Use of the Flame Photometric Detector for Determining Residues of Omite [2-(*p-tert*-Butylphenoxy)cyclohexyl Propargyl Sulfite] in Various Crops

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A gas chromatographic method is described for the determination of Omite [2-(*p-tert*-butylphenoxy)-cyclohexyl propargyl sulfite] residues in various crops. After extraction and column cleanup, Omite is determined using a flame photometric detector equipped with a sulfur filter. Recovery of Omite from various fruits was 96 ± 12% and from nuts it was 75 ± 16%. Results from the method compare favorably with exhaustive extractions of field-treated samples. The method is sensitive to 0.1 ppm for all crops tested.

Omite [2-(*p-tert*-butylphenoxy)cyclohexyl propargyl sulfite] is a new acaricide recommended for the control of phytophagous mites. Previous residue work had been performed with a gas chromatograph and a Dohrmann microcoulometric sulfur cell (Lane, 1968). However, the introduction of the flame photometric detector by Brody and Chaney (1966) showed promise of a less troublesome and more sensitive method of analysis. A very recent report by Westlake *et al.* (1971) employed the flame photometric detector for the determination of Omite residues in citrus and processed citrus samples. This paper describes the resultant procedure for determining residues of Omite in various crops.

EXPERIMENTAL

Apparatus. A Micro-Tek MT-220 gas chromatograph equipped with a flame photometric detector and a sulfur filter (394 mμ) was employed for the analyses. Flame gas flows were as follows: H_2 = 150 ml/min, O_2 = 20 ml/min, and air = 20 ml/min. Chart speed was 0.5 in./min. The various columns and chromatographic conditions which have been used for chromatographing Omite are listed in Table I. The columns were glass, U-shaped tubes.

ANALYTICAL PROCEDURES

Watery Samples. Samples were ground in a food chopper and thoroughly mixed. A 100-g subsample was extracted in a Waring blender for 3 × 10 sec with 200 ml of a 1:1 mixture of hexane:2-propanol, stopping for 5 sec between each 10-sec blend. The homogenate was then filtered through four layers of cheesecloth into a 2-l. separatory funnel. Any remaining solvent was squeezed out. The mixture was washed twice with 1 l. of 3% NaCl solution and the aqueous phases were discarded. The recovered hexane was measured in a graduated cylinder and passed through a funnel containing 30 g of anhydrous Na_2SO_4 into a beaker. The graduated cylinder and Na_2SO_4 were both rinsed with 3 × 10 ml of hexane. The hexane extract was then evaporated to approximately 15 ml on a steam bath with the aid of a stream of air.

A 11-mm i.d. chromatographic column was prepared by adding a plug of glass wool and 10 g of Florisil (PR grade, 60/80 mesh, Floridin Company, heated overnight at 130° C). The Florisil was rinsed with 30 ml of benzene, and as the benzene level reached the column, the concentrated extract was added. The beaker was rinsed with 2 × 10 ml of benzene and then 100 ml of additional benzene were added to the column. When the benzene level reached the top of the column, the receiver was changed and Omite was eluted with 80 ml of 2% acetone in hexane. The eluate was then evaporated to an appropriate volume and set aside for gas chromatographic analysis.

Nut Samples. Nut samples were shelled and then ground in a Wiley Mill equipped with a 2-mm sieve. After thorough mixing, a 100-g subsample was macerated in a Waring blender for short intervals (5 sec) after adding 150 ml of nitromethane, 5 g of Na_2SO_4, and 1 g of $Na_2S_2O_3$ until a pulpy mush was obtained. The homogenate was filtered through Whatman No. 1 filter paper and the volume of nitromethane recovered was measured. The nitromethane was quantitatively transferred to a separatory funnel, and 30 ml of hexane was added. After shaking for 1 min, the lower nitromethane layer was filtered through Whatman No. 1 paper and evaporated to approximately 5 ml. After adding 50 ml of toluene, evaporation was continued until about 20 ml of solvent remained.

Florisil did not clear up a nut extract sufficiently and so the concentrated extract was passed through 5 ml of alumina (Alcoa, F-20) in a 11-mm i.d. chromatographic column topped with 0.5 ml of Na_2SO_4. When the concentrated extract had just passed into the Na_2SO_4, 30 ml of benzene was added. The eluates were combined and evaporated to an appropriate volume and set aside for gas chromatographic analysis.

RESULTS AND DISCUSSION

The extraction method suggested by Lane (1968) gave an indication of only surface residues of Omite. By this method, whole fruit was extracted for 15 min on a ball mill with hexane

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Table I. Chromatographic Columns and Conditions Used for Omite Determination

Parameter	(1) 2% SE-30	(2) 11% DC-200 (2.5 MCS) + 0.01% Versamid 900	(3) 2% QF-1
Support	Chromosorb W	Gas Chrom Q	Anakrom ABS
Column size	6 ft × 3/16 in. i.d.	4 ft × 1/8 in. i.d.	6 ft × 3/16 in. i.d.
Oven temperature	190° C	200° C	165° C
Inlet temperature	225° C	225° C	225° C
Detector temperature	160° C	160° C	160° C
Carrier gas flow	120 ml/min	120 ml/min	110 ml/min
Retention time, min (approximate)	6.0	6.5	7.0

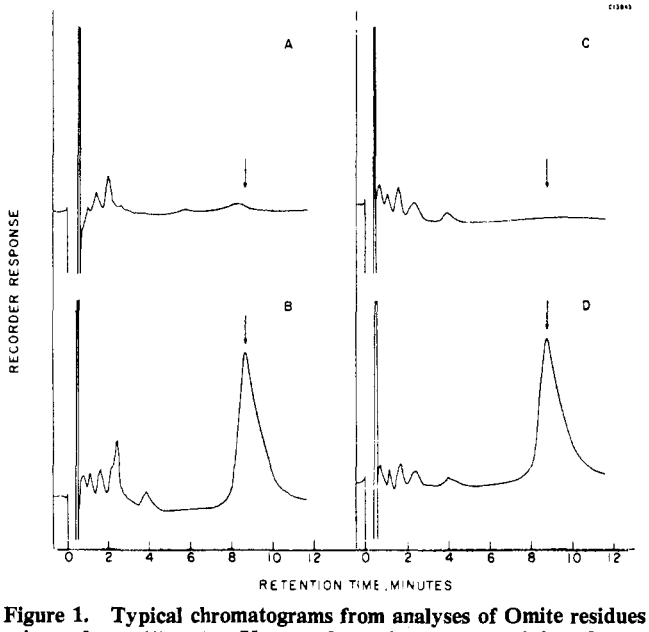

Figure 1. Typical chromatograms from analyses of Omite residues using column (1). A. Untreated peaches, 158 mg injected. B. Treated peaches, containing 0.37 ppm Omite, 148 mg injected. C. Untreated plums, 121 mg injected. D. Treated plums, containing 0.59 ppm Omite, 116 mg injected

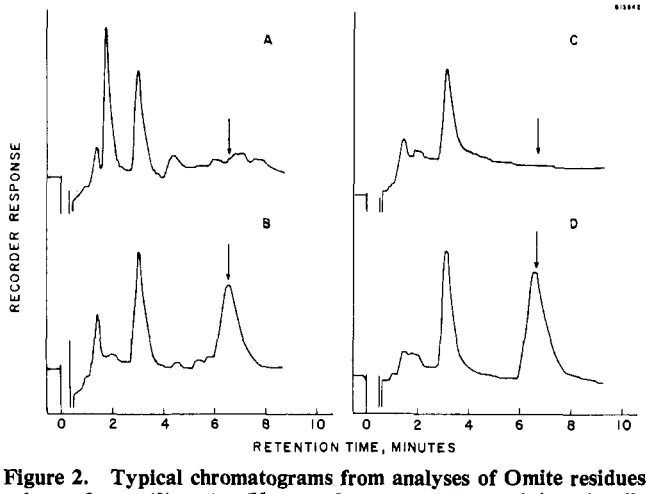

Figure 2. Typical chromatograms from analyses of Omite residues using column (2). A. Untreated orange, 88 mg injected. B. Treated orange, containing 0.26 ppm Omite, 86 mg injected. C. Untreated grapefruit, 87 mg injected. D. Treated grapefruit, containing 0.42 ppm Omite, 85 mg injected

in a 2:1 ratio (fruit:solvent). The hexane was dried with Na_2SO_4 and an aliquot was evaporated for analysis. Even though Omite is not a systemic insecticide, the possibility exists that Omite penetrates the skin of various fruits. Therefore, a comparison of results for field-treated fruits was made between the maceration method described here and the surface strip method of Lane (1968). Omite residues for 16 peach samples and 10 plum samples were compared. The maceration method gave results about 10% higher for the peach samples and about 25% higher for the plum samples. Hence, the maceration procedure gave higher residue levels of Omite than the surface-strip extraction method.

Glc columns 1 and 2, described in Table I, have been used extensively for successful residue determination of Omite residues. The QF-1 column was employed only recently, when it became necessary to separate Omite from various pesticides during specificity studies. Since the flame photo-

Table II. Summary of Recovery Data for Omite

Crop	Fortification, ppm	Recoveries, no.	Average recovery, %	Range, %
Plums	1.0	4	93	73–106
	0.5	5	90	70–120
Peaches	1.0	3	97	76–107
	0.5	6	101	94–110
Oranges	5.0	2	100	90, 111
	1.0	7	98	86–104
	0.5	2	87	76–98
	0.25	1	104	
Grapefruit	1.0	6	97	85–109
	0.5	4	91	72–106
	0.25	1	100	
Potatoes	0.5	2	86	97, 74
	0.1	1	130	
Apples	1.0	2	88	86, 90
	0.5	3	102	96–110
Cherries	1.0	1	89	
	0.5	1	98	
Strawberries	3.0	1	87	
	1.0	1	100	
Apricots	3.0	1	70	
Grapes	10.0	1	103	
Almonds	0.1	1	81	
Walnuts[a]	0.6	2	89	88, 89
	0.2	1	85	
	0.1	1	50	
Almonds[a]	0.2	2	76	68, 85
	0.1	1	50	

[a] Data were obtained using a Dohrmann microcoulometric sulfur cell.

Table III. Comparison of Proposed Method with Exhaustive Extraction

	ppm found	
	Plums	Oranges
Exhaustive extraction		
0–2 hr	7.62	3.51
2–8 hr	ND[a]	ND
Total	7.62	3.51
Maceration	7.18	3.25

[a] ND = Not detectable, less than 0.1 ppm.

metric detector is not linear in the sulfur mode, samples are quantitated by comparing the peak area with a standard curve of Omite. The standard curve is checked periodically but generally remains constant during a day's run.

Table II presents a summary of recovery data for various crops using the described methods. Recovery of Omite from fruit averaged 96 ± 12% and from nuts 75 ± 16%. Figures 1 and 2 present typical chromatograms of several different treated and untreated crop samples. There have been no chromatographic peaks from untreated samples which would interfere with Omite determination in all crops examined.

The extraction efficiency of Omite from field-treated samples by the proposed procedure was compared with that by a Soxhlet extraction. Twenty-five grams each of a plum and an orange sample were extracted in a Soxhlet apparatus with 150 ml of a (1:1) hexane:2-propanol mixture for 2 hr. The samples were then extracted for six additional hours with 150 ml of fresh extraction mixture. The two extracts from each crop were then processed separately through the remainder of the procedure, *i.e.*, washing with 2 × 1 l. 3% NaCl solution and Florisil cleanup. The results of the exhaustive extractions and those from the described method are summarized in Table III. There is excellent agreement between the described extraction method and an exhaustive extraction.

Specificity studies were performed with apricots, strawberries, grapes, and almonds. Omite, at its proposed tolerance, and all FDA approved pesticides at their maximum tolerance levels were added to an untreated crop sample which was then analyzed according to the described procedure. An untreated sample, fortified with all tolerance pesticides at their maximum tolerance levels, was used as a control. Omite could be quantitatively recovered without interference for the three fruits using column 1. However, column 3 had to be used for almonds to separate Omite at 0.1 ppm from a higher level of EPN. When this column (QF-1) was used, there were no interferences in detecting Omite in almonds.

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