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ELECTRON CAPTURING IMPURITIES IN FENITROTHION FORMULATIONS

by

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INTRODUCTION

The polychlorinated biphenyls (PCB's), a mixture of about 200 compounds derived from the aromatic hydrocarbon biphenyl, containing chlorine on any of the ten positions, are ubiquitous pollutants of the atmosphere, waterways, oceans and soil and are present in marine life and in the food chain. Preliminary studies (Sundaram and Davis 1974) showed that they are distributed in the forest environment along with other organochlorines such as DDT. Our knowledge of their presence in various components of the forest, their toxicological significance and exact environmental impact are only fragmentary at the moment. One possible source of their introduction, as contaminants in the forest environment, is probably through the spray applications of various insecticide formulations to control forest pests containing chlorobiphenyls as impurities. In order to find out the possible sources of PCB contamination, a preliminary analytical study using gas liquid chromatography (GLC) has been made to ascertain their presence in the samples of technical fenitrothion insecticide and the diluents, Arotex ®, Atlox ® and the Esso Fuel Oil No. 4 etc. used in the spray mixture.

Fenitrothion is used extensively in Canadian forest pest control programs since 1969 (Fettes 1968, Fettes and Buckner 1972, Fettes 1975, Anonymous 1975) and the inadvertent presence of traces of persistent PCB's in the spray mixture will enhance the contamination of the forest ecosystem. Consequently, periodic checking of the spray formulations for contaminants, especially to electron capturing impurities like PCB's, is an integral part of the environmental monitoring program undertaken

by the Chemistry Section at the Chemical Control Research Institute (CCRI). This report describes a GLC method used for determining the possible presence of PCB's (Aroclor 1254) as contaminants in technical fenitrothion and the diluents, Arotex® (a petroleum fraction) oil, Atlox® emulsifier and Esso Fuel Oil # 4 used in preparing the spray formulation.

MATERIALS AND METHODS

Chemicals and Solvents

Arotex®, Atlox® and Fuel Oil # 4 were collected from different scientists at CCRI. The technical samples of fenitrothion insecticide were supplied by Dr C.H. Buckner. Pesticide grade benzene was obtained from the Caledon Laboratories. Analytical grade fenitrothion, and its two metabolites (oxon and the nitrocresol) and the Aroclor® 1254 (one of the primary standards for the quantitation of PCB's) were supplied respectively by Sumitomo Chemical Company in Japan and Monsanto in U.S.A.

Gas Chromatograph

Hewlett-Packard (H.P.) Model 5710A gas chromatograph fitted with Ni-63 electron capture detector.

Column	:	Borosilicate glass 1.22 m x 6 mm O.D. (2 mm I.D.) packed with 3% DC 200 on 80/100 mesh Gas Chrom W, preconditioned 48 hours at 250°C.	
Temperature (°C):		Injection post	200
		Column oven	200
		Detector	250

Carrier gas	:	Argon/methane (95/5%) pressure of 50 psi and flow rate of 31.25 ml/min.	
Instrument Settings	:	Attenuation	16
Chart span	:	1 Mv	
Chart speed	:	0.5 in/min	
Retention times (min)	:	Nitrocresol	1.81
		Fenitrooxon	3.39
		Fenitrothion	3.54

Standardization of the Gas Chromatograph

The gas chromatograph was standardized by injecting 2 ul of standard solutions of 3-methyl-4-nitrophenol (0.25 ng), fenitrooxon (0.2 ng) and fenitrothion (0.10 ng) in benzene. The retention times (min) were measured from the chromatographic profile in Fig. 1 and were found to be 1.81, 3.39 and 3.54 respectively. The oxon separation was unsatisfactory and appeared as a shoulder to the fenitrothion peak.

A 2 ul shot of the Aroclor® 1254 in benzene gave eighteen well defined peaks (Fig. 2) (numbered according to their RT's) instead of the fifteen peaks observed elsewhere (Hutzinger et al 1974, pp 18 and 19). If the three shoulders observed in Fig. 2 are ignored then the chromatogram contained only fifteen peaks. A rough estimation of the PCB's present in the fenitrothion (tech), Arotex, Atlox and Fuel Oil # 4 samples was made on prorata basis by comparing the area of the 18 peaks for 4 ng weight of the standard Aroclor 1254 with the area of peaks measured for the same weight of the above samples injected into the gas chromatograph

(for experimental details see Sundaram and Volpé, 1976). This procedure is very qualitative and is assumed to be adequate for the present study. No correction factor is applied for the overlapping peaks that could have arisen due to the other electron capturing impurities such as DDT and DDE. The peak # 6 in the Aroclor 1254 standard (Fig. 2) nearly corresponded to the RT's of fenitrothion and its oxon. Arotex and Fuel Oil # 4 also showed peaks similar to them. Such interferences were deliberately ignored to simplify the quantitation procedure.

Table 1

Analysis of Fenitrothion Formulations for PCB's

Chemicals Analysed	Density	Peaks Observed in the Chromatograms	Area of Peaks (cm^2)	Weight of the Chemicals Injected in GLC (ng)	Conc. of PCB's Wt. %
Aroclor 1254 standard	1.495	1-18 (Fig. 2)	38.52	4	-
Fenitrothion (Tech) 1-B	1.320	3, 4 (Fig. 3)	0.37	8	0.50
Fenitrothion (Tech) 1-J	1.320	1, 3, 4 (Fig. 4)	0.49	8	0.60
Arotex ®	0.940	4 (Fig. 5)	0.61	20	0.0003
Atlox ®	1.016	4 (Fig. 6)	0.05	20	0.00002
Esso Fuel Oil # 4	0.923	2 (Fig. 7)	0.14	20	0.00008

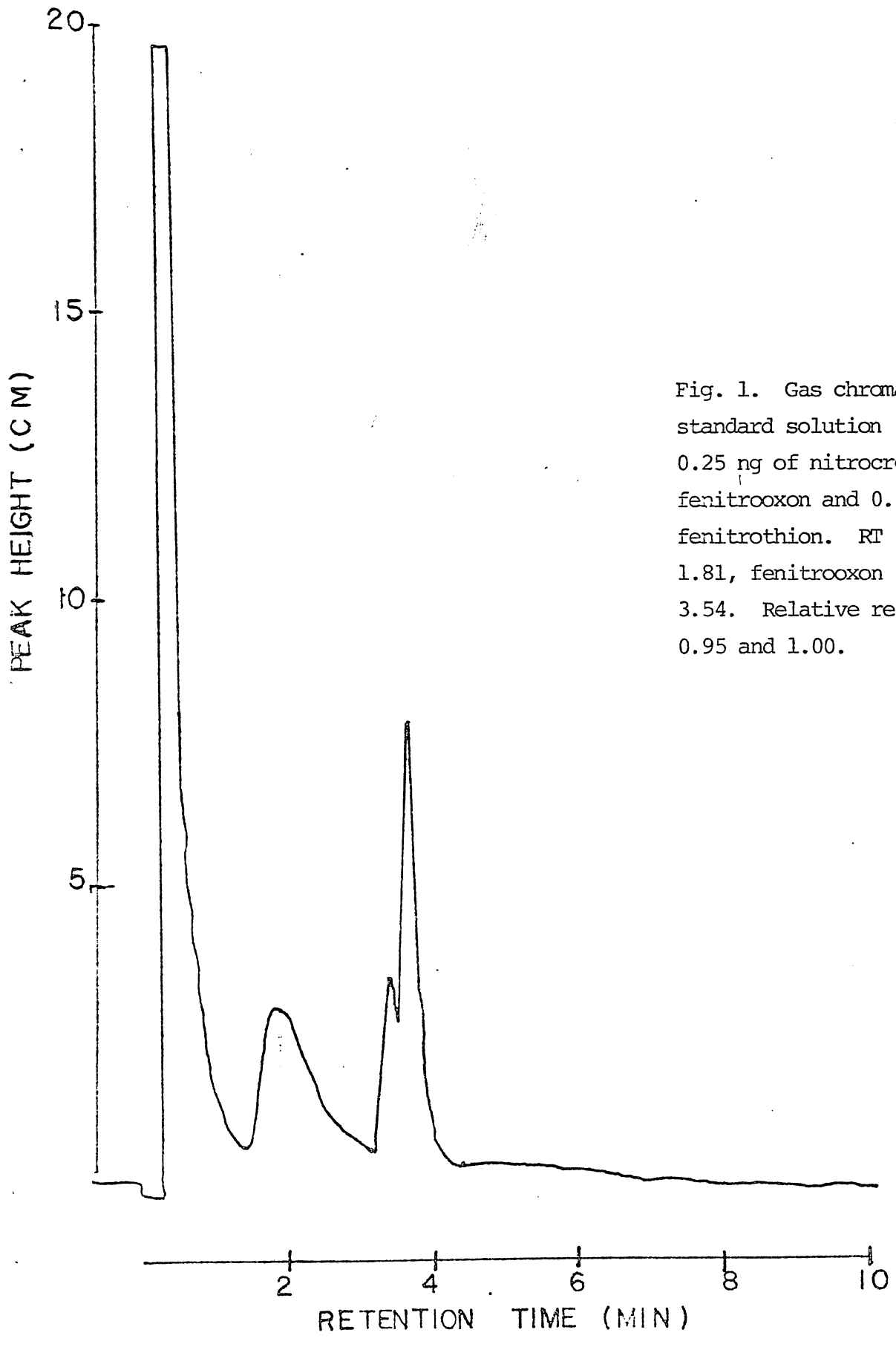

Fig. 1. Gas chromatogram of a standard solution (2 ul) containing 0.25 ng of nitrocresol, 0.20 ng of fenitrooxon and 0.10 ng of fenitrothion. RT (min): Nitrocresol 1.81, fenitrooxon 3.39 and fenitrothion 3.54. Relative retention time: 0.51, 0.95 and 1.00.

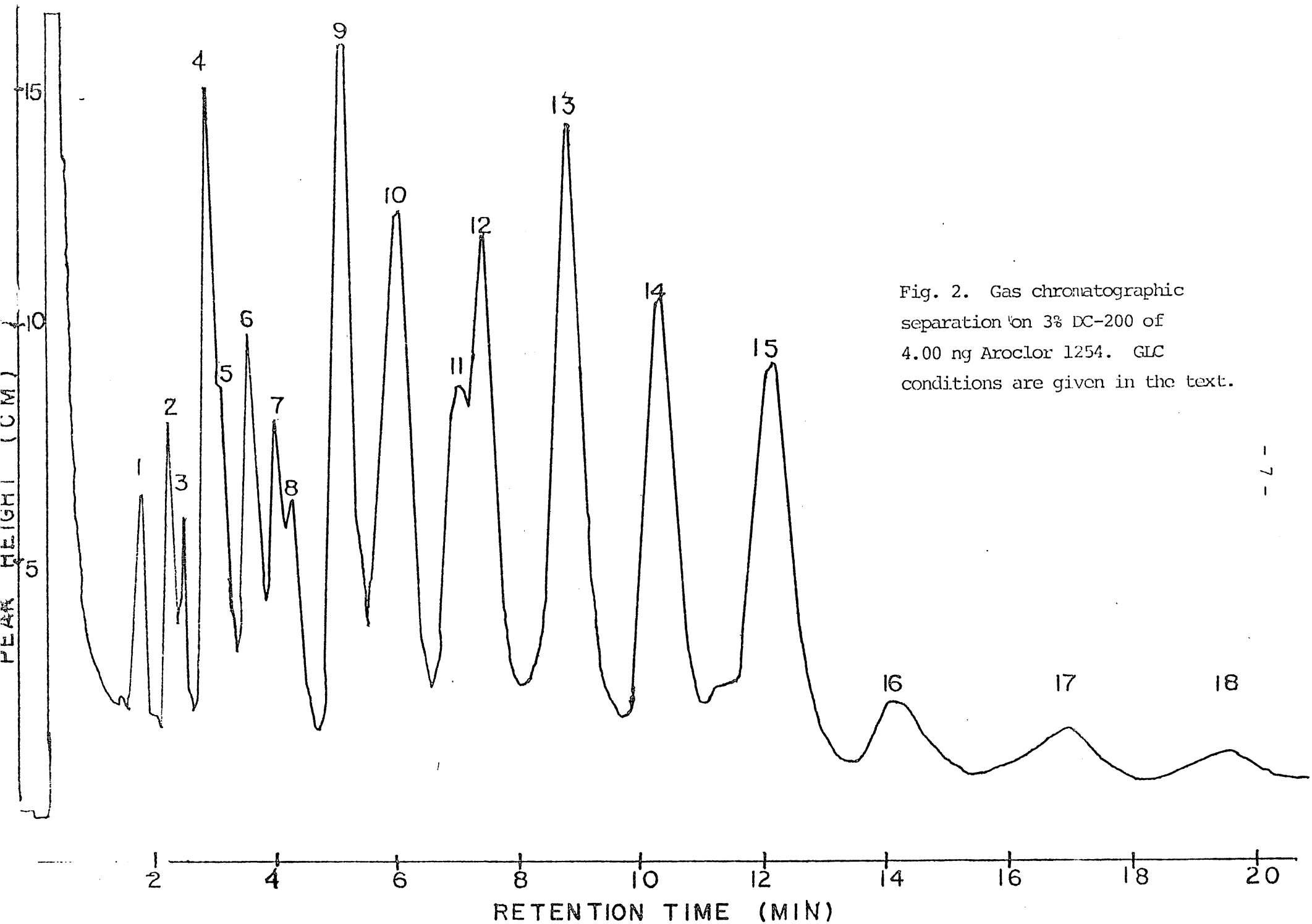

Fig. 2. Gas chromatographic separation on 3% DC-200 of 4.00 ng Aroclor 1254. GLC conditions are given in the text.

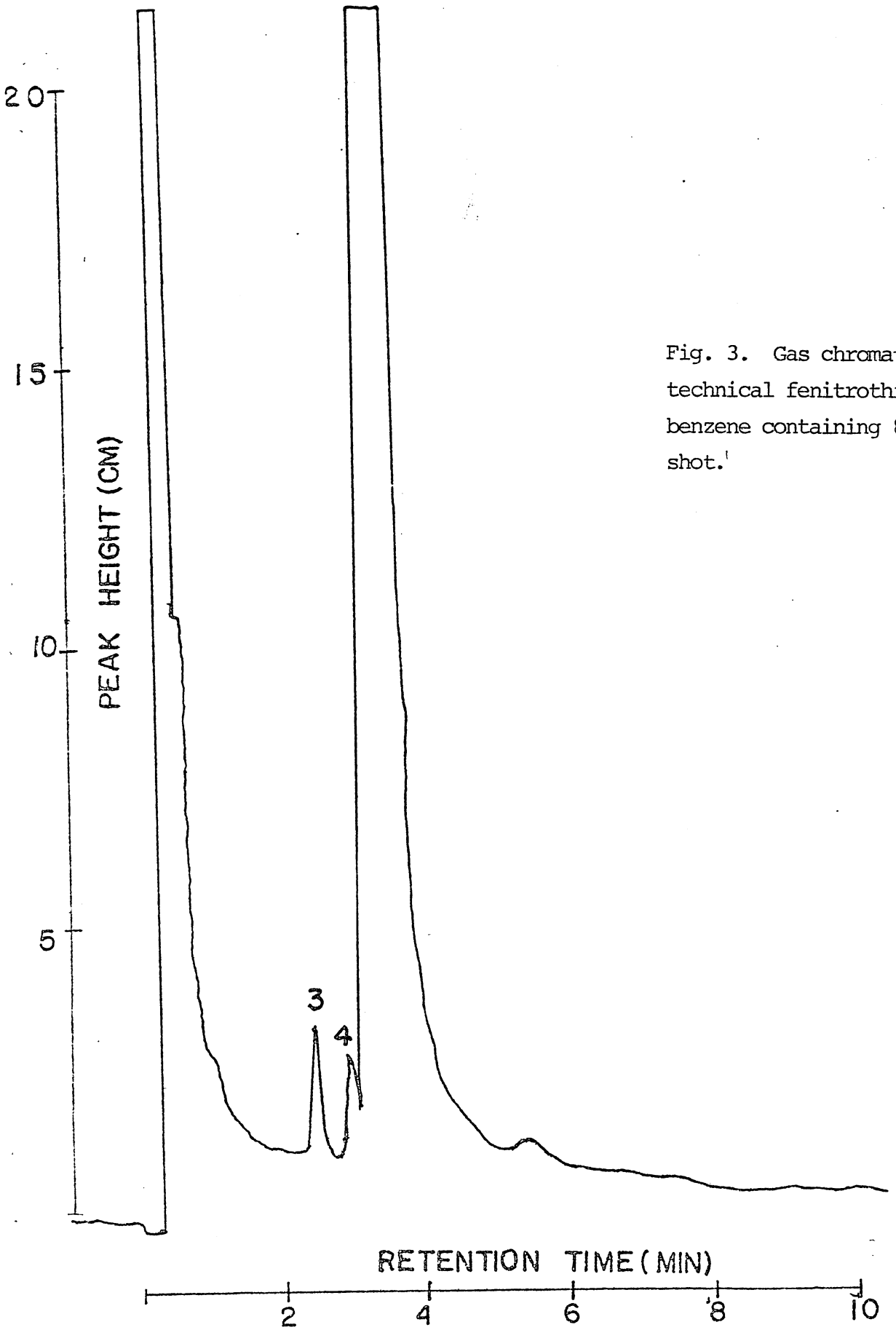

Fig. 3. Gas chromatogram of technical fenitrothion (1-B) in benzene containing 8 ng per 2 ul shot.

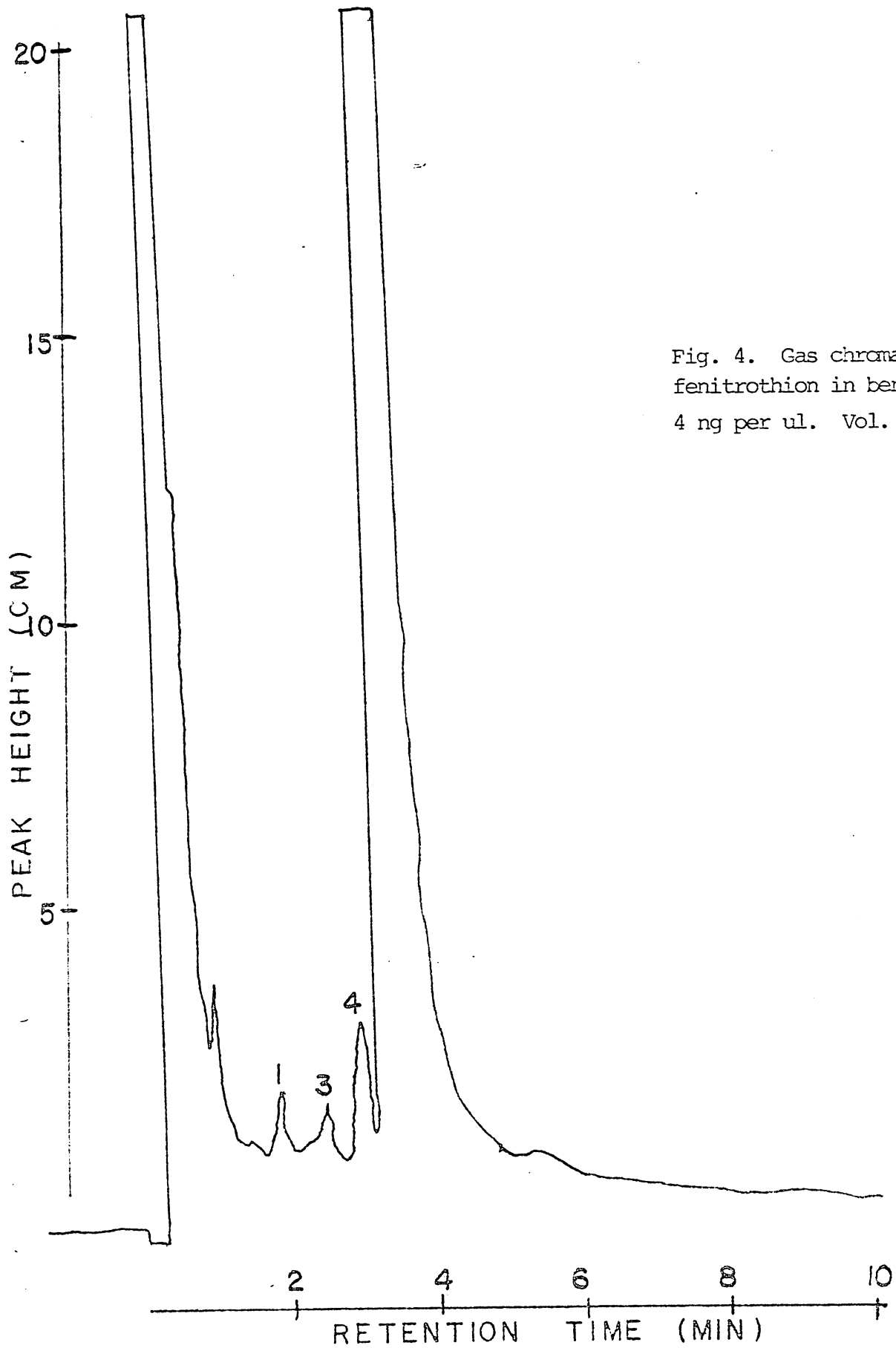

Fig. 4. Gas chromatogram of technical fenitrothion in benzene (1-J) containing 4 ng per ul. Vol. of the shot: 2 ul.

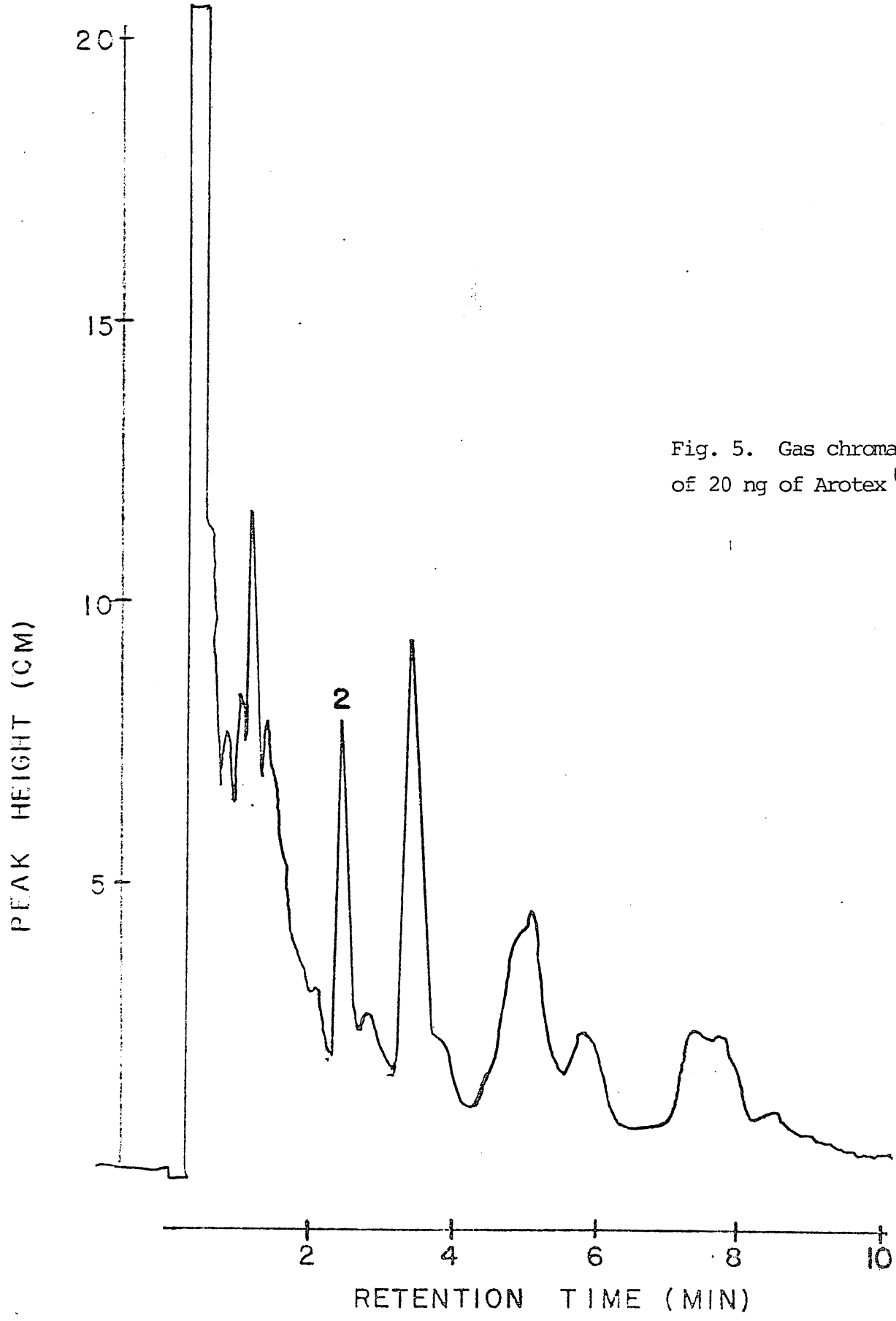

Fig. 5. Gas chromatographic profile of 20 ng of Arotex ® in benzene.

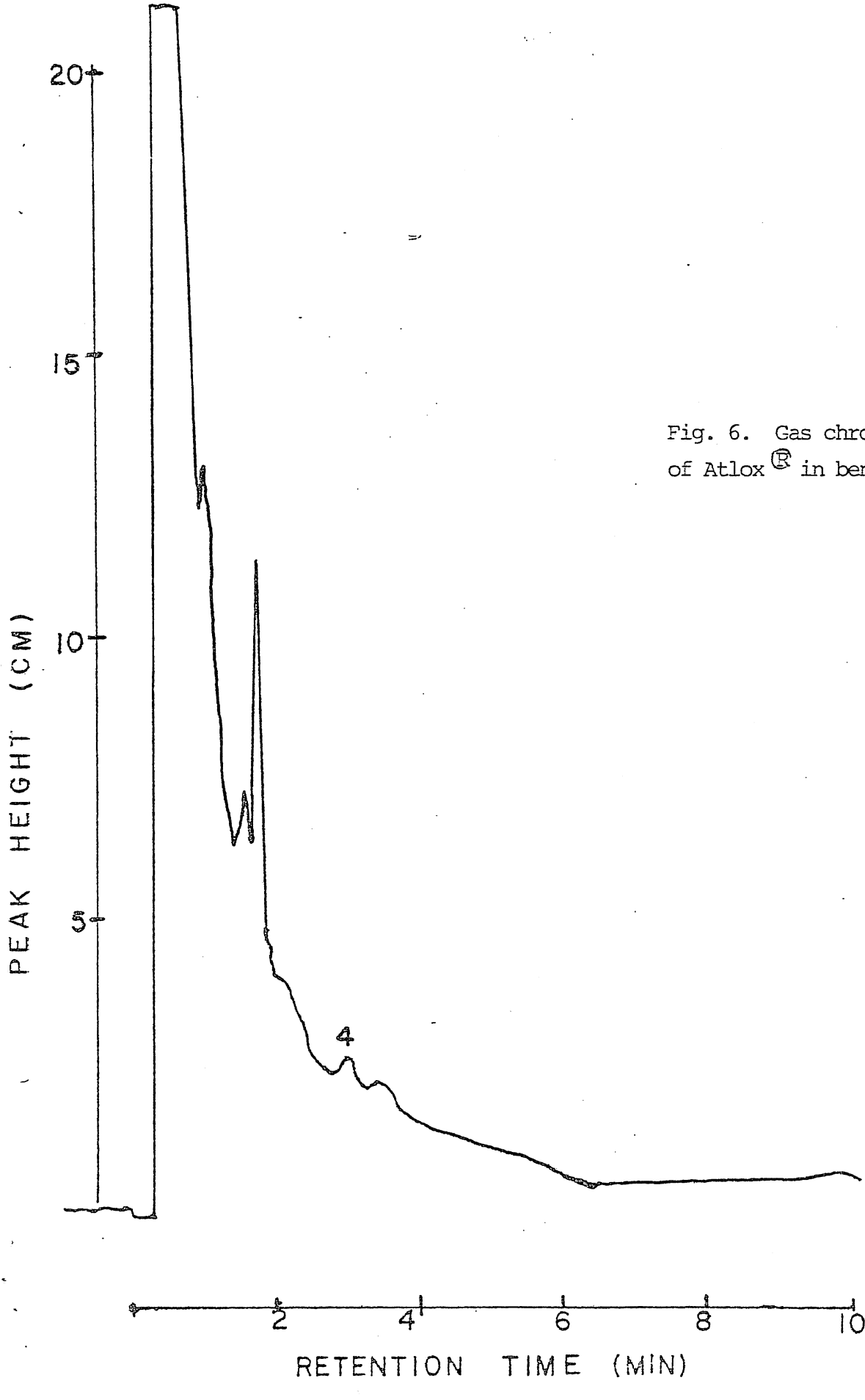

Fig. 6. Gas chromatogram of 20 ng of Atlox® in benzene.

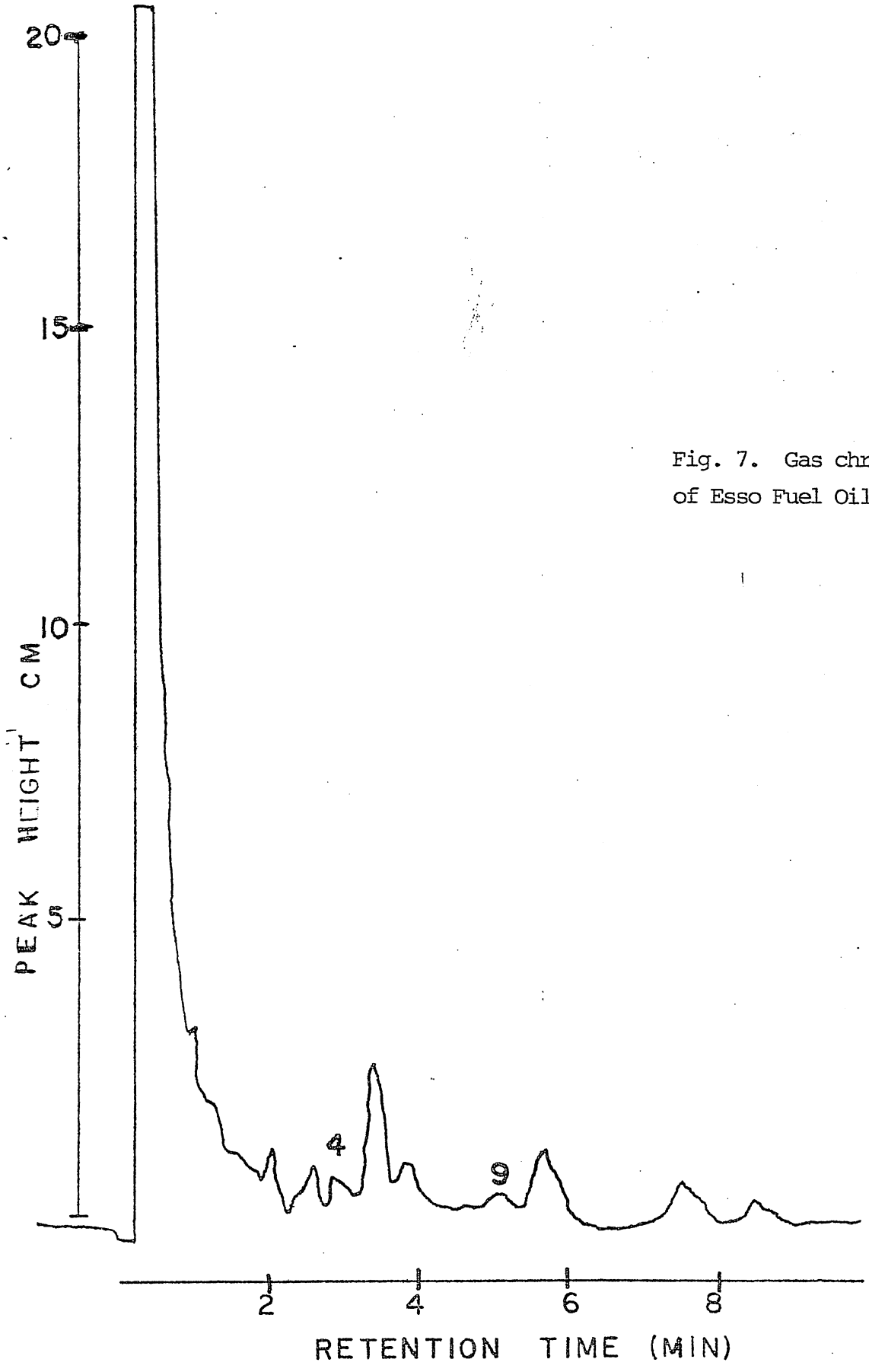

Fig. 7. Gas chromatogram of 20 ng of Esso Fuel Oil # 4 in benzene.

RESULTS AND DISCUSSION

The GLC responses of the two technical fenitrothion samples, Arotex (petroleum distillate) Atlox emulsifier and the Esso Fuel Oil # 4 solvent are given in Figs. 3 to 7 respectively. One of the fenitrothion technical materials (1-B) (Fig. 3) showed peaks 3 and 4 where as the other sample (1-J) showed (Fig. 4) peak 1 in addition to the other two. Arotex showed peak 2, Atlox peak 4 and the chromatogram of the fuel oil carrier contained peaks 4 and 9. From the measured peak areas of each chromatogram (Figs. 3-7), the concentrations of PCB's were calculated, as shown below using the area for the Aroclor 1254 standard obtained from Fig. 2.

4 ng Aroclor 1254 standard gave a peak area (Fig. 2) of 38.5 cm

Therefore, 0.37 cm peak area (Fig. 3, Table 1) will correspond to 4 x 0.37/38.5 = 0.038 ng of PCB (Aroclor 1254)

8 ng of fenitrothion (tech) 1-B sample contains 0.038 ng of PCB

Percent of PCB present = 0.038 x 100/8 = 0.50 (Expressed as Aroclor 1254)

Using similar calculation procedures, the amount of PCB's present in other samples were calculated and the results are recorded in Table 1. From the results it is evident that the technical material contained *ca* 0.5% of PCB's or impurities with similar retention times. The diluents such as Arotex®, Atlox® and the fuel oil, contained negligible amounts of the electron capturing impurities.

Although gas chromatography is the method of choice for the

detection of PCB's, additional confirmation is necessary due to the numerous assumptions made earlier in this investigation. Mass spectrometry coupled with gas chromatography is frequently used to confirm the identity of PCB's. The instrumentation is rather expensive and currently not available at our laboratories. Unless a better confirmative technique (derivatization, mass spectrometry etc.) is developed and applied in the present investigation, the results recorded above are of qualitative nature only without much significance. They only show the presence of some electron capturing impurities with similar retention times as the PCB standard used. Until then, it is wise to assume that little is known about the nature of impurities present in the technical fenitrothion samples analysed.

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