A METHOD FOR THE DETERMINATION OF TRACES OF METALS.

III. STUDIES OF THE DISTILLATION OF AMALGAMS.

By

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Experimental Work By:

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Based on a Portion of a Collected Paper Submitted 1946.
Revised October 1947.

Contribution of
Princeton University Analytical Group
Frick Chemical Laboratory
Princeton, N. J.

For inclusion in the
National Nuclear Energy Series
Distribution Limited
III. Studies of the Distillation of Amalgams.

Introduction.

In the first paper of this series the general procedure for electrolyzing metals into mercury and their recovery by draining the small mercury cathode into a silica boat and distilling in a current of nitrogen has been described and the apparatus has been indicated. In the early development of the procedure it was noted that the weights of the distillation residues were in general greater than the weights of the metals that were known to have been deposited by electrolysis. The excess weight was known to be due in some cases to partial oxidation of the residue and in others to mercury retained by certain metals such as zinc, at the temperatures that were chosen for distillations. The recoveries of known amounts of Cd, Pb, Co, Cu, Ni, Zn and Fe were repeatedly found to be as good as the methods that were used for their estimation when the range of weights involved were in the microgram or milligram range. A precision of 3 to 5 parts per hundred was attained with these small amounts of materials and the temperature was not controlled rigorously in the polarographic work. Recoveries ranged from 95 - 105 per cent of the substances added.

It became of interest later to study the distillation procedure more critically with milligram quantities of various metals. These experiments indicate the advantages and disadvantages of the procedure as applied to the recovery of various metals when their amounts are in the milligram range.
Experimental.

Procedure Applicable to Co, Cu, Fe and Ni. The behavior of each metal was studied separately but the procedure was as follows for all of them: A measured amount of a standard solution equivalent to 5.00 mg. of the metal was evaporated to dryness with 0.15 ml. of conc. sulfuric acid added. The dry residue was dissolved by adding 0.5 ml. of conc. sulfuric acid and 125 ml. of water. The solution was electrolyzed over night with a 2 ml. mercury cathode and a platinum anode at 10 volts applied, current density approx. 0.08 amps. per sq. cm.

The amalgam was drained into a weighed silica combustion boat and the mercury was distilled off in a stream of nitrogen gas at a temperature that never rose to 380°C. The boat was weighed after cooling and the residue was analyzed for the particular metal under consideration. The residual solution was analyzed polarographically or colorimetrically to determine the amount of metal remaining in the solution and by difference the amount of metal that had deposited in the mercury. Table I contains the data for cobalt, copper, iron and nickel.

Cobalt in the residue from the distillation was estimated colorimetrically by the procedure of Potratz and Motta (a) by extracting the cobalt-thiocyanate-tetraphenyl arsonium complex to chloroform and measuring extinction of the blue extract at 620 μμ with a Beckman quartz spectrophotometer. Copper was determined by electrolysis to a platinum cathode from a nitric-sulfuric acid solution. Iron was determined by the 1, 10 phenanthroline colorimetric method by
the extinction measured at 615 μ. Nickel was determined by the conventional gravimetric procedure with dimethyl glyoxime. The recovery of these four metals was complete within the limits of error of the methods. Cobalt, iron and nickel were oxidized to a large extent during the distillation, since no attempt was made to free the nitrogen from traces of oxygen, or to exclude air rigorously from the distillation apparatus.

Table I.

<table>
<thead>
<tr>
<th>No.</th>
<th>Item</th>
<th>Cobalt</th>
<th>Copper</th>
<th>Iron</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Metal taken, mg.</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>3.</td>
<td>Weight of metal found in aqueous solution, mg.</td>
<td>0.002</td>
<td>0.052</td>
<td>0.011</td>
<td>0.006</td>
</tr>
<tr>
<td>4.</td>
<td>Weight of metal deposited in the mercury,(1)minus(3)</td>
<td>5.00</td>
<td>4.95</td>
<td>4.99</td>
<td>4.99</td>
</tr>
<tr>
<td>5.</td>
<td>Temperature range during distillation, degrees C.</td>
<td>365-370</td>
<td>355-375</td>
<td>360-367</td>
<td>358-367</td>
</tr>
<tr>
<td>6.</td>
<td>Appearance of residue from distillation</td>
<td>black</td>
<td>orange; black, metallic compact</td>
<td>black, compact</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Weight of residue, mg.</td>
<td>5.98</td>
<td>5.01</td>
<td>6.47</td>
<td>5.34</td>
</tr>
<tr>
<td>8.</td>
<td>Weight of metal found in residue</td>
<td>4.87</td>
<td>5.10</td>
<td>4.94</td>
<td>4.89</td>
</tr>
<tr>
<td>9.</td>
<td>Apparent recovery Item (8) divided by Item (4), per cent</td>
<td>97.5</td>
<td>103.</td>
<td>99.</td>
<td>98.</td>
</tr>
</tbody>
</table>

Lead. Using the procedure that has been outlined for Co, Cu etc. poor results were obtained for lead because an appreciable amount of lead sulfate remained undissolved in the solution. Therefore lead amalgam was formed by direct addition of lead to mercury.
in a silica boat, followed by distillation. 15.75 mg. of lead was added to 30 g. of mercury in a silica boat, and the distillation was made in the usual manner with temperature ranging from 360 to 410°C. The residue weighed 16.07 mg. It was dissolved and the lead was precipitated as the chromate from acetic acid solution. The lead chromate found was equivalent to 15.24 mg. of lead or a recovery of 96.8 per cent. This rather low recovery is attributed to solubility losses, etc.

Zinc. 5.00 mg. of zinc was electrolyzed and no detectable amount of zinc was found polarographically after electrolysis. The zinc amalgam was distilled and the temperature rose to 400°C during the distillation. The residue was gray and weighed 4.99 mg. The residue was converted to zinc sulfate and the weight of the latter was equivalent to 5.25 mg. of zinc. The recovery was therefore between 99.8 and 105 per cent.

If a zinc amalgam is distilled at temperatures below 380°C, the amalgam is not completely decomposed. In one case after two distillations at a temperature not above 380°C, 15 mg. of zinc gave a residue weighing 26 mg. When the residue was treated with hydrochloric acid a globule of mercury remained. If zinc and cadmium are present it is undesirable to allow the temperature to rise above 380°C. If the complete recovery of cadmium is of interest.

Mercuric ion is undesirable if the polarographic method is to be used because the mercury wave obscures the portion of the polarogram that is of interest in estimating Cd, Pb, etc.
It was found that the mercury that was retained by the zinc could be volatilized in the form of mercuric chloride by heating on a hot plate in a hood at 300°C. or a little above without loss of zinc. This method was tested with 5 mg. quantities of zinc and mercury. Recoveries of 95 - 100 per cent were obtained for zinc and it was proved by hydrogen sulfide test that the mercury had been removed. The zinc was weighed as zinc sulfate.

Cadmium. The distillation of the cadmium amalgams in an air stream was not found effective. When cadmium amalgams are distilled in a nitrogen stream it is important to observe the last stages of the distillation closely. The golden yellow color of the heated amalgam changes to a bluish cast when the last visible traces of mercury have distilled. If the heating is prolonged much beyond this point cadmium may vaporize. If the distillation is completed at 360°C. or slightly below and the temperature lowered immediately when the mercury appears to have distilled, the recoveries of milligram amounts of cadmium are good.

The results of a series of determinations by the electrolysis-distillation and polarographic procedure are given in Table II.

Table II.
The Recovery of Cadmium by the Electrolytic-Polarographic Procedure.

<table>
<thead>
<tr>
<th>Cadmium Present mg.</th>
<th>Maximum temp. °C.</th>
<th>Weight of Residue mg.</th>
<th>Color of Residue</th>
<th>Cadmium Recovered mg.</th>
<th>Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>370</td>
<td>1.21</td>
<td>yellow</td>
<td>0.935</td>
<td>93.5</td>
</tr>
<tr>
<td>2.00</td>
<td>350</td>
<td>2.22</td>
<td>blue-brown</td>
<td>1.94</td>
<td>97</td>
</tr>
<tr>
<td>3.00</td>
<td>330</td>
<td>3.23</td>
<td>blue-brown</td>
<td>3.95</td>
<td>102</td>
</tr>
<tr>
<td>4.00</td>
<td>315</td>
<td>4.33</td>
<td>red-brown</td>
<td>5.94</td>
<td>99</td>
</tr>
<tr>
<td>5.00</td>
<td>300</td>
<td>5.26</td>
<td>blue</td>
<td>7.99</td>
<td>96</td>
</tr>
</tbody>
</table>
These results indicate the tendency of slight loss of cadmium to occur if the temperature is much above 360°C, although the recoveries are almost within the attainable precision of the polarographic method as carried out without rigorous temperature control. A final temperature of 360°C or slightly below gave good recoveries repeatedly in the microgram range.

It was found that 5 mg. each of iron and cadmium could be electrolyzed simultaneously and distilled without complications. In a similar experiment in which 5 mg. each of cadmium and zinc were electrolyzed the residue weighed 47.5 mg., but there was no loss of cadmium when the mercury was removed as the chloride.

Indium. It was observed that indium retains mercury when the amalgam is distilled at 360°C. The amalgam was liquid at the end of the apparent completion of the distillation of the mercury.

Conclusions. It has been shown that milligram quantities of cobalt, copper, iron, lead, nickel or zinc may be recovered by mercury cathode electrolysis and distillation of the residue. Due to the insolubility of lead sulfate and the tendency of lead to go to the anode in the absence of an oxidation-reduction buffer, it is not likely that milligram quantities of lead will be found in the cathode by the procedures that were developed for various substances.

Zinc amalgams are not broken up at 360°C, and the amount of mercury that is retained is roughly proportional to the amount of zinc present. Cadmium retains a small amount of mercury at this temperature during the distillation. Mercury may be removed as mercuric chloride during the preparation of the residue for polarography.
After the removal of the mercury that is held by the metals, the residue is evaporated with hydrochloric acid and potassium chloride present at 100°C. in order to have a slightly acidic residue that gives upon solution a suitable medium in which to detect cadmium and lead by polarography.

Indium retains mercury under the conditions that were chosen as most likely to avoid loss of cadmium.

The loss of cadmium during distillation of the mercury can be avoided by lowering the temperature from 360°C. as soon as the mercury appears to have distilled.

The result of these studies indicate that amounts of Cd, Co, Cu, Fe, Pb, Ni and Zn from a few micrograms to 5.00 mg. may be handled with the equipment that has been described. There is no apparent reason why still larger amounts of metals might not be handled by this general procedure provided equipment of adequate size is available.

A careful visual examination of the residues after distillation often gives an approximate idea of the major components of the mixture. Iron is usually completely oxidized to ferric oxide and is generally found as discrete specks or aggregates that apparently flocculate during the distillation from the colloidal dispersion of the iron in the mercury. Nickel and cobalt behave in the same fashion as iron. Copper, cadmium, lead and zinc do not oxidize appreciably during the distillations. The film of zinc amalgam that remains has a characteristic silvery appearance.
It should be emphasized that the procedure was developed primarily as a method for recovering amounts of metals in the range from a few microgram to 0.2 mg.

The present studies indicate that the procedure might be used effectively for somewhat larger amounts of the electrolyzable metals.

Summary.

It has been demonstrated that the electrolysis-distillation stages of the procedure that has been developed for traces of metals may be utilized, with certain precautions, to recover milligram quantities of cadmium, cobalt, copper, iron, nickel, and zinc. Lead remains partially as undissolved lead sulfate and hence the recovery of amounts ranging from 1 - 5 mg. is not advisable by this procedure.

References.

(1) Cf. Section I of this series of papers.
(2) Bricker, C. E. and Furman, N. H., CC75, May 12, 1942.