[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

DETERMINATION OF MERCURY AS METAL BY REDUCTION WITH HYDRAZINE OR STANNOUS CHLORIDE

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Introduction

The principal errors in determining moderate and large amounts of mercury gravimetrically by reduction to metal are caused by: (1) loss through volatility during the process of reduction, if it is carried out at an elevated temperature; (2) loss in the process of filtration—fine particles going through the filter; (3) loss through volatility in the process of drying. The loss of mercury from hot solutions of its salts, from suspensions of fine particles of mercury, and from metallic mercury on drying has been sufficiently emphasized by Howard[1] as early as 1904. Therefore, the reaction and the conditions for reduction, filtration and drying must be so chosen that the whole process can be carried out at room temperature, that the precipitated mercury is not in too fine a state of division and that the time of drying is as short as possible.

The following reducing agents were tested: sodium arsenite, phosphorous acid, hypophosphorous acid, hydrogen peroxide, stannous chloride, hydroxylamine and hydrazine. Hydrazine hydrate in an ammoniacal solution and stannous chloride in a hydrochloric acid solution were found most satisfactory.

Hydrazine Reduction.—Jannasch[2] has shown that mercury can be separated from such metals as copper, bismuth, lead, cadmium, arsenic, antimony, zinc and metals of the iron group by reduction with hydrazine in an ammoniacal or a weakly acid solution. However, on account of the danger of loss he weighed the mercury as sulfide.

The separation of mercury from other metals by reduction with hydrazine has also been studied by Knoevenagel and Ebler.[3]

In their work on the atomic weight of mercury, Easley and Brann[4] and later Hönigschmid, Birckenbach and Steinheil[5] removed mercury from the solutions of its halides by reduction with hydrazine. The former found that some of the precipitated mercury was always in such a fine state of division that it passed through the densest filters.

Duccini[6] applied the reaction to the quantitative determination of mer-

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[1] Howard, *J. Soc. Chem. Ind.*, **23**, 151 (1904).

[2] Jannasch, *Ber.*, **31**, 2377 (1898); "Prakt. Leitfaden d. Gewichtsanalyse," Veit and Co., Leipzig, **1904**.

[3] Knoevenagel and Ebler, *Ber.*, **35**, 3055 (1902).

[4] Easley and Brann, THIS JOURNAL, **34**, 137 (1912).

[5] Hönigschmid, Birckenbach and Steinheil, *Ber.*, **56**, 1212 (1923).

[6] Duccini, *Gazz. chim. ital.*, **43**, 693 (1913).

cury, weighing it as metal. Briefly, his procedure consisted in precipitating mercury from a potassium hydroxide solution with an excess of hydrazine sulfate, filtering through a small paper filter after six to eight hours' standing, washing first with dilute hydrochloric acid, then with water, alcohol and ether, drying for five to six hours in a desiccator over calcium chloride and weighing. Under these conditions the finely divided mercury settles very slowly, and this method of drying can hardly be recommended.

In this work the question of drying precipitated mercury was first studied. Dick[7] recommends washing precipitates with alcohol and ether, followed by drying in a vacuum desiccator. This procedure was not considered advisable, because it requires two wash solutions, the use of a vacuum desiccator, and because even pure ether usually contains enough peroxide to tarnish the surface of mercury. It is strange that the use of acetone in preference to alcohol and ether has not found a wider application for drying precipitates. Barnebey[8] in a note on the use of acetone for drying chemical utensils, recommended it in place of alcohol and ether. Easley[9] showed that a single globule of mercury could be dried without loss by washing with acetone and warming up to 30–35° for half an hour.

Experimental

In this work the method of drying was as follows: the crucibles and precipitates were washed five times with redistilled acetone and air-dried at room temperature on the suction flask by sucking through them for five minutes air previously dried by calcium chloride (see Fig. 1).

The reproducibility of the weights is shown in Table I. A slight difference between the "acetone-dried weight" and the "oven-dried weight" is undoubtedly due to a trace of acetone being adsorbed by the pores of

TABLE I

DRYING OF CRUCIBLES

Crucible	First acetone drying	Second acetone drying	Oven drying at 120°
1	17.1666	17.1665	
2	15.5768	15.5768	
3	16.1287	16.1286	
4	16.0821	16.0821	
5	13.8332	13.8333	13.8329
6	17.0914	17.0914	17.0912
7	16.3581	16.3580	16.3581
8	17.9009	17.9010	17.9006
9	13.2854	13.2854	13.2852
10	16.3556	16.3556	16.3554

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[7] Dick, *Z. anal. Chem.*, **77**, 352 (1929).

[8] Barnebey, THIS JOURNAL, **37**, 1835 (1915).

[9] Easley, *ibid.*, **31**, 1207 (1909).

the crucible. Whenever the chemical nature of the precipitate permits the use of acetone, and especially when heating must be avoided, the use of this simple and rapid method is recommended.

Attention was next turned to the process of filtration. The precipitation was always carried out in the cold. Filtered concentrated ammonium hydroxide was first added, and then roughly twice the theoretical amount of hydrazine hydrate. The rate of precipitation was found to increase with the hydroxyl-ion concentration. The speed of settling and the coarseness of the particles of precipitated mercury increased at first, but decreased with further increase in concentration of ammonium hydroxide, due, undoubtedly, to adsorption of hydroxyl ions on the surface of the particles of mercury, preventing them from coalescing.

For optimum conditions, 10 cc. of freshly filtered ammonium hydroxide (sp. gr. 0.90) should be added to every 50 cc. of the neutral solution. The precipitation is most conveniently carried out in a tall narrow beaker. It is preferable to keep the volume of the solution as small as possible (50 to 100 cc.).

Under these conditions the precipitate settles completely in one to two hours, but may stand longer if preferred. The heavy gray powder can be filtered as it is or changed into droplets (to facilitate transfer and filtration) by adding to the solution 35 cc. of concentrated hydrochloric acid, stirring for a minute and making ammoniacal again. When time is an important factor, the precipitation is carried out in a centrifuge cup, the solution stirred for a minute to ensure complete reduction, and centrifuged for five minutes. All the mercury then collects into one or two large globules, except a few milligrams, which always remain in the form of a fine gray powder.

The precipitate is conveniently filtered through a porcelain filtering crucible, type A1,[10] previously dried with redistilled acetone and dry air, as already described. A Gooch crucible with asbestos or with precipitated gold mat and a Munroe crucible were used with equal success, but the porcelain filtering crucibles were finally used exclusively, because their weight is most reproducible.

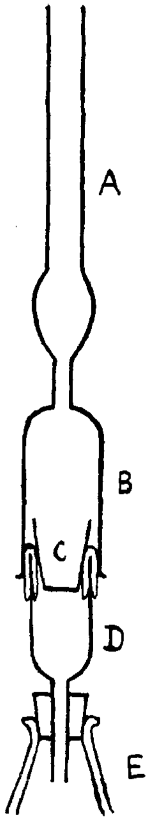

Fig. 1.—Apparatus used in drying crucibles. A, calcium chloride tube; B, glass adapter sealed to the calcium chloride tube and fitting tightly over the rubber Gooch tubing of the crucible holder; C, crucible; D, crucible holder; E, suction flask.

After filtering, the precipitate is thoroughly washed with cold water.

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[10] Manufactured by the Staatliche Porzellanmanufaktur, Berlin.

The mercury in the crucible can be caused to collect into one drop by gently shaking the crucible, thus simplifying the washing; a few milligrams of mercury will, however, always remain in the form of a fine gray powder sticking to the pores of the crucible. The water is then washed out with pure redistilled acetone and the crucible air-dried for five minutes, as described above. After standing in the balance case for two minutes the crucible can be weighed.

The analyses of pure mercuric chloride solutions (prepared from 99.98% pure $HgCl_2$) and of nitrate solutions (prepared by dissolving specially redistilled mercury in nitric acid) are given in Table II.

TABLE II

DETERMINATION OF MERCURY BY REDUCTION WITH HYDRAZINE HYDRATE IN AN AMMONIACAL SOLUTION

No.	Mercury, g. Taken	Found	Corrected	Error, mg.
		Chloride Solutions		
1	1.8821	1.8801	1.8814	−0.7
2	1.3662	1.3652	1.3665	+ .3
3	1.2416	1.2405	1.2418	+ .2
4	1.0175	1.0168	1.0181	+ .6
5	0.5112	0.5096	0.5109	− .3
6	.1827	.1811	.1824	− .3
7	.1751	.1739	.1752	+ .1
8	.1533	.1519	.1532	− .1
9	.1132	.1120	.1133	+ .1
10	.0700	.0686	.0699	− .1
		Nitrate Solutions		
1	2.2247	2.2232	2.2245	− .2
2	1.8285	1.8282	1.8295	+1.0
3	1.5168	1.5146	1.5159	−0.9
4	0.8045	0.8033	0.8046	+ .1

From this table it is evident that the amount of mercury found is always less than the theoretical by a practically constant amount. That this loss was due only to volatility was proved by testing in each case the original beaker, the filtrate and the washings with ammoniacal sulfide, after first adding concentrated nitric acid to dissolve the mercury. In every case the transfer of the precipitate from the beaker to the crucible was found to be complete, and no mercury could be detected either in the filtrate or washings. Furthermore, in several experiments the air with which the mercury was dried was passed through a gas wash-bottle containing nitric acid. This was tested for mercury, and a distinct test could be obtained in every case. Because of the constancy of this loss over a wide range of conditions, it was considered justifiable to apply a correction for it; this correction, calculated from the average of twelve analyses, is +1.3 mg. The results corrected for volatility in this manner are quite accurate, the error seldom exceeding 0.1%.

Stannous Chloride Reduction.—The determination of mercury by reduction to metal with stannous chloride was described as early as 1839 by Rose.[11] More recently it was used by Farup[12] and by Schumacher,[13] who filtered mercury on a gold-asbestos filter, but the method has been unfavorably criticized and little used. Thus Fresenius[14] finds that "this method gives accurate results only when conducted with the greatest care. In general, a little mercury is lost," while Howard[15] states that "stannous chloride is not at all a suitable reducing agent for the estimation of mercurial salts, as the reduction takes place very slowly and is apt to give variable results."

In this work the conditions were found under which this method gives accurate results. Using a large excess of stannous chloride, in a strongly acid solution, the reduction was found to be strictly quantitative and practically instantaneous, the precipitate was easy to filter and the results were accurate both in pure mercuric chloride solution and in the presence of nitrate, sulfate, iron, lead, cadmium, copper, antimony or bismuth.

TABLE III

DETERMINATION OF MERCURY BY REDUCTION WITH STANNOUS CHLORIDE IN AN ACID SOLUTION

No.	$HgCl_2$, g.	Mercury, g.			Error, mg.	Remarks
		Found	Corrected	Calcd.		
1	1.7002	1.2544	1.2554	1.2559	−0.5	
2	1.1585	0.8548	0.8558	0.8558	.0	
3	1.0748	.7931	.7941	.7939	+ .2	
4	0.9876	.7285	.7295	.7295	.0	
5	.7893	.5824	.5834	.5830	+ .4	
6	.6824	.5028	.5038	.5041	− .3	
7	.5968	.4399	.4409	.4408	+ .1	
8	.3765	.2773	.2783	.2781	+ .2	
9	.3334	.2457	.2467	.2463	+ .4	
10	.1998	.1466	.1476	.1476	.0	
11	1.1073	.8165	.8175	.8180	− .5	0.5 g. Fe, 0.9 g. SO_4
12	0.7123	.5256	.5266	.5262	+ .4	.1 g. Pb
13	0.8523	.6285	.6295	.6296	− .1	.5 g. Cd
14	1.0616	.7836	.7846	.7842	+ .4	.25 g. Bi, 0.22 g. NO_3
15	1.2234	.9026	.9036	.9037	− .1	.1 g. Cu, 0.15 g. SO_4
16	1.2272	.9056	.9066	.9065	+ .1	.05 g. Cu, 0.08 g. SO_4
17	1.1936	.8809	.8819	.8818	+ .1	.25 g. Sb
18	1.3989	1.0328	1.0338	1.0334	+ .4	.1 g. Sb

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[11] Rose, "Handbuch des anal. Chem.," 2d ed., **1839**, Vol. II, pp. 169–172.

[12] Farup, *Arch. expt. Path. Pharm.*, **44**, 272 (1900).

[13] Schumacher, *Z. anal. Chem.*, **39**, 12 (1900).

[14] Fresenius, "Quant. Chem. Anal.," translation of the 6th German ed. by Cohn, John Wiley and Sons, New York, **1904**, Vol. I, p. 366.

[15] Howard, *J. Soc. Chem. Ind.*, **23**, 151 (1904).

The preferred procedure is as follows: to 50 cc. of the cold neutral solution add 25 cc. of concentrated hydrochloric acid and 5 cc. of freshly filtered stannous chloride solution, containing 1.125 g. of $SnCl_2 \cdot 2H_2O$ per cc., dissolved in hydrochloric acid (sp. gr. 1.09) and kept over metallic tin. Stir and let settle (or centrifuge). Settling is usually complete in thirty minutes to an hour. Filter through a filtering crucible, previously dried with acetone and dry air, wash with 1:1 hydrochloric acid to prevent hydrolysis of tin salts, then with water and finally with acetone. Dry for five minutes by sucking through the crucible air dried by calcium chloride and weigh. The volatility correction in this method, determined from the average of twenty analyses, is +1.0 mg.—somewhat lower than in the hydrazine method. This may be due to the larger size of the particles. The results are shown in Table III.

Summary

1. Conditions are given for the accurate gravimetric determination of mercury after reduction to metal by hydrazine in ammoniacal solution or by stannous chloride in hydrochloric acid solution.

2. In the latter method iron, cadmium, bismuth, copper, lead, antimony, nitrate and sulfate do not interfere.

3. There is always a definite constant loss due only to volatilization of mercury during filtration and drying, for which an accurate correction can be made.

4. A rapid method of drying is described, using acetone and dry air.

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THE SODIUM PEROXIDE-CARBON FUSION FOR THE DECOMPOSITION OF REFRACTORIES

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The usual methods for decomposing refractory materials are far from being ideal, in that they require considerable manipulatory skill, are time-consuming, and frequently do not effect complete decomposition in a single treatment; in fact, for some commercial refractories several types of fusions must be used in succession to obtain this result. Alkaline and acid fusions are frequently carried out in platinum crucibles, entailing considerable expense where a number of analyses must be carried on at once, while nickel, iron or porcelain crucibles are usually badly attacked under similar circumstances. The temperatures obtainable in a fusion are in general limited to those furnished by a gas flame or an electric heating element, commonly not above 1100°. In view of these considerations, a method