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CHEMICAL ANALYSIS OF MATACIL® IN FISH SAMPLES RECEIVED FROM THE ACCIDENT INVESTIGATION TEAM OF QUEBEC GOVERNMENT

by

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INTRODUCTION

During the 1976 Quebec spray program, a report of Macacil® (Fig. 1) poisoning to fish has been brought to the attention of Dr. R. Sarrazin of the Department of Tourism, Fish and Game, Government of Quebec. The two frozen dead fish samples were sent to the Pesticide Chemistry Section at the Chemical Control Research Institute for Matacil® residue analysis. This report briefly describes the chemical analysis made on the two fish samples received from Dr. Sarrazin.

EXPERIMENTAL

Extraction

Each fish sample was allowed to thaw, pressed on folds of filter paper to remove the adsorbed water and weighed. Both the samples were homogenized separately twice with 100 ml of acetronitrile in a Sorvall-Omni-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 flash-evaporated to 1 ml and transferred quantitatively to a graduated centrifuge tube for the gas chromatographic (GC) analysis.

Gas Chromatographic Analysis

Gas chromatographic analysis of Matacil present in the fish extracts was carried out using a Tracor Model 550 gas chromatograph fitted with a Hall (Model 310) detector. Operating parameters are given in Table 1.

The gas chromatograph was standardized on the same day as the samples were analysed by injecting freshly prepared aliquots (2-5 ul) of (Fig.2) Matacil standards (analytical grade supplied by Chemagro) in benzene, 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 was concentrated by dry air-evaporation to the desired concentration for GC analysis. Quantitative result of the extracted sample was obtained by measuring the peak height after injection (4 ul), under the same operating conditions, and reading the concentration from the calibration curve (Fig. 3).

Solvents and Chemicals

All organic solvents used were either pesticide grade (P.G.) chemicals or freshly distilled in glass. Especially the benzene used was made anhydrous by distilling the P.G. grade with Dean-Stark condenser.

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.

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS

GC	:	TRACOR MODEL 550
DETECTOR	:	HALL MODEL 310 (NITROGEN MODE)
COLUMN	:	1.83 M x 6 MM O.D. PYREX GLASS PACKED WITH 6% SE 30 ON CHROMOSORB W, H.P., MESH 80/100
SOLVENT	:	15% ISOPROPANOL IN DISTILLED WATER
RATE	:	1 ML/MIN
TEMP (°C)		
OVEN	:	210
OUTLET	:	280
INLET	:	215
CARRIER GAS (ML/MIN)	:	He, 100
GAS FLOW (ML/MIN)	:	H_2, 150
ATTENUATION	:	2
RANGE	:	1
RECORDER	:	LINEAR INSTRUMENTS, 1 MV
CHART SPEED	:	30
RETENTION TIME	:	3.25

Table II

Recovery Study of Matacil in Fish*

Fortification Level (ppm)	Matacil Conc. Recovered (Percent)	Remarks
1.0	84	
2.0	88	Av. recovery 85% with coefficient of variation 6

* Average of triplicate determinations.

Table III

Analysis of Matacil® Residues from

Fish Samples Received from Quebec Spray Program - 1976

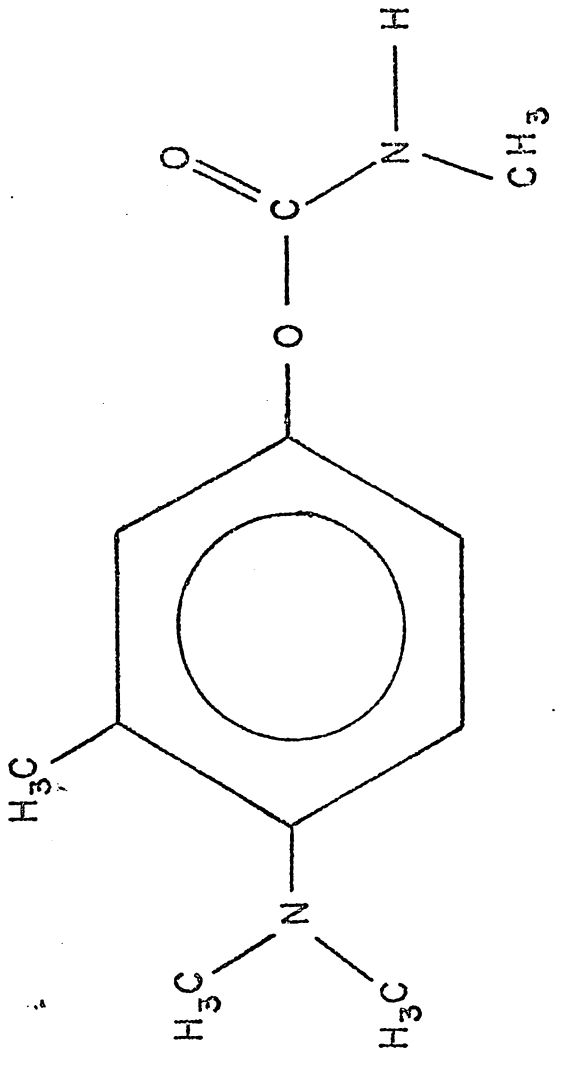
CCRI No.	Sample Description	Matacil® Conc. ppm
18/76/198/369	Club Beausoleil, 8-6-76 1er Bassin	N.D.
18/76/199/370	Club Beausoleil, 8-6-76 2 éme Bassin	N.D.

N.D. Not Detected

MDL 0.3 ppm (Hall Detector)

FIG. I

MATACIL® - AMINOCARB



4-Dimethylamino-3-methylphenyl methylcarbamate

FIG. 2 GAS CHROMATOGRAM OF 10 NG (4 UL) OF MATACIL® STANDARD IN BENZENE

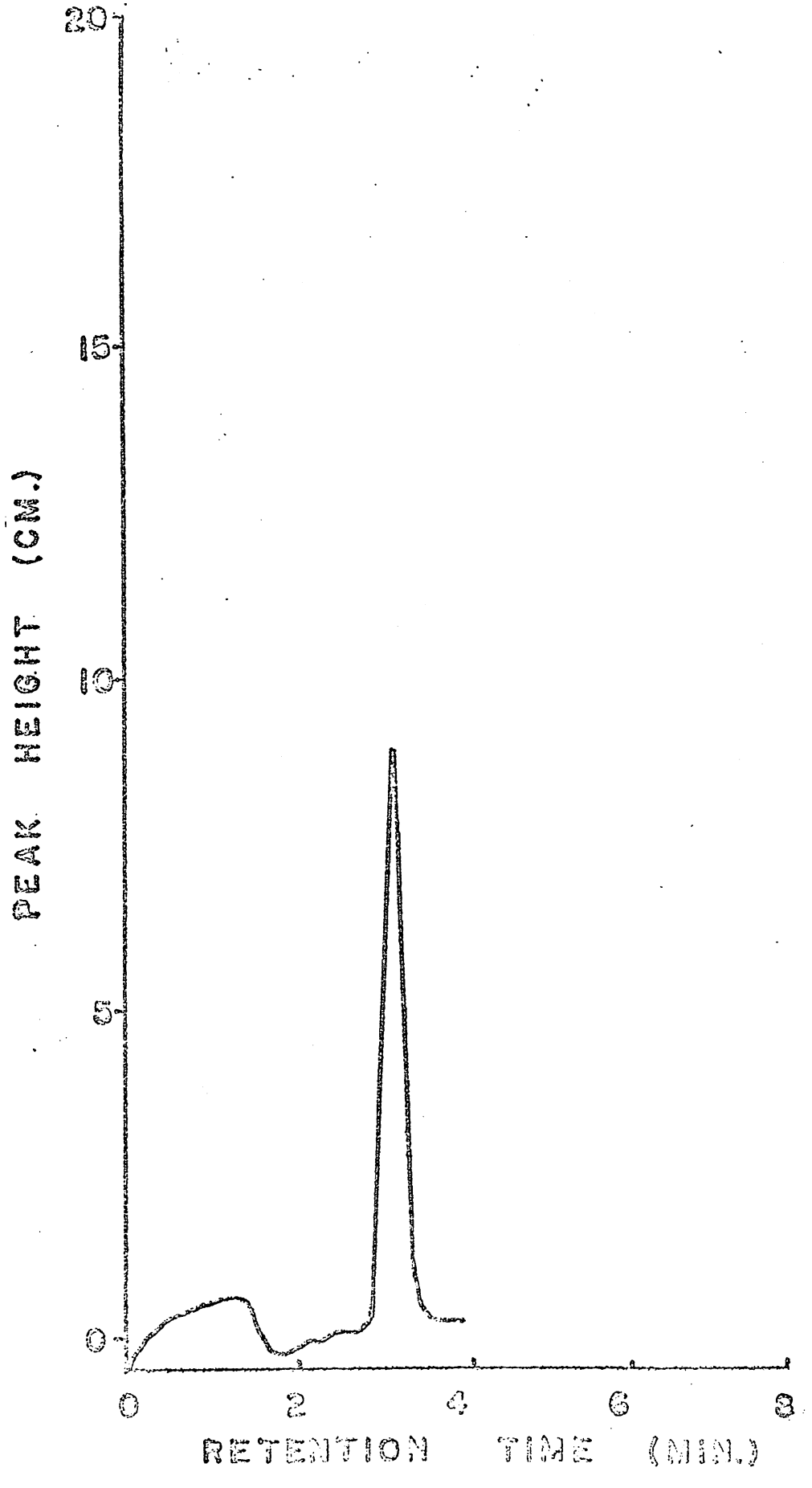


FIG. 3 GAS CHROMATOGRAPHIC CALIBRATION CURE FOR MATACIL® OBTAINED WITH THE HALL DETECTOR

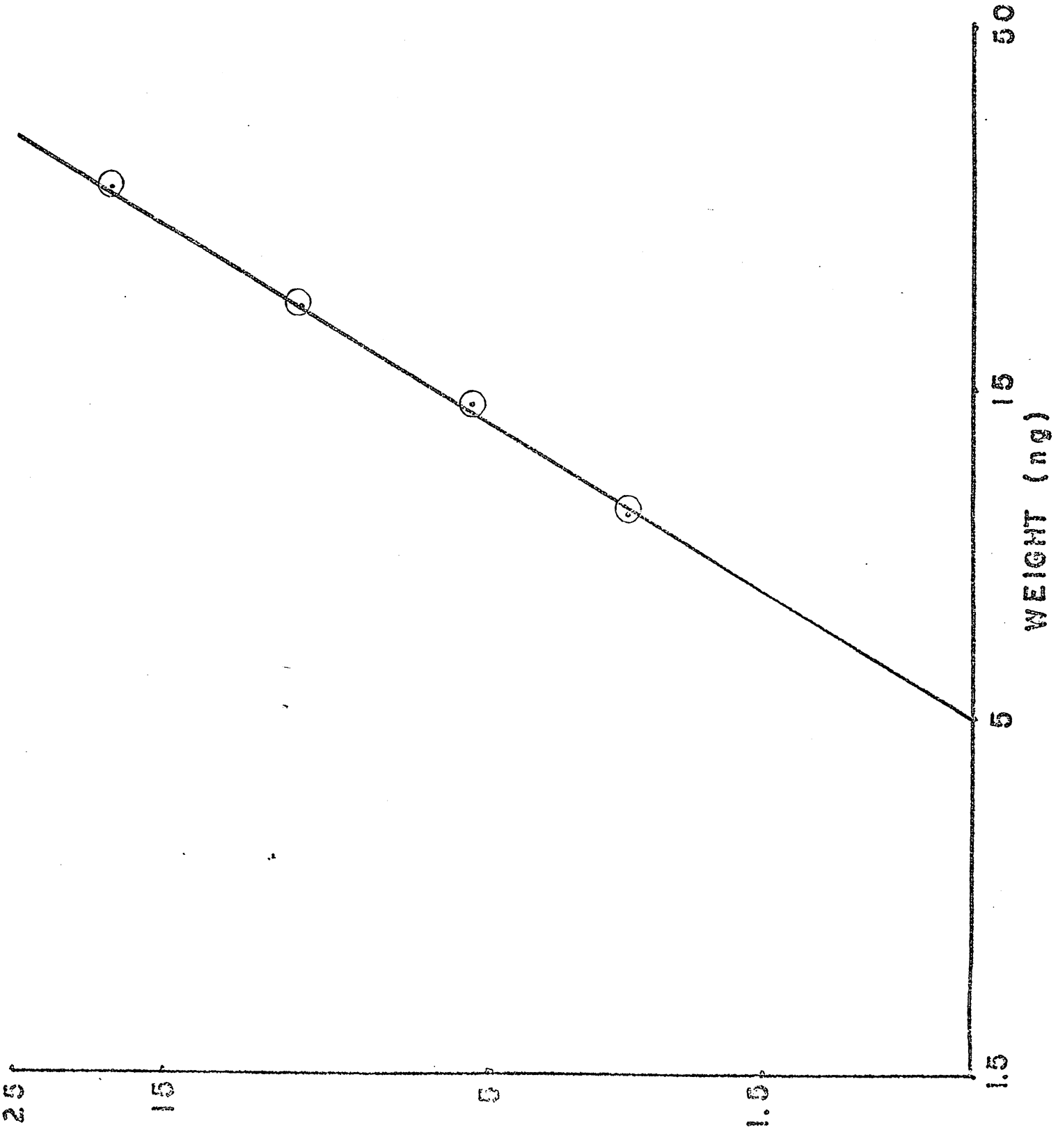


FIG. 4

CHROMATOGRAM OF AN EXTRACT OF FISH TISSUES FORTIFIED WITH MATACIL AT THE LEVEL OF 1.0 PPM

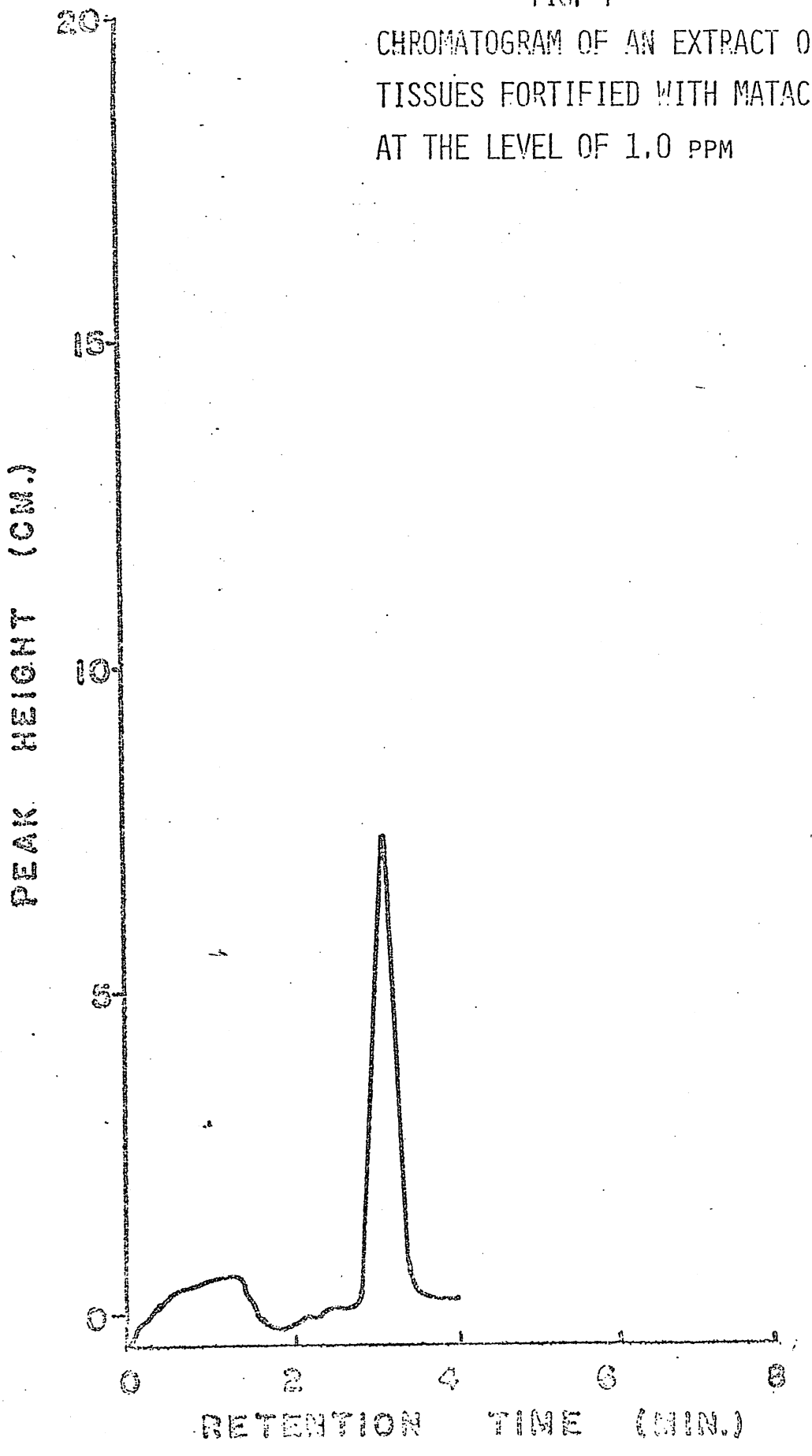
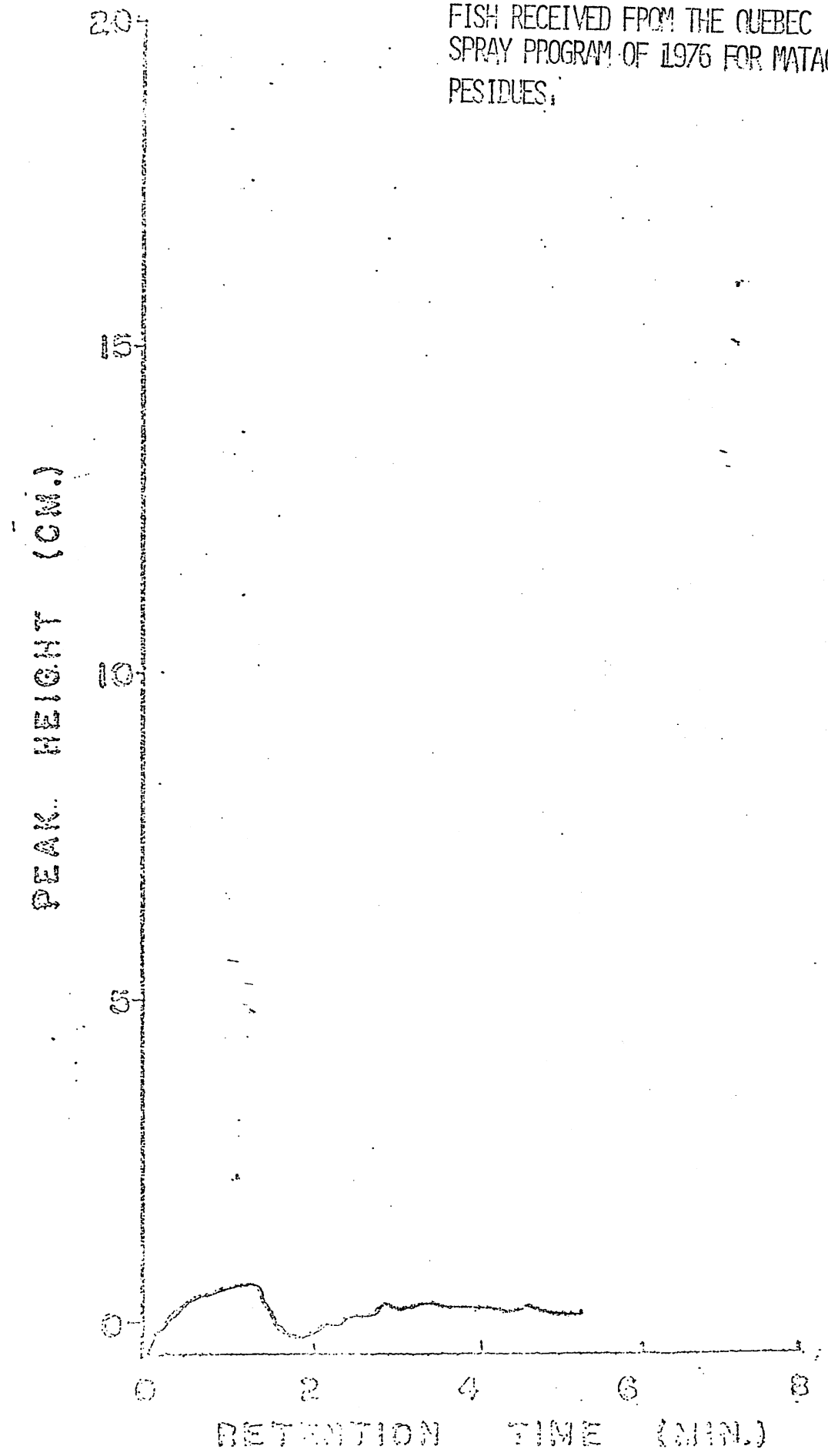


FIG. 5 GAS CHROMATOGRAM OF AN EXTRACT OF FISH RECEIVED FROM THE QUEBEC SPRAY PROGRAM OF 1976 FOR MATACIL RESIDUES.



RESULTS AND DISCUSSION

For recovery studies fish samples (rainbow trout-*Salmo gairdnerii*) were collected from a Matacil-free lake, fortified with the insecticide at 1.0 and 2.0 ppm levels and analysed by the method described. The average recovery was 85% with a coefficient of variation of 6. The minimum detection limit was found to be 0.30 ppm at the above concentration range for 10g of the fish used in the recovery studies. The results of the recovery study are recorded in Table II.

The chromatographic profile of the spiked fish extract is given in Fig. 4. The average percent recovery was found to be 85 with a coefficient of variation 6 (Table II). The method is reasonably sensitive with minimum interference and is satisfactory for the analysis of Matacil® residues present in fish at above 0.3 ppm concentration level. Below this level, the method is not sensitive.

The fish extracts received from the 1976 Quebec spray program through Dr. R. Sarrazin were analysed by injecting 4 ul samples in the Hall-GLC and the results are recorded in Table III. Both the chromatograms (Fig.5) did not show any measurable peak with retention time 3.25 min. corresponding to the presence of Matacil® as observed in the spiked sample (Fig. 4) showing that the fish samples did not contain detectable levls of Matacil®.

CONCLUSION

Under the experimental conditions described above, the two fish samples received from the 1976 Quebec spray program through Dr. R. Sarrazin did not contain measuable levels (0.30 ppm) of Matacil® residues.

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