Infrared Determination of *p*-Chlorobenzyl *p*-Chlorophenyl Sulfide and Its Oxidation to Its Sulfone on Pears

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Residues on pears of the acaricide *p*-chlorobenzyl *p*-chlorophenyl sulfide have been evaluated with infrared techniques. Chromatographic isolations permitted the quantitative establishment of a half life of 11 days for the parent sulfide and of 7 days for the direct sulfone oxidation product formed *in situ*. Details of the analytical procedures are presented.

THE COMPOUND *p*-chlorobenzyl *p*-chlorophenyl sulfide (also known as Chlorparacide, Chlorbenside, and Mitox) has been described as promising for the control of tetranychid mites (*1*), and shows promise for the control of the European red mite, *Metatetranychus ulmi* (Koch), on apples and pears. The normal oxidation products of *p*-chlorobenzyl *p*-chlorophenyl sulfide (I), *p*-chlorobenzyl *p*-chlorophenyl sulfoxide (II), and *p*-chlorobenzyl *p*-chlorophenyl sulfone (III), are reported (*1*) to have biological properties similar to the parent compound. Some properties of the carefully purified compounds in question are listed in Table I. Detailed ultraviolet absorption characteristics are reproduced in Figure 1.

The establishment of magnitudes of persisting residues of acaricides on and in treated foodstuffs is important. Two types of "total" methods are available for the establishment of the maximum amount of parent *p*-chlorobenzyl *p*-chlorophenyl sulfide that could exist in a treated substrate, regardless of ordinary alterations from metabolism or oxidation. These are any of the several "total-chlorine" methods (*2*) and the colorimetric method of Higgons and Kilbey (*3*, *4*), in which the residue is oxidized to the sulfone and then nitrated, and the absorption of the nitration product in alkaline solution is determined at 575 mμ. Because of the reported oxidation *in situ* of the parent sulfide both to the sulfoxide and to the sulfone (*1*), it is desirable to determine magnitudes and locales of these oxidation products in aged residues on and in foodstuffs.

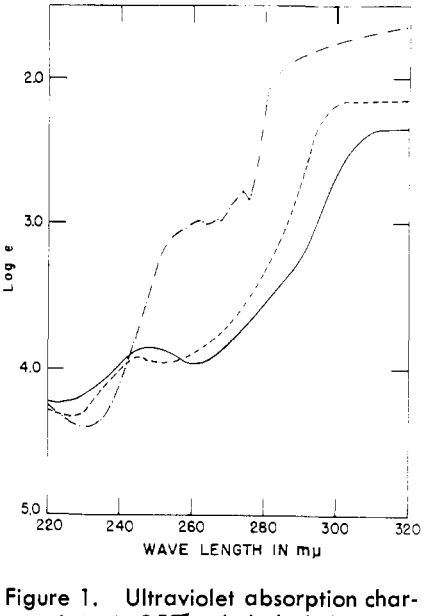
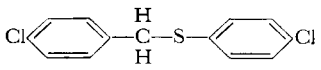
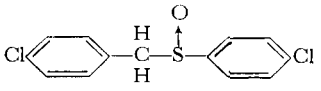
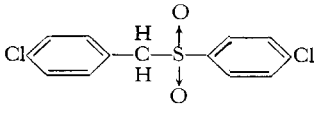


Figure 1. Ultraviolet absorption characteristics in 95% ethyl alcohol: - - - - *p*-chlorobenzyl *p*-chlorophenyl sulfoxide, — · — · — *p*-chlorobenzyl *p*-chlorophenyl sulfone, and ——— *p*-chlorobenzyl *p*-chlorophenyl sulfide

Examination of the infrared absorption spectra of compounds I, II, and III (see Figures 2, 3, and 4) disclosed that whereas all three compounds absorb strongly in the 1095 to 1085-cm.$^{-1}$ region, the sulfone absorbs also at 1155 cm.$^{-1}$ and the sulfoxide absorbs at 1055 cm^{-1}. During the analytical segregation of these compounds from extraneous pear extractives by selective adsorption on Attaclay, the sulfide and sulfone were separately isolated, whereas the sulfoxide remained very strongly adsorbed on the Attaclay. Amounts of the sulfide and sulfone present were therefore determined by their absorption at 1094 and 1155 cm.$^{-1}$ respectively. The sulfoxide was not determined in this study because of difficulties of elution from the Attaclay.

Table I. Properties of Compounds

No	Structural Formula	Mol. Wt.	M. P., °C.	$A_{cm}^{1\%}$ in 95% Ethyl Alcohol	$A_{cm}^{1\%}$ in 2,2,4-Trimethylpentane
I.		269.2	75–6	9300/261.5 mμ	8667/261.5 mμ
II.		285.2	126–7	9347/253 mμ	7695/262.5 mμ
III.		301.2	151–2	1012/264.5 mμ	Insoluble

[a] Absorptivity or extinction value, molar.

Reagents

Petroleum ether (boiling range 60° to 80° C.).

Benzene. Distill before use.

Attaclay. Obtainable from Attapulgus Clay Co., Philadelphia, Pa.

Hyflo Super - Cel. Obtainable from Johns-Manville Co., New York, N. Y.

Attaclay-Hyflo Super-Cel mixture (3 to 2 by weight).

Activated Attaclay-Hyflo Super-Cel mixture (3 to 2 by weight). Heat the

mixture for 16 hours at 180° to 200° C. to activate.

Light petroleum ether (boiling range 30° to 60° C.).

Acetonitrile. Add 1 ml. of glacial acetic acid to 500 ml. of a commercial grade of acetonitrile. This amount of acid reduces emulsion formation.

p-Chlorobenzyl *p*-chlorophenyl sulfide (melting point 75–76° C.). A standard sample was furnished by the Upjohn Co., Kalamazoo, Mich.

p-Chlorobenzyl *p*-chlorophenyl sulfoxide (melting point 126–127° C.). A standard sample was furnished by the Upjohn Co., Kalamazoo, Mich.

p-Chlorobenzyl *p*-chlorophenyl sulfone (melting point 151–152° C.). A standard sample was furnished by The Upjohn Co., Kalamazoo, Mich.

Carbon disulfide (Spectro grade).

Special Apparatus

Infrared Spectrophotometer. A Perkin-Elmer Model 21 infrared spectrophotometer with a 1.0-mm. rock salt microcell was used with rock salt optics. Instrument settings were resolution 927, response 1 to 1, gain 5.5, speed 2 minutes per micron, and suppression 2.

Kuderna-Danish evaporative concentrator (*2*).

Chromatographic column, 25 × 300 mm., with coarse porosity, fritted-glass disk (*2*).

Experimental Procedures

Separation. Filter a measured volume of petroleum ether (boiling range 60° to 80° C.) stripping solution through 1 gram of anhydrous sodium sulfate and a plug of glass wool in a Gooch crucible holder into a 500-ml. ⅁ Erlenmeyer flask and concentrate by evaporation on a steam bath through a three-bulb Snyder column to less than 100 ml. Attach a suction flask to the bottom of the chromatographic column and apply gentle suction to the side arm. While tapping the column, add anhydrous sodium sulfate until a layer 0.5 cm. thick is formed, then add unactivated Attaclay–Hyflo Super-Cel mixture to a depth of 20 cm. Add a top layer of 3 cm. of anhydrous sodium sulfate and lightly press the surface of the adsorbent, using a flat-ended glass rod. Percolate 100 ml. of petroleum ether with suction through the column until the liquid level falls to within 1 cm. of the surface of the adsorbent. Release the vacuum, remove the flask, and replace it with a clean dry flask.

Quantitatively transfer the concentrated stripping solution to the column, using enough petroleum ether to bring the total volume to 100 ml. Apply suction until the liquid level passes just below the top of the upper sodium sulfate layer. At once wash the sides of the column with 10 ml. of petroleum ether and again draw the liquid level just below the top of the sodium sulfate layer. Repeat the washing, then add 300 ml. of petroleum ether and draw it through the column as above. The eluate contains all the *p*-chlorobenzyl *p*-chlorophenyl sulfide.

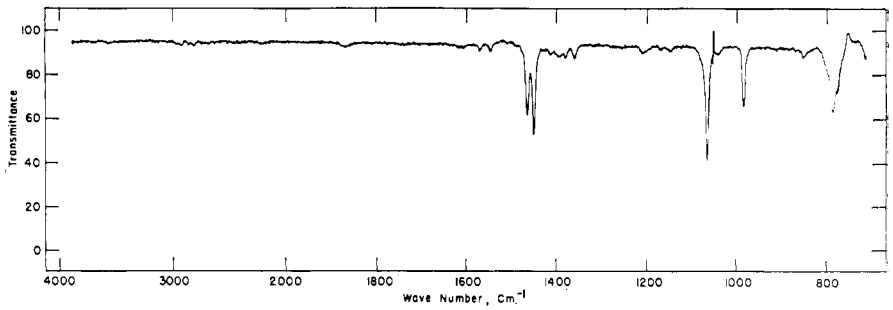


Figure 2. Infrared absorption characteristics of p-chlorobenzyl p-chlorophenyl sulfide (20 mg./ml. in CCl_4 from 4000 cm.$^{-1}$ to 1400 cm.$^{-1}$; 20 mg./ml. in CS_2 from 1400 cm.$^{-1}$ to 700 cm.$^{-1}$)

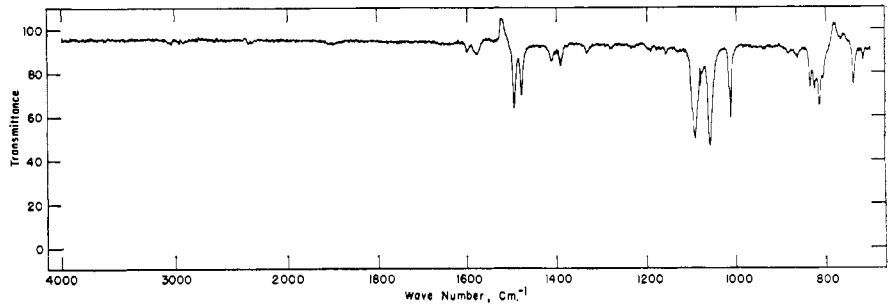


Figure 3. Infrared absorption characteristics of p-chlorobenzyl p-chlorophenyl sulfoxide (20 mg./ml. in CCl_4 from 4000 cm.$^{-1}$ to 1400 cm.$^{-1}$; 20 mg./ml. in CS_2 from 1400 cm.$^{-1}$ to 700 cm.$^{-1}$)

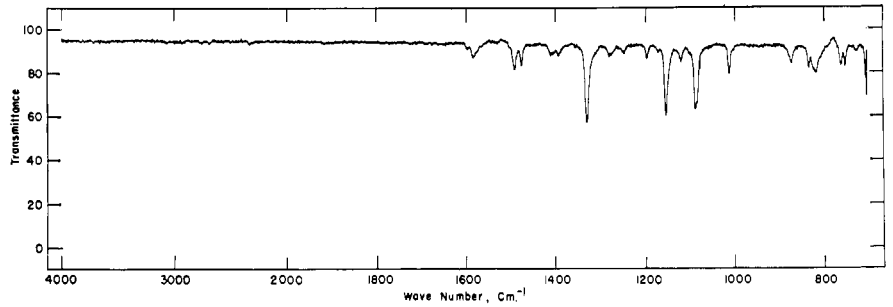


Figure 4. Infrared absorption characteristics of p-chlorobenzyl p-chlorophenyl sulfone (10 mg./ml. in CCl_4 fom 4000 cm.$^{-1}$ to 1400 cm.$^{-1}$; 10 mg./ml. in CS_2 from 1400 cm.$^{-1}$ to 700 cm.$^{-1}$)

At this point, change the container and add 75 ml. of benzene and draw it through the column until the liquid level again drops just below the top of the sodium sulfate layer. Change the container and discard the eluate. Draw an additional 100 ml. of benzene through the column as above. This eluate contains all the *p*-chlorobenzyl *p*-chlorophenyl sulfone. The *p*-chlorobenzyl *p*-chlorophenyl sulfoxide is retained tenaciously on the adsorbent and is not eluted under these conditions.

Determination of *p*-Chlorobenzyl *p*-Chlorophenyl Sulfide. By evaporation concentrate the petroleum ether eluate on a steam bath through a three-bulb Snyder column to less than 100 ml. Transfer quantitatively to a column prepared exactly as above but with activated Attaclay–Hyflo Super-Cel mixture as adsorbent, using enough petroleum ether to bring the total volume to 100 ml. Pass this solution through the column until the liquid level drops just below the top of the sodium sulfate layer. Wash the sides of the column with 10 ml. of petroleum ether and draw through the column as above. Repeat the washing, then add 130 ml. of petroleum ether and draw it through the column until the liquid level approaches the top of the sodium sulfate layer. Discard this eluate. Change the receiver to a Kuderna-Danish evaporative concentrator, add 300 ml. of petroleum ether, and draw it through the column

until the liquid level again falls just below the top of the sodium sulfate layer. Evaporate this eluate to dryness on a steam bath, using a gentle jet of air to remove the last traces of solvent. Dissolve the residue in from 0.2 to 1.0 ml. of carbon disulfide and record the spectrum from 1150 to 1000 cm^{-1}. Determine the absorbancy by the base-line technique at 1094 cm^{-1}. A standard curve can be prepared from purified *p*-chlorobenzyl *p*-chlorophenyl sulfide.

Determination of *p*-Chlorobenzyl *p*-Chlorophenyl Sulfone. Evaporate the benzene eluate to dryness on a steam bath through a three-bulb Snyder column, but remove the Snyder column for the last stages of evaporation. Dissolve the residue in 100 ml. of petroleum ether and extract with two 25-ml. portions of acetonitrile. Dilute the combined acetonitrile solutions with 250 ml. of water and extract with 150 ml. of light petroleum ether (boiling range 30° to 60° C.). Wash the petroleum ether solution with three 100-ml. portions of water, filter it through 1 gram of sodium sulfate into a Kuderna-Danish evaporative concentrator, then evaporate it on a steam bath to dryness, using a gentle jet of air to remove the last traces of solvent. Dissolve the residue in from 0.2 to 1.0 ml. of carbon disulfide and record the spectrum from 1200 to 1050 cm^{-1}. Determine the absorbancy by the base-line technique at 1155 cm^{-1}. A standard curve can be prepared from purified *p*-chlorobenzyl *p*-chlorophenyl sulfone.

Comments on Procedures

Separation. When a petroleum ether solution of *p*-chlorobenzyl *p*-chlorophenyl sulfide, its sulfoxide, and its sulfone is passed through a column of unactivated Attaclay-Hyflo Super-Cel mixture (3 to 2), the sulfide passes through the column with the first 100 ml. of eluate after the initial charge. The sulfoxide and sulfone remain strongly adsorbed throughout the petroleum ether elution. When benzene is used to elute the column the sulfone comes through with the 100 to 150-ml. fraction, but the sulfoxide remains strongly adsorbed and cannot be eluted with this solvent.

Determination of *p*-Chlorobenzyl *p*-Chlorophenyl Sulfide. When a petroleum ether solution of *p*-chlorobenzyl *p*-chlorophenyl sulfide is passed through a column of freshly activated Attaclay-Hyflo Super-Cel mixture (3 to 2), the compound emerges in the eluate with the 350 to 500-ml. fraction, whereas any interferences from pear extractives remain strongly adsorbed or pass through the column in the first 250-ml. fraction.

A calibration curve for *p*-chlorobenzyl *p*-chlorophenyl sulfide in carbon disulfide conforms to Beer's law at 1094 $cm.^{-1}$ from 100 to 2000 γ, with a slope of 550 γ per 0.1 absorbance unit when 1.00 ml. of carbon disulfide is used. Greater sensitivity can be obtained by using a volume of 0.20 ml. of carbon disulfide for the final solution. The analytical procedure has an over-all efficiency of from 70 to 80%, based upon recovery of *p*-chlorobenzyl *p*-chlorophenyl sulfide in the presence of pear extractives in petroleum ether (see Table II).

Determination of *p*-Chlorobenzyl *p*-Chlorophenyl Sulfone. Considerable waxy material results from the benzene elution of *p*-chlorobenzyl *p*-chlorophenyl sulfone. While this does not absorb appreciably in the 1155-$cm.^{-1}$ region, it presents mechanical difficulties when final volumes of 0.25 to 0.50 ml. are desired. Partition of the sulfone from petroleum ether into acetonitrile results in negligible amounts of waxy material. Partition distribution data for *p*-chlorobenzyl *p*-chlorophenyl sulfone into acetonitrile from petroleum ether are presented in Table III.

In the procedure as presented, a 98% recovery of the sulfone results from the double partition into acetonitrile.

A calibration curve for *p*-chlorobenzyl *p*-chlorophenyl sulfone conforms to Beer's law at 1155 $cm.^{-1}$ from 100 to 2000 γ, with a slope of 485 γ per 0.1 absorbance unit when 1.00 ml. of carbon disulfide is used. Greater sensitivity can be obtained by using a volume of 0.20 ml. of carbon disulfide for the final solution. The analytical procedure has an over-all efficiency of from 85 to 90%, based upon recovery of *p*-chlorobenzyl *p*-chlorophenyl sulfone in the presence of pear extractives (see Table IV).

Table II. Recovery of *p*-Chlorobenzyl *p*-Chlorophenyl Sulfide from Pear Extractives

Added		Recovered		
γ	P.p.m.	γ	P.p.m.	%
470	1.18	390	0.98	83
500	1.25	405	1.03	81
94	0.24	68	0.17	72

Table III. Percentage Partition of *p*-Chlorobenzyl *p*-Chlorophenyl Sulfone into Acetonitrile from 1.00 Volume of Petroleum Ether

Comparative Volume Acetonitrile	Sulfone, % in Acetonitrile
1.00	95.0
0.50	92.6
0.33	89.8
0.25	86.6

Table IV. Recovery of *p*-Chlorobenzyl *p*-Chlorophenyl Sulfone from Pear Extractives

Added		Recovered		
γ	P.p.m.	γ	P.p.m.	%
124	0.31	105	0.26	85
200	0.50	180	0.45	90
200	0.50	180	0.45	90

Table V. Residues on Pears

Days after Treatment	Average Weight per Pear, Grams[a]	*p*-Chlorobenzyl *p*-Chlorophenyl Sulfide, P.P.M.[b,c]	*p*-Chlorobenzyl *p*-Chlorophenyl Sulfone, P.P.M.[b,c]
1/2	143	2.2, 2.2, 1.4	<0.1, <0.1, <0.1
7	154	1.1, 0.8, 1.1	0.4, 0.6, 0.5
14	186	0.6, 0.7, 0.9	0.2, 0.3, 0.4
21	211	0.6, 0.5, 0.1	0.2, 0.1, 0.1

[a] For calculating growth-dilution of residues, if desired.
[b] DDT-treated controls at all stages of growth showed 0.0 p.p.m. background for both compounds.
[c] Corrected for recovery.

Discussion of Field Results

The persisting residues of *p*-chlorobenzyl *p*-chlorophenyl sulfide and its sulfone encountered on pears in current practice are collated in Table V and plotted in Figure 5.

Full-coverage hand-sprayed applications were made to mature Bartlett pear trees on June 7, July 6, and August 8. Approximately 800 gallons of spray solution, consisting of 2 pounds of 20% Chlorparacide wettable powder and 1 pound of 50% DDT wettable powder per 100 gallons of water, were applied per acre. Samples were taken immedi-

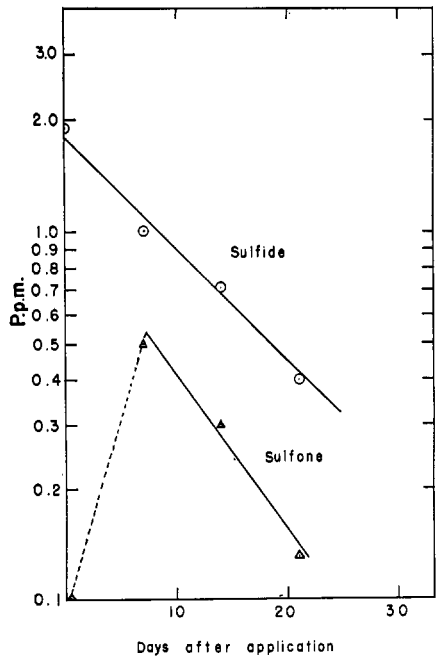


Figure 5. Residues of *p*-chlorobenzyl *p*-chlorophenyl sulfide and *p*-chlorobenzyl *p*-chlorophenyl sulfone on pears

ately after the deposits from the third application were dry, and then after 7, 14, and 21 days. The last sampling coincided with harvest.

The samples were collected as follows. Two pears within reach of the ground were taken from each quadrant of three trees for a total of 24 fruits per sample. Samples were taken in triplicate each time. Two control samples were taken for each set of samples from trees that were in the same orchard but had been sprayed with 1/4 pint of Systox and 1 pound of 50% DDT. The initial samples were placed in polyethylene bags, but paper sacks were used for subsequent samples.

All samples were processed immediately by grinding, mincing 2-pound subsamples with petroleum ether (boiling range 60° to 80° C.), equilibrating, and filtering in the usual manner (*2*). Stripping solutions were stored at 10° C. awaiting analysis. Polyethylene bags from the initial samples were rinsed with solvent, a proper aliquot of which was added to the stripping solution from the corresponding initial subsample; in this manner loose initial deposits were recovered.

From Figure 5 it can be seen that the sulfide has a residue half-life value (*2*) of 11 days, while the sulfone has a residue half-life value of 7 days.

Because these half-life values are expressed in terms of micrograms of the compound in question per gram of Bartlett pear, they incorporate both growth-dilution and decomposition-attenuation factors. In Table V are also recorded the average grams per fruit from each 24-fruit sample replicated five times; these values may be used to calculate and plot the comparative magnitudes of the growth dilution of the residues. Thus, assuming uninterrupted and regular growth of the pears, the growth-dilution half-life value of the sulfide is about 40 days, as contrasted with the above actual half-life value of 11 days.

The chromatographic procedure would adapt itself to either of the total methods (*2*, *4*) mentioned previously. When coupled with a suitable total method for the unchromatographed stripping solution, the sulfoxide may be implied by subtraction.

Acknowledgment

The authors express their thanks to The Upjohn Co., Kalamazoo, Mich., for initial infrared curves, and to this company as well as to the Boots Pure Drug. Co., Ltd., Nottingham, England, for providing samples of *p*-chlorobenzyl *p*-chlorophenyl sulfide, *p*-chlorobenzyl *p*-chlorophenyl sulfoxide, and *p*-chlorobenzyl *p*-chlorophenyl sulfone. They also acknowledge the assistance of C. R. Ash of this station in the field aspects of this work, and of Greta B. Wacker of this station in laboratory analyses.

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Received for review April 6, 1956. Accepted August 23, 1956. Paper No. 927, University of California Citrus Experiment Station, Riverside, Calif. Irrespective of the information contained in this report, the pesticide chemicals discussed may not be used unless a tolerance has been established or an exemption from the requirement of a tolerance has been granted for each specific use.

PESTICIDE RESIDUES

Determination of Ethylene Dibromide in Fumigated Fruit

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Ethylene dibromide is recovered from fumigated fruit by steam distillation and extraction with benzene. It is decomposed with sodium hydroxide in ethyl alcohol–benzene solution, and the liberated bromide is oxidized to bromate, which is determined iodometrically.

For fumigating fruits for the destruction of the larvae and eggs of the fruit fly, a method for the determination of ethylene dibromide in air (*2*) involved absorption in ethyl alcohol and decomposition with sodium hydroxide to yield one mole of inorganic bromide from each mole of ethylene dibromide. The liberated bromide was estimated by the Volhard thiocyanate method.

A number of methods for determining ethylene dibromide in fumigated fruit have been published, but a reasonably rapid and accurate method has not been available. Sinclair and Crandall (*3*) determined total bromide iodometrically after hydrolysis, ashing, and oxidation to bromine. Recoveries of ethylene dibromide added to orange peel or pulp varied from 93 to 105%. However, inorganic bromide liberated in the fruit after fumigation was also included. Tanada, Matsumoto, and Scheuer (*4*) avoided such interference by distilling the ethylene dibromide into ethyl alcohol, refluxing the ethanolic solution with potassium iodide, and titrating the liberated iodine. However, their recoveries of ethylene dibromide added to a number of fruits were low (70 to 79%).

The method described in this paper involves refluxing the sample with water, using a special reflux head in which benzene extracts the ethylene dibromide from the condensate before it is returned to the flask. After decomposition with sodium hydroxide in ethyl alcohol–benzene, the solution is evaporated to dryness. Besides sodium hydroxide and bromide, the residue probably contains traces of sodium salts of acids derived from volatile esters, but these do not interfere if the residue is adequately heated. The Volhard thiocyanate method is not sufficiently sensitive for analysis of fumigated fruit, and instead the bromide is oxidized to bromate with sodium hypochlorite. Excess hypochlorite is reduced with sodium formate and the bromate is determined iodometrically. This procedure is based on that of Alicino, Crickenberger, and Reynolds (*1*), and has the advantage that six equivalents of iodine are liberated for each mole