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ANALYTICAL EVALUATION OF MATACIL[®]
IN FISH COLLECTED FROM THE INSECTICIDE
TREATED AREA IN QUEBEC

By

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File Report No. 34

February, 1976

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INTRODUCTION

In the summer of 1975, the Emergency Investigation Team of the Environmental Impact Project at the Chemical Control Research Institute (CCRI) brought to the Chemistry Section a frozen fish sample received from Dr. R. Sarrazin of the Department of Tourism, Fish and Game, Government of Quebec for Matacil[®] (4-dimethylamino-m-tolyl-methylcarbamate - common name aminocarb) analysis. The only background information supplied with the sample was that it had been reportedly exposed to the insecticide during a forest insect control operation in the province of Quebec. It was the responsibility of the Chemistry Section at CCRI to analyse the fish sample for Matacil and to prepare a report on the findings. This publication gives a brief account of this study.

EXPERIMENTAL

The direct application of gas-liquid chromatography (GLC) is generally unsatisfactory for the quantitation of Matacil because of the on-column decomposition of the molecule and the weakness of detector response. These difficulties have been averted by converting the molecule to a stable heptafluorobutyric anhydride (HFBA) derivative (Fig. 1) which gave good response to electron capture (EC) detector. Using this technique the following analytical method has been used in the analysis of Matacil supposedly present in the fish sample.

Extraction and Cleanup

The sample was allowed to thaw, pressed on folds of white adsorbent paper to remove the water and weighed (15 g). It was homogenized twice with 100 ml of acetonitrile in a Sorvall-Omi-Mixer for 2 min at speed 6. The slurries were filtered under suction, rinsed with the solvent (20 ml), combined and the acetonitrile flashed down under low pressure to 5 ml. The concentrate was transferred quantitatively to 500 ml separatory funnel, 200 ml of 0.5N sulphuric acid was added, shaken, the acid layer extracted three times with 50 ml of ethyl ether saturated with water followed by 50 ml of chloroform once, and all the extracts discarded. The pH of the aqueous fraction was adjusted to 7.5 by addition of saturated NaHCO_3 solution while stirring with a magnetic stirrer. The resulting aqueous solution was then extracted four times with 50 ml of benzene each time. The benzene extracts were pooled, washed repeatedly with distilled water saturated with NaCl and dried employing a benzene azeotrope procedure for about 90 min. using a Dean-Stark condenser.

The colourless dried extract was solvent stripped to *ca* 2 ml and transferred quantitatively with the aid of anhydrous benzene to a 15 ml screw-capped, calibrated centrifuge tube and 0.5 ml of *fresh* heptafluoro butyric anhydride (HFBA)* was added. The tube

* The reagent is unstable and is decomposed rapidly in presence of moisture, storing the material in a desiccator did not help much. For better results, a fresh ampoule should be opened for each set of experiments.

containing ca 10 ml of the reaction mixture was sealed with a cap containing teflon lining and heated in a temperature controlled oil-bath at 120°C** for two hours. Afterwards the tube was removed cooled, flash-evaporated gently to dryness and the residue⁺ was taken up either in dry ethyl acetate or benzene for EC-GLC analysis.

Gas Chromatographic Analysis

Gas chromatographic analysis of Matacil present in the fish sample after complete cleanup and derivatization was carried out using a Hewlett-Packard Model 5750 gas chromatograph fitted with a Ni 63 electron capture (E.C.) detector. Operating parameters were as follows:

Column:	183 m x 6 mm (6 ft. x 0.24 in.) O.D. Pyrex glass packed with 6% SE-30 on Chromosorb G 70/80 mesh, AW-DMCS, preconditioned overnight at 190°C.
Temperature (°C):	Injection port 225 Column oven 190 Detector 260
Gas Flow:	Carrier gas - Argon / methane (95/5%) at pressure 50 psi and flow rate of 75 ml/min. Purge gas - Argon / methane (95/5%) at pressure 50 psi and flow rate of 125 ml/min.

** Temperature control is important to avoid the decomposition of the reagent and the derivative.

⁺ The HFBA derivative is also unstable. GLC analysis of the material should be carried out immediately.

Instrument Settings: Attenuation 32
 Range 10
 Pulse rate 150
 Electrometer 4×10^9 amp at
 full scale deflection with a 1 Mv
 recorder from Linear Instruments.
Chart Speed (cm/hr): 76.2 (30 in / hr)
Retention Time (RT) (min): 3.95

The gas chromatograph was standardized on the same day as the samples were analysed by injecting *fresh* HFBA derivatized aliquots (2-5 ul) of (Fig. 2) Matacil (analytical grade supplied by Chemagro), measuring the peak heights, and preparing a calibration curve by plotting peak heights *vs* concentration (Fig. 3). The calibration was checked intermittently. The fish extract, after derivatization with HFBA was concentrated by dry air-evaporation to the desired concentration for GC analysis. Quantitative result of the extracted and derivatized sample was obtained by measuring the peak height after injection (4ul), under the same operating conditions, and reading the concentration from the calibration curve (Fig. 3). Since the HFBA derivative was not very stable, the analysis was done immediately after the derivatization.

Solvents and Chemicals

All organic solvents used were either pesticide grade (P.G.) chemicals or freshly distilled in glass. Especially the benzene used in preparing the HFBA derivative was made anhydrous by distilling the P.G. grade with Dean-Stark condenser. Being hygroscopic and unstable, the HFBA reagent was stored in a desiccator and a fresh vial was used

at each set of experiments. All the chemicals used in the analysis met with the American Chemical Society specifications. The anhydrous sodium sulphate used was of reagent grade from Fisher, heated at 150° overnight and stored in air-tight glass-stoppered bottles.

Laboratory sources of contamination of chemicals, glassware, solvents etc. was found to be negligible during the period of study.

RESULTS AND DISCUSSION

For recovery studies fish samples (rainbow trout - *Salmo gairdnerii*) were collected from a Matacil-free lake, fortified with the insecticide at 0.2, 0.5 and 1.0 ppm levels and analysed by the method described. The average recovery was 98% with a coefficient of variation of 4. The minimum detection limit was found to be 0.05 ppm at the above concentration range for 10g of the fish used in the recovery studies. The results are recorded in Table I.

Table I

Analysis of Matacil in Fish

Particulars	Matacil Conc. (ppm)	Remarks
Recovery*		
0.2 ppm	0.18	
0.5 "	0.48	Av. recovery 98% with coefficient of variation 4
1.0 "	1.10	
Fish extract from Quebec	N.D.	

* Average of multiple determinations
N.D. Not detected (<0.05 ppm)

The chromatographic profiles for the blank and spiked extracts of fish are given in Figs. 4 and 5 respectively. An artifact (peak height 0.5 cm) with the same RT (3.95 min) but of negligible magnitude appeared in the chromatogram (Fig. 4) of the unspiked fish sample thereby decreasing the sensitivity of the method. Otherwise a minimum detection limit of 0.01 ppm could have been attained.

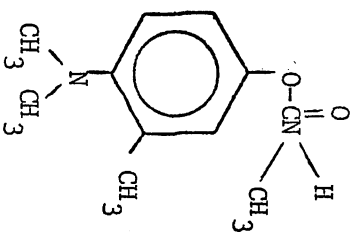
The derivatized fish extract received from Quebec was analysed by injecting 4 ul samples in the EC-GLC and the chromatogram obtained was very similar to Fig. 4 with similar magnitude of the artifact, thus showing that the sample of fish received from Quebec did not contain any detectable amounts (0.05 ppm) of Matacil.

CONCLUSION

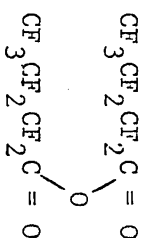
Under the experimental conditions described above, the single fish sample received from the Quebec spray operation did not contain detectable levels (0.05 ppm and above) of Matacil.

ACKNOWLEDGEMENTS

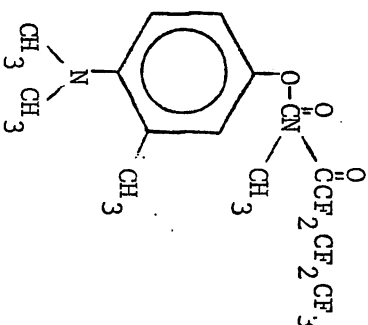
My colleague, Mr. Y. Volpe collaborated actively in extending the Matacil methodology to fish samples. The technical assistance of Messrs. G. Smith, P.E. Lecompte and M. Bryan is greatly appreciated.



MATAcIL



HFBA



4-(dimethylamino)-3-methylphenyl-N-heptafluoro butyryl, N-methyl carbamate

Figure 1: Conversion of Matacil to a Stable Gas-Liquid Chromatographic Derivative.

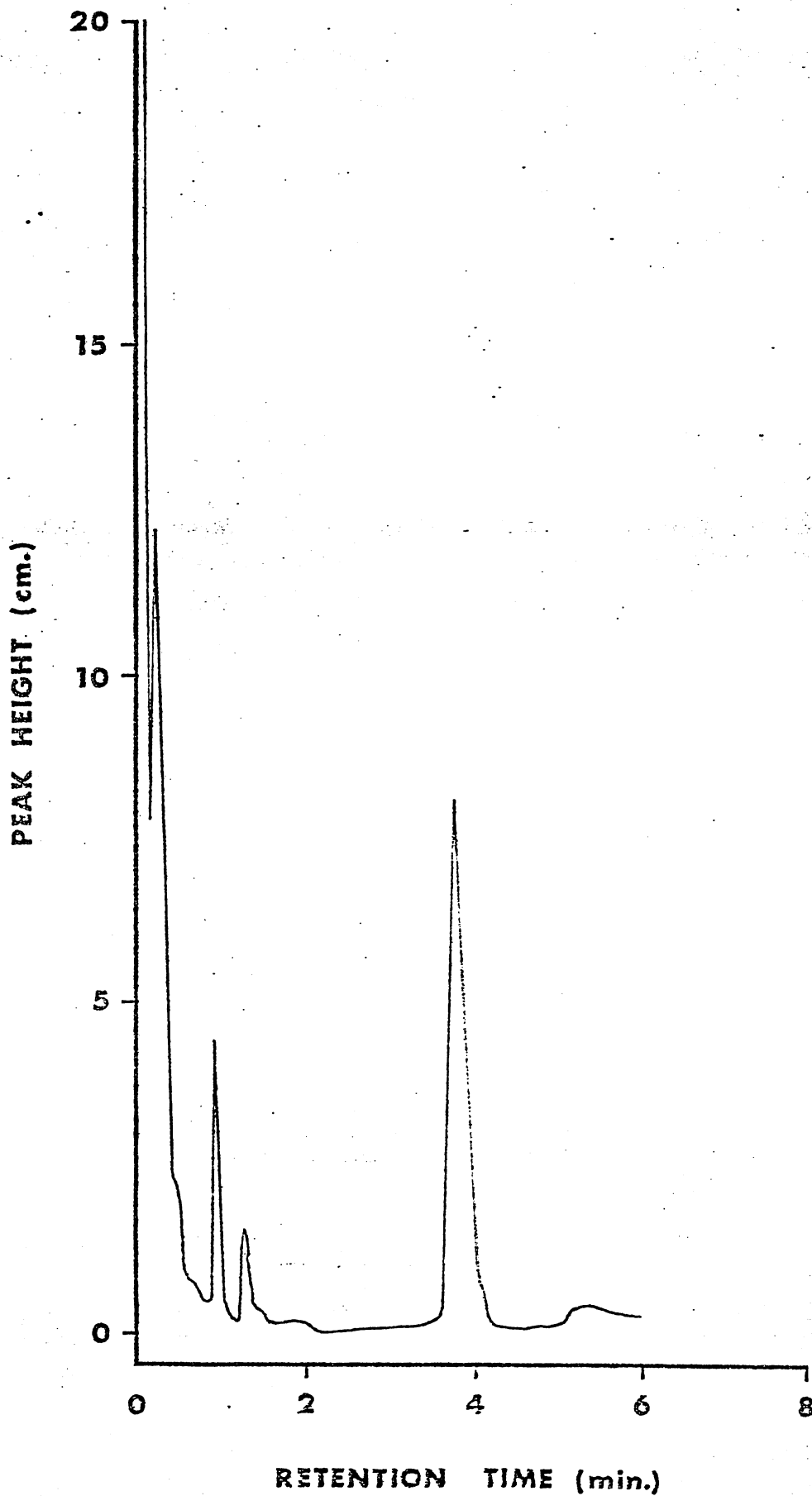


Figure 2: Gas chromatogram of 5ng (2 ul) of Matacil standard in benzene. Peak height 8.1 cm; Retention time 3.95 min.

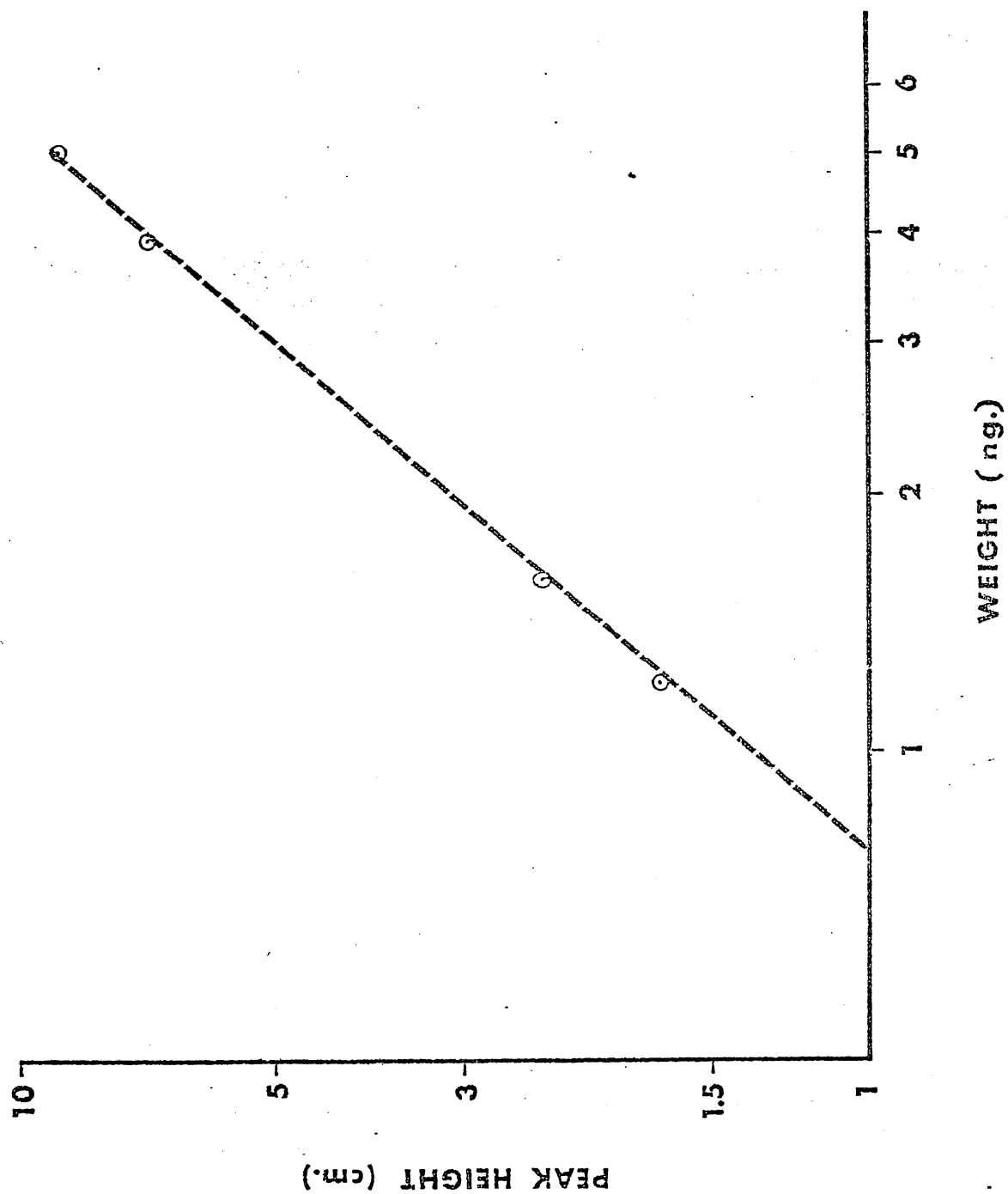


Figure 3: Gas chromatographic calibration curve for Matacil obtained with the EC detector.

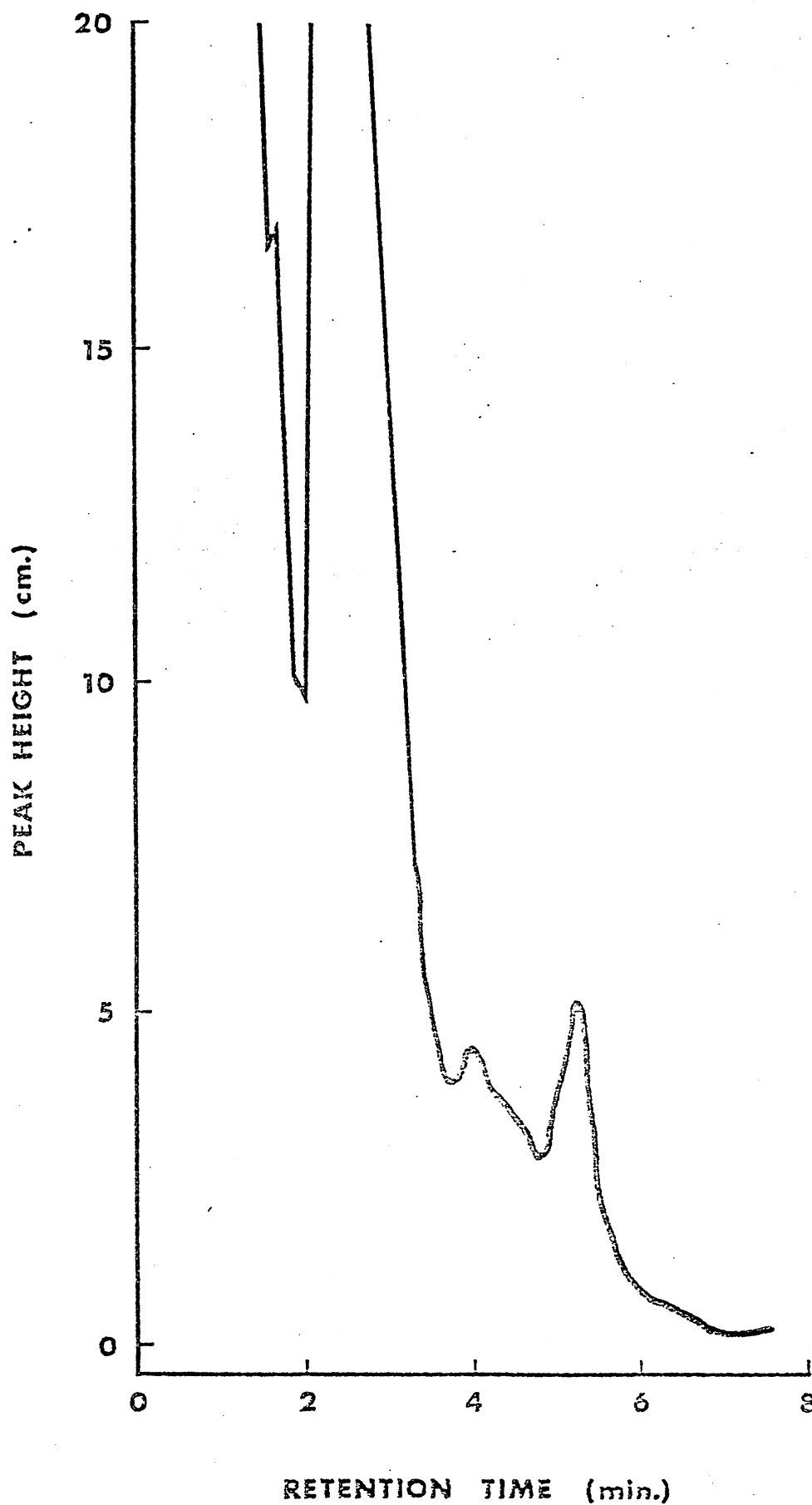


Figure 4: Gas chromatogram of an extract of 4 mg of fish tissues free from Matacil.

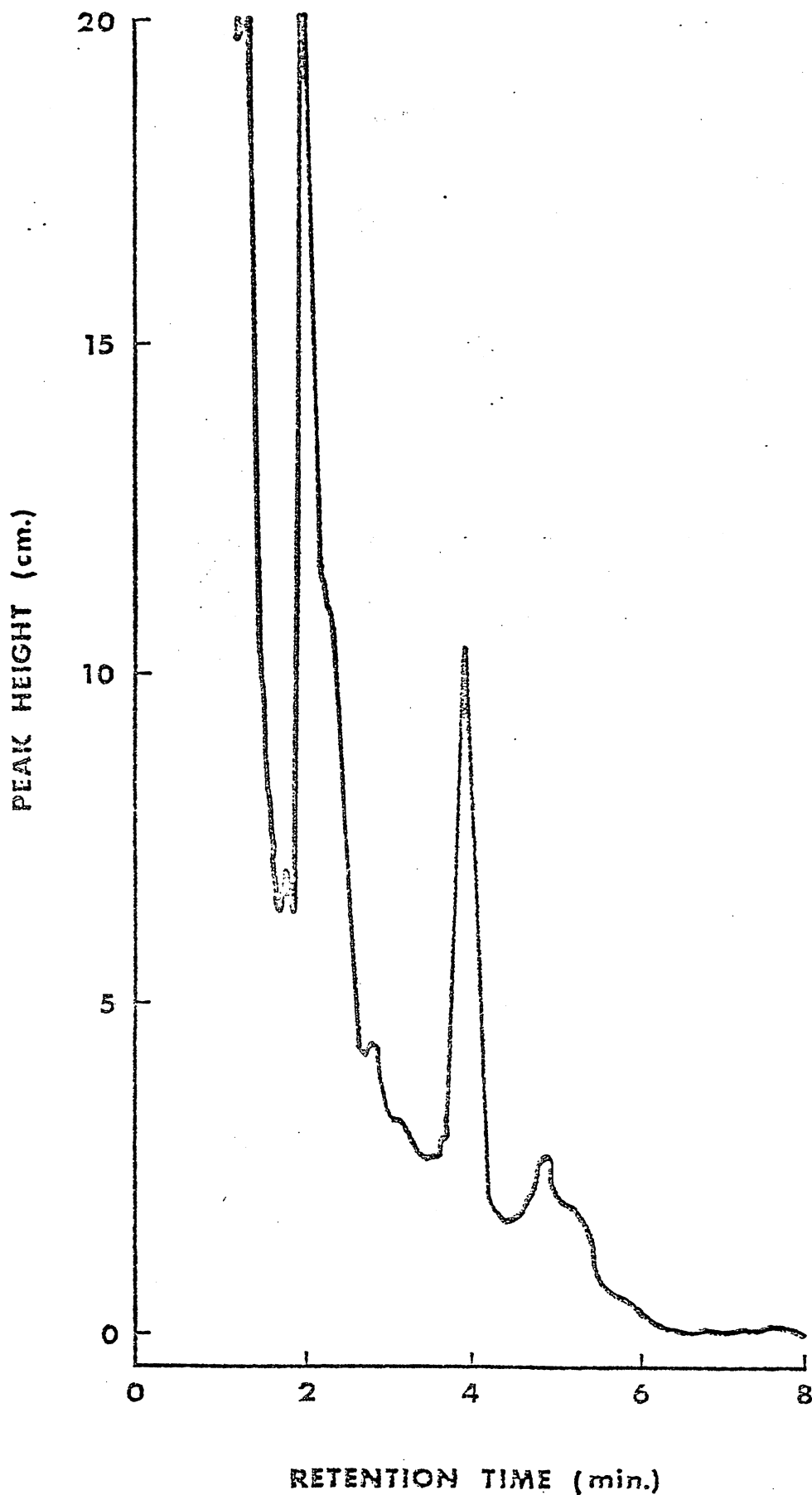


Figure 5: Gas chromatogram of a fish extract fortified with Matacil at the 0.5 ppm level.