

For testing the equality of the volume of the bubbles a useful accessory is a piece of capillary tube of suitable internal diameter, which is placed horizontally against a scale and calibrated by a mercury thread in the usual manner. One end of this capillary is bent vertically downward and expanded into a bell-shaped mouth. This dips below the water in the bath and enables a single bubble to be caught. The other end of the capillary is also bent downward and carries a stopcock. When the tube is filled with water, it acts as a siphon and by opening the stopcock the bubble caught in the bell may be brought to a convenient place in the tube for measurement of its volume.

A serious limitation on the usefulness of the apparatus lies in the necessity for the constancy of the total volume of gas in the tubes of the counter and any apparatus to which it is connected. Also this gas volume must not be too large or a series of bubbles is formed at each emission instead of a single one. A gradual change in this gas volume can be allowed for by measuring the volume of the bubbles at various times by means of the accessory capillary tube; but, where this gas volume is not subject to change, the apparatus is very convenient for such purposes as the measurement of reaction velocity by gas evolution, since both the total volume of gas evolved and also the rate of evolution of the gas are easily obtained by readings of the dial.

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INACCURACY IN THE DETERMINATION OF MERCURY BY DIRECT PRECIPITATION AS MERCURIC SULFIDE FROM ACID SOLUTION¹

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The direct precipitation of mercury as sulfide from acid solution is a procedure whose accuracy has for many years remained apparently unquestioned.²

¹ This paper is constructed from a portion of the doctorate thesis of Edward P. Fenimore, University of Pennsylvania, 1929.

² Fresenius-Cohn, "Quantitative Chemical Analysis," John Wiley and Sons, Inc., New York, 1903, Vol. I, p. 366; Rüdistsile, "Nachweis, Bestimmung und Trennung der chemischen Elemente," Drechsel, Bern, 1913, Vol. II, p. 412; Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1924, Vol. II, 6th ed., p. 172.

It was planned to use this method for control purposes in the development of a new distillation procedure (to be described in a later paper) for determination of mercury in organic compounds. Trials with known amounts of mercury, however, yielded results which were too high. Continued study confirmed this unexpected finding, and showed the sulfide to be contaminated, *e. g.*, with chlorine, the impurity being greater in the presence of dissolved salts in quantity.

Experimental

The concentration of mercury was in all trials less than 0.1 g. per 100 cc. Precipitations were made in Erlenmeyer flasks, hydrogen sulfide being introduced under slight pressure at room temperature. The washed precipitates were extracted for one to two hours in a Wiley apparatus; a second extraction was found to be without effect. The Gooch crucibles were prepared with thick mats of fine asbestos, with underlying disks of filter paper.³

Each crucible was conditioned by passing through it a solution whose composition, etc., duplicated that of the liquid to be filtered in the analysis; these wash-liquids, however, contained no hydrogen sulfide. This treatment was repeated until it was certain, after drying at 100–105°, that the weight was constant within 0.0001 g.

The materials analyzed were two specimens of mercuric chloride and one of precipitated oxide, all of determined purity.

Results obtained with various conditions of precipitation are given in Table I.

TABLE I
ANALYTICAL RESULTS

| Conditions | Mercury taken, g. | Mercuric sulfide, g. | Mercury found, g. | Error, g. |
|--|-------------------|----------------------|-------------------|-----------|
| 1 Precipitation from solution about 0.2 <i>N</i> in HCl, and free from salts | 0.36378 | 0.42275 | 0.36449 | +0.0007 |
| | .2218 | .2577 | .2222 | + .0004 |
| | .2216 | .2586 | .2230 | + .0014 |
| | .2216 | .2581 | .2225 | + .0009 |
| | .3695 | .4294 | .3702 | + .0007 |
| | .3226 | .3756 | .32385 | + .0012 |
| | .3384 | .3940 | .3397 | + .0013 |
| | .3631 | .4227 | .3645 | + .0014 |
| Variations in procedure | | | | |
| (a) Solution saturated with H ₂ S in cold, boiled, cooled and resaturated | .2225 | .2596 | .2238 | + .0013 |
| | .2237 | .2608 | .2249 | + .0012 |
| (b) Dilute solution: 0.09 g. of Hg in 400 cc. | .0902 | .1052 | .0907 | + .0005 |
| | .0890 | .1042 | .0898 | + .0008 |
| (c) Dilute Hg solution added slowly to excess H ₂ S water | .2219 | .2585 | .2229 | + .0010 |
| | .2216 | .2578 | .2223 | + .0007 |

³ White, THIS JOURNAL, 42, 2355 (1920).

TABLE I (Concluded)

| Conditions | Mercury taken, g. | Mercuric sulfide, g. | Mercury found, g. | Error, g. |
|--|-------------------|----------------------|-------------------|-----------|
| 2 Precipitation from solution acid with H_2SO_4 and containing $MnSO_4$, as in method of White | 0.0923 | 0.10885 | 0.0939 | +0.0016 |
| | .1389 | .1632 | .1407 | + .0018 |
| | .1022 | .12015 | .1036 | + .0014 |
| | .1345 | .1572 | .1355 | + .0010 |
| 3 Precipitation from acid solution containing KI and much NaCl and Na_2SO_4 , as in distillation method | .0980 | .1208 | .1042 | + .0053 |
| | .1205 | .1470 | .1268 | + .0063 |
| 4 Modified Volhard method, in presence of KI | .2262 | .2644 | .2280 | + .0018 |
| | .2223 | .2585 | .2229 | + .0006 |
| 5 Double precipitation: HgS from iodide solution rich in salts dissolved in Na_2S and reprecipitated by NH_4NO_3 | .0943 | .1141 | .0984 | + .0041 |
| | .1122 | .1347 | .1161 | + .0039 |

Discussion

The average error of the first eight trials, made under conditions most favorable to accuracy, was +0.34%. The larger error (about 1%) in series 2 will affect gravimetric results by White's method, though it may in practice be compensated by loss of mercury during the decomposition or by loss in weight of Gooch crucibles not properly conditioned. Presence of iodide or of salts in excess (series 3, 4, 5) increased the positive error markedly. The unfavorable effect of iodide was reported by Wegelius and Kilpi,⁴ and several methods to avoid its interference have been proposed, including the solution of the impure sulfide in sodium sulfide and reprecipitation by Volhard's method.⁵

The Volhard procedure, when applied to solutions which contain only the mercury salt and at most the salts from neutralization of a little acid, has been established as accurate. Trials by Rauschenbach⁶ yielded results only 0.06% low. One of the writers (W.) has tested the method in comparison with the thiocyanate titration, with several electrolytic methods,⁷ and against purified mercuric chloride, results by the several methods being practically identical.

Some of the sulfide precipitates of series 1 were in part removed from the crucibles, ignited with lime and tested for chlorine. A considerable contamination was shown (9.8 mg. of $AgCl$); a blank on the lime, etc., was negative.

An explanation for the lack of purity of mercuric sulfide precipitated from acid solution is suggested by the intermediate "compounds" whose

⁴ Wegelius and Kilpi, *Z. anorg. Chem.*, **61**, 413 (1909).

⁵ Dunning and Farinholt, *THIS JOURNAL*, **51**, 804 (1929); Johns, Peterson and Hixon, *ibid.*, **52**, 2820 (1930); Pretzfeld, *ibid.*, **25**, 198 (1903).

⁶ Treadwell-Hall, *Ref. 2*, 3d ed., 1911, p. 170.

⁷ Smith, "Electro-Analysis," P. Blakiston's Sons, Philadelphia, 1918, 6th ed., pp. 101, 103, 104.

visible formation is a feature of the precipitation. The mechanism of mercuric sulfide formation was studied by Smith and Semon,⁸ who concluded that five consecutive reactions are involved. The intermediate compounds were represented to be (1) $[\text{Hg}(\text{SH})_2 \cdot \text{Hg}]X_2$, (2) $[\text{HgSHg}]X_2$, (3) $[\text{Hg}(\text{SHg})_2]X_2$, (4) $[\text{Hg}(\text{SHg})_2](\text{SH})_2$. It is clear that pure mercuric sulfide will result only if none of these intermediate compounds survives.

There must be considered also the ability of mercuric sulfide to combine with or adsorb other molecules. Striking evidence of this was provided by qualitative tests⁹ in which freshly precipitated and well-washed mercuric sulfide was introduced into solutions of mercuric chloride, sulfate, nitrate and acetate, and the mixtures well shaken and filtered, the filtrates in every case being free from mercury. During the precipitation of mercury by hydrogen sulfide the newly formed sulfide would probably be especially active in this way. The success of Volhard's method in the absence of salts in excess may be due to the circumstance that sulfide formation requires only transposition of $[\text{SHgS}]\text{Na}_2$ to the ammonium compound, which on heating decomposes irreversibly due to escape of ammonia and hydrogen sulfide.

Summary

The direct precipitation of mercuric sulfide from acid solution by hydrogen sulfide yields an impure product which is too heavy. In the presence of salts in excess, and of iodide, the positive error is increased. These effects appear to be due to the ability of precipitated mercuric sulfide to cause co-precipitation of other molecules, and perhaps to the nature of the mechanism by which the sulfide is formed. Volhard's procedure is accurate when applied to solutions which contain the mercury salt and not much else, but presence of salts in quantity, and especially of iodide, leads also to high results.

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⁸ Smith and Semon, *THIS JOURNAL*, **46**, 1325 (1924).

⁹ Privately communicated by Dr. J. H. Müller.