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A MODIFICATION OF THE AVERY-BEANS METHOD FOR DETERMINING TOTAL ARSENIOUS OXIDE IN PARIS GREEN.

BY J. K. HAYWOOD.

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INTRODUCTION.

UNTIL recently, nearly all methods for determining total arsenious oxide in Paris green, in so far as the author has been able to find by careful search of chemical literature, were based upon the oxidation of all arsenic to the "ic" condition and a subsequent precipitation with magnesia mixture, followed by a gravimetric determination as magnesium pyroarsenate. Some oxidized with hydrochloric acid and potassium chlorate and determined the arsenic in the presence of copper; some oxidized with fuming nitric acid and determined the arsenic in the presence of copper, and others first removed the copper by boiling with sodium hydroxide and oxidized the filtrate with hydrochloric acid and potassium chlorate, but all finally precipitated the arsenic with magnesia mixture and weighed as magnesium pyroarsenate.

While a few chemists determined the arsenic by precipitation along with copper as the sulphide and a subsequent separation of the two sulphides, this method, on account of inherent difficulties, was seldom employed.

During 1899 Smith[1] devised a volumetric method based on a titration of the arsenious oxide in Paris green after all of the copper had been removed and the arsenic reduced to the "ous" condition. This method was a great improvement over the old ones in that one could make a determination of the total arsenious oxide in a single sample of Paris green in about forty-five minutes.

During September, 1900, the author[2] published a paper upon "The Adulteration and Analysis of Arsenical Insecticides" in which a comparison was made of the Smith method and two or three of the old methods mentioned above. It was shown by this study that the old methods based on the magnesium precipitation

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[1] This Journal, **21**, 769.

[2] *Ibid.*, **22**, 568.

gave low results, while the Smith method always gave correct results, if a few simple precautions were taken that had not been mentioned by Smith in his original article.

In 1901, Avery and Beans[1] published a method for determining total arsenious oxide in Paris green. Since this method is the one that is to be critically studied, it will be given in full.

Method.—Sample the Paris green (as one would an ore for assaying) down to about 1 gram. Pulverize this small sample in an agate mortar and weigh out 0.2 to 0.3 gram in a beaker of, say, 300 cc. capacity. Add 25 cc. of water, and to the green suspended in the water add, with constant stirring, concentrated hydrochloric acid till solution is just effected. Six to twelve drops are usually sufficient. Now add to the acid solution sodium carbonate solution till a slight permanent precipitate is formed. Dissolve this precipitate by adding 2 to 3 grams of sodium potassium tartrate in solution. Now dilute to about 200 cc., add solid sodium bicarbonate and starch solution, and titrate with iodine in the usual way.

In a critical study that was made of this method in comparison with others, by the Association of Official Agricultural Chemists, it was shown by the author and other chemists that most excellent results were obtained when pure samples of Paris green were examined, but that when samples of greens containing considerable quantities of free arsenious oxide were examined, the method always gave low results. This was due to the fact that the free arsenious oxide was not dissolved by hydrochloric acid in the cold. Since any method that is to be used for determining total arsenious oxide in Paris green should include the free arsenious oxide, which is one of the most common adulterants, it at once became evident that the method would have to be modified to admit of its application in general work, especially in station control work. As this method, with pure Paris greens, is accurate as well as extremely short (only about five minutes being required for a single determination), it appeared to the author that any slight modification of it which would allow of its application to Paris greens containing free arsenious oxide, would be well worthy of some study. With this end in view, the following experimental work was carried out.

EXPERIMENTAL WORK.

Experiment 1.—It was at first thought the method might be modified in the following manner: Carry the manipulation down

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[1] This Journal, 23.

to the point where hydrochloric acid has been added, a drop at a time, to get the Paris green in solution. At this point all Paris green will be dissolved, while most of the free arsenious oxide will remain undissolved. Now add a slight excess of sodium carbonate and boil to get all arsenious oxide into solution, cool, acidify with hydrochloric acid, a drop at a time, add sodium bicarbonate until a faint precipitate is apparent, then sodium potassium tartrate, then an excess of sodium bicarbonate and after dilution titrate with iodine in the ordinary way.

Working in this way upon a Paris green that had been shown to contain 67.98 per cent. total arsenious oxide by the Smith method, of which 27.50 per cent. was free arsenious oxide, the following results were obtained: 66.55 per cent.; 67.50 per cent.; 67.15 per cent.; and 67.70 per cent. It at once became evident that, while this method sometimes gave practically correct results, the tendency was toward low results, so that it was not to be depended upon unless the factors that caused the variation could be discovered and controlled.

Since prolonged boiling of arsen*ious* compounds with alkalies is apt to cause the formation of arsen*ic* compounds, it was thought that the length of time of boiling the solution might cause the reduction in the amount of arsenious oxide found. To test this, definite weights of the Paris green were treated as above, using 1 gram of sodium carbonate for each determination, and the boiling was continued for varying lengths of time. The following results were obtained:

Time of boiling. Minutes.	Arsenious oxide. Per cent.
4	67.26
8	67.26
10	63.95
20	63.43
30	Decided reduction of the copper.

It appeared then, from the above table, that the longer the boiling was continued the lower the results, and that the low results were caused by the action of sodium carbonate on the Paris green, resulting in the reduction of the copper and consequent oxidation of part of the arsenious oxide.

Since only slightly low results were obtained when the green was boiled for from four to eight minutes with 1 gram of sodium carbonate, it was thought that by reducing the amount of the sodium carbonate and only boiling from four to eight minutes, the error due to the action of the sodium carbonate upon the Paris green might be so reduced as to be negligible. Working upon this basis, the following results were obtained:

Time of boiling. Minutes.	Amount of sodium carbonate used in excess of that necessary to neutralize the hydrochloric acid.	Arsenious oxide found. Per cent.
7	7 drops of a saturated sodium carbonate solution.	67.39
7	4 drops of a saturated sodium carbonate solution.	67.44

Even in this case, with a minimum of sodium carbonate and a minimum time of boiling, low results were obtained and it was evident that the method was worthless.

Experiment 2.—An attempt was made to use sodium bicarbonate instead of sodium carbonate; the method in all its other details was the same as described in Experiment 1.

Working in this way upon the same Paris green, the following results were obtained where definite weights of the green were used; a definite quantity of sodium bicarbonate (10 grams) was added in each determination and the time of boiling was varied.

Time of boiling. Minutes.	Arsenious oxide. Per cent.
5	67.44 (a few flakes of arsenious oxide undissolved.)
10	67.96
10	67.96
15	67.35
20	66.92
40	63.43 (decided reduction of copper.)

It appeared from the above table that five minutes' boiling was not sufficient to cause all of the free arsenious oxide to go into solution; that ten minutes' boiling gave theoretical results, while with fifteen, twenty and forty minutes' boiling the results were progressively lower, until at forty minutes a marked reduction of the copper and consequent oxidation of arsenious oxide were shown.

The ten-minute period of boiling with 10 grams of sodium bicarbonate was tried with various other Paris greens, but low results were obtained in so many cases that it was seen that the time of boiling must be altered for different samples, thus rendering the method valueless.

An attempt was made to reduce the amount of sodium bicarbonate and so get correct results, but it was found that unless the sodium bicarbonate was present in comparatively large quantities, the free arsenious oxide went into solution very slowly, so that a prolonged boiling was necessary, which always resulted in a slight reduction of the copper of the Paris green.

Experiment 3.—The only other way of applying the Avery-Beans method of analysis to Paris green containing free arsenious oxide that suggested itself to the author was to separate the undissolved, free arsenious oxide and the dissolved arsenious oxide and to determine them separately. To do this the following method of analysis was used: Sample the Paris green (as one would an ore for assaying) down to about 2 grams. Pulverize this small sample in a mortar and place from 0.3 to 0.4 gram in a beaker. Add about 25 cc. of water and, while constantly stirring, add concentrated hydrochloric acid, a drop at a time until all the Paris green is in solution and the free arsenious oxide remains as a residue. Filter and wash the residue. The arsenious oxide in the filtrate is determined in exactly the same manner as is given in the original Avery-Beans method. The filter and contents are dropped back into the beaker, which also receives the water used in washing the funnel. Five grams of sodium bicarbonate are added and the solution boiled until the arsenious oxide is completely dissolved (this takes from five to ten minutes). The resulting solution is cooled and acidified, using a drop of methyl orange to read the change. It is then made alkaline again with sodium bicarbonate, starch is added and the arsenious oxide titrated in the usual way with standard iodine. By this method the results given in the following table were obtained. There are also given the results obtained by the Smith method, which we know to be correct, and a determination of the free arsenious oxide by the sodium acetate extraction method and by the ten-day water extraction method.

	Soluble As_2O_3 sodium acetate extraction.	Soluble As_2O_3 10-day water extraction.	Total As_2O_3 Smith method.	Total As_2O_3 modified Avery-Beans method.
Sample No. 1...	7.25	8.75	58.98	59.17
" " 2...	13.50	14.90	61.71	61.68
" " 3...	26.00	28.00	67.60	67.42
" " 4...	7.18	8.19	59.86	59.87

It will thus be seen that by modifying the Avery-Beans method as above, it can be applied to Paris green containing free arsenious oxide and will give results which are strictly comparable with the Smith method. While this modification increases the time of carrying out the analysis on a single sample from about five to twenty minutes, it still results in a method which is much shorter than any known by the author for this class of compounds.

Now that the above modification has been worked out, it appears so simple and obvious that the author almost feels reluctant to publish it. When it is taken into consideration, however, that the Avery-Beans method has been before the Association of Official Agricultural Chemists for two years and that, although its limitations were spoken of, no one suggested the above change; that the author has also worked with the method for about two years without previously thinking of the change and that finally Avery and Beans, the originators of the method, did not suggest the above simple modification so that it might be applied to Paris green adulterated with arsenious oxide, it seems that the results are worthy of publication, especially since a shorter time and fewer manipulations are involved than in any other method for determining arsenious oxides in Paris green at present known to the author.

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A MODIFICATION OF THE BABCOCK-BLASDALE VISCOSITY TEST FOR OLIVE OIL.

BY HERBERT ABRAHAM.

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ACCORDING to Blasdale, Prof. Rising was the first to suggest the possibility of using the factor representing the viscosity of the soap solution formed from a fixed amount of olive oil, saponified by a definite amount of potassium hydroxide, for detecting adulterated samples. At his suggestion Babcock, who had in 1886[1] examined a number of samples of butter and its principal adulterants, tested also a few of the most common fatty oils. His results show that butter gave the soap of lowest viscosity, and he also remarked that among the fatty oils, olive gave one of about the highest viscosity. The method was, at this time, used simply

[1] Reports N. Y. State Agricultural Experiment Station, 1886, p. 338; and 1887, p. 380.