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Stability of pyrethroid pesticides in freeze-dried river sediment

PREPARATION, HOMOGENEITY AND FIRST INVESTIGATIONS OF THE STABILITY STUDY

W.A. House & I.S. Farr

ABSTRACT

1. A 30 kg batch of 0.5 mm sieved freeze-dried river sediment has been prepared and homogenized.

2. The homogeneity of the batch has been assessed using X-ray fluorescence and organic matter analysis at the 1 g level.

3. 12 bottles of 50 g sub-samples of sediment have been stored at -20°C, room temperature and 40°C. The concentration of the pesticide, cis-permethrin, has been determined at the start of the stability trial.

4. The concentration of permethrin in the sediments stored at three different temperatures has been evaluated after the first storage interval.

5. No significant differences could be detected between the concentration of the pesticide in the sediments stored at different temperatures. The results indicate that if losses are occurring, then the low rates necessitate a longer-term study to permit quantification.

CONTENTS

1. SEDIMENT PREPARATION

1.1 Sediment selection

A survey conducted prior to this study had identified a river site where the sediment and water contained a number of pesticide residues. Preliminary analysis of the sediment indicated levels of cis-permethrin in excess of 20 $\mu g\ g^{-1}$. The site, a mill pool with a large back eddy, contains banks of sandy sediment which are readily accessible.

1.2 Sediment collection

The sediment was collected using a pond net (1 mm mesh). The water content of each collection was partially drained through the net before transfer of the sediment to a 5 mm mesh galvanized screen mounted over a hard plastic tray. The sediment passing the screen was collected in the trays and tapped to encourage settlement. Supernatant water was then discarded.

Approximately 75 kg of wet sediment was transported to the River Laboratory within five hours of sampling. Vibration during the transport caused further settlement in the trays. The supernatant water was discarded before the sample was divided into 15 kg batches for overnight storage at 5°C. The moisture content of the sample was approximately 30%.

1.3 Sediment drying and sub-sampling

The following morning the entire batch of sediment was divided into approximately 1 kg amounts which were placed in aluminium trays and then transported for freeze-drying. This was performed using an Edwards Supermodulyo system in two batches over a period of 12 days. The dried samples were then re-sieved, first through a stainless-steel sieve of 1 mm mesh then through a 0.5 mm mesh brass sieve.

A 30 kg batch of sieved sediment was then collected and thoroughly mixed using stainless steel scoops. The collection method, sample division for freeze-drying and sieving procedures, ensured that the sediment was adequately mixed for subsampling.

50.00 g (± 0.01 g) subsamples of the dry sediment were weighed on a mechanical top-pan balance (Mettler P1210) into 60 ml amber glass powder bottles. These were flushed with nitrogen before and after filling, then sealed with lined Bakelite screw caps.

Bottles were then assigned a number (BCR #) at random. Bottles were then selected at random and assigned to the different storage conditions as specified in the contract:

(a) 4 bottles were set aside for zero-time analysis.

(b) 12 bottles were assigned to each of the storage temperatures used; 40°C, room temperature (RT) and -20°C.

(c) 10 bottles were assigned to element analysis using X-Ray Fluorescence.

(d) 10 samples (5 g each) were also taken from the batch and sub-sampled at the 1 g level to assess the variation in organic content.

The source batch of sediment was mixed using stainless steel scoops after each sampling.

The remaining source batch (approximately 25 kg) was transferred to a dry plastic, 25 litre container previously washed with methanol, acetone and hexane. The container was flushed before and after filling with nitrogen gas. After sealing the container with a plastic screw insert, it was encased in black polythene and stored at 5 °C in the dark.

A further three (50 g) samples were later taken from the source batch of sediment for a second reference-time analysis. The 25 kg batch was subsequently flushed with nitrogen and resealed.

2. HOMOGENEITY STUDY OF THE PILOT MATERIAL

The homogeneity of the freeze-dried sediment was evaluated by both x-ray fluorescence spectrometry and measurement of the organic matter content of sub-samples from the bulk material.

2.1 Results of the X-ray Fluorescence Analysis (XRF)

Ten bottles containing 50 g of sediment were selected at random from the batch collected for pesticide stability trials. The samples were then analysed for Si, Al, Fe and Mn. Five replicate measurements of each of the elements were performed on each pellet to assess the variance of the measurements on each sample. The results of the measurements for the 2 major elements (Si, Al) and trace elements (Fe and Mn) are collected together in Table 1. The sample codes refer to the BCR number of the bottle from the original batch of 50 samples. The results for Mn are expressed in ppm.

The data were analysed to obtain basic statistical parameters (Tables 2 and 3). The analysis of variance (MINITAB statistical package) produced the results shown in Tables 4 and 5. The sample variance was calculated from the mean of squares deviation (MS) for the samples and the within sample variance, $\hat{\sigma}_w^2$.

$$\hat{\sigma}_s^2 = (ms - \hat{\sigma}_w^2)/n$$

where n = 5.

Table 4 shows that for the major elements the coefficient of variation is low and satisfactory homogeneity of the bulk sample has been achieved. For the trace elements, Fe and Mn, the variance is larger. The results for all the elements indicate that the major contribution to the uncertainty is the sample variability rather than errors associated with the instrument measurement. For all the elements, the variance due to be measurement is <2% of the total variance. The F-Test is not meaningful for the analysis because of the extremely small measurement error i.e. within sample variance. The coefficients of variability (CV) are expected to decrease considerably for 50 g samples used in the pesticide analysis when compared with the 1 g samples used here. Because of the exhaustive sieving and mixing of the bulk sediment sample prior to sub-sampling, the homogeneity at the 1 g level for trace elements could only be improved by grinding the sample. This was not considered to be a practical alternative because of the possibility of large losses of pesticide during the grinding and the problems of ensuring homogeneous grinding of a large batch (>25 kg) of sediment.

Table 1 Results of the x-ray fluorescence analysis of BCR samples 3, 10, 14, 17, 19, 22, 33, 39, 40 and 48. Si, Al, Fe in units of % by mass. Mn in ppm.

ROW	CODE	Si	Al	Fe	Mn
1	3	94.6630	2.88649	1.21581	261
2	3	94.61146	2.87296	1.23579	264
3	3	94.5472	2.88121	1.21808	260
4	3	94.5755	2.87278	1.24999	261
5	3	94.4688	2.89658	1.22867	263
6	10	93.8912	3.05181	1.38678	291
7	10	93.8552	3.02037	1.42076	293
8	10	93.8953	3.03714	1.39795	291
9	10	93.8971	3.01636	1.40359	289
10	10	93.9448	3.03941	1.41754	292
11	14	93.8538	3.12613	1.59295	228
12	14	93.8539	3.11050	1.57213	227
13	14	93.8711	3.11941	1.58683	230
14	14	93.8605	3.122151	1.59532	227
15	14	93.8685	3.10247	1.60961	231
16	17	93.9342	3.05697	1.68847	284
17	17	93.9275	3.06387	1.66035	278
18	17	93.9133	3.05705	1.68866	280
19	17	93.9115	3.05548	1.67911	283
20	17	93.8909	3.06036	1.68703	281
21	19	93.7420	3.01998	1.57653	338
22	19	93.7362	3.02527	1.58058	341
23	19	93.7218	3.01112	1.58207	340
24	19	93.6966	3.02823	1.61009	339
25	19	93.6904	3.01749	1.58737	341
26	22	93.3349	3.06684	1.82403	422
27	22	93.3532	3.06456	1.83728	419
28	22	93.3611	3.07518	1.82593	422
29	22	93.3719	3.06928	1.81276	420
30	22	93.3600	3.06107	1.81835	419
31	33	93.9516	2.88711	1.57894	265
32	33	93.9446	2.89759	1.59163	263
33	33	93.9530	2.89374	1.57033	267
34	33	93.9518	2.88047	1.58772	265
35	33	93.9666	2.87663	1.56692	264
36	39	93.8067	2.98789	1.61646	384
37	39	93.7904	2.98020	1.60583	381
38	39	93.7834	3.00343	1.62300	384
39	39	93.7966	3.00147	1.60488	385
40	39	93.7805	2.99348	1.60242	385
41	40	93.8885	3.01374	1.63060	304
42	40	93.8534	3.02142	1.62419	303
43	40	93.8414	3.01059	1.62874	304
44	40	93.8581	3.00640	1.61473	307
45	40	93.8661	3.01723	1.61748	306
46	48	93.7193	3.06509	1.70750	405
47	48	93.6977	3.09286	1.67853	403
48	48	93.6820	3.06561	1.70627	405
49	48	93.6804	3.09531	1.68109	407
50	48	93.7032	3.06369	1.69879	405

Table 2. Statistical information on the results of the XRF analysis of silicon and aluminium. N is the number of replicates and STD DEV is the standard deviation of the replicates.

BCR#	Si N	Si Mean	Si STD DEV	Si MINIMUM	Si MAXIMUM
3	5	94.594	0.083	94.547	94.663
10	5	93.897	0.031	93.855	93.945
14	5	93.862	0.044	93.854	93.871
17	5	93.915	0.044	93.891	93.934
19	5	93.717	0.094	93.690	93.742
22	5	93.356	0.031	93.335	93.372
33	5	93.953	0.088	93.945	93.967
39	5	93.792	0.070	93.780	93.807
40	5	93.862	0.108	93.841	93.889
48	5	93.697	0.099	93.680	93.719
ALL	50	93.864	0.331	93.335	94.663

BCR#	Al N	Al MEAN	Al STD DEV	Al MINIMUM	Al MAXIMUM
3	5	2.8820	0.0102	2.8728	2.8966
10	5	3.0330	0.0146	3.0164	3.0518
14	5	3.1160	0.0095	3.1025	3.1261
17	5	3.0587	0.0035	3.0555	3.0639
19	5	3.0204	0.0067	3.0111	3.0282
22	5	3.0674	0.0053	3.0611	3.0752
33	5	2.8871	0.0089	2.8766	2.8976
39	5	2.9933	0.0097	2.9802	3.0034
40	5	3.0139	0.0058	3.0064	3.0214
48	5	3.0765	0.0162	3.0637	3.0953
ALL	50	3.0148	0.0744	2.8728	3.1261

Table 3. Statistical information on the results of the XRF analysis of trace elements, iron and manganese. N is the number of replicates and STD DEV is the standard deviation of the replicates.

BCR#	Fe N	Fe MEAN	Fe STD DEV	Fe MINIMUM	Fe MAXIMUM
3	5	1.2297	0.0139	1.2158	1.2500
10	5	1.4053	0.0141	1.3868	1.5208
14	5	1.5914	0.0136	1.5721	1.6096
17	5	1.6807	0.0120	1.6603	1.6887
19	5	1.5873	0.0133	1.5765	1.6101
22	5	1.8237	0.0093	1.8128	1.8373
33	5	1.5791	0.0107	1.5669	1.5916
39	5	1.6105	0.0088	1.6024	1.6230
40	5	1.6231	0.0069	1.6147	1.6306
48	5	1.6944	0.0138	1.6785	1.7075
ALL	50	1.5825	0.1565	1.2158	1.8373

BCR#	Mn N	Mn MEAN	Mn STD DEV	Mn MINIMUM	Mn MAXIMUM
3	5	261.80	1.63	260.00	264.00
10	5	291.20	1.47	289.00	293.00
14	5	228.60	1.83	227.00	231.00
17	5	281.20	2.38	278.00	284.00
19	5	339.80	1.31	338.00	341.00
22	5	420.40	1.52	419.00	422.00
33	5	264.80	1.47	263.00	267.00
39	5	383.80	1.64	381.00	385.00
40	5	304.80	1.63	303.00	307.00
48	5	405.00	1.40	403.00	407.00
ALL	50	318.14	63.17	227.00	422.00

Table 4. Analysis of variance of XRF data

Element	$\hat{\sigma}_w^2$	$\hat{\sigma}_s^2$	$\hat{\sigma}_t^2$	SD	CV(%)
Si	0.00049	0.09512	0.09562	0.3092	0.33
Al	0.000095	0.005927	0.006022	0.0776	2.57
Fe	0.000141	0.026500	0.026643	0.1632	10.31
Mn	2.7	4342.5	4345.0	65.92	20.72

Si, Al and Fe measured as % by mass
Mn measured as ppm by mass

Table 5. Percentage of Total Variance

Element	Within sample	Between samples
Si	0.5	99.5
Al	1.6	98.4
Fe	0.5	99.5
Mn	0.1	99.9

Definitions

$\hat{\sigma}_w^2$ Average variance of replicates within same sample

$\hat{\sigma}_s^2$ Average variance of different samples

$\hat{\sigma}_t^2$ Estimated total variance of material in whole matrix

$$\hat{\sigma}_t^2 = \hat{\sigma}_s^2 + \hat{\sigma}_w^2$$

SD Standard deviation $(\hat{\sigma}_t)$

CV Coefficient of variation $(\hat{\sigma}_t / \bar{X}_t)$

where $\bar{X}_t$ is the mean of all the determinations for a particular element.

2.2 Results of the Organic Matter Determination

The organic matter of the sediment was measured by combustion at 550°C. Ten 5 g sub-samples were taken at random from the bulk sediment. These were then stored in 60 ml bottles prior to analysis. A 1 g quantity of sediment was taken from each bottle and the organic matter determined. All weighings were made on a four-decimal place Mettler AE2000 electronic balance. The results of the analysis are shown in Table 6. The organic content of the sediment was found to be low (0.89 ± 0.04%) with a coefficient of variability of 3.9%. Considering the small sample size (1 g) and low content of organic matter, this result is very satisfactory and indicates sufficient homogeneity of the sediment with respect to organic material.

3. ANALYSIS

3.1 Extraction technique

Three 50 g samples in numbered bottles were selected at random from each of the thermostated stores at each sampling interval. The sediments were transferred to the extraction flasks (500 ml Quickfit (B24//29) conical flasks). After the sediment had settled, the residues in the bottles and funnels were washed into the extraction flasks with a series of 15 to 20 ml aliquots of acetone to a total volume of approximately 150 ml per flask. The flasks were then shaken for 1 hour on an automatic shaker (STUART Flask Shaker SF1, setting 6). The solids were allowed to settle for at least 1.5 hours and then the acetone was decanted through pre-washed No.4 porosity sintered glass filters (chromic acid cleaned, acetone and hexane rinsed) set in Quickfit Buchner flasks under slight negative pressure (<0.2 KPa) and transferred, with 2 ml acetone washes, to a 250 ml round-bottomed (RB) flask.

The acetone extract was reduced to a low volume (c. 10 ml) by rotary evaporation (Jobling Rotary Evaporator, type 349/2) at 45°C. The remaining sediments in the extraction flasks were rinsed with 50 ml acetone. The solids were allowed to settle before the acetone layer was decanted through the respective filters. Residue on the sintered filter was leached with 5 ml acetone and all leachate and rinse solutions were transferred to the respective RB flask.

The extraction was then repeated with a further 150 ml acetone and 50 ml rinse. Extensive further extractions yielded less than 10% additional permethrin from sediments. Residues in the RB flasks were taken to dryness by rotary evaporation then redissolved in 10 ml of a solution of 5% acetone in hexane dried over anhydrous sodium sulphate (5% acetone/hexane) ready for further clean-up.

3.2 Sample clean-up procedure

The extracts of the sediments were usually highly coloured and unsuitable for direct use in gas-liquid chromatography (glc). To prevent contamination of the injection port, column and detector and to allow detection of trace pesticide peaks, further separation of determinands from the background organics was required.

Table 6. Results of Organic Matter Determination

Sample number	Weight sediment /g	Weight Ash /g	% Organic matter
1	1.0699	1.0601	0.91
2	1.0228	1.0141	0.85
3	1.0187	1.0098	0.87
4	1.0590	1.0500	0.85
5	1.0147	1.0057	0.89
6	0.9836	0.9747	0.90
7	1.1843	1.1735	0.91
8	1.1846	1.1733	0.95
9	1.0259	1.0170	0.87
10	1.0181	1.0086	0.93

Mean percentage organic matter content is 0.89 ± 0.04 (SD)

A two stage clean-up procedure using a Florisil adsorbent was adopted. Previous research had shown this to be a reliable method for permethrin analysis of organic sediments. The procedure was as follows:

(a) Columns Bond-Elut, Analytichem International Part No. FL944006 Code 0690) were mounted in a Vac-Elut solid phase extraction (SPE) unit (Analytichem International model AI6000) and conditioned with 10 ml dry hexane followed by 10 ml 5% acetone/hexane.

(b) The extract in the RB flask (dissolved in 5% acetone/hexane) was loaded on to the column and the non-adsorbed solutes drawn through under reduced pressure (< 5kPa). The eluate was collected in a 100 ml beaker. The RB flask was washed with a further six (5 ml) aliquots of 5% acetone/hexane and the washings transferred to the adsorbent column.

(c) Many of the coloured components were retained on the SPE column. Permethrin, together with other pyrethroids and several organo-chlorine insecticides were eluted directly. GlC of the eluate with electron capture detection, (ECD), revealed a high-level of background interference, particularly in the region of the chromatogram where organo-chlorine pesticides elute.

(d) A second stage clean-up using Florisil activated at 160°C has been found to reduce interference to an acceptable level.

Glass columns (5 mm i.d., 120 mm in length, fitted with taps) were filled with dry hexane. A wad of glass wool (washed with acetone then hexane) was inserted followed by a 5 mm layer of granular $NaSO_4$ dried at 160°C. Florisil (100-200 mesh) activated at 160°C for more than 12 hours was added whilst hot and allowed to settle, with tapping, to give a bed depth of 100 mm. Finally 10 mm dry $NaSO_4$ was added to protect the Florisil from atmospheric moisture.

(e) 40 ml dry hexane was passed through the column and discarded before the sample was loaded.

(f) The eluate from the first (Bondelut) column was returned to the respective RB flask and taken to dryness on the rotary evaporator taking care to remove condensing solvent.

(g) The sample residue was dissolved in dried hexane (10 ml) and applied to the Florisil column. Remaining residues were washed from the flask with two (5 ml) aliquots of hexane. The 20 ml hexane eluate from the column (column wash) contains much of the interfering background organic solutes. It has been found that permethrin and some organochlorine pesticides would require 40 ml or more hexane for elution.

(h) The permethrin isomers were eluted with a 20 ml 5% acetone/hexane mixture. The column was then eluted with a further 20 ml 5% acetone/hexane. All eluate fractions were retained separately in 20 ml vials for later analysis. The sample volume was checked before glc analysis. The distribution of cis-permethrin between the three column eluates was found to be as follows:

Wash: 0%; 1st 20 ml 5% acetone/hexane eluate: 95.4 ± 1.96%; 2nd 20 ml 5% acetone/hexane eluate: 4.6 ± 1.96%.

3.3 Efficiency of the extraction and clean-up procedure

The overall efficiency of the extraction and clean-up for analysis of permethrin has been investigated in separate studies. In brief this was performed as follows:

25 g of a freeze-dried, highly organic sediment (code BPS, 22.2% organic matter) was spiked with permethrin at levels of 1 $\mu g\ g^{-1}$ and 0.02 $\mu g\ g^{-1}$. The results of the analysis using the procedure described above are satisfactory at both permethrin concentrations.

Permethrin isomer	Spike concentration in sediment /$\mu g\ kg^{-1}$	Recovery %
Trans	1000.0	>100
Cis	20.0	89 *

* This spike concentration is more appropriate to the present work.

4. GLC ANALYSIS OF THE PILOT MATERIAL EXTRACTS FOR PERMETHRIN

Sediment extracts were analysed using a Perkin-Elmer glc model 8700 fitted with a split/splitless injector and ECD. The first 5% acetone/hexane eluate from the clean-up column were examined. Volumes of stored eluates were checked and adjusted as necessary. 2.0 ml were spiked with an internal standard (10 μl of 10 mg dm^{-3} aldrin). The extracts were also analysed to check for the presence of aldrin.

Each sample analysis was preceded by an analysis of a standard pesticide mixture including the internal standard at 0.05 mg dm^{-3} to calibrate the instrument.

4.1 Instrument configuration and chromatography conditions

Configuration:

Injector - Split/splitless
Column - DB5 Jones Chromatography
Detector - ECD (Electron Capture Detector)

Oven conditions:

Oven temperature ($^{\circ}C$)	50	170	240	280
Isothermal time (min)	2.0	0.0	7	2
Ramp rate ($^{\circ}C\ min^{-1}$)	30.0	10.0	2.0	

Injector conditions:

Temperature 310$^{\circ}C$
Splitless for 30 seconds

Detector condition:

Temperature 350$^{\circ}C$

Gases:

Makeup: N_2
Carrier: He
Septum purge ≅ 5 ml min^{-1}
Flow rate ≅ 50 ml min^{-1}

A chromatogram of a sample extract is shown in Figure 1.

Figure 1

Details of the cis-permethrin and internal standard peaks plotted with reference standard peaks are shown in Figures 2 and 3.

4.2 Confirmation of the presence of cis-permethrin by mass spectroscopy

The identity of the peak assigned to cis-permethrin was confirmed using gc/ms combinations: (a) Hewlett-Packard 5890 series I gc with TRIO I quadrupole mass spectrometer referred to as TRIO I, (b) Hewlett-Packard 5890 series II gc with HP/MSD quadrupole mass spectrometer referred to as HP/MSD. TRIO I was run with a 15 m DB5 (5% phenylmethylsilicone) and HP/MSD with a 25 m HP5 column and similar stationary phase.

The mass spectrum of permethrin obtained under electron impact conditions is shown in Figure 4. The largest peak in the spectrum is the base peak at m/z 183 corresponding to the phenoxyltropylium ion. This is the preferred ion for selective-ion-monitoring (SIM). A much less intense ion at m/z 163 (≅30% relative intensity) is also present, i.e. 3-(2,2 - dichloro vinyl) -2,2- dimethyl cyclopropylium fragment.

The confirmation of the assignment was based on the following criteria:

(1) The retention time of the cis peak obtained in the analysis of the sediment extract must be the same as the peak in the standard chromatogram.

(2) The ions in the mass spectrogram must have the correct mass to charge ratio, viz ion at m/z 163 and 183.

The results of the analysis of sample BCR27 using the HP/MSD system are shown in Figure 5. The m/z 163 and 183 chromatograms, together with the retention time data, confirm the peak assignment of cis and trans isomers of permethrin. Excellent separation is evident with a satisfactory signal to noise ratio, i.e. better than 20:1. The TRIO I system produced similar results with the shorter 15 m column giving slightly poorer separation of the isomers (Figure 6).

4.3 Compound recognition during glc with ECD

Recognition of a peak as a particular compound is on the basis of the match of retention time relative to an internal standard retention time (relative retention time, RRT) compared to a standard calibration run. RRTs have been found to be stable to within ±0.001 during a single day, but to drift 0.002 over several days. Prior to every sample analysis RRT values were calibrated with an injection of a mixed pesticide standard. Several calibrations were performed each day.

Peaks are recognised as a particular compound if RRT values are within ±0.001 units for organo-chlorine pesticides (including the internal standard Aldrin) or ±0.002 units for pyrethroid compounds.

4.4 Quantification

Replicate analyses of a standard solution of cis-permethrin (0.05 mg dm^{-1}) using the internal standard (aldrin) method gave the following precision for the glc analysis:

Mean area of peaks 4.0069 + 0.1456 S.D. (3.63%), n=4.
Mean measured concentration 0.04795 mg dm^{-3} + 0.00204 S.D. (4.2%), n=4.

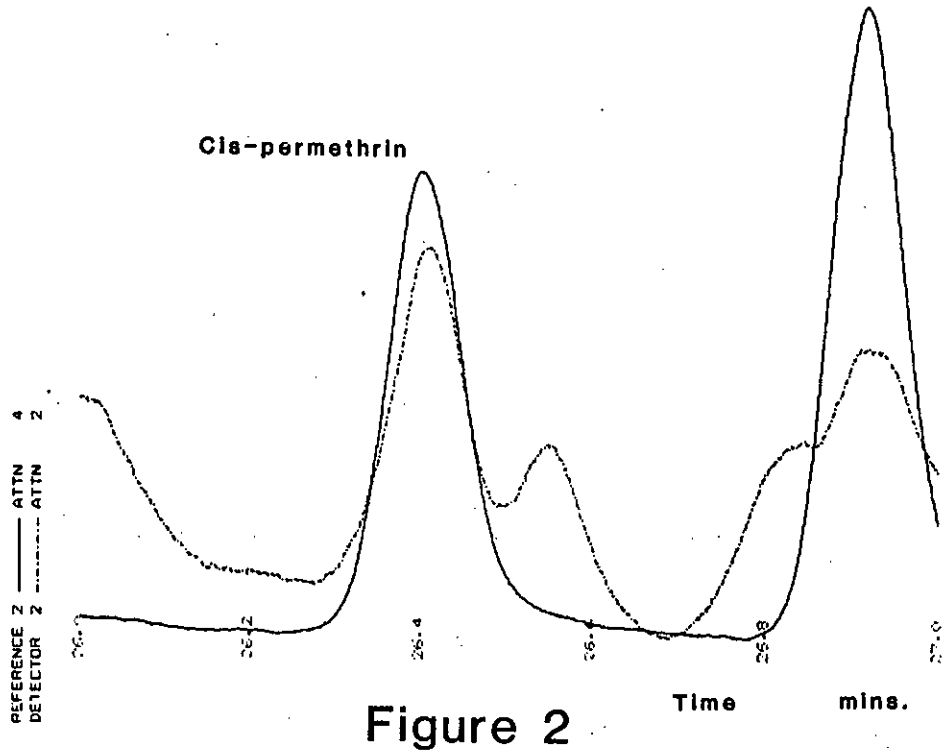


Figure 2

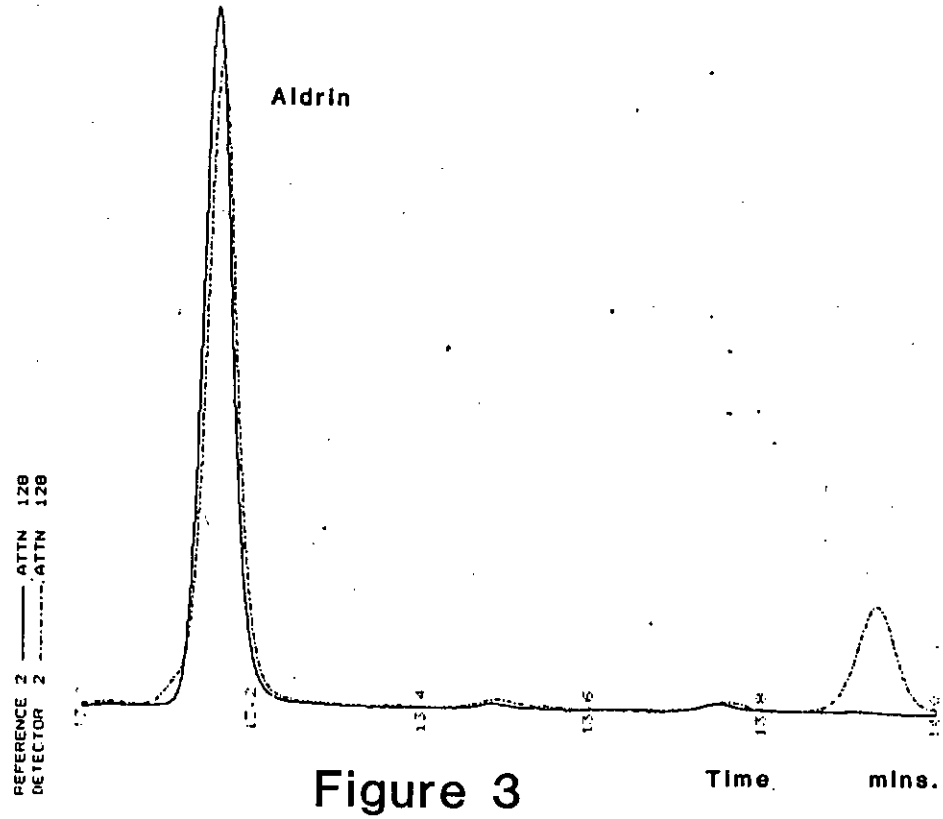


Figure 3

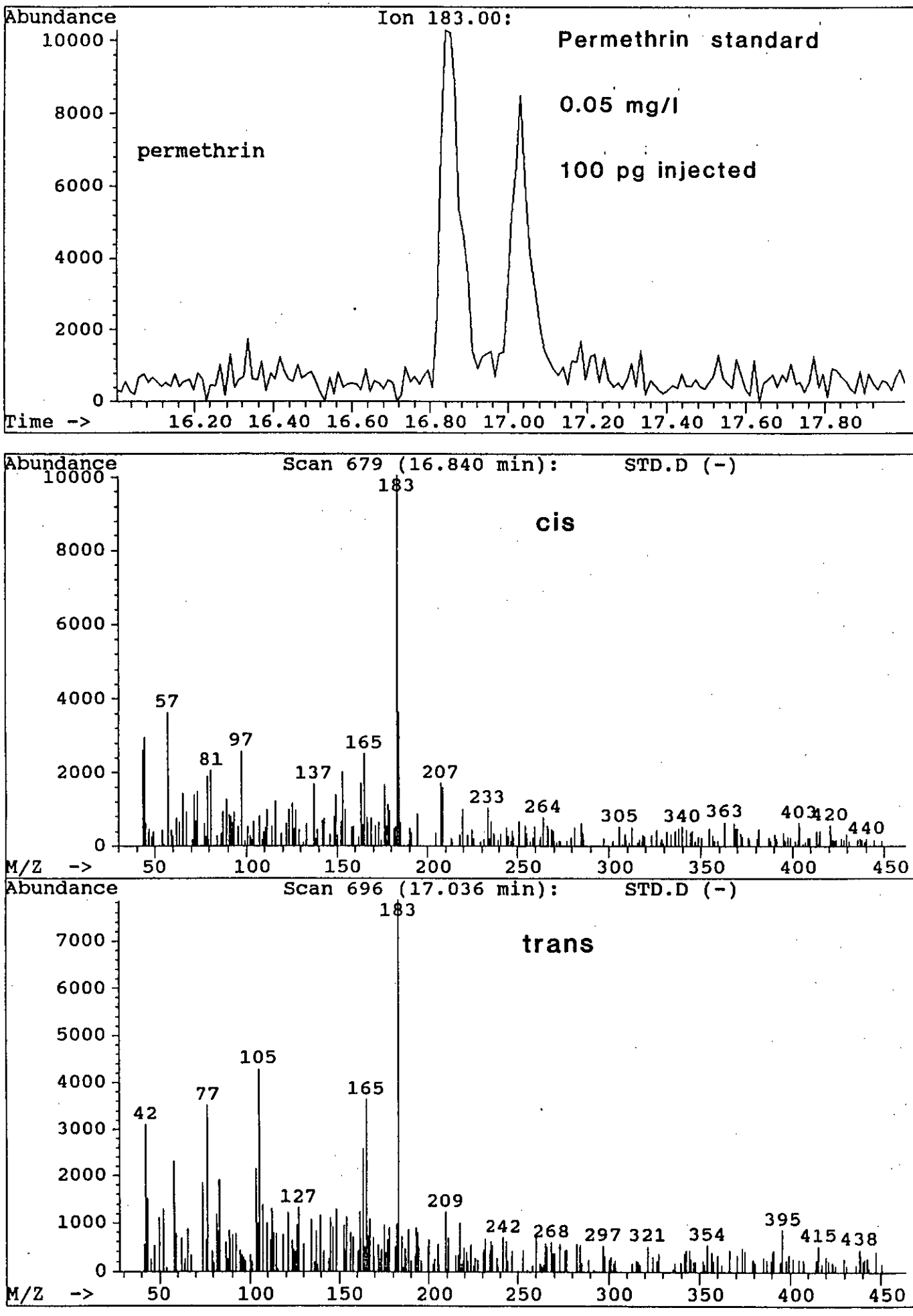
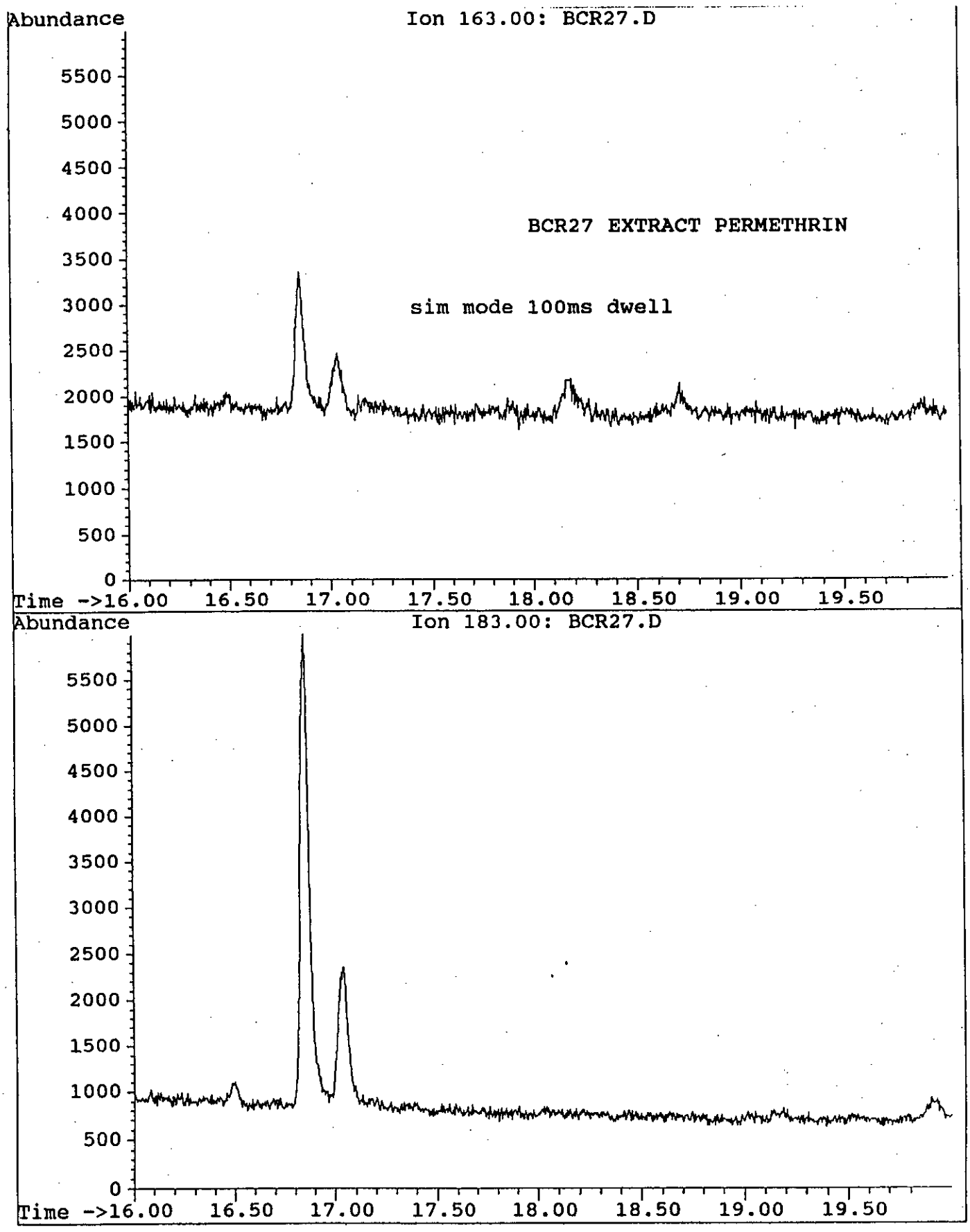


Figure 4 Standard Chromatogram (HP/MSD)

Figure 5 BCR27 Chromatogram in SIM m/z 163 & 183

(HP/MSD)



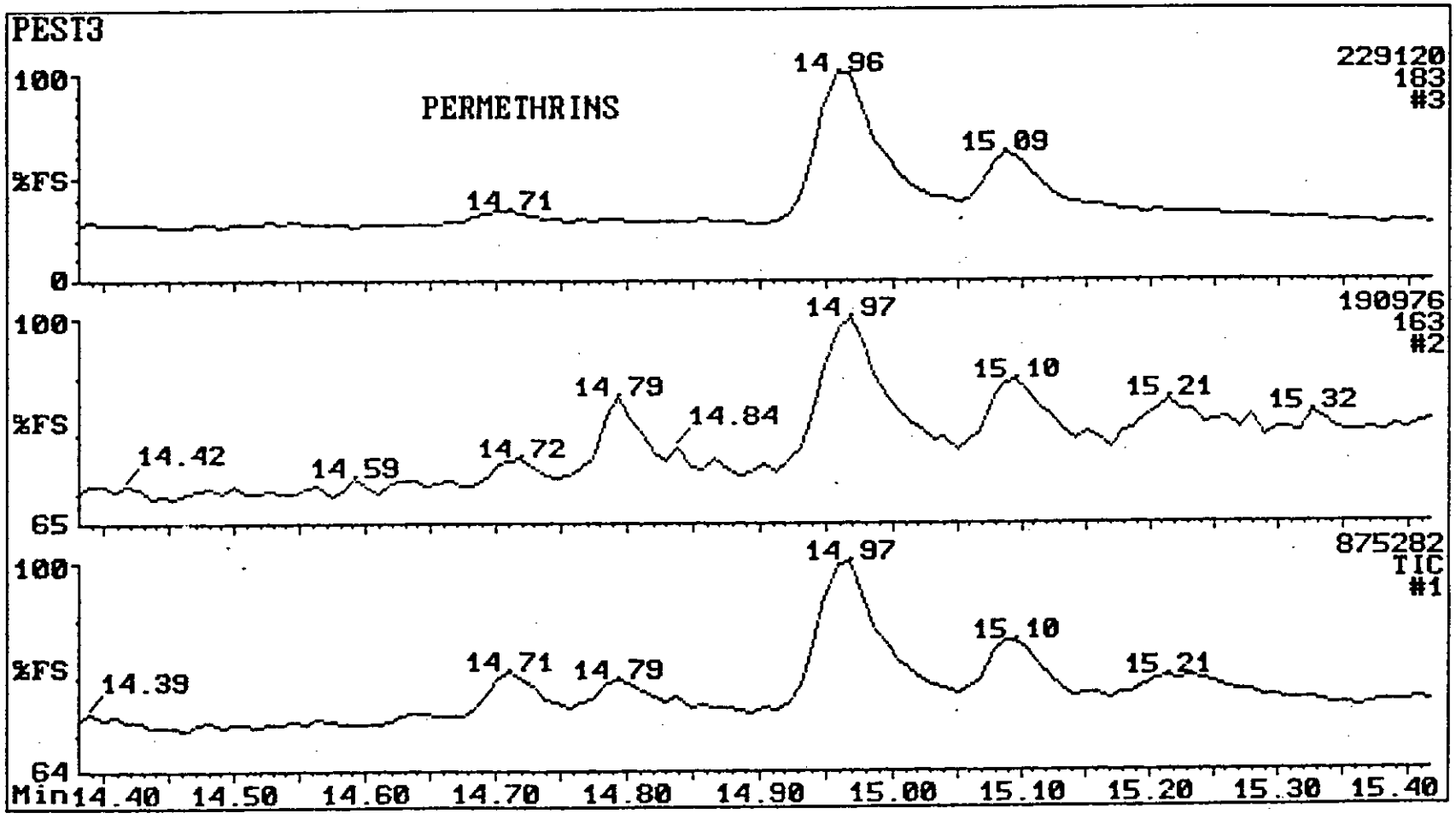


Figure 6 BCR27 Chromatogram in SIM m/z 163& 183 (TRIO1)

For the sediment extract analysis, the cis-permethrin appears fused with a following component. Integration of the cis-isomer peak using an automatic "valley to valley" baseline assignment underestimates the area. Slight variations in the extract composition precludes an exact prediction of the position of valley base points for acceptable quantification. Chromatograms are therefore examined individually and baseline assigned manually as indicated in Figure 7.

5. RESULTS OF THE ANALYSIS OF THE PILOT MATERIAL FOR CIS-PERMETHRIN

The concentration of permethrin in the sediments was determined at the following times:

Storage temperature °C	Date extracted	Storage interval before extraction
5°C	4.11.89	29*
40°C	19.11.89	46
R.T.	20.11.89	47
-20°C	24.11.89	51

*Reference time for analysis

5.1 Reference time analysis

The results are shown in Table 7. Analysis of the second (5% acetone/hexane) eluates gave a mean residual cis-permethrin content of the sediment of 0.49 ± 0.23 (S.D.) $\mu g\ kg^{-1}$.

The variation in the measured cis-permethrin concentration in the pilot material at the reference time (S.D. ± 3.6%) was similar to the variation in the replicate injections of the permethrin standard (S.D. ± 4.2%).

5.2 Analysis of the pilot material after the first storage interval

The results of the analysis of the sediments stored at three different temperatures are shown in Table 8. The variance in the determination at 40°C is significantly different from the value obtained at the reference time at a significance level of 0.05 whereas the variance at R.T. and -20°C is not significant at the 0.05 level. None of the mean values for the three temperatures were significantly different from the concentration determined at the reference time. This has been confirmed using a t-test at a level of significance of 0.05. However, the chromatogram from the analysis of BCR21 (40°C storage) (Figure 8), indicated the presence of a component which may be co-eluating with permethrin but with a significant lower RRT. This led to larger peak areas and concentrations (see Table 8). If this sample is discounted for the moment, then the results are as follows:

Storage temperature/°C	Storage interval/d	Concentration of cis-permethrin/$\mu g\ kg^{-1}$
40	46	8.42 ± 1.42 (SD)
RT	47	10.57 ± 1.14 (SD)
-20	51	9.61 ± 1.65 (SD)

The mean concentration of permethrin in the samples stored at 40°C is slightly lower than obtained at the reference time. However, considering the standard error of the determinations, the value is not significantly

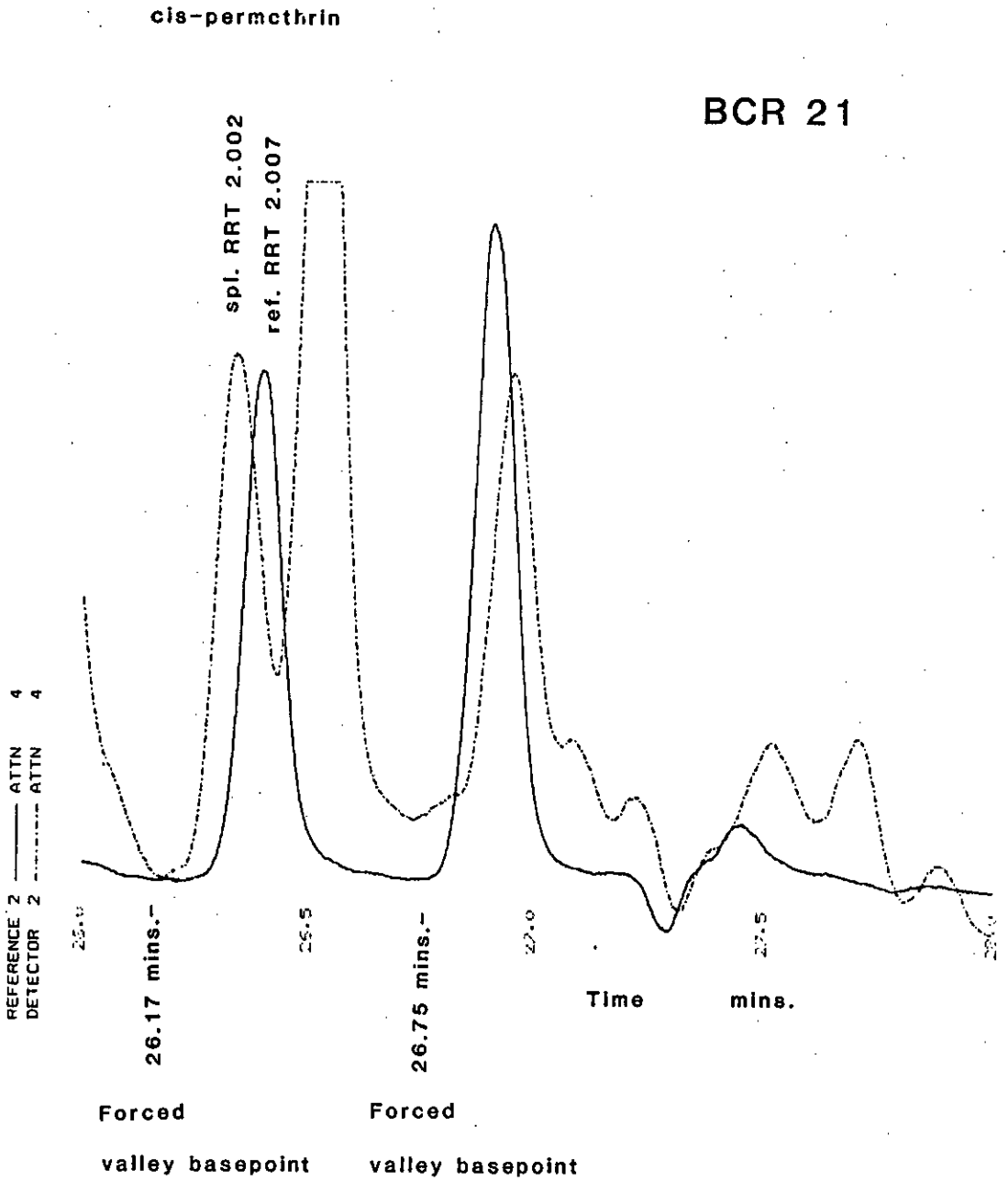

cis-permethrin
BCR 21
spl. RRT 2.002
ref. RRT 2.007
REFERENCE 2 ——— ATTN 4
DETECTOR 2 ------ ATTN 4
26.17 mins.-
26.75 mins.-
Time mins.
Forced valley basepoint
Forced valley basepoint

Figure 7

Table 7 Results of the analysis of the sediments measured at the reference time.

Sample designation	Concentration of cis-isomer in extracts/mg dm^{-3}	Cis-isomer content of sediment $\mu g\ kg^{-1}$
BCR 27	0.0259	10.35
BCR 29	0.0256	10.24
BCR 31	0.0242	9.68
Blank	No cis-isomer peak identified	
	Mean ± S.D.	10.09 ± 0.36

Table 8 Results of the measurement of permethrin in the sediments stored at different temperatures.

Sample designation	Storage temperature °C	Storage interval/d	Concentration of cis-isomer in extracts/mg dm^{-3}	Cis-isomer content of sediment $\mu g\ kg^{-1}$
BCR 02	40	46	0.0236	9.421
BCR 04	40	46	0.0165	7.42
BCR 21	40	46	0.0378	14.8*
Blank	No cis-isomer peak identified			
			Mean ± S.D.	10.55 ± 3.12
BCR 12	R.T.	47	0.0239	9.56
BCR 16	R.T.	47	0.0314	12.57
BCR 24	R.T.	47	0.0239	9.58
Blank	No cis-isomer peak identified			
			Mean ± S.D.	10.57 ± 1.14
BCR 06	-20	51	0.0207	8.27
BCR 26	-20	51	0.0215	8.62
BCR 46	-20	51	0.0299	11.95
Blank	No cis-isomer peak identified			
			Mean ± S.D.	9.61 ± 1.65

* Second component dominant, RRT of cis-permethrin low

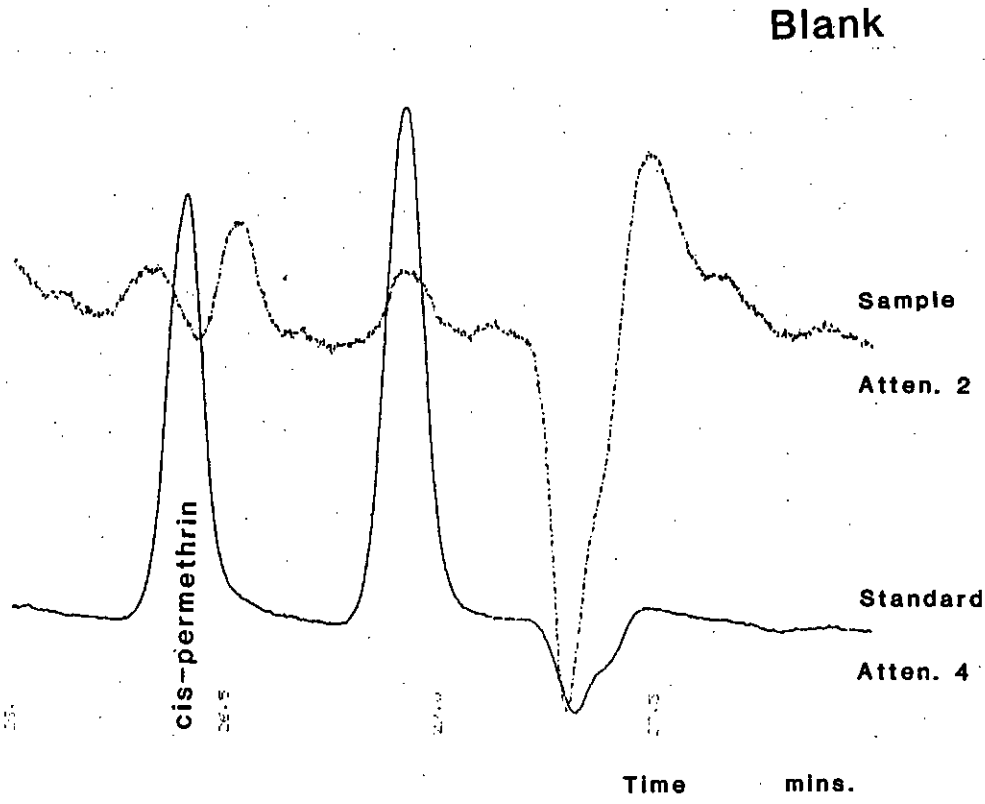

Blank
Sample
Atten. 2
Standard
Atten. 4
cis-permethrin
Time
mins.

Figure 8

different. The results obtained so far indicate that the maximum loss of pesticide (assuming the sample stored at -20°C is stable) is of the order 25.9 ng kg^{-1} d^{-1} for a storage temperature of 40°C. This rate is tentative and further study is required to establish the stability of permethrin in this sediment.

As shown in Table 8 and Figure 9, no permethrin could be detected in the blank samples.

6. CONCLUSIONS

The results obtained so far are inconclusive. No significant loss of permethrin could be detected for the samples stored at different temperatures. There is some evidence that losses of permethrin may be occurring at the highest storage temperature (40°C) but a longer-term study is needed to evaluate the rate of loss of permethrin in different storage conditions before any assessment of the stability can be made.

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