

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE
UNIVERSITY OF PENNSYLVANIA]

AN ANHYDROUS DISTILLATION METHOD FOR THE DETERMINATION OF CERTAIN METALS IN ORGANIC COMPOUNDS. I. THE DETERMINATION OF MERCURY¹

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In the method described below, the sample is decomposed by concentrated sulfuric acid and ammonium (potassium) persulfate in a special apparatus, and mercury is distilled out as chloride by passing a stream of hydrogen chloride and heating to the temperature of distillation of the sulfuric acid (external temperature about 260–310°). The mercuric chloride is collected in water, and is determined by an adaptation of Jamieson's iodate method. Presence of chlorine or bromine introduces no difficulty, but that of iodine necessitates certain changes in the procedure. The method is believed to be general.

It appears that no similar procedure has been described. The volatilization of certain metals as anhydrous halides is employed in the analysis of minerals which are advantageously decomposed by heating in a stream of chlorine, carbon tetrachloride, etc. The wet distillation of metallic chlorides volatile with steam is familiar in the case of arsenic, and Biltz² separated arsenic, antimony and tin in this way. Strecker and Riedemann³ observed mercuric chloride to pass over in part with arsenic, and upon this fact Strecker and Conradt⁴ based a procedure for quantitative (though relatively slow) distillation of mercury in steam containing hydrochloric and hydrobromic acids.

In the elaboration of a complete procedure including the decomposition and anhydrous distillation outlined above, it was necessary finally to determine mercury in a solution containing hydrochloric and sulfuric acids and sulfur dioxide, or the salts formed by their neutralization. The nature of the solution excluded Volhard's thiocyanate titration. The iodimetric method of Rupp⁵ yielded in five trials with pure mercuric chloride results which were concordant but somewhat high. Isolation of mercury as metal by excess stannous chloride, the washed globules being dissolved in nitric acid and titrated with thiocyanate,⁶ was subjected to trial,

¹ This paper is constructed in large part from the doctorate thesis of Edward P. Fenimore, University of Pennsylvania, 1929.

² Biltz, *Z. anal. Chem.*, **81**, 82 (1930).

³ Strecker and Riedemann, *Ber.*, **52**, 1935 (1919).

⁴ Strecker and Conradt, *ibid.*, **53**, 2113 (1920).

⁵ Rupp, *ibid.*, **39**, 3701 (1906); **40**, 3276 (1907); *Chem.-Zig.*, **32**, 1077 (1908); Smith, *Am. J. Pharm.*, **83**, 311 (1911); Kolthoff and Keyzer, *Chem. Abstracts*, **14**, 3035 (1920); Kolthoff, *ibid.*, **17**, 1106 (1923).

⁶ The method of Krieckhaus: Low, "Technical Methods of Ore Analysis," John Wiley and Sons, Inc., New York, 1922, 9th ed., p. 159.

a filter being used to retain floating particles of mercury otherwise lost during the washing by decantation. Results were satisfactory when the quantity of mercury was 0.2–0.3 g. (average error, -0.1%), but with 0.1 g. or less of mercury the results were barely acceptable or considerably too low.⁷

Determination of mercury as sulfide by precipitation with hydrogen sulfide was found to yield high results. With dilute solutions of mercuric chloride about 0.03 normal in hydrochloric acid the errors averaged $+0.34\%$, and in presence of salts the errors were larger. This matter is discussed in another paper.⁸

The iodate method of Jamieson,⁹ in which mercury is precipitated as $\text{ZnHg}(\text{SCN})_4$, which is titrated with standard iodate solution in presence of hydrochloric acid, was found to be satisfactory, the small errors averaging 0.0001 g. For precipitation from the solution obtained in the distillation method, an increase in the concentration of the precipitating reagent was found necessary. The accuracy under the conditions adopted was nearly as high as that of the original method. For comparison purposes the method of White was adopted.¹⁰ The sample, in warm (not hot) concentrated sulfuric acid, was decomposed by addition of powdered permanganate in small portions, the diluted liquid cleared by chlorine-free hydrogen peroxide, and the mercury titrated with thiocyanate solution standardized under the same conditions against pure mercury metal. Tests of this procedure, using pure (99.98%) mercuric acetate, and sucrose to provide oxidizable matter, showed it to be satisfactory, results for mercury averaging 0.04% low. This comparison method is not applicable to compounds which contain halogen, presence of which both increases danger of loss of mercury during the rather vigorous decomposition and excludes the convenient thiocyanate titration.

Distillation Method for Determination of Mercury in Organic Compounds.—The complete apparatus is illustrated in the figure.

1. **Decomposition and Distillation.**—Receiver M contains about 20 cc. of water, and the trap N about 5 cc. Stopcock P is closed. Tube p extends just to the surface of the water in M, and the latter is supported in a beaker of cold water.

⁷ Willard and Boldyreff, *THIS JOURNAL*, **52**, 569 (1930), determined mercury gravimetrically as metal following reduction by stannous chloride, and, using quantities of mercury never less than 0.14 gram, found it necessary to apply an additive correction of 0.0010 g.

⁸ Fenimore and Wagner, *ibid.*, **53**, 2453 (1931).

⁹ Jamieson, *J. Ind. Eng. Chem.*, **11**, 296 (1919); "Volumetric Iodate Methods," The Chemical Catalog Co., Inc., New York, 1926, p. 42.

¹⁰ White, *THIS JOURNAL*, **42**, 2350 (1920). The method of Eschka, in the modification described by Whitmore ("Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, 1921, p. 365), proved to be somewhat uncertain. The lime method is cumbersome and inclined to yield low results, and the modification by Bouton and Duschak [U. S. Bur. Mines Technical Paper No. 227, 1920] for mineral analysis has not been developed for use with organic mercury compounds.

The sample, containing not more than 0.15 g. of mercury, is weighed in a small glass cup, introduced into the decomposition flask G, and dissolved in 4-5 cc. of fuming sulfuric acid, with warming if necessary. To the cooled liquid is added 10 g. of powdered ammonium persulfate (or 12 g. of potassium persulfate), and then 15 cc. of concd. sulfuric acid is introduced in such way as to wash off any powder adhering to the ground surface H.¹¹ The decomposition flask is put in place, funnel F is charged with 5 cc. of concd. sulfuric acid, and connections are made as shown in the figure.

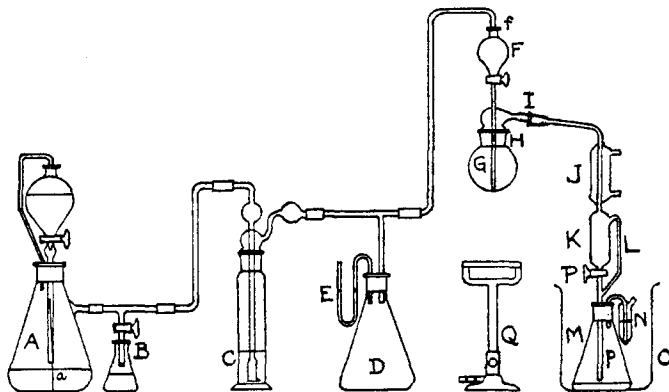


Fig. 1.—A, HCl generator; NH_4Cl and concd. HCl in flask, concd. H_2SO_4 in funnel. Rod *a* causes acid to enter steadily and not by drops; B, pressure release; flask contains water; C, concd. H_2SO_4 drier and bubble-counter; D, safety flask; E, manometer (concd. HCl); F, funnel of 25 cc. capacity; G, decomposition flask of 100 cc. capacity; H and I, ground joints; J, water condenser; K, reservoir of 6-7 cc. capacity; L, vapor by-pass; M, receiver, capacity 150 cc.; N, trap, capacity 15 cc.; O, cooling bath; Q, ring burner.

Flask G is heated cautiously until oxidation starts, shown by gentle effervescence, and decomposition is completed by judicious heating, with occasional cooling if necessary. When active bubbling ceases, the stopcock F is opened, a stream of hydrogen chloride (2 or 3 bubbles per second) is started, and the flask is heated rapidly until sulfuric acid distils. Mercuric chloride volatilizes in part far below its boiling point, collecting at first in the upper parts of the flask. As the temperature rises the mercuric chloride passes over rapidly, and eventually most of it is washed into reservoir K by the sulfuric acid which distils. When 5-6 cc. of acid has collected in K, the heating is stopped, the stream of hydrogen chloride is checked, and the apparatus separated at I, the receiving unit being kept assembled.

For compounds which decompose normally the operations just described can be completed in less than thirty minutes. There should be no odor of hydrogen chloride, as the generator sketched permits good control of the gas stream, and as absorption of hydrogen chloride in M is complete.

¹¹ If the substance is too actively attacked by the oxidizing mixture to permit addition of all the persulfate at one time, the sample is treated with 5 cc. of fuming acid and 10 cc. of concd. sulfuric acid, and persulfate is added in small portions while cooling the (open) flask. The ground surface is then rinsed with 5 cc. of concd. sulfuric acid, and the analysis continued as described above.

2. **Determination of Mercury in Absence of Iodine.** (a) **Precipitation of Zinc Mercuric Thiocyanate.**—The acid in K is allowed to enter M by drops, regulated by the stopcock, the flask being rotated and cooled during the addition. The parts JKL are washed out partially with water (about 10 cc.) introduced at I. Tube p is thrust to the bottom of the flask, a rubber tube is attached to the outlet of the trap, and the acid liquid is forced up into JKL by gentle blowing, and is then allowed to recede. This is repeated several times, to dissolve any lumps of mercuric salt adhering to the glass. The flask M is disconnected and the associated parts washed with numerous small portions of water. If the foregoing operations have been completed properly, the volume at this point will be about 60 cc., and should not exceed 80 cc.

To oxidize sulfur dioxide, fresh bromine water is added (or, if the volume already approaches the stated maximum, vapors from the mouth of a bromine bottle are "poured" into the flask) until a yellow color persists. The solution is neutralized with pure sodium hydroxide, added as a saturated solution and with cooling until the yellow color disappears. The liquid is then barely acidified with hydrochloric acid (yellow color), and an excess of 5 cc. of 6 *N* hydrochloric acid is added.¹²

To the cold solution, whose volume should not exceed 100 cc., there is added 25 cc. of the stronger Jamieson reagent (a filtered solution containing 73 g. of $ZnSO_4 \cdot 7H_2O$ and 125 g. of KSCN per liter), the liquid is mixed and allowed to stand for thirty minutes or longer. The precipitate is filtered with gentle suction on a 9-cm. paper supported by a filter cone. The flask is rinsed with wash liquid (2 cc. of the stronger Jamieson reagent in 450 cc. of water), and precipitate and filter paper are washed five or six times with the same liquid.

(b) **Titration.**—The filter paper and precipitate are put into a 250-cc. glass-stoppered Erlenmeyer flask, treated with 45 cc. of cold hydrochloric acid (1 volume of water and 3.5 volumes of concd. acid) and 6–7 cc. of chloroform, and titration with standard potassium iodate solution (about 25 g. per liter, standardized as suggested below) is begun at once, with continual rotation of the flask. After the color has become pale, titration is continued cautiously, with shaking of the stoppered flask after each addition, until the last tint in the chloroform is just discharged. The end-point is very sharp.

Standardization of Iodate Solution.—If pure iodate is used the solution will have almost exactly the theoretical mercury equivalent ($Hg \approx 6KIO_3$). It seems better, however, to standardize the solution against pure mercury or mercuric salt by the Jamieson procedure. For this purpose the mercuric solution is acidified with 5 cc. of 6 *N* hydrochloric acid, diluted to 50 cc., precipitated with 25 cc. of Jamieson's reagent (the weaker reagent, see paragraph 3), and the filtration and titration conducted as outlined above.

Accuracy tests of the distillation procedure applied to pure mercuric chloride are summarized in Table I.

TABLE I

ACCURACY TESTS OF DISTILLATION PROCEDURE USING PURE MERCURIC CHLORIDE^a

HgCl ₂ taken, g.	Hg taken, g.	Hg found, g.	Error, g.
0.1479	0.1092	0.1094	+0.0002
.1249	.0922	.0920	— .0002
.1363	.1006	.1006	.0000
.0997	.0736	.0736	.0000

^a No organic material was present, and no persulfate was used; otherwise the procedure described was employed.

¹² The small excess of free bromine is later reduced by the thiocyanate.

Results for organic mercury compounds are given in Table III. An analysis can be completed in less than two hours.

3. Determination of Mercury in the Presence of Iodine.—Most of the iodine volatilizes before mercuric chloride does so in quantity. The formation of mercuric iodide in the receivers makes it necessary to wash them out with potassium iodide solution. The mercury then cannot be precipitated by Jamieson's reagent. It is therefore first separated as metal by addition of zinc dust, excess of zinc dissolved in dilute hydrochloric acid, mercury and residual zinc dissolved in nitric acid, and mercury precipitated by Jamieson's original method. The procedure is as follows.

After the distillation, reservoir K is emptied into M, 10 cc. of 10% potassium iodide solution introduced at I, and liquid from M forced up into JKL and held there until all mercuric iodide has dissolved. These parts and the trap are washed with water as described in 2(a). The volume of the liquid should be about 75 cc.

To oxidize sulfur dioxide a strong solution of iodine in potassium iodide is added until the color persists. One gram of zinc dust is suspended in a little water and added in small portions to the solution. The flask is covered, and when evolution of hydrogen moderates (five to ten minutes) the amalgam, excess zinc, and a small brown precipitate (apparently mercuric sulfide) are filtered with suction on a glass filtering crucible (30 cc.), and washed well with water. The crucible is placed upright in a 150-cc. beaker, and 25 cc. of 6 *N* hydrochloric acid added (about 5 cc. in the beaker and 20 cc. in the filtering crucible). The beaker is covered and the acid warmed (not boiled) until the amalgam is reduced to a small mass, stiff in consistency and mossy in appearance. If this treatment is continued until the amalgam becomes liquid, and especially if the acid is boiled, there is danger of loss of mercury. The filtering crucible is replaced in its holder, the acid drawn through, and filter and amalgam washed well with water. The lump of amalgam is dropped into flask M, and the filtering crucible is replaced in its holder, with flask M beneath as receiver. The crucible is treated with several cc. of strong bromine water (no suction), and then with about 2 cc. of hot concd. nitric acid. This treatment dissolves any particles of amalgam and also the small dark precipitate. After a minute the liquid is drawn through the filter, which is treated with several successive portions of hot concd. nitric acid, using in all about 5 cc. of nitric acid. The filter is finally washed with two small portions (1–2 cc.) of water. The flask is warmed until the amalgam dissolves, the solution diluted to about 25 cc. and cooled. Bromine water is added until the color persists.

The liquid is neutralized with strong sodium hydroxide solution, and acidified with 2 cc. of 6 *N* hydrochloric acid; an acidity much higher than this may lead to interaction of nitric acid and thiocyanate during the precipitation. The solution is cooled, diluted to 50 cc., and mercury precipitated by addition of 25 cc. of Jamieson's reagent (29 g.

TABLE II
ACCURACY TESTS OF SEPARATION OF MERCURY FROM STRONGLY ACID SOLUTION BY ZINC DUST^a

Hg taken, g.	KI present, g.	Hg found, g.	Error, g.
0.1042	None	0.1041	–0.0001
.1042	None	.1045	+ .0003
.1042	2	.1046	+ .0004
.0521	2	.0517	– .0004
.0521	2	.0518	– .0003
.1033	2	.1032	– .0001

^a The mercury solutions contained 10 cc. of concd. hydrochloric acid and 5 cc. of concd. sulfuric acid, but no sulfur dioxide; otherwise the procedure was that described.

of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 50 g. of KSCN per liter, obtained by diluting two volumes of the stronger reagent with three volumes of water). The liquid becomes deep red due to iron from the zinc. After an hour or more the precipitate (yellow-tinted when obtained by this procedure) is filtered, washed and titrated as outlined in 2(a) and (b).

Accuracy tests of the zinc separation of mercury are summarized in Table II.

Results for determination of mercury in presence of iodine are given in Table III.

TABLE III
DETERMINATION OF MERCURY IN ORGANIC COMPOUNDS

Compound	Distillation method Sample, g.	Mercury, %	Comparison method Mercury, %
Diacetatomercuriphenol	0.1508	66.36	
	.1537	66.40	66.43
	.1522	66.36	66.29
	.16045	66.41	
	.14895	66.30	
		Av. 66.37	Av. 66.36
Mercury <i>p</i> -ditolyl	0.19945	51.74	
	.1984	51.76	51.92
	.19335	51.98	51.85
	.2004	51.73 ^a	
	.1998	51.87 ^a	
	Av. 51.82	Av. 51.89	
<i>n</i> -Butyl mercury mercaptide	0.2000	61.14	Contained HgCl_2 : not analyzable
	.2206	61.06	
		Av. 61.10	
Mercurated fluorescein Na-salt	0.3048	31.23	30.63
	.3045	31.19	30.66
		Av. 31.21	Av. 30.65
<i>p</i> -Aminophenylmercuriacetate	0.2009	59.78	60.05
	.2055	59.84	60.06
		Av. 59.81	Av. 60.06
Mercuric cyanide	0.1534	79.34	79.44
			79.35
			Av. 79.39
Mercurated <i>p</i> -nitrotoluene (mostly HgO)	0.1311	89.66	89.32
	.1363	89.74	89.49
		Av. 89.70	Av. 89.41
Dibromo-hydroxymercurifluorescein	0.3576	27.89	
	.3543	27.71	27.87 ^b
	.3599	27.71	27.66 ^b
		Av. 27.77	Av. 27.77
Diacetatomercuriphenol with 0.1 g. <i>diiodofluorescein</i> added in trials by distillation method	0.1505	66.35	
	.1421	66.41	
	.1454	66.35 ^c	
	.1448	66.54 ^c	
	Av. 66.41	(66.36)	

^a These two analyses run in ninety-three minutes each. ^b Mercury determined as sulfide following hot decomposition by White's method. ^c These two analyses together were completed in six hours elapsed time, with eighty-minute precipitation intervals.

4. **Analytical Results for Some Organic Mercury Compounds.**—Results by the new method, in comparison with those obtained by the comparison method, are shown in Table III.

Comments.—The use of potassium dichromate for the oxidation gave satisfactory decompositions, but it was found impossible to distil out all the mercury as chloride, retention by anhydrous chromic sulfate seeming to occur. The use of persulfate and concd. sulfuric acid for decomposition of organic samples was apparently new at the time this work was first described (1929), though several chemists had earlier used persulfate with water or dilute sulfuric acid.¹³ Recently Thompson and Oakdale¹⁴ applied persulfate and fuming sulfuric acid in the determination of halogens in organic compounds by a modification of the Baubigny-Chavanne-Robertson method.

In presence of iodine, the preliminary displacement of mercury from the distillate liquid requires zinc *dust*. Qualitative trials showed that 1 g. of finely granular zinc was ineffective, whereas half as much zinc dust added as a suspension removed mercury completely in a few minutes.

The principal impurities in the zinc dust were iron (0.03%) and lead (0.1%). As these metals are concentrated in the zinc amalgam during the hydrochloric acid treatment, their effects upon results by Jamieson's method were studied. Iron yielded of course a strongly colored solution, and the precipitate was tinted, but the effect of even ten times the iron present in 1 g. of zinc dust was nil. In the presence of lead the precipitate was yellow-tinted, as it was in analyses following separation of mercury by zinc, and a positive error rather regularly entered the results. No relationship could be established between the quantity of lead and the magnitude of the error, although the color of the precipitate deepened as the quantity of lead was increased. These results, however, indicate the advisability of using zinc dust as free as possible of impurities.

The trap N is probably not essential, no evidence of presence of mercury in it having been obtained.

Acknowledgment is made to Dr. H. S. Lukens and to Dr. W. M. McNabb for helpful suggestions.

Summary

In the method described for determination of mercury in organic compounds the sample is decomposed by persulfate and concentrated sulfuric acid, mercury is distilled out as chloride by heating in a stream of hydrogen chloride, and is precipitated as zinc mercuric thiocyanate and determined by iodate titration. In presence of iodine, mercury in the distillate liquid is

¹³ Newbery, *J. Chem. Soc.*, **127**, 1751 (1925); Duret, *Compt. rend.*, **167**, 129 (1918); Rupp and Lehmann, *Arch. Pharm.*, **251**, 1 (1913); *Chem. Abstracts*, **7**, 1151 (1913); H. Meyer, "Analyse," Springer, Berlin, 1922, 4th ed., p. 313.

¹⁴ Thompson and Oakdale, *THIS JOURNAL*, **52**, 1195 (1930).

first precipitated by zinc dust, excess zinc dissolved in hydrochloric acid, the residual amalgam dissolved, and mercury determined by the iodate method.

Trials of the procedure with a variety of compounds and in presence of halogens and of sulfur showed it to be apparently of general applicability. The method has the advantage that in presence of halogens it eliminates the danger (which otherwise attends decompositions by acid agents) of loss of mercury by volatilization.

Presence of iodine prolongs the analysis, but in its absence the method is at least as rapid as others of comparable accuracy and applicability.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF BRITISH COLUMBIA]

STUDIES IN THE RARE EARTHS. I. THE PREPARATION OF THE BROMATES OF CERIUM GROUP RARE EARTHS

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Historical

The method of separating the rare earth elements that proved successful in permitting of the concentration of illinium was a fractional crystallization of samarium rich fractions obtained from a double magnesium nitrate series of rare earths, as the bromates, the cerium, lanthanum and praseodymium having been removed completely prior to the conversion to the double magnesium nitrate. This latter crystallization permitted of the separation of the bulk of the neodymium from the remaining elements but experience seems to prove that in such a series the illinium concentrates with the neodymium, rendering its detection difficult, the order of solubility of these salts being such that we have an increase with increasing atomic weight.²

From such a study, then, it would appear to be most advantageous to submit the original material to a preliminary, rather than to a subsequent crystallization as the bromates. The serial order of solubilities would then become, erbium, lanthanum, yttrium, holmium, praseodymium, dysprosium, neodymium, terbium, illinium, gadolinium, samarium, and europium (least soluble), thus permitting of a more efficient separation of the illinium and neodymium.^{2,3}

Introduction

The standard method of preparing the bromate is that of James, and was used extensively by him in his classical work on the yttrium group earths.

¹ National Research Fellow.

² Harris with Hopkins, *THIS JOURNAL*, **48**, 1585 (1926).

³ James, *ibid.*, **48**, 2871 (1926).