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INTRODUCTION

On June 26, 1975, the emergency investigation team of the Environmental Impact Project headed by Dr C.H. Buckner brought to the Pesticide Chemistry Section at C.C.R.I., eight fresh field samples in Mason jars - 2 red pine foliage, 2 soils, 2 fish and 2 sediments - collected from a farm located near the Larose Forest for the analysis of Orthene residues. The Larose Forest had been sprayed earlier with an aqueous formulation of Orthene at a dosage level of 8 oz AI/acre for control of spruce budworm, Choristoneura fumiferana (Clem.). The eight samples were stored in a freezer until suitable analytical methodologies had been worked out for the Orthene and its metabolite (Monitor) from the substrates.

EXPERIMENTAL

Aliquot (20-10 g) quantities of the samples were either macerated

(foliage) in a Hobart chopper or cut into small pieces (fish) and homogenized in a Sorvall for 5 min at speed 6 in presence of 2 x 100 ml of ethyl acetate. The homogenates were filtered under suction using "S and S sharkskin" filter paper. After washing the residues with 20 ml portions of the extractant, they were discarded. The extracts of individual samples were pooled spearately, passed through columns of Na_2SO_4 (50 g), which were rinsed with 2 x 25 ml of the solvent and flash evaporated to ca 10 ml. The concentrated extracts were transferred quantitatively to 250 ml separatory funnels along with 100 ml of CH_3CN and equilibrated with 3 x 25 ml of hexane. The non-polar phases were discarded and the polar ones were evaporated gently to dryness under vacuum using a rotary evaporator.

The chromatographic adsorbent column cleanups were achieved by dissolving each sample residue in 4 x 25 ml of diethyl ether and passing it through a Shell type glass column (26 cm x 2 cm) containing 15 g of E. Merck silica gel (0.05 - 0.22 mm extra pure 70-325 mesh ASTM for column chromatography) sandwiched between 10 g Na_2SO_4 and prewashed with 50 ml ether. The columns were first eluted with 100 ml 5% CH_3OH in ether and all the eluates collected so far were discarded. The final eluations were done by using 250 ml of 10% CH_3OH in ether which brought down the residues of Orthene and its metabolite Monitor. The eluates were flash evaporated gently to dryness, the residues were dissolved in methyl isobutyl ketone* (MIK) and analysed by GLC.

Gas Chromatographic Conditions

GC	:	HP Model 810
Detector	:	FPD (P-mode)
Column	:	18" x 0.25" (I.D.) coiled Teflon,

* Later on we found that ethyl acetate was a better solvent than MIK in GLC analysis.

		1% Reoplex - 400 on Gaschrom Q (100/200 mesh)
Temp (^{o}C)		
(Program)	oven-initial	: 130 (Hold 1 min)
	oven-final	: 180 (Hold 4 min)
	Rate	: 15 / min
	Timing	: 8 min. 20 sec.
	Detector	: 200
	Inlet	: 200
Carrier gas (ml/min)		: Nitrogen - 40
Gas Flow (ml/min)		: H_2 - 150
		: Air - 75
		: O_2 - 12
Attenuation		: 32
Range		: 10^3
Recorder		: Linear Instruments
		: Span 1 Mv
Chart speed (in/hr)		: 16
Retention time (min)		: Monitor 4.28
		: Orthene 5.91
Relative retention time		: Monitor 0.72
		: Orthene 1.00

The chromatographic profile for the Orthene (4 ng) and Monitor (30 ng) standards are given in Fig. 1. The peaks are narrow and symmetrical with good reproductivity and absence of any additional peaks.

The method developed at this Institute has been used to extract

and quantify spiked forest soils, natural waters and coniferous foliage samples containing Orthene and Monitor at 5 and 10 ng/g levels respectively. The percent recoveries for triplicate analysis of the three substrates with respective coefficient of variations are given below.

Substrate	Percent Recovery	Coefficient of Variation
Water*	94	5
Foliage	87	6
Soil	84	9

* Ethyl acetate was used for the extraction after forming a slurry with anhydrous Na_2SO_4. Chloroform also appears to be a good solvent for extracting the residues from the slurry. Preliminary studies showed a recovery of 98 ± 2% recovery.

Recovery studies for spiked fish and sediments have not been carried out during the course of this investigation due to lack of time and facilities. Such studies will be undertaken as soon as the current pressure on the section is decreased. In all probability, it is assumed that the percent recoveries in these two substrates will be above 80% with a coefficient of variation of 5.

RESULTS

Serial No	Sample No	Sample Description	Residue conc. (ppm) "as sampled" Orthene	Monitor	Total
1	1198 - A	Red Pine* Foliage	1.25	0.15	1.40
2	1198 - B	Red Pine* Foliage	0.70	T	0.70
3	1199 - A	Soil* + (sand)	N.D.	N.D.	N.D.
4	1199 - B	Soil* + (sand)	N.D.	N.D.	N.D.
5	1200 - A	Fish	N.D.	N.D.	N.D.
6	1200 - B	Fish	N.D.	N.D.	N.D.
7	1201 - A	Sediment * +	N.D.	N.D.	N.D.
8	1201 - B	Sediment * +	N.D.	N.D.	N.D.

* Moisture Content : Foliage 55%, Sand 42%, Sediment 52%

\+ pH : Soil 5.3, Sediment 6.6

N.D. : Not Detectable

T : Traces (< 0.05 ppm)

DISCUSSION

The recoveries of Orthene and Monitor from spiked samples of foliage and soil were good. The method developed is manageable and sensitive enough to detect up to 0.05 ppm levels of the parent insecticide and its degradation product. Below this level, the noise level increased considerably due to the coextractive impurities present in the final concentrate and the detection became extremely difficult and the results, if reported, would be unreliable. It was also noted that the polar Reoplex

GC column was not only easily poisoned due to the impurities but also bled quickly while operating due to the temperature fluctuations and required frequent costly but unavoidable replacements, thus delaying considerably the progress of work and increasing the overall cost of analysis.

Except for the two foliage samples analysed, none of the other six contained any Orthene or its degradation product above the detectable level (0.05 ppm). The GLC responses for the four types of substrates analysed are shown in Figs. 2-5 and the calibration curves for the insecticides are given in Figs. 6 and 7. The background interferences in the chromatograms are negligible showing that the extraction, separation, cleanup and the GLC operations were excellent and the procedure is adequately suitable for the residue analysis of Orthene and Monitor from the forest environmental samples.

ACKNOWLEDGEMENTS

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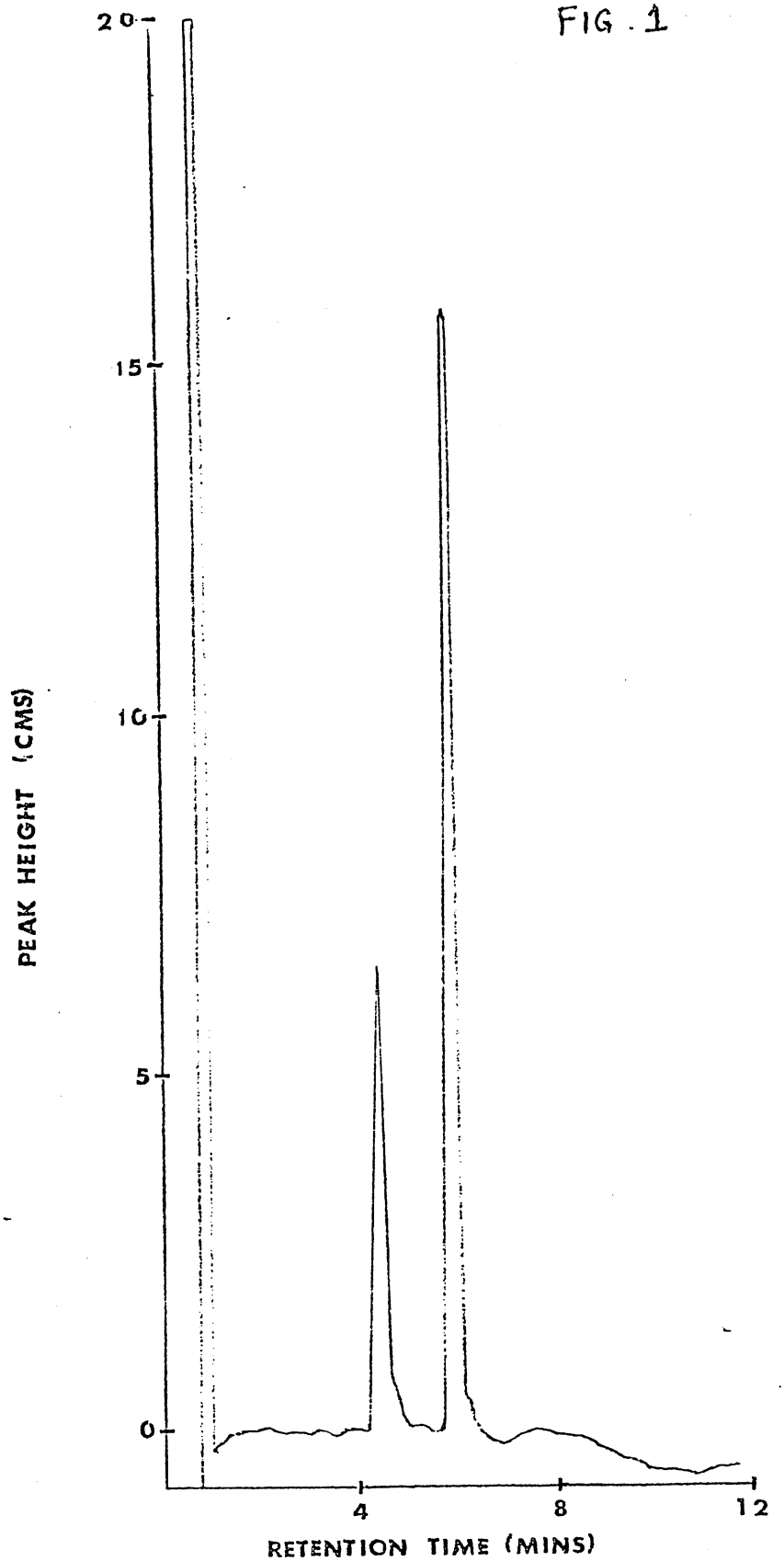
2 λ ORTHENE 2N9/λ → 4N9
MONITOR 15N9/λ → 30N9

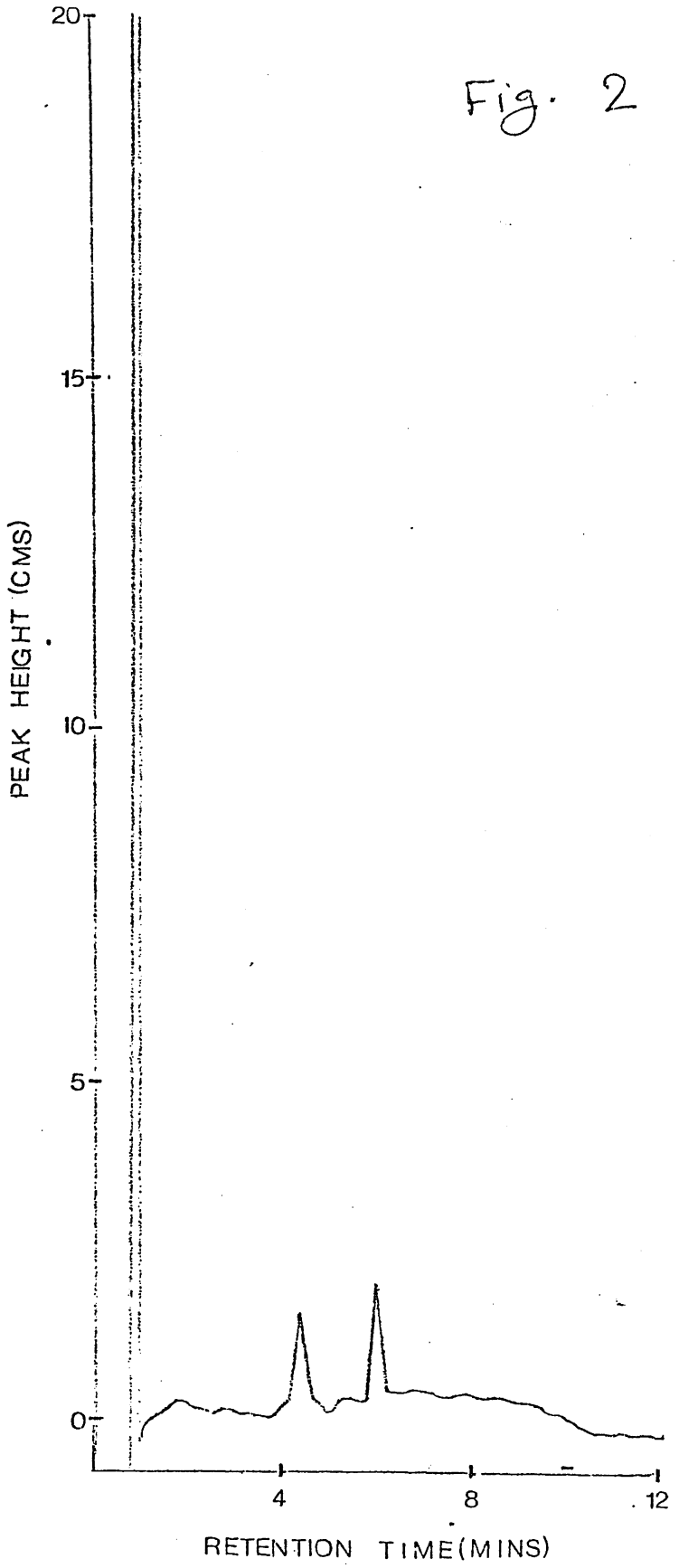
FIG. 1



4λ 1198A →10 MLS RED PINE

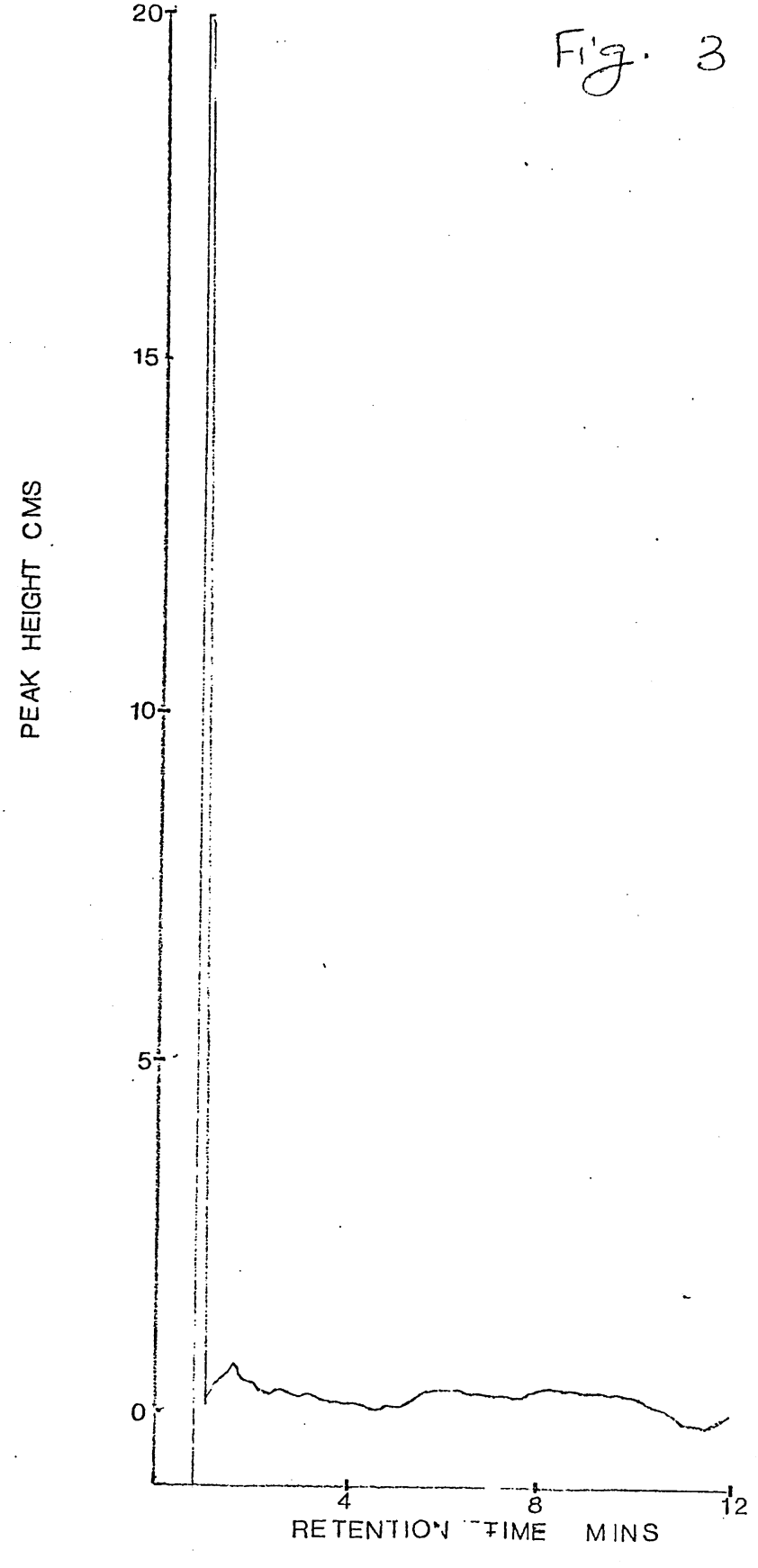
MONITOR →0·15 PPM
ORTHENE →1·25 PPM

Fig. 2



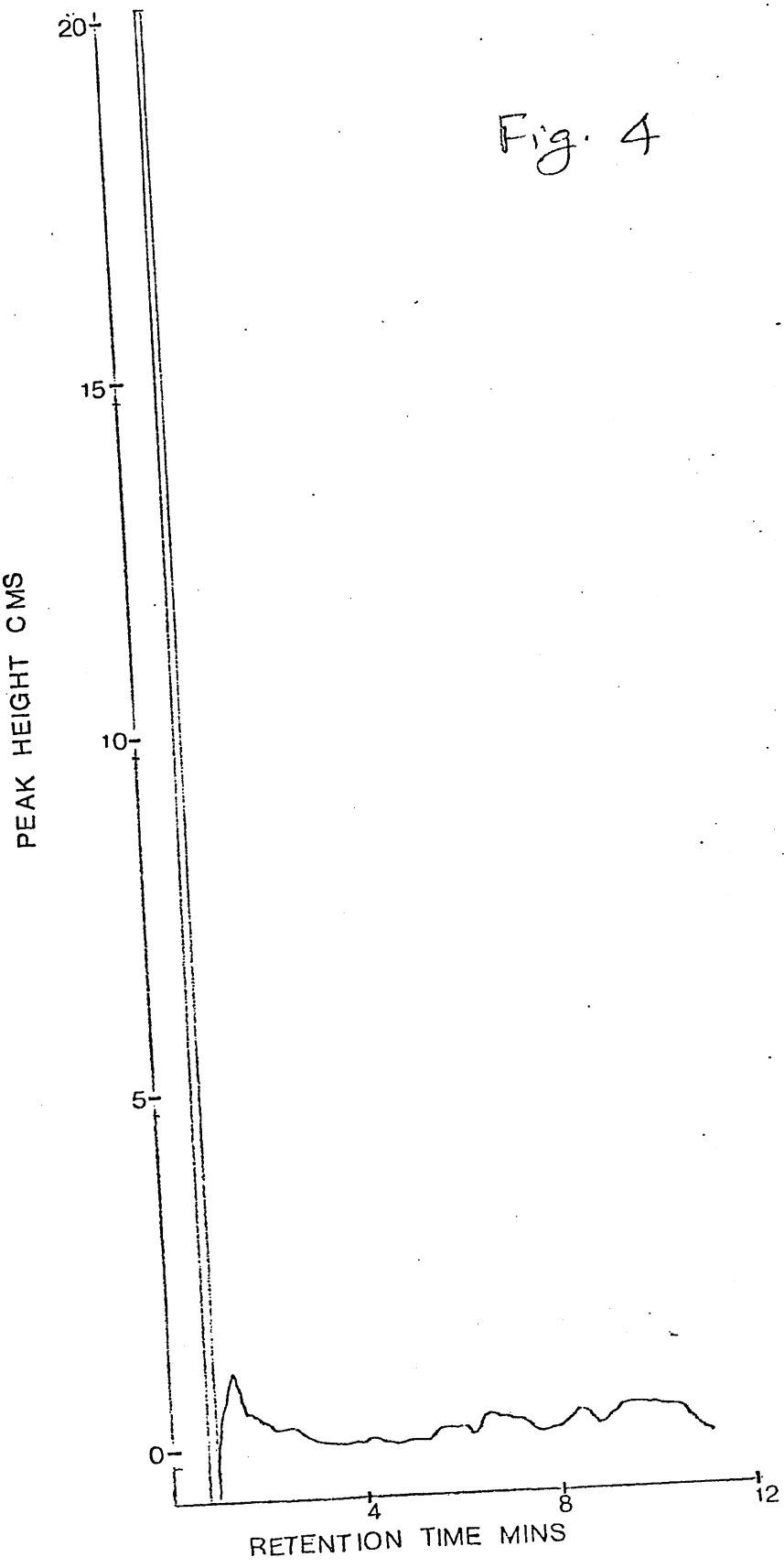
4 λ 1199A ⟶ 1ML SOIL SAND
MONITOR ⟶ N D
ORTHENE ⟶ N D

Fig. 3



4 λ 1200 → 1ML FISH
MONITOR → ND
ORTENE 1 → ND

Fig. 4



1201 → 1ML SEDIMENT
MONITOR → ND
ORTHENE → ND

Fig. 5.

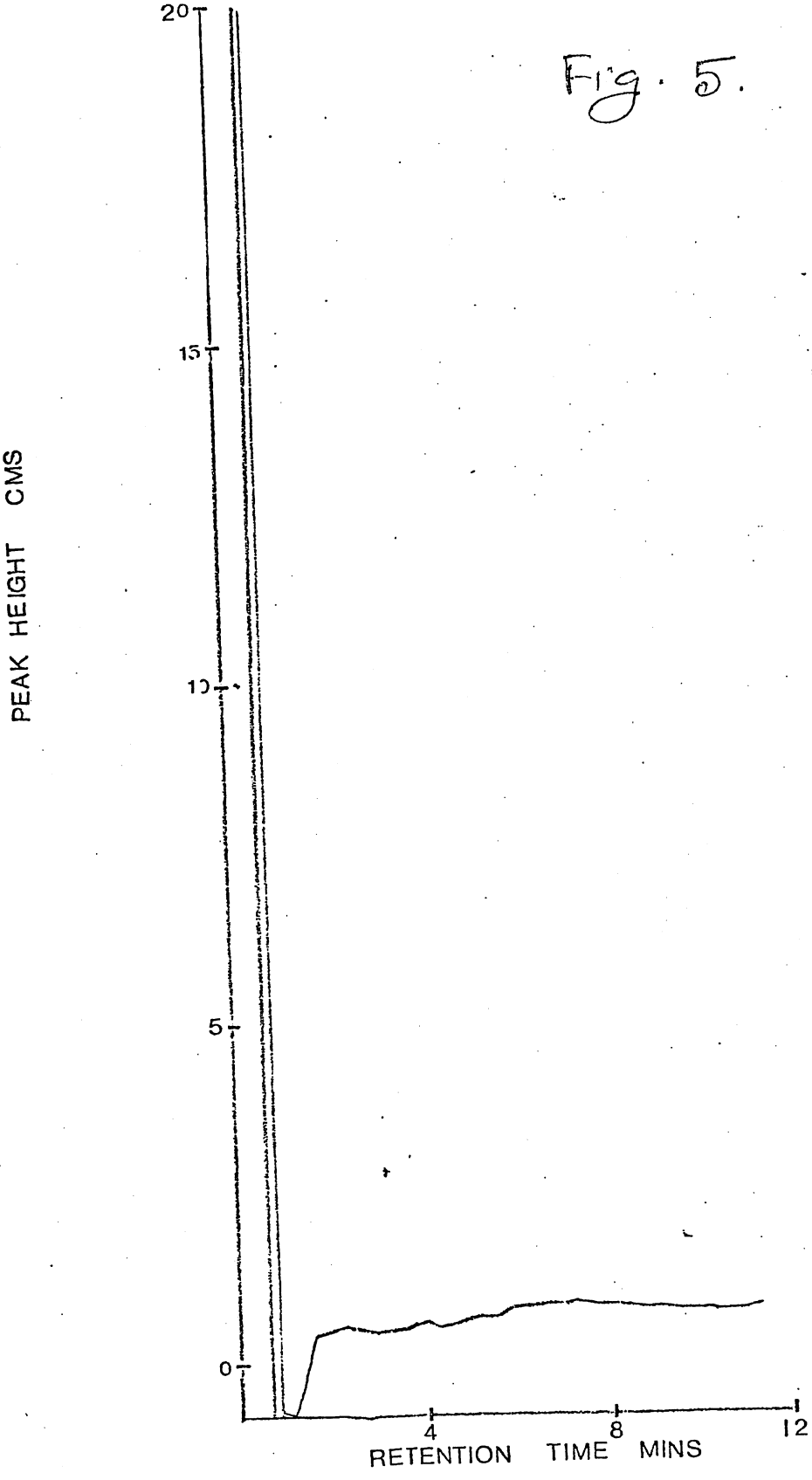
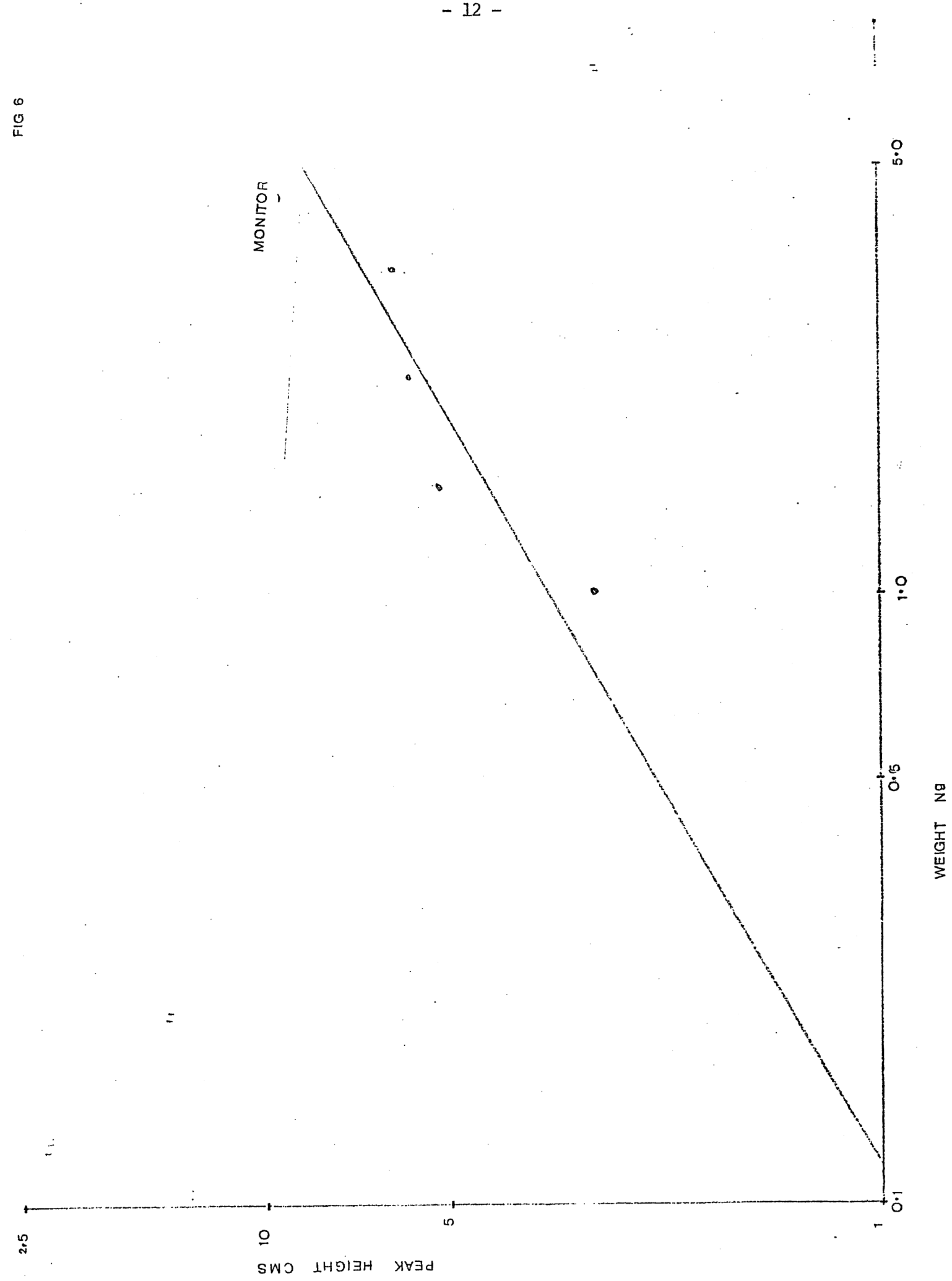
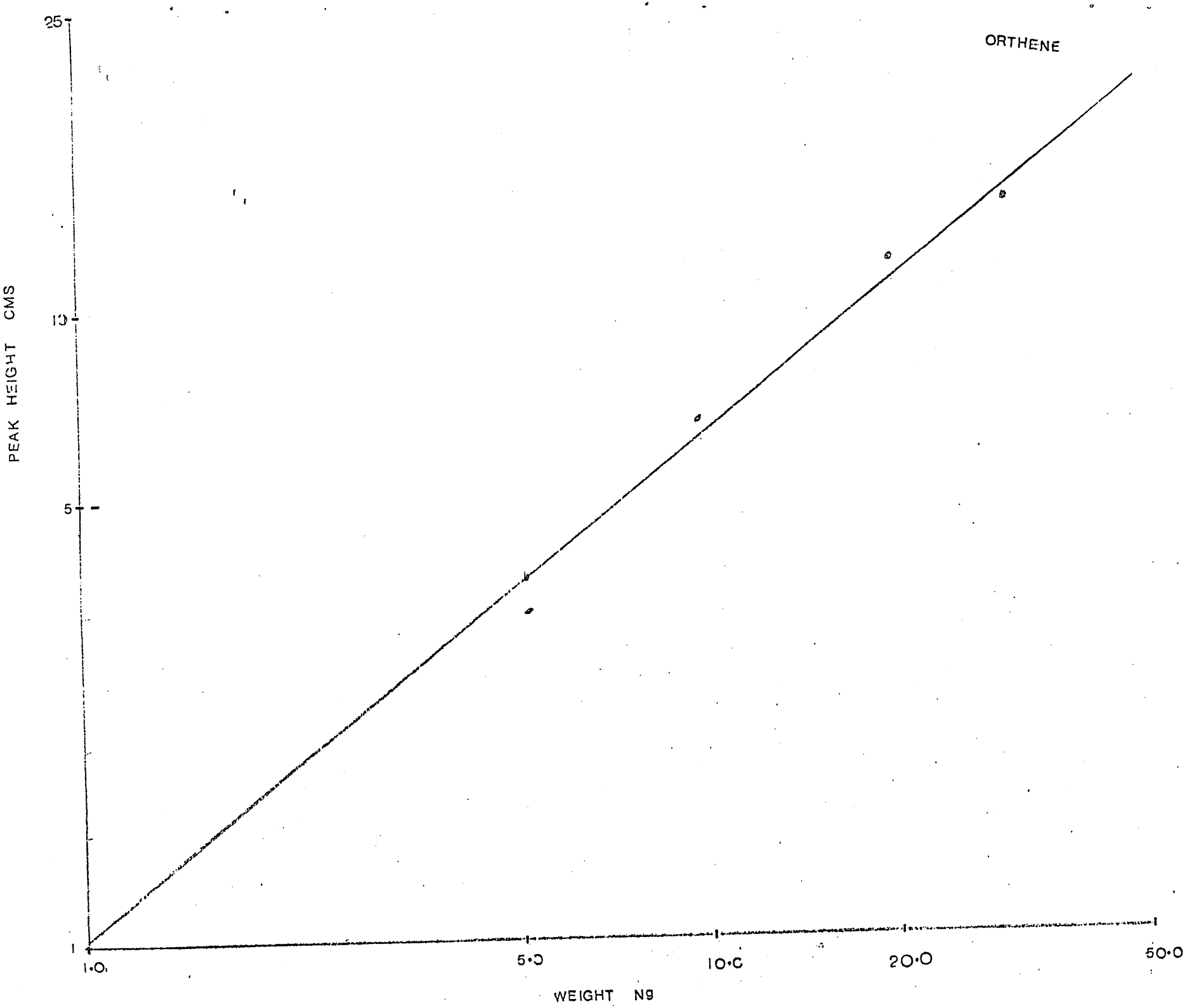


FIG 6




ORTHENE
PEAK HEIGHT CMS
25
10
5
1
1·0
5·0
10·0
20·0
50·0
WEIGHT Ng