

XXXIII.—*Note on the Arsenates of Lead and Calcium.*

By SPENCER U. PICKERING, M.A., F.R.S.

As an insecticide for leaf-eating insects, lead arsenate has lately come into general use, since it does not scorch foliage in the same way as does Paris green or London purple. It is made by precipitating sodium arsenate with the acetate or nitrate of lead; but, unfortunately, so many different instructions have been issued by various authorities, both in this and other countries, as to the proper proportion in which these reagents should be used, that the matter has been reduced to a state of confusion. This is all the more to be regretted, as excess of the soluble arsenate, and, to a lesser extent, excess of the lead salts, is injurious to foliage.

Some account of an investigation on this subject has been published in the Sixth Report of the Woburn Experimental Fruit Farm, 1906, p. 157, but the details of the chemical facts established may be more appropriately recorded here.

The sodium arsenate listed by manufacturers, either without specification, or as "pure," "cryst," or "hydrated," is the disodium ortho-arsenate, generally containing 7 molecules of water of crystallisation, but, occasionally, 12. In the case of four samples out of five which were obtained from different manufacturers, the salt was found to be the heptahydrate; in the fifth, it was dodecahydrate. Determinations of the water contents by prolonged drying at 100°—the results of which are given in Table I, Col. II, samples A to E—indicated that these samples all attained a high standard of commercial purity, although they differed from each other slightly in alkalinity. Sample X was one which was prepared by careful recrystallisation.

As the values in the table imply, the whole of the water of crystallisation may be driven off at 100°, although it is generally stated that a temperature of 200° is necessary for this purpose, and even 300°, according to the British Pharmacopœia, 1898, should be employed. When the crystallised salt is allowed to fuse during dehydration, there

is considerable difficulty in driving off all the water at 100° , but, if it is partially desiccated before being heated, no such difficulty is experienced. On further heating to 150° , it begins to change into the pyroarsenate, and this change is rapid at 300° . The theoretical loss of water in the conversion of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ into $\text{Na}_4\text{As}_2\text{O}_7$ is 43.30 per cent.; the values found with sample X at 300° were 43.21 and 43.17. No fusion occurs if the hydrated arsenate is dehydrated slowly. Thus, the temperature for drying prescribed in the British Pharmacopœia is much too high, and the only sample of this medicinal arsenate which was examined was found, in consequence, to consist mainly of pyroarsenate, instead of orthoarsenate.

TABLE I.—*Precipitation of Sodium Arsenate by Crystallised Lead Acetate.*

Arsenates. I.	Pure Cryst. Na ₂ HAsO ₄ . II.	The sample. III.	Weight of lead acetate required for 1 gram of		
			Hydrated arsenate present. IV.	Na ₂ HAsO ₄ present.*	
				Before heating. V.	After heating. VI.

"Pure hydrated" samples.

Heptahydrates :

Theory for Na ₂ HAsO ₄ , 7H ₂ O ..	59.60	—	1.822	3.056	—
X. (Recryst.)	{ 59.75	1.823	1.846	3.098	3.116
	{ 59.68	1.853	1.876	3.149	2.958
A	59.41	1.696	1.703	2.854	—
B	59.79	1.739	1.724	2.917	—
C	59.84	1.761	1.768	2.943	—
D	59.24	1.798	1.787	3.035	—
Mean	59.62	1.779	1.784	2.999	—

Dodecahydrate :

Theory for Na ₂ HAsO ₄ , 12H ₂ O.	46.27	—	1.414	3.056	—
E	46.48	1.389	1.383	2.987	—

"Pure anhydrous" samples.

Theory for Na ₂ HAsO ₄	100.00	—	—	3.056	—
F. (Fused)	101.53	3.014	—	2.966	—
G. (Exsic. B. P.)	102.96	3.194	—	3.102	—

"Crude anhydrous" samples.

H	103.31	2.583	—	2.500	2.601
I	101.38	2.539	—	2.505	2.538
J	92.33	3.027	—	3.278	3.237
K	86.76	2.757	—	3.180	3.316
Theory for Na ₄ As ₂ O ₇	105.09	—	—	3.212	—

* Or its equivalent of $\text{Na}_4\text{As}_2\text{O}_7$.

In the earlier determinations, which were published in the Report of the Woburn Experimental Fruit Farm, some of the samples used

were overheated in drying, and the water contents, consequently, appear too high. The values have been corrected for this error in the present communication, or fresh determinations have been substituted for them.

The amount of crystallised lead acetate required for the precipitation of 1 gram of the various samples of sodium arsenate was determined by running a standard solution of the acetate into a solution of the arsenate. Filtration was necessary after each addition. The final reaction is not very clearly marked, lead arsenate not being a very insoluble substance; duplicate determinations, however, never differed by more than 1 or 2 per cent. of the total.

The results of the precipitation are given in Table I. These show that the lead arsenate precipitated must be the triplumbic salt. The equation $2\text{Na}_2\text{HAsO}_4 + 3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, 3\text{H}_2\text{O} = \text{Pb}_3(\text{AsO}_4)_2 + 2\text{C}_2\text{H}_4\text{O}_2 + \&c.$ requires 3.056 parts of lead acetate for one part of anhydrous arsenate present, and the mean of the values found with the various samples is 2.999 (Col. V). This is the reaction which had been accepted as correct in Canada and the United States. According to it, for one part of the heptahydrated and dodecahydrated arsenate 1.822 or 1.414 parts, respectively, of lead acetate would be required. The Board of Agriculture and Fisheries (Leaflets 4, 20, 62, and 69) recommends the use of three parts of lead acetate to every one part of crystallised sodium arsenate; this would, obviously, give an unnecessary, and, as I have shown elsewhere, an injurious excess of lead salt. The use of two parts of acetate to every one part of crystallised arsenate would be amply sufficient to ensure the precipitation of all the arsenate in every case.

The reaction is the same whether the acetate is added to the arsenate, as above, or *vice versa*. Thus, with the samples A and C the values obtained on adding acetate to arsenate were 2.854 and 3.095; mean, 2.915; and on adding arsenate to acetate, 2.912 and 3.074; mean, 2.943. A similar identity of results was obtained with various samples of crude arsenate.

The results with two "pure anhydrous" samples are next given in the table. Sample G is that prepared by drying at about 300°, and sold as "Exsic. B.P., 1898"; the other is sold as "fused," and is prepared at a somewhat lower temperature. Both of these samples, on redrying at 300°, lost less water than they should have done if they had consisted of the orthoarsenate, and, consequently, the arsenic acid present in them represents more than 100 per cent. of orthoarsenate; they were, however, not entirely in the condition of pyroarsenate, as 100 parts of this represent 105.09 parts of orthoarsenate, and 102.96 was the highest value found. The results obtained on precipitating this sample with lead acetate give a value (3.194) approximating that required by the pyroarsenate, which is 3.212.

Some samples of "crude anhydrous" sodium arsenate were examined, in order to ascertain how much lead acetate would be required in practice for their precipitation. It will be seen from the water determinations, that two of these appeared to consist partially of the pyroarsenate; the other two contained a notable amount of water. The latter, J and K, give values, on precipitation (Col. V), agreeing fairly well with the results with pure samples, although both are somewhat high, this, no doubt, being due to the presence of an excess of arsenic acid; for all the samples the crude arsenates gave an acid, instead of an alkaline, reaction. The other two samples, H and I, gave values too low to be reconcilable with the action being the same as in other cases. With both of them the lead acetate required was 2.5 parts to every one of $\text{Na}_2\text{H}(\text{AsO}_4)$ present, and this proportion agrees well with that required if the lead arsenate precipitated were a mixture of equal molecular proportions of $\text{Pb}_3(\text{AsO}_4)_2$ and $\text{Pb}_2\text{H}_4(\text{AsO}_4)_2$, the calculated requirement in such a case being 2.546. Further reference to this point will be made below.

It will be seen that another set of values for the lead acetate required for precipitation are given in the last column of the table. These apply to samples of the arsenate after they had been heated to 300° . They were made because some previous determinations—those published in the Report of the Woburn Experimental Fruit Farm—had indicated that a higher lead value was obtained after the sample had been heated, suggesting that the pyroarsenate formed by the heating of the salt remained as such when dissolved in water (like a pyrophosphate), and reacted with the lead acetate in a manner different from the orthoarsenate. The present determinations do show a difference in the lead values in this same direction, but it is too small to be of any significance, especially as similar determinations with the pure arsenate, X, showed no such difference, the mean of the duplicate values in that case (Cols. V and VI) being 3.124 and 3.087, before and after heating, respectively.

For practical purposes it would not be safe to take less than 3.5 parts of lead acetate for 1 part of crude arsenate if the precipitation of all the arsenate is to be ensured, although, often, a good deal less might suffice (see Col. III).

On examining the same samples of sodium arsenate by precipitation with lead nitrate, instead of with lead acetate, it was evident that a different reaction occurred. The values given by the five hydrated samples (Table II) give, as a mean, 1.743 parts of nitrate to every 1 of anhydrous arsenate present in them. This indicates that the arsenate formed must be the diplumbic (PbHAsO_4), and not the triplumbic salt, since the formation of the latter would necessitate the use of 2.669 parts of the nitrate, whereas that of the former requires 1.780

parts. The values in the individual cases are not very concordant, but they leave no doubt as to the general nature of the reaction, although the diplumbic salt formed may be mixed in some cases with a certain amount of the triplumbic salt, and, in others, with some of the monoplumbic salt. The variations in the values are not, however, due to chance circumstances, such as temperature or the proportion of the water present; for duplicates wherein these circumstances were varied did not show differences of more than 2 per cent., whereas the differences observed in the table extend to 10 per cent.; they can, therefore, be accounted for only by differences in the nature of the different samples, and it will be noticed that the three commercial

TABLE II.—*Precipitation of Sodium Arsenate by Lead Nitrate.*

Arsenate.	Weight of lead nitrate required for 1 gram of		
	The sample.	Hydrated arsenate present.	Na_2HAsO_4 present.
<i>"Pure hydrated" samples.</i>			
Heptahydrates:			
Theory for $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$...	—	1·061	1·780
If PbHAsO_4 formed			
X. (Recryst.).....	1·084	1·096	1·839
A.....	1·005	1·008	1·691
B.....	0·902	0·899	1·509
C.....	1·092	1·096	1·822
D.....	1·097	1·095	1·855
Mean	1·036	1·038	1·743
Dodecahydrate:			
Theory for $\text{Na}_2\text{HAsO}_4 \cdot \text{H}_2\text{O}$	—	0·823	1·780
E.....	0·900	0·896	1·936
<i>"Pure anhydrous" samples.</i>			
Theory for Na_2HAsO_4 :			
If $\text{Pb}_3(\text{AsO}_4)_2$ formed	—	—	2·669
If $\text{Pb}_5\text{H}_2(\text{AsO}_4)_4$ formed ...	—	—	2·224
If PbHAsO_4 „	—	—	1·780
If $\text{PbH}_2(\text{AsO}_4)_2$ „	—	—	0·890
F. (Fused)	1·922	—	1·894
G. (Exsic. B. P.)	1·896	—	1·889
<i>"Crude anhydrous" samples.</i>			
H.....	1·946	—	1·883
I.....	2·150	—	2·121
J.....	2·257	—	2·447
K.....	2·210	—	2·547

samples which required the largest amount of lead nitrate—C, D, and E—are the same which required the largest amount of lead acetate.

With the two "pure anhydrous" samples, F and G, the lead nitrate required is, on the average, somewhat greater, and it is even slightly

greater than what would be required if the sodium arsenate were present entirely as the pyro-salt, for the pyro-salt requires only 1.870 parts of lead nitrate, whereas the samples in question took about 1.9 parts. But the end reaction in the case of precipitation with lead nitrate, is less well marked than where the acetate is used, and the values, consequently, are less certain. The diplumbic arsenate appears to be more soluble than the triplumbic salt, and, before the whole of the arsenic acid is precipitated, some excess of lead nitrate must be added. A mixture of the two reagents may be obtained, in which turbidity will be caused by the addition of more of either of them.

Determinations with the samples of the crude sodium arsenate are also given. The amount of lead nitrate required by these varies considerably, and in two cases, J and K, it is nearly equivalent to that required for the formation of the triplumbic salt. With sample H, the diplumbic salt was precipitated, as in the case of the samples of pure arsenate, whilst with the sample I we get a value intermediate between the di- and triplumbic salts.

Mr. F. J. Smith (*Ann. Rep. Mass. Board of Agriculture, and Ann. Rep. of the Hatch exp. Station of Mass. Agri. Coll.*, 1897, 357) gives the reaction between sodium arsenate and lead nitrate as resulting in the formation of a mixture, or compound, of the triplumbic and diplumbic arsenates in equivalent proportions, $Pb_3(AsO_4)_2 + Pb_2H_2(AsO_4)_2$, or $Pb_5H_2(AsO_4)_4$. Such an arsenate might very conceivably exist, either as a molecular compound or otherwise; but it seems evident that the lead arsenate formed—at any rate when the materials are pure—is simply the diplumbic salt, and it is only with one sample out of the twelve here examined (and that a sample of crude arsenate, I), that a value was obtained agreeing fairly with the formation of the complex arsenate—2.121 against 2.224; at the same time, it may be observed, the values obtained by precipitation with lead acetate indicated, both in the case of this sample and in that of H, the formation of the same complex lead arsenate. It is clear, however, that we cannot establish the correctness of a chemical reaction, and, still less, the existence of a new salt, on the strength of determinations with crude and obviously very impure substances. Whether Mr. Smith's results were based on the examination of crude samples, and what value he attached to his equation, as representing an actual reaction, or merely as indicating the proportions required in practice, I am unable to determine, as I have been unable to obtain a copy of his paper, and my information on the subject is derived from Dr. Felt, State Entomologist to the United States. An abstract of Mr. Smith's paper will be found in the *Experimental Station Records*, 1899, p. 567, but it gives no information on the point in question.

As with lead acetate, so with the nitrate, it appears that the reaction

with sodium arsenate is substantially the same, whether the lead salt is added to the arsenate, or *vice versa*. Three of the samples of arsenate gave the following values for the lead nitrate required to precipitate one part of anhydrous arsenate present in them :

	When nitrate is added to arsenate.	When arsenate is added to nitrate.
Sample A (pure)	1.691	1.679
„ J (crude).....	2.447	2.407
„ K („).....	2.547	2.196

Whichever reagent is added to the other, some excess of it will be required before precipitation is complete ; when, therefore, the lead nitrate is added to the arsenate, the amount of it required will appear greater than when the process is reversed ; the difference, however, is not great, except in the case of the sample K.

In order to ensure the precipitation of the whole of the arsenate when lead nitrate is used as the precipitant, I should recommend that in practice $1\frac{1}{4}$ parts of it be used for every one part of crystallised sodium arsenate, or $2\frac{1}{4}$ parts for every one part of crude arsenate.

Calcium Arsenate.

It is probable that the lead in lead arsenate is of little or no value for insecticidal purposes, and that the cheaper calcium arsenate would be equally effective, if it were suitable in other respects ; indeed, it has already been used for this purpose in the United States. A brief note of the chemical facts elucidated in the examination of calcium arsenate will be sufficient.

When calcium nitrate or calcium chloride is added to sodium arsenate, a bulky flocculent precipitate is gradually formed, and at the same time minute crystals are deposited on the side of the vessel. The weight of precipitate formed, when increasing amounts of the calcium salt are added to an equivalent of sodium arsenate, increases until $1\frac{1}{2}$ equivalents of the calcium salt is reached, but increases no further with any excess of the latter up to $4\frac{1}{2}$ equivalents. This shows that the calcium arsenate which separates, is the tricalcium salt, the reaction for its formation requiring $1\frac{1}{2}$ equivalents of calcium to one of sodium arsenate. The calcium arsenate, however, is far from being very insoluble, and the amount precipitated does not approach the total amount formed, unless the liquid is concentrated. With 1 gram of hydrated sodium arsenate, and a total volume of 100 c.c. of liquid, the calcium arsenate precipitated amounts to only one-third of the calculated amount, and if the total volume is 300 c.c. no precipitate at all is formed. Judging by these results, the solubility of calcium arsenate should be about 1 in 200, and an arsenate of this solubility

would be useless for spraying trees, owing to the scorching effect which it would have on the foliage.

In the presence of lime, however, the whole of the calcium arsenate is precipitated from the solution. Thus, when lime water is added to sodium arsenate, no arsenate remains in solution so long as the proportion of lime added is slightly in excess of $1\frac{1}{2}$ equivalents to 1 equivalent of the arsenate. Here, again, it is evidently the tricalcium arsenate which is formed. The precipitate when first thrown down is bulky, flocculent, and opaque, but it soon shrinks and clots together, becoming more transparent and semi-crystalline. Its condition then is not such as would render it suitable for use in a spraying machine.

By using milk of lime, however, and keeping the lime in considerable excess, a mixture is obtained which would appear quite manageable for spraying purposes. Using pure lime, it was found that about three equivalents to every one of arsenate are sufficient to insure the precipitation of the whole of the arsenic acid, the excess of calcium salt in this case being necessitated by the particles of lime becoming coated with arsenate, and being thus prevented from becoming easily available for the reaction. In practice, where an impure lime would be used, it would be advisable to increase the proportions of lime still further, say, to double the amount mentioned above, which would mean mixing equal weights of lime and crystallised sodium arsenate.
