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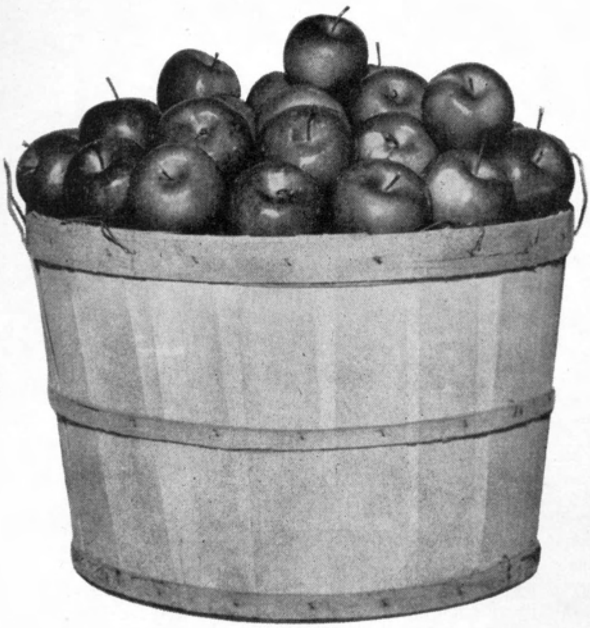
QUALITY OF APPLES

as affected by sprays



by

Philip Garman
L. G. Keirstead
W. T. Mathis

THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION, NEW HAVEN, CONNECTICUT

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QUALITY OF APPLES AS AFFECTED BY SPRAYS

by

Philip Garman, L. G. Keirstead and W. T. Mathis[1]

To begin this discussion, it will be necessary to define what is meant by quality in apples. To be of top quality, an apple should be well colored, of good flavor, and contain enough sugar, minerals and acid to please. It must also be a good cooker, since many of the apples consumed today go into sauce or pie. We have come to realize that a highly colored apple sells better than a poorly colored one. Actual consumption, however, may depend in large measure on such factors as flavor, aroma, texture and cooking quality.

What influence do sprays, as such, actually have on quality? To obtain a full answer to this question much more investigation will be required. However, our work to date, which is reported here, definitely establishes the fact that sprays can affect the quality of apples.

The current discussion deals only with the effect of pesticides and does not include fertilizer, nutritional, or hormone sprays. Pesticide sprays used on apples consist primarily of an insecticide and a fungicide, together with additives to make the mixture safer or more adhesive, or to provide greater spread. Each component naturally plays its part in the over-all effect, and should be taken into consideration.

Furthermore, every ingredient needs to be considered in the light of its effect on metabolism of the plant. An ingredient may have nutritive properties; for example, some spray components contain nitrogen or phosphorus. Some spray materials are anti-metabolites, which may substitute for chemicals necessary in the synthesis of sugars, acids, or other essentials. Other ingredients have a general shading effect, which prevents the full action of sunlight. Still others may clog the stomata or breathing pores in the leaves and prevent proper functioning.

Our most extensive investigations on chemical constituents were made in 1952, when individual trees in randomized plots were analyzed separately, making it possible to pair trees by location and row, so that results could be subjected to analysis of variance. Most of the discussion following refers to this 1952 work, although the 1951 experiments are also reported in considerable detail, and some reference is made to investigations carried on in 1950.

Flavor testing was actually begun in 1949. Methods were improved as the work progressed; as a result the flavor and chemical analyses may be

[1]The senior author is an entomologist: Mr. Keirstead and Mr. Mathis are analytical chemists, all of The Connecticut Agricultural Experiment Station staff.

considered more and more accurate each year since 1949. An example of this is seen in flavor comparisons between thiram- and sulfur-sprayed fruit from the "dwarf" orchard. Likewise, chemical examination of the fruit from the Burton Orchard is now beginning to show differences of considerable significance.

EFFECT OF SPRAYS ON CHEMICAL COMPOSITION

Effect of the Insecticide on Sugars

In tests made prior to 1952 there appeared to be little effect of the insecticide on the sugar content of fruit. Paired comparisons of arsenical

TABLE 1. PAIRED COMPARISONS (BETWEEN DIFFERENT TREATMENTS) IN THE PERCENTAGE OF SUGAR IN MCINTOSH APPLE

	Per cent sugar		Difference in favor of non-arsenical
	Non-arsenical	Arsenate	
	7.30	7.56	— .26
	7.51	7.11	+ .40
	7.09	6.33	+ .76
	7.09	7.33	— .24
Picked	7.39	7.33	— .06
July 21	6.66	7.76	—1.10
	5.92	6.79	+ .87
	6.54	6.84	— .30
	7.65	6.88	+ .77
	7.32	7.02	+ .30
	7.05	7.09	.11
	8.03	7.82	+ .21
	8.03	7.38	+ .65
	8.07	8.24	— .17
Picked	8.74	8.19	+ .55
August 15	8.64	8.09	+ .55
	8.12	7.86	+ .26
	8.92	8.21	+ .71
	8.83	8.21	+ .62
	8.40	8.07	+ .33
	8.42	8.00	.41
	9.48	11.03	—1.55
	11.02	9.84	+1.18
	11.02	10.54	+ .48
	10.65	10.41	+ .24
Picked	11.74	10.41	+1.33
Sept. 15	10.82	11.69	— .87
	11.71	11.10	+ .61
	10.29	10.53	— .24
	11.98	10.53	+1.45
	11.03	11.25	— .22
	11.03	10.81	+ .22
	10.98	10.74	.24

Differences are not significant except Aug. 15

TABLE 2. EFFECT OF THE INSECTICIDE ON TOTAL SUGARS, PAIRED REPLICATES BY ROWS AND LOCATION

Per cent sugar: Non-arsenical-sulfur-ferbam	Per cent sugar: Lead arsenate-sulfur-ferbam	Difference in favor of non-arsenical
8.22	8.20	+ .02
8.03	7.82	+ .21
8.53	8.09	+ .44
8.61	8.21	+ .40
6.96	6.53	+ .52
7.08	7.11	— .03
6.86	6.99	— .13
7.11	6.88	+ .29
10.54	11.03	— .51
10.92	9.84	+1.08
11.68	11.10	+ .58
10.70	11.25	— .55
		.19

Differences are not significant

TABLE 3. EFFECT OF LEAD ARSENATE ON SUGARS, BASED ON AVERAGES OF THE SEVERAL TREATMENTS

Per cent sugar: Non-arsenical	Per cent sugar: Arsenate	Difference in favor of non-arsenical
10.83[1]	10.80	.03
11.07	10.80	.27
7.35	6.88	.47
6.74	6.88	—.14
8.20	8.08	.12
8.50	8.08	.42
11.79	10.80	.99
7.09	6.88	.21
8.40	8.08	.32
		.30

P[2] at the .02 level

[1]These figures are means of several trees in each randomized treatment. In the column labelled "non-arsenical" they are averages of several means.

[2]P=probability. If P is .05 or less, differences are considered significant. If P is .01 or less, they are highly significant. If P is .051 or more, differences are probably not significant.

and non-arsenical treatments (1952) by rows and location showed only slight differences which proved not to be significant for two of the three series of analyses. In the August 15 series, however, the differences were substantial, indicating that there may have been a slight trend (Table 1). Analysis of the differences in connection with the fungicides, however, indicated that fungicides would have to be considered in making the comparisons of insecticides. This was particularly true of *Crag 341*.[1] For

[1]The chemical designation of this and other proprietary insecticides and fungicides is given in the appendix. Official name now glyodin.

this reason, lead arsenate-sulfur-ferbam was compared with treatments receiving the same fungicide but a different insecticide (Tables 2 and 3). These comparisons showed some differences in favor of the non-arsenicals. Differences in Table 2 are not significant. Those in Table 3 are at about the .02 level.

Effect of the Fungicide on Sugars

By comparing treatments receiving lead arsenate plus several different fungicides, it was possible, as already noted, to pick out some that obviously were increasing the sugar content of the fruit. The most conspicuous differences in total sugars seemed to be between lead arsenate-*Crag 341* and lead arsenate with other fungicides. These differences paired by rows and location are shown in Tables 4 and 5. The difference between lead arsenate-*Crag 341* and lead arsenate-sulfur-ferbam (Table 4) is barely significant, but compared with all other fungicides used with lead arsenate (Table 5), the increase in sugar when *Crag 341* was used is highly significant. The differences in July were unexpected, but show that *Crag 341* begins to affect total sugars fairly early (Table 36).

Analyses of apple juice made in previous years, showed that the juice of *Crag 341*-sprayed fruit rated second highest of eight treatments in sugar content in 1951 and was second highest of six treatments from Poughkeepsie in 1950 (Table 6).

Table 4. Effect Of "Crag 341" On Total Sugars

Per cent sugar: Lead arsenate-*Crag 341*	Per cent sugar: Lead arsenate-sulfur-ferbam	Difference in favor of *Crag 341*
7.56	6.53	1.03
7.76	7.11	.65
7.02	6.88	.14
9.04	8.20	.84
8.19	7.82	.37
8.07	8.21	—.14
12.07	11.03	1.04
11.69	9.84	1.85
10.81	11.25	—.44
		.59

P just under .05

Having seen the increase in sugar on comparing lead arsenate-*Crag 341* treatments with lead arsenate plus other fungicides, it becomes of interest to compare the lead arsenate-*Crag 341* treatment with non-arsenicals. Unfortunately, the series did not include a non-arsenical plus *Crag 341*. However, the comparison made between lead arsenate-*Crag 341* and non-arsenates plus sulfur-ferbam shows the treatment with *Crag 341* to be significantly higher in sugar at just above P=.01 (Table 36).

The conclusion is that total sugars in apples were increased from the use of *Crag 341* in the spray mix.

TABLE 5. EFFECT OF "CRAG 341" ON TOTAL SUGARS. PAIRED COMPARISONS OF LEAD ARSENATE-"CRAG 341" WITH LEAD ARSENATE AND OTHER FUNGICIDES

Per cent sugar		
Lead arsenate-*Crag 341*	Lead arsenate-other fungicides	Difference in favor of *Crag 341*
9.04	8.20	.84
9.04	8.16	.88
9.04	8.47	.57
8.19	7.82	.37
8.19	8.24	—.05
8.19	7.38	.81
8.07	8.21	—.14
8.07	7.94	.13
8.07	7.86	.21
7.56	6.53	1.03
7.56	6.90	.66
7.56	7.29	.27
7.76	7.33	.43
7.76	7.11	.65
7.76	6.33	.43
7.02	6.84	.18
7.02	6.88	.14
7.02	6.54	.48
		.34

P less than .01 in favor of *Crag 341*

Highly significant

TABLE 6. EFFECT OF SPRAYS ON COMPOSITION OF APPLE JUICE

Variety McIntosh—Poughkeepsie—1951

	3 Flotation sulfur throughout	4 Flotation sulfur, ferbam	5 *Crag 341*, lime throughout	6 Ferbam throughout	7 *Phygon*, ferbam	8 *Tag*, ferbam
Ash gm/100 cc	.20	.18	.20	.19	.16	.16
Acidity gm/100 cc	.38	.37	.38	.35	.27	.42
Invert sugar gm/100 cc	8.03	6.89	7.33	7.14	7.40	7.02
Sucrose gm/100 cc	2.46	2.77	2.42	2.34	2.11	2.46
pH	3.48	3.45	3.48	3.50	3.55	3.30
K ppm	950.	860.	980.	910.	790.	730.
Mg ppm	38.	37.	38.	38.	37.	36.
P ppm	84.	68.	76.	76.	76.	72.
Fe ppm	13.	8.	10.	7.	7.	7.
Cu ppm	1.0	.8	1.0	1.3	1.2	1.4
B ppm	2.1	1.2	2.0	1.2	.8	1.2
Ca ppm	38.	32.	25.	28.	28.	36.
Zn ppm	2.9	1.8	1.7	3.6	1.8	1.4

Sprays Used (Table 6)

Lead arsenate was used throughout as the insecticide. The variables were fungicides.

	Treatments[1]		*Picking dates*[2]
3	Flotation sulfur 12-100 early:	8-100 cover sprays	Sept. 17-20
4	Flotation sulfur 12-100 early:	ferbam 1½-100 cover sprays	Sept. 24-25
5	*Crag 341* and lime 3 pts. 3 lbs.-100 early :	2 pts.-3 lbs. cover sprays	Sept. 17-20
6	Ferbam 1½-100 throughout		Sept. 26-27
7	*Phygon* ½ lb.-100 plus sticker ½ lb.-100 early :	ferbam 1½-100 cover sprays	Sept. 24-25
8	*Tag* ½ pt.-100 early :	ferbam 1½-100 cover sprays	Sept. 26-27

[1]Two magnesium sulfate sprays on all plots following bloom. A sulfur-lead arsenate dust on all plots August 9

[2]Picking dates determined by maturity criteria, such as pressure and respiration, applied by the New York Agricultural Experiment Station.

Effect of the Insecticide on Acids

Differences in titratable acidity[1] appear to be very small. Those apparent on comparing arsenical and non-arsenical sprays (using the same fungicide in each) show a slight trend towards more acid for the non-arsenicals. These differences for McIntosh were not significant in 1952. Analyses made previous to 1952 on pressed juice showed a much more definite trend towards lower acids from the use of arsenicals. Table 7 gives averages in titratable acidity from 1949 through 1952. The figures, although not too extensive, are significant since all except one show an increase from use of non-arsenicals.

There is a possibility that the reduction in acids by arsenicals may be due to depression of phosphorus. Table 8 shows that phosphorus and acidity were directly correlated in two of three analyses. The reduction in phosphorus content following application of arsenicals is shown in Table 12.

Effect of the Fungicide on Acids

Fungicides evidently have more influence in acid formation than was suspected. The figures obtained in 1952 indicate a strong reduction in acids from a complete schedule of *Phygon*-lead arsenate (Table 9, Figure 1). There was no such reduction from the use of *Crag 341* or *Captan*. It should be pointed out, however, that *Phygon* was used throughout the season and not as an early season spray as is commonly recommended. A similar trend was noted, however, in Hudson Valley fruit sprayed on a split schedule, with *Phygon* early and ferbam late.

A further comparison of *Captan* with sulfur-ferbam gave the results reported in Table 10, which show a strong tendency towards increased

[1]Krotkov *et al.*, 1951, shows that about 80 per cent of the titratable acidity of the McIntosh apple is malic acid.

TABLE 7. EFFECT OF SPRAYS ON TITRATABLE ACIDITY

	1949 McIntosh	
Non-arsenical (av. of 5 trees)	Arsenical (av. of 2 trees)	Difference in favor of non-arsenical
% .52	% .41	% .11
	1950 McIntosh	
Non-arsenical (av. of 3 trees)	Arsenical (av. of 3 trees)	
.65	.60	.05
	1951 McIntosh	
Non-arsenical (av. of 4 trees)	Arsenical (av. of 4 trees)	
.56	.53	.03
	1952 McIntosh	
Non-arsenical (av. of 14 trees)	Arsenical (av. of 12 trees)	
.82 (July 21)	.82	.00
.75 (August 15)	.72	.03
.74 (September 15)	.71	.03
	1950 Baldwins	
Non-arsenical (av. of 3 trees)	Arsenical (av. of 3 trees)	
.66	.58	.08

TABLE 8. RELATION OF PHOSPHORUS AND TOTAL ACIDITY

	Acidity per cent	Phosphorus ppm	
7/21	.60 — .70	156	
	.71 — .80	132	No difference
	.81 — .90	124	
	.91 — 1.00	137	
8/15	.60 — .70	110	
	.71 — .80	119	Trend upwards
	.81 — .90	130	
9/15	.61 — .70	100	
	.71 — .80	99	Trend upwards
	.81 — .90	121	
	.91 — 1.00	132	

acids when *Captan* was used. The results are probably more important because the data includes results from non-arsenical-sulfur-ferbam treatments, which have in general shown a tendency to increase acids (Table 7).

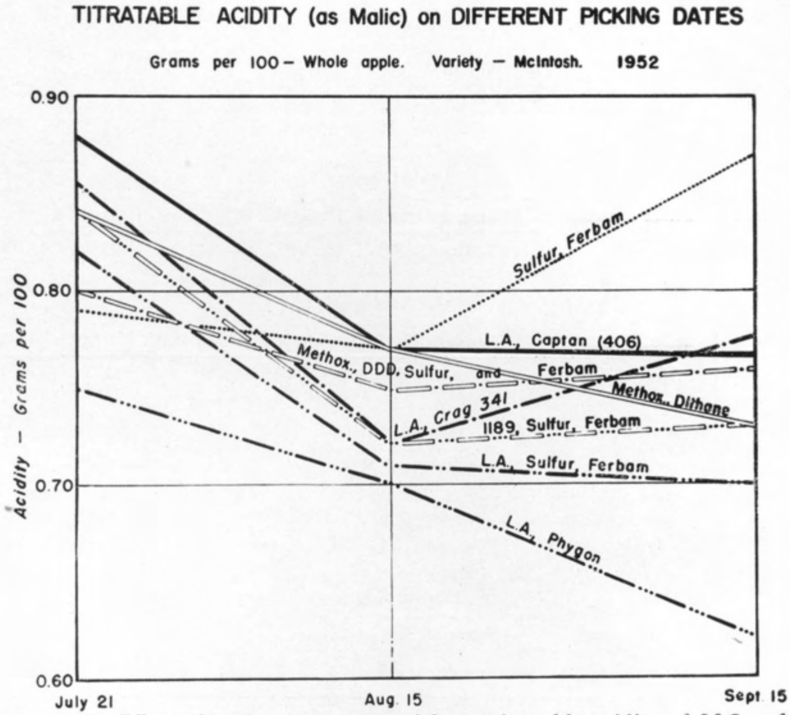

Figure 1. Effect of various spray materials on titratable acidity of McIntosh apples.

TABLE 9. EFFECT OF SPRAYS ON TITRATABLE ACIDITY OF APPLES. COMPARISON OF LEAD ARSENATE-"PHYGON" AND LEAD ARSENATE-OTHER FUNGICIDES

Lead arsenate-other fungicides[1]	Lead arsenate-*Phygon*	Difference in favor of other fungicides
%	%	
.88	.80	.08
.96	.79	.17
.78	.66	.12
.74	.76	–.02
.69	.61	.08
.81	.70	.11
.69	.76	.07
.68	.56	.12
.78	.70	.08
.81	.63	.18
.67	.58	.09
.77	.69	.11

P below .01 – highly significant

[1]Averages of three treatments receiving either *Captan, Crag 341,* or sulfur-ferbam combined with lead arsenate.

TABLE 10. EFFECT OF LEAD ARSENATE PLUS "CAPTAN" AND OTHER FUNGICIDES ON TITRATABLE ACIDITY

Lead arsenate-*Captan*	Sulfur-ferbam[1]	Difference in favor of *Captan*
%	%	
.72	.70	.02
.83	.79	.04
.75	.66	.09
.90	.88	.02
.92	.84	.08
.82	.72	.10
.81	.68	.13
.75	.75	.00
.75	.66	.09
.81	.74	.06

Very highly significant

[1]With or without lead arsenate – average of 3 treatments.

Effect of Pesticides on Ascorbic Acid Content

Ascorbic acid determination was made on each of four ripe apples (picked in September, 1950) from each of six pesticide treatments, involving two varieties, using the Morrell modification of Bessy's method for reduced ascorbic acid. The findings are shown in Table 11. The analysis of variance showed no differences due to either the insecticide or the fungicide.

TABLE 11. ASCORBIC ACID CONTENT OF RAW APPLES FROM SIX PESTICIDE TREATMENTS Mg. per 100 gm. Edible Portion

	Variety			
	McIntosh		Baldwin	
Treatment	Mean[1]	Range	Mean[1]	Range
Lead arsenate-sulfur	3.17	2.56 – 3.62	10.62	7.31 – 13.56
Lead arsenate-thiram	1.88	1.25 – 2.31	9.20	7.44 – 11.31
Lead arsenate-thiram-*Karathane*	3.09	1.94 – 5.31	11.30	9.44 – 12.63
DDD-chlordane-sulfur	2.39	1.62 – 2.81	10.67	9.81 – 12.56
DDD-chlordane-thiram	2.42	1.75 – 3.38	10.62	9.00 – 13.25
DDD-chlordane-thiram-*Karathane*	1.70	1.25 – 2.25	10.23	8.00 – 12.56
Insecticide components:				
Lead arsenate	2.71		10.38	
DDD-chlordane	2.17		10.51	
Fungicide components:				
Sulfur	2.78		10.65	
Thiram	2.15		9.91	
Thiram-*Karathane*	2.40		10.77	

[1]Each mean is the average value for four apples analyzed individually.

Effect of Sprays on Mineral Content

Changes in the mineral content of apples sprayed with different chemicals were first noticed in 1951 (Table 12). The principal differences were apparently between arsenicals and non-arsenicals, and the minerals affected were potassium, calcium, phosphorus and boron. Analyses in 1952 both of leaves and fruit confirmed these findings (Tables 13 and 14).

TABLE 12. EFFECT OF INSECTICIDES ON MINERAL CONSTITUENTS OF THE APPLE
1951 — Figures are ppm[1]

Treatment	Potassium	Calcium	Phosphorus	Boron
Non-arsenical	992	43	101	2.2
Arsenical	906	32	94	1.5

[1]Analyses made after the fourth year in which the trees had been sprayed with arsenicals and non-arsenicals. All figures are averages of four treatments; samples from three or four plots in each treatment were combined.

In the case of fruit (Tables 12 and 13), these elements were increased by non-arsenical sprays in every comparison but one. In the leaves (Table 14), the non-arsenical treatments produced a higher mineral content in every comparison. Trees receiving no insecticide at all produced fruit containing more minerals than those treated with non-arsenicals. The same general trend occurred in the leaves, but was not so consistent.

Studies of data from leaves and fruits in 1952 failed to reveal any outstanding relation between fungicide and mineral levels. *Phygon* does show a slight tendency to diminish potassium and boron, but the data are not significant statistically and are not presented here.

TABLE 13. EFFECT OF SPRAYS ON THE MINERAL CONSTITUENTS OF APPLES
McIntosh—Burton Orchard—1952
Figures are ppm

Spray	Date Collected	K	Ca	P	Mg	B	
Arsenical	July 21	1451	93	123	104	1.7	
	Aug.15	1136	113	113	80	2.0	Av. of
	Sept. 15	1120	81	110	69	2.3	14 trees
Non-	July 21	1579	98	140	110	2.1	
Arsenical	Aug. 15	1273	109	119	86	2.4	Av. of
	Sept. 15	1179	74	113	68	2.8	12 trees
No	July 21	1796	129	166	117	2.1	
Insecticide	Aug. 15	1203	108	137	86	2.9	Av. of
	Sept. 15	1316	66	134	76	3.2	3 trees

Fruit:

K Significance — P below 0.1 level
Ca Significance — P to .05 level (not significant)
P Significance — P to .01 level
Mg Significance — P to .01 level
B Significance — P to .01 level

TABLE 14. EFFECT OF SPRAYS ON MINERAL CONSTITUENTS OF APPLE LEAVES
McIntosh—Burton Orchard—1952

Spray	Date Collected	K	Ca	P	Mg	B
		%	%	%	%	ppm
Arsenical	May 26	1.67	.69	.23	.22	14
	June 12	1.54	.60	.17	.24	12
Non-Arsenical	May 26	1.90	.81	.29	.25	17
	June 12	1.73	.66	.21	.25	16
No Insecticide	May 26	1.84	.89	.23	.27	14
	June 12	1.58	.80	.20	.24	15

Based on dry weight

Relation Between Some Minerals, Sugar and Ascorbic Acid in Sprayed Apples

The relation between the quantities of minerals, sugar and ascorbic acid found in fruit juice (regardless of treatment) is shown in Table 15. The correlations have been grouped as negative and positive. For example, when calcium content was high, magnesium content was low, and vice versa. The same appeared to be true of calcium and boron. There was a positive correlation between the content of boron and sucrose, and magnesium and phosphorus. Many of these relationships could not be demonstrated by analysis of the entire apple. However, the positive correlation between boron and sucrose in juice was also found in apples (Table 16). In addition, there was a positive correlation between boron and potassium (Table 17).

TABLE 15. RELATION OF SEVERAL ELEMENTS IN SPRAYED APPLES

Source of Apples	New York 1950 - 51	New York 1950 - 51	Conn. cider from several varieties	Conn. Delicious	Conn. McIntosh
	Negative Correlation[1]				
Calcium-magnesium	×	×	×	×	?
Calcium-boron	×	?	×	×	×
Phosphorus-copper	?	×	×	—1	?
Sucrose-copper	?	×	×	?	?
Ascorbic acid-copper	×	—	—	—	—
	Positive Correlation[2]				
Sucrose-boron	?	×	×	?	×
Phosphorus-boron	×	×	×	×	×
Magnesium-phosphorus	×	×	×	×	×
Magnesium-boron	×	×	×	×	×

[1]The higher the calcium, the lower the magnesium, etc.
[2]The higher the sucrose, the higher the boron, etc.

Table 16. Relation Of Boron And Sucrose In McIntosh Apples
Burton Orchard—1952[1]

Analysis of Whole Apples

Picked 8/15		Picked 9/15	
Boron ppm	Sucrose Per cent	Boron ppm	Sucrose per cent
.9 – 2.0	1.50	1.6 – 2.0	2.98
2.1 – 3.0	1.57	2.1 – 3.0	3.04
3.1 – 3.7	1.73	3.1 – 4.0	3.21

[1]Analyses made from ground pulp including juice.

Table 17. Relation Of Potassium To Boron In The Whole Apple
Analyses of McIntosh Apples Sprayed with
Non-arsenical Sprays—Picked August 15, 1952

Boron ppm	Potassium ppm
1.3 – 2.0	1010
2.0 – 2.5	1280
2.5 – 3.0	1315
3.0 – 3.1	1489

The thought naturally occurs that these relationships may occur earlier than harvest or during growth and maturation. With this in mind a series of chemical analyses was made on apples picked at monthly intervals. The positive correlation between boron and magnesium did not appear in apples picked July 21, but began to be apparent in the August 15 collection. There was also a definite trend in the relation between boron and sucrose in the August 15 and September 15 harvest (Table 16), which did not occur in the July 21 collection. As can be seen in Figure 2, there is, as the season progresses, a definite downward trend in certain mineral constituents of the apple except for boron. This was thought at first to mean that the fruit is drawing continually on the leaves for boron. However, our figures (Table 18) indicate the same upward trend of boron in the leaves so that boron is apparently not being taken at the expense of the foliage. It would seem logical to supply boron at this time to be sure of an adequate amount, especially in view of the depressing effect of lead arsenate. Boron is known to form rather easily such compounds as boro-arsenites,[1] boro-tungstates, and boro-tartrates. This offers a possible explanation of boron depression by arsenates, especially if such reactions occur before the boron reaches the leaf or fruit.

[1]Thorpe, J. F., and Whitely, M. A. Dictionary of Applied Chemistry, Vol. II, p. 47.

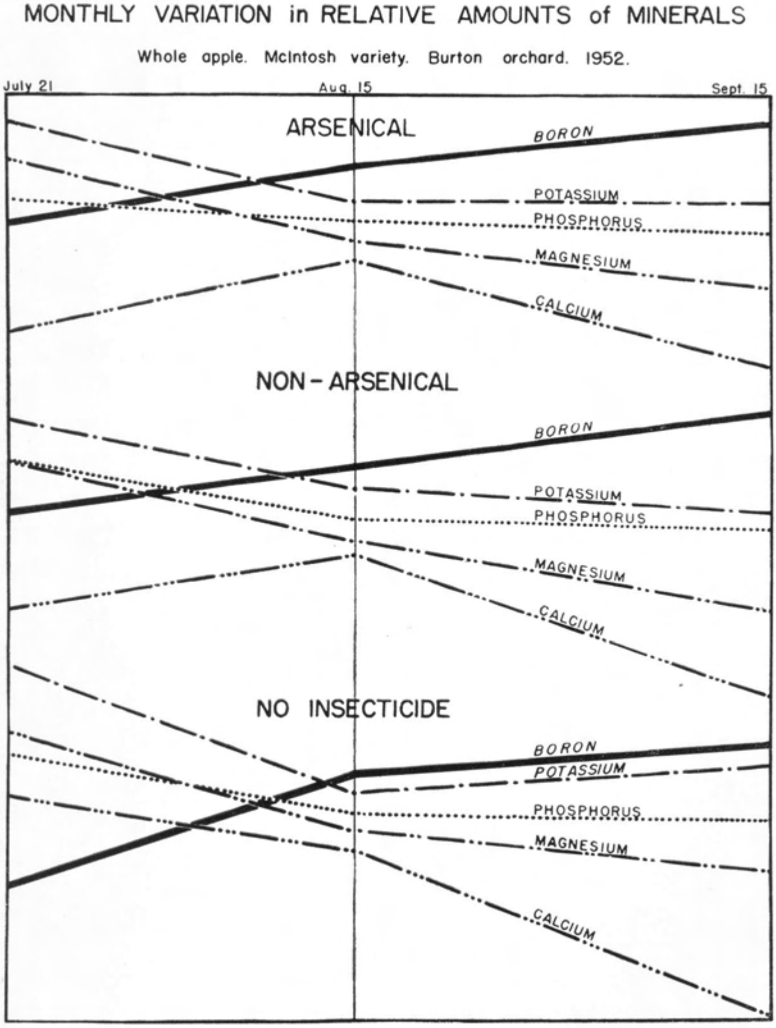

Figure 2. Effect of spray materials on amounts of mineral constituents of McIntosh apples.

Low boron is said (Smith and Reuther, 1951) to retard potassium and accentuate magnesium accumulation in citrus. Low boron as associated with low potassium in apples was not noticed until August, 1952 (Table 17). An examination of these figures shows that there is evidently a rather serious derangement in the mineral nutrition of the apple as evidenced by depression of boron by lead arsenate.

TABLE 18. TRENDS IN BORON CONTENT OF McINTOSH LEAVES WITH DIFFERENT TREATMENTS—1952

Treatment	Dates	Boron ppm
Lead arsenate-sulfur-ferbam	June 5	11
	June 12	13
	July[1]	18
	August[1]	18
	September[1]	20
Lead arsenate-*Phygon*	June 5	13
	June 12	12
	July[1]	22
	August[1]	24
	September[1]	30
Methoxychlor-nabam[2]	June 5	29
	June 12	17
	July[1]	18
	August[1]	21
	September[1]	20
"1189"-sulfur-ferbam	June 5	11
	June 12	16
	July[1]	32
	August[1]	28
	September[1]	28

[1]Composites of several collections.
[2]*Dithane.*

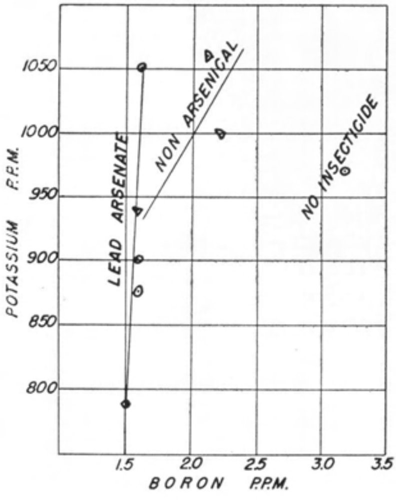

Figure 3.
Relation between amounts of boron and phosphorus in McIntosh apples sprayed with lead arsenate, non-arsenical insecticides and no insecticide.

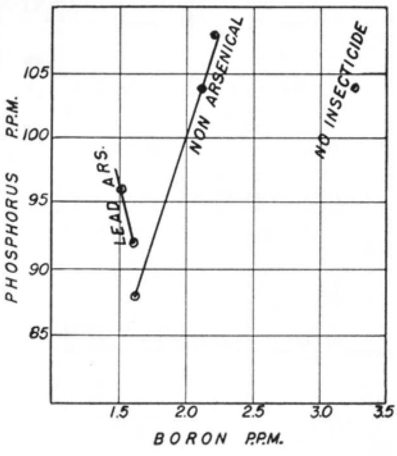

Figure 4.
Relation between boron and potassium content of McIntosh apples sprayed with lead arsenate, non-arsenical insecticides and no insecticide.

TABLE 19. TRENDS IN POTASSIUM CONTENT OF McINTOSH LEAVES WITH DIFFERENT TREATMENTS, 1952 (INDIVIDUAL TREES)

Treatment	Dates	Potassium Per cent dry wt.
Lead arsenate-sulfur-ferbam	May 26	1.69
	June 12	1.50
	July[1]	1.17
	August[1]	1.31
	September[1]	1.14
Lead arsenate-*Phygon*	May 26	1.58
	June 12	1.54
	July[1]	1.45
	August[1]	1.26
	September[1]	1.18
Methoxychlor-nabam[2]	June 5	1.72
	June 12	1.66
	July[1]	1.41
	August[1]	1.07
	September[1]	1.03
"1189"-sulfur-ferbam	June 5	2.26
	June 12	1.80
	July[1]	1.59
	August[1]	1.45
	September[1]	1.31

[1]Composites of several collections.
[2]*Dithane.*

According to Goodall and Gregory (1947), boron deficiency in fruit may occur when the boron content is 3 and 4 ppm, though symptoms have apparently been reported at higher figures. Heinicke *et al.* (1942) found deficiency symptoms in McIntosh apples with 2.48 ppm, but none from 4.62 to 5.43 ppm. Three of our four lead arsenate treatments averaged below 2.48 ppm in 1952, but none of the non-arsenical treatments were below that figure. The only ones approaching 4.62 ppm were non-arsenicals (4.5 ppm) and only one of the arsenical-sprayed group reached 3 ppm. Heinicke *et al.* suggest that boron levels not quite low enough to cause deficiency symptoms in the fruit might cause premature fruit drop. It is evident, therefore, that apples on the border line of deficiency would be harmed considerably by arsenicals unless efforts were made to increase boron by sprays or ground applications.

Similarly, potassium levels in the leaves during May and June were frequently below levels for optimum growth (1.7 per cent[1]) in the trees treated with arsenicals, whereas the non-arsenicals were above. (Refer to Table 14).

After two years of investigation, the following general conclusions in regard to the effect of pesticides on the mineral content of apples seemed to be indicated:

[1]Goodall and Gregory, p. 17.

1. Lead arsenate depressed the uptake of minerals, such as potassium, calcium, phosphorus, and boron.

2. Boron is evidently very important in the metabolism of the apple and is probably associated with formation of sugar.

3. Certain negative and positive relationships showed up on pairing the various elements and plotting one against the other. This finding resulted from analyses of juices, not whole apples.

4. Examination of the graphs (mentioned in 3) indicates that some of the relationships are altered by the use of insecticides, especially lead arsenate.

EFFECT OF SPRAYS ON PHYSICAL APPEARANCE AND YIELD

Effect of Sprays on Russetting

Going back to 1948 and comparing McIntosh apples sprayed with non-arsenical-sulfur, and with lead arsenate-sulfur, we found that a reduction in total russetting resulted from omission of arsenical sprays. In Baldwin this reduction was from 71 to 55 per cent and in Gravenstein from 41 to 2 per cent. During 1949, we were able to reduce russetting in Baldwins sprayed with arsenicals by addition of soy bean oil or silica gel buffers. Lead arsenate-sulfur caused 36 per cent russet and parathion-sulfur only 15 per cent.

In 1950 russetting on Gravensteins was reduced from a 12 to 25 per cent range where sulfur was used with lead arsenate to an average of 1.8 per cent for non-sulfur-lead arsenate. On Baldwins the average for sulfur-lead arsenate was 39.6 per cent, whereas non-sulfur-lead arsenate treatments varied from 6.5 to 13.5 per cent. For non-arsenical-sulfur the figures were 13.2, 18.9 and 25.5 per cent.

So far indications were, therefore, some reduction in russetting from omission of either sulfur or lead arsenate. Direct comparison of non-sulfur-lead arsenate with non-arsenate-sulfur showed less russet with non-sulfur sprays, indicating stronger action of the sulfur in the spray mix.

Logically, substitution for both arsenate and sulfur should give the smoothest Baldwins, provided neither substitute russetted. Our 1952 results showed least russetting from a combination of lead arsenate and *Captan* confirming previous results in regard to sulfur. However, complete substitution, using in this case methoxychlor and nabam, did not help, though omission of lead arsenate from the combination with sulfur-ferbam and substitution of methoxychlor again reduced the russett by about half. For complete substitution, combinations of materials other than methoxychlor and nabam are indicated.

During the years under which russeting has been under observation there has been a rather wide variation in the actual amounts appearing at harvest due to at least two factors. Spray russetting appears to be profoundly affected by midsummer temperatures, since there has usually been a marked increase between fruit thinned in June or July and harvested fruit. Another factor may be amount of fruit on the trees, but to date our information on this point is not too indicative.

For Red Delicious, the picture seems to be different. Dropping lead arsenate from the schedule reduces conspicuous russetting of the type shown in Figure 5. The question arose as to whether methoxychlor combined with various fungicides might also give trouble. Results of this work are given in Table 20. Marked increases in russetting occurred with some combinations as suspected; others, like the methoxychlor-*Captan* mixtures, showed no russetting. Whether the combination or the fungicide is responsible for the high percentage of russetting shown in the last two entries in Table 20 is not apparent in this test.

TABLE 20. EFFECT OF DIFFERENT FUNGICIDES COMBINED WITH METHOXYCHLOR ON RED DELICIOUS RUSSETTING

Material and dosage	Per cent russet
Methoxychlor[1] – *Captan* (3 lbs./100 gals.)	0.0
Methoxychlor – *Crag 341* (1 pt./100 gals.)	1.2
Methoxychlor – thiram (1½ lbs. 75%/100 gals.)	2.3
Methoxychlor – ferbam (1½ lbs. 75%/100 gals.)	0.0
Methoxychlor – nabam (1 qt./100 gals.)	14.9
Methoxychlor – *Phygon* (½ lb./100 gals.)	40.5
Spray dates: April 30, May 14, 28, June 4, 11 (TEPP only), 21, 30, August 5.	

[1]Methoxychlor 3 lbs. to 100 gals, throughout.

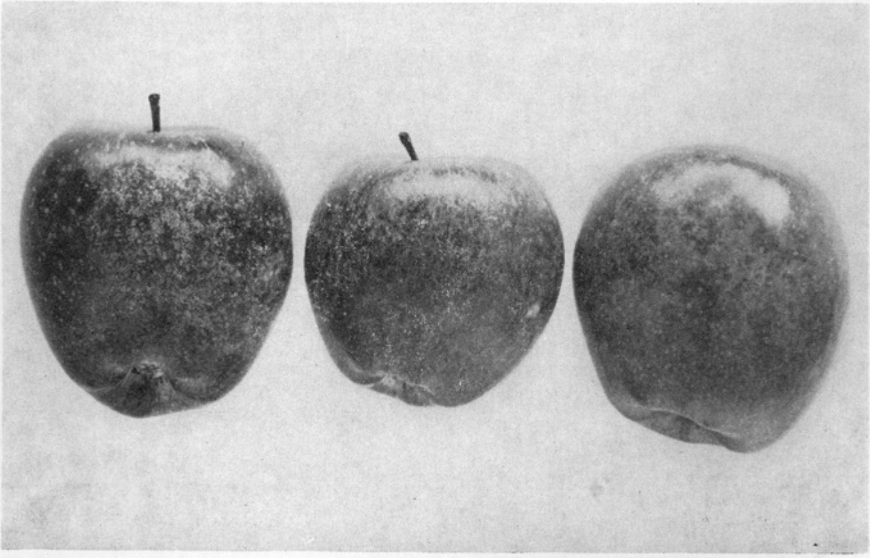

Figure 5. Spray russet on Red Delicious caused largely by lead arsenate.

Effect of Sprays on Sun Scald

Another feature of importance in appearance of the fruit at harvest is sun scald (Figure 6). Our experiments indicate that this condition is definitely associated with applications of sulfur in hot weather. Table 21 gives some of our 1952 results which correspond with those obtained in previous years. 1952 was a particularly bad year for this trouble, and it occurred regardless of variety.

TABLE 21. EFFECT OF SPRAYS ON SUN SCALD

Treatment	Per cent sun scald	
	McIntosh	Baldwin
Lead arsenate – sulfur – ferbam	4.2	8.5
Lead arsenate – *Captan*	.5	.1
Lead arsenate – *Phygon*	.2	.1
Lead arsenate – *Crag 341*	.1	.2
Methoxychlor – sulfur – ferbam	3.9	15.9
Methoxychlor – nabam	.2	.4
"1189" – sulfur – ferbam	5.2	10.8
No insecticide – sulfur – ferbam	1.7	10.6

Probability that *Captan* is better than any other: .02.

Probability that *Captan* is better than any other omitting *Phygon:* .02.

Probability that non-sulfurs are better than sulfurs: less than .01 and nearer .001.

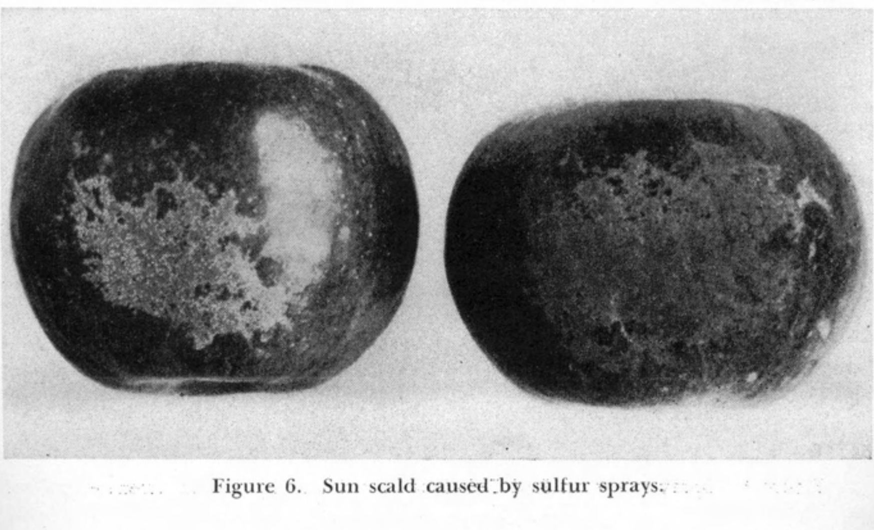

Figure 6. Sun scald caused by sulfur sprays.

Effect of Sprays on Yield

Size and yield are both affected by sprays. Production increases in Connecticut followed the substitution of mild sulfur for lime sulfur in the 1930's. A similar increase recently began to be apparent following substitution of ferbam for sulfur, wherever the substitution was reasonably complete. Similar trends are apparent in experimental blocks following substitution of thiram for sulfur. Increases are especially appar-

Figure 7. Effect of sprays on Delicious apple yield. Upper trees were sprayed with lead arsenate-sulfur, while the trees in the lower picture received applications of lead arsenate-thiram.

Figure 8. Trees in the upper photograph were sprayed with parathion-thiram; those in the lower picture with parathion-sulfur. Note the reduction in yield resulting from the use of sulfur.

ent in the "off" year of trees with a biennial bearing habit, and can be readily detected by the amount of bloom in the "off" season (Figures 7 and 8). The theory has been advanced that ferbam enhances production by reason of the nitrogen contained in the molecule. This may be true. The actual percentage of nitrogen in ferbam is about 10 per cent. At the rate of 1½ pounds of 75 per cent wettable powder per 100 gallons and 10 gallons per tree, this would be the equivalent of only .0125 pounds per tree per application or .125 (1/8 pound) of nitrogen for 10 sprays. Ten pounds of 10-10-10 fertilizer would equal 1 pound of nitrogen per tree per season as compared with .125 pound. Urea, on the other hand, contains 45 per cent nitrogen and applied at the rate of 5 pounds per 100 gallons (10 gallons per tree) would be equivalent to .225 pounds per tree—18 times as much as would be supplied by one spray of ferbam and about twice (1.8) as much as 10 sprays of ferbam. However, the possibility that the nitrogen in ferbam is beneficial cannot be completely ruled out, especially in view of the improvement in tree foliage following application of nitrogen-containing fungicides such as *Karathane* and thiram. Thiram contains 11.6 per cent nitrogen and *Karathane* about the same. Stimulation of tree growth from *Karathane* has been marked, though no check has been made by us on increased yield. It should be noted here that all improvements in yield as shown in Table 22 came from trees that were fertilized in the usual manner each year.

TABLE 22. YIELD OF RED DELICIOUS IN THE "OFF" YEAR FOLLOWING APPLICATIONS OF SEVERAL INSECTICIDE-FUNGICIDES THE PREVIOUS SEASON[1]

Treatment	Yield
Sulfur-lead arsenate	1/5 box
Ferbam-lead arsenate	8½ boxes
Thiram-lead arsenate	3½ boxes
Sulfur-methoxychlor	1½ boxes
Ferbam-methoxychlor	2½ boxes
Thiram-methoxychlor	3 boxes

[1]All trees bearing equally in 1951. Increase from ferbam-lead arsenate probably above normal. See also Figures 7 and 8.

Effect of Sprays on Color

Color in apples is dependent on a number of factors which are sometimes difficult to separate. One of these is the kind of spray. Another is nutrition as influenced by fertilizers, location, and variety or strain of apple. Sprays may affect color in several ways: (1) by blocking action of sunlight, (2) by bleaching, and (3) by changes in the rate of ripening. Any black material, if it remains on the fruit continually throughout the summer, will produce a blotchy apple at harvest. This is shown in Figure 10. Experiments at the Henry Orchard in Wallingford indicate an increase in 75 per cent-colored fruit of the Opalescent variety sprayed with thiram-lead arsenate as compared with ferbam-lead arsenate (Table 23). The Opalescent is a variety that colors well normally, and the figures are perhaps not too impressive. Nevertheless, comparison of these two materials on other varieties such as Baldwin, McIntosh, and Delicious support strongly the evidence obtained in the Henry Orchard.

Bleaching effects are particularly noticeable with sulfur sprays (Figure 9). Such action is more pronounced in hot weather and is probably the same kind of action that produces sun or sulfur scald (Figure 6).

Influence on the rate of ripening is best seen in such compounds as *Tag*, which is known to delay the date of harvest, and *Crag 341* which hastens it. Even sulfur-lead arsenate sprays seem to have some delaying action on the rate of coloring.[1] This was particularly noticeable in 1950 and 1951 following heavy applications. There is a strong tendency for complete sulfur-lead arsenate sprays to produce an apple which either has less color or a dull, unattractive finish. This has been seen not only from Mt. Carmel, but also in several samples from Poughkeepsie, N. Y. The dull finish mentioned is perhaps more noticeable in Baldwin than in McIntosh, but occurs even where part of the sulfur is left out and ferbam substituted. It has been largely eliminated by substituting either a non-sulfur fungicide or a chlorinated hydrocarbon insecticide.

In view of the above, it would seem to be inadvisable to use sulfur after the first or second cover spray—to avoid sun scald, bleaching, and possibly reduced production.

Table 23. Effect Of Sprays On Color
Variety Opalescent

Treatment	Estimated color		
	75%	50%	25%
75% ferbam-lead arsenate	57.4	35.5	7.1
50% thiram-lead arsenate	65.1	28.6	6.2

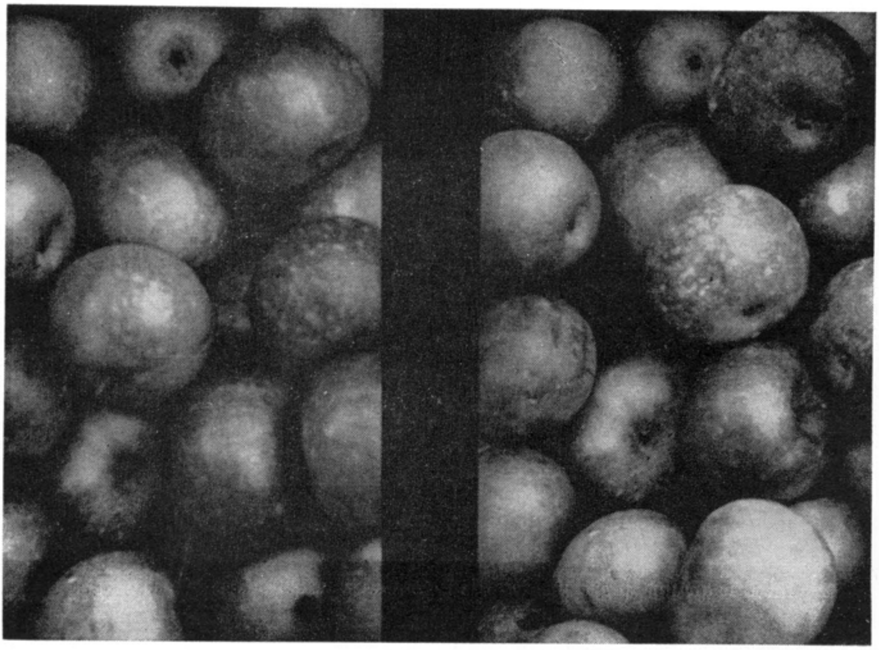

Figure 9. Excessive spray residue. Left, wiped; right, unwiped fruit.

[1]This in spite of a slight advance in maturity dates for sulfurs compared with ferbam.

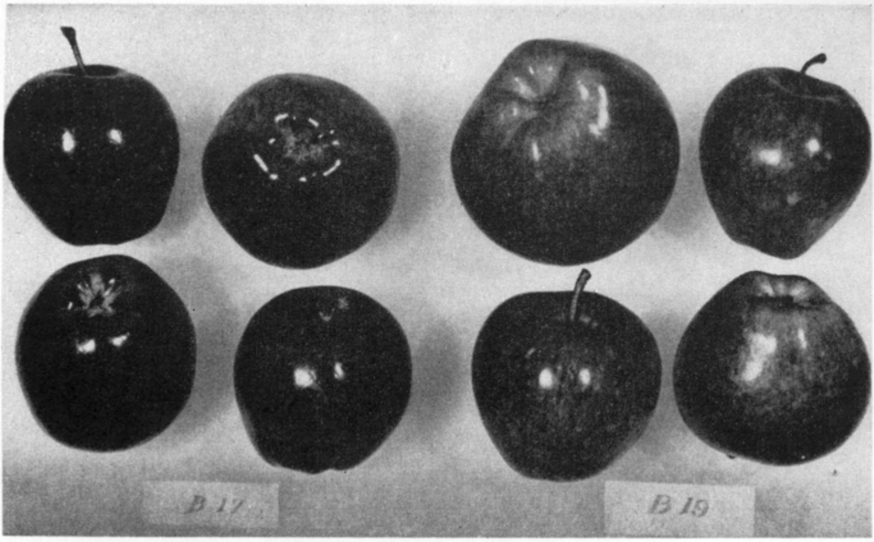

Figure 10. Mottling resulting from the use of ferbam and methoxychlor throughout the season is shown in the four apples on the right. Apples at left were treated with thiram and methoxychlor.

EFFECT OF SPRAYS ON FLAVOR

It has usually been assumed that sprays had no effect on the flavor of fruit unless an "off-flavor" was produced. It is evident, however, that pesticides may influence the content of sugars, acids, and possibly other constituents of the fruit, and thereby affect flavor.

The only method of determining flavor has been by means of taste or preference tests. However, preferences may vary from individual to individual and from time to time in the same individual. During the course of the investigations reported here, methods were improved, with the final system (devised by Dr. Chester I. Bliss)[1] designed so that fruit from each treatment is compared directly with fruit from every other and tested in reverse order in replications.

The original tests were made using fresh apples. When more than one apple was selected from a treatment, the difference between apples was sometimes as great as between treatments. The use of sauces or purées, prepared in a standard manner, made it possible to obtain a more homogeneous and representative sample.

Maturity of the fruit was also a serious problem. Use of a pressure gauge for selection of apples of uniform firmness helped solve this problem. No apple was used that fell above or below a limit of plus or minus one pound on the gauge.

It was also found that when apples were held in cold storage, differences in flavor became less distinct. To overcome this, sauce was made early in the season and frozen.

[1]Biometrician, The Connecticut Agricultural Experiment Station.

Palatability Test Procedures and Some Preliminary Findings

Three series of taste tests were carried out on apples from different spray treatments at the Storrs Agricultural Experiment Station and the School of Home Economics of the University of Connecticut in the fall of 1950. The procedures developed here were followed in general in subsequent tests both at Storrs and at The Connecticut Agricultural Experiment Station. The spray treatments involved were:

1. Lead arsenate-sulfur
2. Lead arsenate-thiram
3. Lead arsenate-thiram-*Karathane*
4. DDD-chlordane-sulfur
5. DDD-chlordane-thiram
6. DDD-chlordane-thiram-*Karathane*

Two varieties of apples thus treated were tested, namely, McIntosh and Baldwin. Two groups served as tasters: (a) students and faculty members at the University and (b) sixth, seventh, and eighth grade children in an elementary school. The apples were tasted both in the raw state and as sauce by the first group, only in the raw state by the children.

The fruit was washed in a detergent suds and rinsed thoroughly. Apples for tasting raw were sectioned and each section wrapped in cellophane. Apples for sauce were quartered, cored, and cut into sixteenths. Sections from each of 10 apples, to make a 300-gm. portion, were boiled in 150 ml. of water for 15 to 18 minutes, then sieved. All samples were at room temperature when tasted. The six samples (only four at a time for the children), presented at random, were ranked in order of preference, with no ties allowed. Previous to analysis, the ranks were transformed to scores for normalizing ordinal data.

A summary of the results with the adult tasters is presented in Tables 24 and 25. It is obvious that these tasters preferred fruit sprayed with DDD-chlordane over that sprayed with lead arsenate. In the apple sauce, but not in the raw apples, thiram-*Karathane* was preferred over thiram alone, and sulfur-sprayed fruit had the lowest score. Baldwin apples showed greater differences as a result of the different sprays than did McIntosh.

The palatability scores for the sixth and seventh grade children showed no significant differences between treatments. In the eighth grade DDD-chlordane treatment was preferred to lead arsenate, but no significant preference was indicated for any fungicide.

Relation Between Chemical Analysis and Flavor

It is possible to compare preference for fruit with the results of determinations of pH, and content of minerals, sugars, and acids.

TABLE 24. TOTAL PALATABILITY SCORES (ADULT TASTERS) FOR APPLESAUCE ARRANGED BY DATES

			Spray components						
			Insecticides			Fungicides			
Date	No. of tasters	Variety	Lead arsenate	DDD-chlordane	Significance	Sulfur	Thiram	Thiram-*Karathane*	Significance
Nov. 6	26	McIntosh	.72	–.72	. . .	8.86	–6.97	–1.89	. . .
9	28	McIntosh	–16.08	16.08	P<.01	–9.93	9.87	.06	P<.20
20	27	McIntosh	3.16	–3.16	. . .	–15.03	11.00	4.03	P<.05
27	25	McIntosh	1.88	–1.88	. . .	4.55	–12.24	7.69	P<.10
Total	106	McIntosh	–10.32	10.32	. . .	–11.55	1.66	9.89	. . .
Dec. 12	27	Baldwin	–21.86	21.86	P<.001	–11.61	14.32	–2.71	P<.05
14	29	Baldwin	–21.68	21.68	P<.001	6.67	–5.58	–1.09	. . .
Jan. 18	25	Baldwin	4.57	–4.57	. . .	–11.75	–8.38	20.13	P<.001
24	26	Baldwin	–12.74	12.74	P<.01	–30.29	15.07	15.22	P<.001
Total	107	Baldwin	–51.71	51.71	P<.001	–46.98	15.43	31.55	P<.001
Grand Total	213		–62.03	62.03	P<.001	–58.53	17.09	41.44	P<.001

TABLE 25. TOTAL PALATABILITY SCORES (ADULT TASTERS) FOR RAW APPLES ARRANGED BY DATES

Date	No. of tasters	Variety	Spray components						
			Insecticides			Fungicides			
			Lead arsenate	DDD-chlordane	Significance	Sulfur	Thiram	Thiram-*Karathane*	Significance
Nov. 2	28	McIntosh	6.05	–6.05	. . .	2.56	–2.92	.36	. . .
13	28	McIntosh	6.17	–6.17	. . .	3.42	–8.10	4.68	. . .
17	32	McIntosh	–6.99	6.99	. . .	19.04	–23.45	4.41	P<.001
Total	88	McIntosh	5.23	–5.23	. . .	25.02	–34.47	9.45	P<.01
Dec. 4	30	Baldwin	–6.17	6.17	. . .	3.74	13.54	–17.28	P<.01
7	30	Baldwin	–10.64	10.64	P<.10	–14.82	12.43	2.39	P<.05
Jan. 15	30	Baldwin	–18.00	18.00	P<.01	–2.06	1.26	.80	. . .
22	26	Baldwin	–18.66	18.66	P<.01	2.31	4.01	–6.32	. . .
Total	116	Baldwin	–53.47	53.47	P<.001	–10.83	31.24	–20.41	P<.05
Grand Total	204		–48.24	48.24	P<.01	14.19	–3.23	–10.96	. . .

Relation Between pH and Flavor

In 1951, nine samples of cider were tested by 51 growers, and the four best were then submitted to a trained panel for selection of first, second and third prizes. The cider was analyzed (Table 26) and the samples selected as the four best were observed to have a high pH and were also high in calcium, magnesium, total solids and sucrose.

However, in 1952, analyses of fruit sprayed with different materials showed no differences in pH attributable to treatment, and preferences shown by taste panels were not associated with high pH. Considerably more study of this phase therefore seems to be indicated.

TABLE 26. ANALYSES OF APPLE CIDERS

Sample	Solids, gm./100cc.	Ash, gm./100cc.	Total acidity as malic acid, gm./100cc.	Invert sugar, gm./100cc.	Sucrose, gm./100cc.	pH	Selected by panel
A	12.19	0.21	0.36	9.14	1.42	3.55	
B	12.33	0.22	0.35	7.91	1.85	3.58	*
C	12.43	0.23	0.36	9.09	1.61	3.60	*
D	12.67	0.21	0.36	8.91	1.90	3.50	
E	1.49	0.17	0.48	0.30	0.00	3.32	
F	11.65	0.19	0.26	7.84	1.22	3.65	*
G	10.64	0.20	0.35	8.26	0.99	3.52	*
H	10.61	0.20	0.36	8.22	0.88	3.53	
J	11.51	0.20	0.36	8.65	1.11	3.52	

Sample	Alcohol, per cent by volume	K, ppm	Ca, ppm	Mg, ppm	P, ppm	Fe, ppm	Cu, ppm	B, ppm	Zn, ppm	
A	....	650	30	40	68	1.9	2.0	2.0	5.0	
B	....	580	32	49	68	4.0	1.1	2.3	3.3	*
C	trace	760	33	50	84	2.7	1.3	2.0	5.0	*
D	....	540	31	52	84	2.6	2.1	2.0	3.9	
E	5.14	770	29	52	68	2.5	1.6	1.8	1.9	
F	....	830	31	43	116	2.8	1.6	4.0	4.1	*
G	....	970	36	38	56	5.4	2.3	1.8	5.0	*
H	....	860	32	42	56	5.4	2.4	1.7	2.5	
J	....	830	30	47	84	4.3	1.5	1.1	2.3	

Relation Between Minerals and Flavor

Variations in mineral content probably have little influence on consumer preference except indirectly. For example, as already mentioned, high boron content is usually associated with high sucrose content, and thus boron may have an indirect influence on flavor. In view of occasional preferences obtained for fruit treated with lead arsenate-*Crag 341* over the standard with sulfur-ferbam only, taste panel results were compared with mineral contents in this particular series to determine whether there might possibly be any direct connection. None could be seen. The only evident differences in mineral content are those listed in Tables 13 and 14, comparing arsenicals and non-arsenicals.

These are significant by statistical analyses. Whether these differences are or have been responsible in any way for preferences in the first few years for non-arsenicals (seen in fruit from Waltham, Masachusetts) is unknown. Flavor seems to depend much more on sugars and acids, and minerals as such probably have little influence except where directly correlated with sugars or acids.

Relation Between Sugars and Flavor

That total sugars influence acceptability in an apple appears almost self-evident. It is believed to be largely responsible for preferences for certain varieties or for apples that have been allowed to become tree ripened (Table 27). Evidence for this preference in sprayed fruit is often apparent in non-arsenicals, which frequently rate higher in sugar content than arsenicals. On the other hand, lead arsenate-*Crag 341*, which increased the sugar definitely in 1952 has been somewhat erratic in its performance when presented to taste panels, a fact not completely understood at this time. Many preferences for fruit sprayed with it have been registered, however.

TABLE 27. EFFECT OF SUGAR CONTENT ON FLAVOR. TASTE PREFERENCES IN RELATION TO TOTAL SUGARS FROM ANALYSES OF JUICE

Poughkeepsie—McIntosh—1950

Total sugars	Titratable acidity	Percentage of taste tests rating better than standard[2]
11.15[1]	.39	66.7
11.12	.39	78.6
11.11	.39	61.3
10.92	.49	60.6
9.93	.39	31.8
10.19	.38	52.6
10.91	.43	42.1

[1]Sugar content of the standard was determined as 10.52 per cent.
[2]Unless the rating was better than 50 per cent in these tests, they were considered no better than the standard. All of those rating above 60 per cent had ferbam only in the cover sprays.

Relation Between Acids and Flavor

Several years' results with taste panels convinces us that acids also play an important part in taste selection of apples. For example, McIntosh apples treated with sprays containing *Phygon* plus lead arsenate in 1952 showed a low titratable acidity throughout the season. These apples rated low in taste panel preferences, in spite of the fact that sugars were high (equal to five of the eight non-*Phygon* treatments, only lower than two). This evidence indicates that the low acidity was at least partly responsible for the poor showing of the treatment.

Figure 2 shows the trend in acid content of apples sprayed with the different treatments. According to Krotkov (1951) the titratable acidity drops almost continuously after mid-July. His charts (Figures 2 and 4) do, however, show a temporary rise in acidity during the first half of September, although what the meaning of it is, is not clear or explained. (Spray treatments are not given.)

It is evident from our work that different titratable acidities are produced with different sprays and that acidity is a factor in determining preferences (Table 28). That acid content at harvest may possibly be correlated with firmness at the end of storage is also indicated (Table 29).

TABLE 28. EFFECT OF TITRATABLE ACIDITY ON PREFERENCE IN TASTE TESTS. TOTAL SUGARS EQUAL IN AMOUNT

Titratable acidity		
A	B	Preference for A over B
.70	.62	2.3 to 1
.76	.62	2.0 to 1
.76	.70	1.5 to 1
.78	.77	1.1 to 1

TABLE 29. RELATION BETWEEN TOTAL ACIDITY AND PRESSURE WHEN TAKEN FROM STORAGE FIVE MONTHS LATER

	Total acidity at start	Pressure after 5 months
1	.87	9.2
2	.78	8.7
3	.77	8.9
4	.76	8.6
5	.73	8.5
6	.73	8.4
7	.70	8.25
8	.62	8.16

The Sugar-Acid Ratio

Differences in the sugar/acid ratio as found in the 1952 McIntosh from the Burton Orchard are given in Table 30, from the September 15 harvest.

The high ratio for lead arsenate-*Phygon* is probably the result of low titratable acidity, and it reflects the taste panel preferences since No. 1 was rated low and No. 8 fairly high. No. 2 (lead arsenate-sulfur-ferbam) is significantly lower in the 1952 taste tests than all others. No. 1 was considerably below No. 2 in preference and also below No. 6. It cannot be safely assumed, however, that such a table of sugar-acid ratios will always give us an accurate index of taste preferences, because it is plainly possible to get the same figures with either a high or a low sugar content.

TABLE 30. SUGAR/ACID RATIO IN APPLES AS INFLUENCED BY SPRAYS

	Spray	Sugar/acid ratio
1	Lead arsenate-*Phygon*	17.5
2	Lead arsenate-sulfur-ferbam	15.4
3	Lead arsenate-*Captan*	15.0
4	Lead arsenate-*Crag 341*	14.8
5	*"1189"*-sulfur-ferbam	14.8
6	Methoxychlor-TDE-sulfur-ferbam	14.6
7	Methoxychlor-nabam	14.1
8	Sulfur-ferbam, no insecticide	13.6

Effect of Individual Spray Materials on Quality

Lead Arsenate

In view of consistent results over a number of years, including 1952, and in view of data already presented on depression of minerals and titratable acidity, it is apparent that more flavorsome fruit of some varieties can be produced without arsenate of lead. From the first, these differences have been more apparent in Gravenstein and Baldwin than other varieties, but they also showed up in 1951 in Cortland and in 1952 in McIntosh. Of the varieties tested, McIntosh was least affected. Note the significance in Tables 24 and 25.

In this connection it would be well to refer to Table 20 and Figure 5, which show the increased russetting and the type of injury produced by lead arsenate-sulfur. From this, it would seem that substitution for lead arsenate wherever possible would be beneficial from the quality standpoint *provided* no reactions occurred which produced results worse than lead arsenate (off-flavor, russet, scald, etc.) However, the fungicide used with it has sometimes shown a tendency to counteract the ill effects of lead arsenate (see under thiram, p. 36).

Parathion

Plots in the dwarf orchard at Mt. Carmel have been sprayed with parathion sprays for a number of years. While complete chemical analyses of apples from these plots so far have not been possible, it is interesting to note the preference in taste tests (Cortland and Baldwin) for fruit sprayed with parathion over lead arsenate-sprayed apples when combined with either sulfur or thiram. Differences have been small, however, and are probably not significant. Leaf injury to certain varieties is severe, unless the parathion is safened, and the quality of the fruit obtained may depend on this factor.

Chlorinated Hydrocarbons

Materials in our experiments which fall into the chlorinated hydrocarbon class are methoxychlor, chlordane, TDE (DDD) and *"1189"*. Since 1950 there has been a rather pronounced taste panel preference in varieties such as Gravenstein and Baldwin for apples sprayed with chlorinated hydrocarbons (other than benzene hexachloride) instead of lead arsenate. This is sometimes but not always true of the McIntosh; it *was* true in 1952 (methoxychlor-DDD-sulfur-ferbam preferred over lead arsenate-sulfur-ferbam).

Better color is often apparent and a better finish *nearly always* results from substitution for lead arsenate.

Ferbam

The increased yield has already been noted wherever there was substitution of ferbam for sulfur, as has the improved color compared with sulfur-lead arsenate and the blotchiness of Delicious (from late sprays) compared with thiram (Figure 10.) Apparently these conditions affect flavor little, if any. Ferbam-sprayed McIntosh apples received from Poughkeepsie in 1950 were higher in total sugar than sulfur-sprayed fruit, but were lower in 1951. Ferbam-sprayed fruit kept in storage was, however, readily separated by tasters in 1952. It is believed that ferbam-sprayed fruit is usually superior to sulfur-sprayed apples, but the evidence is somewhat conflicting on the basis of processed apples. Selection of fresh unprocessed fruit seems to be easier.

Injury to the surface of some tender skinned fruit sometimes occurs with lead arsenate-ferbam (Figure 11).

In view of the danger of blotchiness from sprays of ferbam after July 1, it is advisable to use either a spreader to even out the deposit or another fungicide which allows the sun to penetrate and color the apple.

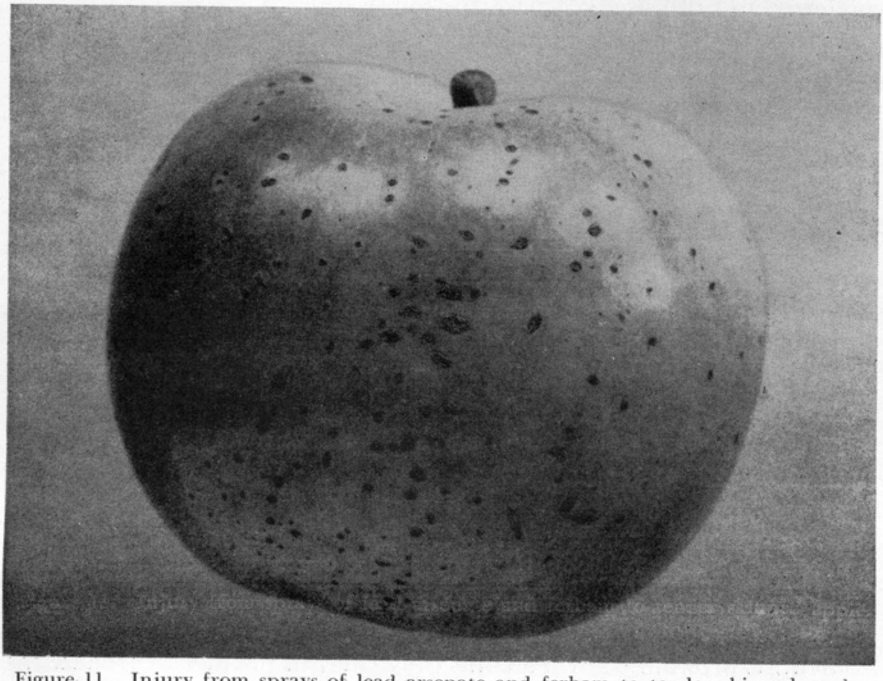

Figure 11. Injury from sprays of lead arsenate and ferbam to tender skinned apple.

Thiram

Thiram-sprayed fruit (combined with lead arsenate or parathion) was preferred in 1950 and 1952 over sulfur. According to the data obtained in 1951, the preference for lead arsenate-thiram over methoxychlor-sulfur-ferbam in Baldwins was highly significant. In Cortlands the preference for lead arsenate-thiram over lead arsenate-sulfur was highly significant and parathion-thiram over parathion-sulfur was just significant. The variety Delicious was an exception to these results in 1951, but the preference ratings agreed with those on other varieties in 1952.

The reason for the preferences noted is not entirely clear. Analyses of total sugars in Cortland and Baldwins showed only slight differences between sulfur-lead arsenate and thiram-lead arsenate, although much greater differences were recorded between lead arsenate-thiram and parathion-sulfur.

The question of maturity naturally enters the picture. Our 1952 tests with Cortlands were made on apples which tested 11.1 to 11.8 pounds, while Delicious fruit tested between 15.7 and 16.2 pounds. All fruit was tree ripened. Yet in spite of these similarities (within varieties) the differences in favor of thiram over sulfur are very pronounced (Tables 31 and 32).

Thus, in view of preferences obtained over a three-year period with a number of varieties, it seems fair to conclude that thiram-sprayed fruit is preferred to sulfur-sprayed. In this connection the increased yields and slightly better color should not be forgotten (Table 22 and Figure 9).

There is no need for omission of or substitution for thiram in midsummer as noted for sulfur and ferbam.

TABLE 31. PREFERENCES FOR THIRAM OVER SULFUR
Mt. Carmel—1952[1]

Variety	Combination	Preference
Delicious	Thiram-parathion vs. Sulfur-parathion	2.8 to 1
Delicious	Thiram-lead arsenate vs. Sulfur-lead arsenate	2.4 to 1
Cortland	Thiram-parathion vs. Sulfur-parathion	1.3 to 1
Cortland	Thiram-lead arsenate vs. Sulfur-lead arsenate	1.5 to 1

[1]All apples selected on basis of pressure.

"Crag 341"

Our first flavor tests with *Crag 341*-sprayed apples were somewhat unfavorable compared with sulfur-lead arsenate. In spite of the high sugar content, as determined in 1952, this fungicide did not always produce the same preferences either in fruit from Mt. Carmel or Poughkeepsie. In

TABLE 32. COMPARISON OF PREFERENCES IN APPLES RECEIVING DIFFERENT SPRAYS

Subject	Number of times each was preferred					
	A Lead arsenate-sulfur-ferbam	B Lead arsenate-thiram	A Lead arsenate-sulfur-ferbam	C Methoxychlor-sulfur-ferbam	B Lead arsenate-thiram	C Methoxychlor-sulfur-ferbam
1	0	4	1	3	4	0
2	1	3	2	2	3	1
3	1	3	4	0	3	1
4	0	4	3	1	4	0
5	0	4	0	4	2	2
6	3	1	3	1	3	1
7	1	3	2	2	4	0
8	3	1	1	3	1	3
9	2	2	4	0	4	0
10	2	2	2	2	3	1
11	3	1	2	2	4	0
12	1	3	0	4	0	4
13	0	4	2	2	4	0
14	3	1	0	4	2	2
15	0	4	4	0	4	0
16	1	3	3	1	4	0
Totals	21	43	33	31	49	15

other words, there seems to be considerable variation in evaluation by taste panels, so far.

There is some tendency with this fungicide to produce a rough finish, but there has been great variation in smoothness of the fruit from year to year. In one 1952 test, however, on McIntosh apples, those sprayed with *Crag 341* were preferred significantly to those sprayed with other combinations.

On the other hand, the increased sugar content as indicated in the 1952 analysis is of great interest, and the advance in ripening date needs to be considered by anyone using this fungicide.

"Phygon"

Phygon-sprayed McIntosh from Poughkeepsie had a low level of acceptance or preference in 1951, possibly because of tree injury from the *Phygon* as reported by Dr. Palmiter. These apples were harvested by maturity. *Phygon*-lead arsenate-sprayed Baldwins from Mt. Carmel (1952) were preferred equally to those receiving sulfur-ferbam-lead arsenate. Apples from Poughkeepsie (McIntosh) obtained in 1952 were processed when they tested 9 to 10 pounds pressure; Baldwins from Mt. Carmel at 10.4 to 11.3 pounds. Tests on 1952 McIntosh from the Poughkeepsie plots did not correspond to the 1951 results, indicating that the leaf injury may have been responsible for the low preference in 1951. Much investigation remains to be done with *Phygon*, but its performance on McIntosh in relation to total acidity (Table 9) should be considered. The tendency to lower total acidity was noted also in apples from Poughkeepsie received in 1951.

TABLE 33. POUGHKEEPSIE McINTOSH PREFERENCES. FUNGICIDE PLOTS[1] (1951)

Fungicides compared		
A	B	Preference A over B
Flotation sulfur	Flotation sulfur Ferbam late	1.2 to 1
Flotation sulfur	*Crag 341*	1.1 to 1
Flotation sulfur	Ferbam	1 to 1
Flotation sulfur	*Phygon*	*4 to 1*
Flotation sulfur	*Tag 331* — Ferbam	1 to 1.4
Flotation sulfur-ferbam	*Crag 341*	1.6 to 1
Flotation sulfur-ferbam	Ferbam	1.5 to 1
Flotation sulfur-ferbam	*Phygon*	*1.6 to 1*
Flotation sulfur-ferbam	*Tag*-ferbam	1.1 to 1
Crag 341	Ferbam	1 to 1
Crag 341	*Phygon*	*2.4 to 1*
Crag 341	*Tag 331*-ferbam	1 to 1
Ferbam	*Phygon*	1 to 1
Ferbam	*Tag*-ferbam[2]	1 to 1.4
Phygon	*Tag*-ferbam[2]	1.7 to 1

[1]Insecticide: lead arsenate in all plots.
Injury noted in the *Phygon* plots.

[2]Many off flavors reported. See Table 34.

Phygon should evidently not be used in a complete program of sprays on McIntosh, but it is not yet apparent how much *can* be used without reducing acidity. Flavor tests on McIntosh from Poughkeepsie indicate that *Phygon* can be used early in the season without noticeably affecting flavor, although acid reduction in this fruit has already been noted.

Sulfur

Sulfur appears to affect the apples on which it is sprayed in the following ways:

1. By producing sun scald in hot weather (Table 21, Figure 6).
2. By russetting, especially in combination with insecticides (Figure 5).
3. By reducing yields, in comparison with thiram (Figures 7 and 8).
4. By bleaching the color and making a blotchy surface as shown in Figure 9.
5. Minor effects on flavor and slight advance in maturity are apparent.

So far the influence of sulfur on flavor has been difficult to detect, although the difference between sulfur and thiram-sprayed fruit has been highly significant in our taste tests. The difference between a full sulfur spray schedule and other fungicides has sometimes been marked in the Poughkeepsie fruit, even though selected on the basis of maturity. Variations from season to season also seem to occur, probably because of variable weather.

The most conspicuous feature about fruit sprayed with sulfur throughout the season is the frequency of a dull finish which may be worse in some seasons than others. Heat is the contributing factor here, and injury to leaves and fruit is much greater in extremely hot weather. Also, the insecticide combined with sulfur plays an important part, as discussed previously.

The evidence seems to indicate avoidance of sulfur in any form after mid-June, but early season sprays do not seem to be harmful.

Sulfur-Ferbam

Standard use of this combination became popular in 1952. So far as we have determined, this combination does not have as deleterious an effect on the fruit as the straight sulfur program. It has sometimes been difficult to separate sulfur-ferbam-sprayed fruit from others, and it would, therefore, seem to be a much better fungicide than sulfur alone from the standpoint of quality.

However, the combination of sulfur and ferbam did not prevent scald, as shown by our 1952 results (Table 21), and the russetting problem still remains with the combination.

It would seem wise on this account to observe the same precautions here as with sulfur alone.

"Tag 331"

Two years of testing apples from the Poughkeepsie fungicide plots showed a different taste panel preference in 1950 and 1952 for those treated with *Tag.* Apples obtained in 1952 compared favorably with others of the series as regards color, sugar, total solids and pressure test for firmness, but taste panels rated them lower than any other spray combination.

It is well known that sprays of *Tag* or related compounds delay the ripening dates considerably. This fact was taken into consideration in planning harvest dates in 1952.

The above indicates caution with *Tag 331,* avoidance of incompatible combinations which produce foliage injury, or sprays in hot weather, or too many applications. The McIntosh received in 1952 from Poughkeepsie had seven *Tag* applications up to the cover sprays when ferbam was substituted. There were four in 1950. Fruit from these plots showed a marked increase in off-flavors in 1952 compared with fruit from other plots handled in the same way. Table 34 below gives an idea of the increase.

TABLE 34. EFFECT OF FUNGICIDES ON "OFF-FLAVOR"
Insecticide, Lead Arsenate—1952

Fungicide treatment	Total taste tests	Number off-flavor reports	Per cent off-flavor[1]
3 Flotation sulfur	162	5	3
4 Flotation sulfur-ferbam	134	5	4
5 *Crag*-lime	78	4	5
6 Ferbam-ferbam	120	7	6
7 *Phygon*-ferbam	106	4	4
8 *Tag*-ferbam	154	26	17

[1]Described as bitter, rotten, fermented, metallic, musty, tinny, chemical, woody, medicinal, or oily by various tasters.

Flavor as a Factor in Commercial Grades

At the 1952 annual meeting of the Connecticut Pomological Society, a number of boxes of apples were brought in and graded by experts. The purpose of this was to determine how the fruit from various orchards met market standards for the industry. Among these were 15 boxes of McIntosh, only three of which graded U. S. No. 1. Samples of all 15 boxes were then brought to New Haven and submitted to a taste panel as fresh fruit and as sauce. Several interesting facts became evident.

None of the fruit rated high by taste panels corresponded with the ones which met the commercial grade. This seems to confirm the suspicion that fruit which meets the commercial grade may or may not be top quality from the flavor standpoint. At least two of the samples examined were preferred as fresh fruit, only to receive a low sauce rating. Probably the sauce determination should carry more weight than the fresh fruit preference, but this test also indicates the necessity for more complete examinations from the flavor standpoint.

While this type of investigation is far from complete, it does indicate the importance of considering flavor in connection with commercial apple grades.

Occurrence of Off-Flavors

Table 35 gives some of our results with "off-flavors" based on fruit produced at Mount Carmel in 1952. Similar results may be found in Table 34 from Poughkeepsie fruit. All tests in 1952 were on frozen sauce.

The main difference in the two lots of fruit is the absence of non-arsenical treatments in the Poughkeepsie samples. In the Mt. Carmel tests, there was a noticeable decline in the percentage of off-flavor reports when methoxychlor-TDE or *"1189"* was substituted. However, the high rating of the control (sprayed with sulfur-ferbam only) casts some doubt on the

Table 35. Effect Of Sprays On Objectionable Flavors[1]
Sauce from McIntosh Apples—Burton Orchard—1952

Treatments	Number of runs	Runs with off-flavor	Per cent runs with off-flavor	Number individual taste tests	Per cent objectionable
Lead arsenate-sulfur-ferbam	14	7	50	228	3
Lead arsenate-*Crag 341*	12	5	41	141	6
Lead arsenate-*Phygon*	5	2	40	63	11
Lead arsenate-*Captan*	6	1	16	77	9
Sulfer-ferbam	4	2	50	59	5
'1189'-sulfur-ferbam	5	1	20	76	1
Methoxychlor-TDE-sulfur-ferbam	10	1	10	150	1

[1]Designation: bitter, rotten, fermented, metallic, musty, tinny, chemical, woody, medicinal, oily.

value of the percentages. In the case of the Poughkeepsie fruit (Table 34), the very large increase in percentage of off-flavor reports with *Tag*-ferbam (insecticide, lead arsenate) may have some meaning. If we total the number of tests on the Mount Carmel lead arsenate-sprayed fruit, the per cent off-flavor of the 509 individual tests is 5.6. A similar percentage of the 600 Poughkeepsie fruit tests, excluding those treated with *Tag*-ferbam, is 4.0 per cent. Including the *Tag*-ferbam, the per cent is 6.8, both figures being near the fruit from Mount Carmel. The increase from either of these averages to 17 per cent or the reduction from them to 1 per cent is interesting and suspicious, though not necessarily significant.

SUMMARY AND CONCLUSIONS

During 1950 we examined apples from Poughkeepsie, N. Y., Waltham, Mass., and Mount Carmel. Apples from the various plots were picked on approximately the same dates in several locations. In 1951 taste and chemical determinations were made on apples from the same localities. The varieties included were McIntosh, Baldwin, Gravenstein, Cortland and Delicious. Results did not seem to be completely in line with those obtained in 1950, but definite trends began to appear and some interesting data were obtained.

In 1952, a more detailed chemical examination was made of the fruit from Mount Carmel. This work involved eight different spray programs in one orchard and four in another. Apples were again received from Poughkeepsie, but none from Waltham.

Several things have become apparent during these investigations. The need for repeated taste panel preference tests over a period of years and covering processed and unprocessed fruit before and after refrigeration has become clear. The selection of fruit on a maturity basis has also become increasingly important and a careful examination of the trees themselves (to eliminate those not in good condition)[1] is indicated. Pressure testing each apple before submitting it to the taste panel or making it into sauce seems to have some value.

Comparison of the relation between mineral elements and sugars and acids, as determined by analyses, is interesting. The connection between boron and sugars is important, though how to make use of it is not completely clear at this time. Changes in both acids and sugars as determined by 1952 analyses shows that two of the more important elements affecting quality may be altered by sprays. The low preference for commercially graded McIntosh by taste panels in 1952 indicates the importance of flavor analyses.

All the above seems to show that we may be leaf-feeding the apple tree with almost any pesticide; that some have little effect while others have much; that those having the greatest effect are frequently detected in fruit by taste panels; and finally, that it may be possible to correct for deficiencies at least in part by changes in the spray.

[1]Large trunk scars sometimes have a marked influence in lowering quality.

From our work to date, the following conclusions may be drawn:

(1) No significant effect of the insecticide on sugars could be detected but there is a slight trend towards increased sugars from the non-arsenicals. Some fungicides increase sugars strongly. *Crag 341* was the most notable in this regard.

(2) Total acidity appears to be depressed slightly by arsenicals. This is more apparent from analyses of the pressed juice than of the whole apple, and was more apparent in the 1950 and 1951 analyses than in the 1952. Some fungicides also effect acids strongly; for example, a complete schedule of *Phygon*-lead arsenate reduced acid content. Others such as lead arsenate-*Captan* or lead arsenate-*Crag 341* gave no indication of depression; in fact, a slight increase was noted for *Captan* (Table 10).

(3) No differences could be detected in ascorbic acid content due to treatments.

(4) Minerals are depressed by arsenical sprays. Other elements in the spray mix have not been demonstrated to have any effect. Depression of boron in particular appears to be very important from a number of standpoints.

(5) Both insecticide and fungicide may affect the physical appearance of the apple as by russetting (arsenates, sulfur), sun scald (sulfurs), color reduction (any black spray too late in the season), and bleaching (sulfurs). Some combinations reduce yield while others containing nitrogen may increase it (Figures 7 and 8).

(6) Lead arsenate has consistently affected flavor unfavorably in Baldwin and Gravenstein, but not so much in McIntosh. Very significant preferences for thiram-sprayed fruit when compared with sulfur (in combination with both lead arsenate and parathion) developed over the three-year period and were relatively consistent from year to year.

(7) Flavor tests require careful operation and are sometimes difficult to evaluate. Complete examination of fruit, processed and unprocessed, refrigerated and fresh, is indicated. Examination for off-flavors as well as general preferences should be considered.

APPENDIX

Tables 36 and 37 contain analyses of fruit on a seasonal basis, arranged by spray programs. Some of the data are quoted in preceding pages or illustrated graphically. They present, however, a more complete picture than has been given before and are, therefore, included here.

TABLE 36. CHEMICAL ANALYSIS OF MCINTOSH APPLES
Whole Fruits Picked July 21, 1952—Burton Orchard

Constituent	Lead ars.-sulfur-ferbam	Lead ars.-*Crag 341*	Lead ars.-*Captan*	Lead ars.-*Phygon*	*"1189"*-sulfur-ferbam	Methoxy.-DDD-sulfur-ferbam	Methoxy.-nabam	Sulfur-ferbam only
Total sugar %	6.88	7.45	7.02	6.52	7.35	6.74	7.23	7.09
Acidity (as malic) %	.82	.86	.88	.75	.84	.80	.84	.79
Ash %	.39	.38	.41	.37	.43	.41	.45	.42
K ppm	1500	1493	1433	1335	1578	1493	1568	1827
Ca ppm	101	97	77	91	82	113	100	129
Mg ppm	109	106	96	101	99	111	118	117
P ppm	127	121	123	118	135	130	156	166
Fe ppm	4.9	4.8	5.3	5.1	5.8	5.1	6.9	6.9
Cu ppm	3.5	4.8	4.4	4.8	4.7	4.3	5.5	5.3
B ppm	2.0	1.9	1.8	1.4	2.2	1.7	2.5	2.1
Zn ppm	5.4	3.8	2.7	1.8	6.6	1.5	8.3	2.1

Note: Figures are averages of 3 to 4 replicates in each treatment.

TABLE 37. CHEMICAL ANALYSIS OF MCINTOSH APPLES
Whole Fruits Picked August 15, 1952—Burton Orchard

Constituent	Lead ars.-sulfur-ferbam	Lead ars.-*Crag 341*	Lead ars.-*Captan*	Lead ars.-*Phygon*	*"1189"*-sulfur-ferbam	Methoxy.-DDD-sulfur-ferbam	Methoxy.-nabam	Sulfur-ferbam only
Total sugar %	8.08	8.43	8.11	7.80	8.20	8.50	8.49	8.40
Acidity (as malic) %	.71	.72	.77	.70	.72	.75	.77	.77
Ash %	.36	.36	.38	.34	.39	.36	.40	.37
K ppm	1188	1190	1193	1003	1263	1260	1298	1203
Ca ppm	103	108	107	130	110	106	107	109
Mg ppm	78	90	77	78	90	79	88	86
P ppm	118	113	110	117	123	110	125	137
B ppm	2.4	2.0	1.7	1.8	2.4	2.4	2.5	2.9
Al ppm	54	58	54	49	62	53	60	52

All analyses on the whole apple

TABLE 37. CHEMICAL ANALYSIS OF MCINTOSH APPLES (Continued)

Constituent	Lead ars.-ferbam sulfur-	Lead ars.-*Crag 341*	Lead ars.-*Captan*	Lead ars.-*Phygon*	*"1189"*-sulfur-ferbam	Methoxy.-DDD-sulfur-ferbam	Methoxy.-nabam	Sulfur-ferbam only
				Picked September 15				
Total sugar %	10.80	11.52	10.93	10.88	10.83	11.07	10.32	11.79
Acidity (as malic) %	.70	.78	.77	.62	.73	.76	.73	.87
Ash %	.26	.29	.26	.24	.25	.27	.28	.28
K ppm	1132	1190	1086	1072	1190	1282	1067	1316
Ca ppm	86	88	78	74	69	75	79	66
Mg ppm	68	74	60	74	69	65	73	76
P ppm	111	94	97	102	117	102	120	134
B ppm	2.4	2.9	2.0	2.1	2.7	2.5	3.2	3.2
Al ppm	46	45	43	46	56	53	48	60
Zn ppm	1.5	1.4	1.2	1.4	1.8	1.3	1.8	2.0

All analyses on the whole apple

The following are the chemical designations of the spray materials used in this bulletin.

Captan	N-trichloromethylthio-tetrahydrophthalimide, formerly "406".
Crag 341[1]	2-Heptadecylglyoxalidine
DDD-TDE	2:2-Bis (*p*-chlorophenyl)-1:1-dichloroethane
"1189"	Oxygenated dimer of hexachlorocyclopentodiene
Ferbam	Ferric dimethyldithiocarbamate
Karathane	Dinitro capryl phenyl crotonate
Nabam	Disodium ethylene bis (dithiocarbamate) (*Dithane*)
Phygon	Dichloronaphthoquinone
Tag	Phenylmercuric acetate
TEPP	Tetraethyl pyrophosphate
Thiram	Tetramethyl thiuram disulphide

[1]Official name now glyodin.

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