

### Procedure

Chlorine gas from a cylinder passes through a flask used as a safety trap and then is condensed in a large test tube (or flask for larger amounts) by surrounding it with a mixture of acetone or ether and solid carbon dioxide. The powdered iodine is added slowly and immediately is converted to flocculent, orange, iodine trichloride which settles gradually. When the liquid space is filled with the trichloride, the excess chlorine is evaporated into a second container where the process may be repeated.

### Properties

The product is a fluffy orange powder decomposing rapidly at 47 to 62°C. and should be immediately placed in a dry bottle. A sample prepared in this way analyzed for chlorine, 45.7 per cent (calc. 45.61 per cent) and for iodine, 54.5 per cent (calc. 54.39 per cent). The yield is 100 per cent based on the iodine used.

### Reference

1. THOMAS and DEPUIS: *Compt. rend.*, **143**, 282 (1906).

## 58. THE PERIODATES OF SODIUM, POTASSIUM, AND BARIUM

SUBMITTED BY H. H. WILLARD\*

CHECKED BY E. H. HUFFMAN† AND LOUIS GORDON†

The periodates of the alkali metals<sup>1</sup> are best prepared by oxidation of iodate by chlorine.<sup>2</sup> The oxidation can also be effected by persulfate,<sup>3</sup> but this is inferior as a preparative method and is to be recommended only when no ready supply of chlorine is available.

### Procedure

**Sodium Iodate.** This compound, from which all of the following are prepared, may be readily obtained by oxida-

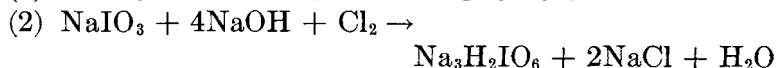
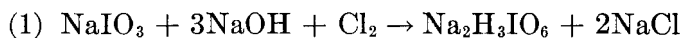
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tion of iodine with an excess (at least 20 per cent) of sodium chlorate.

In a 5-l. flask, 125 g. of pure sodium chlorate is dissolved in 500 ml. of water at 45°C. After acidification with 2 ml. of concentrated nitric acid, 100 g. of iodine is added. The mixture is warmed until reaction just begins (at 50°C., if the acidity is correct). To prevent loss of iodine, the mouth of the flask is lightly closed with an inverted beaker. Provision should be made for immersing the flask in cold water in case the reaction becomes too vigorous. Complete disappearance of the iodine ordinarily requires 10 or 15 minutes. The iodate solution is then ready to be oxidized to periodate.

#### A. SODIUM PARAPERIODATE, CHLORINE METHOD



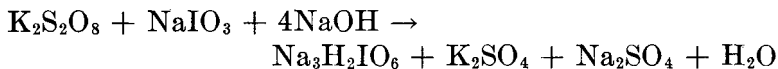
The best yields are obtained when the alkali concentration is near that expressed by (2). Under these conditions, nearly pure  $\text{Na}_3\text{H}_2\text{IO}_6$  is formed although a small amount of the other salt may be present.

To a solution of sodium iodate from 100 g. of iodine are added 140 g. of solid sodium hydroxide and, if necessary, 100 to 200 ml. of water to allow ready mixing. The mixture is heated to boiling, and chlorine is passed in as rapidly as possible without spattering. This is best accomplished by passing the chlorine in through a glass tube not less than 1 cm. in inside diameter, which is used as a hand stirrer. (A smaller tube is apt to clog.) Best yields are obtained when the solution is boiled rapidly and stirred vigorously. The reaction is finished when the alkali has been neutralized and chlorine is no longer absorbed (10 to 15 minutes).

The solution is made slightly alkaline with sodium hydroxide (to change any  $\text{Na}_2\text{H}_3\text{IO}_6$  to the less soluble  $\text{Na}_3\text{H}_2\text{IO}_6$ ), cooled, and filtered. The precipitate is washed several times with cold water (below 20°C.) and dried at

110°C. The yield is about 225 g. (97 to 98 per cent). The  $I_2O_7$  content is 62.2 to 62.8 per cent;  $Na_3H_2IO_6$  demands 62.23 per cent.\*

#### B. SODIUM PARAPERIODATE, PERSULFATE METHOD†



To the sodium iodate solution from 100 g. of iodine 40 g. of sodium hydroxide is added in portions.‡ After dilution to 1200 ml., the solution is heated to boiling and vigorously stirred mechanically while 213 g. of potassium persulfate is added and then 170 g. of sodium hydroxide in small portions. The boiling is continued for 15 minutes. The solution is cooled to 40°C., filtered on a fritted-glass filter (or decanted), and the precipitate is washed with cold water. If cooled below 40°C., large amounts of sulfate crystallize. Even when prepared as described, the precipitate usually gives a test for sulfate after numerous washings. After drying at 110°, the yield is 223 to 227 g. of 94 to 97 per cent purity, based on the  $I_2O_7$  content.

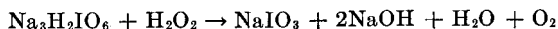
#### Sodium Metaperiodate.



For each 100 g. of sodium paraperiodate, 200 ml. of water and 55 ml. of concentrated nitric acid (a 50 per cent excess)

\* The  $I_2O_7$  content of the periodates described is determined as follows: The weighed sample is covered with 20 ml. of water, and 5 to 10 drops of 6N HCl is added to hasten solution. No chlorine is liberated from the acid of this concentration. The solution is diluted to 100 ml., made just alkaline to phenolphthalein paper with borax, buffered with borax and boric acid (MÜLLER and WEGELIN: *Z. anal. Chem.*, **52**, 755-759 (1913), and an excess of potassium iodide is added. Under these conditions, the periodate is reduced to iodate. The liberated iodine is titrated with 0.1N arsenite.

The basicity of sodium paraperiodate is determined by titration with acid after reduction to iodate by boiling with neutral hydrogen peroxide:



† The presence of ammonium salts is very detrimental to this reaction.

‡ Some precipitation occurs as a result of oxidation by the chlorine formed in the preparation of the iodate.

are added. If not clear, the solution is filtered through asbestos and evaporated on a steam bath until crystals appear. The solution is cooled to 20°C., filtered, and the precipitate is washed with cold water, centrifuged, and dried at 110°C. It forms brilliant, clear crystals.

If the solution is cooled to too low a temperature, white crystals of  $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$  are formed. The transition point is 34.4°C.,<sup>1</sup> but the solution can be cooled much below that point if none of the trihydrate phase is present.

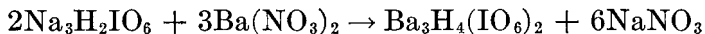
Yields of 61 to 62.1 g. (84 to 86 per cent) are obtained, of purity 99.5 to 99.8 per cent. The remaining periodate may be separated from the sodium nitrate by adding potassium nitrate, which precipitates potassium periodate. This gives an additional 10 to 12 g. (13 to 15 per cent).

**Potassium Metaperiodate.** This compound can be obtained in good yield by oxidation of the iodate with chlorine in alkaline solution. Since the soluble salt  $\text{K}_4\text{I}_2\text{O}_9$  exists in alkaline solution instead of the insoluble  $\text{KIO}_4$ ,<sup>1</sup> no precipitation occurs until all of the alkali is neutralized.

The directions for the preparation differ from those for the preparation of sodium paraperiodate only in that 135 g. of potassium chlorate is used and 195 g. of pure potassium hydroxide. Since the latter always contains water, its percentage purity must be known. The yield is nearly 180 g. (98 to 99 per cent), and the purity is 99.5 per cent.

Impure periodate residues are conveniently recovered by adding potassium nitrate to the acid solution, as described under sodium metaperiodate.

#### **Barium Paraperiodate.**



The sodium periodate from 100 g. of iodine (about 225 g.) is suspended in a liter of boiling water containing 10 ml. of concentrated nitric acid (to increase the solubility of the periodate). A moderate excess of barium nitrate (325 g.) dissolved in hot water is added, and the solution is boiled for 1½ to 2 hours with vigorous stirring. The solution

then is neutralized with barium hydroxide and allowed to cool. The barium periodate which crystallizes is washed with hot water several times by decantation (stirring up the crystals each time) and then on a Büchner funnel. If the salt gives more than a faint flame test for sodium, it is again boiled with barium nitrate solution containing nitric acid and treated as before.

The yield is nearly quantitative. Although the salt cannot be analyzed directly for  $I_2O_7$  because of its insolubility in the buffered solution, a nearly pure product is indicated by the results obtained when it is used to prepare periodic acid.

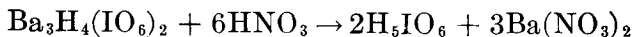
The same salt may be prepared from potassium metaperiodate by adding two equivalents of potassium hydroxide and proceeding as with the sodium salt.

If the salt is to be used for preparing periodic acid, it need not be dried.

#### References

1. HILL: *J. Am. Chem. Soc.*, **50**, 2678 (1928).
2. LANGLOIS: *Ann. chim. phys.*, [3], **34**, 257 (1852); *Ann.* **83**, 153 (1852).
3. MÜLLER and JACOB: *Z. anorg. Chem.*, **82**, 308 (1913).

### 59. PERIODIC ACID



SUBMITTED BY H. H. WILLARD\*

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Of the older methods for the preparation of periodic acid, the most satisfactory for obtaining large quantities is the electrolytic oxidation of iodic acid at an anode of platinum plated with lead dioxide, the cathode solution being dilute nitric acid.<sup>1</sup> The iodic acid for this preparation is conveniently prepared by the electrolytic oxidation of iodine.<sup>1</sup> However, periodic acid prepared in this way often contains

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considerable iodic acid after a year, even when carefully protected from light and dust, doubtless due to traces of platinum derived from the electrode.

The following method of making periodic acid is adapted to large-scale preparation, and the acid so prepared is stable at least over a period of several years. It depends upon the fact that barium nitrate is insoluble in nitric acid of sp. gr. 1.42, whereas periodic acid is readily soluble:

Temp., C.	H <sub>5</sub> IO <sub>6</sub> , g. per 100 ml.	H <sub>5</sub> IO <sub>6</sub> , g. per 100 g. solution
-12° ± 1°	5.68	3.95
26° ± 0.05°	7.82	5.41

The solubility rises rapidly above 25°C. and is about ten times as great in water as in concentrated nitric acid. If dry barium periodate is treated with concentrated nitric acid, the barium nitrate is so finely divided that it is difficult to filter and wash. This is avoided by using more dilute acid or by treating the moist salt with concentrated acid.

### Procedure

One hundred grams of barium periodate is moistened with 75 ml. of water and treated with 200 ml. of colorless\* nitric acid (sp. gr. 1.42). The mixture is kept at 60 to 70°C. for an hour with frequent stirring, cooled to 30 to 40°C., and the barium nitrate filtered off on a fritted-glass Büchner funnel. It is washed with colorless, concentrated nitric acid until free from periodate, which is best done by thoroughly stirring it with the washing acid.

The filtrate and washings are concentrated at 60 to 70°C. *in vacuo* (water pump). If the solution becomes cloudy

\* It is essential that the acid used in this preparation be free from nitrous fumes and nitrous acid, which reduce periodic acid to iodic acid, which may also be formed if the temperature gets too high at any time. If, in spite of precautions, some iodic acid is formed, it may be removed from the periodic acid by recrystallization from colorless, concentrated nitric acid, in which it is but slightly soluble.

because of the separation of a little barium nitrate or iodic acid, it is filtered, the precipitate is washed with nitric acid, and the filtrate and washings are evaporated until periodic acid begins to separate. Sometimes a little more barium nitrate separates first and must be removed. Upon cooling, clear, brilliant crystals of periodic acid are formed. The solution shows a great tendency to supersaturation, and ample time should be allowed after cooling before the crystals are removed. These are centrifuged and dried in the air or *in vacuo* at 50°C. The mother liquor is evaporated for a second recovery. The yield is 46 to 51 g. (90 to 96 per cent), and the purity 99.5 to 99.9 per cent. The addition of potassium nitrate to the second mother liquor recovers the remaining periodic acid as potassium metaperiodate.

As much as 500 g. of barium periodate can easily be carried through this process.

The preparation conveniently starts with iodine which can be converted through the sodium and barium salts to the acid without drying the intermediate products. From 200 g. of iodine, 302 to 326 g. of periodic acid (about a 90 per cent yield) can be obtained. A run can easily be made in a day. The principal losses are due to the volatilization of iodine in the first step, the solubility of sodium periodate, and reduction of the acid to iodic acid. The barium nitrate and much of the nitric acid are recovered for further use.

Finely divided platinum catalyzes the decomposition of periodic acid, so even traces of this metal must be avoided.

A satisfactory vacuum-distillation apparatus is one that resembles a vacuum desiccator with a tube ground into the cover and having a side arm.\* If the ground surface between vessel and cover is improved by grinding with the finest carborundum or emery flour and then with rouge, it will hold a vacuum sufficiently well without any lubricant—

\* An apparatus of this type is sold by the Corning Glass Works.

an essential feature, because periodic acid is so readily reduced.

It is essential that the hot nitric acid shall not come into contact with rubber, in order that no nitrous acid may be formed. To avoid this, the top of the tube ground into the cover is sealed off, and the side-arm delivery tube lengthened to at least 25 cm. The side arm is then inserted 7 to 8 cm. below the water-cooled part of the condenser tube, which should allow of very little clearance, in order that no nitric acid may come in contact with the rubber stopper joining the two.

The still is conveniently heated by placing on an asbestos pad over an electric hot plate with adjustable temperature control. If much refluxing occurs, an asbestos shield should be formed around the still.

#### Reference

1. WILLARD and RALSTON: *Trans. Electrochem. Soc.*, **62**, 239 (1932).

## 60. METALLIC RHENIUM

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Two methods are in common use for the production of metallic rhenium. The first of these involves a direct reduction of commercial potassium perrhenate (procedure A) and yields a product that usually contains a small amount of alkali but is pure enough for most preparative purposes. The second method (procedure B) is slightly more complicated in that a preliminary precipitation of rhenium heptasulfide is followed by conversion to ammonium perrhenate which is subsequently reduced to the metal.<sup>1,2</sup> Metallic rhenium so produced is usually purer than that prepared by direct reduction of the potassium salt.

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