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Mercury may be quantitatively precipitated as mercuric periodate, $Hg_{5}(IO_{6})_{2}$, from 0.15 N nitric or 0.1 N sulfuric acid solution. It may be weighed in this form, or determined volumetrically by iodometric methods. Moderate amounts of aluminum, cadmium, zinc, copper, nickel, calcium, and magnesium do not interfere.

berg (7) who treated mercuric oxide with a nitric acid solution of periodic acid. It was described as an orange-red salt having the composition $Hg_{5}(IO_{6})_{2}$, not decomposed at 100° C., but completely volatile on ignition. It was insoluble in water.

ERCURIC periodate

was first prepared in

1834 by Bengieser

(2) by the action of sodium

periodate on mercuric nitrate.

Later it was prepared by

Lautsch (6) and by Rammels-

In the course of an investigation on periodates in progress in this laboratory this salt was studied, particularly with reference to its suitability for the quantitative determination of mercury.

Experimental Data

Mercuric nitrate, dissolved in nitric acid of varying concentrations, was precipitated by the addition of excess of sodium periodate. Precipitation was complete at concentrations not greater than 0.15 N. At 100° C. the salt was appreciably soluble in water, but below 50° C. the solubility was practically negligible.

A sample of the salt was thoroughly washed with hot water, dried at 100° C. for 4 hours, and analyzed gravimetrically for iodine and mercury. It was dissolved in dilute nitric acid, tartaric acid was added, and the solution made ammoniacal. A slight excess of sulfite was added to reduce the periodate and the mercury was precipitated from the hot ammoniacal solution by hydrogen sulfide. After standing one hour, the mercuric sulfide was filtered through a filtering crucible with porous porcelain bottom, washed with hot water containing a little hydrogen sulfide, then with pure water, dried 2 hours at 100° C., and weighed. The filtrate was oxidized to sulfate by pure hydrogen peroxide, the excess removed by boiling, a little arsenite added to reduce any iodate, and after acidifying with nitric acid, the iodide was precipitated and weighed as silver iodide. The results were: found, 74.75, 74.73, 74.76 per cent of HgO, average 74.75 per cent, which is the theoretical value; 25.30, 25.26 per cent of I₂O₇, average 25.28 per cent, theory 25.25 per cent. The salt is thus shown to be the pentamercuric paraperiodate, Hg₅(IO₆)₂.

Some of this salt was recrystallized by dissolving it in concentrated nitric acid and diluting with water. The bright red crystals were washed and dried. They proved to be less pure than the precipitated salt. Analysis showed 73.83, 73.50, 73.76, 73.90 per cent of H₂O, average 73.75 per cent, compared with the theoretical 74.75 per cent; and 25.26, 25.38, 25.30, 25.28 per cent of I₂O₇, average 25.30 per cent, compared with 25.25 per cent.

The iodine in mercuric periodate was determined volumetrically in two ways:

¹ Received August 12, 1931. Presented before the Division of Physical and Inorganic Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

² From a dissertation submitted by J. J. Thompson to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of doctor of philosophy. Method A—The salt was dissolved in excess of potassium iodide, acidified with hydrochloric acid, and the liberated iodine titrated with thiosulfate:

 $\begin{array}{l} Hg_{5}(IO_{6})_{2}+34KI+24HCl\\ =5K_{2}HgI_{4}+8I_{2}+24KCl+12H_{2}O\end{array}$

Method B—The salt was dissolved in an excess of standard arsenite by adding considerable concentrated hydrochloric acid, and the excess was titrated back with iodate using a little chloroform as indicator (1, 5):

$$\begin{array}{l} \mathrm{Hg}_{t}(\mathrm{IO}_{6})_{2}+6\mathrm{H}_{3}\mathrm{AsO}_{3}+12\mathrm{HCl}=5\mathrm{Hg}\mathrm{Cl}_{2}+\\ 2\mathrm{ICl}+6\mathrm{H}_{3}\mathrm{AsO}_{4}+6\mathrm{H}_{2}\mathrm{O}\end{array}$$

In six titrations of the precipitated salt by these methods the maximum variation from the theoretical value was only. 0.02 per cent.

Quantitative Determination of Mercury

Mercury is usually weighed as metal or as mercuric sulfide. Precipitation of the latter in hydrochloric acid solution is not entirely satisfactory (3), especially in the presence of zinc, cadmium, and copper, because of contamination with other sulfides. Volumetrically mercury may be determined in a number of ways, most of which are not particularly accurate, the thiocyanate titration (4) being a common and accurate one.

It has been found that mercury can be determined gravimetrically or volumetrically by precipitation as mercuric periodate, $Hg_6(IO_6)_2$, in the presence of aluminum, zinc, cadmium, nickel, copper, calcium, and magnesium. The method is rapid, convenient, and accurate, and the end point in the volumetric method is very sharp. Iron interferes because it is precipitated as ferric periodate. Attempts were made to keep it in solution as the complex fluoride, but under these conditions the mercury was not completely precipitated. Chloride and other halides must be absent, because they prevent complete precipitation of mercury, doubtless owing to the slight ionization of mercuric halides. The maximum permissible acidity for complete precipitation is 0.15 N nitric or 0.1 N sulfuric acid, and under these conditions a large excess of periodate is required.

Table I-Gravimetric Determination of Mercury as Hg₅(IO₆)₂

· MER	CURY			
Taken	Found	Error	ACID PRESENT	
Gram	Gram	Mg.		
0.0497	0.0497	0	Nitric	
0.1243	0.1240	- 0. 3	Nitrie	
0.1563	0.1563	0	Nitric	
0.2904	0.2903	- 0.1	Nitrie	
0.3882	0.3885	+ 0.3	Nitric	
0.5493	0.5492	- 0.1	Nitric	
0.5721	0.5721	0	Nitric	
0.4799	0.4798	- 0.1	Sulfuric	
0.6313	0.6311	-0.2	Sulfuric	
0 4852	0 2563	-228.9	Hydrochloric ^a	

^a Effect of hydrochloric acid in preventing precipitation is shown.

PROCEDURE—A sample of pure mercury was dissolved in nitric acid, sp. gr. 1.2, and the solution evaporated to dryness. It was taken up with 150 cc. of 0.15 N nitric acid or 0.1 N sulfuric acid, heated to boiling, and the mercury precipitated by adding slowly, with constant stirring, 2 grams of sodium or potassium periodate dissolved in 50 cc. of water. It was cooled, filtered through a filtering crucible with a sintered-glass or porous porcelain bottom, washed with warm water, dried at 100° C. for 2 or 3 hours, and weighed as $Hg_5(IO_6)_2$. The results are shown in Table I.

Volumetric Determination

Method A—The filtered and washed precipitate of mercuric periodate in the crucible was treated with 2 or 3 grams of solid potassium iodide and 10 to 15 cc. of water, stirring until all the periodate had dissolved. The solution was washed into a 150-cc. conical flask (most conveniently a suction flask), acidified with 10 cc. of 2 N hydrochloric acid, and the liberated iodine titrated with 0.1 N sodium thiosulfate, using starch as indicator.

Method B—The precipitate in the crucible was treated with an excess of standard arsenite and then concentrated hydrochloric acid added until it dissolved, about 35 cc. being required if the volume at the end of the titration is about 100 cc. The solution was washed into a 150-cc. glassstoppered conical flask, and titrated with 0.1 N potassium iodate until it had a light brown color. Four or five cubic centimeters of chloroform were then added and the titration continued, shaking after each addition until the purple color of the iodine just disappeared $(1, \delta)$. The solution at the

ILLARD

manganese can be determined

colorimetrically by oxidation

to permanganate with a small

excess of periodate. The so-

lution thus obtained is stable

Greathouse (4)

have shown that

and

end point should contain between 28 and 45 cc. of hydrochloric acid, sp. gr. 1.18, per 100 cc.

The results, both with pure mercury and in mixtures with other metals, are shown in Table II. In the first three experiments method B was used; in all others, method A. The mercuric salt was precipitated from a nitric acid solution.

Table	II—Volumetric	Determination	oť	Mercury	as	Hg5(IO6)2
rabic	II VOIGHICCIIC	Determination	0.	moreury	40	1190(100)2

MERCURY		OTHER METALS			
Taken	Found	PRESENT	Error		
Gram	Gram	Gram	Mg.		
0.3645	0.3646		+0.1		
0.2071	0.2070		-0.1		
0.0513	0.0513	0.20 Ni	0		
0.2556	0.2558	0.15 Al	+0.2		
0.1327	0.1327	0.18 Cd	0		
0.1903	0.1902	0.17 Zn	-0.1		
0.1064	0.1065	0.13 Cu	+0.1		

If a chloride solution is to be analyzed, the mercury may first be precipitated as metal or sulfide and then converted into nitrate or sulfate.

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Volumetric Determination of Manganese after Oxidation by Periodate^{1,2}

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Manganese up to 30 mg. can be determined by oxidation to permanganate with periodate in either phosphoric or sulfuric acid solution, removal of excess periodate by precipitation as mercuric salt, and reduction of the permanganate by standard ferrous sulfate. The reaction goes best in a phosphoric acid solution, in which case less than a milligram of chromium does not interfere. Cobalt, cerium, and chloride must be absent.

for weeks, a fact confirmed by **must be absent**. others (3). It seemed desirable, therefore, to make this the basis of a volumetric method by removing the excess of periodate. This was accomplished by precipitation as mercuric periodate, after which the permanganate was titrated by adding excess of standard ferrous sulfate and back titrating with permanganate. Although bismuth periodate is the least soluble of all, its presence caused certain errors which made its use for this purpose impossible.

Precipitation of Periodate as Bismuth Salt

A known volume of standard permanganate was reduced with ferrous sulfate in a dilute sulfuric acid solution, and the manganous salt was then oxidized to permanganate by adding 0.3 gram of sodium metaperiodate, NaIO₄, and boiling gently for 15 minutes. After cooling to room temperature,

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² From a dissertation submitted by J. J. Thompson to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of doctor of philosophy. the excess periodate was precipitated by the addition of bismuth perchlorate, as a white, voluminous precipitate of bismuth periodate. The solution was immediately titrated with standard ferrous sulfate. To make the end point more distinct in the presence of the precipitate,

alphazurine (Erioglaucine A) (2) was added just before the end point. Too little ferrous sulfate was always used, showing that some permanganate had been reduced, because other experiments proved that oxidation was complete. The surprising fact was that in the presence of iodate some of the permanganate was used in the oxidation of bismuth. In the presence of bismuth periodate only, no such error occurred. Both bismuth and iodate are necessarily present because the latter is formed by reduction of the periodate by manganous ion (4). It could not be completely removed by precipitation as silver iodate. If standard permanganate to which as much as 0.6 gram of sodium periodate had been added was treated with a bismuth salt, and, without filtering, titrated with ferrous sulfate, accurate results were obtained. If, however, excess of the latter was added and back titrated with permanganate, the results indicated that the excess of ferrous salt was slowly oxidized by the precipitate of bismuth periodate even in cold solution.

There are, therefore, two errors to be considered: oxidation of the excess reducing agent by iodate or insoluble