[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE U. S. DEPART-MENT OF AGRICULTURE, NO. 38. SENT BY H. W. WILEY.]

THE ADULTERATION AND ANALYSIS OF THE ARSEN-ICAL INSECTICIDES.

BY J. K. HAYWOOD, Received July 6, 1900.

I N the following paper I will first give a résumé of what has been done in the analysis of insecticides, showing which are usually pure and which often adulterated, and laying particular stress on the arsenical insecticides, which are of the most importance now on the market. This will be followed by a series of carefully-tested methods for the analysis of the more common insecticides, with the results indicated.

Various groups of insects act harmfully on plants and require special methods of treatment to kill them. Among these classes of insects may be mentioned subterranean insects, household pests, animal parasites, internal feeders, etc. The insects which principally injure plants, however, and for which insecticides are usually applied, are external feeders, which include "biting" and "sucking" insects.

For the first, or "biting" insects, some substance is used which can be sprayed on the parts of the tree attacked, and then eaten by the insect with its food. Such substances are Paris green, Scheele green, London purple, lead arsenate and arsenite, barium arsenite, arsenious oxide, etc.

For the second group, or "sucking" insects, substances must be used which will act externally on the bodies of the insects and smother them either by closing their pores or filling the air around with poisonous vapors. Among the latter insecticides may be mentioned insect powder, sulphur, kerosene, hydrocyanic acid, carbon disulphide, ammonia, formalin, etc. Experience has proved that a great many of the insecticides mentioned above are nearly always pure as they occur in commerce. There are certain ones, however, which often show adulteration, among them being cupric carbonate (impure because of faulty methods of manufacture), potassium cyanide, potash lye (which is often sodium hydroxide), formalin (which should be a 40 per cent. solution of formaldehyde, but often is not), and most of the arsenical preparations. I will not attempt to go into the adulteration of all the articles mentioned above, but will lay particular stress on the adulteration of the arsenicals. These include Paris green, Scheele green, London purple, arsenious oxide, lead arsenate, white arsenoid, pink arsenoid, green arsenoid, paragrene, etc.

Paris green is supposed to be copper acetoarsenite and to contain 31.29 per cent. copper oxide, 58.65 per cent. arsenious oxide, and 10.06 per cent. acetic acid.

Scheele green is supposed to be copper hydrogen-arsenite and to contain 42.37 per cent. copper oxide, 52.32 per cent. arsenious oxide, and 4.81 per cent. water.

London purple is a by-product in the manufacture of the aniline dyes and is thought to be composed mainly of calcium arsenite with some coloring impurity, mostly rosaniline arsenite.

Besides London purple there are two other preparations, Paris and English purple, which have practically the same composition.

Of course arsenious oxide should be nearly pure, but in the crude state it may contain from 8 to 10 per cent. of cinders and other impurities.

White arsenoid is supposed to be barium arsenite; pink arsenoid is supposed to be lead arsenite; and green arsenoid is supposed to be copper arsenite:

Paragrene is a patented article which is said to be free from the objectionable features of Paris green, in that it never scorches the foliage.

Excepting the arsenious oxide, all of the above preparations may be, and often are, adulterated in one of three ways:

1. Some colored substance may be used to represent the compound, which will contain none of the elements which should be in the true compound. For example, samples have been analyzed which were labeled Paris green, but which contained neither arsenious oxide nor copper. Such imitations are usually harmless to the plant, but are equally harmless to the insect. Such a fraud as the above was noticed at the Alabama Station,¹ where a sample, called Paris green, was found to be composedof Prussian blue, chrome-yellow, and some inert substance, such as clay or chalk.

1 Bulletin No. 58. 10-22 2. Some substance or substances may be added to the insecticides to increase their weight or to change their color, for use in making pigments. For example, Paris green is often adulterated with calcium sulphate, calcium carbonate, lead chromate', etc. This second form of adulteration is practiced more often in Germany than in America.

3. There may be arsenical insecticides containing a low per cent. of arsenious oxide in combination. It will be noticed that I say in combination. Many of the insecticides contain enough arsenic to include them in the class of high-grade articles, but this arsenic is often not in combination as it should be, but present as free arsenious oxide, thus forming a substance which will scorch the foliage of the tree.

The last of these three forms of adulteration is the most common in America, and must be considered as a fraud when we remember that free arsenious oxide not only scorches the foliage, but is usually much cheaper than the compound, which ought to be present. Sometimes it appears that the free arsenious oxide is added purposely; sometimes it is free because of faulty methods of manufacture.

Paris green, or copper acetoarsenite, has been repeatedly analyzed at the New Jersey Argricultural Experiment Station,¹ and has been found to range in percentage of arsenious oxide from 41.54 to 68.59 per cent. The excessively high percentage of arsenious oxide indicates that this cheaper substance had been added to the Paris green. Again, a sample of Paris green has been recently analyzed at the California Agricultural Experiment Station,² which contained 31.25 per cent. copper oxide and 52.90 per cent. arsenious oxide, but 23.60 per cent. of arsenious oxide, or nearly one-half, was in the free state. There were, besides, small amounts of impurities, including lime, soda, silica, sulphur trioxide, zinc oxide, etc. This most likely represents a sample where faulty methods of manufacture were used.

Another sample of Paris green, analyzed at the New Hampshire Station,³ was found to have the following composition :

² Bulletin No. 126.

¹ Report, 1897. pages 397-492.

³ Bulletin No. 43.

Arsenious oxide (does not say whether free or combined).. 30.00 Insoluble in hydrochloric acid...... 43.30

This insoluble portion was composed mainly of silica and oxides of iron and alumina, thus indicating that clay was the adulterant used.

Again at the Massachusetts Hatch Experiment Station,¹ two samples of so-called pure Paris greens were analyzed, which, not including various small amounts of impurities, had the following compositions:

	Per cent.	Per cent
Water at 100°	5.00	4.29
Arsenious oxide	58.44	63.98
Copper oxide	8.30	6.60
Calcium oxide	14.50	15.98
Sulphur trioxide	7.56	5.80

The above analyses, of course, show adulteration with calcium sulphate. Samples of Paris green analyzed in Germany have been found to contain calcium sulphate, barium sulphate, lead chromate, lead sulphate, calcium carbonate, etc. One especially contained 25 per cent. of barium sulphate and 6.56 per cent. of lead chromate.²

As to Scheele green, the same adulterants are found as in Paris green. In a sample which I have just analyzed, the arsenious oxide and copper oxide appear in nearly theoretical proportions, but 17 per cent. of the arsenious oxide is in the free condition, thus making the sample worthless, unless previously treated with lime.

As to London purple, a sample analyzed at the New Jersey Station showed the following composition :

	Per cent.
Water	3.27
Arsenious oxide	41.44
Calcium oxide	24.32
Alumina and iron	· 3.37
Sulphur trioxide	• 0.31
Dye by difference	27.97

The arsenic in this sample was found to be present in the form $Ca_s(AsO_s)_s$, or the normal arsenite, but about 15 per cent.

² Stillman : Chem. News, 80, Nos. 20,087 and 20,088.

Per cent.

¹ Bulletin No. 38.

was soluble; therefore, although this sample was not adulterated, the analysis shows very careless making, as the manufacturers could just as easily have boiled with enough lime in the beginning. The process of manufacture, by the way, is to boil a waste product consisting of dye and arsenious oxide with lime, to make the insoluble calcium arsenite. Samples of London purple have been analyzed at the Cornell Station,¹ South Carolina Station,² the Florida Station,³ and elsewhere, and wherever soluble arsenious oxide was determined it was found to be present in large amounts. It will also be easily seen that, owing to the intense color of London purple, various substances might be added to increase the weight without being perceptible to the naked eye.

White arsenoid, which is supposed to be barium arsenite, has recently been analyzed at the California Station⁴ and found to possess the following composition :

	Per cent
Barium carbonate	• 44.05
Barium chloride	• 13.05
Barium oxide	. 8.18
Arsenious oxide, free	· 27.64
Lead carbonate	. 1.86
Silica	• 0.20
Water	• 4.00

It will be seen that the only substance giving to this preparation any value as an insecticide is arsenious oxide, and since this is in the free state, it is harmful to the foliage. The barium salts are present only to give weight.

Pink arsenoid is supposed to be lead arsenite. A recent analysis made at the California Agricultural Experiment Station⁴ showed that it had the following composition :

I I I I I I I I I I I I I I I I I I I	er cent
Lead oxide	49.58
Arsenious oxide, combined	40.02
Arsenious oxide, free	3.24
Water	0.31
Organic matter from aniline residue and lead sulphate	6.85

- ¹ Bulletin No. 18.
- ² S. C. Report, 1888, page 142.
- ³ Florida Station Bulletin No. 14.
- 4 Bulletin No. 126.

This preparation is evidently unadulterated and has given very good results.

Green arsenoid, or copper arsenite, analyzed at the California Station,¹ showed the following composition :

	rer cent
Arsenious oxide	61.33
Copper oxide	· 28.83
Water	2.77
Silica	0.40
Organic material, sodium sulphate, etc	6.67

7.82 per cent. of this arsenious oxide was soluble.

Paragrene has also recently been analyzed at the California Station and found to owe its poisonous properties mainly to arsenious acid and copper oxide. It contains 23.46 per cent. copper oxide and 40.60 per cent. of arsenious oxide, but 23.08 per cent. of this is free. It also contains 19.31 per cent. of gypsum to add weight. The preparation is therefore harmful to the plant.

In the Canada Experimental Farm Report of 1895, page 220, mention is made of lead arsenate. This substance is obtained by the action of sodium arsenate on lead acetate. It is there stated that there is no reason lead arsenate so manufactured should contain impurities, but that it often does, however, because of the original impurities in the sodium acetate, a byproduct obtained in the manufacture of aniline dyes.

Arsenious oxide, because of its method of preparation, may, in the crude state, contain from 2 to 10 per cent. of arsenious sulphide and ore dust as impurities, it being usually prepared by roasting mispickel or tin ores.

I must not leave this subject without calling attention to two insecticides, called respectively "Peroxide of Silicates" and "Hammond's Slug Shot." The first, on analysis at the Vermont Station,² was shown to have the following composition:

I CI CCHC
· 1.44
• 1.47
0,28
. 36.43
. 52.29
1.40
· 1.93
• 4.76

1 Bulletin No. 126.

² Bulletin No. 12.

Der cent

It is needless to say that this sample, composed mostly of calcium sulphate, did not give good results.

"Hammond's Slug Shot," by an analysis made at the Vermont Experiment Station," was shown to have the following composition:

	Per cent.
Water of hydration	• 14.76
Arsenious oxide	· 1.58
Cupric oxide	• о.бо
Lime	30.24
Sulphur trioxide	• 43.02
Ferric oxide and aluminum oxide	• 0.79
Sodium chloride	· 2.83
Insoluble	· 1.38
Organic and volatile matter (mostly dead oil by difference)	· 4.79

Here again it will be seen that in buying the above substance one is paying a pretty good price for an article composed almost entirely of calcium sulphate.

I have gathered together a bibliography of the arsenical insecticides, of which the examples presented above form only a small fraction. These are, however, fairly representative of the different classes of adulterants.

ANALYSIS OF INSECTICIDES. (Paris green and Scheele green.)

Recently it became necessary for me to make analyses of various arsenical insecticides, but on looking up the matter I found that few good methods had been published. Many of the Stations had partially analyzed these substances, but even the methods employed in these partial analyses were not given. I therefore decided to test some of the few more promising methods which are known, and where methods were not known, try to work them out on the following substances: Paris green, Scheele green, London purple, and white arsenic.

An analysis of Paris green would include determinations of total and soluble arsenious oxide, copper oxide, moisture, acetic acid, and matter insoluble in dilute hydrochloric acid. An analysis of Scheele green would include determinations of all the substances named above, except acetic acid. An analysis

¹ Bulletin No. 12.

574

of white arsenic would, of course, include only the determinations of water and total arsenious oxide to ascertain the purity.

A determination of the moisture in Paris green is made in the usual way by drying for twelve to fifteen hours, at the temperature of boiling water. On two samples the results were :

	A. Per cent.	B. Per cent.
Moisture	• 1.30	0.99

1. For a determination of the total arsenious oxide, I first tried the well-known method, as given by Fresenius, of dissolving in hydrochloric acid, oxidizing to arsenic acid with potassium chlorate, driving off the chlorine at a gentle heat, making ammoniacal, precipitating with magnesia mixture, filtering and washing in a Gooch crucible, putting a cap on the crucible drying first at 100° and then at 130° C., heating on a sand-bath, then on an iron plate, and finally heating over the blast-lamp and weighing as magnesium pyroarsenate. This method, however, in the first place, is very long because of the time taken in getting rid of the chlorine and in igniting the precipitate by degrees; secondly, there is great danger of loss of the arsenic, as arsenious chloride; and thirdly, the precipitate of ammonium magnesium arsenate is somewhat soluble in the ammonia wash and has not quite the theoretical composition. After obtaining rather varying results, this method was abandoned.

2. I next tried to determine the arsenic by the following method: Oxidize the Paris green in a small flask, closed with a funnel on the steam-bath, by means of fuming nitric acid. Pour out in a dish and evaporate to dryness; take up with hydrochloric acid and proceed as in the first method, finally weighing the arsenic as magnesium pyroarsenate. This plan shortens the time necessary to determine the arsenic and rids one of the danger of loss as arsenious chloride, but there is still present the third source of error, mentioned above. Proceeding in this way, I obtained the following results on two samples of Paris green ("A and B"), and on a sample of dry, chemically pure arsenious oxide:¹

¹ In every case where the arsenic was weighed as magnesium pyroarsenate, a correction was made of 0.0008 gram magnesium pyroarsenate, for each 30 cc. of ammoniacal filtrate containing an excess of magnesium mixture as suggested by Fresenius.

J. K. HAYWOOD.

	Arsenious oxide. Per cent.
Paris green, "A"	···· { 56.03 56.03
Paris green, "B"	$\cdots \left\{ \begin{smallmatrix} 56.68 \\ 56.69 \end{smallmatrix} ight.$
Arsenious oxide, C. P	\dots { 99.33 99.18

3. I next tried a method suggested by Thorn Smith.¹ As described by himself, the method is as follows :

"Two grams of Paris green are weighed out and about 100 cc. of water and 2 grams of sodium hydroxide added. The solution is brought to a boil and the boiling is continued for a few minutes (thus precipitating copper as cuprous oxide). It is then allowed to cool to room temperature and the solution made to 250 cc. The well-shaken liquid is filtered through a dry filter and 50 cc. taken for analysis. This portion is concentrated to about one-half of its volume and allowed to cool to about 80° C. An equal volume of strong hydrochloric acid is then added, accompanied by 3 grams of potassium iodide, and the whole allowed to stand for ten minutes (to reduce the arsenic oxide to arsenious oxide). The deep red solution is slightly diluted with water to dissolve the precipitate caused by the potassium iodide, and a dilute solution of sodium hyposulphite added, until the color just disappears. This solution is then made neutral by the addition of dry sodium carbonate and finally an excess of sodium bicarbonate is added. Tenth normal iodine is dropped in and the end reaction noted by the starch solution."

In applying this method, I used one or two precautions, not mentioned by Smith; namely, instead of making neutral with dry sodium carbonate and very likely getting in an excess, I added dry sodium carbonate until the bubbles came off slowly, showing that the acid was really neutralized, and then sodium bicarbonate to neutrality and some in excess. This was done, because if any free sodium carbonate is present it will itself act on the iodine solution. Again, after using up the iodine which was set free in reducing the arsenic to arsenious oxide by sodium hyposulphite, the solution was immediately diluted, since the air

1 This Journal, 21, 769.

is apt to act on the hot, concentrated solution of hydriodic acid and set free some iodine if this is not done.¹

On applying this method to the two samples of Paris green ("A" and "B") and the dry, chemically pure arsenious oxide the following results were obtained :

	Arsenious oxide. Per cent.
Paris green "A"	$\dots \left\{ \begin{array}{c} 56.85\\ 56.96 \end{array} \right.$
Paris green "B"	$\dots \left\{ \begin{array}{c} 57.63\\ 57.45 \end{array} \right.$
Arsenious oxide, C. P. ²	$\dots \left\{ \begin{array}{c} 100.10\\ 100.10\\ 99.86 \end{array} \right.$

It will not be out of place here to speak of the standardization of the iodine solution, since it is upon the correctness of this standardization that the accuracy of the above method depends. A great many text-books give the following method for standardizing the iodine solution :

Weigh out a small portion of dry, chemically pure arsenious oxide, dissolve in sodium hydroxide, make slightly acid with hydrochloric acid, and then add an excess of sodium bicarbonate. Run in the iodine solution, using starch as an indicator, until the blue color appears.

I used this method of standardizing at first, but it soon seemed to me that perhaps it was not correct, since the literature on the subject speaks of the alkali arsenites being partially oxidized to the ''arsenates'' upon boiling the solution, exposed to the air. I therefore used a dry, chemically pure portion of arsenious oxide and carried it through by the Thorn Smith method, standardizing my iodine solution against the arsenious oxide, as finally reduced by potassium iodide. In every case, I found that on adding potassium iodide to the hydrochloric acid solution of the arsenite some iodine was set free, showing that a small amount of arsenate had been formed, which should be reduced before running in the iodine solution.

Applying these two methods to an approximately tenth-normal

¹ Gooch and Browning : Am. J. Sci., 40, 66 (1890).

² The iodiue solution for the determination of arsenic trioxide in the chemically pure arsenic trioxide was not standardized against arsenious oxide, but against sodium hyposulphite, which had in turn been standardized against the amount of iodine set free, when potassium iodide acts on a weighed quantity of potassium dichromate in the presence of hydrochloric acid.

iodine solution, I obtained by the old method of standardization I cc. iodine solution = 0.012607 gram iodine, and by the Smith method of standardization I cc. iodine solution = 0.012484 gram iodine. It will at once be seen that the errors caused by the sodium arsenite partially oxidizing to sodium arsenate is larger than should be allowed in a standard solution.

A determination of the copper oxide in Paris green was made in the following well-known manner :

The cuprous oxide obtained in the Thorn Smith method by boiling the Paris green with sodium hydroxide was poured on the filter (after taking an aliquot portion of the solution for the determination of arsenious oxide) and well washed with hot water. It was then dissolved with hot dilute nitric acid and made to a volume of 250 cc., one-fifth being taken for analysis. The copper in solution was determined either by means of the galvanic current or, when that was not handy, in the following manner:

The nitric acid solution was made alkaline with sodium carbonate, then made slightly acid with acetic acid, and about ten times the weight of the copper in potassium iodide added. When it was all dissolved, the free iodine was titrated with a standard solution of sodium hyposulphite, using starch as indicator. The full details of this method are given in Sutton's "Volumetric Analysis," third edition, page 133. The results on the two samples of Paris green by this method were as follows:

	Cupric oxide. Per cent.
Paris green "A"	$\cdots \begin{cases} 29.79 \\ 30.37 \\ 30.15 \end{cases}$
Paris green "B"	$ \cdot \cdot \begin{cases} 29.79 \\ 29.79 \\ 29.79 \\ 29.79 \end{cases} $

The figure for acetic acid in Paris green is usually obtained by subtracting the sum of total arsenious oxide, water, cupric oxide, and residue left after treating with dilute hydrochloric acid, from 100.

As to the determination of soluble arsenic in Paris green, I could find very little in the literature on the subject which was of any value. I therefore tried several schemes:

578

1. I weighed 1 gram of Paris green on a filter-paper and washed it with cold water. Each time 200 cc. were obtained, sodium bicarbonate was added and the solution titrated with iodiue solution. After about 2,000 cc. of wash liquor had been used the filtrate was still slowly gaining in arsenious oxide. The method was therefore abandoned as impracticable.

2. I weighed out several 1-gram samples of Paris green and treated these in flasks with 500 cc. of water. The flasks were stoppered and occasionally shaken each day. Every few days an aliquot portion of 100 cc. was filtered off from one of the flasks and the arsenious oxide titrated with iodine after the addition of sodium bicarbonate. The results on the samples of Paris green ("A" and "B") were as follows:

			Time. Days.	Arsenious oxide extracted. Per cent.
Paris	green	"A"	2	1.01
" "		•••	••••• 4	1.68
" "	" "	··· · · · · · · · · · · · · · · · · ·	8	2.69
" "	" "	···	· · · · · · · · · II	4.02
" "	"	"	14	4.02
" "	" "	"В"		3.41
"	"	· · · · · · · · · · · · · · · · · · ·	I2	4.86
" "	6 4		14	4.86

It will thus be seen that this method finally gave constant and very likely correct results. It is rather long, but very little attention or time had to be given after the first weighing out.

3. To expedite matters, I next tried the following method for determining the soluble arsenious oxide. One-half gram of Paris green was weighed out, placed in a flask and treated with about 200 cc. of water. This was digested with occasional shaking on the water-bath at 50° to 60° C., and each day all of the water poured off through a filter, and, after returning all of the substance from the filter to the flask, a fresh portion of water was added and the digestion continued. The arsenious oxide was determined by means of a standard iodine solution. The results on the samples of Paris green ("A" and "B") were as follows:

			Time. Days.	Arsenious oxíde extracted. Per cent.
Paris	greeu	''A''	• I	3.41
"	4.4	··	• 2	3.41 + 2.14 = 5.55
"	" "	··· · · · · · · · · · · · · · · · · ·	•• 3	5.55 + 1.56 = 7.11
"	"	" · · · · · · · · ·	·· 4	7.11 + 1.17 = 8.28
" "	• •	··	• 5	8.28 + 1.26 = 9.54
" "		"·······	6	9.54 + 1 .56 = 11. 10
" "		•••••••••••••••••••••••••••••••••••••••	• 7	Still gaining.
• •	\$ \$	'''B''·····	· · I	2.24
" "	4.4	·· · · · · · · · · · ·	• 2	2.24 + 1.46 = 3.70
" "	**	··	•• 3	3.70 + 1.26 = 4.96
4 6		·· · · · · · · ·	·· 4	4.96 + 1.17 = 6.13
" "	÷ +	·· ·····	. 5	6.13 + 1.17 = 7.30
" "		·· · · · · · · · · · · · · · · · · · ·	. 6	7.30 + 1.56 = 8.86
" "	" "	·· · · · · · · · · · ·	•• 7	Still gaining.

It will thus be seen that a hot extraction can not be used, since the Paris green either breaks up or goes into solution in the presence of hot water, the amount of arsenious oxide going into solution each day being finally nearly constant.

The same methods for determining the constituents of Scheele green were used as those for Paris green mentioned above. On one sample the moisture was 5.27 per cent.

The total arsenious oxide was as follows :

By Method	1. Oxidation	with HCl and KClO3	 Not tried
By Method	2. Oxidation	with $HNO_3 \dots$	· { 50.63 50.80
By Method	3. Thorn Smit	h	$\begin{cases} 51.39 \\ 51.27 \end{cases}$

The determination of the cupric oxide by the method mentioned above gave the following results :

Cupric oxide \cdots $\begin{cases} 38.04\\ 38.23 \end{cases}$

The soluble arsenious oxide determination gave the following results by the various methods:

1. Washing on filter. Not tried.

2.	Extracting with 500 cc. cold water :		
	Time. Days.	Arsenious P	oxide extracted. er cent.
	6	• • • • • • • • •	13.09
	9	• • • • • • • • • •	14.30
	13	••••••	16.26
	21		16.73
	34		17.82
	36		17.70

3. Extracting with water at 50° to 60° C.:

Time Days	:.																									A	rsenious oxide extracted. Per cent.
I	• •	•	•	•	•	•	•	•	•	•	• •		•	•	•	•	•	•	•	•	•	•••	•	•	••	•	13.43
2	• •	•	•	•	•	•	•	•			• •	•	•	•	•	•	•,	• •	,	•	• •	• •	•	•	••		13.43 + 3.70 = 17.13
3	• •	•	•	•	•	•	•	•	,	•	•		• •	•	•	•	•	•	•	•	•	•••	• •	• •	•••	•	17.13 + 1.85 = 18.98
4	•	• •	•	•	•	•	•	•		•	•		• •	•	•	•	•	•	•	•	•	•		• •	•	•	$18.98 \pm 0.87 = 19.85$
5	• •	•	•	•	•	•	•	•	•	•	• •		• •	•	•	•	•	•	•	·	•	• •		• •	••	•	$19.85 \pm 0.78 = 20.63$
6	•	• •	•	•	•	•	•	•	•	•				•	٠	•	•	•	•	•	•	• •	• •	• •	• •	•	$20.63 \pm 0.58 = 21.21$
7	۰.	•	•	•	•	•	•	•	• •			•	•	•	•	•	•	• •	•	•		• •	•	•	• •		21.21 + 0.49 = 21.70
8	•		•	•	•	•	•	•	•	•	• •		• •	•	•	•	•	•	•	•	•	••	• •	•	••		$21.70 \pm 0.39 = 22.09$
9	•		•	•	•	•	•	•	•	•	• •	•	•	•	•	•	•	•	•	•	•	• •	•	• •	••	•	$22.09 \pm 0.39 = 22.48$
10	•		•	•	•	•	•	•	•	•	•			•	•	•	•	•	•	•	•	•		• •	• •		$22.48 \pm 0.39 = 22.87$
II	•		•	•	•	•	•	•	•	•			•	•	•	•	•	•	•	•		• •	• •	•	•	•	Still gaining.

From the above work I would draw the following conclusions :

1. Water can be determined in Paris green and Scheele green by drying at the temperature of boiling water for twelve to fifteen hours.

2. The best method for determining the total arsenious oxide in Paris and Scheele greens is the Thorn Smith method, marked 3 above.

3. The best method for determining the soluble arsenious oxide in Paris and Scheele greens is by extracting with 500 cc. of water at room temperature.

4. Hot water extraction can not be used to extract soluble arsenious oxide.

5. A good method for determining copper in Paris and Scheele greens is the volumetric method based on the titration of the iodine set free from potassium iodide by a copper salt in acetic acid solution.

Appended is a condensed statement of the work done :

	Total arsenic.						
Water.	Oxidation with potas- sium chlorate.	Oxidation with nitric acid.	Method of Smith.	_			
Per cent.		Per cent.	Per cent.				
Paris green ''A''····· 1.30	Abandoned	56.03	56.90				
Paris green "B" 0.99	" "	56.69	57.54				
Scheele green 5.27	"	50.66	51.33				
Arsenious oxide, C. P. None		99.25	100.02				

A. L. WINTON.

Soluble arsenious oxide.

	Wash on filter.	500 cc. cold water. Per cent.	Water at 50°-60° C.	Cupric oxide, Per cent.	Insoluble in hydrochloric acid.
Paris green "A"	Abandoned	4.02	11.10+	30.07	None
Paris green "B"	"	4.86	8,86+	29.79	None
Scheele green	" "	17.76	22.87+	38.14	None
Arsenious oxide, C. P.					None

A continuation of this paper will appear during the next few months, which will have for its object the creation and improvement of the methods of estimating the various constituents of London purple as well as a study of the improved method of estimating arsenic gravimetrically by Martha Austin,¹ which has only come to my notice since the above work was completed.

THE DETECTION OF COAL-TAR DYES IN FRUIT PRODUCTS.

BY A. L. WINTON. Received July 5, 1900.

S OON after its discovery fuchsine came into use for coloring wines and replaced to a large extent the vegetable dyes which from very early times had been employed for this purpose. More recently various other coal-tar dyes, particularly the azocolors, have been extensively used in wines although fuchsine and acid fuchsine are still preferred by some makers.

Within the past few years the use of coal-tar dyes in articles of diet has attracted the attention of food analysts in the United States. In the case of confectionery, pastries, and some other products they serve merely to render the articles more attractive to the eye without deceiving the purchaser, but as a rule they give imitation products the appearance of the genuine or, to use the legal phraseology, "they make the products appear better or of greater value than they really are."

Some of the results obtained by Winton, Ogden, and Mitchell, in the examination of foods at the Connecticut Agricultural Experiment Station, illustrate the fraudulent use of dyes. In 1898, sixty-three samples of jellies purporting to have been made from fruit were examined, and of these, twenty-eight were spurious mixtures colored with coal-tar dyes. Some of the most remarkable samples, labeled "strawberry jelly," "raspberry

1 Zischr. anal. Chem., 23, heft 2.