Journal of Agricultural and Food Chemistry

© Copyright 1980 by the American Chemical Society

Volume 28, Number 6 November/December 1980

Utilization of an Infrared Detector for Selective Liquid Chromatographic Analysis. Formulation Analysis of the Pyrethroid Insecticides Resmethrin, Permethrin, and Fenvalerate

Euphemia Papadopoulou-Mourkidou,* Yutaka Iwata, and Francis A. Gunther

The pyrethroid insecticides resmethrin [(5-benzyl-3-furyl)methyl *cis,trans*-(±)-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate], permethrin [3-phenoxybenzyl *cis,trans*-(±)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], and fenvalerate [(±)-α-cyano-3-phenoxybenzyl (±)-2-(4-chlorophenyl)-3-methylbutyrate] in formulated material were analyzed by using high-performance liquid chromatography with a silica column (10-μm Partisil) and carbon tetrachloride mobile phase containing 0.85, 1, and 2.5% (v/v) acetonitrile, respectively, for the three insecticides. The in-line detectors used were an infrared (IR) detector operated at the carbonyl or the C–O absorption band of the insecticides and an ultraviolet detector operated at 280 nm. The selectivity of the IR detector was demonstrated in that aromatic solvents in the formulation did not interfere in the analysis. Minimum detectable levels for the IR detector were 1 μg for resmethrin and permethrin and 2 μg for fenvalerate.

The pyrethroid insecticides are promising new compounds for chemical insect control. Residue and formulation analytical methods are needed as the available published literature for these compounds is still limited. Three pyrethroids of economic importance are resmethrin, permethrin, and fenvalerate.

Resmethrin formulation analysis has been reported (Heath, 1972) by gas chromatography with a flame ionization detector, and the cis/trans ratio was determined from the nuclear magnetic resonance spectrum of chrysanthemic acid formed after hydrolysis of resmethrin. The same analytical system was used (Simonaitis and Cail, 1975) for resmethrin residue determination in fortified food samples after extensive extract cleanup by liquid–liquid partitioning and adsorption column chromatography. Extensive cleanup procedures were also necessary for the formulation analysis of permethrin (Simonaitis et al., 1977), permethrin residue determination in fortified crop samples (Chapman and Harris, 1978; Fujie and Fullmer, 1978) and bovine tissue (Oehler, 1979), and fenvalerate residues in cabbage and lettuce samples (Lee et al., 1978), using gas chromatography with a flame ionization, electron capture, or a Coulson electrolytic conductivity detector.

Gas chromatographic analysis of the pyrethroid insecticides is hampered by the nonspecific nature of available detectors, the thermal instability of most pyrethroids at elevated temperatures, and, consequently, the need for elaborate column conditioning (Kikta and Shierling, 1978)

Department of Entomology, University of California, Riverside, Riverside, California 92521.

0021-8561/80/1428-1043$01.00/0 © 1980 American Chemical Society

and extensive sample cleanup. High-performance liquid chromatography (LC) is a new and promising technique for pyrethroid analysis since it can operate at ambient temperatures and provide high resolution of the analyte from interfering material. Only the use of an ultraviolet (UV) detector has been reported for pyrethroid analysis. A need for a simple, rapid, and dependable method for formulation and residue determinations for pyrethroids is of unquestionable importance to pesticide analysts. Our objective was to develop such a method using liquid chromatography for cleanup and separation and tandem infrared (IR) and UV detectors for detection and quantitation. The IR detector can provide selectivity over interfering material and give better assurance of positive identification than can be provided by a UV detector. Although generally less sensitive than the UV detector, current technology can alleviate this existing shortcoming of the IR detector. Reported herein are data obtained for the formulation analysis of resmethrin, permethrin, and fenvalerate.

EXPERIMENTAL SECTION

trans-Resmethrin (100% analytical standard), technical-grade resmethrin (84.5% pure), and a 2EC formulation (2 lb of resmethrin/gal, 0.24 kg/L) were obtained from Penick Corp. Also, technical-grade resmethrin (89.4% pure) was obtained from Fairfield American Corp.

cis-Permethrin (MRV 645) and *trans*-permethrin (MRV 449), 99% analytical standards, and a Pounce 3.2EC formulation (2 lb of permethrin/gal) were obtained from FMC Corp.

Fenvalerate (99.4% analytical standard), technical-grade fenvalerate, (93.6% pure; WL 43775), and a Pydrin (SD 43775) formulation (2.4 lb/gal, 0.29 kg/L) were obtained from Shell Development Co.

All solvents were distilled in glass from Burdick and Jackson Laboratories, Inc., and degassed by sonification under reduced pressure just prior to use. Degassing was of greater importance for the UV detector than for the IR detector. Standard solutions and dilutions of formulations were made by using CCl_4.

The liquid chromatograph consisted of two Waters Associates Model 6000A pumps controlled by a Waters Associates Model 660 solvent programmer. A 5 cm × 4.6 mm i.d. tube packed with glass wool was connected between the pumping system and the injector to ensure that the solvent effluent from the pumps was thoroughly mixed. A septumless injector (Precision Sampling Corp., Baton Rouge, LA) was directly connected to a guard column to allow direct injection onto the guard column and, hence, minimize sample dilution. A 5 cm × 4.6 mm i.d. Whatman HC Pellosil guard column was used to protect the 25 cm × 4.6 mm i.d. 10-μm Partisil analytical column. The analytical column was connected to the IR and UV detectors, respectively. Column fittings were low dead volume unions, and the lengths of the 0.25 mm i.d. tubing used to make connections were minimized to minimize band broadening.

A Wilks Miran-1A (Foxboro, El Monte, CA) variable-wavelength infrared spectrophotometer was used with a 3-mm path length, 9-μL capacity NaCl flow cell. A dual-wavelength (254 and 280 nm) Model 151 Altex ultraviolet detector was used with a 9-μL capacity flow cell.

The mobile phase was CCl_4 containing 0.85 (resmethrin), 1.0 (permethrin), or 2.5% (fenvalerate) acetonitrile. The mixtures were prepared by using the solvent programmer and two pumps, one pumping pure CCl_4 and the other pumping 5% acetonitrile in CCl_4. All injections were 10-μL volumes. All elutions were made under isocratic conditions at 1.2 mL/min flow rate and at ambient temperature.

RESULTS AND DISCUSSION

An unusual molecular structure common to the chrysanthemate pyrethroid insecticides is the substituted cyclopropane ring moiety. The cyclopropane ring has two characteristic ring-vibration absorption bands in the mid-infrared region of the electromagnetic spectrum. One band occurs between 9.45 and 9.8 μm (1058–1020 cm^{-1}); a stronger band, which is not consistently present and has been suggested as arising from a ring deformation mode, occurs between 11.1 and 12.5 μm (900–800 cm^{-1}) (Bellamy, 1958). Examination of the infrared spectra of *d*-allethrin, cypermethrin, decamethrin, permethrin, *d*-phenothrin, and resmethrin showed that in each case, one band was present in each of the above regions. The absorption frequency of one band was solvent dependent and occurred at 1053, 1058, and 1064 cm^{-1} in $CHBr_3$, CCl_4, and CS_2, respectively. The absorption frequency of the other band was relatively invariant at 847–848 cm^{-1}. The infrared absorption bands can potentially provide a highly selective means of detection and quantitation for the chrysanthemate pyrethroids. Currently available commercial infrared instruments based on interferometry should be capable of providing the requisite sensitivity for use as a detection device. As the necessary instrumentation for utilizing the cyclopropane ring absorption bands was lacking, the two strongest absorption bands in the infrared spectra of three pyrethroids were used to demonstrate the selectivity and utility of an infrared spectrophotometer used in conjunction with a high-performance liquid chromatograph. The two bands used were the absorption bands arising from the carbonyl stretching vibration (1785–1720 cm^{-1}, 5.6–5.8 μm) and from the C–O stretching vibration (1160–1143 cm^{-1}, 8.6–8.75 μm). The three pyrethroids studied were resmethrin, permethrin, and fenvalerate, and results are separately presented below for each insecticide.

A disadvantage inherent in the liquid chromatographic system described herein is the toxicity of the carbon tetrachloride. It should be possible, however, under other chromatographic conditions or with better instrumentation to utilize safer solvent systems. For example, Parris (1979) used a gradient elution with acetonitrile–dichloromethane in a nonaqueous reversed-phase liquid chromatographic system with an IR detector for the separation of saturated triglycerides and alkanes.

Resmethrin. Resmethrin eluted from the liquid chromatograph was measured by using the C–O absorption band at 8.6 μm rather than the carbonyl absorption band at 5.6 μm. Although both bands were of essentially equal intensity in the infrared spectrum determined with resmethrin in CCl_4 solution, the C–O absorption was greater under the liquid chromatographic conditions used. It is speculated that the use of acetonitrile in the mobile phase decreased the available infrared energy through absorption. This lower sensitivity of the carbonyl absorption does not preclude its use. The UV detector on-line following the IR detector was operated at 280 nm.

The mobile phase was 0.85% (v/v) acetonitrile in CCl_4. At lower acetonitrile content, the resolution of *cis*- and *trans*-resmethrin was initially much better than that shown in Figure 1, but the retention time increased rapidly with column use and the consequent band broadening resulted in poor resolution. With the 0.85% acetonitrile, the retention times remained constant after 24 h of use. If any changes occurred, the column could be deactivated by passing 30 mL of 5% acetonitrile through the column and used after equilibrating the column with the 0.85% acetonitrile until the initial base-line condition was achieved.

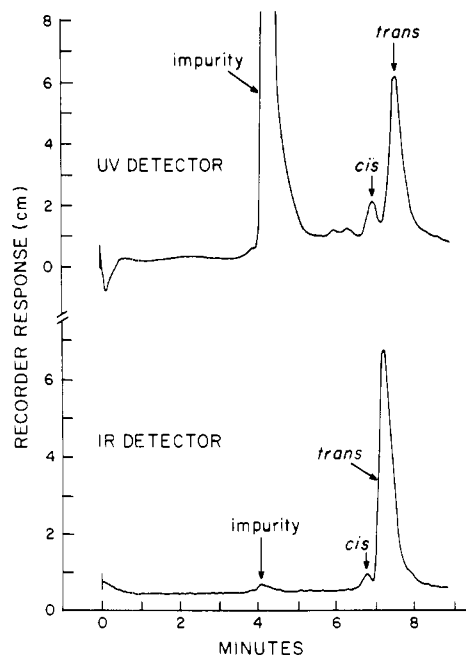

Figure 1. Liquid chromatograms obtained after injection of 60 μg of technical-grade resmethrin in 10 μL of CCl_4. The IR detector was operated at 8.6 μm and 0.1 AUFS; the UV detector was operated at 280 nm and 0.08 AUFS.

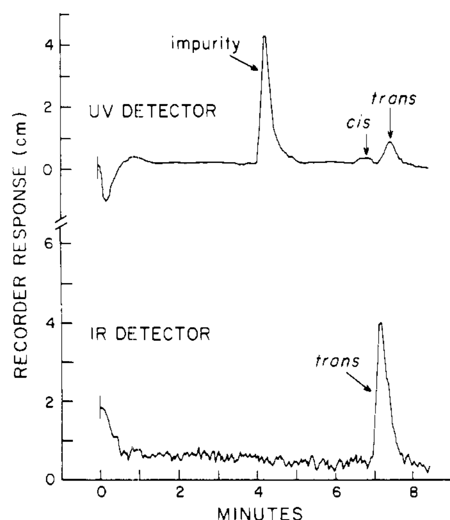

Figure 2. Liquid chromatograms obtained after injection of 8 μg of technical-grade resmethrin in 10 μL of CCl_4. The IR detector was operated at 8.6 μm and 0.025 AUFS; the UV detector was operated at 280 nm and 0.08 AUFS.

Alternately, 30–50 μL of absolute ethanol could be injected onto the column, and then the column could be used after equilibration with 50 mL of 0.85% acetonitrile.

The *trans*-resmethrin peak on the chromatograms obtained by using the technical-grade (Figures 1 and 2) and formulated (Figures 3 and 4) materials was assigned based on the retention time obtained for the single peak resulting from injection of a *trans*-resmethrin standard. *cis*-Resmethrin was not available. Figure 1 shows that in addition to *cis*- and *trans*-resmethrin the UV detector indicates the presence of three impurities at retention times of 4.2, 5.7, and 6.1 min. The major UV-detector peak is only a small peak on the IR chromatogram while the two minor UV-detector peaks are totally absent on the IR chromatogram. This is an example of the selectivity achievable by using the IR detector which is responding, in this case, to only elutants which have a C–O bond. The example is more dramatic with the chromatograms obtained by using a resmethrin formulation. Figures 3 and 4 show that whereas a large UV-detector peak nearly obscures the *cis*- and *trans*-resmethrin peaks, the IR chromatogram only shows the resmethrin peaks. The UV peak results from the "66.4% aromatic hydrocarbons" in the formulated material. The major UV-detector peak in both the technical-grade and formulated materials has the same retention time as xylene which actually passes unretarded through the highly polar silica column.

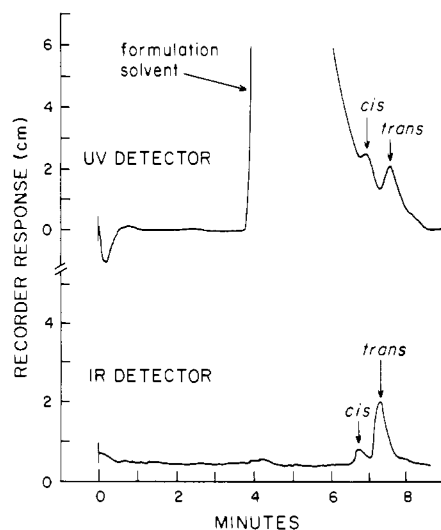

Figure 3. Liquid chromatograms obtained after injection of 10 μL of a 0.8% (v/v) solution of SBP-1382 resmethrin formulation in CCl_4. The IR detector was operated at 8.6 μm and 0.1 AUFS; the UV detector was operated at 280 nm and 0.08 AUFS.

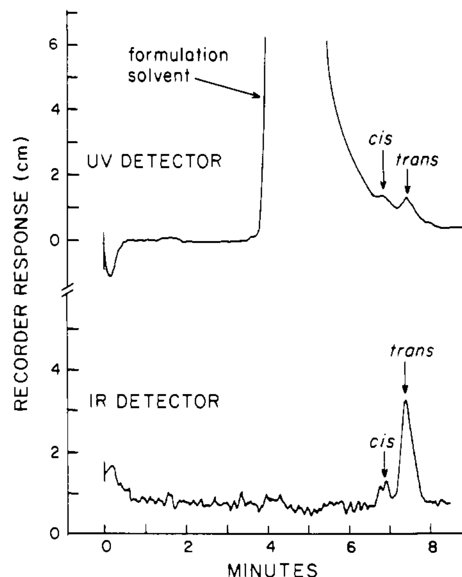

Figure 4. Liquid chromatograms obtained after injection of 10 μL of a 0.3% (v/v) solution of SBP-1382 resmethrin formulation in CCl_4. The IR detector was operated at 8.6 μm and 0.025 AUFS; the UV detector was operated at 280 nm and 0.08 AUFS.

Two possible impurities of resmethrin are the synthetic precursors 5-benzyl-3-furylcarbinol and ethyl chrysanthemate. The alcohol did not elute from the column under the conditions used. *cis/trans*-Ethyl chrysanthemate produced two peaks with retention times of 6.4 and 7.0 min; the 6.4-min peak was half the height of the 7.0-min peak. Injection of 1:1 (w/w) ethyl chrysanthemate–resmethrin mixtures by using technical-grade and formulated resmethrin showed that ethyl chrysanthemate did not interfere in the quantitation of either resmethrin isomer.

Table I. Comparison of IR and UV Detectors Tandem in a High-Performance LC System for the Analysis of Analytical-Grade *trans*-Resmethrin (A) and Technical-Grade Resmethrin (B)

detector[a]	range, AUFS	compd	min detectable, µg		linear range, µg, trans	sensitivity, cm/µg	
			cis	trans		cis	trans
IR	0.1	A[b]		4	4-80		0.1
	0.025			1	1-20		0.5
UV	0.08	A[b]		4	4-60		0.1
IR	0.1	B[c]	5	4	4-80	0.1	0.1
	0.025			1	1-20		0.44
UV	0.08	B[c]	5	4	4-60	0.1	0.1

[a] IR and UV detectors were operated at 8.6 µm and 280 nm, respectively. [b] Three replicate 10-µL injections were made of 0.1, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, and 10 mg/mL solutions of *trans*-resmethrin in CCl_4. [c] *trans*-Resmethrin in the technical-grade material was obtained by analysis using the *trans*-resmethrin analytical standard. *cis*-Resmethrin in the technical-grade material was obtained by difference using the given value for total resmethrin in the technical-grade material.

This was a result of differing retention times for the four peaks and the lower sensitivity of the IR detector to ethyl chrysanthemate at the wavelength used.

When solutions of 4, 6, 8, and 10 mg of technical-grade resmethrin/mL of CCl_4 were injected and the *trans*-resmethrin analytical standard was used for quantitation, the amount of *trans*-resmethrin in the formulated material was calculated. On the basis of the specified total resmethrin content given, the amount of *cis*-resmethrin was calculated by difference. The calculated trans/cis ratio was then 3.4 ± 0.6, in agreement with the specified composition of the technical-grade material.

Under the conditions specified above, *trans*-resmethrin had a retention time of 7.2 min. The cis isomer whose identity is essentially indirect evidence had a retention time of 6.8 min. The retention times were 0.1 min longer with the on-line UV detector. For the trans and cis isomers, the bandwidths obtained on the IR detector were 0.8 min (0.96 mL) and 0.6 min (0.72 mL), respectively, and the bandwidths obtained on the UV detector were 0.85 min (1.02 mL) and 0.62 min (0.75 mL), respectively.

Table I gives data comparing the minimum detectable level, linearity, and sensitivity (slope of the standard curve) of the IR and UV detectors. The linearity range for the two detectors was comparable. The minimum detectable level with a 10-µL injection was 1 µg for the IR detector and 4 µg for the UV detector. The lowest workable range was 0.025 AUFS for the IR detector and 0.08 AUFS for the UV detector. The inadvertant introduction of air affected the performance of the UV detector to a greater degree than that of the IR detector; the presence of air caused irregular base lines.

The sensitivity of the trans isomer was 0.5-cm peak height/µg in the 0.025-AUFS range of the IR detector and 0.1-cm peak height/µg in the 0.08-AUFS range of the UV detector; both detectors were operated at the lowest workable range. Thus, under the conditions used, the IR detector was 5 times more sensitive to *trans*-resmethrin than the UV detector. The conditions used, however, were selected for obtaining good results with the IR detector and not with the UV detector. The UV detector was not operating at the absorbance maximum for resmethrin at ~225 nm as the IR-compatible mobile phase, CCl_4, strongly absorbs UV light below 280 nm. On the other hand, at a 225-nm setting, any compound with a multiple bond or unshared electron pair will respond to the UV detector and the potential for interfering peaks in the analysis is greatly enhanced.

Table II. Results of the Analysis of SBP-1382 2EC (2 lb/gal) Resmethrin Formulation Using a High-Performance LC System with Tandem IR and UV Detectors

detector[a]	range, AUFS	SBP-1382 dilution used, %	results, lb/gal[b]		
			trans	cis	total
IR	0.1	0.5	1.52	0.72	2.24
		0.8	1.56	0.60	2.16
		1.0	1.52	0.60	2.12
		2.0	1.52	0.60	2.12
	mean ± SD:		1.53 ± 0.03	0.63 ± 0.06	2.16 ± 0.06
UV	0.08	0.5	1.20	0.82	2.02
		0.8	1.20	0.64	1.84
		1.0	1.30	0.71	2.01
		2.0	1.10	0.71	1.81
	mean ± SD:		1.20 ± 0.08	0.72 ± 0.08	1.92 ± 0.11

[a] IR and UV detectors were operated at 8.6 µm and 280 nm, respectively. [b] Results are a mean of three 10-µL injections. Quantitation used the *trans*-resmethrin analytical standard and the calculated *cis*-resmethrin content in the technical-grade material (see Table I).

Figure 1 shows the chromatograms obtained on the IR and UV detectors after injection of 60 µg of technical-grade resmethrin. The UV chromatogram shows an intense peak at 4.2 min due to an impurity, but due to the selective nature of the IR detector this impurity is almost nondetectable on the IR chromatogram. Figure 2 shows the chromatograms obtained for 8 µg of technical-grade resmethrin. The fivefold better sensitivity of the IR detector over that of the UV detector is demonstrated. Whereas the most prominent peak in the UV chromatogram is the impurity, in the IR chromatogram the only peak obtained is the active ingredient, the trans isomer. Figure 3 shows chromatograms obtained for an 0.8% (v/v) solution of an emulsifiable concentrate resmethrin formulation in CCl_4. With the UV detector, both resmethrin isomers appear as small peaks on the tail of the strongly absorbing aromatic hydrocarbon peak whereas the IR detector only records the two resmethrin peaks. Figure 4 shows chromatograms obtained for a 0.3% (v/v) solution of the resmethrin formulation. Whereas the UV detector was unamenable to quantitative work, both resmethrin isomers were quantitatively and reproducibly measured with the IR detector.

The results of a formulation analysis are given in Table II. Five dilutions [0.3, 0.5, 0.8, 1.0, and 2.0% (v/v)] of the formulated material in CCl_4 were analyzed; the 0.3% dilution could not be reproducibly measured with the UV detector (see Figure 4). The cis isomer in the technical-grade material, whose content was determined by difference as discussed above, was used as a secondary standard for the formulation analysis. On the basis of IR analysis, the formulation contained 1.53 ± 0.03, 0.63 ± 0.06, and 2.16 ± 0.06 lb/gal of *trans*-, *cis*-, and total resmethrin, respectively. The corresponding values based on UV analysis were 1.20 ± 0.08, 0.72 ± 0.08, and 1.92 ± 0.11 lb/gal, respectively. There is a statistically significant difference at the 1% level for the results obtained by using the two detectors for the *trans*- and total resmethrin analyses; the difference was not significant for the *cis*-resmethrin values at the 10% level. The formulation used was a 2 lb of resmethrin/gal of emulsifiable concentrate. The differences in the results from the two detectors arise principally

Table III. Comparison of the IR and UV Detectors Tandem in a High-Performance LC System for the Analysis of *cis*- and *trans*-Permethrin

detector	range, AUFS	min detectable, μg[a]	linear, range, μg[a]	sensitivity, cm/μg[b] cis	trans
IR, 5.75 μm	0.1	5	5-50	0.09	0.10
	0.025	1	1-10	0.32	0.35
IR, 8.65 μm	0.1	5	5-50	0.10	0.16
	0.025	1	1-10	0.34	0.57
UV, 280 nm	0.16	<1	1-10	1.5	1.5

[a] Both cis and trans isomers. [b] A minimum of three 10-μL injections were made by using 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, and 10 mg of each isomer/mL of CCl_4 solution.

from the difficulty in reproducibly measuring the peaks obtained on the UV detector due to the presence of the large aromatic hydrocarbon peak.

No comparison of the overall system described herein with other high-performance LC systems described in the published literature on resmethrin analysis can be given due to the lack of reported quantitative data. Zehner and Simonaitis (1976) described a method for the determination of resmethrin and the cis/trans ratio in formulated and technical-grade resmethrin using reversed-phase high-performance LC and a UV detector operated at 254 nm and a 60 °C column temperature. In this system, *trans*-resmethrin has a retention time of more than 50 min, and consequently there was a loss of sensitivity due to band broadening. Gunew (1978) reported a method for bioresmethrin (*trans*-resmethrin) residue determination in wheat samples using a high-performance LC–UV system after extensive extract cleanup and use of a backflush system without extract cleanup.

Permethrin. Unlike the case with resmethrin, both the cis and trans isomers were separately available for use. The IR spectra showed that each isomer had a slightly different λ_{max} for both the carbonyl and C–O absorption bands. The λ_{max} values for the carbonyl absorption were 5.8 and 5.75 μm for the cis and trans isomers, respectively. The λ_{max} values for the C–O absorption were 8.8 and 8.65 μm for the cis and trans isomers, respectively. Since the trans isomer is the one which is insecticidally active, and hence the compound of more interest, analyses were conducted at 5.75 and 8.65 μm. The UV detector was operated at 280 nm.

The mobile phase was 1% acetonitrile in CCl_4. The retention times on the IR chromatogram were 5.2–5.3 and 6.1–6.2 min for the cis and trans isomers, respectively. The bandwidths were the same as those reported above for resmethrin.

Data on the minimum detectable levels, linearity ranges, and detector sensitivities are given in Table III. Data were obtained by using a 1:1 (w/w) mixture of the two isomers; results obtained by using individual isomers were identical with those for the mixture. The minimum detectable level for the two isomers was 1 μg for the IR detector at either of the two wavelengths used. The UV detector had a 10-fold better minimum detectability (0.1 μg) for both isomers at the 0.08-AUFS range.

The sensitivities of the IR detector to *trans*-permethrin for the 5.75- and 8.65-μm wavelengths, respectively, were 0.10- and 0.16-cm peak height/μg at 0.1 AUFS and 0.35 and 0.57 cm/μg at 0.025 AUFS. Thus, there is greater sensitivity at the 8.65-μm wavelength. No apparent difference in sensitivities was noted at the two wavelengths for the cis isomer. A typical standard curve is shown in Figure 5.

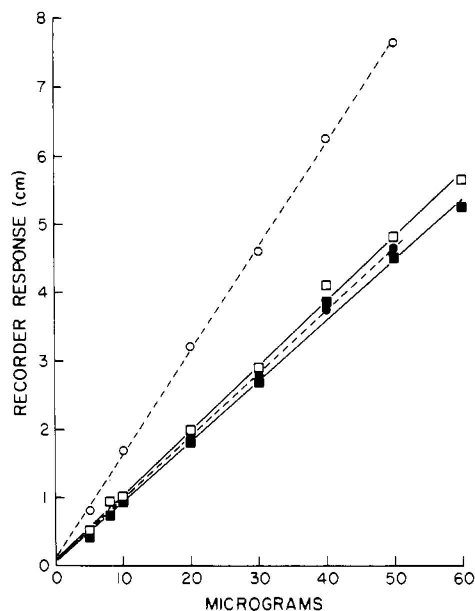

Figure 5. Typical standard curves for permethrin obtained by using the IR detector operated at 5.75 (solid line) and 8.65 (dashed line) μm; open symbols represent data for the trans isomer, and the closed symbols represent data for the cis isomer. Data were obtained at 0.1 AUFS, and each point represents the mean value obtained from three replicate sample determinations.

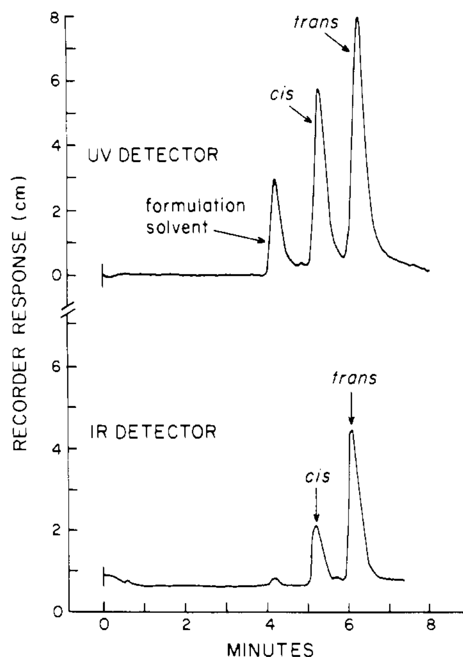

Figure 6. Liquid chromatograms obtained after injection of 10 μL of a 1% (v/v) solution of Pounce permethrin formulation in CCl_4. The IR detector was operated at 8.65 μm and 0.1 AUFS; the UV detector was operated at 280 nm and 0.64 AUFS.

Pounce 3.2EC permethrin formulation was analyzed by direct injection of the formulated material which had been diluted with CCl_4. Quantitation was by separate injections of analytical standards. Figure 6 shows the IR and UV chromatograms obtained after injection of a 1% (v/v) solution of Pounce 3.2EC in CCl_4. The UV analysis for permethrin is not complicated by the UV-absorbing formulating solvent, as was the case with resmethrin, due to the greater UV absorption of permethrin relative to resmethrin. Figure 7 shows the chromatograms obtained after injection of a 0.2% (v/v) solution of Pounce 3.2EC in CCl_4. The IR detector response at both the 5.75- and 8.65-μm

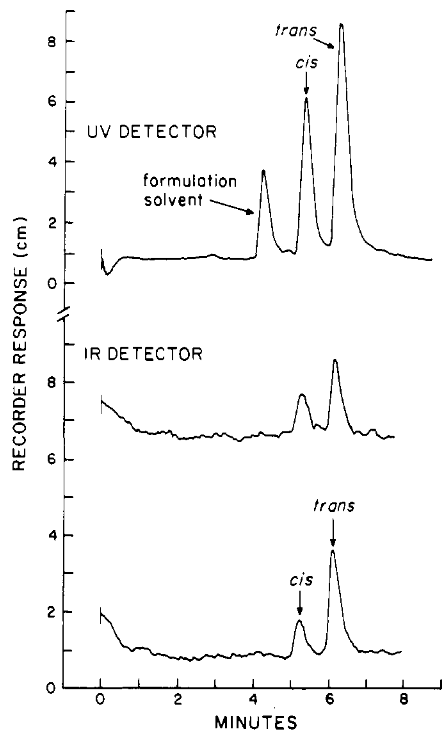

Figure 7. Liquid chromatograms obtained after injection of 10 μL of a 0.2% (v/v) solution of Pounce permethrin formulation in CCl_4. The IR detector was operated at 5.75 (top) and 8.65 (bottom) μm and 0.025 AUFS; the UV detector was operated at 280 nm and 0.16 AUFS.

Table IV. Results of the Analysis of Pounce 3.2EC Permethrin Formulation Using a High-Performance LC System with Tandem IR and UV Detectors

detector	range, AUFS	Pounce dilution used, %	results, lb/gal: cis	trans	total
IR, 8.65 μm	0.1	1.0	1.4	2.1	3.5
		1.5	1.3	2.0	3.3
	0.025	0.1	1.4	2.1	3.5
		0.2	1.3	2.0	3.3
IR, 5.75 μm	0.1	1.0	1.3	2.0	3.3
		1.5	1.3	2.0	3.3
	0.025	0.1	1.6	2.1	3.7
		0.2	1.4	2.4	3.8
		mean ± SD:	1.4 ± 0.1	2.1 ± 0.1	3.5 ± 0.2
UV, 280 nm	0.16	0.1	1.3	2.0	3.3
		0.1	1.6	2.2	3.8
		0.2	1.4	2.1	3.5
		0.2	1.5	2.1	3.6
		0.5	1.4	2.0	3.4
		mean ± SD:	1.5 ± 0.1	2.1 ± 0.1	3.5 ± 0.2

settings is shown. The ~50% greater response obtained at the 8.65-μm wavelength over the 5.75-μm wavelength is evident. Both wavelengths are equally usable, and selection would depend on the nature of the interfering material present in a sample. Table IV gives the results from the formulation analysis for the 3.2EC. The values for *cis*-, *trans*-, and total resmethrin were 1.4 ± 0.1, 2.1 ± 0.1, and 3.5 ± 0.2 lb/gal, respectively, by IR detection and 1.5 ± 0.1, 2.1 ± 0.1, and 3.5 ± 0.2, respectively, by UV detection. There was no statistical difference in the values obtained with the two detectors.

Kikta and Shierling (1978) described a high-performance LC–UV system for the analysis of permethrin. They used reversed phase at 40 °C and normal phase at ambient temperature. The authors suggested that both systems could be used for residue determinations if proper cleanup procedures are used comparable to those required for gas chromatographic systems with an electron-capture detector. They did not report any quantitative data.

Table V. Comparison of IR and UV Detectors Tandem in a High-Performance LC System for the Analysis of Fenvalerate Standard

detector	range, AUFS	min detectable, μg	linear range, μg	sensitivity, cm/μg
IR, 5.7 μm	0.1	6	6-80	0.05
	0.025	2	2-40	0.22
UV, 280 nm	0.64	0.5	0.5-20	0.38

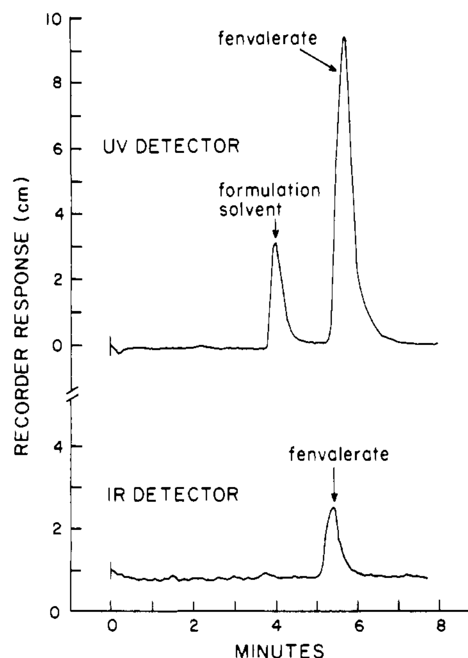

Figure 8. Liquid chromatograms obtained after injection of 10 μL of a 1% (v/v) solution of Pydrin fenvalerate formulation in CCl_4. The IR detector was operated at 5.7 μm and 0.1 AUFS; the UV detector was operated at 280 nm and 0.64 AUFS.

Fenvalerate. Even though fenvalerate is not a cyclopropanecarboxylic acid ester, it is still considered a pyrethroid. The infrared spectrum of fenvalerate in CCl_4 solution has two strong absorption bands, one at 5.7 μm and the other at 6.5 μm. All measurements were made at 5.7 μm since the mobile phase absorbed too strongly at 6.5 μm. The UV detector was operated at 280 nm.

With a mobile phase consisting of 1% acetonitrile in CCl_4, it was possible to separate the two diastereomers, and their retention times were 10.6 and 11.4 min. As individual standards were not available and there was no necessity in quantitating each diastereomer in the formulation, a 2.5% acetonitrile mobile phase was used to obtain a single fenvalerate peak. Under these conditions both analytical and technical-grade fenvalerate standards gave a single peak at 5.4–5.5 min on the IR detector and a single peak on the UV detector.

Table V gives data on the minimum detectable levels, linearity ranges, and sensitivities for fenvalerate. The minimum detectable amount was 2 μg with the IR detector and less than 0.25 μg with the UV detector. Figure 8 shows IR and UV chromatograms obtained after injection of a 1% (v/v) solution of Pydrin fenvalerate formulation in CCl_4. Table VI gives the results of the formulation analysis with quantitations made by separate injections of standards. The mean values obtained were 2.5 ± 0.2 and 2.4

Table VI. Results of the Analysis of Pydrin Fenvalerate Formulation Using a High-Performance LC System with Tandem IR and UV Detectors

detector	range, AUFS	Pydrin dilution used, %	fenvalerate, lb/gal
IR, 5.7 μm	0.1	0.5	2.37
		0.5	2.84
	0.025	0.5	2.33
		0.5	2.47
		0.5	2.77
		0.5	2.35
		mean ± SD:	2.5 ± 0.2
UV, 280 nm	0.64	0.5	2.22
		0.5	2.42
		0.5	2.27
		0.5	2.67
		0.5	2.32
		mean ± SD:	2.4 ± 0.2

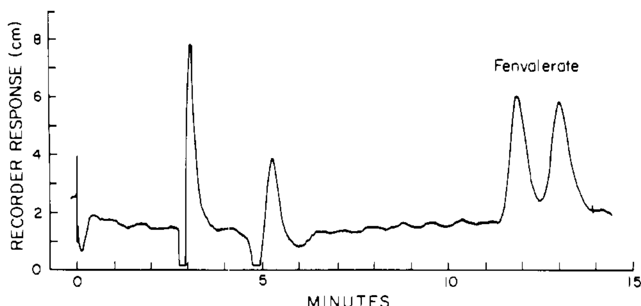

Figure 9. Liquid chromatogram obtained after injection of 6 μg of fenvalerate in 10 μL of CCl_4. The two fenvalerate diastereomers are shown at 11.5- and 12.6-min retention times. A UV detector was operated at 280 nm and 0.08 AUFS. The mobile phase was 80% cyclohexane, 19% CCl_4, and 1% acetonitrile at a flow rate of 1.2 mL/min.

± 0.2 lb/gal for the IR and UV detector analyses, respectively. There was no statistical difference in the two values. The two detectors were comparable in accuracy and reproducibility for the formulation analysis.

Fenvalerate is unstable under gas chromatographic conditions (Mourot et al., 1979). Formulation analysis was reported by Mourot et al. (1979) and involved direct analysis with high-performance LC–UV using both reversed and normal-phase conditions. It was reported that with reversed phase, aside from interference from the alkylbenzene in the formulation, the diastereomers were not separated; with normal phase retention times could not be kept constant but slowly decreased. No quantitative data were present for use in comparison with the system reported herein.

If a UV detector is used, a mobile phase of 80% cyclohexane, 19% CCl_4, and 1% acetonitrile can be used to separate the fenvalerate diastereomers; all other instrument conditions are the same as reported for the other studies reported herein. This system with retention times of 11.5 and 12.6 min for the two diastereomers is comparable to that of Mourot et al. (1979) in terms of analysis time and resolution but yields constant retention times. Figure 9 shows a sample chromatogram.

LITERATURE CITED

Bellamy, L. J. "The Infrared Spectra of Complex Molecules"; Wiley: New York, 1958; pp 29–30.
Chapman, R. A.; Harris, C. R. *J. Chromatogr.* **1978**, *166*, 513.
Fujie, G. H.; Fullmer, O. H. *J. Agric. Food Chem.* **1978**, *26*, 395.
Gunew, D. S. *Anal. Methods Pestic. Plant Growth Regul.* **1978**, *10*, 19–29.
Heath, R. R. *J. Assoc. Off. Anal. Chem.* **1972**, *55*, 1328.
Kikta, E. J., Jr.; Shierling, J. P. *J. Chromatogr.* **1978**, *150*, 229.
Lee, Y. W.; Westcott, N. D.; Reichle, R. A. *J. Assoc. Off. Anal. Chem.* **1978**, *61*, 869.
Mourot, D.; Delepine, B.; Boisseau, J.; Gayot, G. *J. Chromatogr.* **1979**, *168*, 277.
Oehler, D. D. *J. Assoc. Off. Anal. Chem.* **1979**, *62*, 1309.
Parris, N. A. *J. Chromatogr. Sci.* **1979**, *17*, 541.
Simonaitis, R. A.; Cail, R. S. *J. Assoc. Off. Anal. Chem.* **1975**, *58*, 1032.
Simonaitis, R. A.; Cail, R. S.; Zehner, J. M.; Bry, R. E. *J. Assoc. Off. Anal. Chem.* **1977**, *60*, 9.
Zehner, J. M.; Simonaitis, R. A. *J. Assoc. Off. Anal. Chem.* **1976**, *59*, 1101.

Received for review May 13, 1980. Accepted August 5, 1980. This research was partially supported by Regional Research Project W-45.

An Electron Capture Gas Chromatographic Method for Determination of Residues of 1,2-Dibromoethane in Fumigated Grapefruit

Jimmie R. King,* Donald L. von Windeguth, and Arthur K. Burditt, Jr.

An analytical procedure was developed for determining residues of 1,2-dibromoethane or ethylene dibromide (EDB) in grapefruit. The method involves steam distillation from a benzene–water mixture for separation and cleanup. When a gas chromatograph equipped with a nickel-63 electron capture detector was used to determine the concentration of EDB present in fortified samples of grapefruit, residues as low as 0.00038 mg/kg could be detected. The method was used to study the effect of storage time and temperature on the residue of EDB in fumigated grapefruit. Residues in fiberboard carton material were also determined.

The recent Rebuttable Presumption Against Registration (RPAR) for 1,2-dibromoethane [commonly referred to as ethylene dibromide (EDB)] by the Environmental Protection Agency (1977) greatly enhances the need for appropriate residue data. Likewise, the recommendation of the FAO/WHO Joint Meeting (FAO/WHO, 1967) that no residues of EDB be allowed to reach the consumer indicates the need for highly sensitive analytical methodology.

Subtropical Horticulture Research Unit, Science and Education Administration, Agricultural Research, U.S. Department of Agriculture, Miami, Florida 33158.

This article not subject to U.S. Copyright. Published 1980 by the American Chemical Society