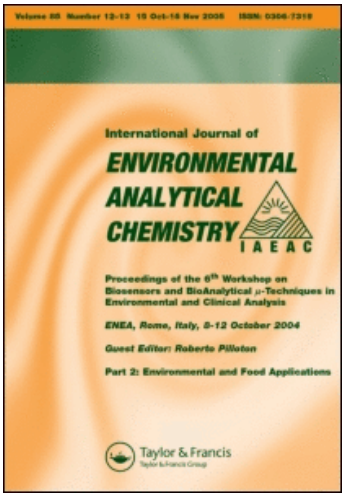

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Determination of Permethrin in Environmental Waters by Gas Chromatography-Selected Ion Monitoring-Mass Spectroscopy Using Ion Counting Detection

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Traces of permethrin in wastewater have been quantitated by GC-SIM-MS using direct ion counting detection. Under the recommended conditions, the detection limit for permethrin is 50 picograms with a signal-to-noise ratio of 6:1. This level of detection permits the determination of about 0.05 ppb permethrin in raw wastewater samples which have been concentrated and cleaned up by column chromatography. The method has been found sensitive and specific for permethrin in the presence of a variety of co-eluting substances. Details of the equipment and data system are described. The method has general utility.

KEY WORDS: Permethrin, environmental waters, ion counting detection, selected ion monitoring, gas chromatography-mass spectroscopy, FMC33297, Pounce® (Technical), NRDC 143, synthetic pyrethroids.

INTRODUCTION

Analytical techniques of highest sensitivity and specificity are often required for the trace analysis of the synthetic pyrethroid insecticide permethrin in the environment. Permethrin is the common name for 3-phenoxybenzyl (±)-*cis*, *trans*-3-(2,2-dichlorovinyl-2,2-dimethylcyclopropanecarboxylate. It is also known as NRDC 143 and FMC 33297 and is marketed by FMC as Pounce® (Technical). High sensitivity is required because some governmental agencies have set 4 ppb

as the maximum acceptable level of permethrin in environmental waters. This low level coincides with the LC_{50} level for a number of species of fish. Highest degrees of specificity are required because environmental samples often have very complex matrices.

A number of clean-up and chromatographic techniques have been reported which successfully quantitate permethrin present in crop residues, animal tissues and samples of environmental origin. Gas chromatographic (GC) techniques using flame ionization (FI) detection,[1-3] electron capture (EC) detection[4-7,16] and Coulson electrolytic conductivity (CEC) detection[7] have been described. The use of Hall detection is presently being studied.[8] Reported detection limits for FI, EC and CEC detectors are ~0.1 ppm, ~0.01 ppm and ~0.05 ppm, respectively, based upon GC methods which resolve the two isomeric forms of permethrin. High pressure liquid chromatographic techniques have also been reported[9,10] which have a detection limit of ~0.01 ppm.

Environmental water samples often contain hydrocarbons and halogenated contaminants which cannot be completely removed by clean-up procedures and which frequently have the same GC retention times as the geometrical permethrin isomers. In many cases, these interferences distort or saturate the EC, CEC and Hall detector responses. In order to circumvent these problems, we developed the highly specific and sensitive technique of Gas Chromatography-Selected Ion Monitoring-Mass Spectroscopy using ion counting detection and a data system (GC-SIM-MS-IC-DS) for experimental control, data acquisition and reduction.

This method is both selective and sensitive enough to analyze permethrin at the sub-ppm level in the presence of many co-eluting components. It also obviates the need for finding new GC conditions whenever new co-eluting compounds interfere when using standard GC detectors.

ADVANTAGES OF ION COUNTING[11-14]

Ion counting is an integration process in which the ions impinging upon the electron multiplier dynodes generate high frequency pulses which are counted as discrete events over a short preset time interval. The ion counting detection technique has been chosen because it is the most sensitive, efficient and direct method for measuring low level ion intensity mass chromatographic data. Advantages of ion counting include the discrimination of dark current electron-multiplier noise from that of ion signals; ease in computer interfacing due to the digital nature of the ion signal; ion counting accuracy in the presence of electron-multiplier bias drift; absence of electrometer-preamplifier baseline drift in the presence of

low level signals; high sensitivity (single ion detection); and large linear dynamic range. All these advantages can be routinely achieved by simple modification of existing mass spectrometers with commercially available high sensitivity ion (photon) counting hardware. Figure 1 illustrates the signal-to-noise improvement of ion counting vs. analog recording of a PCB (polychlorinated biphenyl) mixture (Aroclor 1254) run under identical GC and MS conditions. The signal-to-noise improvement in this case of ion counting relative to analog recording is about 25 times.

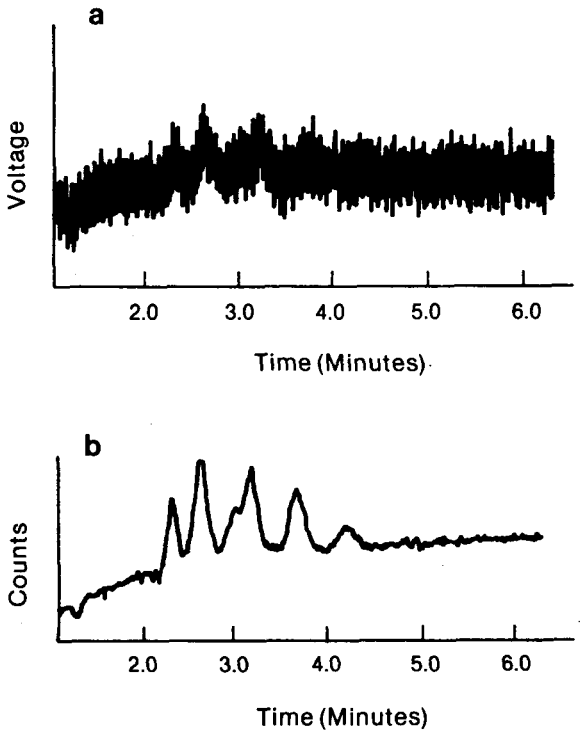

FIGURE 1 Comparison of analog detection (*a*) and ion counting detection (*b*) of 1 ng PCB (polychlorinated biphenyl) mixture (Aroclor 1254) at M/Z 326 under identical GC-MS conditions.

SAMPLE PREPARATION

A brief description of the procedure for concentration and clean-up of the wastewater samples follows. Wastewater samples were passed through a column packed with XAD-2 macroreticular resin. The eluted water was cycled through another equivalent column packed with XAD-2 resin.

Adsorbed components were then eluted with ethyl ether. The water layer in the eluate was separated from the ether layer and extracted with ether. All ether fractions were combined and concentrated in a modified Kuderna–Danish evaporative concentrator in which a straight column replaced the Snyder condenser. The concentrated ether extract was passed through a column of untreated Florisil® with a 90% hexane/10% ethyl ether solvent mixture to remove polar interferences and then concentrated in another modified Kuderna–Danish evaporative concentrator to about a 1 ml volume. Using this clean-up procedure, spiked water samples containing permethrin routinely have recoveries of 95% with concentration factors of about 10^3.

Standards of *cis*- and *trans*-permethrin were prepared by preparative high pressure liquid chromatography and fractional crystallization. The isomer purities were >99%. The physical properties of the *cis*- and *trans*-isomers were in agreement with those found in the literature.[15] Mixtures of the permethrin isomers were made up in hexane and used as standards for quantitating the wastewater samples.

METHODOLOGY

The wastewater extracts were injected into a GC using a packed column known to resolve the *cis*- and *trans*-isomers of permethrin. (For detailed conditions, see the section below entitled Apparatus Operating Conditions.) The components present in the extract elute from the column, enter the mass spectrometer at their respective retention times and are ionized and fragmented. By dwelling on characteristic ions of permethrin under low resolution mass spectral conditions, a mass chromatogram is generated. This method, known as selected ion monitoring (SIM), is very sensitive and specific.[15] Additional sensitivity enhancement is attained by the use of ion counting and data smoothing with the computer-based data system. Additional specificity can be achieved by dwelling on more than one ion, viz., multiple ion monitoring.

Figure 2 is a mass spectrum of permethrin obtained under electron impact conditions (70 eV ionization voltage). By far, the largest peak in the mass spectrum is the base peak at M/Z 183, corresponding to the 3-phenoxytropylium ion. This is the preferred ion for selected ion monitoring. When additional specificity is desired, the much less intense ion at M/Z 163 can be also monitored (30% relative intensity). This ion corresponds to the 3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropylium fragment ion.

In the described GC-SIM-MS scheme, the following criteria had to be

met when dwelling on both the 183 and/or 163 peaks in order for a component to be considered as permethrin:

a) Retention times must agree with those of the *cis*- and *trans*-isomers of permethrin.
b) The isomer intensity ratios observed in the mass chromatogram must agree with the known values, if available.
c) Ions observed must have the correct mass to charge ratios as found in the mass spectrum of permethrin, viz., ions at M/Z 163 and/or 183.
d) Ion intensity ratios must correspond to those found in the mass spectrum of permethrin.

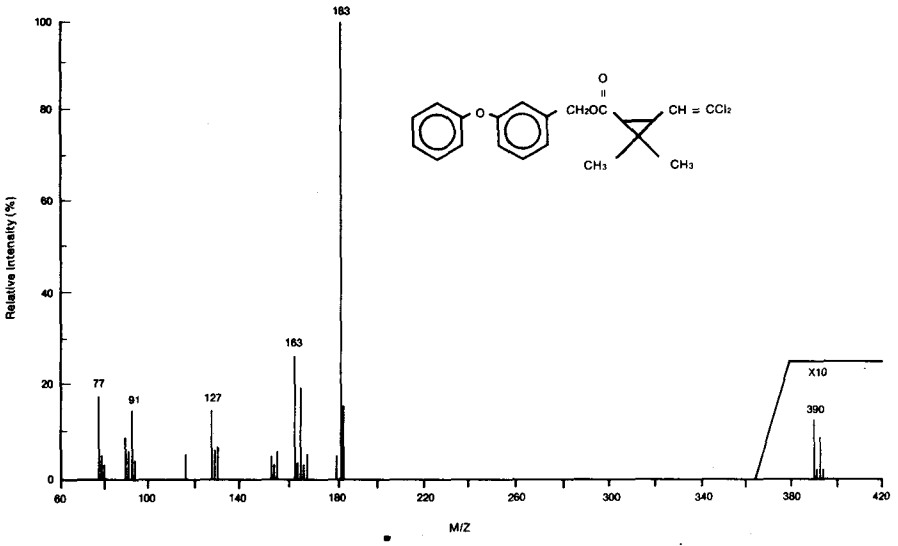

FIGURE 2 Electron impact (70 eV) mass spectrum of permethrin.

To confirm the mass chromatographic peaks considered to be that of permethrin, the unknown sample was spiked with about an equivalent amount of permethrin considered to be present in the unknown sample. If the peaks considered to be that of permethrin grew symmetrically and in proportion to the quantity of the spike, the peaks were confirmed to be that of permethrin.

Tests on pure permethrin samples, using the above described technique, indicate a detection limit of at least 50 and 300 picograms with a signal-to-noise ratio of 6:1 on the 183 and 163 peaks of permethrin, respectively. These figures correspond to a detectable concentration of about 50 and

300 ppt for the 183 and 163 ions, respectively (using a 1 μl injection of the wastewater extracts).

APPARATUS

The ions having a M/Z of 183 and 163 were monitored using an LKB 9000 GC-MS modified to acquire spectral information in the ion counting mode. The ion counting hardware which replaced the LKB electron-multiplier pre-amplifier consisted of a Princeton Applied Research (PARC) Model 1121 Amplifier-Discriminator and a PARC Model 1109 Photon Counter. The LKB accelerating voltage and electron-multiplier power supplies were replaced with a TREK (Barker, N.Y.) Model 608A High Voltage Programmable Power Supply and a Brandenberg (Thornton Heath, Surrey, U.K.) Model 2707 Regulated High Voltage Power Supply, respectively.

The data system used to collect, process and record the data consisted of a Digital Equipment Corporation (DEC) Model PDP 11/70 Mini-computer, Hewlett-Packard (HP) Model 2648A Graphics Terminal and a Tektronix Model 4632 Hard Copy Unit and an in-house designed Mass Spectrometer-Computer Interface Unit. Figure 3 is a block diagram illustrating the hardware used for selected ion monitoring.

The Mass Spectrometer-Computer Interface Unit is designed to accept data from the DEC PDP 11/70 Mini-computer and format it to drive the high speed, high voltage Programmable Power Supply, TREK 608A. The Interface Unit also accepts data from the PARC 1109 Counter and transmits this data to the PDP 11/70 Mini-computer as well as exercising start control over the PARC 1109 Counter. The Interface Unit contains the circuitry to implement multiple transmission Baud rates, serial (RS 232 data stream) to parallel conversion (seven bit ASCII character), a digital-to-analog converter (DAC) for control of the TREK 608A Power Supply voltage, variable trigger delays for the PARC 1109 Counter, selectable pre-set voltages for setting the TREK 608A Power Supply voltages, and self-test features. Figure 4 is a block diagram illustrating the Mass Spectrometer-Computer Interface Unit hardware.

DATA SYSTEM SOFTWARE FEATURES

The DEC PDP 11/70 has a multi-user, multi-task operating system (RSX-11M). The software designed for this system is written in FORTRAN IV. The software system initiates the trigger for data acquisition to begin. The integrated ion counts from the PARC 1109 Counter on command is then transferred to the DEC PDP 11/70. This data is then displayed in real-

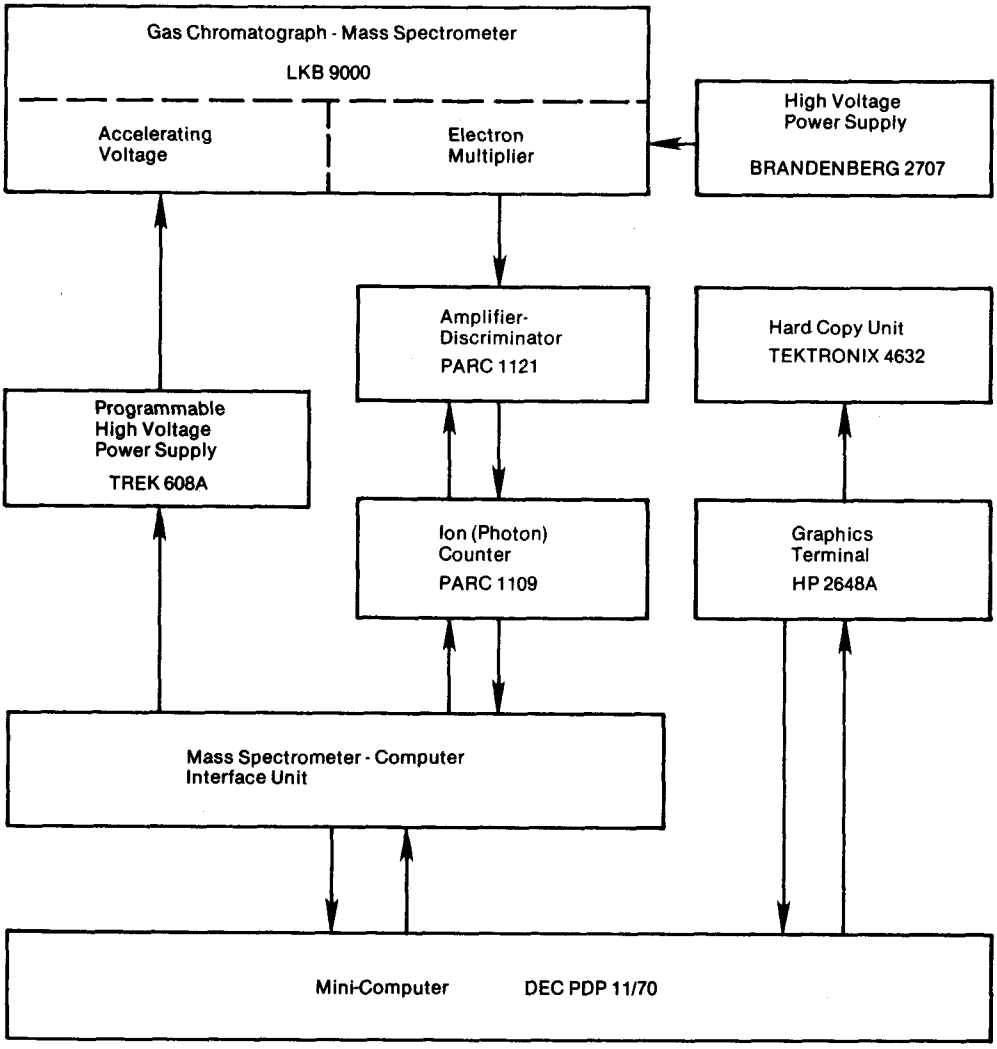

FIGURE 3 Block diagram of GC-SIM-MS-IC-DS hardware.

time on the HP 2648A Graphics Terminal in the form of ion counts vs. retention time. Routines for scanning and staircasing the DAC are provided for calibrating the mass axis and/or monitoring pre-selected ions. Software for data analysis is also included. Among the available analysis routines are baseline subtraction, integration of selected ion mass chromatogram peak areas, peak intensities, retention times, outlier

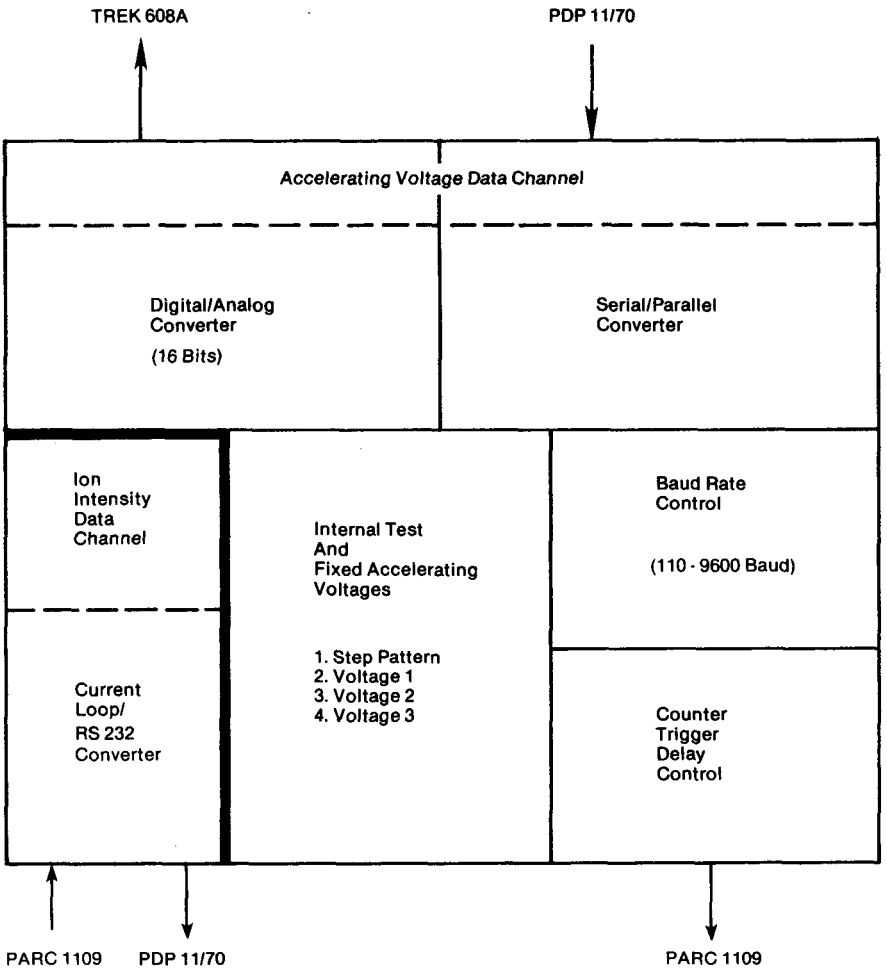

FIGURE 4 Block diagram of the Mass Spectrometer-Computer Interface Unit.

removal algorithm, running quadratic and median smoothing routines, resolution enhancement, analysis of the time axis data, band deconvolution and summation, cross- and auto-correlation of chromatograms, and spectral mathematics (addition, subtraction, division and multiplication of chromatographic data with constants or other chromatographic data).

This software was based upon a software package obtained from the National Institutes of Health[16] which was considerably modified and

enhanced. The major software modifications included the software necessary to control and acquire the digital data from the PARC 1109 Photon (Ion) Counter, algorithms for the calibration of the mass axis and routines for data reduction and analysis.

APPARATUS OPERATING CONDITIONS

The operating conditions for the LKB 9000 Mass Spectrometer and the operating conditions for the LKB 9000 Gas Chromatograph are given in Table I. The trigger delay and integration time for the PARC 1109

TABLE I

GC and MS operating conditions for LKB 9000 GC-MS used for selective ion monitoring

LKB 9000 MS operating conditions		
Ionization mode	Electron impact	
Filament voltage	7.2 aJ (45 eV)	
Filament current	120 μA	
Mass marker reading	209.2 calibrated at an accelerating voltage of 3564 V	
Accelerating voltage	4584 V for M/Z 163	
	4045 V for M/Z 183	
Electron multiplier voltage	4500 V	
GC-MS interface	Jet separator, 300°C	
Mass spectral resolution	~200	
LKB 9000 GC operating conditions		
Column	1% SP-2250 on Supelcoport, U.S. standard sieve 150–180 μm (80/100 mesh), 1.8 m (6 ft) × 2 mm I.D.	
Carrier gas	Helium at 25 ml · min^{-1}	
Injector temperature	275°C	
Isothermal temperature	230°C	
Temperature program	Initial temperature	200°C
	Initial hold	2 min
	Temperature rate	8°C · min^{-1}
	Final temperature	260°C

Counter was set at 4 ms and 0.5 sec, respectively, and the discriminator level on the PARC 1121 Amplifier-Discriminator was set to 0.1 mV.

Optimization of the GC conditions, though desirable, was not necessarily required for the quantitation of permethrin in the waste waters studied because the GC-SIM-MS-IC-DS technique was found to be specific and sensitive enough for the analysis. The major criterion for choosing the packed column liquid phase was its ability to resolve the *cis*- and *trans*-permethrin isomers. SP-2250, a 50% methyl/50% phenyl silicone GC liquid phase mixture, satisfied this criterion well.

GC INJECTION AND SAMPLING PROCEDURES

The following GC injection and sampling procedure was followed for analysis of permethrin in wastewater extracts:

a) The 183 and/or 163 ions of permethrin were identified by scanning the accelerating voltage using the very low-level residual permethrin typically in the instrument background from previous work.
b) A mass chromatogram of a permethrin standard was run to check the number of ions generated with previously run standard samples.
c) Step (*a*) was repeated to check and correct for magnet drift.
d) A wastewater extract believed to contain permethrin was run.
e) Step (*c*) was repeated.
f) A spiked wastewater extract was run.
g) Step (*c*) or (*b*) was repeated.

Since external calibration techniques were used, the precision of each injection of the extract was checked in the following ways:

a) The impurity peaks present in the wastewater were used as internal standards to check the self-consistency of the sample sizes of the spiked and unspiked extracts.
b) Agreement between the number of counts in a known permethrin standard and the computed number of counts attributed to permethrin in the spiked extract was also checked.

DETERMINATION

Permethrin concentrations were computed from the integrated areas of the mass chromatographic peaks identified as the *cis*- and *trans*-forms of permethrin relative to that of a standard sample of permethrin. The integrated areas were computed after baseline corrections were made for instrumental background and GC column bleed. The following expression is used for computing the concentration of permethrin in ppm in wastewaters relative to a permethrin standard:

$$\text{Permethrin concentration in PPM} = \frac{\text{IA(Sample)} \cdot \text{NG(Standard)}}{\text{IA(Standard)} \cdot \text{V(Sample)} \cdot \text{D(Sample)} \cdot \text{CF} \cdot \text{RF}} \quad (1)$$

where IA is the integrated mass chromatographic peak area in units of counts-minutes; NG is the number of nanograms of standard injected; V

is the number of microliters of sample concentrate injected; D is the density of the original water sample in $mg/\mu l = gm/cm^3$, essentially unity; CF is the concentration factor of the sample (CF = initial volume of raw sample/final volume of extracted sample); and, RF is the recovery factor (RF = mass of permethrin in extracted sample/mass of permethrin in the raw sample) determined in separate experiments with permethrin standards.

In the quantitation of low levels of permethrin, the largest experimental errors are associated with the reproducible determination of the integrated areas for the standard and sample. Typically, the relative standard deviation in the reported values for the concentration of permethrin range from 5–20% and can be computed from

$$R_{ppm} = [R^2_{IA(Sample)} + R^2_{IA(Standard)}]^{1/2} \tag{2}$$

where R_{ppm} is the relative standard deviation in ppm due to corresponding relative standard deviations in the integrated areas of the sample and standard, $R_{IA(Sample)}$ and $R_{IA(Standard)}$.

In cases where either the *cis*- or *trans*-components are masked by large overlapping mass chromatographic peaks or are faintly visible on the shoulder of larger peaks, the presence of permethrin was confirmed by spiking experiments and quantitated by integrating the area of the deconvoluted components associated with the *cis*- and *trans*-isomers of permethrin. The deconvolution procedure consisted of fitting the experimental data by non-linear least squares using a Gauss–Newton algorithm.[16] The Gaussian function was chosen since it generally describes the band contour of gas chromatographic peaks.[17] The number of Gaussian functions chosen to describe a mass chromatogram was estimated from the band shape. The Gaussian function is defined as:

$$A = \hat{A} \exp[-\ln 2 \cdot (t - t_0)^2 / b^2] \tag{3}$$

where the variables A and t are the number of counts and time, respectively, and the fitted constants are $\hat{A}$, t_0 and b where $\hat{A}$ is the peak maximum (maximum ion counts), t_0 the peak center (retention time) and b is the peak half-width at half the peak maximum. The integrated Gaussian peak area is given by:

$$IA = \int_{-\infty}^{+\infty} A \, dt = (\pi/\ln 2)^{1/2} \hat{A} b = 2.12893 \hat{A} b. \tag{4}$$

ANALYSES OF WASTEWATER SAMPLES

a) Analyses of wastewater sample containing halogenated compounds (Sample A)

Permethrin, when analyzed on methyl silicone type GC columns, co-elutes with some halogenated pollutants found in wastewaters, e.g., tetradifon (*p*-

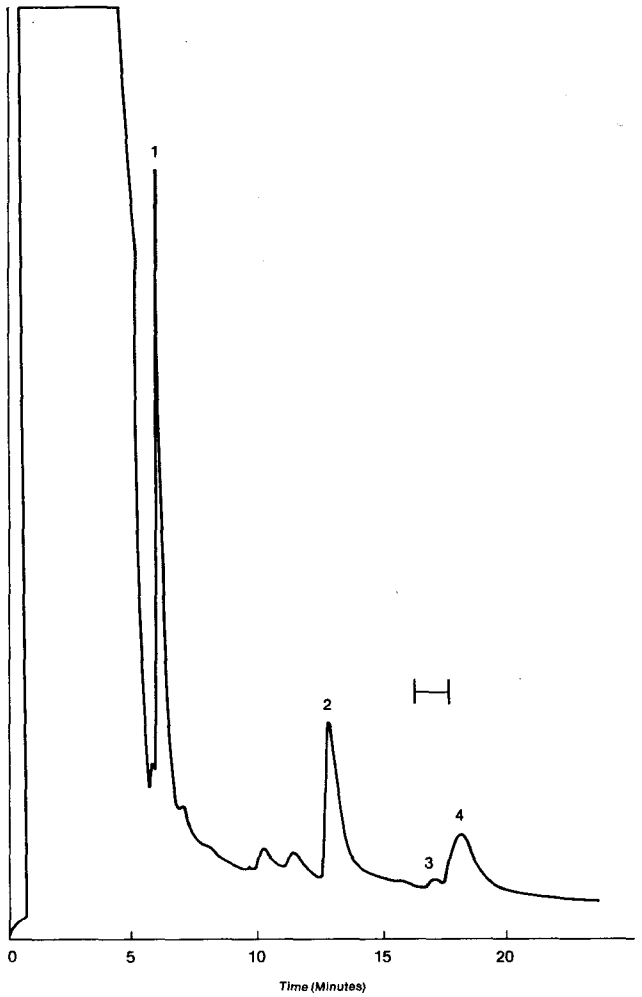

FIGURE 5 FI detection gas chromatogram and mass spectral assignments for Sample A. The retention time window for permethrin is indicated by the bar from 16.0–16.8 minutes GC conditions: 6′ 5% SP-2330, 80°C initial temp. programmed at 12°C/minute to 265°C and held. Mass spectral assignments: 1-2,6-di-tert-butyl-4-methyl phenol, 2-dioctyl phthalate, 3-dichloro analog of tetradifon, 4-tetradifon.

chlorophenyl 2,4,5-trichlorophenyl sulfone). It was found that this interference could be resolved from permethrin on cyanopropyl silicone type columns. However, after this column was in use for some time, chlorine containing tetradifon analogs began to appear in some of the wastewater samples which co-eluted with permethrin. Figure 5 is a temperature-programmed gas chromatogram of a wastewater sample obtained with a flame ionization detector. The components were identified by electron impact and chemical ionization mass spectroscopy. The retention time window for permethrin and tetradifon analogs is 16.0–16.8 minutes. Both EC and Hall detection methods were not reproducible for this sample and often the detectors saturated due to the chlorine containing interferences.

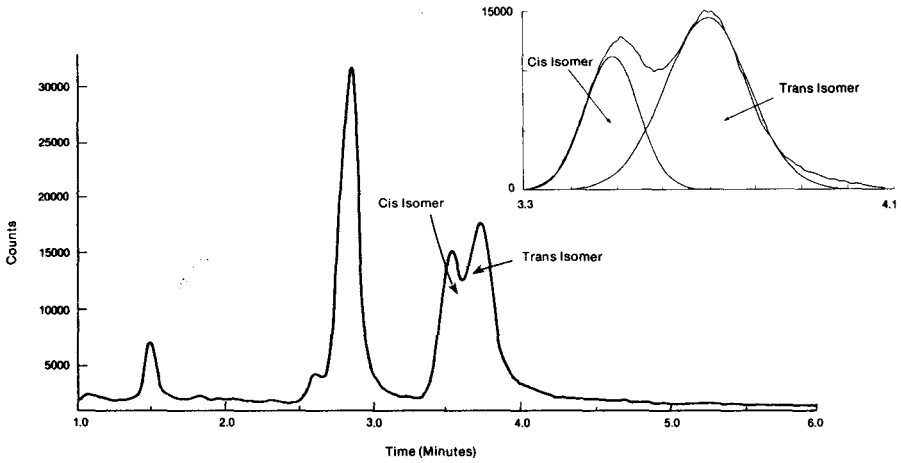

FIGURE 6 Mass chromatogram of 1.0 μl of Sample A run under isothermal GC conditions of Table I. Inset is an expanded, baseline corrected and deconvoluted mass chromatogram of the *cis*- and *trans*-permethrin isomers.

Figure 6 is a mass chromatogram of the sample obtained under the isothermal GC-SIM-MS conditions described in Table I and also shows the deconvoluted mass chromatogram. A calibration standard consisting of 3.25 ng of permethrin run under the same isothermal conditions is illustrated in Figure 7. Note the sensitivity of the method to permethrin.

Figure 6 clearly illustrates the generality of the GC-SIM-MS method. In spite of the fact that tetradifon analogs co-elute with permethrin, they have no fragment ion at M/Z 183, hence, the components eluting at 3.5 and 3.7 minutes are attributed to the *cis*- and *trans*-isomers of permethrin. The experimental and deconvoluted integrated areas are tabulated in Table II. The concentrated wastewater extract analyzed as 42.4 ppm

permethrin which corresponded to 0.11 ppm permethrin in the raw wastewater sample. The *cis/trans*-isomer ratio obtained from the deconvolution data is 33/67. Further verification of these values can be obtained by observing the less sensitive M/Z 163 fragment ion of permethrin under identical GC-SIM-MS conditions.

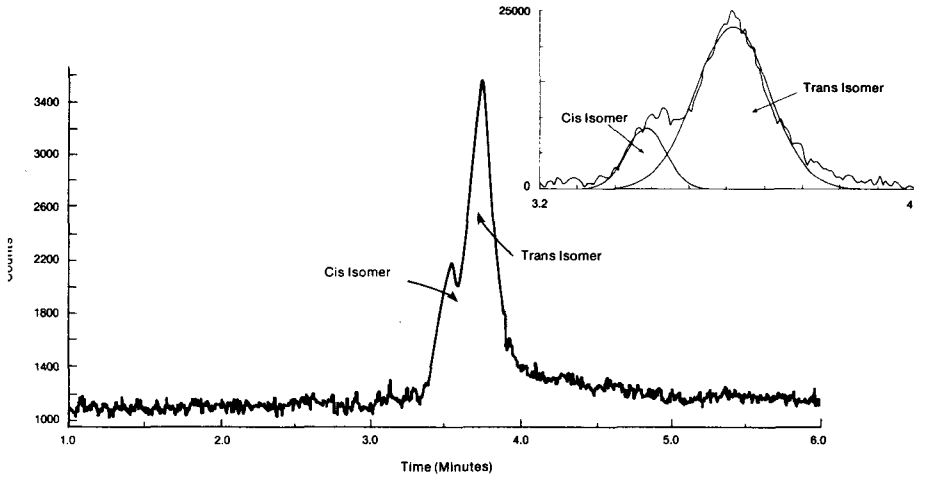

FIGURE 7 Mass chromatogram of a 3.25 ng sample of permethrin obtained under the isothermal GC conditions described in Table I. Inset is an expanded, baseline corrected and deconvoluted mass chromatogram.

b) Analysis of wastewater sample contaminated with phthalate esters and hydrocarbons (Sample B)

Some wastewater samples are highly contaminated with phthalates and hydrocarbons. The temperature-programmed gas chromatogram obtained on such a sample is illustrated in Figure 8. The assignments indicated were made from electron impact and chemical ionization mass spectra. These contaminates were not readily removed by the previously described clean-up procedure. In addition, they often saturated the EC and Hall GC detectors or made them behave in a non-reproducible fashion. The problem of reproducibility with this type of sample can be overcome readily by GC-SIM-MS. However, due to the large number of interferences, illustrated here, it was necessary to study this sample under temperature-programmed GC conditions in order to achieve better separation of permethrin from the interferences.

Figures 9, 10 and 11 are typical mass chromatograms of 1.8 ng of permethrin (Standard), a wastewater extract and the extract spiked with

TABLE II

Typical analyses of permethrin in wastewaters

Samples	Integrated experimental area[c]	Integrated deconvoluted areas[c]			Concentration of extract (PPM)	Concentration factor (CF)	Recovery factor (RF)	Concentration of raw wastewater sample (PPM)
		Cis-isomer (%)	*Trans*-isomer (%)	Total				
Standard (3.25 ng)	604	110 (17)	544 (83)	653				
Sample A[a] (1.0 μl)	5210	1710 (33)	3450 (67)	5160	42.4	258	0.95	0.11
Standard (1.8 ng)	4240	859 (20)	3470 (80)	4330				
Sample B[b] (3.0 μl)	NI	759 (36)	1370 (64)	2130	0.448	1210	0.95	0.00026
Sample B[b] (7.0 μl) + standard (0.90 ng)	NI	2000	5600	7600				

Consistency check on Sample B[b] using the spiked sample

[I] = [IA Sample B[b] (7.0 μl) + IA standard (0.90 ng)] − 1/2 [IA standard (1.8 ng)] = 5430 CM

[II] = 7/3 [IA Sample B[b] (3.0 μl)] = 4970 CM

$$\text{Maximum relative error} = \frac{[\text{I}] - [\text{II}]}{([\text{I}] + [\text{II}])/2} \times 100 = 8.8\,\%$$

[a]Sample A corresponds to the wastewater sample containing halogenated compounds.

[b]Sample B corresponds to the wastewater sample containing phthalate esters.

[c]Area unit is counts · minutes, CM.

NI = Not integratable—interference present.

IA = Integrated area.

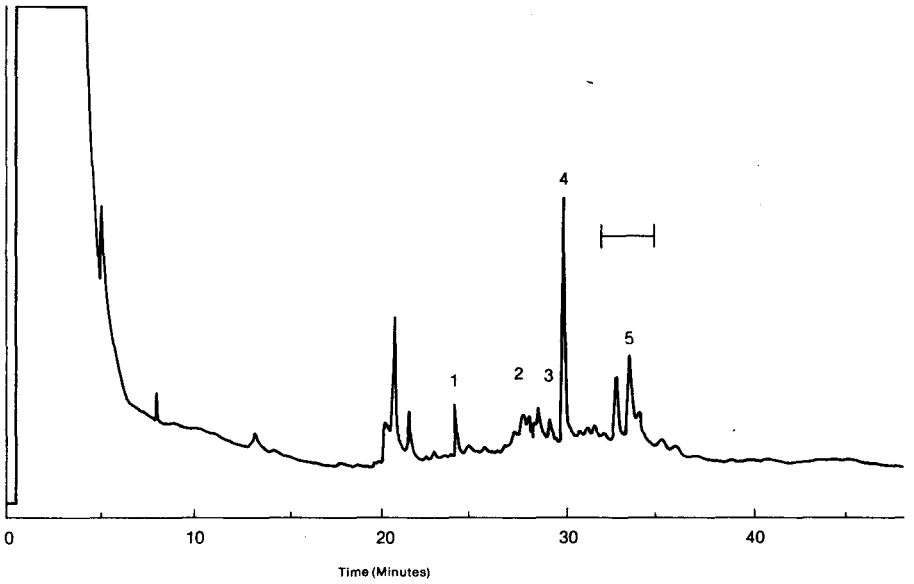

FIGURE 8 FI detection gas chromatogram and mass spectral assignments for Sample B. The retention time window for permethrin is indicated by the bar. GC conditions: 6′ 1% SP-2250 50°C initial temp., held for 4 minutes, programmed at 8°C/min., to 260°C and held. Mass spectral assignments: 1-dibutyl phthalate, 2-hydrocarbons. 3-$(Cl_2C_3H_5O)_3P{=}O$, 4-dioctyl phthalate, 5-MW 410, unknown structure.

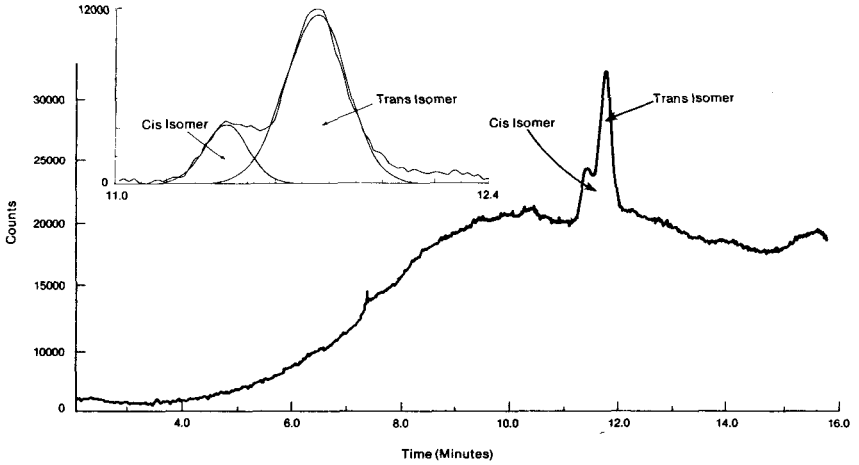

FIGURE 9 Mass chromatograms of a 1.8 ng sample of permethrin obtained under the temperature programmed conditions described in Table I. Inset is an expanded, baseline corrected and deconvoluted mass chromatogram.

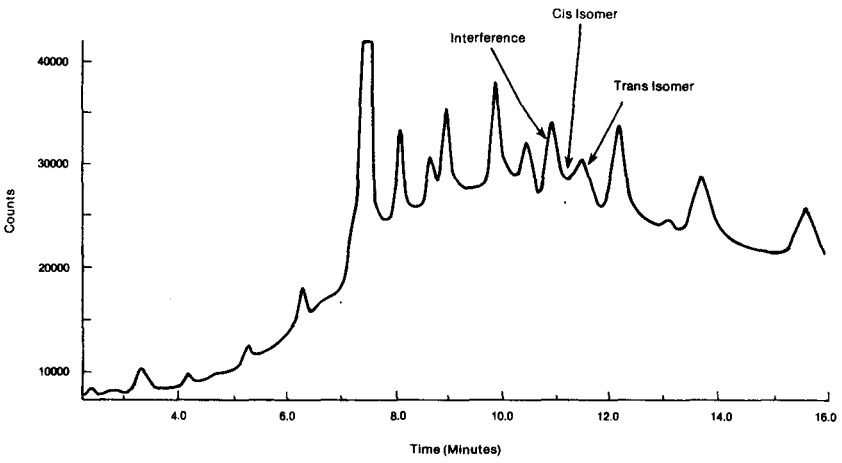

FIGURE 10 Mass chromatogram of 3.0 μl of Sample B run under the temperature programmed GC conditions listed in Table I.

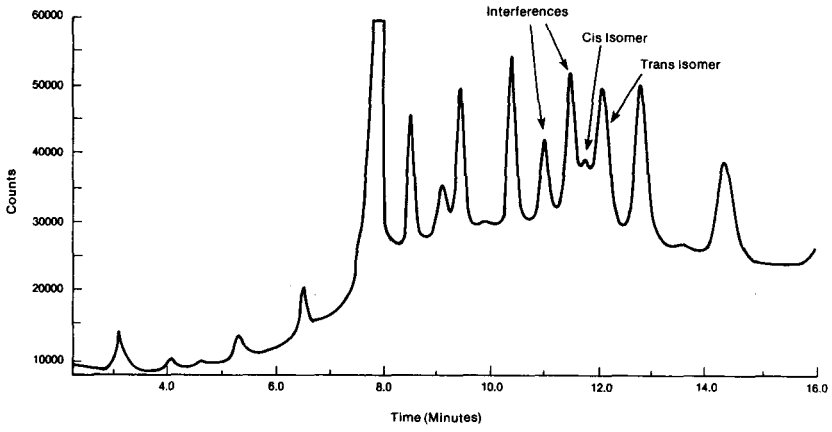

FIGURE 11 Mass chromatogram of 7.0 μl of Sample B spiked with 0.90 ng of permethrin run under the temperature programmed GC conditions listed in Table I.

permethrin run under the temperature programmed GC-SIM-MS-IC-DS conditions described in Table I. The rising and then plateauing baseline is due to GC column bleed. Slight differences in retention times are due to matrix effects, operator injection delays and non-linearity and reproducibility of the GC temperature programmer of the LKB 9000 GC-MS.

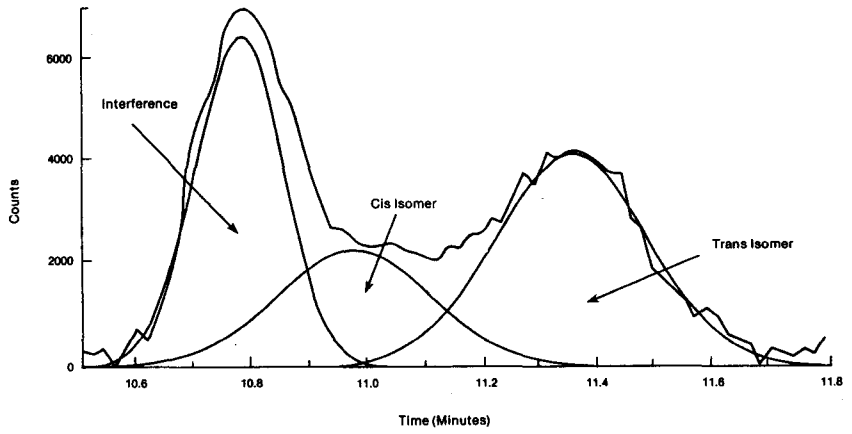

FIGURE 12 Expanded, baseline corrected and deconvoluted mass chromatogram of the permethrin retention time window of 3.0 μl of Sample B. Compare with Figure 10.

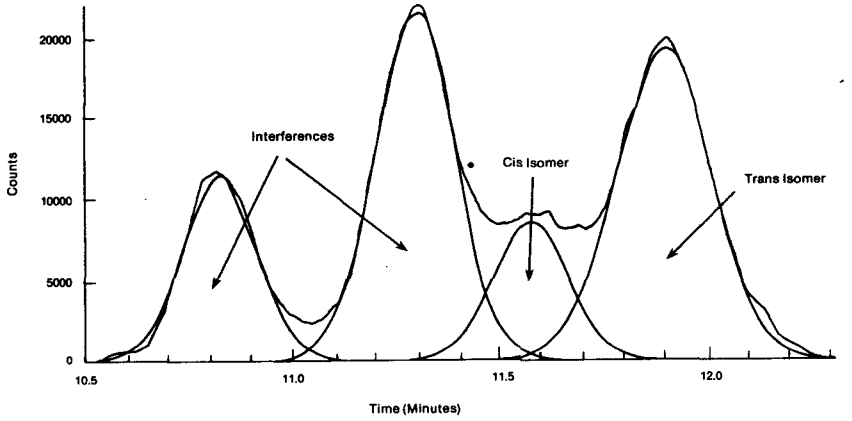

FIGURE 13 Expanded, baseline corrected and deconvoluted mass chromatogram of the permethrin retention time window of 7.0 μl Sample B spiked with 0.90 ng permethrin. Compare with Figure 11.

By comparing the unspiked and spiked samples, Figures 10 and 11, the retention time windows for the *cis*- and *trans*-isomers of permethrin can be identified. Due to the large impurity peak in Sample B at about 10.8 minutes, the *cis*- and *trans*-isomers are not resolved. To quantitate accurately this sample, it was necessary to deconvolute the regions of interest in the mass chromatograms using the method described

previously. Figures 12 and 13 illustrate the deconvolution curves for the unspiked and spiked samples. The quantitative data are listed in Table II. The concentrations of the concentrated extract and raw wastewater samples were computed relative to the integrated area of the 1.8 ng permethrin standard using Eq. (1). These data were checked for consistency by comparing the integrated areas of the concentrated extract with that of the spiked extract. These calculations are illustrated at the bottom of Table II. Note that the calculations include corrections due to the different volumes of the extract and spiked extract. The maximum difference between the two experiments and their mean is about 9 %.

The concentrated wastewater extract was found to contain 0.448 ppm permethrin which corresponds to 0.00026 ppm (0.26 ppb) permethrin in the raw wastewater sample. The *cis/trans*-isomer ratio of permethrin in the sample calculated from the deconvolution data is 36/64.

SUMMARY

Analytical techniques of highest sensitivity and specificity are often required for the analyses of permethrin in environmental matrices. GC-SIM-MS techniques using an LKB 9000 GC-MS modified for ion counting detection with a data system has been demonstrated for the low level quantitation of permethrin. Ion counting extends the detection limits over that of the analog GC-MS system by a factor of about 25 times. The data system controls the experiments, acquires and reduces the data, thereby reducing operator interaction and aiding in data interpretation. With clean-up and concentration procedures, levels in raw environmental water samples above 0.05 ppb of permethrin can be routinely quantitated.

This apparatus and methodology has been applied generally to the analysis of other trace components present in very complex matrices of environmental origin and found to be similarly sensitive and to give useful analytical results.

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