metrical triakyl phosphorotetrathioates, $(RS)_3PS$; unsymmetrical dimethyl alkyl phosphorotetrathioates, $(CH_3S)_2P(=S)-SR$; and unsymmetrical methyl dialkyl phosphorotetrathioates, $CH_3S-P(=S)(SR)(SR')$. To compare the fungitoxicities of these compounds, the average inhibitions of eight fungi at 100 p.p.m. were used. Although there were variations between fungi, examination of the data in Table II shows that the variations generally were small and that the structure-toxicity relationships are consistent.

Figure 1 shows these structure-toxicity relationships graphically for the first two groups of compounds in Tables I and II. Curve I represents the symmetrical compounds and shows the linear relationship among CH_3, C_2H_5, and i-C_3H_7. The same superiority of branched chains over straight chains is shown again in curve 2 for the dimethyl propyl phosphorotetrathioates and the dimethyl hexyl phosphorotetrathioates. The differences here are not so exaggerated, however, because of the overwhelming effect of the two methyl groups. The increase in toxicity with the *n*-decyl side chain is not surprising, as this phenomenon occurs in many other toxicity-structure relationships. It is interesting to note, however, that there is a linear relationship with the *n*-decyl, *n*-undecyl, and *n*-dodecyl groups.

In view of the many reactions and modes of action in which these compounds could be involved it would be unwise to infer too much from these preliminary screening results. It is clear, however, that these compounds have significant biological activity, particularly those with small alkyl groups, and are worthy of further investigation.

Acknowledgment

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FUNGICIDE RESIDUES

Rapid Determination of Mercury in Apples by Modified Schöniger Combustion

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A modified Schöniger combustion of dried apple tissue replaces wet ashing prior to the determination of mercury. Loss of mercury by volatilization is eliminated in the closed combustion flask. Apple tissue is dried on cellophane overnight under vacuum, then burned in an oxygen-filled flask with a balloon attached for pressure control. Mercury is determined spectrophotometrically after extraction of the absorbing solution with dithizone. About 12 samples can be burned and analyzed in one day. Recovery of mercury from apples in the 0.3- to 0.6-p.p.m. range averaged 83.6%. Up to 0.18 p.p.m. of mercury was found in apples treated with mercurial fungicides for scab control.

MERCURIAL FUNGICIDES have been used in New York during the past three seasons for control of scab in apples. During analysis of these apples for mercury residues this laboratory was unable to recover small amounts of mercury consistently by wet-ashing procedures. Although oxidizing conditions were always maintained, mercury was lost by volatilization during acid digestion of apple tissues. Attempts to reduce this loss by the use of a low temperature initial digestion, hydrogen peroxide, selenium, and various condensing systems proved unsuccessful.

Southworth, Hodecker, and Fleischer (*4*) recently determined mercury in organic compounds by combustion in a Schöniger flask (*2, 3*). In the work reported a modified Schöniger flask is used to determine mercury in apples. Apple tissue containing organic mercury fungicides is dried on cellophane and burned in an oxygen-filled flask. The combustion products are absorbed in 0.1*N* hydrochloric acid and mercury is determined spectrophotometrically after extraction of the absorbing solution with dithizone (*1*). Loss of mercury by volatilization cannot occur in the closed system and recovery of mercury is consistently good.

Combustion Flask

The combustion flask and platinum holder are shown in Figure 1.

The flask is round-bottomed, of 5-liter capacity, and made of borosilicate glass. A 40/35 standard-taper, female ground joint is sealed on the neck. A side arm (1 cm. in inside diameter, 4 cm. long) is

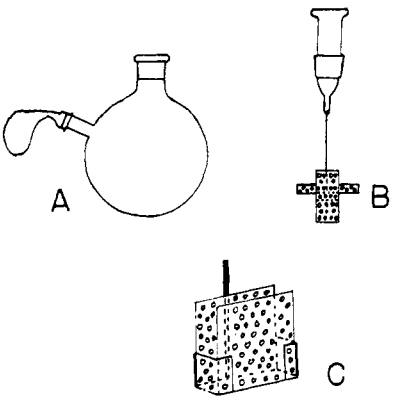

Figure 1. Combustion equipment

A. Flask
B. Platinum holder open
C. Platinum holder closed

Table I. Per Cent Recovery of Mercurial Fungicides[a] from Apples

Apple Variety	Phenylmercuric Acetate	Phenylmercuric Oxyquinolate (Quinex)	Di(phenylmercuric) Ammonium Oxyquinolate (Metasol DPO)
MacIntosh	81.9		
	71.5		
	84.9		
	80.0		
	81.7		
	79.7		
	74.7		
	78.5		
	82.9		
	82.2		
Cortland	89.3	85.0	
	84.1	83.2	
	79.2	75.0	
		80.6	
		80.6	
Red Delicious	82.9	76.8	80.7
	84.1	83.8	80.5
	86.9	63.5	103.9
		89.6	106.3
		70.1	
Rome Beauty	83.9	77.2	94.7
	85.6	89.8	100.8
	82.5		93.8
			109.9
Rhode Island Greening	77.8	76.7	98.8
	91.9	69.3	63.5
	85.4		

[a] 0.60 p.p.m. (calculated as mercury) of fungicide added to each sample except first two samples of MacIntosh apples treated with phenylmercuric acetate, to which 0.30 p.p.m. was added.

Table II. Residues of Mercury in Apples Treated with Organic Mercurial Oxyquinolate

Apple Variety	Phenylmercuric Oxyquinolate (Quinex)	Di(phenylmercuric) Ammonium Oxyquinolate (Metasol DPO)
	(P.p.m.)	
Cortland[a]	0.03	
	0.00	
	0.07	
	0.05	
Red Delicious[a]	0.06	0.00
	0.05	
Rome Beauty[a]	0.04	0.00
	0.05	
	0.02	
Rhode Island Greening[a]	0.04	0.00
	0.04	
	0.02	
Cortland[b]	0.13	
	0.06	
	0.15	
	0.14	
Red Delicious[b]	0.15	
	0.18	
Cortland[c]	0.00	
	0.00	
Red Delicious[c]	0.02	0.00
	0.00	0.00
Rome Beauty[c]		0.05
		0.02
Cortland[d]	0.02	
	0.04	
Red Delicious[d]	0.03	
	0.03	

[a] 7 applications through May 26; apples sampled July 16.
[b] 7 applications through May 26 with bimonthly thereafter; apples sampled July 16.
[c] 7 applications through May 26; apples sampled September 16.
[d] 7 applications through May 26 with bimonthly applications until August 16; apples sampled September 16.

sealed to the flask as illustrated. A rubber balloon, about 8 cm. long, is secured to the side arm with a rubber band.

The platinum holder is constructed by sealing a 12-cm. length of No. 16 B. and S. gage platinum wire onto a 40/35 standard-taper, male ground joint drawn out 8 cm. below the ground portion. A piece of Style 4, perforated platinum sheet (J. Bishop and Co., Platinum Works, Malvern, Pa.), 2.5 cm. wide and 7.5 cm. long, and bent as shown is electrically welded to the last 3 cm. of this wire. Two platinum tabs (1.25 × 2.5 cm.) are welded on to form the two remaining sides of the holder and to keep the sample compressed. The bottom of the resulting holder is 1 × 2.5 cm. and the holder is 3 cm. deep.

Procedure

Preparation of Sample for Combustion. Blend apples in their own liquid until a homogeneous mixture is obtained. Spread a 10-gram portion of the mixture on a 3 × 3 inch square of cellophane (Du Pont No. 300, MSAT No. 87 is satisfactory) supported on a watch glass. Place the watch glass and sample in a desiccator containing sulfuric acid. Several samples may be dried at once. Evacuate the desiccator and allow the samples to remain under vacuum overnight.

Combustion and Determination of Residues. Remove the sample from the desiccator and wrap the cellophane around it by folding the opposite sides up. Place the package in the partially open platinum holder and compress by bending the tabs around it. Insert a fuse cut from filter paper (0.5 × 10 cm.) into the sample. Place 200 ml. of 0.1*N* hydrochloric acid and an egg-shaped, magnetized stirring bar ($2^1/_2$ inches long, Teflon-sealed) in the combustion flask. Place the flask on a magnetic stirrer and support it from a ring stand. Thoroughly purge the flask with oxygen. Light the fuse and place the holder in the flask as soon as about 1 inch of the fuse has burned. Hold the top on until combustion is complete and the balloon has collapsed. Start the magnetic stirrer and operate it fast enough to wash the inside surface of the flask with the splashing solution. Stirring from 7 to 10 minutes is usually sufficient. Remove the flask from the stirrer and tilt it to rinse the upper portion of the flask. Do not allow the acid to enter the balloon, as rubber absorbs mercury. Remove the platinum holder. The magnetized stirring bar is best removed by using a large horseshoe magnet externally to draw the bar out of the flask. Pour the absorbing solution into a 500-ml. separatory funnel while rinsing the platinum holder. Rinse the flask, holder, and balloon with 50 ml. of 0.1*N* hydrochloric acid and add the rinse solution to that in the funnel. Repeat with a second 50-ml. portion of the acid. Carry each sample separately through the procedure from this point.

To the combined acid solution in the funnel add 10 ml. of 20% hydroxylamine hydrochloride and 5 ml. of 30% acetic acid and mix. Add exactly 25 ml. of dithizone in chloroform (4 mg. per liter) and shake exactly 1 minute. Drain the lower layer through a cotton pledget placed in the stem of the funnel into a 5-cm. cuvette. Measure the absorbance of the solution at 490 mμ with dithizone in the reference cell. Use fresh dithizone with each sample.

Prepare the calibration curve (0 to 10 γ of mercury) as follows:

Pipet 0, 1, 2, 3, 4, and 5 ml. of a standard mercuric chloride solution in 0.1*N* hydrochloric acid (2 γ of mercury per ml.) into a series of 500-ml. separatory funnels, and add 0.1*N* hydrochloric acid to make a total volume of 300 ml. Proceed as in the analysis of samples, beginning with addition of the hydroxylamine solution.

Results and Discussion

The method was used to recover phenylmercuric acetate, phenylmercuric oxyquinolate (Quinex), and di(phenylmercuric) ammonium oxyquinolate (Metasol DPO) from apples. These fungicides have been used here for the control of apple scab.

Solutions of these fungicides in glacial acetic acid were added to the 10 grams of apple tissue on the cellophane before drying. The recoveries obtained after drying and combustion of the tissue are shown in Table I.

The check value for 29 analyses averaged 0.037 p.p.m. of mercury. The method will detect about 0.01 p.p.m. of mercury in a 10-gram apple sample.

During 1959, several varieties of apple trees and fruit were treated with Quinex and Metasol DPO for scab control. Quinex was formulated with $^1/_4$ pint of a 20% active liquid formulation contained in 100 gallons of water. Metasol DPO was formulated with $^1/_2$ pint of a 10% active liquid formulation contained in 100 gallons of water. About 12 gallons of this dilute spray was applied to each tree (about a gallon per bushel of fruit). Seven applications were made between April 11 and May 26, 1959. In one experiment spray applications were not continued after May 26 and fruit was

sampled on July 16 and September 16. In a second experiment spray applications were continued bimonthly until August 16, samples being taken on July 16 and September 16. Table II shows the residues of mercury found in replicate samples following analysis.

Some varieties in Table II were not available for the September sampling.

The weight of dried apple burned was about 2 grams, which represented about 10 grams of fresh apple tissue. If a larger weight of tissue was used, combustion was incomplete. Expansion of gases into the balloon allowed the combustions to be carried on safely. The size of the sample and the rapid rate of burning of cellophane necessitated the use of a balloon, which was replaced after about five combustions. Nearly 200 combustions have been conducted in the flask. About 12 samples can be burned and analyzed in a day.

Acknowledgment

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FUNGICIDE RESIDUES

Effects of Treatment Conditions on *o*-Phenylphenol Residues in Oranges

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Sodium o-phenylphenate is effective as a postharvest fungicide in controlling decay of citrus fruits, but it sometimes causes peel injury. A study was made of the effects of treatment conditions on residues of o-phenylphenol in oranges. Residues increased with concentration, temperature, and length of treatment, but decreased as pH was raised. By control of treatment conditions residues can be maintained at any desired level. Peel injury was not a problem when residues were below the legal tolerance of 10 p.p.m.

ORTHO-PHENYLPHENOL and its sodium salt are effective as postharvest fungicides for citrus fruits when applied from aqueous solutions (*8*). A major problem has been injury to the peel by these materials (*7*). Efforts to prevent this injury have been directed toward adjustment of formulation (*9*) and use of additives such as hexamethylenetetramine (*5*). Recently it has been found (*6*) that both peel injury and fungicidal effectiveness are related to the pH of sodium *o*-phenylphenate solutions used for treatment of oranges.

The authors found (*4*) that addition of sodium *o*-phenylphenate to the water used for hydrocooling oranges was effective in reducing subsequent decay. The search for optimum conditions has been extended to study the effects of concentration, temperature, pH, and length of treatment on residues of *o*-phenylphenol and extent of peel injury of oranges.

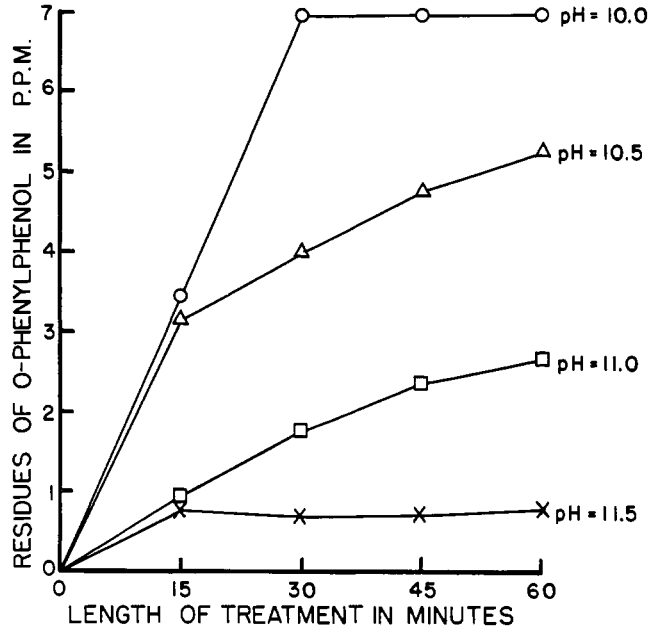

Figure 1. Effect of length of treatment on o-phenylphenol residues in oranges treated with 0.1% Dowicide A at 40° F. at various pH levels

Fruit Handling

Oranges used in these experiments came from groves of the Citrus Experiment Station. The entire series of experiments was run using Pineapple oranges, a midseason variety, and repeated with Valencias, which mature much later. Fruit was washed, dried, graded, and automatically packed in 4/5-bushel fiberboard cartons using small, commercial-type machinery in the experimental packinghouse. Storage before and after fungicidal treatments was at 70° F.

Low temperature treatments were