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## RESEARCH PAPERS

### THE ARSENIC LIMIT TESTS OF THE BRITISH PHARMACOPŒIA

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LIMIT tests for arsenic were first introduced into the British Pharmacopœia, 1914. In the Pharmacopœias of 1932 and 1948 the application of these tests was much extended and the limits were made more stringent, but the general method has remained substantially unchanged, as have the several procedures for preparing solutions suitable for testing. The methods appear to have been based primarily on the work of Hill and Collins<sup>1</sup>. They advocated the use of hydrochloric acid containing a small amount of stannous chloride to ensure reduction of the arsenic, and also to promote a steady evolution of hydrogen, in the Gutzeit test. For tests of materials containing iron or other metals which interfere with the test, they recommended distillation with hydrochloric acid and a slight excess of stannous chloride as a means of obtaining the arsenic in a suitable solution.

In those cases where preparation of the test solution involves exposure to oxidising agents, it is to be expected that the arsenic will be converted into the pentavalent form, and numerous workers have stated that the official test then fails to give correct results. Thus, Bird<sup>2</sup> tested equivalent quantities of arsenic in the forms of arsenite and arsenate and found the stain from the latter to develop much more slowly, and to be of a different colour from that produced from arsenite. Gotthelf<sup>3</sup> confirmed Bird's findings and recommended pre-reduction of pentavalent arsenic by warming the solution with sulphurous acid before applying the test. Sanger and Black<sup>4</sup> also studied the matter, and showed only 40 to 50 per cent. of arsenic, originally present in the pentavalent form, to be detected after 30 minutes, even when the reaction mixture was maintained at 90°C. They found the addition of stannous chloride, or of potassium iodide, to effect no improvement, and, like Gotthelf, recommended pre-reduction with sulphurous acid.

More recently, the Association of Official Agricultural Chemists<sup>5</sup> has recommended, for those cases where the test solution is prepared by wet oxidation, the addition of small amounts of stannous chloride and of potassium iodide to the cold solution before subjecting it to the test. Davies and Maltby<sup>6</sup> have also confirmed that pentavalent arsenic was

incompletely reduced in the Gutzeit test; that stannous chloride in the cold, or at water-bath temperature, did not improve the results; and claimed that the A.O.A.C. method was entirely successful. However, these authors preferred pre-reduction with sulphurous acid. They also discussed the possible effect of variation in the "sensitivity" of the zinc used, and suggested that such variation could be eliminated by conducting the test at 40° to 60°C. Stainsby and Taylor<sup>7</sup> also have recommended the use of stannated hydrochloric acid containing potassium iodide when dealing with solutions containing pentavalent arsenic, and use of zinc "activated" by a preliminary treatment with hydrochloric acid. On the other hand, Taylor and Hamence<sup>8</sup> have claimed that use of zinc containing 0.3 per cent. of copper eliminated all need for any special pre-treatment of the test solution.

Electrolytic methods, eliminating any possible variations arising from the use of zinc, have also been employed. Thorpe<sup>9</sup> devised an apparatus having platinum electrodes, but found that the method failed to reduce pentavalent arsenic. This was confirmed by Trotman<sup>10</sup> who recommended zinc electrodes, and by Sand and Hackford<sup>11</sup> who recommended lead, zinc, or iron electrodes, as capable of effecting complete reduction. More recently, Roche Lynch<sup>12</sup> has claimed satisfactory results with platinum electrodes, provided that pre-reduction with sulphurous acid was applied. Monier Williams<sup>13</sup> found lead electrodes to be satisfactory, and claimed that solutions containing iron, which normally interferes with the reduction, could be tested directly if organic matter was present or added. It was found that lead electrodes became insensitive after use and gave erratic results. Callan<sup>14</sup> investigated this phenomenon and claimed that it could be avoided by appropriate treatment and care of the electrodes. These methods had been employed for the Marsh-Berzelius test, but Evers<sup>15</sup>, applying the recommendations of Callan and others, devised an electrolytic Gutzeit apparatus with lead electrodes which was claimed to give quantitative recovery of arsenic, even where the solution contained iron, or had been exposed to oxidising conditions. He added cadmium sulphate to the solutions as a catalyst.

Although, in the above references, there appears to be general agreement that the Gutzeit test fails in those cases where pentavalent arsenic is present, and that special treatment is then necessary, there is no agreement on what this treatment should be; nor does it appear that stannous chloride, on which the B.P. tests are based, is capable of ensuring reduction of pentavalent arsenic in the Gutzeit test. There must be few analysts who have not encountered anomalous and disturbing results in applying the official tests in such cases. It is therefore rather surprising, especially in view of the numerous publications quoted above, that the official tests have remained virtually unchanged during nearly 40 years.

Our interest in this matter arose from the use of ferric chloride as a source of ferric hydroxide for the manufacture of iron scale preparations. These latter were found, on occasion, to contain excessive amounts of arsenic, although all the deliveries of ferric chloride used had been tested by the B.P. test (as for solution of ferric chloride) and apparently con-

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tained little or no arsenic; this applied also to the other materials used in the process. Since the ferric chloride seemed to be the most likely source of the trouble, it was decided to investigate the official test for solution of ferric chloride. The B.P. 1948 describes the preparation of the test solution as follows: "Heat 4 g. in a porcelain dish with 1 ml. of *sulphuric acid AsT.*, until white fumes are given off; cool, add an equal volume of *water*, and again heat, until white fumes are given off; cool, and dissolve the residue in 10 ml. of *water* and 15 ml. of *hydrochloric acid AsT.*; transfer to a small flask, add *solution of stannous chloride AsT.*, until the yellow colour disappears, connect to a condenser, and distil 20 ml.; to the distillate add a few drops of *solution of bromine AsT* in order to oxidise any sulphurous acid, remove the excess of bromine by a few drops of *solution of stannous chloride AsT.*, and add 40 ml. of *water.*" Tested by this method, solution of ferric chloride is required to contain not more than 2.5 p.p.m. of arsenic\*.

Two samples of ferric chloride were selected. The first (1), which had given satisfactory scale preparations, was believed to be practically arsenic-free; whereas the other (2), from the arsenic content of products made from it, was calculated to contain 5 p.p.m. of arsenic. Each was used to make two samples (A and B) of solution of ferric chloride B.P. In each case, 5 p.p.m. of arsenic (as dilute solution of arsenic AsT.) was added to sample B. The four samples were each tested several times by the B.P. test; the results, given in Table I, confirmed that the test was unsatisfactory.

TABLE I  
ARSENIC LIMIT TESTS ON SOLUTION OF FERRIC CHLORIDE B.P.

Sample	Arsenic content(p.p.m.)	
	Expected	Found
1A ... ..	nil	nil
1B ... ..	5	0 to 2
2A ... ..	5	0 to 2
2B ... ..	10	0 to 3

Solution of ferric chloride, if made by nitric acid oxidation of ferrous chloride solution, is liable to contain dissolved oxides of nitrogen. It is presumably to expel these latter that the preliminary evaporation with sulphuric acid is prescribed. Since the samples tested were unlikely to contain oxides of nitrogen, it seemed remotely possible that the arsenic might be present in the arsenious form and be lost during the evaporation process. Accordingly, the evaporation was conducted in a small flask attached to a condenser; the distillate showed no trace of arsenic on subjection to a Gutzeit test. In addition, 5 per cent. v/v of nitric acid

\* Throughout this paper, and following the practice of the B.P., the term "arsenic" refers to arsenious oxide, As<sub>2</sub>O<sub>3</sub>.

B.P. was added to each sample and the tests repeated; the results agreed with those in Table I.

On the assumption that the trouble lay solely in the evaporation procedure, it was at this stage decided to examine the B.P. test for potassium nitrate. This includes the evaporation stage, but not the distillation and subsequent bromine treatment applied to solution of ferric chloride:—  
“Heat 5 g. in a porcelain dish with 5 ml. of *sulphuric acid AsT.* and 5 ml. of *water*, until white fumes are given off; cool, add 5 ml. of *water*, and again heat, until white fumes are given off; cool, and add 50 ml. of *water* and 5 ml. of *stannated hydrochloric acid AsT.*”

Tests were conducted on potassium nitrate A.R., to which 2 p.p.m. of arsenic (as dilute solution of arsenic AsT.) had been added; the results varied from nil to less than 1 p.p.m. It was noted that the evolution of hydrogen and the development of the stain were much slower than in a normal test; after 40 minutes there was usually no stain, and to obtain results even of the above low order it was necessary to allow the reaction to proceed for at least 2 hours. Evidently the arsenic had been oxidised to the pentavalent state. Further tests were carried out, incorporating the various procedures recommended to deal with such a case, and the results are shown in Table II.

TABLE II  
ARSENIC LIMIT TESTS ON POTASSIUM NITRATE CONTAINING 2 P.P.M. OF ARSENIC

No.	Details of test	Arsenic found (p.p.m.)
1	B.P. test ... ..	nil to 0·8
2	B.P. test, but using a zinc-copper couple ... ..	nil to 0·8
3	B.P. method for preparation of test solution; this tested in Evers's <sup>14</sup> electrolytic apparatus ... ..	nil to 0·4
4	B.P. test, but adding potassium iodide (1g.) to prepared test solution at room temperature ... ..	2
5	B.P. test, but prepared solution diluted with water to 120 ml., sodium sulphite (1g.) added, and the mixture digested on a boiling water-bath for 30 minutes. Finally, the solution was boiled until all sulphur dioxide was expelled, and the volume was reduced to about 60 ml.; cooled ... ..	2
6	Heated with sulphuric acid according to the B.P. test, and diluted with water (10 ml.); added hydrochloric acid AsT. (15 ml.) and solution of stannous chloride AsT. (5 drops). Distilled 20 ml., and added water (40 ml.), and solution of stannous chloride AsT. (5 drops) ... ..	1
7	As No. 6, but added solution of stannous chloride AsT. (1 ml.) before distillation ... ..	2
8	As No. 6, but added solution of stannous chloride AsT. (0·5 ml.) before distillation ... ..	2

Similar tests were also applied to dilute solution of arsenic AsT. In each case, 1 ml., after the pre-treatment described, was subjected to the test as for a standard 1 ml. stain; the results (Table III) are expressed as percentage recoveries by comparison with normal standard stains.

The results given in Tables II and III confirmed that arsenic was oxidised (presumably to the pentavalent state) on heating in the presence

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of nitric acid; and that the B.P. test failed to detect more than part of such material. Recovery of the arsenic was not improved by using a zinc-copper couple in the test; and was even poorer using Evers's electrolytic apparatus. Of the other treatments previously recommended, the addition of potassium iodide<sup>5,6,7</sup> to the prepared solution at room temperature, or

TABLE III

ARSENIC LIMIT TESTS ON 1 ML. PORTIONS OF DILUTE SOLUTION OF ARSENIC AsT.

No.	Details of test	Arsenic recovered (per cent.)
9	Diluted with water (5 ml.) and nitric acid AsT. (1 ml.); evaporated to dryness. Residue dissolved in water (50 ml.) and stannated hydrochloric acid AsT. (10 ml.)	30 to 40
10	Diluted with water (5 ml.), sulphuric acid AsT. (1 ml.) and nitric acid AsT. (1 ml.); proceeded as for potassium nitrate by B.P. test, but adding stannated hydrochloric acid AsT. (10 ml.) finally	30 to 40
11	As No. 10, but using a zinc-copper couple	30 to 40
12	As No. 10, but solution tested in Evers's electrolytic apparatus	10 to 30
13	As No. 10, but omitting the nitric acid	100
14	As. No. 10, but adding potassium iodide (1g.) to prepared test solution at room temperature	100
15	As No. 10, but prepared solution diluted with water to 120 ml., sodium sulphite (1g.) added, and the mixture digested on a boiling water-bath for 30 minutes. Finally, the solution was boiled until all sulphur dioxide was expelled, and the volume was reduced to about 60 ml.; cooled	100
16	As No. 10, but prepared solution treated with solution of stannous chloride AsT. (0.2 ml.), and left at room temperature for 30 minutes. (Similar experiments, using larger volumes of solution of stannous chloride AsT., failed owing to the formation in the Gutzeit test of a spongy mass of tin which coated the zinc and stopped the evolution of hydrogen)	30 to 40
17	Initial evaporation procedure as for No. 10. Cooled residue diluted with water (10 ml.); added hydrochloric acid AsT. (15 ml.) and solution of stannous chloride AsT. (5 drops). Distilled 20 ml., and added water (40 ml.), and solution of stannous chloride AsT. (5 drops)	40 to 50
18	As No. 17, but added solution of stannous chloride AsT. (1 ml.) before distillation	100
19	As No. 17, but added solution of stannous chloride AsT. (0.5 ml.) before distillation	100

heating the prepared solution with sulphurous acid<sup>3,4,6</sup> and finally boiling off excess of sulphur dioxide were entirely satisfactory in securing complete recovery of arsenic in the B.P. test; the potassium iodide method commended itself on the grounds of simplicity. Stannous chloride in the cold appeared quite ineffective, but distillation in the presence of a sufficient excess also secured complete recovery of arsenic in the B.P. test. The significance of this in regard to those B.P. tests incorporating such a distillation is referred to later in this paper.

At this stage, it seemed likely that application of one or other of these procedures would suffice to remove any error from those B.P. arsenic limit tests, relatively small in number, involving heating with oxides of nitrogen in the preparation of the test solution. In the case of solution of ferric chloride, distillation with a sufficient excess of stannous chloride was the obvious choice, representing only a small modification of the present

official procedure. This method was therefore applied to the samples mentioned in Table I; the results are given in Table IV.

TABLE IV

ARSENIC LIMIT TESTS ON SOLUTION OF FERRIC CHLORIDE B.P. BY THE OFFICIAL TEST, BUT USING 1 ML. OF SOLUTION OF STANNOUS CHLORIDE AS<sub>2</sub>T. IN EXCESS OF THAT REQUIRED TO DECOLORISE THE SOLUTION BEFORE DISTILLATION

Sample	Arsenic content (p.p.m.)	
	Expected	Found
1A ... ..	nil	nil
1B ... ..	5	1 to 3
2A ... ..	5	1 to 3
2B ... ..	10	2 to 4

These results were most disappointing, and it seemed clear that another source of error must be involved. This seemed the more likely since, as already mentioned, these samples were unlikely to contain nitric acid, and hence the added arsenic was unlikely to have been oxidised during the heating with sulphuric acid.

It had already been noted that bromine oxidation of the distillate was peculiar to this and one or two similar tests where the presence of sulphur dioxide was likely. It was therefore decided to repeat the tests as described in Table IV, but omitting bromine treatment of the distillate. Instead, the latter was diluted with water to 120 ml., and concentrated by boiling to a volume of about 60 ml. (in order to remove any sulphur dioxide) and finally treated with solution of stannous chloride As<sub>2</sub>T. (5 drops). In all four cases, the expected results were obtained, recovery of the arsenic present being quantitative.

It thus appeared that bromine, even in the cold, was capable of oxidising arsenic to a form in which it was not fully recovered in the B.P. test. This important possibility, which does not appear to have been considered before, if correct would obviously introduce errors into a much larger number of B.P. arsenic limit tests, and clearly required full investigation. Accordingly, a series of tests was performed on dilute solution of arsenic As<sub>2</sub>T. Each test was performed on a 1 ml. quantity and the results (Table V) are expressed as percentage recoveries by comparison with normal standard stains.

The results in Table V confirmed that bromine, in the cold, seriously interfered with the accuracy of the test. It was observed that evolution of hydrogen was very slow in such cases, and it was necessary to allow the reaction to proceed for at least 2 hours to obtain even the partial recoveries indicated above. The results also showed that the same treatments effective after nitric acid oxidation were successful in this case also, the use of potassium iodide again commending itself as the simplest procedure.

It was now apparent that a much larger number of B.P. arsenic limit tests were likely to give inaccurate results; the very considerable number

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involving the use of bromine at any stage required consideration along with those incorporating any other oxidation procedure in the prepara-

TABLE V

ARSENIC LIMIT TESTS ON 1 ML. QUANTITIES OF DILUTE SOLUTION OF ARSENIC AS<sub>T</sub>.

No.	Details of test	Arsenic recovered (per cent.)
20	Diluted with water (50 ml.); treated with hydrochloric acid As <sub>T</sub> . (10 ml.) and solution of bromine As <sub>T</sub> . (5 drops); excess of bromine removed by adding solution of stannous chloride As <sub>T</sub> . (5 drops)	30 to 40
21	As No. 20, but adding potassium iodide (1g.) to the prepared test solution at room temperature ... ..	100
22	As No. 20, but prepared solution diluted with water to 120 ml., sodium sulphite (1g.) added, and the mixture digested on a boiling water-bath for 30 minutes. Finally, the solution was boiled until all sulphur dioxide was expelled, and the volume was reduced to about 60 ml.; cooled ... ..	100
23	As No. 20, but adding solution of stannous chloride As <sub>T</sub> . (0.3 ml.) and leaving at room temperature for 30 minutes ... ..	30 to 40
24	Diluted with water (10 ml.); added hydrochloric acid As <sub>T</sub> . (15 ml.) and solution of bromine As <sub>T</sub> . (5 drops); excess of bromine removed by adding solution of stannous chloride As <sub>T</sub> . (5 drops plus 0.5 ml. in excess). Distilled 20 ml., and added water (40 ml.) and solution of stannous chloride As <sub>T</sub> . (5 drops) ... ..	100

tion of the test solution. A review of the B.P. tests showed that no fewer than 76 merited such consideration. They are tabulated in the following groups based on the procedure involved:—

*Group A:* Those involving direct treatment with brominated hydrochloric acid As<sub>T</sub>., excess of bromine being removed by adding slight excess of solution of stannous chloride As<sub>T</sub>. in the cold (30 tests involved):—

Ammonii Bicarbonas	Potassii Bicarbonas
Calcii Carbonas	Potassii Hydroxidum
Calcii Hydroxidum	Potassii Tartras Acidus
Creta	Sodii Benzoas*
Extractum Malti	Sodii Bicarbonas
Gelatinum	Sodii Carbonas
Glucosum Liquidum	Sodii Carbonas Exsiccatus
Liquor Ammoniaë Dilutus	Sodii Hydroxidum
Liquor Ammoniaë Fortis	Sodii Salicylas*
Liquor Magnesiaë Bicarbonatis	Sulphur Praecipitatum†
Magnesii Carbonas Levis	Sulphur Sublimatum†
Magnesii Carbonas Ponderosus	Theobromina et Sodii Salicylas
Magnesii Oxidum Leve	Theophyllina et Sodii Acetas
Magnesii Oxidum Ponderosum	Zinci Oxidum
Mistura Magnesiaë Hydroxidi	Bromine Reagent†

\* first carbonized and residue used for test.

† special procedure, *q.v.*

*Group B:* Those involving direct treatment with brominated hydrochloric acid As<sub>T</sub>., excess of bromine being removed by adding slight

excess of solution of stannous chloride AsT., and distillation of the mixture. (2 tests involved):

Bismuthi Carbonas

Bismuthi Oxychloridum

*Group C:* Those involving ignition with calcium hydroxide AsT. and dissolution of the residue in brominated hydrochloric acid AsT., excess of bromine being removed by adding slight excess of solution of stannous chloride AsT. in the cold. (18 tests involved):

Acidum Acetylsalicylicum

Saccharinum Sodium

Acidum Benzoicum

Succinylsulphathiazolum

Acidum Mandelicum

Sulphacetamidum

Acidum Nicotinicum

Sulphacetamidum Sodium

Acidum Salicylicum

Sulphadiazina

Mersalylum

Sulphadiazina Sodium

Methylthiouracilum

Sulphathiazolum

Nicotinamidum

Sulphathiazolum Sodium

Saccharinum

Thiouracilum.

*Group D:* Those involving ignition with calcium hydroxide AsT., dissolution of the residue in brominated hydrochloric acid AsT., excess of bromine being removed by adding slight excess of solution of stannous chloride AsT., and distillation of the mixture. (6 tests involved):

Bismuthi et Sodii Tartras

Ferri Carbonas Saccharatus

Bismuthi Salicylas

Ferri et Ammonii Citras

Bismuthi Subgallas

Iron Citrate Reagent.

*Group E:* Those involving distillation with stannated hydrochloric acid AsT., the distillate being treated with slight excess of solution of bromine AsT., and excess of bromine removed by adding slight excess of solution of stannous chloride AsT. in the cold. (4 tests involved):

Cupri Sulphas

Ferri Sulphas Exsiccatus

Ferri Sulphas

Liq. Ferri Perchloridi.\*

\* After preliminary evaporation with sulphuric acid AsT.

*Group F:* Those involving heating with sulphuric acid AsT., and/or nitric acid AsT., followed by treatment with slight excess of solution of stannous chloride AsT. in the cold. (5 tests involved):

Acidum Nitricum

Iodoxyllum

Injectio Diodoni

Potassii Nitras

Sodii Nitris.

*Group G:* Those involving heating with sulphuric acid AsT. and nitric acid AsT., and distillation of the mixture with stannated hydrochloric acid AsT. (5 tests involved):

Methylthioninæ Chloridum

Suraminum

Phenolphthaleinum

Viola Crystallina

Viride Nitens.

*Group H:* Those involving treatment with hydrochloric acid AsT. and



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potassium chlorate AsT., excess of chlorine being removed by gentle warming followed by treatment with slight excess of solution of stannous chloride AsT. in the cold. (4 tests involved):

Acidum Hypophosphorosum Dilutum      Sodii Metabisulphis  
Potassii Chloras                              Sodium Thiosulphate Reagent.

*Group I:* Those involving treatment with hydrochloric acid AsT. and potassium chlorate AsT., excess of chlorine being removed by gentle warming followed by treatment with slight excess of solution of stannous chloride AsT., and distillation of the mixture. (2 tests involved):

Bismuthum Præcipitatum                      Ferrum

On the basis of the work already described, the following modifications to the official methods of preparing the test solutions are suggested:—

*Group A:* Add potassium iodide (1 g.) to the test solution at room temperature.

*Group B:* Add solution of stannous chloride AsT. (1 ml., in excess of that required to remove the excess of bromine) prior to distillation. As an additional safeguard, add potassium iodide (1 g.) to the final test solution at room temperature.

*Note:* In applying the present official method, some analysts may unwittingly have complied with this requirement; whereas others, interpreting strictly such directions as “a few drops,” “sufficient to decolorise the solution,” etc., would not. Discrepancies between laboratories would thus be explained, since a sufficient excess of stannous chloride is essential in order to secure correct results.

*Group C:* As for Group A.

*Group D:* As for Group B.

*Group E:* As for Group B. In addition, since traces of sulphur dioxide may be present in the distillate, add slight excess of solution of bromine AsT., remove the excess of bromine by adding a few drops of solution of stannous chloride AsT., and add potassium iodide (1 g.) to the final test solution.

*Note:* It is worth recording that direct oxidation of sulphur dioxide in the distillate with hydrogen peroxide, in place of bromine, was found also to cause low results, unless potassium iodide was added.

*Group F:* As for Group A.

*Group G:* As for Group E.

*Group H:* As for Group A.

*Group I:* As for Group B.

Substances from each group were tested both by the B.P. method and by the suggested modified method. In each case, the substances were tested (a) as received, and (b) after adding (as dilute solution of arsenic

AsT.) the maximum quantity of arsenic permitted by the B.P. limit. In these laboratories it has been the practice for many years to add the test solution at room temperature to the Gutzeit apparatus, and to stand the latter on a warm surface so that the liquid temperature at the end of the reaction period is between 65° and 70°C. This procedure, which probably counteracts any variations in the "activity" of the zinc used (cf. Davies and Maltby<sup>6</sup>), was applied throughout this series of tests, the results of which are given in Table VI:—

TABLE VI  
COMPARATIVE ARSENIC LIMIT TESTS BY THE B.P. METHODS AND BY THE MODIFIED METHODS

Group	Material	Arsenic added (p.p.m.)	Arsenic detected by	
			B.P. method (p.p.m.)	Modified method (p.p.m.)
A	Calcii carbonas ... ..	nil	nil	nil
"	" " " " " " " " " "	5.0	2.0	5.0
"	Calcii hydroxidum ... ..	nil	1.5	3.0
"	" " " " " " " " " "	5.0	4.0	8.0
"	Gelatinum* " ... ..	nil	nil	nil
"	" " " " " " " " " "	1.4	0.7	1.4
"	Sodii benzoas ... ..	nil	nil	nil
"	" " " " " " " " " "	2.0	0.4	2.0
"	Sulphur sublimatum ... ..	nil	1.5	1.5
"	" " " " " " " " " "	5.0	3.0	6.5
B	Bismuthi carbonas ... ..	nil	nil	nil
"	" " " " " " " " " "	2.0	1.6	2.0
C	Acidum acetylsalicylicum ... ..	nil	nil	nil
"	" " " " " " " " " "	2.0	0.8	2.0
"	Saccharinum ... ..	nil	nil	nil
"	" " " " " " " " " "	5.0	1.5	5.0
D	Ferri et ammonii citras ... ..	nil	nil	0.5
"	" " " " " " " " " "	5.0	3.5	5.5
E	Ferri sulphas ... ..	nil	nil	trace
"	" " " " " " " " " "	2.0	0.6	2.0
"	Liquor ferri perchloridi ... ..	nil	1.0	5.0
"	" " " " " " " " " "	2.5	2.0	7.5
F	Potassii nitras ... ..	nil	nil	nil
"	" " " " " " " " " "	2.0	0.8	2.0
G	Methylthioninae chloridum ... ..	nil	nil	trace
"	" " " " " " " " " "	10.0	7.0	10.0
H	Sodii metabisulphis ... ..	nil	nil	nil
"	" " " " " " " " " "	5.0	2.5	5.0
I	Ferrum ... ..	nil	nil	4.0
"	" " " " " " " " " "	200.0	140.0	200.0

\* The general method proposed for Group A substances did not give entirely satisfactory results for gelatin. The results recorded above were obtained by the following special method which is recommended for gelatin:—Heat 7 g. on a boiling water-bath for 15 minutes with 5 ml. of hydrochloric acid AsT. and 3 ml. of solution of bromine AsT.; cool. Add 10 ml. of water and 15 ml. of hydrochloric acid AsT.; transfer to a small flask, add 1.5 ml. of solution of stannous chloride AsT., connect to a condenser, and distil 20 ml.; to the distillate add a slight excess of solution of bromine AsT. in order to oxidise any sulphurous acid, remove the excess of bromine by a few drops of solution of stannous chloride AsT.; add 40 ml. of water and 1g. of potassium iodide AsT.

The results given in Table VI confirm that the B.P. arsenic limit tests give very low results in those cases where preparation of the test solution involves exposure to oxidising conditions at any stage. On the other hand, they show that the simple modifications to these tests, proposed above, give entirely satisfactory results. The need for revision

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of the B.P. tests is emphasised. Adoption of the modified tests proposed would require the specification of an additional reagent, potassium iodide AsT., to be defined as material which, when exposed to the B.P. test, gives no visible stain. The material used in the present work complied with this requirement.

The purpose of the lead acetate paper in the Gutzeit test is, of course, to trap any traces of hydrogen sulphide which may be generated. Provided care is taken to avoid the presence of sulphurous acid in the test solution, no appreciable amount of hydrogen sulphide is likely to be generated; in the present work this has applied. However, an open cylinder of lead acetate paper does not appear to be the best device for "scrubbing" a gas stream; and the use of plumbised cotton wool, as recommended by Evers<sup>15</sup>, would appear to be more efficient. Both devices are in use in these laboratories, though the official lead acetate paper has been used in the work described. It is recommended that the official apparatus be modified to require the use of plumbised cotton wool.

It has not been possible, in the time available, to apply the comparative methods to more than the small selection of suspected tests listed in Table VI, but there is good reason to suppose that the results obtained are typical. However, it is possible that other substances may, like gelatin, require special treatment. It is hoped, therefore, similarly to examine all the other substances listed in groups A to I, and to report the results at a later date. Although the B.P. arsenic limit tests applied to substances other than those in these groups appear to be satisfactory, it seems possible that in cases where the materials have been manufactured by methods involving oxidising conditions, the arsenic present might be in a form not fully detectable by the official tests. It is therefore recommended that in all the B.P. arsenic limit tests the modification of adding 1 g. of potassium iodide AsT. to the final test solution at room temperature be adopted.

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### REFERENCES

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## DISCUSSION

In the unavoidable absence of Dr. Mitchell the paper was read in abstract by Mr. H. Deane.

THE CHAIRMAN (Mr. A. D. Powell) said that certain oxidising substances required excess of stannous chloride, usually followed by distillation, in order to obtain correct results. He also had used potassium iodide in the manner described by the authors, and could confirm the efficiency of the method. The possibility of re-oxidation by bromine water was a valuable point brought out by the paper.

DR. E. F. HERSANT (Dagenham) said that many arguments he had had over arsenic limits had been due to the incomplete reduction of the arsenic when present in the pentavalent state. He would emphasise the advantages of using plumbised cotton wool instead of lead acetate paper as had been observed in testing potassium iodide. The more carefully the lead acetate paper was inserted, so that it was in a roll, the more easily the top paper was contaminated by minute splashes of hydriodic acid, but with plumbised cotton wool the droplets of hydriodic acid were entirely eliminated and the results were much more satisfactory.

DR. D. C. GARRATT (Nottingham) said he thought that most analysts were agreed that the B.P. arsenic tests were inadequate, and that higher results were obtained by other techniques. The standard technique of the Society of Public Analysts, which he thought was recognised as being good when applied to organic materials, gave erratic results in some cases, for example, gelatin, and they had sanctioned the use of sulphite as reducing agent. He advocated the use of sulphite rather than iodide. It was simple to use, there was very little chance of the further complication of blanks and also it was cheaper.

DR. R. E. STUCKEY (London) said that one should not be too critical of some of the arsenic limit tests, as they worked well in the hands of someone who knew the technique. Up to a few years ago he had been very critical of the B.P. technique and had advocated a wholly electrolytic procedure. He had been surprised by the accuracy and reproducibility of the B.P. method in the hands of an experienced worker who was familiar with the technique. Many people did not adhere to the exact detail which was necessary. For example, the exact amount of hydrochloric acid and water specified must be strictly adhered to, or one would get the hydrochloric acid too concentrated and start to lose arsenic before distillation had commenced.

DR. G. E. FOSTER (Dartford) supported what Dr. Stuckey had said with regard to hydrochloric acid. Many years ago they had had a dispute with a German firm about arsenic in a preparation. The discrepancies in their results were found to be due to the fact that the Germans were not using constant-boiling hydrochloric acid, but hydrochloric acid which fumed, and they had lost all the arsenic before it had started to distil over.