

VI.

CONTRIBUTION FROM THE LABORATORY OF S. P. SHARPLES.

SCHWEINFURT GREEN:

SOME EXPERIMENTS ON THE ACTION OF ARSENIC TRIOXIDE ON COPPER ACETATE, WITH THE VIEW OF INVESTIGATING THE COMPOSITION OF THE ABOVE COMPOUND.

By E. R. HILLS.

Read by title, November 8, 1876.

AFTER the completion of the paper on Scheele's Green by Professor S. P. Sharples, I became interested to know something about the composition of the closely allied substance, Schweinfurt green, — as to whether it was perfectly definite in its composition, or whether it varied in a similar manner to Scheele's green. I therefore obtained a sample of Schweinfurt green from the Massachusetts Institute of Technology, which was procured by them in the market for analysis.

This was submitted to a careful analysis, and gave as follows: —

ANALYSIS NO. I.

	Per cents.
Copper oxide,	25.82
Arsenic trioxide,	45.18
Acetic anhydride ($C_4H_6O_3$),	15.40
Sulphuric anhydride (SO_3)	1.76
Barium sulphate,	11.44
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	99.60

If now we deduct from this the sulphuric anhydride and barium sulphate, and calculate the percentages anew, we have, —

	Per cents.	Atomic Ratios.
Copper oxide,	29.88	4.26
Arsenic trioxide,	52.30	3.00
Acetic anhydride,	17.82	1.98
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	100.	

A sample of Schweinfurt green was then obtained from Messrs. Folsom & Co. of this city. This sample was said to be perfectly pure, and was made in their works. It was of a much brighter shade than the preceding, and gave on analysis:—

ANALYSIS No. II.

	Per cents.	Atomic Ratios.
Copper oxide,	30.97	4.43
Arsenic trioxide,	52.82	3.00
Acetic anhydride,	16.03	1.79
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	99.82	

This is very nearly the same as the preceding sample, calculated as pure *copper aceto-arsenite*. It corresponds quite nearly to the formula,



which calculated to percentages is thus:—

	Per cents.	Atomic Ratios.
Copper oxide,	33.19	5.
Arsenic trioxide,	49.73	3
Acetic anhydride,	17.08	2.
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	100.	

It will be seen by comparing the percentages that both samples analyzed contain more arsenious acid than is called for by the formula: this is most probably due to the difficulty of washing out the excess of arsenic in process of manufacture.

The formula given in the books for Schweinfurt green is,—



which was based upon the following analysis:—

	Per cents.	Atomic Ratios.
Copper oxide,	31.24	3.96
Arsenic trioxide,	58.62	3.00
Acetic anhydride,	10.13	1.00
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	100.	

This analysis was made by E. Ehrmann in the laboratory of Professor Von Liebig, and the results were published in "Der Annalen der Pharmacie,"* in 1834, in which paper Ehrmann, after giving the

* Der Annalen der Pharmacie, Band XII., 1834, Seite 72.

origin of the salt, gives a formula for its preparation, and then the composition as determined by him.

The receipt he gives is as follows, which he states works as well in small amounts as in large:—

“10 parts verdigris are mixed with as much water at 50–55° as is necessary to produce a moderately thin emulsion: this is then passed through a fine hair sieve, to separate the marc of the grape or the small particles of copper from the basic acetate of copper.

“This emulsion is poured still warm into a solution of 8 parts of powdered arsenious acid in 100 parts water, which is kept in a state of brisk ebullition in a copper kettle. The mixing is done quickly, and meanwhile the fire must be kept bright and hot, so that the boiling of the solution of arsenious acid may not be interrupted. The color appears in a few minutes. If the verdigris is added cold, or the boiling of the arsenious acid is interrupted, the precipitate is of a dull yellow-green color, in which case some acetic acid must be added to the solution, boiling a few minutes longer, and allowed to stand to cool by itself, after which the dull precipitate becomes crystalline, and is converted into Schweinfurt green.

“On account of the difficulty with which the arsenious acid dissolves in pure water, many makers add to the water, with the 8 parts of arsenious acid, $\frac{1}{8}$ parts (that is, to 8 pounds 1 oz.) of pure potash; but, before the addition of the verdigris, the solution must be made neutral with acetic acid. . . .

“If a boiling solution of neutral acetate of copper and one of arsenious acid in water, the amounts of each being equal, are mixed, a very voluminous precipitate of a dull olive-green color occurs immediately: if the supernatant liquid be allowed to stand in contact with this some hours, or cool slowly with it, it loses its gelatinous condition, sinks together, becomes crystalline in granular crystals, and assumes the useful color of Vienna green.

“The compound acquires a still more brilliant color, if an equal volume of cold water is added to the liquid after mixing.

“If the mixture, instead of standing by itself, be boiled a few minutes, the conversion to the crystalline salt is accomplished in a very short space of time.

“The difference in the shades of color is due mainly to the size of the crystalline grains: when rubbed to a fine powder on a color-slab, their appearance is similar. . . .

“The pure compound which was obtained by the preceding method was submitted to analytical investigation. . . .

"Schweinfurt green is a double salt of acetic acid, arsenious acid, and oxide of copper: it is entirely insoluble in water. All mineral acids, and even concentrated acetic acid, extract the oxide of copper from it, leaving the white arsenious acid behind. It is also decomposed by fixed alkalies, except that in this case oxide of copper remains behind. If the alkaline liquid, which has dissolved the arsenious acid, is boiled with the precipitated oxide of copper, this is reduced to the suboxide by the arsenious acid: the oxide, which is at first black, becomes orange-red by boiling. . . . Ammonia dissolves it without decomposition, with the well known blue color of copper."

Some Schweinfurt green was now prepared by the first of these receipts.

Experiment No. 1.

Took 20 grams verdigris and made it into a thin paste with water, rubbing it well in a mortar to break up any lumps and mix thoroughly. 16 grams of arsenic trioxide were dissolved in water, to which about 1 gram of potassium carbonate was added: then the emulsion of verdigris was added to the boiling solution of arsenic trioxide, which was made acid with acetic acid. At first yellow-green copper arsenite was precipitated: this, on boiling, very gradually changed to the aceto-arsenite, at first crystallizing in a pellicle over the surface; finally, with the addition of a little acetic acid, the whole mass became more dense and crystalline, leaving a blue solution, from which the precipitate was separated by a filter. The precipitate was washed with boiling water, till no arsenic was found in the filtrate on testing the acidulated liquid with sulphuretted hydrogen. The filtrate contained copper, arsenic trioxide, and potassium acetate.

The precipitate was dried at 100° C. for twenty-four hours, and then analyzed.

ANALYSIS NO. III.

	Per cents.	Atomic Ratios.
Copper oxide,	32.00	4.33
Arsenic trioxide,	55.63	3.00
Acetic anhydride,	12.31	1.29
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	99.94	

The precipitate was of a pale green color, inferior to the samples previously examined, and its specific gravity was much lower.

The above receipt was now varied by substituting the neutral copper acetate for verdigris: the manipulation is much easier than with the basic acetate.

Experiment No. 2.

80 grams arsenic trioxide dissolved in water.

100 „ copper acetate „ „ „

The copper salt was added to the solution of arsenic trioxide: as in the former case, a yellow-green flocculent precipitate was produced, which was gradually converted by boiling into the brilliant acetoarsenite. The filtrate from the pigment was acid, of a deep blue color, and contained arsenic trioxide, copper, and acetates.

The precipitate was dried at 100° C. as before, and gave on analysis these results:—

ANALYSIS NO. IV.

	Per cents.	Atomic Ratios.
Copper oxide,	32.12	4.56
Arsenic trioxide,	56.08	3.00
Acetic anhydride,	10.37	1.07
Hydroscopic water.	.61	
	99.18	

These two salts approximate to Ehrmann's formula, although they vary somewhat from it. In 1858,* "N. Reilter found in four commercial Schweinfurt greens (No. I. was pure, II.-IV. were mixed with heavy spar and gypsum, all four samples showed the presence of free arsenious acid, they were washed before analysis), after deducting the water and impurities:—

	I.	II.	III.	IV.
Copper oxide,	33.97	34.94	33.83	33.65
Arsenic trioxide,	57.52	58.18	54.31	57.93
Acetic anhydride,	8.51	7.88	11.86	8.42
	100.00	101.00	100.00	100.00

"He says it follows from these numbers that Schweinfurt green consists of monarsenite of copper, combined with varying amounts of basic (not *mono*) copper acetate."

It will be seen, by comparison of these results with those obtained by Ehrmann, that they with one exception contain less acetic anhydride and more arsenic trioxide and copper oxide, while they do not approach the composition of the commercial samples analyzed by myself. This is, I think, partly due to an admixture of free arsenic trioxide.

* Jahresbericht der Chemie, 1858, Seite 651.

Experiment No. 3.

The filtrate in Experiment No. 2 contained copper, arsenic trioxide, and acetates. To this solution, in which no precipitate occurred on the addition of more arsenic trioxide, sodium carbonate was added to faint alkaline reaction. A yellow-green precipitate fell, which was collected on a filter, washed until the filtrate was free from arsenic trioxide. Dried, the composition was, —

ANALYSIS NO. V.

	Per cents.	Atomic Ratios.
Copper oxide,	50.69	3.31
Arsenic trioxide,	38.13	1.00
Water,	11.88	
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	100.70	

This is copper arsenite of the following formula, $\text{Cu}_3\text{As}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, with about 4 per cent of hygroscopic water, and contained, as far as could be ascertained by careful testing, *no* acetic acid.

The question then arose, Does sodium arsenite precipitate pure copper arsenite from copper acetate in all cases, or does it also carry down some basic copper acetate with it? This led to

Experiment No. 4.

Copper acetate,	33 grams.
Sodium carbonate,	50 "
Arsenic trioxide,	18 "

The arsenic trioxide was dissolved in the sodium carbonate, and the solution mixed with the copper acetate solution, both being near the boiling point. A yellow-green precipitate fell, the supernatant liquid contained acetates, arsenic trioxide, and carbonates, and was slightly yellow. The precipitate was separated by a filter, and washed till no arsenic trioxide was found in the wash-water. This was much like the product obtained in Experiment No. 3, except that the color was a little brighter and of a bluer shade, and when analyzed gave: —

ANALYSIS NO. VI.

	Per cents.	Atomic Ratios.
Copper oxide,	52.06	10.35
Arsenic trioxide,	37.81	3.00
Acetic anhydride,	2.70	.40
Water,	8.21	7.08
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	100.78	

This shows that when sodium arsenite acts on copper acetate, if there is not a large excess of arsenic trioxide, we get copper arsenite, which contains some basic copper acetate, as is the case with the copper sulphate under like conditions, and that the acetic acid gives a brighter shade to the color.

To answer the question as to whether an excess of copper acetate would produce, when mixed with arsenic trioxide, a salt containing more basic copper acetate, we have

Experiment No. 5.

Copper acetate,	250 grams.
Arsenic trioxide,	50 „

Dissolved in water separately, and mixed the boiling solutions and boiled an hour. The precipitate was green, the filtrate from it was blue, and contained arsenic trioxide, copper, and acetates. The precipitate had this composition:—

ANALYSIS No. VII.

	Per cents.
Copper oxide,	50.00
Arsenic trioxide,	35.57
Acetic anhydride,	2.47
Water,	11.07
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	99.11

This result, deducting hygroscopic water and calculating the per cents anew, gives:—

	Per cents.	Atomic Ratios.
Copper oxide,	52.06	10.80
Arsenic trioxide,	37.04	3.00
Acetic anhydride,	2.57	.39
Water,	8.33	7.38
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	100.00	

This is a mixture of copper arsenite and basic copper acetate, almost of exactly the same composition as that obtained by the action of sodium arsenite on copper acetate in Experiment No. 4, and, instead of containing a considerable amount of copper acetate, has a very small amount.

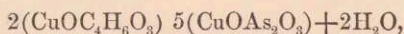
Experiment No. 6.

To the filtrate from the pigment obtained in Expt. No. 5, 50 grams of arsenic trioxide were added and some free acetic acid: a new formation of the well-known color of Schweinfurt green occurred after a prolonged boiling; this was allowed to stand over night in contact with the solution from which it was precipitated; it was then filtered off and washed free from the excess of arsenic trioxide. The filtrate was blue, and acid, containing copper, arsenic trioxide, and acetates; on the addition of more arsenic trioxide, no precipitate fell, but, on neutralizing, one was produced having the color of the one in Expt. No. 3, and it was probably of similar composition, but was in too small an amount for analysis. The composition of the pigment obtained was:—

ANALYSIS NO. VIII.

	Per cents.	Atomic Ratios.
Copper oxide,	31.00	7.09
Arsenic trioxide,	54.48	5.00
Acetic anhydride,	11.32	2.00
Combined water,	2.55	2.56
Hydroscopic water,	.65	.70
	<hr/> 100.00	

This is very near the formula, —



which when calculated in percentages is:—

	Per cents.	Atomic Ratios.
Copper oxide,	31.12	7.00
Arsenic trioxide,	55.43	5.00
Acetic anhydride,	11.43	2.00
Water,	2.02	2.00
	<hr/> 100.00	

This was the first hydrated copper aceto-arsenite obtained, excepting the resulting pigments from Expts. Nos. 5 and 6, which may be considered as mixtures; for, although there was a small amount of water in nearly all samples, it was hydroscopic water, and was entirely driven off by heating to 105° C.

This experiment was repeated, giving:—

ANALYSIS No. IX.

	Per cents.	Atomic Ratios.
Copper oxide,	31.53	7.05
Arsenic trioxide,	55.03	5.00
Acetic anhydride,	10.16	1.76
Combined water,	2.28	2.32
Hydroscopic water,	.64	.60
	<hr/> 100.04	

This is a confirmation of the preceding result, and seems to prove the existence of a hydrated copper aceto-arsenite.

Having experimented on an excess of copper acetate with a small amount of arsenic trioxide, the other extreme was now tried, and, as the proportion was 5 to 1 in preceding case, so here 5 to 1 was used.

Experiment No. 7.

Copper acetate,	25 grams.
Arsenic trioxide,	125 „

Dissolved separately, added the copper solution to the arsenic trioxide, and boiled; the reaction was as in the preceding cases; first copper arsenite, changing to aceto-arsenite; this precipitate was filtered off and washed with hot water; the filtrate contained a trace of copper and a large amount of arsenic trioxide. When the excess of arsenic trioxide was washed out of the precipitate, the latter was dried at 100° C. and analyzed.

ANALYSIS No. X.

	Per cents.	Atomic Ratios.
Copper oxide,	31.19	4.85
Arsenic trioxide,	46.47	3.00
Acetic anhydride,	14.05	1.76
Combined water,	7.05	4.85
Hydroscopic water,	1.15	
	<hr/> 99.91	

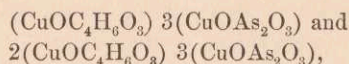
This agrees with the formula, —



which, calculated in percentages, gives, —

	Per cents.	Atomic Ratios.
Copper oxide,	30.90	5.00
Arsenic trioxide,	46.22	3.00
Acetic anhydride,	15.88	2.00
Water,	7.00	5.00
	100.00	

This salt is in color the most brilliant of all the samples in my possession, and of a decidedly different shade from the samples of the formulæ, —



being more grass-green, having less blue in it. It comports itself with acids and alkalis in a similar manner to the last-mentioned salt, but is a little more dense; it holds to its five molecules of water strongly, it not being decomposed at 120° C. When heated for a long time at this temperature, it oxidizes slowly and gains steadily in weight. This is probably the salt existing in the commercial samples examined minus the water, and is the nearest approach to them I have been able to make, the exact formula for their production being a trade secret.

“* Wagner states that the formula given by Ehrmann is only empirical, because a portion of the copper is present as the suboxide, and a portion of the arsenic as arsenic acid.”

To test this statement, I examined my samples of Schweinfurt green in the following manner: In each case a weighed amount of the green was dissolved in pure hydrochloric acid, made alkaline with ammonia water and “magnesia mixture” added, and in each case a precipitate occurred. After allowing this to stand over night, it was filtered off and washed with aqua ammonia dissolved in hydrochloric acid, and neutralized with ammonia, then acidulated with acetic acid, and acetate of uranium solution of known strength added, testing in the usual way for an excess, with ferrocyanide of potash. The first drop of uranium solution gave a brown coloration when tested with the ferrocyanide, and an excess gave no precipitate, proving beyond a doubt the absence of arsenic pentoxide.

The precipitate obtained by the “magnesia mixture” was doubtless basic magnesium sulphate and magnesia itself.

* Handbook Chemical Technology, Rudolf Wagner, Ph. D. Translated by W. Crooks, F.R.S. Appleton & Co., N. Y., 1872. Page 58.

Therefore I conclude that the formulæ do represent the composition, both empirically and rationally, and that there is *no* suboxide of copper present, as also *no* arsenic acid.

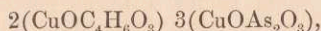
Wagner, after giving Ehrmann's receipt, publishes the following from M. Braconnot: "15 kilos of sulphate of copper ($\text{CuSO}_4 + 5\text{H}_2\text{O}$) are dissolved in the smallest possible quantity of boiling water, and mixed with a boiling and concentrated solution of arsenite of soda or potash, so prepared as to contain 20 kilos of arsenious acid. There is immediately formed a dirty greenish-colored precipitate, which is converted into Schweinfurt green by the addition of some 15 litres concentrated wood-vinegar. This having been done, the precipitate is filtered off and washed. . . .

"It thus appears that the preparation of this pigment aims first at the least expensive preparation of neutral arsenite of copper, which is then converted into aceto-arsenite of copper, by digesting the precipitate with acetic acid."

Now this is very probably the method, by which the sample obtained from the Massachusetts Institute of Technology was made, and accounts for the basic copper sulphate found in it. The insoluble matter is used to dilute the color and as adulteration.

These latter are therefore impurities, and are to be disregarded in speaking of its composition.

Now with regard to the pure pigment: Ehrmann's analysis is without doubt correct, and is sustained by two samples prepared by myself; but this cannot be regarded as the universal composition of the salt, and does not, as has been already said, cover the commercial samples that I found in the market. Therefore we must look farther, and we find there is another salt having the formula, —



in two commercial samples; hence we infer that the composition varies between these salts, that it may be $\text{CuOC}_4\text{H}_6\text{O}_3 \ 3(\text{CuOAs}_2\text{O}_3)$, or $2(\text{CuOC}_4\text{H}_6\text{O}_3) \ 3(\text{CuOAs}_2\text{O}_3)$, or something between the two; and we also see that the amount of arsenic trioxide may vary considerably, from the difficulty with which it is removed by washing, even with hot water, in process of manufacture.

In the extract from N. Reilter, we have a series of results which vary from any obtained by Ehrmann and myself (with one exception), where the amounts of acetic acid are much less. And he states that Schweinfurt green is copper mono-arsenite combined with varying amounts of basic copper acetate. We have a variance of from

7.88% — 17.82% of acetic anhydride, a variance of nearly 10%. As the salt is crystalline, and is formed out of different proportions of the materials used, with the same composition, as it was in several cases where no *great* change was made, it appears as a definite chemical compound, and the variation is, I think, best explained by considering the existence of several definite salts. Also in three cases I have found water chemically combined, which shows still more variance, but these salts also appear definite, and agree with very simple formulæ.

Pure Schweinfurt green may therefore be composed either entirely of the salt having the formula $(\text{CuOC}_4\text{H}_6\text{O}_3)_3 (\text{CuOAsO}_3)$, or entirely of that having the formula $2(\text{CuOC}_4\text{H}_6\text{O}_3)_3 (\text{CuOAs}_2\text{O}_3)$, or may have a composition between the two, from a mixture of these salts, and it may contain combined water having this formula, $2(\text{CuOC}_4\text{H}_6\text{O}_3)_3, 5(\text{CuOAs}_2\text{O}_3) + 2\text{H}_2\text{O}$, or may have the formula $2(\text{CuOC}_4\text{H}_6\text{O}_3)_3 (\text{CuOAs}_2\text{O}_3) 5\text{H}_2\text{O}$. And all these results may be varied again still more by a mechanical mixture of arsenic trioxide, from the difficulty of removing the same by washing. That the arsenic is present as trioxide, it contains no arsenic pentoxide so far as I have been able to find in this investigation. The salts of the formulæ $2(\text{CuOC}_4\text{H}_6\text{O}_3)_3 (\text{CuAs}_2\text{O}_3)$ and $2(\text{CuOC}_4\text{H}_6\text{O}_3)_3 (\text{CuOAs}_2\text{O}_3) + 5\text{H}_2\text{O}$ are more brilliant than the other two with less basic copper acetate in them, the difference being quite marked.

Therefore this beautiful pigment is not so definite as has been previously supposed, but may vary some ten per cent in its amount of acetic acid, twelve per cent in its arsenic trioxide, and five per cent in its amount of copper oxide; while some samples contain chemically combined water, in one specimen going up to seven per cent. And all of these would be taken by an observer for Schweinfurt green, and can only be distinguished by a slight difference in shade of color and chemical composition, which latter shows there exists three definite salts.

In the analyses of this paper, the following methods were employed:

A weighed portion was dissolved in an excess of nitric acid, the solution boiled some time in order to oxidize the arsenic trioxide, the solution was then made alkaline with caustic potash, which precipitated the copper as oxide, which if the acids are all oxidized is black; if not, orange-red, in which case the separation is not as perfect, and it cannot be manipulated with as much ease, as when the oxidation is perfect. The fluid with the precipitate is boiled and

filtered, the precipitate washed with hot water, dissolved in dilute sulphuric acid, and the metallic copper precipitated by a battery.

The filtrate containing the arsenic is made acid with acetic acid, and titrated with uranium acetate solution.

This method was carefully tested against others and itself, and proved to give the most satisfactory results.

The acetic anhydride was determined by ignition with lead chromate as in an organic analysis, collecting the carbonic acid and water, and weighing the same; the excess in weight of water above that formed from the combustion of the acetic acid, gave the total water. The hygroscopic water was determined by drying the salt for three or four hours in an air-bath at 100° — 105° C. until a constant weight was obtained, of course deducting the hygroscopic from the total water, gives that which is combined.

I owe my sincere thanks to Professor S. P. Sharples, for his kindness in allowing me the use of his very convenient laboratory, his library, and for some suggestions as the investigation progressed.

Boston, October 24, 1876.