Some Experiments on the Determination of Lead in Lead Amalgam.

M. G. Mellon and H. F. Reinhard.

In working with lead amalgams several types of procedure have been employed by various individuals for obtaining the concentration of the lead in the amalgams. These methods may be conveniently classified as electrolytic, gravimetric, and physico-chemical. There follows a brief outline of the principles involved in the three types of procedure.

Electrolytic Methods. One electrolytic method takes advantage of the scheme used for preparing the amalgam. Under certain conditions Stähler and Alders[1] found that lead deposits in a mercury cathode. They maintain that the amalgam formed may be washed with water, alcohol, and ether, and weighed. Knowing the original weight of the mercury serving as the cathode, the increase in weight represents the amount of lead deposited. From these two weights the concentration of the lead may be calculated. In using this procedure Vortmann[2] encountered difficulties from the oxidation of the amalgam when the electrolyte was alkaline. The authors have had similar trouble when working with lead amalgams in which the lead was deposited from aqueous solutions of lead nitrate. The above procedure is ultimately a method of preparing an amalgam in which the concentration of the element deposited in the mercury is known, rather than a method of analysis.

A somewhat similar method has been employed by Richards and Wilson[3] for amalgams of thallium, indium and tin. As in the above method, the amalgams were prepared by depositing the different elements electrolytically in a mercury cathode. The concentration of the metal deposited was obtained by means of a silver coulometer included in the electrical circuit during the electrolysis, the assumption being that the element deposited in the mercury was equivalent in amount to the silver deposited in the coulometer. The percentage composition of the amalgam could then be calculated from the weights of silver and of the mercury serving as cathode.

A third electrolytic method is that suggested by Smith.[4] It involves the solution of the amalgam in nitric acid and the deposition of both elements. With properly arranged apparatus, and under suitable conditions, the lead deposits at the anode as the peroxide and the mercury at the cathode.

Gravimetric Methods. The methods outlined here for the gravimetric estimation of the concentration of lead in lead amalgams involve

---

[1] Ber. 42, 2685 (1909).

[2] Ibid. 22, 2756 (1891).

[3] Carnegie Inst. Pub. 118, 1 (1909).

[4] Electro-Analysis, p. 229 (1918).
Smith and Moyer—J. Anal. Ch. 7, 252 (1893); Z. anorg. Ch. 4, 267 (1893).
Smith and Heidenreich—Ber. 29, 1585 (1896); Z. Elektrochem, 3, 151 (1897).

the solution of the amalgam and the subsequent separation of the two elements by the precipitation of one of them. The first of these is based upon the fact that mercuric sulfide is insoluble in dilute, boiling nitric acid (Sp. G. 1.2-1.3), while lead sulfide is soluble. For this determination Treadwell,[1] and also Scott,[2] recommended the precipitation of the elements from their solution (the mercury being present entirely in the mercuric form) by hydrogen sulfide. The precipitate is filtered off, washed with hydrogen sulfide water, transferred to a dish and boiled for a considerable time with the dilute nitric acid. The solution is then diluted, the mercuric sulfide filtered off and washed with water containing nitric acid. Certain precautions are necessary in the final determination of the two elements.

As a second gravimetric method Crookes[3] suggests the addition of sulfuric acid to the solution containing the lead and mercury, followed with alcohol to form about one-sixth the volume of the solution. The precipitated lead sulfate requires washing with dilute alcohol containing a little sulfuric acid. The separation of the lead by this means is based upon the insolubility of its sulfate and the solubility of the mercuric sulfate. Horsford used this method.[4]

Physico-Chemical Methods. Richards and Wilson[5] have measured the densities of lead amalgams as a means for obtaining the concentration of the lead. From these results they were then able to obtain this concentration by reference to a curve showing the variation in density of the amalgam with change in the amount of lead present. Such a method is based upon the fact that the physical property being measured varies with, or is a function of, the concentration of the constituent being determined.

Meyer[6] and Richards and Forbes[7] have investigated a second, interesting physico-chemical method. Their work included the elements zinc, cadmium, lead, tin, copper, and sodium. The principle of the method has as its basis the familiar equation for electrode potentials as developed by Nernst. When applied to concentration cells in which the two electrodes are amalgams or alloys it has the form—

$$E = \frac{RT}{nF} \ln \frac{c_1}{c_2}$$

in which the various terms all have their usual significance. In such a combination as

$$Zn.\,Hg\ (C_1) — ZnSO_4\ (Sat.\ Sol.) — Zn.\,Hg\ (C_2)$$

one will find a given potential whose magnitude will depend upon the concentrations of the two amalgams and the temperature, as the chief factors. To apply the above equation in calculating the concentration of a given element in an amalgam, one would set up a combination such as that mentioned for zinc amalgams, using an amalgam of accurately

[1] Treadwell-Hall—Analytical Chemistry II, p. 194 (1915).
[2] Standard Methods of Chemical Analysis, p. 271 (1917).
[3] Select Methods in Analytical Chemistry, p. 324 (1894).
[4] Am. J. Sci. [2] 13, 305 (1852).
[5] Carnegie Inst. Pub. 118, 1 (1909).
[6] Z. phys. Ch. 7, 477 (1891).
[7] Carnegie Inst. Pub. 56, 1 (1906).

known concentration for one of the electrodes and the one of unknown concentration for the other. The potential E could then be measured for the combination. This leaves as the one unknown quantity in the equation the concentration of the amalgam being measured, and its value may readily be calculated.

Hulett and Minchin[1] have made use of this scheme in their study on the distillation of amalgams and the purification of mercury. They state that one part of zinc can be detected with certainty in ten billion parts of mercury, and that the method is probably the most delicate analytical procedure known.

Criticism of Methods. None of the preceding methods seemed to meet the requirements, as to ease and accuracy, for certain work that is being conducted in this laboratory. As already noted, the first electrolytic method was unsuitable because of oxidation of the amalgam during washing and drying.

For the method involving the electrolytic separation of the lead and mercury, or the gravimetric separation, either of the mercury as mercuric sulfide, or of the lead as lead sulfate, the amalgams under investigation contained entirely too much mercury. There was generally present from 30 to 50 grams of this element and only about 0.5 gram as the maximum amount of lead. For an electrolytic separation this amount of mercury would require altogether too much time, even if there were involved no other undesirable features. Likewise, in the gravimetric methods which involve a separation by precipitating one of the constituents, the mechanical difficulties of handling a solution containing such a large proportion of mercury would be too great to insure a high degree of accuracy in the determinations.

Two distinct difficulties are evident in the method involving the determination of the density of the amalgams. In the first place, it is not easy to handle lead amalgams without oxidation of the surface. The difficulty is increased if the amalgam is wet and must be dried during the procedure. In the second place, the densities of lead and mercury are so near each other that a considerable change in density of the amalgam does not result from a small change in the concentration of the lead in the amalgam. This means that the accuracy in determining the concentration of the lead by this method would not be so great as in the case of such elements as cadmium and zinc, whose densities are much less than that of lead.

Although the method based upon the measurement of the potentials of amalgams apparently may be very accurate, distinct precautions must be observed in making such determinations. Rather elaborate electrical apparatus is required along with an accurately controlled thermostat for holding the temperature factor constant. No attempt was made to use the method in the present work, although it is hoped a later study may be made on concentration cells with lead amalgams. Previous[2] work has indicated that, under certain conditions, a very constant and reproducible potential is obtained for a saturated lead amalgam.

---

[1] Phys. Rev. 21, 388 (1905).

[2] Mellon and Henderson—J. Am. Chem. Soc. 42, 676 (1920).

Present Work.

Oxidation of Lead Amalgams. As already stated, in the course of some work in this laboratory with lead amalgams, it was not found possible to handle them according to the method of Stähler and Alders without having marked evidence of oxidation, even with only a few hundredths of a gram of lead present. Amalgams prepared electrolytically were always bright, and remained so during washing with water and alcohol. When washed with ether, however, there often formed on the surface of the amalgam a dark film which was easily lost on further washing. If washed immediately and quickly with the ether, not much of the film formed; but the longer the time of washing, the more film there was present. It was difficult to avoid losing it when washing by decantation; and if much was present, some was always lost. On standing any length of time following the washings with just water and alcohol, there was always considerable oxidation.

To show this oxidation of the amalgam on standing, and the resulting loss in weight with washing, the following determinations are typical, except that the errors are considerably exaggerated due to the length of time the amalgams stood before washing. These amalgams were made up by dissolving a known weight of lead in a known weight of mercury and allowed to stand in a beaker 48 hours. After washing with the liquids mentioned, the amalgams were dried in a desiccator and reweighed, with the results shown in Table I. Numbers 1 and 2 were washed once with 10 cc. of water and twice with 10 cc. portions of alcohol, while numbers 3 and 4 had, in addition to this, two washings with ether.

Table I.

Loss in Weight of Amalgams During Washing.

No.	Weight of Mercury	Weight of Lead	Loss
1	43.0182	0.8496	0.0138
2	40.8870	1.0832	0.0076
3	57.2745	1.0357	0.0162
4	39.2819	0.8600	0.0227

Development of Method of Analysis. On account of the defects inherent in the methods already outlined for the analysis of lead amalgams, it seemed desirable to have available a method for determining the concentration of the lead involving some procedure by which the element could be brought easily from the amalgam into aqueous solution, and then determined gravimetrically in this solution. A solution of copper nitrate was selected as a promising possibility for obtaining the replacement of the lead in the amalgam by another element, thus bringing it into aqueous solution from which it could be precipitated. Copper sulfate was rejected because it brought about the formation of lead sulfate very shortly, which seemed to retard the replacement process. The procedure adopted consisted in covering the amalgam in a beaker with 25 cc. of a 10 per cent solution of copper nitrate for a period of 15 to 24 hours, decanting the solution, and washing the remaining amalgam. Copper is less soluble in mercury than lead, and

many of the determinations showed considerable brownish-red material on the surface of the amalgam, after standing in contact with the solution of copper nitrate for several hours. This was found to be largely copper, along with some mercury, and the solution was always filtered from this precipitated material.

Determination of Lead in the Amalgam as Lead Sulfate. In trying out the method for displacing the lead from the amalgam by means of a solution of copper nitrate, the first attempt to precipitate the lead was with sulfuric acid. Amalgams containing known weights of lead stood four days in contact with 40 cc. of a 10 per cent solution of the copper nitrate. After decanting the resulting solution, an additional 10 cc. portion of the copper nitrate stood on the amalgams for 30 minutes. From the total, warm solution the lead was precipitated with dilute sulfuric acid. The weight of lead sulfate was determined by filtering it on a Gooch crucible, the ignition being accomplished by supporting the crucible in an asbestos ring placed in a larger crucible and heating the latter to dull redness for 15 minutes. The weight of lead was found to be uniformly low, as shown in Table II.

TABLE II.

Determination of Lead in Lead Amalgam as Lead Sulfate.

No.	Lead Taken	Lead Found	Percent Loss
1	0.5650	0.5606	0.78
2	0.4748	0.4704	0.92
3	0.5108	0.5058	0.98
4	0.5024	0.4977	0.93

Solubility of Lead Sulfate in a Solution of Copper Nitrate. Assuming that the low values for the lead found resulted from the solubility of the lead sulfate in the solution of copper nitrate, definite weights of prepared lead sulfate were allowed to stand four days in a 10 per cent solution of the copper nitrate. The precipitate was then filtered off and weighed as before. The results shown in Table III are only preliminary and more accurate determinations will be made under varying conditions, but the increase in solubility with increase in concentration of copper nitrate is evident.

TABLE III.

Solubility of Lead Sulfate in a Solution of Copper Nitrate

No.	Vol. of Sol. of $Cu(NO_3)_2$	$PbSO_4$ Taken	$PbSO_4$ Found	Percent Loss
1	25cc	0.7000	0.6764	3.39
2	50	0.7000	0.6556	6.33
3	50	0.7000	0.6533	6.61

Solubility of Lead Chromate in a Solution of Copper Nitrate. The foregoing work on the determination of the lead as lead sulfate and on its solubility in solutions of copper nitrate indicated that the results might be due to a failure of the lead to change entirely from a

metallic solution as amalgam to aqueous solution as lead nitrate, that is, a state of equilibrium was established, leaving part of the lead still in the amalgam from which it did not precipitate as the sulfate; or it might be due to the solubility of the lead sulfate in the excess of copper nitrate, or to a combination of the two. The method seemed to be useless for quantitative determinations and no further work was attempted with it.

With the idea that lead might be precipitated quantitatively as the chromate in the presence of copper nitrate, the solution of lead nitrate being used as electrolyte was analyzed for its concentration of lead by precipitating the metal, in the presence of a few drops of acetic acid, with potassium dichromate.[1] The precipitate was dried at 120° C. in a Gooch crucible. Then the same volume of solution of lead nitrate was treated as before except for the addition of 20 cc. of the solution of copper nitrate before the precipitation of the lead chromate. The results shown in Table IV indicate either that the solubility of lead chromate in a solution of copper nitrate is very small, or that errors are inherent in the procedure which serve to compensate such solubility.

TABLE IV.

Solubility of Lead Chromate in a Solution of Copper Nitrate

No.	Volume of Solution of Copper Nitrate	Volume of Solution of Lead Nitrate	Weight of $PbCrO_4$
1	None	50cc	0.3316
2	"	"	0.3313
3	20cc	"	0.3312
4	"	"	0.3309
5	"	"	0.3308

Determination of Lead in Lead Amalgam as Lead Chromate. Since there seemed to be only a small amount of lead lost when precipitated as the chromate, in the presence of 20 cc. of a 10 per cent solution of copper nitrate, the next step was to ascertain whether the lead in a lead amalgam could be quantitatively determined as the chromate. Following the procedure used in the attempt to determine the lead as sulfate up to the point of precipitating the lead, a few drops of acetic acid was then added, followed by a solution of potassium dichromate sufficient to complete the precipitation. The amalgam had been made

TABLE V.

Determination of Lead in Lead Amalgam as Lead Chromate

No.	Lead Taken	Lead Found	Difference	Percent Variation
1	0 3153	0.3149	—0 0004	—0.12
2	0.2616	0.2615	—0.0001	—0.04
3	0.2763	0.2761	—0.0002	—0.07
4	0.3013	0.3014	+0.0001	+0.03
5	0.2751	0.2754	+0.0003	+0.11

[1] Scott—Standard Methods of Chemical Analysis, p. 236 (1917).

by adding a known weight of lead to 40 to 50 grams of mercury and allowing it to dissolve in the mercury before the addition of the solution of copper nitrate. The results shown in Table V indicate that the method is satisfactory for a quantitative determination of the lead in a lead amalgam.

Summary.

The material presented in this paper includes:

1. A brief review of some of the methods that have been proposed for determining the concentration of lead in lead amalgams, together with a consideration of the possibility of applying them to the analysis of such amalgams containing a large amount of mercury and a relatively small amount of lead.

2. An account of some experiments made with the object of developing a more desirable procedure for the above determination. This work has involved the following determinations:

a. The loss in weight of lead amalgams during washing.

b. The amount of lead in lead amalgams by weighing the metal as the sulfate and as the chromate.

c. The solubility of lead sulfate and of lead chromate in an aqueous solution of copper nitrate.

Department of Chemistry, Purdue University.