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The Pennsylvania State College

The Graduate School

Department of Agricultural and Biological Chemistry

Residual Arsenic on Pennsylvania Apples in 1932

A Thesis

by

William Searles Hodgkiss

Submitted in partial fulfillment

for the degree of

Master of Science

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Approved:

Jan. 18, 1934 — D. E. Haley per RAD.

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INTRODUCTION

There has been a rather wide-spread interest in the composition and removal of insecticidal residues remaining upon apples at harvest, as a result of suppression operations against the codling moth. To arrange a spraying system it has been necessary to determine the quantities of residual arsenic upon the apple at picking time. This study was intended to determine these factors and to indicate what took place during the season of 1932.

The use of chemicals as spray treatments in codling moth control has a number of limiting factors. Their efficiency depends upon the employment of effective dosages of poison, proper timing of applications to the trees, and thoroughness of spraying. The amount of rainfall during the growing period of the fruits also has an important bearing on the protection of apples by the spray coating applied.

Spray schedules, as a rule, are rather general in scope and have been arranged so that under normal weather conditions maximum insect protection and minimum residues at harvest may be assured. In general there is a wide gap between the degree of control which is obtainable under local orchard conditions and the full control which nearly all authorities assume that lead arsenate is capable of giving. It is also evident that there are important technical factors which may explain the reduced efficiency of lead arsenate in insect control under the conditions mentioned. In this paper any reference to lead arsenate is to be understood as meaning the acid lead arsenate.

In Pennsylvania it has been necessary to use lead arsenate in one spray at the blossom petal fall and in from two to five later spray treatments which are principally for fruit protection. The omission of any one of these poison applications may result in increased codling moth injury to the fruit.

When a complete codling moth program is followed in an orchard there is danger that the arsenical residues on apple fruits at harvest will be above the international tolerance of 0.01 grain of arsenic trioxide per pound of fruits. This is particularly apparent when subnormal conditions of rainfall prevail during the growing season, or if the apples for some other reason fail to develop to a normal size. If, on the other hand, an excess of rainfall occurs or the ordinary growth results in an increased size of the apple fruits, the final residue at harvest built up by the several spray treatments will be below the tolerance.

HISTORICAL

The recognition and employment of chemicals in the control of insect pests in the early years were based on chance discovery rather than results of controlled scientific experiments. Later research has been developed to some extent at least upon the belief that only substances toxic to higher animals would be toxic to insects. Combinations of lead, copper and arsenic came into use not only because of their high toxic values but also because of their comparative cheapness and availability.

On the other hand, substances whose poisonous effect upon higher animals is slight or undetermined have been compounded during the last thirty years. These comprise a number of insecticides of proven worth as poisonous or contact remedies. Examples of this type are the sulfides and polysulfides of barium, calcium, sodium and potassium. Nicotine sulfate and extracts of Pyrethrum and Denis are also in this category.

The type of chemical used as a spray or dust depends upon the insect to be suppressed. At the present time combinations of sprays are more often used and these when applied in the proper manner are effective for several unrelated insect species.

Arsenic in the form of acid lead arsenate is the most widely used of the toxic elements adapted to the control of chewing insects active upon fruit and fruit trees. This combination is successful, not only because of its high toxic action but also because it adheres well and does not break down easily and release arsenic as the water-soluble arsenic acid which is injurious to plant growth. It will react chemically at a slow rate with lime sulfur, a standard fungicide used to make a combination spray for apple trees, and does not appreciably injure the fruits or foliage when applied in large quantities under normal temperature conditions.

The use of arsenical compounds in codling moth control originated in 1878 when it was discovered that the practice of spraying apple trees with Paris green to destroy the spring canker worm not only controlled that pest but also reduced the injury from codling moth[1]. Experiments on the value of this treatment, made by Cook[2] in 1880, indicated that it was highly effective. Other experiments by Forbes[3] in 1886 confirmed the findings of Cook. Paris green was the principal poison used in spraying for codling moth during the period from 1880 to about 1900. Lead arsenate was first compounded for use against the gypsy moth[16] and was employed on apples as early as 1895[4], but the first experiments of consequence for codling moth control were made in the period from 1901 to 1905. It has been used almost exclusively for the past twenty-five years. Practical experience has shown that acid lead arsenate is the safest arsenical insecticide to apply to tender foliage. Many experiments have shown that its' insecticidal properties are very satisfactory. In most of the cases in which arsenic has been prepared in combination with other elements, the unsatisfactory behavior was due to damage to the foliage rather than to poor insecticidal properties[5].

The retention of an arsenical coating upon the fruit surface throughout the season appears to be necessary for control of insect pests of the type under observation. It is also important from the human health standpoint that the residue remaining on the fruit at harvest should be well below the limit considered to be toxic to the human body.

As early as 1891, the presence of spray residue on fruits and vegetables and its possible injurious effect on the consumer were discussed in certain British journals. However, it was not until 1926, after years of agitation, that the British authorities ruled that the maximum amount of arsenic trioxide as a spray residue which would be tolerated on apples was 0.01 grains per pound of fruit. This action had a depressing effect upon those American apple growers who depended upon export trade as an outlet. The ruling aroused much discussion in this country as well as abroad.

In order to protect the interests of apple producers in the United States, the United States Department of Agriculture subsequently set a tolerance of 0.01 grain of arsenic trioxide per pound of apples upon the export fruit and 0.015 grain on all other apples. There was an expressed intention to lower the domestic limit gradually to the world tolerance.

In 1931 the domestic tolerance was lowered to 0.012 grain and in 1932 was placed in agreement with the international standard.

OBJECT OF THE INVESTIGATIONS

The object of this study was to determine quantitatively the amount of residual arsenic on apples which had received six different spray treatments throughout the growing season. The study comprised three phases:

(1) The relation of arsenical residue at harvest to the type of spray treatment.

(2) The relative amount of residue on the fruit at various stages of growth through the season under both a complete and incomplete spray schedule of treatments.

(3) The effect of weathering and growth upon the residue throughout the season.

PLAN OF THE EXPERIMENT

A block was set aside in the College orchard for these experiments. Six spray combinations were applied, one to each of six one-row plots containing six trees each of 15 year old York and Stayman trees. The sprays were applied from a spray gun under a pressure of 350-400 pounds. Care was taken that a complete spray coverage of the tree was made for each application. This averaged 8.3 gallons per tree per application. The sprays were applied June 10, June 20, July 5, July 25 and August 3. Samples for determination of residual arsenic were taken before and after each spray application and at harvest.

In a commercial orchard at Biglerville, Pennsylvania, a similar schedule was carried out on three single row plots containing nine trees of 15 year old Rome and Stayman trees. The trees received an average of 5.5 gallons of spray per application. The sprays were applied May 17, May 27, June 7, June 17, June 29 and July 23. Samples were taken only at harvest.

An analysis was made also on samples collected throughout Pennsylvania at harvest to show the relation between controlled spray practice of the experimental type and the extent of arsenical residues found in general orchard operation.

Collection of Samples

In order to insure complete retention of the spray coating from the time of sampling to the removal of the residue for analytical purposes, it was thought advisable to collect the samples without handling. A collecting device was used consisting of a box with removable strips pierced with sharpened nails arranged so that the apples placed thereon could not touch each other.

When removed from the tree, the apple was held by the stem while still attached to the branch and one of the nails forced into the calyx cavity. The stem was then cut from the branch.

Sampling followed the tree and row arrangement of the spray block with duplicate samples from each of the spray treatments.

Each sample throughout the growing season consisted of ten apples collected from the lower limbs of the trees. These were selected, unblemished, were similar in size and in appearance seemed to hold the maximum residue.

The samples collected at harvest were selected in the same manner although no standard was set as to the number of fruits taken as long as the duplicates were approximately of the same weight.

Removal of the Residue

In preparation for the removal of the residue, the stem and calyx lobes were cut out since they hold an appreciable quantity of the residue. This was necessary since the comparison was to be made throughout the season and these portions do not change in size and shape, thus bearing a greater percentage of the total arsenic on young fruits than on mature apples.

A solution of 3% hydrochloric acid (by volume) at a temperature of 70°-80° C. was used to remove the residue.

About 200 c.c. of the hot acid solution was poured over the sample in a beaker. In order to have a final volume of 500 c.c., the larger apples were washed singly. The solution was held at 70°-80° C. for one minute with continued agitation so as to remove mechanically any visible spray streaks. The apples were then removed from the solution by pressing a glass stirring rod into the calyx cavity and washed carefully with the hot acid solution, with special precautions in cleaning the stem and calyx openings. The solution was then cooled, made to a volume of 500 c.c. and stored for analysis.

Method of Analysis

A modification of the A.O.A.C.[6] and Heidenhain[7] methods for determination of arsenic by the Gutzeit method was used in this study. An aliquot of the sample, such that it contained approximately 0.02 mgm. of arsenic trioxide, was placed into the small Gutzeit generator. Hydrochloric acid was added so that the final volume of the solution was 35 c.c. and the acid content was 2.0 molal. An arrangement, using acid volumes similar to that of Percival and Potter[8] was used to determine the added acid necessary. Four pieces of activated stick zinc were added, the absorption tubes connected and the whole apparatus submerged within 2 cm. of the top of the tube in water at a temperature of 20°C. for $1\frac{1}{2}$ hours. The paper strips were removed and the length of the stain was compared to standard stains produced under like conditions.

Determinative Measurements

In order to determine the surface area of each apple and total in the sample, each apple was measured for average diameter which was considered to be the average between the transverse and vertical diameters. Since the fruit was sampled in a manner so as to take typical apples from each tree, the average diameter of the samples of the ten apples correspond to a reasonable degree. Assuming that an apple is a sphere, a calculation was made for the surface. These calculations, however, are only comparative. The total weight of each sample was measured and the grains of arsenic trioxide per pound was calculated.

From the above calculations, a separation was made to determine the arsenical residue in grams per apple so that the growth factor could be eliminated.

In comparison and as a check upon the calculated surface areas, a water displacement volume was recorded for a number of the samples.

EXPERIMENTS IN THE COLLEGE ORCHARD

A block was set aside in the College orchard for these experiments. It consisted of a plot containing six rows with six trees in each row. The whole plot contained 34 trees, 16 of which were York and 18 of the Stayman variety. The trees were approximately the same age and all had been under the same type of treatment.

The tree and row order are given in the diagram below. Spray treatment and sampling order followed this relationship.

	6	5	4	3	2	1		
	o	x	o	o	o	o	1	
York	o	o	o	o	o	o	2	
	o	x	o	o	o	o	3	Tree
	o	o	o	o	o	o	4	
Stayman	o	o	o	o	o	o	5	
	o	o	o	o	o	o	6	

S → N

x Tree missing

Spray Combinations

In the York-Stayman plots the following mixtures in amounts per hundred gallons of spray were applied:

I. Acid lead arsenate - 3 pounds

Liquid lime sulfur - 1.006 sp. gr.

II.	Acid lead arsenate	-	3 pounds
	Flotation sulfur paste	-	10 pounds
III.	Acid lead arsenate	-	3 pounds
	Flotation sulfur paste	-	10 pounds
	Fish oil	-	1 quart
IV.	Acid lead arsenate with casein	-	3 pounds
	Hydrated spray lime	--	3 pounds
	Liquid lime sulfur	-	1.006 sp. gr.
V.	Acid lead arsenate	-	2 pounds
	Kayso	-	2 pounds
	Sulfocide	-	2 quarts
	Scalecide	-	4 quarts
VI.	Acid lead arsenate	-	3 pounds
	Hydrated spray lime	-	9 pounds
	Liquid lime sulfur	-	1.006 sp. gr.

These spray combinations were arranged to give an idea of the efficiency of certain common spray materials upon the retention of arsenical residues.

Spray I is the standard combination in which the liquid lime sulfur acts as controlling factor for apple scab.

Because of the nauseating odor produced when fish oil and liquid lime sulfur are mixed, flotation sulfur paste was substituted. Spray II was applied as a check between the standard Spray mixture I and Spray III containing fish oil as an adhesive.

Casein is incorporated with the acid lead arsenate in Spray mixture IV. Casein will react with the hydrated lime to form calcium caseinate which acts as an adhesive. The hydrated spray lime acts as a preventative for rapid reactions between acid lead arsenate and liquid lime sulfur. The soluble arsenic formed in this reaction causes injury to the foliage.

Spray VI was used as a check on the casein lead arsenate Spray IV.

Spray V was used to show the effect of a miscible oil in replacement of a portion of the lead arsenate necessary for toxic action.

Table 1 illustrates the manner in which the sprays were applied and the samples were collected.

Table 1

Record of Spray Applications at the College Orchard

Spray Mixtures	Row	York Tree	Stayman Tree	Cover Spray Dates				
				June 10	June 21	July 5	July 25	Aug.3
Check	1	3	4	-	-	-	-	-
I	1	1	6	x	x	x	x	x
	1	2	5	x	x	x	-	-
II	2	1	6	x	x	x	x	x
	2	2	5	x	x	x	x	-
	2	3	4	x	x	x	-	-
III	3	1	6	x	x	x	x	x
	3	2	5	x	x	x	x	-
	3	3	4	x	x	x	-	-
IV	4	1	6	x	x	x	x	x
	4	2	5	x	x	x	x	-
	4	3	4	x	x	x	-	-
V	5	out	6	x	x	x	x	@
	5	2	5	x	x	x	x	-
	5	out	4	x	x	x	-	-
VI	6	1	6	x	x	x	x	x
	6	2	5	x	x	x	x	-
	6	3	4	x	x	x	-	-

x applied
- dropped
@ Found Scalecide to be broken down - free oil liberated - did not make final application

Climatic Factors

The season of 1932 was below normal in rainfall, the local weather records showing subnormal precipitation for the months of June, August and September. In comparison to a 31 year average shown by the records of the State College Station, the rainfall from May 15 to October 20 was 15.81 inches in 1932 while normal was 17.62 inches. During July and October the rainfall was above normal but during September when residue loss is of the greatest importance, the weather approached drought conditions with only four rainy days and a total rainfall of 0.59 inches.

The daily precipitation, dates of spray application, and the length of exposure to the rainfall after spraying, are shown graphically in Figure 1. The subnormal rainfall in the 1932 season must be taken into account in a comparison to other seasons. McLean and Weber[9] found that the time of application of the spray has a far more important effect on the amount of residue than the quantity of spray applied. Hough et al.[10] showed that an arsenical spray applied late in July left an excessive amount of residue even though the August and September rainfall greatly exceeded the normal precipitation, while Magness et al.[11] stated that the amount of residue increased with the number of applications and was greater, the later in the season they were applied.

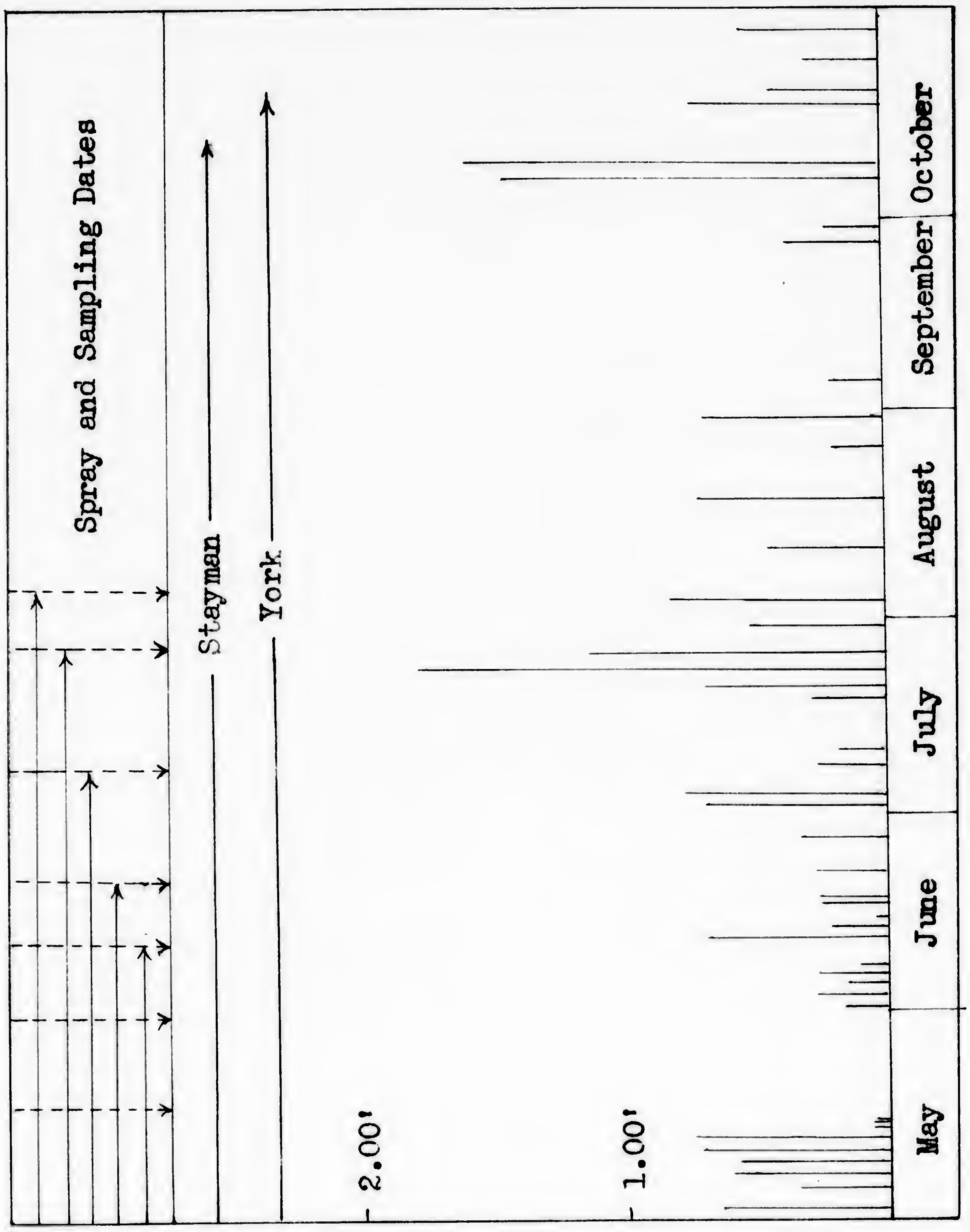

Figure I - Showing dates of spraying, daily precipitation and time of sampling. The horizontal lines indicate the length of time the apples remained on the trees.

Residues at Harvest

Samples were collected at harvest from the plot so that duplicate samples were obtained from the York and Stayman trees. These gave samples from trees receiving six different spray treatments and from those whose spray treatment was incomplete.

A summary of the results of spraying practices on residues at harvest are given in Table 2. These show the variation of arsenical residue with variety of apple, type of treatment and omission of one or both of the last two spray applications. Table 2 includes the results of some 200 chemical analyses calculated as grains of arsenic trioxide per pound of fruits.

It may be well to note that the actual residue at harvest as shown in these data will not correspond to general commercial practices since special precautions were taken to insure the retention of all residue which was not removed by the natural conditions of growth and weathering. This fact is brought out in Table 3.

Table 2

Residues at Harvest Affected by Spray Treatments and Omission of Certain Applications

Spray Mixture	York			Stayman		
	Date of Last Application			Date of Last Application		
	July 5	July 25	Aug. 3	July 5	July 25	Aug. 3
I	.007	-	.014	.012	-	.025
II	.007	.013	.021	.012	.016	.026
III	.015	.022	.043	.016	.027	.049
IV	.006	.012	.026	.012	.013	.034
V	-	.010	-	.009	.010	-
VI	.003	.011	.016	.006	.012	.016

Values in grains As_2O_3 per pound of fruit

Variety of Apple

From Table 2 it is noticeable that there was a decided variation in total quantities of residual arsenic at harvest between the York and Stayman varieties. This relationship is carried throughout the table.

The variation can be explained on the basis that the Stayman apples were much smaller in size than the average York variety and would have therefore a smaller surface area per apple and larger quantities of residue per common weight of fruits. The Stayman samples were collected nine days earlier than those of the York variety, the latter receiving 1.31 inches more of rainfall. Removal by weathering accounts for some of the variation of residues between varieties. It is also an accepted fact that differences in skin texture between varieties accounts for the added adhesive powers of sprays and noticeable variations in total residual arsenic at harvest.

Complete Treatment and Omission of Treatment

Table 2 shows that under the conditions for growth and weathering during the 1932 season, all spray combinations tested left excessive residues of arsenic at harvest when applied in 5 cover sprays ending August 3.

The use of Spray mixtures V and VI might be possible under normal weather conditions. Under seasonal variations that were present during the 1932 season the results indicate that these spray mixtures could not be applied in early August without excessive residues at harvest.

A comparison of treatments I and VI shows that the addition of hydrated lime to the lead arsenate - lime sulfur mixture reduces the retention of arsenic. The residues found where casein was included were considerably larger than where the spray contained no spreader.

Spray mixture III contained fish oil in combination with lead arsenate and flotation sulfur paste. It is comparable to mixture II which contained no fish oil. The residual arsenic at harvest remaining from the fish oil treatment was approximately twice as large as that resulting from treatment II containing no fish oil. The quantity was approximately one-third larger than the residue exhibited by the use of the casein lead arsenate Spray IV. In comparison to the standard lead arsenate - lime sulfur spray mixtures, the residue at harvest from the fish oil treatment was nearly three times as large. Hood[13] stated that, in a series of experiments using fish oil as an adhesive, nearly

75% of the residual arsenic remained on the fruit and leaf surfaces after 102 days and 15.63 inches of rainfall. Thus, even under normal weather conditions, residues remaining from fish oil - lead arsenate treatments applied in early July become excessive and require cleaning operations to reduce the arsenic trioxide below the tolerance level. This fact is quite noticeable in the spray group studied for it is doubtful whether Spray III under the conditions of the experiment would exhibit a below tolerance residue at harvest after a normal season.

The remaining five treatments may be applied July 5 without excessive residues at harvest under seasonal conditions similar to those of 1932. Spray treatments in this group, if applied in late July, will form above tolerance residues at harvest.

Table 3

Loss of Residue by Weathering in the Period between Last Spray Application and Harvest

Spray Mixture	August 3	October 20	Loss	% Loss
I	1164	163	1001	86.0
II	1262	409	853	67.6
III	1178	833	345	29.3
IV	900	505	395	43.6
V	-	-	-	-
VI	1008	296	712	70.6

Grams $X10^{-6}$ of As_2O_3 per apple

Table 3 indicates the loss of residue for each of the six spray treatments under 6.60 inches of rainfall. Samples of the York variety were used. The data are applicable only to seasons, weathering conditions of which are similar to 1932 but the comparison of treatments will hold for any season.

These results indicate that sprays containing adhesives are less subject to weathering loss than others under similar periods and weather conditions.

The relation of residues present at picking time, from Table 2, of treatments I, V and VI, indicates that it is logical to assume that treatment V in Table 3 follows a similar order and should be placed in that order.

From Table 2, it is evident that the six spray combinations may be separated into groups depending upon the total arsenical residues at harvest. This relation is also shown in Table 3. It cannot be considered specific for any season unlike that of 1932 although in general the relation applies to all seasons.

Table 4

Relation of Spray Mixtures to Spray Periods

Group	Spray Mixture	Residual Arsenic	Period for Last Application
1	III, IV		Late June
2	I, II	Maximum Allowed	Early July
3	VI, V(?)		Late July

Table 4 consists of a relative comparison between spray types such that in general the spray treatments noted could not be used after the period cited without undue residual arsenic at harvest under 1932 weather conditions.

Group 1 in Table 4 consists of Spray III containing fish oil and Spray IV containing casein, as adhesives for the protective coating. As has already been noted from Table 2, the use of these sprays later than July 5 under the weather conditions of 1932 would necessitate cleaning operations at harvest to lower the residual arsenic below the tolerance.

Group 2 is made up of spray mixtures I and II. They contain no adhesives although the lime-sulfur and flotation sulfur paste have some adhesive qualities along with their normal fungicidal activities.

Group 3 contains mixture VI and possibly V. The position of mixture V in the table is questionable since no values for residual arsenic could be determined at harvest. Spray VI contains hydrated lime which lowers the adhesive properties of the spray material. This was noted in Table 2. These mixtures may be applied in late July without excessive residues remaining at harvest.

Arsenical Deposit and Loss

In order to determine the proximate quantities of arsenic present on the fruit throughout the season, samples were collected before and after each of the six spray applications.

Duplications of treatments were carried on throughout the season so that comparisons might be made of the residue remaining upon the fruit of the York and Stayman varieties.

Results of the analyses of these samples are given in the Tables 5 to 16. Calculations have been outlined in terms of grains of arsenic trioxide per pound of fruit, grams of arsenic trioxide per square meter of apple surface, and grams of arsenic trioxide per apple. These calculations are the basis for conclusions which follow.

Table 5

Analyses of Residue

Spray I - York Apples

Sampling Date	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	-			.896			108		
" 20	.0586		-	.396		.500	93		15
" 21	-	-		-	-		-	-	
July 5	.0343		-	.308		-	118		-
" 6	.1707	.1364		1.626	1.318		677	559	
" 25	.0425		.1282	.512		1.114	336		341
" 26	.1031	.0606		1.301	.789		838	502	
Aug. 3	.0395		.0636	.516		.785	363		475
" 4	.1245	.0850		1.691	1.175		1164	806	

Table 6

Analyses of Residue

Spray I - Stayman Apples

Sampling Date	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	-			1.194			122		
" 20	.0727		-	.435		.759	93		29
" 21	.2144	.1417		1.563	1.128		357	264	
July 5	.0376		.1768	.341		1.222	129		228
" 6	.2203	.1827		1.665	1.324		576	447	
" 25	.0419		.1784	.435		1.231	230		346
" 26	.1390	.0971		1.524	1.090		808	578	
Aug. 3	.0503		.0897	.588		.936	379		429
" 4	.1274	.0771		1.405	.817		860	481	

Table 7

Analyses of Residue

Spray II - York Apples

Sampling Date	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	–			1.058			112		
" 20	.0599		–	.332		.726	90		22
" 21	.1997	.1398		1.275	.943		292	202	
July 5	.0229		.1768	.389		.886	158		134
" 6	.1120	.0891		1.034	.645		389	231	
" 25	.0313		.0807	.364		.670	239		150
" 26	.0983	.0670		1.148	.784		672	433	
Aug. 3	.0515		.0468	.660		.488	473		199
" 4	.1175	.0660		1.590	.930		1262	789	

Table 8

Analyses of Residue

Spray II - Stayman Apples

Sampling Date	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	-			.999			100		
" 20	.0607		-	.388		.511	86		14
" 21	.2028	.1421		1.313	.925		305	219	
July 5	.0451		.1577	.389		.924	158		147
" 6	.1356	.0905		1.112	.723		402	244	
" 25	.0302		.1054	.311		.801	145		257
" 26	.1094	.0792		1.232	.921		660	515	
Aug. 3	.0795		.0299	.977		.255	538		122
" 4	.1479	.0684		1.587	.610		912	374	

Table 9

Analyses of Residue

Spray III - York Apples

Sampling Date	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	-			1.226			136		
" 20	.0668		-	.434		.792	101		35
" 21	.1835	.1167		1.221	.787		296	195	
July 5	.0579		.1256	.519		.702	203		93
" 6	.1234	.0655		1.018	.499		375	172	
" 25	.0379		.0855	.558		.460	328		47
" 26	.1211	.0852		1.427	.869		875	547	
Aug. 3	.0919		.0292	1.134		.293	850		25
" 4	.1219	.0300		1.563	.429		1178	328	

Table 10

Analyses of Residue

Spray III - Stayman Apples

Sampling Date	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	-			1.126			134		
" 20	.0535		-	.229		.897	76		58
" 21	.1899	.1364		1.188	.959		281	205	
July 5	.0679		.1220	.545		.643	177		104
" 6	.1522	.0843		1.228	.683		422	245	
" 25	.0535		.0987	.576		.652	319		103
" 26	.1571	.1036		1.697	1.121		918	599	
Aug. 3	.0948		.0623	1.083		.614	687		231
" 4	.1101	.0153		1.351	.268		995	308	

Table 11

Analyses of Residue

Spray IV - York Apples

Sampling Date	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	-			.758			78		
" 20	.0600		-	.363		.395	79		-1
" 21	.1350	.0750		.879	.516		199	120	
July 5	.0315		.1035	.282		.597	99		100
" 6	.1145	.0830		.997	.715		385	286	
" 25	.0439		.0705	.513		.484	282		103
" 26	.1199	.0760		1.359	.846		805	523	
Aug. 3	.0542		.0657	.676		.683	469		336
" 4	.1045	.0503		1.235	.559		900	431	

Table 12

Analyses of Residue

Spray IV - Stayman Apples

Sampling Dates	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	-			1.102			118		
" 20	.0661		-	.375		.727	76		42
" 21	.2175	.1514		1.219	.844		314	238	
July 5	.0591		.1584	.491		.728	177		137
" 6	.2346	.1755		1.906	1.415		696	519	
" 25	.0457		.1889	.491		1.415	267		429
" 26	.0542	.0085		.959	.468		338	71	
Aug. 3	.0618		-.0076	.738		.221	514		-176
" 4	.1399	.0781		1.633	.895		948	434	

Table 13

Analyses of Residue

Spray V - York Apples

Sampling Dates	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	-			.768			119		
" 20	.0421		-	.257		.511	58		61
" 21	.1039	.0618		.667	.410		146	88	
July 5	.0238		.0801	.211		.456	76		70
" 6	.0900	.0662		.786	.575		275	199	
" 25	.0184		.0716	.216		.570	129		146
" 26	.0789	.0605		.931	.715		592	463	
Aug. 3	.0322		.0467	.402		.529	303		289
" 4	-			-	-		-	-	

Table 14

Analyses of Residue

Spray V - Stayman Apples

Sampling Date	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	-			1.098			95		
" 20	.0474		-	.289		.809	64		31
" 21	.1432	.0958		.922	.633		227	163	
July 5	.0474		.0958	.372		.550	127		100
" 6	.1126	.0652		.899	.527		275	148	
" 25	.0323		.0803	.269		.630	172		103
" 26	.0741	.0418		.741	.472		362	190	
Aug. 3	.0479		.0263	.488		.253	283		79
" 4	-	-		-	-		-		

Table 15

Analyses of Residue

Spray VI - York Apples

Sampling Date	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	-			.806			95		
" 20	.0324		-	.213		.593	51		44
" 21	.1458	.1134		.998	.785		243	192	
July 5	.0348		.1110	.303		.695	115		128
" 6	.1065	.0717		.986	.683		389	274	
" 25	.0159		.0906	.218		.768	127		262
" 26	.0780	.0621		1.026	.808		677	550	
Aug. 3	.0430		.0450	.561		.465	392		285
" 4	.1008	.0578		1.273	.715		1008	616	

Table 16

Analyses of Residue

Spray VI - Stayman Apples

Sampling Date	As_2O_3 in Grain per Pound	Gain	Loss	As_2O_3 in Grams per $(M)^2$	Gain	Loss	As_2O_3 in Grams $X10^{-6}$ per Apple	Gain	Loss
June 10	-			.915			109		
" 20	.0221		-	.134		.781	33		76
" 21	.1399	.1178		.911	.777		237	204	
July 5	.0382		.1017	.301		.610	115		122
" 6	.1474	.1092		1.013	.712		407	292	
" 25	.0249		.1225	.281		.732	176		231
" 26	.0746	.0497		.806	.525		460	284	
Aug. 3	.0433		.0313	.543		.263	378		82
" 4	.0969	.0536		1.162	.619		795	417	

Growth and Weathering

Conditions for removal of arsenical residues during a growing season depend upon growth recognized by an increase of surface area of the fruit, and upon weathering. The sum of these two factors account for the greater part of the natural loss of residue from the fruit surface.

The rate of growth factor exhibits its effect in early season. As the growth increase becomes smaller, the effect of weather conditions upon the residue becomes more pronounced. In the last two months before harvest the rate of growth is decreasing and in the balance between growth and weathering, the effect of weathering is the more important. These facts have been reported by Hamilton of New Jersey[14] and have been confirmed in this study.

The loss of residue due to growth is a constant factor in any type of spray combination under conditions of normal growth. The weathering factor however is variable depending upon the type of materials used in the spray combination.

Figure II represents the loss of arsenic trioxide in the spray residue due to weather conditions. The total rainfall between applications is shown and compared to the losses at various periods through the spraying season.

Spray I was subject to a greater loss of residue throughout the season of 1932 than any of the other spray combinations. Spray III showed a decreasing loss after the July 5 application. This indicated that under the conditions of the experiment, a drying oil adhesive provides great retentive powers for the residue upon the fruit surface.

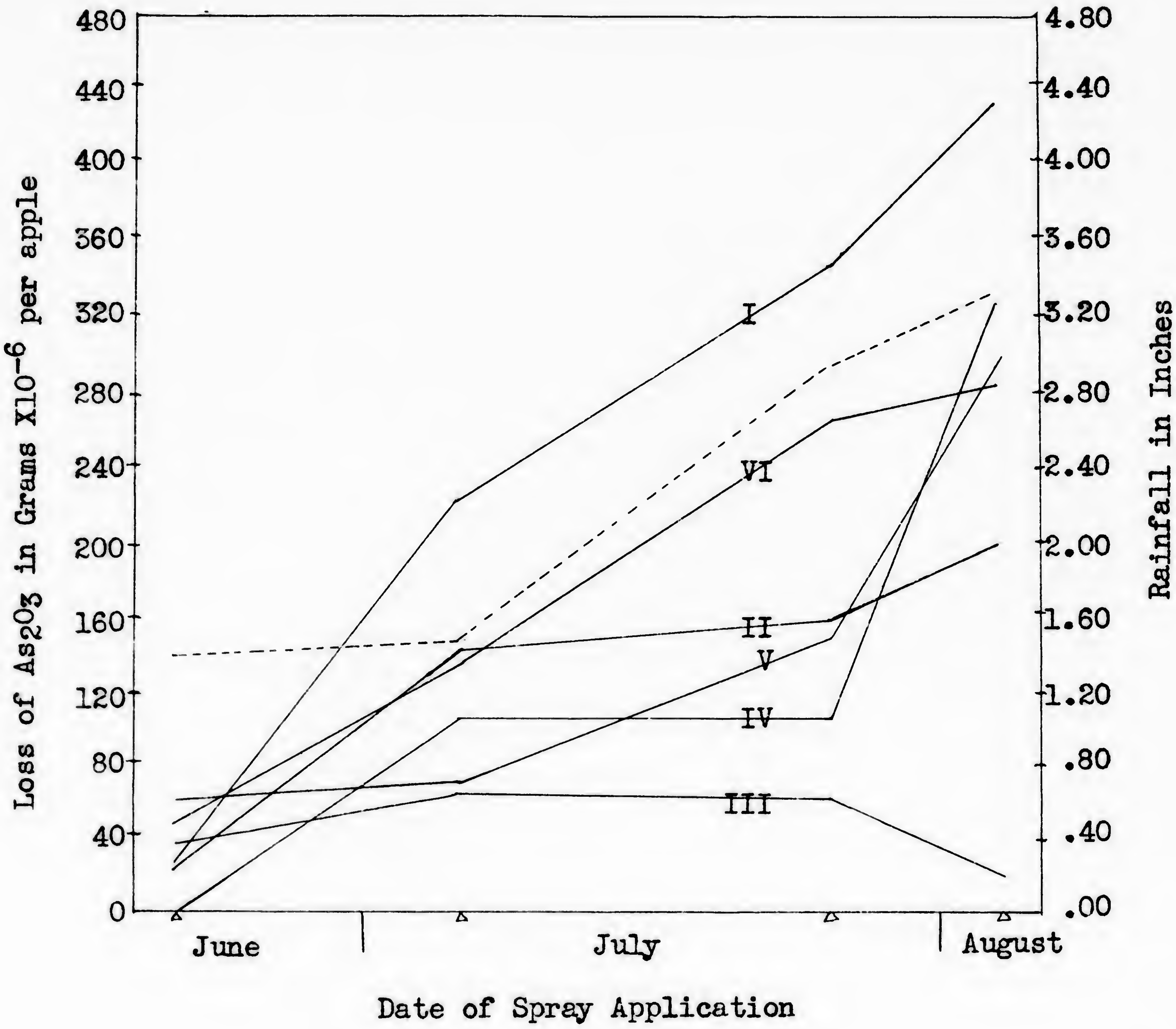

Figure II - Showing the loss of As_2O_3 between spray applications and its relation to the total rainfall between applications for the spray mixtures studied. Broken line indicates total rainfall between applications.

Spray IV containing the casein adhesive showed a greater loss of arsenic trioxide during the last spray period than Spray III. The effect of the casein was therefore not as lasting as that of the fish oil.

The growth - weathering relationship is also shown in Figure II. As the season progressed the losses due to weathering were considerable. The relation follows directly with the curve showing the quantity of rainfall occurring between the spray applications.

The samples were collected just before each application was made. This was the end of the period of effectiveness of the poison. These sampling dates are shown in Table 1 and Figure II.

Based upon calculations similar to those of Hamilton[14], it was found that about 10% of the final surface area had formed at the time of the June 10 application. At this time the increase in surface area was almost 50% during the ten day period to the June 20 application. It is evident that at this time the growth factor was of the greater importance while the proportion of the loss from weathering was slight. By August 3, the date of last spray application, 60% of the final surface area had formed. At this time the growth factor had become less important and the factor of weathering of much greater importance.

The normal reduction of residue due to an increase in surface area was calculated upon this basis. Thus from June 10 to June 20 the area increased 10% of the total or 50% in that period. The residue loss due to growth would then be 50% of the original amount on the apple, June 10. The difference between loss due to growth and total loss was considered to be the loss due to weathering. Table 17 was derived from these calculations.

Table 17

Calculated Percentage Losses Due to Weathering

Between Applications	Spray Combinations					
	I	II	III	IV	V	VI
June 10-20	8.6	25.7	21.1	4.0	25.0	32.0
June 20-July 5	-	56.6	34.0	42.2	44.2	45.5
July 5-25	44.6	41.4	13.7	22.0	47.5	51.0
July 25-Aug.3	78.4	69.0	36.8	74.6	76.9	61.2

Table 17 also indicates the correlation which existed, during the 1932 season, of the relation of total residue at harvest to growth, weathering and spray treatment. The table was included to show the difference in effect of the weathering process upon the various spray combinations. It does not show increasing losses through the various periods since the time ratio between spray applications and the total rainfall during the periods were not constant. It does indicate however that the losses due to weathering increase as the season progressed. Also that certain of the spray combinations, most noticeably spray mixture III were not affected by weathering to the same extent as the others.

EXPERIMENTS AT BIGLERVILLE, PENNSYLVANIA

The methods employed were similar to those followed in the previous experiment. Under conditions in that orchard, it was necessary to use six spray treatments to control the codling moth. In other orchards in Adams County, the infestation did not warrant the use of this number of spray applications during 1932.

Weather conditions favored codling moth development. Rainfall was deficient during June and July. About half of the normal precipitation occurred in August and drought conditions were reached in September. The rainfall in October was extremely heavy.

Worthley[15] has published the codling moth control records for these spray combinations used in the experiments which were a part of this study.

Comparison of Spray Combinations

In the Rome-Stayman plots the following mixtures in amounts per 100 gallons of spray were applied:

Plot I	Acid lead arsenate	3 pounds
	Liquid lime sulfur	1.006 sp. gr.
Plot II	Acid lead arsenate	3 pounds
	Chemical hydrated lime	9 pounds
	Liquid lime sulfur	1.006 sp. gr.
Plot III	Acid lead arsenate	3 pounds
	Flotation sulfur paste	10 pounds

Plot IV	Acid lead arsenate	3 pounds
	Flotation sulfur paste	10 pounds
	Choice light pressed fish oil	1 quart
	(Fish oil omitted in last application)	
Plot V	Acid lead arsenate with casein	3 pounds
	Chemical hydrated lime	9 pounds
	Liquid lime sulfur	1.006 sp. gr.
Plot VI	Acid lead arsenate	2 pounds
	Calcium caseinate	2 pounds
	Sodium sulfide	2 quarts
	Miscible oil	4 quarts
Plot VIII	Acid lead arsenate	3 pounds
	Liquid lime sulfur	1.006 sp. gr.

These spray combinations are similar to those used at State College. Since there were variable factors between this and the previous experiment, due principally to variations in weather conditions, the results determined as residual arsenic were not compared. Samples from this orchard were only collected at harvest.

The results of analyses of samples of Rome apples from the Rome-Stayman block are shown in Table 18. Losses by handling are also shown in the table. These relations, insofar as total residual arsenic at harvest is concerned, refer only to the 1932 seasonal conditions.

Residues at Harvest

Treatment and Picking Operations

Table 18

Arsenic in Grains per Pound of Rome Fruit at Harvest from Spray Treatments and the Loss of Residue by Handling

Plot	Picked without Handling	From Picking Crates	Loss Due to Handling	% Loss due to Handling
1	-	.006	-	-
2	.005	.004	.001	20.0
3	.007	.006	.001	14.3
4	.010	.011	-	-
5	.007	.004	.003	42.9
6	.008	.004	.004	50.0
8	.006	.005	.001	16.6

Spray mixtures applied to Plots I and VIII were the same so the results should be interchangeable.

The table shows the amount of residual arsenic at harvest under ordinary commercial spraying operations. Spray IV,which contained fish oil in all but the last application, showed residual arsenic close to the tolerance. From the results of the previous experiment it is evident that if the oil had been applied with the July 23 treatment, excessive residues would have resulted at harvest. The remainder of the treatments gave residues well below the tolerance.

Losses due to handling of the fruit are included in Table 18. Certain of the losses were nearly 50% of the total residual arsenic present. These results cannot be considered as comparisons between spray types nor can they be considered constant since the degree of mechanical removal has a wide variation. It does appear, however, that the nature of the spray coating afforded by the addition of fish oil is such that ordinary handling results in little, if any, removal of arsenic. The spray coating given by casein is readily subject to mechanical removal. Even in combination with an oil spray (VI), the presence of casein apparently facilitated the mechanical removal of arsenic.

RESULTS FROM COMMERCIAL ORCHARDS

Samples were collected and analyzed from 132 orchards throughout Pennsylvania. The results show the general run of arsenical residues at harvest from spray practices necessary to control the codling moth.

Table 19 shows the results of some of the analyses which indicate the level of arsenical residue found from general commercial orchard operations.

The relative visibility of the arsenical residue is also noted in the table. It is evident from these figures that no correlation can be made between the visible residue and the actual quantity of residual arsenic present on the fruit surface.

Table 19

Sample	Location County	Amount of Visible Residue	As_2O_3 in Grain/lb.
1	Lycoming	light	.001
2	Northumberland	none	.002
6	Mifflin	heavy	.006
10	Dauphin	light	.007
12	Adams	none	.003
14	Adams	light	.018
20	Adams	none	.006
25	Adams	light	.005
32	Adams	heavy	.006
36	Adams	none	.009
46	Franklin	light	.007
51	Franklin	heavy	.008
108	Lancaster	light	.005
110	Lancaster	heavy	.018
113	Lebanon	heavy	.011
114	Lebanon	none	.005
120	Chester	none	.004
121	Chester	light	.002
137	Lehigh	none	.005
138	Lehigh	none	.002
206	Fayette	light	.003
208	Somerset	light	.006
214	Washington	none	.003
219	Allegheny	heavy	.010
222	Jefferson	light	.007
225	Butler	heavy	.007
226	Armstrong	none	.006

SUMMARY

Experiments were conducted at the College Orchard to determine the amounts of residual arsenic present at various stages throughout the growing season and at harvest under complete and incomplete spray treatments. Six spray combinations were used and compared to each other in effectiveness of retention of the arsenical residue.

The data indicate that there is a direct relationship existing between arsenical residue at harvest and the completeness of spray treatment. A dependence is also shown, in the loss of residual arsenic during the season, on the natural removal factors of growth and weathering. The relation of residue loss to growth is very pronounced in early season but becomes less important as the season progresses. At this time the effect of the weathering factor is predominant.

The use of adhesives in spray combinations increases the effective retention of the spray coating. Applications containing fish oil could not be used after July 5 without excessive quantities of residual arsenic being present at harvest.

The weather conditions during 1932 were subnormal. All of the spray combinations used gave above tolerance residues at harvest when the spray was applied as late as August 3.

Results of the analyses of residues present upon York and Stayman fruits were consistently variable. The residual arsenic upon the Stayman fruits was larger. This variation appears to be the result of differences in fruit surfaces and not to the spray material applied.

These comparisons will not necessarily be repeated since the

amount of spray material applied and the completeness of the application will be governed by the conditions under which the treatment is made.

The results of the experiments at Biglerville were made to confirm the relationships given in the preceding experiment and to show the relation between controlled spray practices of the experimental type and those carried out under general orchard operation.

Samples were collected at harvest and the results related to those from the experimental block at the College Orchard. Both of these plots were sprayed with the same spray mixtures although with different quantities of spray material per tree.

With one exception, the residues at harvest were all below the tolerance at Biglerville where weather, variety of fruit and amounts of spray material applied were different from conditions at State College.

An indication is given of the approximate losses of arsenic from the fruit by handling during picking operations.

In codling moth control, the records at Biglerville(15) show fish oil to be a valuable adhesive, and lime to reduce the effectiveness of the spray. If control depends entirely upon the quantity of arsenic applied and remaining upon the foliage and fruit, these results are in agreement with the analytical findings reported in this paper.

CONCLUSIONS

Subnormal weather conditions in 1932 make it impossible to reach definite conclusions regarding the safety and practicability of these spray programs in so far as they concern residual arsenic.

The date of last application and the amount of rainfall between the date of the last application and harvest are factors of maximum importance in determining whether or not arsenical residues will be within the limit of the international tolerance.

Spray combinations containing added adhesives may not be applied after late July under excessively dry weather conditions without excessive arsenical residues at harvest.

Spray combinations containing no added adhesive may be applied as late as August 3 even under very dry conditions without too large an excess of arsenical residue at harvest.

A direct relation exists between the growth of fruit as indicated by increase in surface area and decrease in arsenical residues.

There is a variation in residual arsenic present upon different varieties of fruits. This variation does not depend upon the type of spray applied.

Analytical records from Pennsylvania orchards in 1932 show a level of below tolerance residues.

The visibility of spray deposits is no indication of the relative quantity of poison present.

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