	0.2873	0.2488	0.2483	+0.5	+0.20	3.7–3.8	10.8–11
6	18	0.2873	0.2488	0.2483	+0.5	+0.20	3.9	11.2–11
7	15	0.2874	0.2489	0.2483	+0.6	+0.24	4	13
16	15	0.2885	0.2499	0.2496	+0.3	+0.12	3.8–3.7	11
17	20	0.2889	0.2502	0.2496	+0.6	+0.24	3.8	11
18	180	0.2887	0.2501	0.2496	+0.5	+0.20	2.3–2.1	1.6– 1.5
19	15	0.1137	0.0985	0.0982	+0.3	+0.26	3.8–3.7	11 –11.2
20	16	0.1136	0.0984	0.0982	+0.2	+0.17	4 –3.7	11.4
21	17	0.0567	0.0491	0.0491	±0.0	±0.00	4 –3.7	11.5–11
22	16	0.0563	0.0488	0.0491	–0.3	±0.61	3.9–3.8	11.4–10.8
23	15	0.0569	0.0493	0.0491	+0.2	+0.41	3.9–3.6	11.2–11
24	15	0.0565	0.0489	0.0491	–0.2	–0.41	4 –3.6	11 –10.9
25	15	0.0567	0.0491	0.0491	±0.0	±0.00	3.8–3.6	11.2–11

It is plain that the results of determinations of different amounts of lead agree very well for each definite weight, but it will be discovered on turning to column 6, beginning with the smallest deposit of lead dioxide, that the lead equivalents are too high, and that the error grows gradually with the weight of the deposits until in the case of those approximating 0.58 gram of lead dioxide the lead equivalent is on the average 1.5 mg. too high. This is exactly the opposite of what Hollard[1] observed. He used station-

[1] *Ann. de Chim. Anal.*, 4, 11.

ary electrodes and dried the deposits at 200° C. for a period of fifteen minutes.

In Expt. 18 the cathode was stationary, and the result is in close agreement with the others of its class. It is of interest to note the effect of the increase of temperature upon this deposit.

TABLE IV.

Minutes heated.	Temperature.	Weight of deposit.
30	180–190°	0.2895
30	180–190°	0.2895
15	230°	0.2889
15	230°	0.2887
120	230°	0.2887

These changes led to a study of the weights of all the deposits at different temperatures: 180–190° (Classen), at 200° for fifteen minutes (Hollard), and finally to constant weight at 230°, an idea taken from the work of Carnelly and Walker.[1]

TABLE V.

Experi-ment.	Minutes heated.	Temperature.	Weight of deposit.	Pb present.	Pb/PbO₂ factor.
12	30	180–190°	0.5805		
	90	180–190°	0.5805		
	30	190–210°	0.5799		
	120	190–210°	0.5799		
	30	240°	0.5787		
	180	240°	0.5787	0.4996	0.8633
13	60	240°	0.5789		
	30	240°	0.5789	0.4996	0.8630
14	30	200°	0.5788		
	30	200°	0.5788		
	30	240°	0.5781		
	30	240°	0.5781	0.4992	0.8635
15	30	200°	0.5788		
	30	200°	0.5790		
	30	230°	0.5780		
	120	240°	0.5780	0.4992.	0.8635

Average, 0.8634

The weights of these deposits were not changed by further drying for two hours at 270° C., and consequently show that deposits of lead dioxide approximating 0.5 gram in weight do not really have a constant composition until they have been dried at 230° C.

[1] *J. Chem. Soc.* (London), **53**, 85.

Deposits of lead dioxide approximating 0.288 gram in weight were heated at different temperatures with the following results:

TABLE VI.

Experiment.	Minutes heated.	Temperature.	Weight of deposit.	Pb present.	Pb/PbO$_2$ factor.
5	15	230°	0.2878		
	60	230°	0.2873		
	60	230°	0.2873	0.2483	0.8641
6	30	230°	0.2873	0.2483	0.8641
7	60	200–220°	0.2874		
	40	230–250°	0.2873		
	140	240°	0.2874	0.2483	0.8640
16	30	200°	0.2885		
	30	200°	0.2885		
	30	230°	0.2885		
	30	230°	0.2885	0.2496	0.8651
17	30	200°	0.2889		
	30	200°	0.2889		
	30	230°	0.2889	0.2496	0.8640
18	See Table IV.		0.2887	0.2496	0.8646

Average, 0.8643

It is evident that this quantity of lead dioxide reaches a constant weight when dried at 200°, and that this condition is reached only after it has been exposed to that temperature for more than a half hour.

When the quantity of the lead dioxide deposit is small, say from 0.05 to 0.1 gram, it is hardly necessary to introduce an analytical factor.

The following experiments show the weights of such smaller deposits (1) after washing with absolute alcohol and absolute ether and (2) after they have been dried at 230° to constant weight. They further indicate that there is little probability of the formation of a definite hydrated lead dioxide in such cases.

TABLE VII.

Experiment.	(1).	(2).	Loss.
19	0.1147	0.1137	0.0010
20	0.1150	0.1136	0.0014
21	0.0570	0.0567	0.0003
22	0.0567	0.0563	0.0004
23	0.0569	....	....
24	0.0573	0.0565	0.0008
25	0.0569	0.0567	0.0002

It may be fairly concluded from the preceding experiments that deposits of lead dioxide made in the electrolytic way will be too high unless they have been dried for definite periods at a temperature ranging from 200° to 230° C. Much depends upon the weight of the deposits, but an analytical factor will be necessary.

It is not probable that the excessive weight of the deposits is due to the formation and precipitation of a higher oxide of lead than the dioxide. It is more likely, as is evidenced by Schucht's[1] work also, that the final traces of water, adhering or included, are expelled with difficulty. The fact that the error increases with the density of the deposit might be advanced as an argument in favor of this view.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 109.]

SOME ACYL DERIVATIVES OF HOMOANTHRANILIC NITRILE, AND THE 7-METHYL-4-KETODIHYDRO-QUINAZOLINES PREPARED THEREFROM.[2]

BY MARSTON TAYLOR BOGERT AND ALFRED HOFFMAN.

IN A previous paper, Bogert and Hand[3] have shown that quinazolines can be very easily obtained from anthranilic nitrile. In the present paper, the method is applied to homoanthranilic nitrile with equally successful results.

Homoanthranilic nitrile was prepared from *m*-nitro-*p*-toluidine by converting the latter into *m*-nitro-*p*-tolunitrile by the Sandmeyer reaction, and then reducing the nitro group with stannous chloride and hydrochloric acid:
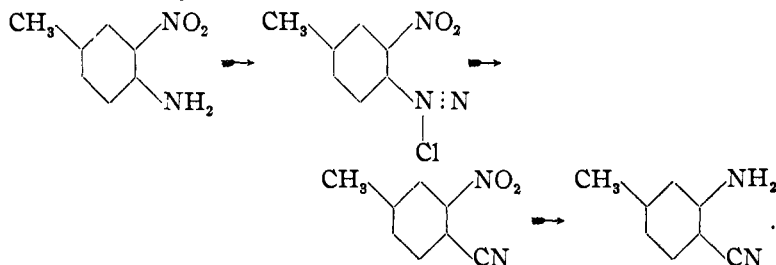
[1] Z. anal. Chem., 19, 4.
[2] Read before the New York Section of the American Chemical Society, May 5, 1905.
[3] This Journal, 24, 1031 (1902).