Oregon Agricultural College
Experiment Station

AGRICULTURAL CHEMISTRY DEPARTMENT

The Calcium Arsenates

By

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Acting Chemist, Oregon Agricultural Experiment Station.

CORVALLIS, OREGON

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INTRODUCTION

Chemical investigations on the calcium arsenates relative to their economic value and practicability as insecticides have been carried on by the department of Agricultural Chemistry of this Station during the past two years. The results obtained from these investigations are presented in this bulletin. The work was supported by the annual funds provided by the Adams Act of the United States Government.

Commercial calcium arsenate is an arsenical now being produced by reliable manufacturers of spray material and offered for sale as a substitute for the arsenates of lead. The value of the latter as a stomachic insecticide has been demonstrated, and it is now used extensively for the successful control of the codling moth, the destruction of the cotton boll worm, the tobacco worm, and the Colorado potato beetle. Previous investigations on the toxic values and killing power of calcium arsenate and lead arsenate indicate equal efficiency.

A consideration of a few figures will show the economic advantages which might be gained if calcium arsenate could be substituted for lead arsenate. A conservative estimate of the quantity of lead arsenate used annually in the United States, as stated by one of the largest manufacturers of spray materials, is probably more than 30,000,000 pounds. Assuming that it is retailed at 12 cents a pound, the actual cost being much more, especially when purchased in small lots, the total value would be $3,600,000. The cost of calcium arsenate, on the other hand, is about half the price of lead arsenate. Consequently, provided it may be substituted for the more expensive spray material, there would be a saving of more than $1,800,000. As these figures are based on prices that prevailed previous to 1916, this saving would not terminate after the war, since the higher price of lead arsenate is chiefly attributed to the excessive value of lead salts over calcium salts. During the past year, due, perhaps, to conditions brought on by the world war, the prices cited above have almost doubled; consequently, we are confronted with the possibility that the use of lead arsenate may be curtailed to the detriment of our orchards and the quality of the crop produced.

Numerous field experiments have been made heretofore, in various sections of the country, to ascertain the practicability of using calcium arsenate as a spray; but in most cases these trial experiments have failed, due to excessive burning of foliage. As a result, the use of this spray material has been discouraged.

As with most arsenicals, the cause of burning is due to the action of arsenic upon the foliage. The high water-soluble content of commercial samples of calcium arsenate indicates the possibility that therein lies the cause of intensive burning of foliage. This difficulty was encountered when the commercial lead arsenates were first used; but a study of the properties of the pure salts prepared in the laboratory enabled manufacturers to produce a high-grade, insoluble lead arsenate that gave orchardists no trouble and caused little burning. A review of the literature, moreover, reveals no investigations on the calcium arsenates that would give information relative to the preparation, stability,
or other characteristics of the material that would explain the cause of the unfavorable results obtained by field experiments. It was thought, therefore, that a more complete knowledge of the composition of the calcium arsenates, together with a study of the methods of preparation, as well as the physical and chemical properties, would give an insight relative to the practicability of their use as a substitute for the arsenates of lead.

Experimental

A review of the literature relative to compounds of calcium and arsenic shows that numerous preparations are discussed from a theoretical standpoint, but that few have actually been obtained in the laboratory. The calcium arsenates that are of vital interest to us from an insecticidal standpoint must necessarily have those physical and chemical properties that indicate a fairly stable salt. Preliminary experiments convinced us that two salts, the tri-calcium arsenate, \( \text{Ca}_3(\text{AsO}_4)_2 \), and the calcium hydrogen arsenate, \( \text{CaHAsO}_4 \), appeared to be the only favorable ones.

Recent work on these two salts is very limited. In 1844 Rammelsberg \(^1\) prepared the pure salt corresponding to the theoretical composition \( \text{CaHAsO}_4 \cdot 2\text{H}_2\text{O} \), containing two molecules of water of crystallization, which was further substantiated at about the same date by the work of Klaproth \(^2\) and Dufet \(^3\). Others, at even an earlier date, obtained different results, indicating variation in amounts of water of crystallization and constitution. Although citations are made giving possible methods of preparing the tri-calcium arsenate, no data containing actual figures of analysis were found. Furthermore, numerous analyses of commercial samples, both the so-called C. P. salts, intended for reagents in chemical work, and those salts sold by manufacturers for spraying purposes, proved to be mixtures of various calcium salts and no two were alike in composition. This point will be further commented upon later.

Previous investigators suggest the preparation of calcium hydrogen arsenate by using calcium chloride, \( \text{CaCl}_2 \), and sodium hydrogen arsenate, \( \text{Na}_2\text{HAsO}_4 \), the reaction being in accordance with the following equation:

\[
\text{CaCl}_2 + \text{Na}_2\text{HAsO}_4 \rightarrow \text{CaHAsO}_4 + 2\text{NaCl}
\]

These salts may, however, also react as represented in the following equation giving the tricalcium arsenate:

\[
3\text{CaCl}_2 + 2\text{Na}_2\text{HAsO}_4 \rightarrow \text{Ca}_3(\text{AsO}_4)_2 + 4\text{NaCl} + 2\text{HCl}
\]

It is obvious, therefore, that both the arsenates may be formed in greater or less amounts when prepared in the above manner. This may account for the variable composition of the commercial arsenates noted above, and emphasizes more strongly the necessity of specific control of conditions in such a manner that one or the other salt will be produced.

Preparation of Calcium Hydrogen Arsenate and Tri-Calcium Arsenate.

In order to make a complete study of those physical and chemical properties of the calcium arsenates that would have an immediate bearing upon their value as a spray material, the preparation of these salts in very pure form is essential.

Numerous methods of preparation were undertaken, but in most cases, mixtures were obtained of varying composition. After trial experiments the following method was found to be satisfactory:
Solutions of calcium chloride and sodium hydrogen arsenate were made, and very slightly acidified with either acetic, hydrochloric or nitric acid. After filtration, to obtain absolutely clear solutions, the cold calcium chloride solution was gradually poured into the sodium hydrogen arsenate solution, being constantly stirred meanwhile. A heavy, voluminous precipitate immediately formed, which slowly settled, whereupon the clear, supernatant liquid was decanted off. It was further washed by decantation several times and finally brought upon a Buchner filter and washed with hot distilled water until free from chlorides. The pure white amorphous powder was then dried at 100°C.

The combined washings were evaporated down to small volume, when crystals of calcium hydrogen arsenate separated out. After removing the mother liquor by suction, the crystals were washed several times with small quantities of boiling water and dried at 100°C.

Analyses made of the samples thus obtained are as follows:

Powder:
- Calcium as CaO — total 28.14%
- Arsenic as As₂O₅ — total 57.91%

Crystals:
- Calcium CaO — total 28.40%
- Arsenic as As₂O₅ — total 58.15%

Theoretical composition of CaHAsO₄·H₂O:
- Calcium as CaO — total 28.24%
- Arsenic as As₂O₅ — total 58.11%

Comparing the results with the theoretical composition of calcium hydrogen arsenate, CaHAsO₄·H₂O, as noted above, we conclude that both samples are pure calcium hydrogen arsenate, containing one molecule of water of crystallization.

When these samples were further dried at 175°C, both lost their water of crystallization, as shown by the following analytical results:

Powder:
- Calcium as CaO — total 31.10%
- Arsenic as As₂O₅ — total 63.80%

Crystals:
- Calcium as CaO — total 31.20%
- Arsenic as As₂O₅ — total 63.88%

Theoretical composition of CaHAsO₄:
- Calcium as CaO — total 31.13%
- Arsenic as As₂O₅ — total 63.86%

A comparison of these results with the theoretical composition of calcium hydrogen arsenate, shows each of the samples to be a pure calcium hydrogen arsenate.

When the heating is continued at 230°C, the tendency to form the pyroarsenate, Ca₂As₂O₇, is observed, as shown by the analysis:
- Calcium as CaO — total 32.01%
- Arsenic as As₂O₅ — total 65.78%

Another method found successful in preparing pure calcium hydrogen arsenate, consists in dissolving a commercial calcium arsenate, which may be a mixture of the two calcium arsenates under discussion, in the smallest quantity possible of either hydrochloric or acetic acid, maintaining as large a volume of water as convenient. When evaporated upon hot plate either amorphous powder or crystals separate out, depending upon rapidity of evaporation.
A simple laboratory method that also proved successful, consists in adding slowly a solution of calcium hydroxide to a clear aqueous solution of arsenic acid, stirring vigorously meanwhile until the acid is about three-fourths neutralized. By slow evaporation, crystals of pure calcium hydrogen arsenate separate out.

The chief precaution that must be observed in order to obtain the pure salt, is to maintain an excess of acid or H. ion in the original solutions. This excess of acid, however, must be at a minimum or the precipitate will redissolve.

In the preparation of tri-calcium-arsenate, Ca₃(AsO₄)₃, various methods suggest themselves from a theoretical standpoint, as indicated by the following equations:

1. When a pure calcium hydrogen arsenate is acted upon by an alkali:
   \[ 3 \text{CaHAsO}_4 + 2 \text{NaOH} \rightarrow \text{Ca}_3(\text{AsO}_4)_2 + \text{Na}_2\text{HAsO}_4 + 2 \text{H}_2\text{O} \]

2. When arsenic acid is completely neutralized with a solution of calcium hydroxide:
   \[ 2\text{H}_3\text{AsO}_4 + 3 \text{Ca(OH)}_2 \rightarrow \text{Ca}_3(\text{AsO}_4)_2 + 6\text{H}_2\text{O} \]

3. When solutions of calcium chloride and sodium arsenate are allowed to react:
   \[ 3 \text{CaCl}_2 + 2 \text{Na}_3\text{AsO}_4 \rightarrow \text{Ca}_3(\text{AsO}_4)_2 + 6\text{NaCl} \]

In all cases cited, if the reaction is permitted to reach an equilibrium, and conditions are controlled as indicated, it is possible that a pure tri-calcium arsenate would result. The last proved to be the most practical, however, and concordant results were obtained. The perfected method is as follows: Cold solutions of both calcium chloride and sodium hydrogen arsenate were prepared, and the former made just sufficiently alkaline so that no calcium hydroxide precipitated out. To the sodium hydrogen arsenate solution just enough sodium hydroxide was added to change completely the salt to sodium arsenate. (Especial care must be taken lest too much sodium hydroxide should be added, as this would form calcium hydroxide when combined with the calcium chloride solution.) Both solutions were then filtered, and the clear calcium chloride solution was added to the sodium arsenate solution. A heavy, voluminous precipitate formed that settled very slowly. This was washed by repeated centrifuging and decanting off supernatant liquid each time. It was finally brought upon a Buchner filter and washed free of chlorides with hot water. After drying in the oven at 100° C. the analysis gave the following results:

- Calcium as CaO, total 38.49%
- Arsenic as As₂O₃, total 52.50%

These results indicate that a salt is produced, containing two molecules of water of crystallization, and agreeing with the formula, Ca₃(AsO₄)₂·2H₂O.

When further dried at 175° C. the pure Ca₃(AsO₄)₂ was obtained, as shown by the following analytical data:

- Calcium as CaO, total 42.16%
- Arsenic as As₂O₃, total 57.73%

Theoretical composition of Ca₃(AsO₄)₂:

- Calcium as CaO, total 42.20%
- Arsenic as As₂O₃, total 57.80%
Specific Gravity, Solubility, and Relative Stability of Calcium Hydrogen Arsenate and Tri-Calcium Arsenate. A spray material in powder form must be in a fine state of subdivision to facilitate efficient spreading on foliage, and must have a specific gravity sufficiently low so that it will remain in suspension in water for a considerable length of time.

The specific gravity was obtained by determining the weight of absolute alcohol displaced by a known quantity of the salt. The alcohol was especially prepared by redistilling the commercial C. P. absolute alcohol over calcium oxide obtained by igniting C. P. calcium carbonate, CaCO₃. All weighings were made at 20° C. with recently standardized weights. The specific gravity for the different salts was found to be as follows:

- CaH₂AsO₄·H₂O at 20°/4°: 3.09
- CaH₂AsO₄ at 20°/4°: 3.48
- Ca₃(AsO₄)₂·H₂O at 20°/4°: 3.23
- Ca₅(AsO₄)₃ at 20°/4°: 3.31

The solubility of an arsenical utilized for insecticidal purposes is an exceedingly important factor. The presence of an excess of soluble arsenic or any salt that would ultimately pass into solution, forming arsenic acid or a soluble arsenate, would cause burning of foliage and render the arsenical useless for spraying purposes. Qualitative tests showed that both calcium hydrogen arsenate and tri-calcium arsenate were slightly soluble, and, like many other calcium salts, the solubility is greater at lower than at higher temperatures. The determinations were made at 25° C. in a constant temperature bath that was fitted with a revolving bottle holder. By means of the latter, four bottles could be submerged and kept in a state of constant agitation during the entire experiment. Various amounts of the samples were introduced into the different bottles and 300cc of conductivity water added to each. They were then placed in the constant temperature bath and allowed to revolve for five days, when 100cc was removed from each bottle and evaporated on a steam bath. The bottles were replaced in the bath and allowed to continue three days longer, when another 100cc was removed and evaporated as before.

Finally, after evaporation, the salts were dried in an electric oven at 100° C and then at 175° C as recorded in Table I.

Table I
The Solubility of the Calcium Arsenates in Water at 25° C.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Temperature Dried</th>
<th>Weight—grams in 100 gms. solute</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaH₂AsO₄</td>
<td>100°</td>
<td>0.3308</td>
</tr>
<tr>
<td>CaH₂AsO₄</td>
<td>175°</td>
<td>0.3108</td>
</tr>
<tr>
<td>Ca₃(AsO₄)₂</td>
<td>100°</td>
<td>0.0140</td>
</tr>
<tr>
<td>Ca₅(AsO₄)₃</td>
<td>175°</td>
<td>0.0133</td>
</tr>
</tbody>
</table>

Analysis of the dissolved material showed that the composition of the latter was the same as that of the original salt used, which indicated no perceptible hydrolysis.

We observe from the results given in Table I that the calcium hydrogen arsenate is far more soluble than the tri-calcium arsenate at 25° C. This point is of considerable practical importance, since the solubility of the calcium hydrogen arsenate proximates the amount shown by field experiments to cause burning of foliage. These data indicate the futil-
ity of attempting to use the pure calcium hydrogen arsenate alone, as a spray. The tri-calcium arsenate, on the other hand, is only slightly soluble, and danger of burning from that source would probably be negligible.

From the standpoint of density and solubility, it is probable that the tri-calcium arsenate could be safely used as a spray material, while the calcium hydrogen arsenate is doubtful. An important factor remains yet to be taken into consideration; namely, the stability of the salts. This was ascertained by a study of the chemical change that resulted when either the calcium hydrogen arsenate or tri-calcium arsenate was shaken at intervals for several days in solutions of acids, both organic and inorganic, ammonium hydroxide, sodium hydroxide, sodium chloride, and similar salts. In all cases tried, the calcium hydrogen arsenate reacted, dissolved, or arsenic in soluble form was found in solution. The tri-calcium arsenate manifested greater stability, however, and in many instances showed only slight reactivity. From the relative stability of the two salts, it may be inferred that both arsenates would, under severe and abnormal climatic conditions, probably yield to the action of carbon dioxide and moisture in the air, with the consequent formation of free arsenic acid. The tri-calcium arsenate, being more insoluble, and more stable than the calcium hydrogen arsenate, would not have the tendency to react so readily, and hence the danger attending its use would be diminished accordingly.

The Effects of Calcium Hydroxide on the Solubility of the Calcium Arsenates. Our investigations thus far indicate favorable possibilities for the use of the calcium arsenates. The presence of any substance that would prevent solubility and reactivity would prove beneficial in the use of tri-calcium arsenate, and almost a necessity in the case of the calcium hydrogen arsenate. Judging from a theoretical standpoint, ordinary quicklime, CaO, would fulfill these requirements. The calcium hydroxide, becoming soluble, would react with any arsenic that goes into solution, forming more calcium arsenate.

In order to corroborate the above assumption, different amounts of the pure salts were introduced into each of several 200cc graduated flasks, together with known quantities of lime, CaO. In some cases calcium carbonate was also added. The flasks were then made up to mark with distilled water and shaken at intervals for two days. After allowing the salts to settle, determinations were made for total arsenic and calcium oxide in the clear supernatant liquid. The results are given in Table II.
Table II
The Solubility of the Calcium Arsenates in Water Containing Lime, CaO, and Calcium Carbonate, CaCO₃.

<table>
<thead>
<tr>
<th>Flask No.</th>
<th>Substances Used</th>
<th>Amount Added (gms.)</th>
<th>Amount As₂O₅ Found (gms.)</th>
<th>Amount CaO Found (gms.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Ca₄(AsO₄)₂</td>
<td>1.0</td>
<td>.0084</td>
<td>.0049</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Ca₃(AsO₄)₂</td>
<td>1.5</td>
<td>nil</td>
<td>.1131</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaCO₃</td>
<td>nil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>CaHAsO₃</td>
<td>1.0</td>
<td>nil</td>
<td>.0554</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaCO₃</td>
<td>nil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>CaHAsO₁</td>
<td>1.0</td>
<td>.0026</td>
<td>.0082</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaCO₃</td>
<td>.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>J. T. Baker's C. P. Cal. Ars.</td>
<td>2.0</td>
<td>nil</td>
<td>.0573</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Inspection of the results given in Table II indicates that wherever calcium oxide is present in even slight excess, so that calcium hydroxide was found qualitatively in solution, no soluble arsenic was detected. The calcium carbonate, furthermore, prevented in no way the solubility of the calcium arsenates. It is quite evident, therefore, if there is an excess of calcium hydroxide in the system, the solubility of both calcium arsenates is inhibited.

In order to substantiate the former results and to ascertain whether or not, by allowing the action to continue for a longer duration of time, the system would come to an equilibrium and continue indefinitely with no arsenic in the solution, a similar set of flasks was prepared. These were allowed to stand two weeks, being shaken occasionally, and then the supernatant liquid was analyzed as before. The quantity of material used, together with the results obtained, is given in Table III:

Table III
The Solubility of the Calcium Arsenates in Water Containing Lime, CaO

<table>
<thead>
<tr>
<th>Flask No.</th>
<th>Substances Used</th>
<th>Amount Added (gms.)</th>
<th>Amount As₂O₅ Found (gms.)</th>
<th>Amount CaO Found (gms.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Ca₄(AsO₄)₂</td>
<td>1.0</td>
<td>nil</td>
<td>.2481</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>CaHAsO₃</td>
<td>1.0</td>
<td>nil</td>
<td>.2451</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>CaHAsO₁</td>
<td>1.0</td>
<td>nil</td>
<td>.2540</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results given in Table III further verify those in the previous experiment and emphasize the fact that a definite point of equilibrium is reached in which the concentration of calcium hydroxide in solution becomes constant. It was found, moreover, that the concentration of calcium hydroxide is the same as the maximum of calcium hydroxide in pure water at the same temperature.
From a practical standpoint, the preventive action of calcium hydroxide on the solubility of the calcium arsenates is of vital importance. The free calcium hydroxide has no harmful effects upon foliage. If, therefore, one part of quicklime, CaO, is added for every two parts of either calcium hydrogen arsenate or tri-calcium arsenate, and sprayed as a combination spray no burning of foliage, due to solubility of the arsenates, should result. The action under severe atmospheric conditions, furthermore, will be greatly diminished, since the carbon dioxide in the air will first react with the calcium hydroxide, forming the harmless calcium carbonate before the calcium arsenates are affected.

**The Action of Carbonic Acid Upon the Calcium Arsenates.** A study of the action of CO₂ upon the calcium arsenates is an important consideration. Although chemical changes due to carbonic acid or saturated solution of CO₂, as noted in laboratory experiments, would be more vigorous than the action of the CO₂ of the atmosphere, a similar but much slower change would probably occur. In order to ascertain if any reaction may result a series of flasks, each of which contained a specific amount of calcium arsenate and 50cc of distilled water, was prepared. The carbon dioxide was then passed through the mixture, which kept the salts in a constant state of agitation. After ten hours the supernatant liquid was boiled to expel excess carbon dioxide, and determination made for arsenic in solution. The results, together with the amounts of arsenic used, are given in Table IV.

**Table IV**

<table>
<thead>
<tr>
<th>Salt Used</th>
<th>Amount Taken</th>
<th>Arsenic as As₂O₃, in 50cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca₃(AsO₄)₂</td>
<td>2.0</td>
<td>0.0208</td>
</tr>
<tr>
<td>CaHAsO₄</td>
<td>2.0</td>
<td>0.0428</td>
</tr>
<tr>
<td>Ca₃(AsO₄)₂+.5 gm. CaO</td>
<td>1.0</td>
<td>0.0012</td>
</tr>
<tr>
<td>CaHAsO₄+.5 gm. CaO</td>
<td>1.0</td>
<td>0.0046</td>
</tr>
<tr>
<td>CaHAsO₄+1.0 gm. CaO</td>
<td>1.0</td>
<td>0.0020</td>
</tr>
</tbody>
</table>

From the above results it is plainly evident that carbonic acid has a solvent action upon the calcium arsenates. When the excess carbon dioxide was boiled off, a precipitate came down that consisted of a mixture of calcium carbonate and a smaller amount of calcium arsenate. The presence of calcium hydroxide, however, diminished the solvent action appreciably.

**The Reaction Between the Calcium Arsenates and Lime-Sulfur Solution.** Combination sprays are of great economic importance since time, labor, and money are thereby saved. The tendency for chemical reaction that destroys or greatly diminishes the efficiency of both spray materials often results, and consequently prevents their use in this manner. Combination of lead hydrogen arsenate and lime-sulfur exemplifies this difficulty as shown by Robinson and Tartar(4). The concentration of the lime-sulfur is reduced; arsenic is found in solution; lead sulfide is precipitated out, thus utilizing part of the lead arsenate; and severe burning of foliage may occur, depending upon climatic conditions.
When pure tri-calcium arsenate was added to dilute lime-sulfur no reaction appeared to occur. G. E. Sanders (3), in field experiments, reports more favorable results obtained with the calcium arsenate-lime-sulfur combination spray, than with lead arsenate-lime-sulfur. Hence a study of the chemical reaction, if any, was initiated. Pure lime-sulfur was prepared in the laboratory from crystallized sulfur and lime, CaO, the latter obtained by igniting CaCO₃. The lime-sulfur produced had a specific gravity of 1.242 or 28.2 Baume, and was diluted to average field spraying strength. Both of the calcium arsenates were prepared in the laboratory in pure form. Into each of several flasks 1 gm. Ca₃(AsO₄)₉, 1 gm. CaHASO₄, or 1 gm. CaHAsO₄+0.5 gm. CaO, was introduced and 200cc of the diluted lime-sulfur added. A check flask containing 200cc of the diluted lime-sulfur only was also prepared. The flasks were then shaken at intervals during two days, after which the salts were allowed to settle and determinations were made for total sulfur, calcium oxide, and arsenic pentoxide in the supernatant lime-sulfur solution. Table V records the results expressed in grams contained in 200cc.

<table>
<thead>
<tr>
<th>Table V</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Solubility of the Calcium Arsenates in Lime-Sulfur Solution</td>
</tr>
<tr>
<td>Check</td>
</tr>
<tr>
<td>gms.</td>
</tr>
<tr>
<td>Sulfur, total</td>
</tr>
<tr>
<td>CaO, total</td>
</tr>
<tr>
<td>As₂O₅, total</td>
</tr>
</tbody>
</table>

The above results proved favorable beyond expectation. There appears to be no chemical change whatsoever in the lime-sulfur solution, all constituents remaining constant and agreeing with results given for the check solution. Barring the possibility of chemical reaction after spraying, we have, in the calcium arsenate, an ideal spray material to be used in combination with lime-sulfur. The efficiency of the latter is not reduced, and the calcium arsenate remains unchanged.

Attention is further brought to the analysis of the liquid in the flask containing CaHAsO₄+CaO. As with CaHASO₄ and Ca₃(AsO₄)₉, no arsenic was found in the lime-sulfur solution and the sulfur content remained constant. The amount of CaO, however, exceeds that obtained in other flasks. This increase of the CaO is equivalent to the solubility of Ca(OH)₂ in pure water at the temperature under observation. Since the addition of lime in no way reacts with either of the other spray materials, it might be advisable to have it present in order to prevent danger of foliage burn, due to severe atmospheric conditions. This would be especially true of the less stable CaHAsO₄. This precaution, however, must be verified by field experiments.

Since the above conclusions were obtained on pure samples, the experiment was repeated using commercial products to ascertain the practicability of their use. A solution of commercial lime-sulfur, having a specific gravity of 1.227 or 26.7 Baume, was diluted in the same proportion as indicated in the previous experiment. A commercial calcium arsenate was used that had the following composition:

- CaO total 39.20%
- As₂O₅ total 48.90%
- CaCO₃ total 1.14%
From these analyses we infer that the sample consisted of over 60% tri-calcium arsenate and the remainder calcium hydrogen arsenate and calcium carbonate.

Treatment was similar to the last experiment and the composition of the lime-sulfur solution is given in Table VI.

### Table VI

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>S</th>
<th>As₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Check (Lime-sulfur only)</td>
<td>0.7821</td>
<td>1.6482</td>
<td>none</td>
</tr>
<tr>
<td>Cal. Ars. and Lime-sulfur</td>
<td>0.7816</td>
<td>1.6474</td>
<td>none</td>
</tr>
</tbody>
</table>

Here again we observe that no apparent chemical action has occurred. No arsenic was found in solution and the total lime and sulfur content remained the same. It is obvious that a commercial sample composed of both calcium hydrogen arsenate and tri-calcium arsenate and possibly other impurities may be combined with commercial lime-sulfur with the same degree of safety as the pure laboratory products.

The use of dry substitutes for lime-sulfur is rapidly becoming prevalent; hence a study of their combination with calcium arsenate would be beneficial. Consequently 0.5 gm. of a commercial “Dry Lime-Sulfur” and the same amount of so-called “Soluble Sulfur” which is composed chiefly of the sulfides of sodium or potassium, was introduced into a 200cc graduated flask together with 1.0 gm. of commercial calcium arsenate. It was then made up to mark with water and after shaking occasionally during two days was allowed to settle and analyzed for arsenic in solution as reported in Table VII.

### Table VIII

<table>
<thead>
<tr>
<th></th>
<th>As₂O₅ in 200cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Check</td>
<td>none</td>
</tr>
<tr>
<td>Dry Lime-Sulfur</td>
<td>none</td>
</tr>
<tr>
<td>Soluble Sulfur</td>
<td>.2300</td>
</tr>
</tbody>
</table>

These results indicate that no chemical changes occurred when calcium arsenate and dry lime-sulfur were combined. The soluble sulfur, however, caused such a large quantity of arsenic to pass into solution that this would make it inadequate for utilization as a combination spray.

The Valuation of Commercial Samples. There are at present on the market various calcium arsenate products offered as substitutes for lead arsenate, together with the so-called C. P. salts used as reagents for chemical work. Complete analyses have been made of these samples, both to ascertain whether or not they approximated the theoretical composition of the pure salt and also to estimate their commercial value as spray materials. Table VIII gives a compilation of the results obtained.
Table VIII

Composition of Commercial Calcium Arsenates

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO</th>
<th>As₂O₅</th>
<th>CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kahibaum, C. P.</td>
<td>36.62</td>
<td>51.50</td>
<td>trace</td>
</tr>
<tr>
<td>Bakers, C. P.</td>
<td>40.96</td>
<td>42.75</td>
<td>7.25</td>
</tr>
<tr>
<td>Commercial No. 1</td>
<td>43.46</td>
<td>40.84</td>
<td>40.00</td>
</tr>
<tr>
<td>Commercial No. 2</td>
<td>39.20</td>
<td>48.86</td>
<td>1.14</td>
</tr>
<tr>
<td>Commercial No. 3</td>
<td>45.61</td>
<td>19.22</td>
<td>8.40</td>
</tr>
</tbody>
</table>

The wide variation in the composition of commercial arsenates is plainly evident from the results given in the table. Both Kahibaum's and J. T. Baker's C. P. samples, supposed to be high-grade salts, are mixtures of the calcium hydrogen arsenate and tri-calcium arsenate with between 10% and 20% water of crystallization or constitution. Kahibaum's, moreover, contained a distinct trace, while Baker's had 7.25% calcium carbonate. Commercial sample Nos. 1, 2, and 3 likewise emphasize the necessity of greater care in their manufacture. Attention is especially called to sample No. 1 that contains 49% calcium carbonate but only 43.46% of total calcium estimated as lime, CaO. These figures indicate that there is insufficient base to combine with the amount of arsenic pentoxide, As₂O₅, present and further examination showed the latter was there as actually As₂O₅ uncombined. It is probable that the manufacturer attempted to prepare the calcium arsenate from As₂O₅ and an impure lime, which was chiefly calcium carbonate. The latter would react very slowly, if at all, and the excess As₂O₅ over the amount required to combine with the calcium hydroxide would remain unchanged, as noted above. If the manufacturers would exercise more complete control of conditions and know definitely what materials are being used, a spray material sufficiently pure for practical use could probably be obtained.

Thus far our investigation has shown the possibility of the calcium arsenates being a practical, economical, and evidently satisfactory substitute for the more expensive lead arsenate. The pure salts contain 57.8% and 63.9% of arsenic calculated as As₂O₅ for the tri-calcium arsenate and calcium hydrogen arsenate respectively, while the basic and hydrogen lead arsenate contain only 25.5% and 33.7% As₂O₅ respectively. In other words, the calcium arsenate contains more than twice as much arsenic, the active killing agent of the insecticide. For practical spraying purposes, therefore, only one-half of the quantity of calcium arsenate should be used compared with lead arsenate. This point, however, must be more definitely determined by field experiments, since there is a bare possibility that the lead has toxic values that the calcium does not have. Relative toxic values and killing efficiency have been recently shown in laboratory experiments with the "common tent caterpillar" by Lovett and Robinson (6) and with the "fall wet worm" by Scott and Seigler (7) indicating killing efficiency of calcium arsenate compared with lead arsenate.

Field spraying experiments have been carried on by several investigators with more or less successful results. This may be due to the use of an unreliable calcium arsenate similar to the one cited above. San-
ders (8), however, reports very favorable results during the past two seasons. Scott and Seigler (7) also obtained encouraging results.*

In cooperation with A. L. Lovett, Entomologist at this Station, preliminary field experiments were tried with the pure salts prepared in the laboratory. Favorable results, especially with tri-calcium arsenate and quicklime, were obtained, but due to insufficient time and lateness in the season the trials were limited. During the coming spraying season more elaborate field experiments will be conducted by Professor Lovett, who will report upon them at a later date.

**Recommendations For Using Calcium Arsenates.** Since past experiments with calcium arsenate are very limited, especial care should be exercised in preparing the spray material for use. Equal parts of the commercial calcium arsenate and quicklime, using for trial experiments 1 1/2 lbs. of each to 50 gal. of water, is perhaps the most efficient proportion. If desired, double the amount of quicklime may be used. The quicklime should first be slaked in a small amount of water, then added to the spray tank containing the 50 gal. of water, and stirred occasionally for an hour before being used. If desired, this may be done the previous day, but the lime should not be in contact with air more than a few days before using. **Immediately before spraying,** the calcium arsenate is added and thoroughly mixed.

When used as a combination spray with lime-sulfur solution or any other spray material, it is advisable to exercise the same precaution as noted above. After diluting the concentrated lime-sulfur as desired, the slaked quicklime is added and stirred occasionally for a short time. Finally, immediately before spraying the calcium arsenate is added.

**Caution.** The author desires to emphasize that thus far field experiments, employing the suggestions herein reported, have been very limited and consequently spraying with calcium arsenate should be done in an experimental way until absolute safety in its use is assured.

**Summary**

In this paper a chemical study of the calcium arsenates is reported.

1. The pure calcium hydrogen arsenate and tri-calcium arsenate have been prepared and methods for their preparation outlined.

2. The specific gravity for calcium hydrogen arsenate was found to be 3.48.
   The specific gravity for tri-calcium arsenate was found to be 3.31.

3. The solubility of calcium hydrogen arsenate in 100 grams of solute at 25° C. was 0.310 grams, and for tri-calcium arsenate was 0.013 grams.

4. A chemical study of relative stability showed that:
   (a) There was no apparent reaction between either calcium hydrogen arsenate or tri-calcium arsenate, and lime-sulfur when combined at a dilution used in field spraying.
   (b) Addition of excess of quicklime to either of the calcium arsenates prevented arsenic from going into the solution.

*Scott and Seigler gave the analysis of the calcium arsenate used, showing only 0.04% soluble arsenic oxide. A possible explanation is that the spray material was prepared from stone lime, (containing 80% CaO), sodium arsenate, and water. A very slight excess of the stone lime would prevent any arsenic becoming soluble as shown in experiments reported above.
(c) Some commercial substitutes for lime-sulfur reacted with both of the calcium arsenates.
(d) The arsenates reacted with, or became soluble in, organic acids and various salts such as sodium chloride, NaCl.
(5) The composition of various commercial arsenates is given and commented upon.
(6) Recommendations have been made for the experimental use of commercial calcium arsenate.

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(5) Sanders, G. E.
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(7) Scott, E. W., and Siegler.
(8) Sanders, G. E.