

REFERENCES

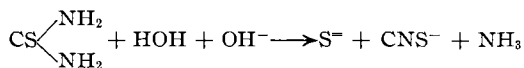
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Assay of Mercuric Chloride

By *Berl S. Alstodt**

Much of the discussion which follows is applicable to other mercury compounds which are generally determined as the sulfide. Some of the work on ammoniated mercury already completed in this laboratory and which will be presented at some future time tends to confirm the conclusions of this study.

The study was prompted by an effort to avoid the use of hydrogen sulfide in the official assay of mercuric chloride. The use of organic compounds which evolve hydrogen sulfide vapors was also to be avoided. It was believed that thiourea would be suitable for this purpose, since thiourea hydrolyzes in an alkaline medium according to the following equation given by Taylor (1):



This reaction does not produce any perceptible odor of hydrogen sulfide.

The thiourea procedure was developed and the utilization of the method was found to be dependent on controlling the p_{H} of the solution during precipitation. If the solution was too alkaline, the results were low and failed to show any degree of reproducibility. The low results are due probably to the solution of mercuric sulfide, forming the complex ion, HgS_2^{--} . If the p_{H} of the solution is controlled so as to render it suffi-

ciently alkaline for hydrolysis according to the above equation, the thiourea method yields precise results, but invariably the results are high. In twenty-five determinations by the thiourea method all results ran over 100%. The precision of the series of determinations was about one per thousand.

Since the results were high by the thiourea method, the mercuric chloride was assayed according to the method of U. S. P. XI. The results, presented in Table I, indicate satisfactory precision, but, as in the thiourea method, exceed 100%. The high results, by both the thiourea method and the U. S. P. method, indicate a constant error in the sulfide precipitation of mercuric chloride. Bassett (2) states that the sulfide determination of mercuric chloride may be high by a few tenths of a per cent.

The U. S. P. directs that the precipitate of mercuric sulfide be treated with carbon tetrachloride for one-half hour, that the carbon tetrachloride be drained and that the precipitate of mercuric sulfide be treated with further portions of carbon tetrachloride, until on evaporating a 1-cc. portion of the filtrate, no visible residue remains. In spite of this treatment, the results are high. The treatment was, therefore, modified so that the precipitate of mercuric sulfide was treated with carbon disulfide from one to twenty-four hours in an arrangement described by Scott (3), whereby the precipitate is subjected to continuous extraction.

Table II shows that the average value was only slightly less when extracted with carbon disulfide than when extracted with carbon tetrachloride, although sulfur is considerably more soluble in the former. This would suggest that the amount of free sulfur present is quite small and that the amount is readily extracted by either carbon tetrachloride or carbon disulfide. If the amount of free sulfur is as small as is indicated, then treatment with either solvent may be unnecessary. A series of determinations was, therefore, made according to the U. S. P., except that the precipitated mercuric sulfide was not treated with carbon tetrachloride, nor was it treated with carbon disulfide. Table II includes the result of this series of nine determinations. The result was about

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one per thousand greater than that obtained by the U. S. P. method, and only about two per thousand greater than the method in which the sulfur is extracted with carbon disulfide. This would indicate that if the high results are to be attributed to the precipitation of sulfur, then most of the sulfur must be in a form which is insoluble in carbon disulfide or carbon tetrachloride, or that the sulfur must be so coprecipitated that it cannot be extracted by merely washing with solvents for sulfur. The latter may be the more probable explanation.

The mercuric chloride was assayed according to the British Pharmacopœia, 1932. The results, Table I, show satisfactory precision. The method is considerably more rapid than the gravimetric procedure and is devoid of any difficulties. It is recommended, however, that the sample of mercuric chloride taken for analysis by the B. P. method should be about 0.5 Gm., rather than 0.3 Gm., since an error of 0.05 cc., which is readily possible in a residual titration, causes a variation of 0.23% for the smaller sample and only about 0.14% for the larger sample.

Since the results were much lower by the method of the British Pharmacopœia than by the method of the United States Pharmacopœia, it was deemed advisable to check the assay by some other method. For this purpose the Rauscher (4) method was adopted. The Rauscher volumetric method, whereby the mercury compound is reduced to metallic mercury, which is subsequently dissolved and titrated with a thiocyanate solution, is modified in that the reduction is carried out at 170–180° C. for 15 minutes by heating in an oil-bath, as recommended by Shukis and Tallman (5). It was found, however, that even the latter method, which improved the original method, leaves tiny particles of mercury which remain on the surface of the monoethanolamine and are lost when the mercury is washed. To overcome this objection, the procedure was modified so that the reaction is carried out in a 500-cc. iodine flask, fitted with a ground 100-cm. condenser tube. The mercuric chloride is reduced in this flask by heating with monoethanolamine in a paraffin bath between 170–180° C. for 15 minutes. When

reduction is complete, the supernatant liquid is decanted through a small filter paper and the nitric acid necessary to dissolve the mercury is passed through the same filter, so that any particles of mercury on the filter paper will be recovered.

In the Rauscher method the potassium permanganate, used to ensure the absence of nitrous acid and mercurous mercury, is destroyed by a dilute solution of hydrogen peroxide. This was modified in that the permanganate is destroyed by a dilute solution of ferrous sulfate, which, being oxidized to ferric ion, subsequently may serve as the indicator during the titration with ammonium thiocyanate.

EXPERIMENTAL

Thiourea Method.—Dissolve about 0.5 Gm. of mercuric chloride, accurately weighed, in 300 cc. of distilled water containing 10 cc. of 1*N* hydrochloric acid. Add 5 drops of methyl red test solution and render just alkaline with 3*N* sodium hydroxide. Heat the solution to almost boiling and add from a burette dropwise with constant stirring 50 cc. of 0.02*M* thiourea solution, gently boiling the solution during the addition of the reagent. Set aside for about one to two minutes and observe whether the supernatant liquid is yellow. If the solution is not yellow, or if the precipitate fails to settle during this time, add 3*N* sodium hydroxide until the solution is distinctly yellow, and boil for another minute. This treatment should be repeated until the supernatant liquid remains yellow when the precipitate settles. Let digest for about one hour and filter through a sintered crucible, containing a small stirring rod. Wash the precipitate of mercuric sulfide with hot water until free of chlorides. Then wash with two 10-cc. portions of alcohol. Add 10 cc. of carbon disulfide, stir well, let stand for about five minutes and then suck through. Treat in a similar fashion with another 10-cc. portion of carbon disulfide. Apply strong suction for about one minute. Treat with 10 cc. of alcohol, mix well and suck the alcohol through. Treat with another 5-cc. portion of alcohol. In similar manner treat with two 5-cc. portions of ether. Apply strong suction for about one to two minutes and dry for one-half hour in an oven at 110° C. Repeat drying to constant weight. The weight of mercuric sulfide multiplied by 1.167 represents the equivalent of mercuric chloride in the sample taken for analysis.

U. S. P. XI Method.—Follow the Pharmacopœia as directed under "Hydrargyri Bichloridum," collecting the precipitate in a sintered crucible (1G3) containing a small stirring rod, and from there on proceed as directed under the Thiourea method with, "Wash the precipitate of mercuric sulfide

with hot water" The calculations are identical with those given under the Thiourea method.

British Pharmacopœia Method.—Follow the method as directed in the British Pharmacopœia, 1932, under "Hydrargyri Perchloridum," using 0.5 Gm. of mercuric chloride, 100 cc. of distilled water, 15 cc. of solution of potassium iodide, 5 cc. of solution of formaldehyde, 20 cc. of solution of sodium hydroxide, 25 cc. of acetic acid and 50 cc. of the volumetric solution of iodine. Otherwise, follow the method as given in the British Pharmacopœia. One cubic centimeter of 0.1*N* iodine solution is equivalent to 0.01358 Gm. of mercuric chloride.

SUMMARY

1. To avoid the vapors of hydrogen sulfide, the hydrolysis of thiourea is used to precipitate mercuric chloride as mercuric sulfide. The method shows satisfactory precision, but yields high results.

2. The U. S. P. method for determining mercuric chloride likewise gives high results. Washing the sulfide precipitate with carbon disulfide instead of carbon tetrachloride

Table I.—Determination of Mercuric Chloride by Various Methods

	Thiourea		U. S. P. XI		B. P. 1932	Rauscher
	CCl ₄	CS ₂	CCl ₄	CS ₂		
Per Cent of HgCl ₂	100.45	100.41	100.31	100.24	99.49	99.54
Av. Dev. of a						
Single Detn.	0.09	0.11	0.14	0.12	0.14	0.16
No. of Detns.	10	15	26	21	10	12

Rauscher's Method.—Transfer about 0.5 Gm. of mercuric chloride, accurately weighed, to a 500-cc. iodine flask, fitted with a ground 100-cm. condenser tube. Add 5 cc. of purified monoethanolamine. Insert the condenser tube, moistening the ground portion with a trace of monoethanolamine, and place 1 cc. of the reagent in the lip of the iodine flask. Heat in an oil or paraffin bath between 170–180° C. for fifteen minutes. Remove the flask from the bath, let cool and wash down the tube and the flask with 100 cc. of water. Disconnect the condenser tube and filter the liquid through a small filter paper, retaining the globule of mercury in the flask. Wash the flask repeatedly with water until the washings are free of chlorides, passing the washings through the filter. Through the filter pass 10 cc. of 16*M* nitric acid and collect it in the iodine flask containing the globule of mercury. Let stand until the mercury is completely dissolved. Wash the filter with several small portions of water, adding the washings to the mercuric nitrate solution. Add 5% potassium permanganate until the solution remains pink for one to two minutes. Add a 1% solution of ferrous sulfate until the permanganate is just decolorized. Dilute with 200 cc. of distilled water, add 2 cc. of ferric ammonium sulfate test solution, and titrate with 0.1*N* ammonium thiocyanate. One cubic centimeter of 0.1*N* ammonium thiocyanate solution is equivalent to 0.01358 Gm. of mercuric chloride.

does not remedy the difficulty. If the precipitate is not washed with carbon disulfide or with carbon tetrachloride the results are only slightly worse.

3. The B. P. method is satisfactory and obviates the difficulties entailed in the sulfide procedures. It is the most rapid of the methods studied.

4. The Rauscher volumetric method is modified so as to overcome any losses of mercury. The method is satisfactory and preferable to the B. P. method in that it is a direct rather than a residual titration.

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Table II.—Hydrogen Sulfide Determinations of Mercuric Chloride

	No. of Detn.	Per Cent of HgCl ₂	Av. Dev. of Sing. Detn.
Washed with CCl ₄	26	100.31	0.14
Washed with CS ₂	21	100.24	0.12
No washing with CCl ₄ or CS ₂	9	100.44	0.24

"You can know little of any idea until you know the history of that idea."—AUGUSTA COMTE.