

gradually from the eutectoid zone towards the core, the use of ferrosilicon in a carburizing material should prove desirable in this respect at least. Cases having only eutectoid composition at the surface and a relatively deep penetration of carbon may be prepared by heating for shorter periods of time at higher temperatures than are ordinarily used for the production of such a case.

The work presented here represents a part of more comprehensive experiments which are in progress at the present time, this investigation forming the basis for a thesis by one of the authors (Spencer) for the Doctorate.

COLLOIDAL ARSENIC TRIOXIDE IN THE ARSENIC DETERMINATION.

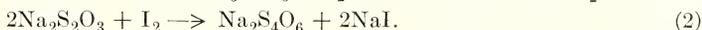
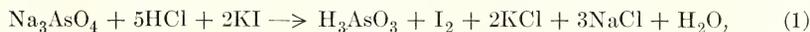
E. G. MAHIN AND A. F. DOYLE, University of Notre Dame.

Arsenic is an essential constituent of various commonly used insecticides. In such materials it may occur in either state of oxidation (trivalent or pentavalent) and as either free acid or combined as salts—arsenites or arsenates. Paris green is a double copper salt of acetic acid and arsenous acid, of variable composition, but the commercial article may contain also cupric arsenate or free arsenous or arsenic acid. As these compounds vary in solubility, insecticidal efficiency and effect upon foliage, methods for their determination are necessary; but one determination that is always of first importance is that of total arsenic.

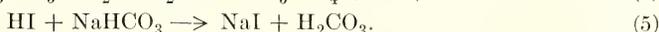
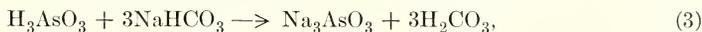
For this determination two methods have at various times been made official by the Association of Official Agricultural Chemists. Until the publication of the revision of 1919, the official method for total arsenic¹ was, in outline, as follows:

The weighed sample is heated with a solution of sodium hydroxide until decomposition is complete. Cuprous oxide is precipitated, the solution then containing sodium acetate, sodium arsenite and sodium arsenate. The last named salt is from oxidized arsenic already existing in the sample, as well as from arsenite which has been oxidized during the process of digestion with the basic solution.

The pentavalent arsenic is then brought to the trivalent form by the addition of hydrochloric acid and potassium iodide, followed by careful removal of liberated iodine by sodium thiosulphate:



An excess of sodium bicarbonate is then added to maintain the solution in a weakly basic condition, after which the arsenic is titrated by standard iodine solution, by the aid of starch as an indicator:



¹ Bur. Chem., Bull. 107, 25 (1908).

This method is convenient and it gives accurate results, but one difficulty is occasionally experienced in routine determinations. At the point where iodine is to be removed from the solution of reduced arsenic (equation (2)) it is not permissible to add starch as indicator, because in the strongly acid solution there would be partial inversion of starch, with the formation of erythro-dextrin, this giving a persistent red color with iodine and thus interfering with the subsequent titration.

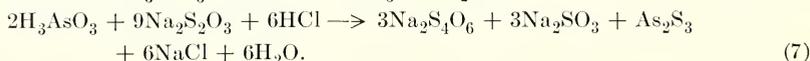
In the absence of starch the exact removal of iodine must be accomplished through observation of the disappearance of the faint yellow color of iodine alone. This may readily be done if the reactions proceed normally. But it sometimes happens that toward the end of this step a yellow color develops from another source and deepens as the addition of sodium thiosulphate proceeds; in such cases it becomes practically impossible to determine when the correct amount of thiosulphate has been added.

With the publication of the revised methods of the Association of Official Agricultural Chemists in 1919 the method as above described was abandoned and that of Roark and McDonnell² was substituted. In this method the sample of Paris green is placed in a distilling flask with hydrochloric acid and cuprous chlorid, the liquid then being distilled and the distillate, containing hydrochloric acid and arsenic trichloride, is later neutralized and titrated with standard iodine solution.

This method is reliable but it requires assembled apparatus, consumes considerable time and requires rather close attention during the progress of the distillation. In the opinion of the present authors the older method is preferable, provided that some method may be found for obviating the difficulty which comes through the development of color as the arsenic is reduced.

It was with the purpose of discovering the cause of this secondary development of color, as well as to find the conditions under which color might or might not develop, that the present investigation was undertaken.

As theoretical possibilities, this color might be due to the formation of sols of either arsenic trisulphide or arsenic triiodide, both of these compounds readily going into the colloidal state:



The details of the (slightly modified) procedure are as follows:³

To 2 gm. of Paris green in a 250 cc. flask add about 100 cc. of a 2-per cent solution of sodium hydroxide. Boil until all of the green compound has been decomposed and only red cuprous oxide remains. Cool, filter into a 250 cc. volumetric flask, washing the paper well, dilute to the mark and mix.

Measure 50 cc. of the solution into a 250-cc. flask and concentrate by boiling to about half the original volume. Cool to 60° and add 10 cc.

² J. Ind. Eng. Chem., 8, 327 (1916); A. O. A. C., "Methods of Analysis," p. 53 (1919).

³ Mahin: "Quantitative Analysis," 3rd ed., p. 245.

of concentrated hydrochloric acid and 1 gm. of potassium iodide. Mix and allow to stand for ten minutes. From a burette carefully add tenth-normal sodium thiosulphate solution until the iodine is all reduced. Starch must not be used but care should be exercised in reaching the end point. If a persistent yellow color develops at this point, use starch solution as an outside indicator, touching drops of the titrated solution to the starch. If the end point has been passed, add iodine solution until the iodine-starch reaction is barely produced.

Allow to stand for five minutes longer and if iodine color reappears, carefully add more thiosulphate solution. Immediately add, as rapidly as may be done without loss by effervescence, 15 gm. of sodium bicarbonate, free from lumps. Titrate at once with standard iodine solution, deferring the addition of starch until near the end point. Calculate the percentage of total arsenic, expressed as arsenic trioxide, in the Paris green.

Experimental. Weighed portions of Paris green were treated as above until the diluted basic solution of arsenic was obtained. Measured portions of this solution were taken for the titrations, the conditions being varied as to temperature and as to the relative amounts of hydrochloric acid and potassium iodide added, other conditions being maintained as already described.

Experiment 1.—The temperature was held at about 20°, instead of the specified 60°. Other conditions being unchanged, potassium iodide was varied in the determinations from the prescribed 1 gm. to a maximum of 40 gm. The solutions remained colorless upon reduction, until the one containing 30 gm. was reached; in this solution a persistent yellow color developed.

Experiment 2.—The temperature was held at 60°, as specified, during the reduction period, and the quantity of potassium iodide was again varied. A yellow color developed as soon as the specified quantity of 1 gm. had been exceeded.

Experiment 3.—With conditions otherwise the same as in the preceding experiment, the quantity of hydrochloric acid was reduced to 5 cc. The results were the same as in the preceding experiment.

Experiment 4.—The amount of acid was further reduced to 2.5 cc. No yellow color developed until the quantity of potassium iodide added had reached 15 gm., but the reduction of arsenic was slow, and probably incomplete.

Experiment 5.—With a temperature of 60° for the reduction period, as in experiments 2, 3 and 4, the potassium iodide was fixed at 2.5 gm. and the acid was varied from a minimum of 1.25 cc. to a maximum of 15 cc. No color was produced after reduction of any of these solutions, but reduction was incomplete in the more dilute acid solutions.

Experiment 6.—The acid was fixed at 5 cc. and the potassium iodide at 3.75 gm., while the reduction temperature was varied between 25 and 90°. No color developed in any of the solutions after reduction.

Conclusions.—The persistent yellow color which is sometimes formed toward the end of the reduction of arsenic acid by potassium iodide, hydrochloric acid and sodium thiosulphate is not due to the formation of sols of arsenic trisulphide, because this colloid is readily flocculated by concentrated hydrochloric acid, which is here present. The conclusion seems obvious that arsenic triiodide is formed in a colloidal state, in presence of an excess of potassium iodide.

With conditions maintained as in the official method, no interfering color is formed during the reduction, unless the specified quantity of 1 gm. of potassium iodide is exceeded. Variation in acidity within reasonable limits has no undesirable effects, so far as development of color is concerned, but it is necessary to exercise care in weighing the iodide to be used in the reduction. No doubt a lack of appreciation of this requirement has been responsible for the apparently erratic results often observed by analysts, who have thought that they were following the same method in all cases.

The older method, as herein outlined, seems preferable to the distillation method of Roark and McDonnell, which is now official. If the analyst will exercise some care in the addition of potassium iodide he will experience no difficulty in obtaining accurate and reliable results.

THE DIFFUSION OF HYDROGEN IN IRON.

E. G. MAHIN, University of Notre Dame.

It is quite well known among metallurgists that metals may dissolve various gases, sometimes in fairly high concentrations. This is especially true for metals in the molten state and gases so dissolved are partly expelled when the metals crystallize during solidification, this action resulting in troublesome "blow holes," which are merely gas pockets occurring through the mass of solid metal.

It seems practically certain that, within ordinary temperature ranges, most gases may enter into metallic solution only if the gas be in the atomic state. But if a gas is liberated from a compound, in direct contact with a clean metal surface and by reaction of the compound with the latter, solution is relatively easy because the gas is then in the nascent state.

This action is especially important in connection with the operation of cleaning sheets of iron or mild steel to prepare them for coating with tin, zinc or enamel. During the process of rolling the metal into sheet it becomes coated with iron oxide which, if not first removed, will effectively prevent the second metal alloying with the iron surface, during the tinning or "galvanizing" process. In order to remove this oxide coating the sheets are "pickled" in hydrochloric or sulphuric acid. The concentration, temperature and duration of application of the acid are so chosen as to effect complete removal of scale, with a minimum of attack upon the metal underneath. But under any circumstances there