date of sodium was prepared and obtained pure after several recrystallizations. The anhydrous material was exposed to hydrochloric acid gas as before with results that indicate a quantitative separation of the acid.

1. 0.1240 gram sodium pyrovanadate heated to 440° in hydrochloric acid gas gave 0.0935 gram of salt instead of 0.0945 gram.

2. 0.2197 gram sodium pyrovanadate gave 0.1669 gram sodium chloride, while theory requires 0.1672 gram.

The sodium chloride from these last two experiments was perfectly white in color, soluble without residue in water, and on examination showed no evidence of the presence of vanadium. The volatile product had the appearance of the compound $2VO_2.3H_2O.4HCl$ obtained by Berzelius when acting on vanadic acid with concentrated hydrochloric acid. If such be really the case we may suppose that in our reaction changes occurred similar to those indicated in the following equations:

$$\text{I. } Na_4V_2O_7 + 4HCl = 4NaCl + V_2O_5.2H_2O,$$

$$\text{II. } V_2O_5.2H_2O + 6HCl = 2VO_2.3H_2O.4HCl + Cl_2.$$

It will, however, be necessary to subject this volatile product to careful analysis before making a positive assertion in regard to its composition.

It is our intention to pursue this study further with the view of ascertaining whether by means of this reaction it will be possible to separate vanadic acid from certain of its associates from which it is now removed with difficulty. From the ease with which the transposition occurs we may hope that the atomic mass of vanadium may be determined after the same fashion as was done in the case of molybdenum.[1]

UNIVERSITY OF PENNSYLVANIA,
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ON SOME OF THE ARSENIC TESTS OF THE U. S. PHARMACOPOEIA (1890).[2]

BY CHARLES O. CURTMAN.

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NOTE.—In applying Bettendorf's test for arsenic, the Pharmacopoeia directs that to a small quantity of the liquid to be tested, which should contain much hydrochloric acid, or should be a solution of the substance

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[1] *Ztschr. anorg. Chem.*, 5, 280.

[2] Report of the Pharmacopoeial Research Committee B.

to be tested in pure, concentrated hydrochloric acid, there should be added an equal volume of a saturated solution of freshly prepared stannous chloride in pure, concentrated hydrochloric acid, ***together with a small piece of pure tin-foil.*** The presence of arsenic is revealed by the production of a brown color or brown precipitate, the appearance of which is hastened by a gentle heat. By an oversight, the direction to add the tin-foil was inserted or left standing in the tests for arsenic in bismuth or antimony salts, in which it leads to false conclusion, as the following paper will show. (Dr. Chas. Rice, Chairman U. S. P. Revision.)

A NUMBER of experiments have been made for the purpose of ascertaining the conditions most favorable to the result of the test for arsenic by stannous chloride (Bettendorf's test and its modifications).

The inquiry was directed to the following points:

1. The limit of sensitiveness of the test in its various modifications.
2. The best proportion of reagent to specimen.
3. The influence of the use of metallic tin together with the stannous chloride.
4. The influence of the presence of other substances in the specimen tested.

I. LIMIT OF SENSITIVENESS.

The following reagents were used:

a. The solution directed for Bettendorf's test by the U. S. P., consisting of a saturated solution of pure stannous chloride in pure, concentrated hydrochloric acid. The specific gravity of this solution was 1.407.

b. Metallic tin, perfectly pure, in thin cylinders, from which shavings of about 0.1 gram were taken as needed.

c. Stannous chloride solution prepared according to the German "Arzneibuch," by saturating a mixture of five parts of crystals of stannous chloride and one part of hydrochloric acid with dry hydrochloric acid gas. The specific gravity = 1.912.

All of the materials used were previously tested for absence of arsenic by Gutzeit's test, so as to exclude any fallacies arising from the introduction of even small traces of arsenic by the reagent, which might cumulate with those in the specimen.

It was easy enough to procure pure metallic tin, but impossible to obtain, from local dealers, hydrochloric acid sufficiently free from arsenic to stand Gutzeit's test for one hour. So that I had to distill from purified sulphuric acid and pure sodium chloride the hydrochloric acid required for the preparation of the reagents.

A number of specimens of arsenic solution were made, containing free trioxide, sodium metarsenite and sodium arsenate in such proportion that each set corresponded exactly to an equal amount of As. They were:

Arsenic trioxide ($As_2O_3 = 197.68$), of which 1.31962 grams contain one gram of As.

Sodium metarsenite, ($NaAsO_2 = 129.82$), of which 1.7332 grams contain one gram of As.

Sodium arsenate, U. S. P. ($Na_2HAsO_4 + 7H_2O = 311.46$), of which 4.51834 grams contain one gram of As.

The solutions used for experiment contained from 0.5 gram to 0.01 gram of As. Of these, one cc. was used for each trial and the amount of reagent mixed with this varied from one cc. to three cc., so as to correspond with the limits prescribed in the pharmacopoeial tests. When metallic tin was added to the reagent, one cc. each of the specimen and the stannous chloride solution was used. In some cases of doubt a ten-fold quantity (10 : 30 cc. etc.) was used to obtain sufficient material for colorimetric comparison.

A uniform application of heat was effected whenever needed by imbedding the series of test-tubes under observation, to an equal depth, in a sand-bath heated to about 80° C.

Whenever comparisons of color became necessary to decide whether a deeper color had been produced than that of the unaffected reagent (as was especially necessary with the yellowish solution of the German pharmacopoeia), or whether a greater or less intensity of color characterized the reaction, narrow graduated cylinders of ten cc. capacity, were used in a dark box with light reflected from beneath, or occasionally for still greater accuracy, a pair of Hehner's colorimeter cylinders of 100 cc. capacity, also placed for observation into a dark box, admitting from beneath light reflected upward by a plate of milk-glass placed at an angle of 45°. With the aid of these appliances the following results were obtained:

a. With the U. S. P. solution of stannous chloride of sp. gr. 1.467, one cc. of each of the three specimens, containing 0.5 mgm. of As, was mixed in the different proportions stated below, and kept at ordinary temperature for one hour.

With one cc. of reagent a sharp reaction had taken place at the end of the hour. With two cc. of reagent the reaction was obtained earlier and was more intense at the end of one hour. With three cc. of the reagent the reaction was still more speedy, and at the end of the hour more intense.

No difference could be noticed either in time or in intensity between arsenic in the state of trioxide or pentoxide.

When the test-tubes were arranged exactly as before, but placed in hot sand, the time was somewhat shortened, and a slight increase of intensity noticed in all of the specimens.

b. When one cc. of the U. S. P. solution was used with one cc. of solutions containing 0.5 mgm. of As, and a small piece of metallic tin added and heat applied, the reaction was almost instantaneous, and in three minutes a very sharp, unmistakable coloration appeared which continued to increase in intensity for about ten or fifteen minutes, but was not notably darker at the end of the hour. No difference appeared in the different solutions containing arsenite and arsenate.

c. When from one to three cc. of the stannous chloride of the German pharmacopeia was used with one cc. of the solutions containing 0.5 mgm. of As, there was a slight darkening of the color in a few minutes, which continued to increase to the end of the hour. No difference was perceivable between the arsenous and the arsenic preparations. At fifteen minutes the specimens treated by the U. S. P. solution and metallic tin showed a much greater intensity of color, but toward the end of the hour there was but little difference perceptible between the color of the specimens treated with three cc. of the German reagent without heat, and that treated with one cc. of the U. S. P. reagent, metallic tin, and heat. The specimens containing less than 2.5 cc. of reagent showed a less intense color.

These experiments were repeated with the three solutions containing 0.05 mgm. of As. in one cc. and resulted as follows:

a. With the U. S. P. solution of stannous chloride: One cc.

gave no reaction during forty-five minutes, then gradual coloration began. If heat be applied the reaction begins in eighteen minutes and at the end of one hour is slightly more intense than when treated without heat. 1.5 cc. of reagent: reaction slightly more rapid and intense than with one cc. 2.0 cc. of reagent: still more rapid and intense, both with and without heating. 2.5 cc. of $SnCl_2$: reaction begins in fifteen minutes at air temperature in less than five minutes when heated. 3.0 cc. of $SnCl_2$: reaction slightly less intense than with 2.5 cc., both hot and cold. 3.5 cc. of reagent: a still further slight decrease in intensity. No difference could be observed in the reaction of As_2O_3 and As_2O_5; the sodium metarsenite appeared to be very slightly more colored than As_2O_3.

b. With one cc. of the U. S. P. solution and a small piece of metallic tin, at a temperature of about 80° C., one cc. of the solutions containing 0.05 mgm. of As, began showing a brownish color at thirteen minutes. At thirty-five minutes the reaction was quite sharp and continued to grow slowly in intensity to the end of the hour. No difference was perceptible between As_2O_3 and As_2O_5.

Three cc. of the solution of the "Arzneibuch" mixed with one cc. of the solutions containing 0.05 mgm. of As, began showing a feeble reaction at thirty-five minutes, and at the end of the hour showed a plain reaction as compared with the unchanged reagent, but did not equal in intensity, the reaction produced by the addition of metallic tin.

On repeating the experiments with solutions containing 0.03 mgm. of As in one cc., a feeble reaction resulted from the use of stannous chloride and metallic tin at the end of an hour, but even after standing over night the other methods gave such a faint reaction that it required close inspection in the colorimeter to perceive the change. A solution containing 0.02 mgm. of arsenic failed to show any reaction. So I think that for practical purposes the utmost limit of reaction is reached at 0.03 mgm. of As in one cc. and that the method employing metallic tin and heat is to be preferred where the presence of antimony or bismuth does not forbid its use. Even the addition of pure, concentrated sulphuric acid, which was recommended when the test was first introduced, has not yielded to me any substantial advantage in detecting the presence of arsenic in greater dilutions.

II. THE BEST PROPORTION OF REAGENT TO SPECIMEN.

In the foregoing experiments and a number of others conducted for that purpose it was observed that both with the U. S. P. solution (without the use of metallic tin) and with that of the German pharmacopoeia, the greatest intensity of color obtained after an hour's reaction occurred when one cc. of the arsenical solution was mixed with 2.5 cc. of the reagent. Between three cc. and two cc. of the German solution hardly any difference could be found. But with the pale U. S. P. solution a very slight difference appeared in favor of two cc. as against three cc. Heat did not appear to affect the proportion needed.

When metallic tin was added it seemed to be best to use equal volumes of specimen and reagent, although the variable amount of dark coating of reduced arsenic adhering to the tin prevented an accurate comparison.

III. INFLUENCE OF THE USE OF METALLIC TIN TOGETHER WITH STANNOUS CHLORIDE.

When metallic tin is heated with pure concentrated hydrochloric acid, a copious evolution of hydrogen results. When heated with the saturated solution of stannous chloride in hydrochloric acid, the evolution of hydrogen is but scant. When arsenic is mixed with the solution, the evolution of gas is perceptible but very feeble. Very little arsine appears to be evolved, for a paper cap with a drop of acidulated silver nitrate does not show any evidence of the reduction by AsH_3 for over fifteen minutes, and even at the end of an hour but a very faint arsenic reaction is seen.

To ascertain whether any of the arsine formed would react with the stannous chloride and thus hasten the reduction of As, I arranged a small apparatus in which a copious current of arsine, mixed with hydrogen, was generated and after passing through a bottle filled with dry cotton, was permitted to bubble through stannous chloride solution of the U. S. P. After more than an hour's time not a trace of coloration could be detected. So that after arsine has once been formed it is not again decomposed by stannous chloride. Hence the prompt action of metallic tin must depend upon the *nascent* hydrogen, which aids the stannous chloride in reducing the trioxide and pentoxide.

But, however satisfactory the action of metallic tin in accelerating and intensifying the reduction of arsenic, it *cannot* be employed to detect arsenic in preparations of *bismuth or antimony.* For *the metallic tin reduces both of these metals*, and precipitates them from their solution as black floccules, which aggregate into small granular lumps. There could be a distinction made between the firm floccules of Sb or Bi and the finely divided brown particles of arsenic, but it would hardly be safe to trust to this appearance for a sufficient evidence of the presence of arsenic, and the preparations of Bi and Sb *must be tested without the aid of metallic tin.*

A number of specimens of pure bismuth and antimony salts were tested with the U. S. P. and the German solution of stannous chloride in various proportions. But neither at ordinary temperature nor when heated did the least coloring occur.

IV. INFLUENCE OF THE PRESENCE OF OTHER SUBSTANCES IN THE SPECIMEN TESTED.

The preceding experiments were made with a solution of either arsenic trioxide or sodium metarsenite or arsenate in water, other substances being absent. But in testing various chemicals for traces of arsenic there are different conditions, as the arsenic forms only a very small portion of the mixture. In the U. S. P. the Bettendorf test is directed for eleven preparations. For hydrobromic, hydrochloric, phosphoric, and sulphuric acids, one cc. of the acid is to be tested by mixing with one cc. of the reagent, adding a small piece of tin-foil and heating. In case of magnesium sulphate, one gram of the dry substance is to be shaken with three cc. of the reagent; metallic tin is then to be added and an hour allowed for the appearance of the reaction; sodium phosphate, and pyrophosphate are treated in like manner, but heat applied and fifteen minutes time given.

In the case of antimony and potassium tartrate, antimony oxide, bismuth subcarbonate, and bismuth subnitrate, it was intended to test with stannous chloride alone for an hour, but by an unfortunate misunderstanding of the transcriber, tin-foil was directed to be added, which will reduce Sb and Bi as well as As.

To find whether any of the chemicals directed to be tested by the stannous chloride method, could influence the detection of arsenic, specimens were prepared containing the pure chemicals shown to be free from arsenic by other tests, and with these small portions of arsenic were mixed and the tests compared with those in which arsenic was present in equal amount without admixture with the chemicals.

In no case could any difference in the intensity of the test be made out, nor were the differences in the time of the occurrence of the coloration sufficiently great or regular to justify the assumption that the reaction was impeded or accelerated by the presence of other salts.

ST. LOUIS, May 27, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY. No. 8.]

THE INFLUENCE OF ALUM, ALUMINUM HYDROXIDE AND ALUMINUM PHOSPHATE, ON THE DIGESTIBILITY OF BREAD.

BY W. D. BIGELOW AND C. C. HAMILTON.

Received June 28, 1894.

THE property which alum possesses of arresting the fermentation of flour, and making it possible to prepare presentable bread from very inferior flour has long been known, and the adulteration of flour by means of alum has been extensively practiced by millers and bakers. Comparatively little attention has been given to this subject in this country, but in Europe, especially in England, the question has been constantly before the minds of the public analysts for at least a quarter of a century. Indeed, as early as 1821 a law was passed prohibiting the addition of alum or any aluminum compound to flour or bread. This law remained in force till 1861 when it was repealed by the passage of a law which made it necessary for the prosecution to prove the injurious quality of the substance added.

It is universally admitted that the presence of alum as such not only impedes digestion but also exercises an injurious effect on the digestive organs. There is one phase of the alum question, however, to which a great deal of attention has been