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THE COMPOSITION AND ANALYSIS OF LONDON PURPLE.

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LONDON purple has, up to the present time, been supposed to consist mainly of calcium arsenite and an organic dye residue. From the work which will appear later on in this article, however, it is shown that the arsenic in London purple is principally in the "ic" condition, so that it consists mainly of calcium arsenate, calcium arsenite, and an organic dye residue. On account of the method of manufacture, as I have mentioned in an earlier paper,[1] some of the arsenic will nearly, or quite, always appear in the free condition. It will thus be seen that an analysis of London purple would include the determination of moisture, total arsenic acid, total arsenious acid, soluble arsenic acid, soluble arsenious acid, calcium, and sand.

DETERMINATION OF MOISTURE.

The moisture of London purple, was determined by drying at 100° for from twelve to fifteen hours. On four samples (A, B, C, and D) examined by me the results were :

	A. Per cent.	B. Per cent.	C. Per cent.	D. Per cent.
Moisture	1.87	4.07	2.76	2.73

DETERMINATION OF TOTAL ARSENIC.

As regards the determination of total arsenic, it will at once be seen that on account of the presence of the organic dye-stuff residue, and of the calcium, the same methods cannot be applied as those mentioned in my earlier paper for Paris and Scheele greens.

I therefore tried to apply to London purple the same method for determining total arsenic as is used for determining phosphoric acid in phosphates, namely :

1. About 0.5 gram of the sample was oxidized with fuming nitric acid, the excess removed by evaporation, molybdate

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[1] "Adulteration and Analysis of the Arsenical Insecticides." This Journal, 22, 568.

solution added and the yellow precipitate carefully washed, and afterwards dissolved in ammonia, magnesium mixture added and the arsenious oxide weighed as magnesium pyroarsenate ($Mg_2As_2O_7$). In carrying out this method, however, I found that the fuming nitric acid did not oxidize all of the organic dyestuff and that consequently all of the yellow molybdate precipitate did not come down. As the results obtained showed that the amount of arsenious oxide was about 10 per cent. below that which I subsequently found to be present, the method was abandoned.

2. I next tried to determine the total arsenic by dissolving the purple in hydrochloric acid, precipitating with hydrogen sulphide, washing, dissolving in ammonia, reprecipitating with hydrochloric acid, washing first with water, then, after drying, with carbon disulphide, and finally weighing as arsenious sulphide. The arsenious sulphide obtained, however, was perfectly black, from contamination with organic matter, hence this method was also abandoned.

3. The next method which I tried was as follows:

About 2 grams of the sample were dissolved in hydrochloric acid (1 : 4) and heated to from 60°-70° C. to get all arsenic in solution (not higher for fear of driving off arsenious chloride). The solution was then filtered to a definite volume, an aliquot portion taken for analysis and the arsenic precipitated by hydrogen sulphide at 70° C. The precipitate was separated by filtration, washed, and finally both filter and precipitate oxidized with fuming nitric acid in a small flask. After all sulphur and organic matter appeared to be oxidized, the solution was evaporated to a small volume, filtered, treated with magnesia mixture prepared according to the Austin formula,[1] and then with a little ammonia. After settling a few hours the precipitate was washed with ammonia water (1 cc. ammonia to 100 cc. of water) on a Gooch crucible, dried, and the Gooch crucible placed in a solid platinum crucible where it was ignited by degrees in the ordinary way.

Employing this method, the following results were obtained on the four samples (A, B, C, and D):

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[1] *Ztschr. anorg. Chem.*, **23**, Heft. 2.

	A. Per cent.	B. Per cent.	C. Per cent.	D. Per cent.
Arsenious oxide......	35.50	37.48	36.47	35.90

Another sample, X, gave results in triplicate, as follows:

Per cent.
33.53
33.32
33.79

Although this method seemed to give fairly good results, I did not feel satisfied for two reasons, namely:

1. The magnesium ammonium arsenate was always dark-colored, showing that the nitric acid had not oxidized all the organic matter, and that consequently when the precipitate was ignited, there would be a loss of arsenic.

2. From the length of time necessary to precipitate the arsenious sulphide (As_2S_3), it appeared to me that some of it at any rate must be in the "ic" condition, and that consequently a method should be employed which would differentiate between the "ous" and "ic" arsenic.

With these two points in view I worked out a method modeled after the Thorn Smith method, mentioned in my earlier paper, but quite different in all of the small details. It is as follows:

3. Two grams of London purple were dissolved in about 80 cc. of water, and 20 cc. of hydrochloric acid at a temperature of from 60° to 70°, just as in the method above described, filtered, and washed to a volume of 300 cc. One hundred cc. of this was treated in a 500 cc. flask with sodium bicarbonate in excess. The contents of the flask were then brought to the mark with water, using a few drops of ether to destroy bubbles, and 250 cc. filtered off. To this was added starch solution, and the standard iodine solution, until the blue color appeared. The result was the arsenious oxide as such, in 50 cc. of the original solution.

Again 50 cc. of the original solution (representing 0.33333 gram) was heated to 80° on the water-bath, and then taken off and 50 cc. of hydrochloric acid, and three grams of potassium iodide added. The mixture was allowed to stand for at least fifteen minutes, the "ic" arsenic thus being reduced to "ous" arsenic by the action of the potassium iodide, in the acid solution, iodine being set free. The solution was then rinsed out in a large beaker, and tenth-normal sodium thiosulphate added, drop by drop, to get rid of the iodine. The end-point here was rather difficult to read on account of the very dark color of the solution, but with a little practice one could determine it very easily, by proceeding as follows:

The sodium thiosulphate was run in a little at a time and occasionally a drop of the solution was added to a drop of starch paste. This would of course give a blue color with the starch, which became fainter and fainter as the iodine was used up. Finally when a drop of the solution only gave the slightest blue color, with the starch, a little starch paste was added directly to the whole solution, and the blue color dissipated with a few drops of thiosulphate. With a little practice one could in this way get the exact end-point every time. The solution was immediately made alkaline with solid sodium carbonate. It was again made slightly acid with hydrochloric acid, taking care that all of the solid particles of the sodium carbonate on the bottom were neutralized by the acid,[1] and finally made alkaline with sodium bicarbonate. Starch paste was now added and tenth-normal iodine until the blue color appeared. This end-point is easily read if the beaker is placed on a white surface between the eye and the light, and iodine run in until a distinct purple color appears. The figure thus obtained gave the total amount of arsenic in the solution as arsenious oxide. Subtracting the first figure from this we have the amount of arsenious oxide corresponding to arsenic oxide in 50 cc. of the original liquid. Working in this way I obtained the following results on the samples (A, B, C, and D).

	Arsenious oxide as such.	Total arsenious oxide present.	Arsenious oxide corresponding to arsenic oxide.	Arsenic oxide present.
Sample.	Per cent.	Per cent.	Per cent.	Per cent.
A	8.16	37.21	29.05	33.77
	8.16	37.21	29.05	33.77
	...	36.78	28.62	33.26

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[1] If all of the sodium carbonate is not used up, it will itself act on the standard iodine subsequently to be added.

Sample.	Arsenious oxide as such. Per cent.	Total arsenious oxide present. Per cent.	Arsenious oxide corresponding to arsenic oxide. Per cent.	Arsenic oxide present. Per cent.
B	17.45	39.97	22.67	26.34
	17.16	40.12	22.82	26.50
	....	40.26	22.96	26.66
C	10.47	38.67	28.20	32.76
	10.47	38.81	28.34	32.93
D	6.40	37.07	30.67	35.62
	6.40	36.92	30.52	35.45
	...	37.21	30.81	35.79

It will thus be seen that this method not only allows of a determination of the arsenious oxide and the arsenic oxide but also gives very good duplicate results, which results are higher than those obtained by the previous methods. One would expect this on account of the loss which very likely takes place in the last method when the magnesium ammonium arsenate is burned in the presence of some organic matter, which has not been removed by the fuming nitric acid.

DETERMINATION OF CALCIUM OXIDE.

In order to determine calcium oxide in London purple, a portion was dissolved in hydrochloric acid (an aliquot portion of the 300 cc. used in the determination of arsenious and arsenic oxides above would do), and hydrogen sulphide passed through. The precipitate was well washed, the filtrate evaporated to small bulk and transferred to a 200 cc. flask, when it was treated with ammonia (to precipitate the iron, etc.) and made to the mark. A 100 cc. portion of this was filtered off and treated with ammonium oxalate in the usual way. In this manner the following results were obtained on the samples (A, B, C, and D).

Samples.	Calcium oxide. Per cent.
A	25.09
B	23.59
C	24.55
D	25.03
On a fifth sample, X, triplicate results were	23.25 23.25 23.40

DETERMINATION OF SOLUBLE ARSENIOUS OXIDE.

To determine the soluble arsenious oxide, the same methods were used as those described in my previous paper for Paris and Scheele greens.[1] On a fifth sample, X, the results were as follows:

Method 1. Washing on the filter not tried.

Method 2. Extracting 1 gram with 500 cc. of water for a number of days at room temperature, and determining arsenious oxide by standard iodine in an aliquot portion of the filtrate.

Sample.	Time.	Arsenious oxide extracted. Per cent.
X	5 days	7.29
	10 days	7.88
	19 days	7.88

Method 3. Extracting 1 gram with successive portions of water at 50°-60° C.

Time.	Arsenious oxide extracted. Per cent.
1 day	7.78
2 days	7.78 + 1.65 = 9.43
3 days	9.43 + 0.87 = 10.30
4 days	10.30 + 0.49 = 10.79
5 days	10.79 + 0.39 = 11.18
6 days	11.18 + 0.29 = 11.47
7 days	11.47 + 0.19 = 11.66
8 days	11.66 + 0.24 = 11.90
9 days	Still gaining.

It will be seen from this that the only method which gave constant results was Method 2, above, just as in the case of Paris and Scheele greens. Applying this method to Samples A, B, C, and D, the following results were obtained:

Sample Nos.	Soluble arsenious oxide. Per cent.
A	2.43
B	13.3
	13.60
C	3.88
D	1.44

DETERMINATION OF SOLUBLE ARSENIC OXIDE.

To determine the soluble arsenic oxide, an aliquot portion of

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[1] "Adulteration and Analysis of the Arsenical Insecticides." This Journal, **22**, 568.

the liquid from Method 2 above, for soluble arsenious oxide (say 200 cc.), was transferred to a flask, made slightly alkaline with NaOH, and evaporated to about 25 cc. on a hot plate. The flask was then removed and allowed to cool to about 80°, and an equal volume of concentrated hydrochloric acid and 3 grams of potassium iodide added. It was allowed to stand fifteen minutes, the iodine set free, exactly used up with tenth-normal thiosulphate (the end-point is easily read without the use of starch), and the solution neutralized with sodium carbonate. It was again made slightly acid with hydrochloric acid, taking care that all lumps of sodium carbonate were acted on, then made alkaline with an excess of sodium bicarbonate, and titrated with iodine, using starch as an indicator. From this figure was subtracted the figure representing the amount of soluble arsenious oxide, and the remainder was calculated as arsenic oxide.

Proceeding in this way I obtained the following results :

Sample.	Soluble arsenic oxide. Per cent.
A	15.81
B	7.12
C	12.56
D	19.56

DETERMINATION OF SOLUBLE CALCIUM OXIDE.

In Method 2 above for soluble arsenious oxide and arsenic oxide, I also determined the per cent. of calcium oxide that had been dissolved by the action of the 500 cc. of water. The results on the samples (A, B, C and D) were as follows :

Sample.	Calcium oxide dissolved by 500 cc. of water. Per cent.
A	7.80
B	6.60
C	7.00
D	10.80

DETERMINATION OF OTHER INORGANIC MATTERS.

The inorganic matter, insoluble in hydrochloric acid, mostly consisting of sand, was determined by dissolving the London purple in hydrochloric acid, filtering, washing, and burning the filter and contents. The results obtained on the samples (A, B, C and D) were as follows:

Sample.	Sand. Per cent.
A	3.54
B	2.61
C	2.46
D	3.55

The following is a condensed statement of the work done:

			Total arsenic[1] calculated as As_2O_3.				
Sample.	Water. Per cent.	Sand. Per cent.	Precipitating as arsenious sulphide, oxidizing with nitric acid. (3) Per cent.	Volumetric iodine method. (4) Per cent.	Total arsenious oxide as such. Per cent.	Total arsenic oxide as such. Per cent.	Total calcium oxide. Per cent.
A	1.87	3.54	35.50	37.07	8.16	33.60	25.09
B	4.07	2.61	37.48	40.12	17.31	26.50	23.59
C	2.76	2.46	36.47	38.74	10.47	32.84	24.55
D	2.73	3.55	35.90	37.07	6.40	35.62	25.03
X	....	....	33.55	....	....	.....	23.30

	Soluble arsenious oxide.			
Sample.	Method 2, extraction with 500 cc. cold water. Per cent.	Method 3, extraction with successive portions of water at 60°-70°. Per cent.	Soluble arsenic oxide, extracting with 500 cc. cold water. Per cent.	Soluble calcium oxide. Per cent.
A	2.43	....	15.81	7.80
B	13.49	....	7.12	6.60
C	3.88	....	12.56	7.00
D	1.44	....	19.56	10.80
X	7.88	11.90	....	....

FORM IN WHICH VARIOUS CONSTITUENTS APPEAR.

Knowing the full inorganic composition of the four samples given above, we are now in a position to determine the form in which they appear in London purple. The calculation is very simple. If we subtract the soluble arsenious oxide from the

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[1] Methods 1 (precipitating with molybdate) and 2 (weighing as arsenious sulphide) were abandoned as unsatisfactory.

total arsenious oxide as such, the soluble arsenic oxide from the total arsenic oxide as such, and the soluble calcium oxide from the total calcium oxide, we have left the insoluble arsenious oxide, the insoluble arsenic oxide, and the insoluble calcium oxide. If the form in which these are united is the normal calcium arsenate, $Ca_3(AsO_4)_2$, and the normal calcium arsenite, $Ca_3(AsO_3)_2$, then the sum of the amounts of calcium oxide, necessary to unite with all the insoluble arsenious oxide to form calcium arsenite, and all of the insoluble arsenic oxide to form calcium arsenate, should be equal to the insoluble calcium oxide as determined.

We will now take up each of the samples and see if such is the case.

A. Total $As_2O_3 = 8.16$ Total $As_2O_5 = 33.60$ Total $CaO = 25.09$
Soluble $As_2O_3 = 2.43$ Soluble $As_2O_5 = 15.81$ Soluble $CaO = 7.80$
Insoluble $As_2O_3 = 5.73$ Insoluble $As_2O_5 = 17.79$ Insoluble $CaO = 17.29$

$$As_2O_3 : 3\,CaO :: 5.73 : x$$
$x = 4.86 =$ CaO necessary to form $Ca_3(AsO_3)_2$
$$As_2O_5 : 3CaO :: 17.79 : x$$
$x = 12.99 =$ CaO necessary to form $Ca_3(AsO_4)_2$
$12.99 + 4.86 = 17.85 =$ CaO theoretically necessary to form $Ca_3(AsO_3)_2$ and $Ca_3(AsO_4)_2$
$17.29 =$ CaO actually found.

B. Total $As_2O_3 = 17.31$ Total $As_2O_5 = 26.50$ Total $CaO = 23.59$
Soluble $As_2O_3 = 13.49$ Soluble $As_2O_5 = 7.12$ Soluble $CaO = 6.60$
Insoluble $As_2O_3 = 3.82$ Insoluble $As_2O_5 = 19.38$ Insoluble $CaO = 16.99$

$$As_2O_3 : 3CaO :: 3.82 : x$$
$x = 3.28 =$ CaO necessary to form $Ca_3(AsO_3)_2$
$$As_2O_5 : 3CaO :: 19.38 : x$$
$x = 14.15 =$ CaO necessary to form $Ca_3(AsO_4)_2$
$14.15 + 3.28 = 17.43 =$ CaO theoretically necessary to form $Ca_3(AsO_3)_2$ and $Ca_3(AsO_4)_2$
$16.99 =$ CaO actually found.

C. Total $As_2O_3 = 10.47$ Total $As_2O_5 = 32.84$ Total $CaO = 24.55$
Soluble $As_2O_3 = 3.88$ Soluble $As_2O_5 = 12.56$ Soluble $CaO = 7.00$
Insoluble $As_2O_3 = 6.59$ Insoluble $As_2O_5 = 20.28$ Insoluble $CaO = 17.55$

$As_2O_3 : 3CaO :: 6.59 : x$

$x = 5.59$ = CaO necessary to form $Ca_3(AsO_3)_2$

$As_2O_5 : 3CaO :: 20.28 : x$

$x = 14.81$ = CaO neccessary to form $Ca_3 (AsO_4)_2$

$5.59 + 14.81 = 20.40$ = CaO theoretically necessary to form $Ca_3(AsO_3)_2$ and $Ca_3 (AsO_4)_2$

17.55 = CaO actually found.

D. Total $As_2O_3 = 6.40$ Total $As_2O_5 = 35.62$ Total $CaO = 25.03$
Soluble $As_2O_3 = 1.44$ Soluble $As_2O_5 = 19.56$ Soluble $CaO = 10.80$

Insoluble $As_2O_3 = 4.96$ Insoluble $As_2O_5 = 16.06$ Insoluble $CaO = 14.23$

$As_2O_3 : 3 CaO :: 4.96 : x$

$x = 4.21$ = CaO necessary to form $Ca_3 (AsO_3)_2$.

$As_2O_5 : 3 CaO :: 16.06 : x$

$x = 11.73$ = CaO necessary to form $Ca_3 (AsO_4)_2$.

$4.21 + 11.73 = 15.94$ = CaO theoretically necessary to form $Ca_3 (AsO_3)_2$ and $Ca_3(AsO_4)_2$

14.23 = CaO actually found.

On another sample E the results were as follows:

10.91 = CaO theoretically necessary to form $Ca_3(AsO_3)_2$ and $Ca_3(AsO_4)_2$,

10.21 = CaO actually found.

It will be seen from the above calculations that the amounts of calcium oxide, arsenious oxide, and arsenic oxide are such in Samples A, B, and E as to closely approximate the formulas $Ca_3(AsO_3)_2$ and $Ca_3(AsO_4)_2$. In Samples C and D the amounts of these three substances do not so closely approximate the formulas $Ca_3(AsO_3)_2$ and $Ca_3(AsO_4)_2$ but show there is a tendency to form compounds in which the amount of lime is less in proportion to the arsenious and arsenic oxides as in $CaHAsO_4$ and $Ca_2As_2O_5$.

I am inclined to believe from this work that the lime, arsenious and arsenic oxides in London purple are *usually* combined as the normal calcium arsenite and arsenate, but that sometimes small quantities of calcium arsenite and arsenate are formed in which the lime is less in proportion to the arsenious and arsenic oxides as in $CaHAsO_3$ and $Ca_2As_2O_5$. The factors that determine this are very likely the time of boiling, the original concentration of the liquor, the presence or absence of an excess of lime and the form in which the arsenic is present in the original dye residue.