

## SOME RELATIONS OF ARSENIC TO PLANT GROWTH: PART 1

JOHN STEWART

*Utah Agricultural Experiment Station*

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### INTRODUCTORY

For at least three-quarters of a century the effect of compounds of arsenic upon plant growth has been a subject of scientific investigation. It was early recognized that arsenic is quite generally found in animal tissue; and, since the animal must have obtained the arsenic from its food, it was soon found that arsenic is present in minute amounts in many plants. Later investigations (2) have shown arsenic to be very widely distributed in the soil, and to have been derived in this case from the original rocks from which the soil was formed.

The fact that arsenic was found to be so generally present in animal and vegetable tissues raised the question as to whether or not arsenic is essential to the life processes. Gautier and Clausmann (1) failed to find arsenic in *some* plants and concluded from this fact that arsenic is not essential to vegetable life. But the more intimately life processes are investigated the more apparent it is becoming that very minute quantities of substances may have a very decided effect on those processes. For example, note the decided effect which the minute amount of iodine in the thyroid gland has on animal life processes. The more recent investigations are thus making it appear that it is still too early to draw definite and final conclusions as to the rôle of arsenic in plant and animal life; and more refined methods of investigation may very probably be expected to reveal the more general presence of arsenic in plants than heretofore found.

But even though arsenic in minute quantities may or may not be useful to plant or animal life, it has been abundantly proved that it is a strong poison to both plants and animals if the quantity absorbed is large. Some years ago it was reported (5 and 6) that orchard trees were dying in Colorado as a result of arsenic poisoning. Since the practice of spraying is resulting in the application of considerable quantities of arsenical compounds to the soil and since smelters in some localities belch forth large amounts of arsenic oxides annually, it thus becomes important from a practical point of view to have more definite information as to the effects of arsenic on plants. Dr. Greaves (2, 3, 4) worked on this problem and has published some of his results in several papers. His work at first dealt with some chemical phases, but later it has dealt with the effects of arsenical compounds on the microörganisms of the soil, ammonifiers and nitrifying organisms.

In 1912 the chemical phase of this investigation was turned over to the author of this paper, who devised a plan of attacking the problem.

It was proposed to determine the solubility of lead arsenate and other compounds of arsenic, likely to be used for spraying purposes, in solutions of the inorganic salts commonly occurring in the soil, a determination being made with each pure salt. Two series of concentrations were to be used, one representing the concentrations which might be expected in an ordinarily rich soil and the other representing concentrations such as might be expected in strongly "alkali" soils. It was also proposed to determine these solubilities in mixtures of all the individual salts used in each of the two series mentioned. Some humus was to be prepared and, after removal of the ammonia, it was to be used in some more determinations with the two series of solutions to test the effect of organic matter of the soil in conjunction with the soluble salts on the solubility of the arsenic compounds. Soils were also to be collected from the principal fruit growing sections of the State. A definite quantity of each soil was to be treated with a definite volume of water and the solubility of the arsenic compounds in these mixtures was to be determined. It was also proposed to build concrete, water tight vessels, sufficiently large for the roots of a mature tree. These were to be built so the top was flush with the surface of the ground, and filled with soil the composition of which was known. Some of the orchard trees, such as apple, peach, pear, etc., were to be grown to maturity in these tanks and then subjected to the usual spraying treatment given to orchards. This treatment was to be continued for about five years or more after the tree commenced to bear, and the effects of the spraying treatment on the tree, the fruit, and the soil were to be noted. A series of tests was also to be made upon a number of young trees and shrubs grown in small vessels. For instance, about twenty to forty apple trees were to be grown in this way. These were to be divided into ten sets of two or four trees each. Each set, except one tree for control, was then to be treated with solutions containing a definite amount of sodium arsenate, each set receiving a different amount. The effect of the treatment was to be studied by means of the appropriate observations and analyses. All kinds of ordinary orchard trees were to be treated in this way. The experiment as planned was intended to be a somewhat exhaustive study of the effects and nature of arsenical poisoning on plants. Results of value from both a practical and scientific standpoint were expected. Some of the work planned has been accomplished, and this paper sets forth these results.

The methods of analysis in such work must be delicate, reliable, and as rapid and simple as possible. To select or develop the most suitable analytical methods was in itself no small task. So before commencing on the experimental part of the investigation the author made a comparative study of the methods for determining arsenic. This resulted in a decision to use the Marsh method as modified by Greaves (3) of this station and the Williamson method mentioned by Sutton (8) as modified by the author of this paper. The Williamson method is fraught with some difficulties, as a reference to the recent literature will show. The means of satisfactorily overcoming these difficulties were worked out in this laboratory. Thoroughly understood, the method becomes a rapid and excellent one, but not suitable for the determination of such minute quantities of arsenic as is the Marsh method. For further information about the analytical methods used in this work, reference must be made to the earlier paper of Greaves (3) and to the author<sup>1</sup> for unpublished information concerning the modified Williamson method.

<sup>1</sup>A paper by the author describing his modification of the Williamson method was accepted for publication by the *Zeitschrift für Analytische Chemie* in the early summer of 1914, but the outbreak of the war seems to have prevented its publication.

## EXPERIMENTAL

*Solubility of lead arsenate in salt solutions*

The modified Williamson method was used for determining the arsenic dissolved in the salt solutions and the soil solutions. The modified Marsh method was used for determining the arsenic absorbed by the plants in the pot experiment, which will be reported in another paper. The lead arsenate used for the solubility determinations was *Sherwin Williams*, guaranteed to contain not less than 25 per cent of arsenic, and not more than  $1\frac{1}{2}$  per cent of water soluble arsenic. It was an impalpable dry powder.

As stated above, solubility in solutions of each salt of two concentrations was determined. Potassium carbonate was used as a starting point for determining the concentrations. The weaker potassium carbonate solution contained 0.10 per cent of  $K_2CO_3$ , the stronger one contained 0.50 per cent of  $K_2CO_3$ . The concentrations of the other salt solutions were then made such that the basic elements were present in all the solutions in chemically equivalent amounts. For example, the weaker series of solutions contained in 2 liters, 2.0000 gm. of  $K_2CO_3$ , 2.1580 gm. of KCl, 1.5340 gm. of  $Na_2CO_3$  etc.; the stronger series of solutions contained 10.0000 gm. of  $K_2CO_3$ , 10.7900 gm. KCl, 7.6700 gm.  $Na_2CO_3$  etc. The solutions of the common salts of potassium, sodium, ammonium, calcium and magnesium prepared in this way were then treated with an excess of lead arsenate and shaken two or more times per day for three weeks or more. The solutions were filtered, one liter treated with 10 cc. of  $HNO_3$  and 10 cc. of  $H_2SO_4$  and evaporated to white fumes. The residue was cooled, the sides of the vessel washed down with water and again evaporated to white fumes. This dilution and re-evaporation are necessary to break down the nitrosyl sulfuric acid and thus completely remove oxides of nitrogen. The dissolved arsenic was then determined.

Some difficulties were encountered in this work and as yet no satisfactory means of entirely overcoming them has been found. Solutions such as  $Na_2CO_3$  which give an alkaline reaction on account of hydrolysis, persistently hold the lead arsenate in colloidal solution and suspension. No way of filtering out this colloidal material was found; after the best filtration possible such solutions were still opalescent. Filtration through Chamberlain-Pasteur filters was not feasible because these retained arsenic which was in true solution. The best way found was to filter through paper. By repeating the filtration several times through the same paper the pores became somewhat clogged with the lead arsenate, and a somewhat clearer filtrate resulted. It was found by Stewart (7) that a good way to filter humus was through paper covered with a thin layer of the soil from which the humus has been extracted. The two cases are identical in principle.

The length of time required to establish equilibrium between the dissolved and undissolved lead arsenate was also an obstacle to rapid work. But even shaking the solutions containing lead arsenate for six days in a shaking machine failed to establish equilibrium so that duplicates would agree satis-

factorily. Variations in temperature also result in slightly different values for the solubility.

The solubility data obtained for the various salt solutions are shown in table 1. The table is in three parts, A, B and C. Part A shows the solubility of the lead arsenate in the weaker concentrations mentioned above; part B, in the stronger concentrations; and part C, in tap water, distilled water and two mixtures of salts. Mixture 1 represents a mixture of the salts of the concentrations used in part A, and Mixture 2, a mixture of the salts of the concentrations used in part B. Some of the salts were precipitated out of solution

TABLE 1  
*Arsenic dissolved in the form of lead arsenate in various salt solutions*

	CARBON- ATES	CHLORIDES	NITRATES	BICAR- BONATES	SULFATES	BISUL- FATES	PHOSPHATES	
							Secondary	Primary
A. Weaker concentrations								
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
K.....	165.2	39.3	4.5	139.9	4.6	241.9	174.2	29.1
Na.....	184.8	51.7	5.3	136.4	5.9	260.9	168.9	11.8
NH <sub>4</sub> .....	175.6	37.0	3.4	136.4	3.5	271.5	177.6	18.7
Ca.....	73.4	54.7	2.0		5.6	296.3	73.9	36.6
Mg.....	4.1	36.6	3.5	37.4	4.5	268.5	93.5	21.0
B. Stronger concentrations								
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
K.....	115.9	156.0	8.1	99.8	5.8	647.2	292.9	78.0
Na.....	131.8	130.5	13.5	96.7	5.6	1016.9	357.0	84.6
NH <sub>4</sub> .....	119.2		5.4	162.5		838.3	392.1	63.0
Ca.....	36.5	105.4	4.3	13.5	4.2	615.2	57.7	67.5
Mg.....	20.1	101.2	3.5	85.4	2.6	572.3	46.1	38.0
C. Other solvents								
							<i>p.p.m.</i>	
Tap water.....							33.8	
Distilled water.....							3.0	
Mixture 1.....							183.8	
Mixture 2.....							324.9	

in both mixtures. The figures in the table represent milligrams of arsenic in a liter of solution.

In the case of sodium, potassium and ammonium carbonates and probably some of the alkali phosphates, the data represent some material that is in colloidal solution as well as that in true solution. In each case the figure in the table represents the average of two to ten determinations. It will be noted that the lead arsenate is only very slightly soluble in distilled water, 3 parts per million. In the presence of nitrates and sulfates the solubility does not appear to be very materially different from that in distilled water, there being possibly a very slight increase in solubility in the presence of these salts. Since lead sulfate is a very insoluble compound, the ionic theory would lead

one to expect such a result as appears in the table in the sulfate column; but as lead nitrate is a soluble compound the ionic theory would *a priori* lead one to expect a larger solubility than appears in the nitrate column in the table. Since a great number of analyses were made from which the data in the table are condensed, there can be no doubt that lead arsenate is not materially more soluble in nitrate solutions than in pure water. The data show that the neutral chlorides increase the solubility of the lead arsenate considerably. The difference between the effect of the chlorides and the nitrates is somewhat surprising, and must apparently be attributed to the specific nature of these salts modifying the solvent. That is, chloride solutions and nitrate solutions have different solvent powers in much the same way that water and alcohol have. As is to be expected, the acid salts such as the bicarbonates, the bisulfates and the acid phosphates cause considerably larger quantities of the lead arsenate to go into solution. Increasing the concentration of the chlorides, the bisulfates and the phosphates also increases the amount of arsenic dissolved; but in the case of the sulfates and nitrates increased concentration appears to have no effect, while in the case of the carbonates and bicarbonates increased concentration as used in these experiments causes a decrease in the amount of arsenic dissolved. Ten times as much lead arsenate was dissolved in tap water as in distilled water. This, of course, shows to some extent what is to be expected to occur in the underground water. The tap water contains 212 parts of solids per million, mostly in the form of bicarbonates of calcium and magnesium.

#### *Solubility of lead arsenate in soil solution*

Soils were collected for this experiment in 1913 from the principal fruit-growing sections of the state. The amount and composition of the water-soluble material in these soils were determined. The treatment with arsenic was as follows: Two hundred fifty grams of each of the soils were treated with one liter of water. An excess of lead arsenate was added to this mixture and the amount of arsenic dissolved determined in the same manner as indicated above for the salt solutions. The data expressed in milligrams of arsenic per liter are in table 2. The soils collected represented light sandy loams, gravelly loams, rich and somewhat heavy loams, and uncultivated alkali land.

Data in table 2 have been grouped roughly according to soil types. The College Farm soil stands alone. The group of nine soils following includes in the main somewhat gravelly bench lands which are more representative of the fruit-growing districts than the other soils mentioned. Next is a group of five light sandy soils without gravel. This is a lighter type of soil than the preceding group. The fourth group includes nine good loam soils from some of the best farming lands in the State. Some of them tend to heaviness, but all are easily tillable. The last two soils in the table represent uncultivated "alkali" land west of Salt Lake City and between Tooele and Grantsville.

The data show that lead arsenate is much more soluble in the soil solution than in pure water, and that it has about the same solubility in the soil water

TABLE 2

*Solubility of lead arsenate in soil solution*

SOIL NUMBER	LOCALITY	SOIL TYPE	ARSENIC PER LITER	COMPOSITION OF SOIL SOLUTION						
				Total solids	Cl	CO <sub>2</sub> (and HCO <sub>3</sub> )	SO <sub>4</sub>	Ca	Mg	K
			mgm.	per cent	per cent	per cent	per cent	per cent	per cent	per cent
78032	College Farm	Gravelly bench loam	44.5	0.238						
78033	College Farm		43.1	0.238						
77939	East of Midvale 1 mi.	Coarse sandy loam	20.4	0.140		0.034	0.008	0.071	0.021	0.013
77942	Tooele (W. side)	Bench loam	23.8	0.214		0.050	0.014	0.084	0.059	0.014
77945	Tooele (N. E. side)	Black, gravelly loam	11.1	0.142		0.040	0.008	0.060	0.027	0.012
77949	S. E. of Provo	Light gravelly loam*	22.0	0.270		0.040	0.046	0.060	0.027	0.017
77950	Provo Bench (Anderson Bros. orchard)	Gravelly bench land	16.0	0.108		0.030	0.025	0.044	0.017	0.013
77954	Orchard S. W. of Ogden		10.5	0.092		0.024	0.017	0.050	0.019	0.006
77956	Pleasant View near Hot Springs		25.4	0.186		0.060	0.022	0.056	0.026	0.012
77962	Near S. city limits of Brigham City		11.1	0.218	0.028	0.040	0.019	0.044	0.027	0.012
77963	Near Brigham City depot		12.1	0.140		0.041	0.014	0.040	0.011	0.007
Averages.....			17.0	0.168		0.041	0.019	0.056	0.026	0.012
77951	2 mi. So. 77950	Light sandy loam	8.1	0.102		0.034	0.016	0.033	0.020	0.007
77946	Clearfield		9.6	0.146		0.022	0.012	0.036	0.027	0.008
77955	Five points	Light loam	16.2	0.124		0.035	0.023	0.052	0.024	0.007
77958	North of Willard		9.4	0.114		0.016	0.017	0.034	0.023	0.010
77960	Dewey (W. of Depot)		12.6	0.142		0.031	0.031	0.056	0.023	0.010
Averages.....			11.2	0.126		0.027	0.020	0.042	0.023	0.008

77938	West Jordan	Heavy loam	26.2	0.230		0.055	0.017	0.075	0.032	0.022
77940	North of Murray near Hussler's mill		23.1							
77944	Grantsville	Heavy black loam	31.8	0.220	0.071	0.061	0.016	0.056	0.031	0.007
77947	Farmington		19.8	0.164		0.014	0.010	0.056	0.026	0.012
77949	Centerville	River bottom loam	14.1	0.140		0.030	0.025	0.049	0.029	0.008
77952	Provo		17.0	0.210		0.060	0.024	0.066	0.022	0.011
77957	North Ogden	Heavy loam	13.3	0.180	0.014	0.050	0.017	0.056	0.024	0.014
77959	Honeyville		16.7	0.188	0.014	0.056	0.035	0.060	0.031	0.009
77961	Garland		26.0	0.412	0.028	0.048	0.043	0.080	0.025	0.070
Averages.....			20.9	0.218	0.032	0.048	0.023	0.062	0.027	0.019
77943	Between Tooele and Grantsville	Alkali (Uncultivated)	64.5	0.216		0.070	0.014	0.071	0.024	0.012
77941	About 1 mi. W. of S. L. C. gas plant		33.2	0.198		0.042	0.012	0.072	0.004	0.021
Averages.....			48.8	0.207		0.056	0.013	0.071	0.014	0.016

\* Soil no. 77954 had a clay substratum.

that it has in tap water. The solubility is shown to be roughly proportional to the percentage of soluble salts in the soil. Thus the third group of soils has the lowest per cent of soluble salts and gives the lowest solubility for the lead arsenate. The second group of soils having the next higher per cent of soluble salts has the next higher solvent power for the arsenate. The fourth group stands next in order in both soluble salts and solvent power, and the College Farm soil follows the fourth group in amount of soluble salts and in solvent power for the arsenate. The two "alkali" soils in the last group break this regularity. These show a somewhat high solvent power for lead arsenate, but the soluble salts in the soils are not shown to be high. In fact, the low per cent of soluble salts found for these two soils is somewhat unexpected, but repetition of the analysis failed to change the result. It is hardly possible to trace any relation between the amount of arsenic dissolved and the individual components of the soil solution, although increase of the carbonate and bicarbonate ions and of the potassium ion is accompanied by increased solution of the arsenate. The fourth group, which contains more chlorides than the second and third, also dissolved more arsenic. These results are in keeping with the finding of Greaves (2).

#### SUMMARY

Lead arsenate is a very insoluble compound. Only three parts of arsenic dissolve in a million parts of pure water. Its solubility is greatly increased by many common salts when these are present in the aqueous solvent, but sulfates and nitrates do not seem to increase materially the solvent power of water for lead arsenate. Acid salts and those which hydrolyze with an alkaline reaction markedly increase the solvent action of water on lead arsenate. The soil solution also has a greater solvent power for lead arsenate than has pure water.

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