ART. XXXI.—*The Stability of Standard Solutions of Tartar Emetic*; by HIPPOLYTE GRUENER.

[Contributions from the Kent Chemical Laboratory of Yale College—XXVI.]

DURING the progress of some investigations on antimony, I found it desirable to know to what extent a solution of tartar emetic could be relied on to retain its strength when kept for a length of time. Accordingly I made up a number of solutions of tartar emetic, whose strength was determined by titration in presence of an alkaline tartrate and bicarbonate with decinormal iodine, standardized against arsenious oxide. These solutions were put aside in stoppered bottles for a number of months, when they were again determined with iodine standardized against the same arsenious oxide.

Solution A was simply tartar emetic in distilled water, 16 grms. to the liter. At the end of five months this was found to have lost strength to a considerable extent, while a deposit, seemingly a mixture of antimonious oxide and of fungus growth had settled at the bottom of the bottle. At the end of fourteen months a still greater loss of strength was observed, corresponding in all to about 3.5 per cent of the tartar emetic, of which 4 grms. were present. The sediment was drained, dissolved in tartaric acid and titrated with iodine. It was found to correspond to .13 gm. of tartar emetic or approximately the amount lost. This shows clearly that under the conditions no great loss is caused by the formation of the pentoxide, in closed bottles at least.

Solution B was slightly alkaline with sodium bicarbonate in presence of sodium tartrate. On this solution after five months there was developed in addition to a fungus growth a

* Min. und Petr. Mitth., xii, No. 3.

deposit, probably antimonious oxide; there was here a slight loss in the strength of the solution, amounting to 1 per cent.

Solution C was acid with tartaric acid only. After ten months the solution was found of the same strength and clearness as it was originally: but four months later there was a slight deposit accompanied by a loss of 1.2 per cent.

Parallel experiments to A gave like results. Two repetitions of C with varying amounts of tartaric acid present showed in each case a decided fungus growth with no loss of strength at the end of five months, whereas at the end of nine months the loss amounted to 1 per cent for the larger amount of tartaric acid and 0.3 per cent for the smaller amount.

It seems then that there is little danger of any oxidation of the antimonious oxide occurring, and provided enough tartaric acid is present to keep all the antimonious oxide in solution, the solution should maintain its strength for at least five or six months. The fungus growth has not been found to interfere in practical work with the solutions, yet it seemed advisable to prevent its formation if it could be done simply. To test the possibility of this, a number of solutions were prepared containing varying amounts of hydrochloric acid, which should act as a sterilizer; enough tartaric acid was added to counteract any tendency toward precipitation. In one series of experiments the solutions were sterilized at the beginning by boiling; in the other series distilled water which had been exposed more or less to the air for a number of days was directly used. Where the solutions had been thus sterilized no sign of fungus growth had appeared at the end of five months, and in the case of the unsterilized solutions there was never more than a trace. Where the hydrochloric acid present was not more than 10 cm³ to 500 cm³ of water, there was at the end of three months only the faintest trace of a deposit and no material loss of strength. Where the hydrochloric acid was present to the extent of 25 cm³ in 500 cm³ of water a decided granular precipitate was observed, accompanied by a loss of strength of about 10 per cent. The granular precipitate dissolved in tartaric acid and titrated accounted almost exactly for this loss.

A number of solutions were prepared under varying conditions and left open to the air for three months, at the end of which time no loss from oxidation was found.

It may be seen that tartar emetic in a solution of 16 grms. to the liter is not oxidized either in closed or open bottles. If it is desired to keep this solution as a standard for a moderate length of time it can be done in presence of enough tartaric acid (20 to 30 grms. to the liter) to prevent precipitation. The addition of 1^{cm} hydrochloric acid to one liter of solution

is enough to prevent any decided formation of fungus growth, at the same time not enough to cause a deposit as happens when large amounts of hydrochloric acid are used.

In the titration of tartar emetic in presence of starch the permanent blue color was taken in every case as the indication of the end reaction, as all other shades of color were found unsatisfactory. It is a well known fact that in the titration of antimony salts the color of the starch iodide is not developed until there is a considerable excess of iodine present, so that as compared with arsenious oxide, iodine gives high results with antimony. Thus, for example, the mean of six series of determinations made at various times and aggregating twenty-nine determinations showed the presence of 43.95 per cent of antimonious oxide in tartar emetic. ($\text{Sb} = 120$ and tartar emetic $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O} = 332$, requiring 43.37 per cent.)

The facts above shown, that tartar emetic may be kept in stable solution by means of tartaric acid and hydrochloric acid in the proportions given, make it possible to use and keep such solutions for standardizing iodine for the determination of antimony, and thus to eliminate the error due to the tardy development of the starch iodide blue in presence of antimony salts, observed when compared arsenious oxide is used as a standard.