THE ANALYSIS OF ARSENOUS IODIDE.*

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Four samples of arsenous iodide were analyzed; only one sample was of acceptable quality although all were labeled as U. S. P.

INTRODUCTION.

The purpose of this article is to call attention to the unsatisfactory quality of some arsenous iodide recently purchased and to present some suggestions regarding methods for the analysis of this U. S. P. chemical.

HISTORICAL REVIEW.

In 1900, R. Dupouy (1) reported that a sample of arsenous iodide when treated with water left a yellow insoluble residue of SbOI, this compound being formed by the action of water on SbI_3 contained in the drug. The insoluble residue from a second sample consisted of SbOI and free arsenic, while a third sample left a residue of free arsenic alone. Another sample contained an excess of free iodine and formed a clear brown solution which gradually became colorless.

In an analysis of a commercial sample of arsenous iodide, Dott (2) found 1.28 per cent of insoluble matter. He reported that some commercial samples contained free arsenic and arsenic trioxide and that there was a tendency toward a deficiency in iodine. In 1903, (3) Duncan mentioned the variability of commercial samples of arsenous iodide.

In connection with a study of Donovan's Solution (4), Husa and Enz examined samples of arsenous iodide purchased in 1927. The products of three different manufacturers were found to differ somewhat in physical properties and rapidity of solution. One of the specimens contained a slight amount of free iodine. The differences noted were not considered serious as each sample yielded Donovan's Solution of U. S. P. strength. Arsenous iodide made by one of the manufacturers was selected for the work in hand and it was thought that variability in the material used would thus be largely eliminated. However, arsenous iodide purchased from the same manufacturer in 1929 showed entirely different properties in some respects (5). Instead of rapidly dissolving and yielding a Donovan's Solution of p_H 1.2 as was the case with the 1927 product, the 1929 product dissolved very slowly and the p_H of Donovan's Solution made from it was 1.3.

EXPERIMENTAL DATA.

Quality of Arsenous Iodide.—When a further study of Donovan's Solution was taken up in 1930 by the present author, the brand of arsenous iodide which had previously been adopted was again used in the beginning. However, it was found that Donovan's Solution made from samples purchased in 1929 and 1930 showed a pronounced deficiency in trivalent arsenic. For convenience we may refer to the manufacturer of this brand as manufacturer A. A detailed study was then made of the samples of this brand, and of the products of two other manufacturers, whom we may designate as B and C.

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Analytical Methods Used.—The trivalent arsenic was determined by titration with $N/10$ iodine and calculated as AsI_3. Total arsenic, calculated as AsI_3, was obtained by the method of Rosin (6). The percentage of moisture was found by drying over conc. H_2SO_4. Total iodide, calculated as AsI_3, was determined by the U. S. P. method.

The determination of free iodine offered some difficulties. When some of the bottles of arsenous iodide were opened, the odor of free iodine was noted. On dissolving such a sample in water the color of the solution was distinctly yellowish at first, becoming colorless in a few minutes, the free iodine apparently being reduced to hydriodic acid through oxidation of some of the arsenous acid to arsenic acid. When some water was placed in a beaker, starch solution added, and solid arsenous iodide added with stirring, a deep blue color was observed, showing the presence of free iodine in the freshly prepared solution. It was thought that the reduction of iodine to HI would be delayed or prevented in acid solution and on this basis the free iodine was determined as follows: 0.5 gram of arsenous iodide was triturated in a mortar with dilute sulphuric acid (4 cc. of the concentrated acid and 96 cc. of water), the mixture washed into an Erlenmeyer flask and titrated with $Na_2S_2O_3$ V.S., using starch as indicator.

The analytical results were as follows:

TABLE I.—SOURCE OF ARSENOUS IODIDE.

	Manufacturer A. Sample I.	Manufacturer A. Sample II.	Manufacturer B.	Manufacturer C.
Trivalent arsenic calcd. as AsI_3	84.5%	88.8%	99.0%	107.6%
Total arsenic calcd. as AsI_3	85.0%	89.0%	99.5%	107.6%
Moisture	0.3%	0.1%	0.4%	0.2%
Free iodine	0.1%	0.1%	0.1%	0.0%
Iodide calcd. as AsI_3 (U. S. P. method)	115.5%	110.2%	98.9%	

DISCUSSION OF RESULTS.

Products of Manufacturer A.—Sample I of manufacturer A was about 15% deficient in arsenic content, and the total iodide calculated as AsI_3 as determined by the U. S. P. method for iodides was about 15% too high. Sample II of the same manufacturer gave results of the same nature. From these results it might seem that the samples were contaminated with the iodide of some metal of lower equivalent weight than arsenic, since the results were low in arsenic and high in iodide. However, on going through the procedure for the qualitative analysis of the common metals, tests were obtained only for calcium, potassium and traces of nickel and sodium. Further investigation would be necessary before the exact nature of the impurities could be ascertained but the results definitely indicate that these samples of arsenous iodide are greatly deficient in arsenic.

Product of Manufacturer B.—The product of manufacturer B was clearly a high-grade product and was adopted for further work on Donovan's Solution which is being reported in another paper. In a minor respect this product did not meet the U. S. P. description which states that arsenous iodide is inodorous; this sample had the odor of free iodine.

Product of Manufacturer C.—As the sample purchased from manufacturer C had been on our shelves for three years after the bottle was originally opened, and

apparently changed somewhat during this time, it is not particularly to the discredit of this manufacturer that the product failed to show proper quality. When originally opened three years before the present tests were made, this product contained a slight amount of free iodine. It is noteworthy that after three years the free iodine was no longer present; in fact this was the only sample of the four that contained no free iodine. A deficiency in iodide content, such as would be caused by the presence of some arsenic trioxide, would account for the high results in trivalent arsenic calculated as AsI_3.

Comments on U. S. P. Assay.—At this point we may consider the suitability of the U. S. P. assay for iodides as applied to arsenous iodide. Since the assay of Donovan's Solution includes an assay for trivalent arsenic, it would seem logical that the arsenous iodide used in its preparation should likewise be analyzed for trivalent arsenic. The percentage of arsenic is obviously of greater importance than the percentage of iodine, although both could be determined if this were deemed advisable. A Committee of the Philadelphia College of Pharmacy has already suggested (7) that the U. S. P. XI adopt an assay which determines the actual arsenic content of arsenous iodide. Likewise the Pharmaceutical Chemistry Sub-Committee has recommended (8) that the next edition of the British Pharmacopœia adopt an assay for arsenous iodide based on titration with $N/10$ iodine.

Another weakness in the present U. S. P. assay of arsenous iodide lies in the fact that the method does not distinguish between chlorides, bromides and iodides. Thus an arsenous iodide contaminated with chlorides or bromides would give misleading results in this assay. In this respect, it would be preferable to use the method of Szancer (9), which is not influenced by the presence of chlorides or bromides, since it is based on the liberation of iodine from iodides by means of nitrous acid. At this time, it is not definitely recommended that Szancer's method be adopted, as a preliminary trial of the method in this laboratory has given results which appear to be low.

CONCLUSIONS.

1. Arsenous iodide, U. S. P., as found on the market shows an undesirable variation in quality. The trivalent arsenic content, calculated as AsI_3, of four samples was 84.5%, 88.8%, 99.0% and 107.6%, respectively.

2. It would be desirable that the U. S. P. XI contain an assay of arsenous iodide for content of trivalent arsenic.

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