The results thus far obtained in this investigation may be briefly summarized as follows :

The Gibbs method of determining the equivalent weight does not give exact results even when the conditions prevailing in different series of determinations are identical.

There is a slight error in the sulphate method of determining the equivalent weights, due to the formation of some acid sulphate.

Of the many methods of partial precipitation which were investigated the following seem to be the most rapid : primary potassium oxalate, potassium trinitride, partial decomposition by fusion of the nitrates with alkali nitrates, and electrolysis of neutral solutions. Magnesia usta causes fractionation of this material, but the progress of the separation can not be easily controlled with the spectroscope as was done by Muthmann in his work on didymium.

One of the best methods for the separation of yttria from the other members of this group is that of fractional precipitation of a neutral solution by potassium chromate. Quite pure yttria may be obtained in this manner at the end of a comparatively short series of fractions.

Unusually rapid separation of the earths of this group is effected by ammonium carbonate and acetic acid. Fractional solution of the hydroxides by means of a saturated ammonium carbonate solution causes quite rapid separation, and if this ammonium carbonate solution be fractionally precipitated by addition of acetic acid, the results are most striking. Ytterbium is the last of the earths to be precipitated by this treatment. Erbium and terbium concentrate in the first fraction.

CORNELL UNIVERSITY,
January, 1902.

# ELECTROLYTIC DEPOSITION OF LEAD FROM A PHOSPHORIC ACID SOLUTION.

BY A. F. LINN.

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LEAD has been successfully deposited as metal, by the electric current, from a solution of the double oxalate, the acetate, the oxide in sodium hydroxide, and also the phosphate dissolved in the latter reagent.[1] From each of these solutions the separa-

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[1] Smith's "Electrochemical Analysis," p. 62.

tion of metal is complete and satisfactory, but the results are almost invariably too high, owing to the tendency of the moist deposit to undergo partial oxidation.

Smith therefore recommends the employment of a nitric acid solution containing from 10 to 20 per cent. of free acid, from which the lead separates as dioxide upon the anode. Some interesting results have been obtained by Smith[1] in the electrolysis of metallic phosphates in acid solution, but as far as the writer is aware, no experiments are recorded showing the deportment of lead toward the current in the presence of an excess of phosphoric acid. Preliminary trials showed that the metal could be deposited from a solution of this kind completely, and in such a form as to warrant a more extended study. The phosphoric acid used had a specific gravity of 1.71. In an excess of acid of this strength lead phosphate, precipitated either by disodium hydrogen phosphate or phosphoric acid, is readily soluble. With such a solution the following experiments were made.

The method of working was to take a definite volume of lead nitrate solution, precipitate the phosphate by disodium hydrogen phosphate or phosphoric acid, dissolve this in an excess of the phosphoric acid, and then electrolyze by a current of known strength. The deposited metal was washed with freshly boiled distilled water, absolute alcohol and ether, and finally dried in an air-bath at 100°–110° C. The deposition of metal took place at ordinary temperatures.

From a solution, prepared by precipitating lead phosphate by phosphoric acid, and then dissolving this in an excess of the precipitant, the lead separates in a partly crystalline and partly spongy condition, but sufficiently adherent to allow of thorough washing. If the amount of lead in the solution is too great, or the current too strong, the deposit is always very spongy and some of it is apt to be carried away in the washings.

On the other hand, from a solution made by adding more than enough disodium hydrogen phosphate for complete precipitation of lead phosphate, and then dissolving this in an excess of phosphoric acid, the lead deposit forms on the platinum dish a smooth, uniform, gray coating similar to that produced from an alkaline solution of lead. In a few experiments some brown discolorations were noticed on the dried deposit. These were taken to indicate

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[1] *Am. Chem. J.*, **12**, 329, and **13**, 206.

oxidation. Throughout the course of this work the tendency of the deposit to oxidize in the drying process did not give much difficulty, if after a thorough washing with ether the latter is evaporated by the heat of the hand before the crucible or dish is placed in the air-bath.

The greatest difficulty encountered was the readiness with which the moist deposit dissolved in the wash-water after the current was interrupted. After a number of trials it was found best to allow the current to act during the washing with water, then to *very rapidly* wash with a small amount of absolute alcohol, and finally with ether as stated above.

When a strong current was used, or even in the case of a weaker current allowed to act for a longer period than is required for the complete deposition of the lead, the deposit gave a test for phosphorus, and the platinum vessel in a number of experiments was found to be stained a light brown color after the solution of the deposited lead in warm moderately concentrated nitric acid. The brown stain seems to be insoluble in any single acid hot or cold. Preliminary tests show that it contains both lead and phosphorus. This substance, probably a phosphide of lead, is under examination at the present time.

Experiments 1–7 show that with a fairly strong current the lead separates in the spongy condition and is especially difficult to wash, without loss due to the solvent action of the wash-water. In No. 2 the lead deposit, after the first weighing, was allowed to stand in contact with 20 cc. distilled water for three minutes, then washed with alcohol and ether, dried and weighed again. The loss in weight was 2 mg., and the washings, which contained no solid particles mechanically removed, showed a strong test for lead with hydrogen sulphide.

In 9–12 the current acted for a much longer time than was required for complete deposition. In each case, the deposited lead when dissolved in moderately concentrated nitric acid gave a test for phosphorus, and the platinum dish showed the brown stains already mentioned.

Experiments 13–18 show that under the conditions given, lead can be deposited satisfactorily from a phosphoric acid solution. The results obtained would indicate that in a solution containing not more than one-tenth gram of lead, and to which about 10 cc. of sodium phosphate, and 12–14 cc. of phosphoric acid (sp. gr.

| No. | Lead taken. Gram. | Lead found. Gram. | Diff. Per cent. | N.D.$_{100}$. Ampere. | Voltage. | Hrs. | Dilution. cc. | $H_3PO_4$. cc. | $Na_2HPO_4$. cc. | Remarks. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0937 | 0.0912 | − 2.6 | 0.018 | 3.5 | 2 | 130 | .. | .. | Very spongy. Not all deposited by current. |
| 2 | 0.0937 | 0.0917 | − 2.1 | 0.018 | 3.5 | 4 | 130 | 10 | 10 | Spongy. Precipitation complete. Pb found in washings by $H_2S$. |
| 3 | 0.0717 | 0.0700 | − 1.8 | 0.018 | 3.5 | 7 | 130 | 10 | 10 | Spongy. Precipitation complete. Pb found in washings by $H_2S$. |
| 4 | 0.0717 | 0.0730 | + 1.8 | 0.018 | 3.5 | 12 | 130 | 10 | 10 | Spongy. Brown spots after drying. |
| 5 | 0.0143 | 0.0150 | + 4.8 | 0.018 | 3.5 | 3 | 130 | 10 | . | Spongy. Brown spots after drying. |
| 6 | 0.0717 | 0.0711 | − 8.3 | 0.018 | 3.5 | 3 | 130 | 10 | .. | Deposition complete. Pb found in washings by $H_2S$. |
| 7 | 0.1151 | 0.1148 | − 0.26 | 0.018 | 3.5 | 4 | 130 | 10 | .. | Spongy but adherent. No test for Pb in washings. |
| 8 | 0.0344 | 0.0369 | + 7.2 | 0.002 | 3 | 20 | 130 | 14 | .. | P in deposit. |
| 9 | 0.0344 | 0.0340 | − 1.1 | 0.011 | 3 | 5 | 130 | 14 | .. | Spongy. Pb found in washings. |
| 10 | 0.0344 | 0.0356 | + 3.4 | 0.002 | 3 | 17 | 130 | 10 | .. | P in deposit. |
| 11 | 0.0562 | 0.0575 | + 2.3 | 0.002 | 3 | 17 | 130 | 14 | .. | P in deposit. |
| 12 | 0.0206 | 0.0205 | − 0.48 | 0.002 | 3 | 4.5 | 130 | 10 | 8 | Deposition complete. |
| 13 | 0.0344 | 0.0342 | − 0.58 | 0.003 | 3 | 5 | 130 | 7 | 5 | Deposition complete. |
| 14 | 0.0562 | 0.0560 | − 0.35 | 0.002 | 3 | 7 | 130 | 12 | 10 | Deposition complete. |
| 15 | 0.0562 | 0.0561 | − 0.17 | 0.002 | 3 | 6 | 130 | 12 | 8 | Deposition complete. Washed with hydrant water.[1] |
| 16 | 0.0937 | 0.0934 | − 0.32 | 0.003 | 3 | 8 | 130 | 12 | 8 | Deposition complete. |
| 17 | 0.0937 | 0.0932 | − 0.53 | 0.003 | 3 | 8 | 130 | 12 | 10 | Deposition complete. Washed with hydrant water. |
| 18 | 0.0562 | 0.0559 | − 0.53 | 0.002 | 3 | 10 | 130 | 8 | 6 | Deposition complete. |

[1] Contains about 28 grains solids per gallon, consisting mainly of the carbonates of calcium and magnesium.

1.71), have been added, the metal can be quantitatively separated by a current having $N.D._{100} = 0.003$ ampere, and voltage 3. The deposition is complete in twelve to fourteen hours.

### SEPARATION OF LEAD FROM MANGANESE.

Phosphate of manganese is readily soluble in an excess of phosphoric acid. With such a solution several trials showed that even strong currents produced no effect other than to develop a pink coloration, suggesting the color of weak permanganate.[1] The current was allowed to act at ordinary temperatures for seventeen hours.

When lead and manganese were in the same solution and electrolyzed with

$N.D._{100} = 0.011$ ampere,
Voltage = 3,
Dilution = 130 cc.,
Phosphoric acid = 14 cc.

manganese dioxide was thrown out on the anode, while the lead deposit gave tests for both lead and manganese.

Further work is now being done to determine whether lead can be separated from manganese in a phosphoric acid solution.

WITTENBERG COLLEGE, SPRINGFIELD, O.,
December 26, 1901.

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[CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

# RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

## (THIRD PAPER.)

BY HENRY L. WHEELER AND HENRY F. MERRIAM.

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IN our first paper[2] we described the results of an examination of rhodanides formed from certain alkylmonohalides and potassium thiocyanate, and showed that it is a simple matter to distinguish normal from isothiocyanates by their behavior with thiol acids.

In the case of monothiocyanates, two reactions were observed. Either a direct addition was obtained with the formation of benzoyldithiourethanes, or along with other products, an ester of thiobenzoic acid resulted. The latter reaction was observed only in the case of certain secondary and tertiary thiocyanates:

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[1] Smith: *Am. Chem. J.*, **12**, No. 5.

[2] This Journal, **23**, 283 (1901).