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Sundaram, K.M.S.

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25 Pickering Place

Ottawa, Ont., K1A OW3

INTRODUCTION

Current chemical control methods in use for control of forest insect pests are, in most cases, more effective and economically feasible than the various other control methods available. Despite such problems as insect resistance, biological magnification and environmental contamination, various chloroorganic, organophosphate and carbamate insecticides are used in increasing amounts in Canadian forest and shade tree spray programs for controlling various insect pests. A large number of synthetic organic insecticides are dispersed aerially in the forest environment in various spray formulations. The two common types of insecticide formulations widely used in aerial spraying are:

(1) The emulsifiable concentrates (EC) containing an insecticide and an emulsifying agent in a suitable solvent, which are dispersed in water

for use, and

(2) solutions of insecticides dissolved in suitable solvents such as petroleum distillates.

The biological activity, stability and distribution of these insecticides in a forest ecosystem depend primarily on the type and nature of formulations used (Van Valkenburg, 1973). To assess the overall efficacy of various insecticides, it has become necessary to analyse and quantify all the pesticide formulations used in spray programs.

During the later part of April 1976, Messrs F. Leduc and G.M. Lévesque of the Environmental Protection Service, Quebec Region of the Environment Canada requested the Chemical Control Research Institute (CCRI) to help them in analysing about 110 samples of technical materials of fenitrothion, Matacil®, dimethoate and phosphamidon insecticides and their spray mixtures.

This report describes the gas-liquid chromatographic (GLC) methods developed and used at CCRI to quantify the four insecticides and several of their spray mixtures and commercial formulations. The GLC method has the advantages of speed and flexibility with minimum interferences from impurities or admixed solvents and emulsifiers and may be used for the rapid and accurate analysis of the insecticides and their formulations.

MATERIALS AND METHODS

Insecticide Materials

Table I lists the various insecticide materials (technical) (emulsifiable concentrates or solutions) and the spray mixtures numbering to 110 used in the GLC analysis. The insecticide materials were collected by Mr G.M. Lévesque from the various spray areas in Quebec and shipped to the pesticide laboratory at CCRI for analysis.

Reagents

Solvents: Pesticide grade solvents distilled in glass obtained from the Caledon Laboratories.

Insecticides: Analytical grade samples of fenitrothion, dimethoate, Matacil® and phosphamidon were obtained from the corresponding chemical companies [Sumitomo (fenitrothion), Chemagro (dimethoate and Matacil®) and Ciba-Geigy phosphamidon].

Apparatus

Gas Chromatograph

The different GC models used in the analysis and their operating conditions are given in pages 6-9.

Calibration Curve

Stock solutions containing 10 mg of the insecticides were prepared separately in 100 ml of benzene (100 µg/ml). Required aliquots of each of the stock solutions were transferred to a 100 ml volumetric flask using pipettes and diluted with benzene and mixed thoroughly.

The concentration (ng/µl) of the insecticides in the resulting standard solution were calculated. The standard and stock solutions were stable for many weeks if they were kept tightly sealed and under refrigeration. The gas chromatograph was calibrated by injecting different volumes of the standard solutions, measuring the peak heights and plotting against the mass (nanogram) of the insecticides on log-log paper. The response of the GC instruments was linear, the peak shapes were good (Figs. 1-4) providing adequate resolution and appropriate retention times. The calibration of the instruments and their responses were checked twice daily in the morning and in the afternoon during the course of the analysis.

Analysis of Insecticides and their Spray Mixtures

Each insecticide (technical) or spray mixture was weighed accurately (40 mg) in a semimicro balance, transferred quantitatively to a 100 ml volumetric flask and a homogeneous stock solution in benzene was prepared. An aliquot of the solution was further diluted in a volumetric flask (10 µg/ml) so that a 4 µl shot of it gave roughly 50% of full-scale recorder deflection at a specific attenuation setting. This requirement and condition were applied for all the samples of formulation and spray mixtures. Four microliters of each of the diluted sample solution in triplicate was injected into the gas chromatograph under the same operating conditions out-lined earlier. Each peak height was measured and found to agree within 2% and the average peak height for each insecticide was calculated. Using the average peak height, the amount of each insecticide (ng/µl) was read from the calibration curve and the weight of active material present in 100 ml of the formulations were calculated and their concentrations expressed as a percentage (weight/weight).

For spray mixtures, in addition to percent active ingredient, the content in ounces or pounds (avoirdupois) in one gallon (U.S.) could be calculated, if required, using the following conversions:

1 ℓ = 0.264 gal (U.S.)

1 g = 0.0353 oz

1 kg = 2.205 lbs

The petroleum solvents, emulsifiers, surfactants and dye tracers present in the formulation did not give any interference and the GLC responses were good. In analysing aqueous emulsions (spray mixtures) the removal of water was not often necessary, but if needed, it was done by passing an aliquot of the prepared stock solution through a column of anhydrous sodium sulphate and making up the eluate to a known volume. No solvent partitions and cumbersome column cleanups were necessary during the analysis and the present method was found to be simple, rapid, efficient, sensitive and direct.

G.L.C. CONDITIONS

FENITROTHION

Column:	5% OV1 on Chromsorb W mesh 80/100 4 ft.
Instrument:	H.P. 7610A
Detector:	F.P.D. P-mode
Temperatures:	Oven - 195°C Detector - 200°C Injection Port - 225°C
Gas Flows:	H_2 150 mls/min. Air 50 mls/min. O_2 18 mls/min.
Carrier Gas:	N_2 30 mls/min.
Attenuation:	32
Range:	10^3
Chart Speed:	0.5 inch/min.
Chart Span:	1 MV
Retention Time:	3.9 min.

G.L.C. CONDITIONS

PHOSPHAMIDON

Column:	20% OV-101 on Chromosorb W mesh 80/100 4 ft.
Instrument:	H.P. 5710A
Detector:	F.P.D. P-mode
Temperatures:	Oven - 190°C Detector - 200°C Injection Port - 250°C
Gas Flows:	H_2 150 mls/min. Air 50 mls/min. O_2 18 mls/min.
Carrier Gas:	N_2 30 mls/min.
Attenuation:	32
Range:	10^2
Chart Speed:	0.5 inches/min.
Chart Span:	1 MV
Retention Time:	trans 4.7 min. Cis 6.1 min.

G.L.C. CONDITIONS

DIMETHOATE

Column:	5% OV1 on Chromosorb W mesh 80/100 4 ft.
Instrument:	H.P. 7610A
Detector:	F.P.D. P-mode
Temperatures:	Oven - 205°C Detector - 200°C Injection Port 225°C
Gas Flows:	H_2 150 mls/min. Air - 50 mls/min. O_2 - 18 mls/min.
Carrier Gas:	N_2 30 mls/min.
Attenuation:	32
Range:	10^3
Chart Speed:	0.5 inches/min.
Chart Span:	1 MV
Retention Time:	1.6 min.

G.L.C. CONDITIONS

MATACIL

Column:	6% SE30 on Chromosorb W mesh 80/100 6 ft. Solvent 15% isopropanol in distilled water at a rate of 1 ml/min.
Instrument:	Tracor 550
Detector:	Hall
Temperatures:	Oven - 210°C Detector - 280°C Injection Port - 215°C
Gas Flows:	H_2 150 mls/min.
Carrier Gas:	He 100 mls/min.
Attenuation:	2
Range:	1
Chart Speed:	0.5 inches/min.
Chart span:	1 MV
Retention Time:	3.15 min.

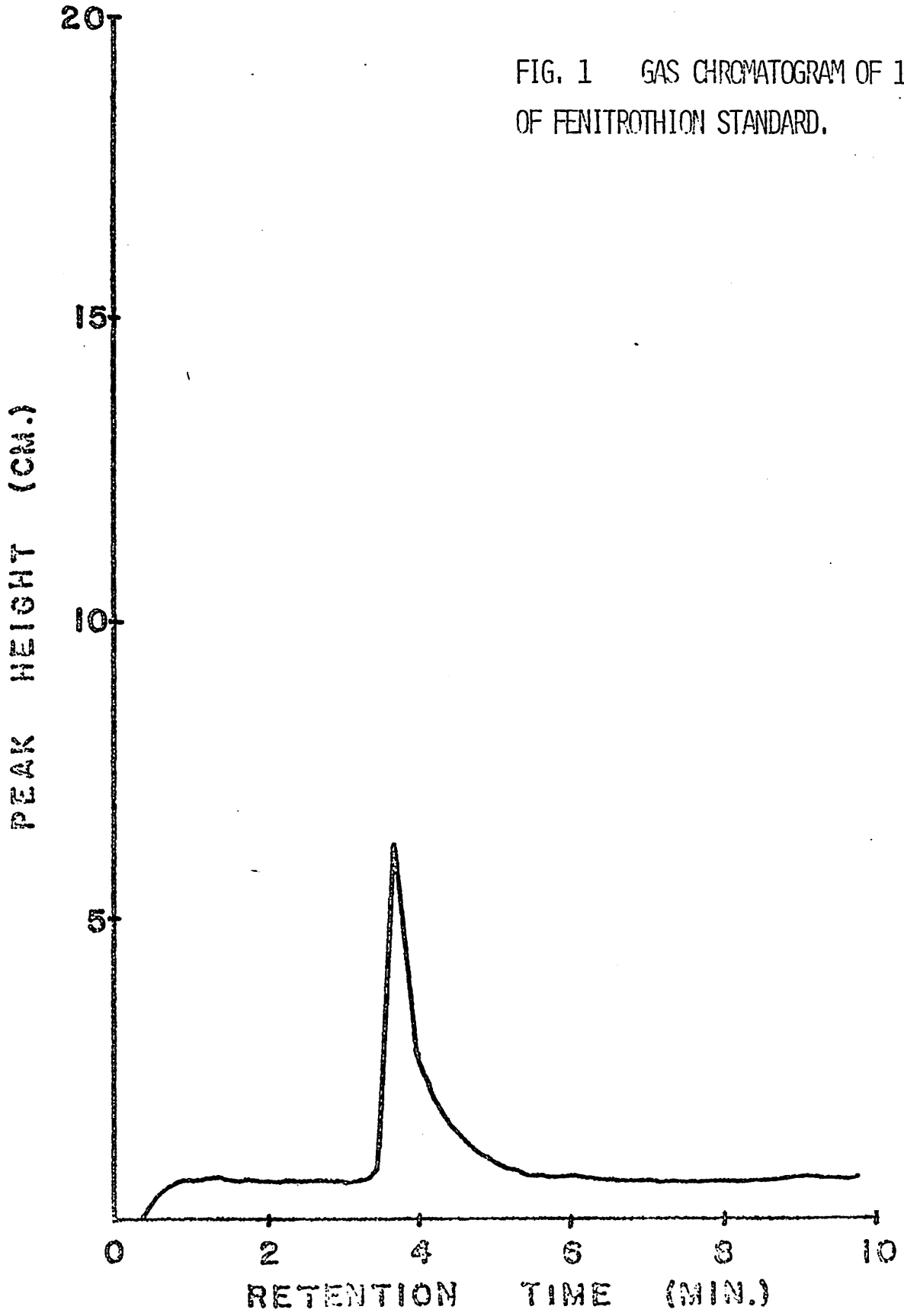


FIG. 1 GAS CHROMATOGRAM OF 10 NG OF FENITROTHION STANDARD.

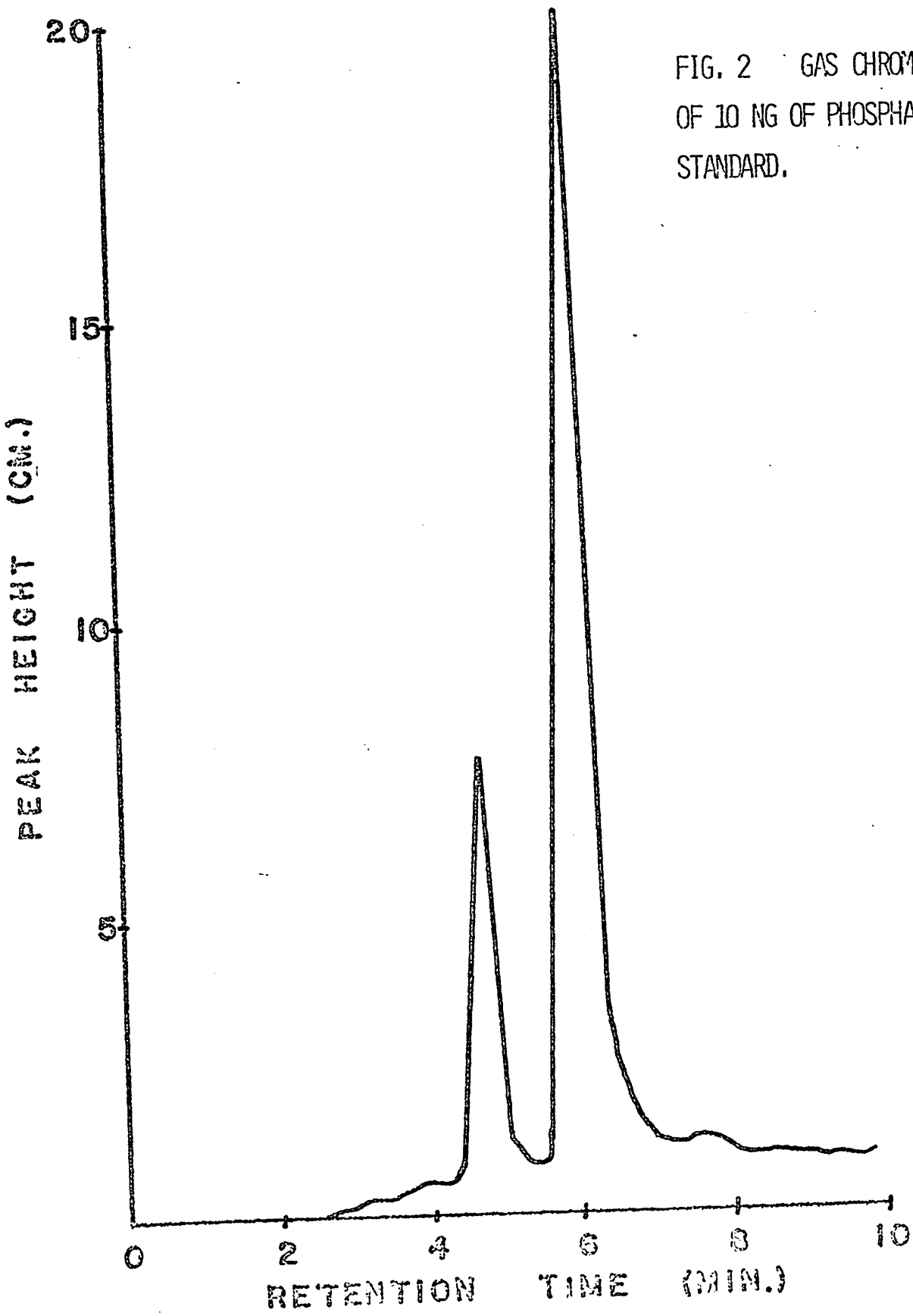


FIG. 2 GAS CHROMATOGRAM OF 10 NG OF PHOSPHAMIDON STANDARD.

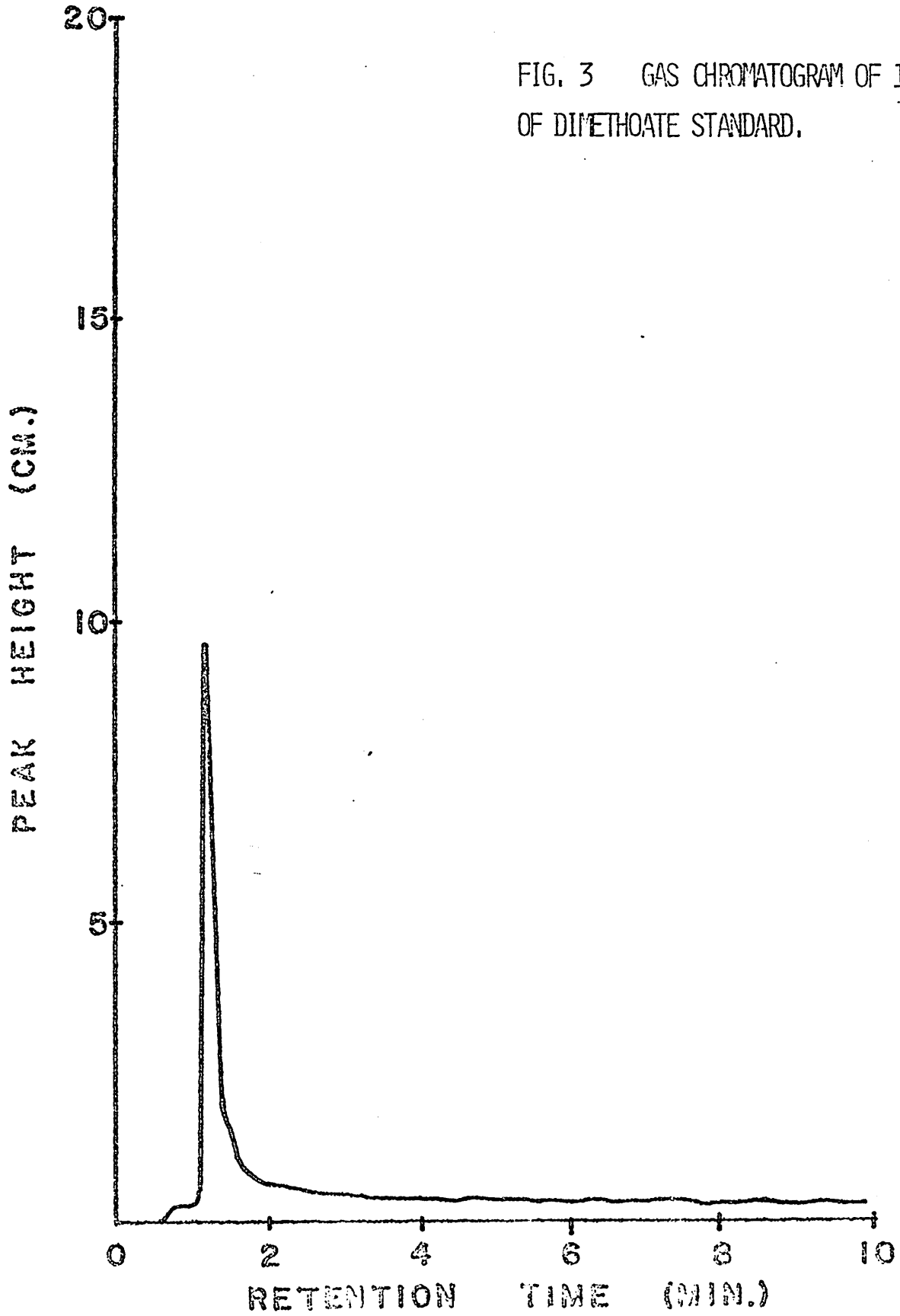
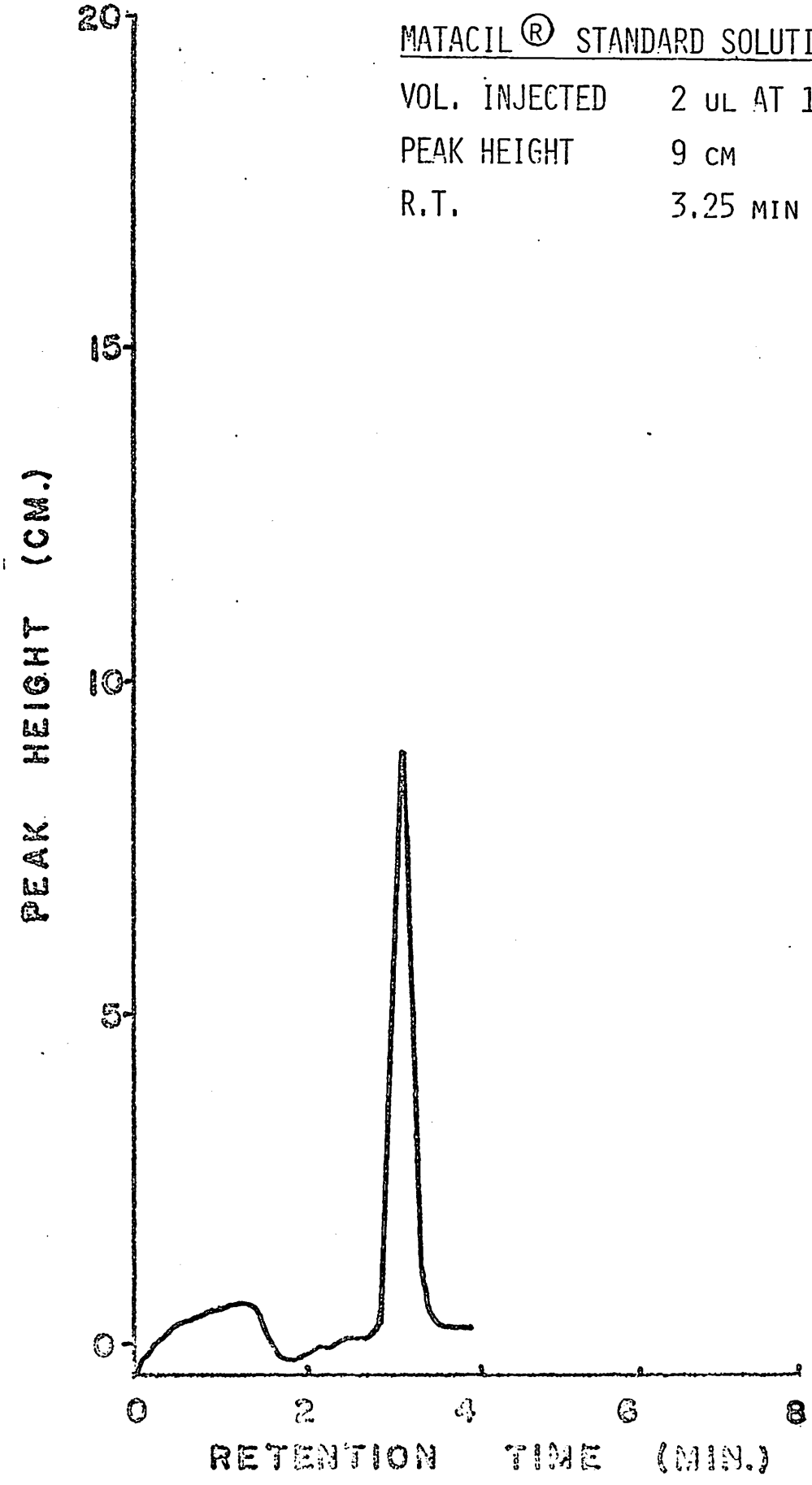


FIG. 3 GAS CHROMATOGRAM OF 10 NG OF DIMETHOATE STANDARD.

FIG. 4

MATACIL® STANDARD SOLUTION

VOL. INJECTED	2 UL AT 10 NG/UL
PEAK HEIGHT	9 CM
R.T.	3.25 MIN



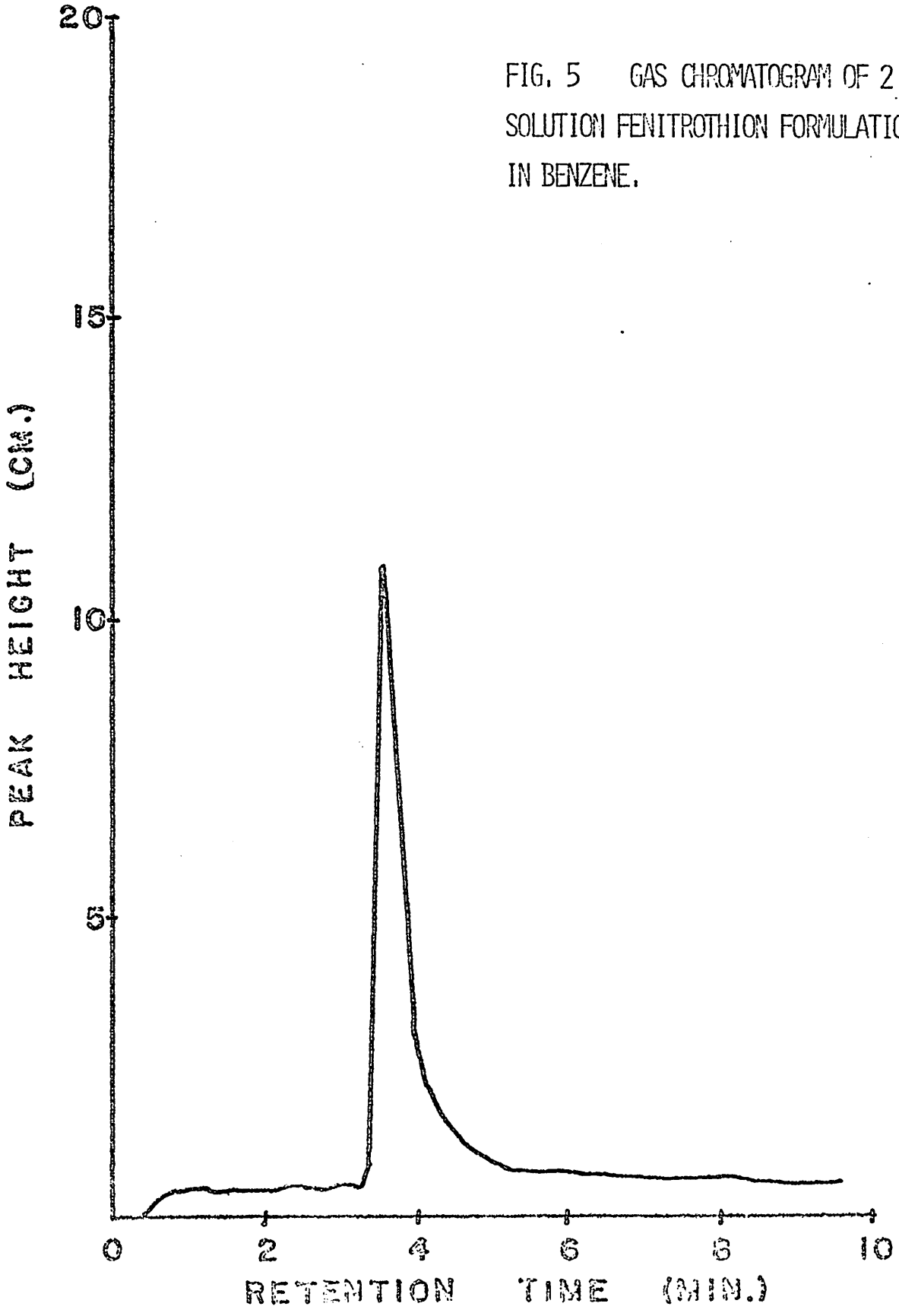


FIG. 5 GAS CHROMATOGRAM OF 2 UL SOLUTION FENITROTHION FORMULATION IN BENZENE.

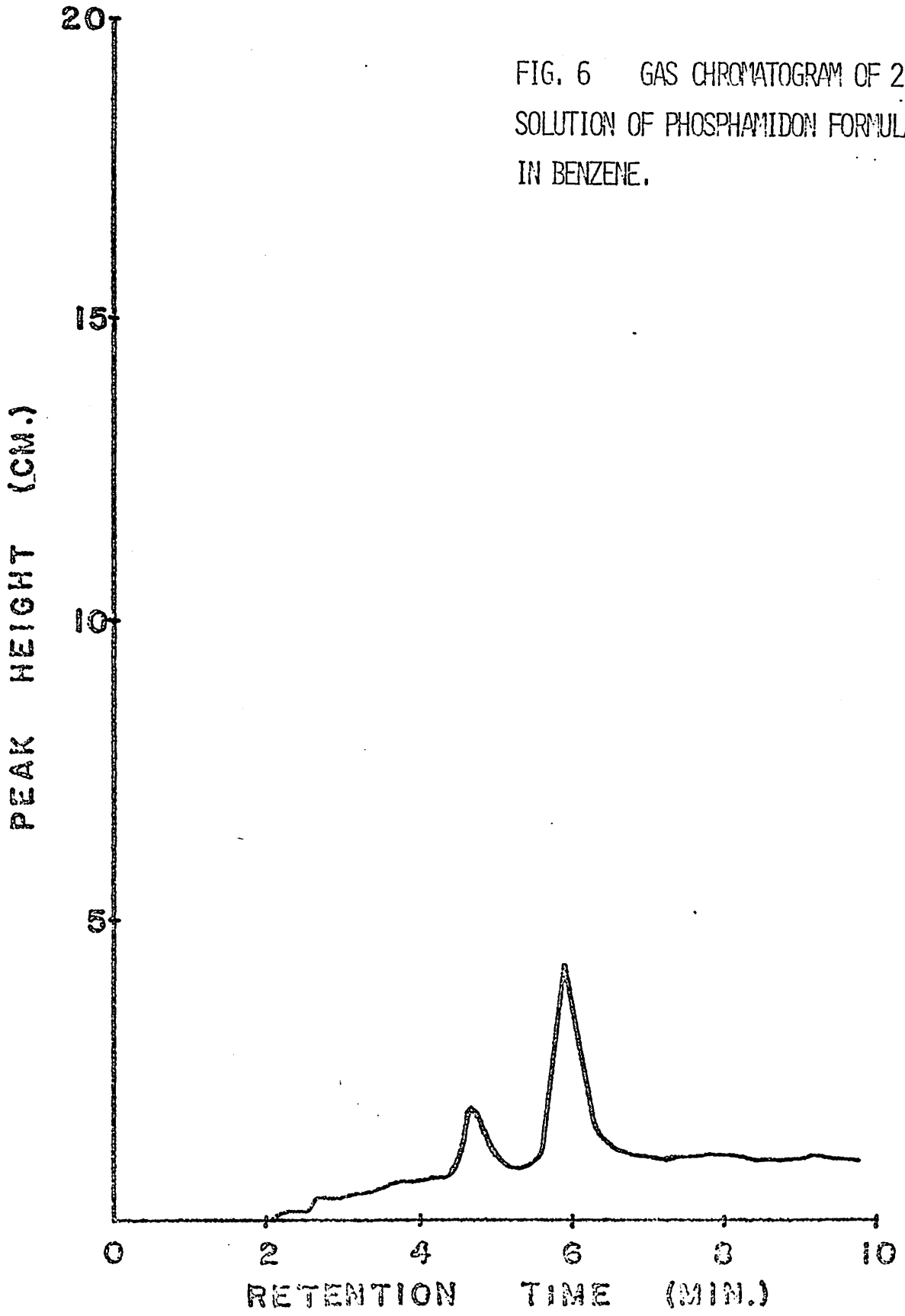


FIG. 6 GAS CHROMATOGRAM OF 2 UL SOLUTION OF PHOSPHAMIDON FORMULATION IN BENZENE.

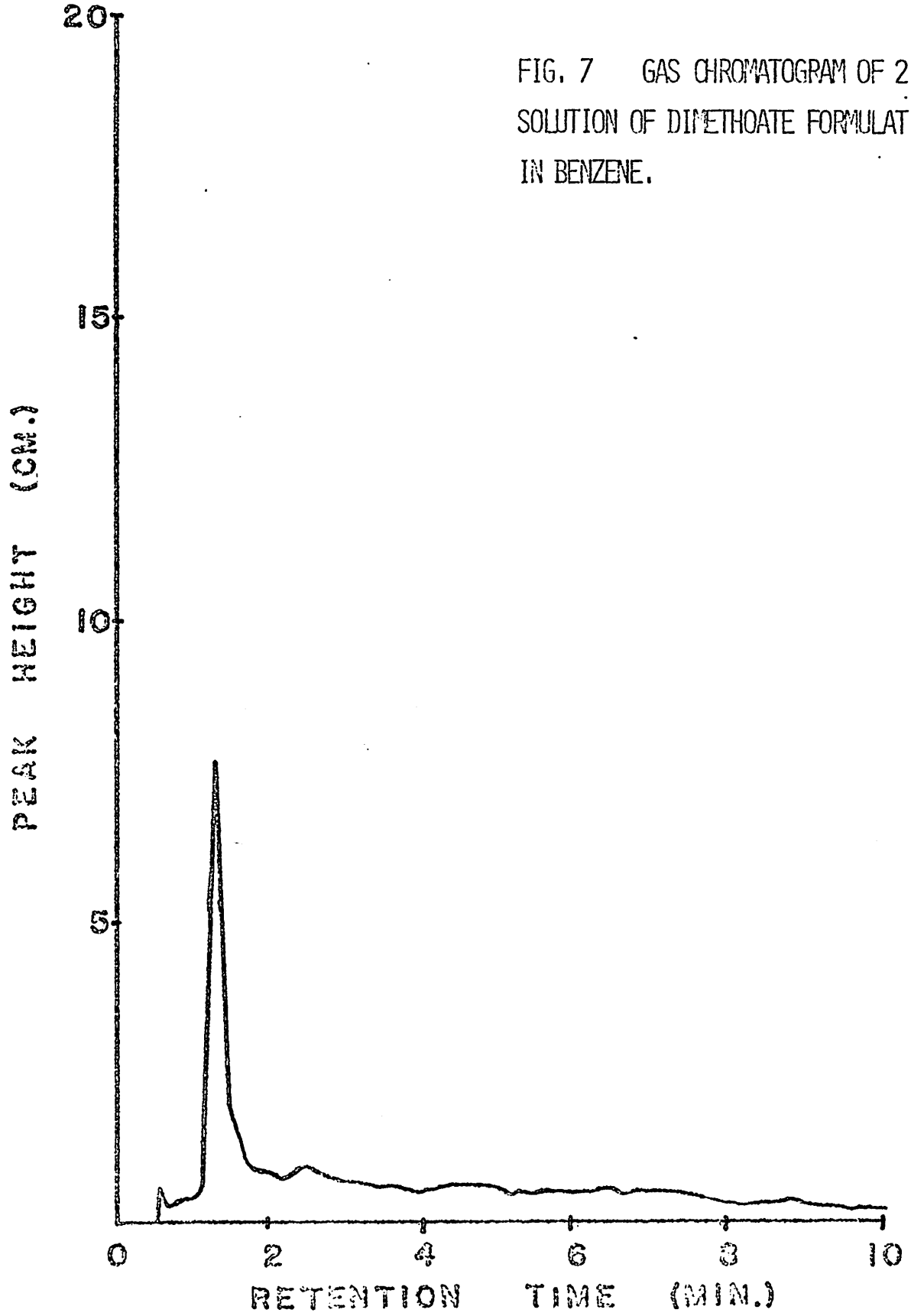


FIG. 7 GAS CHROMATOGRAM OF 2 UL SOLUTION OF DIMETHOATE FORMULATION IN BENZENE.

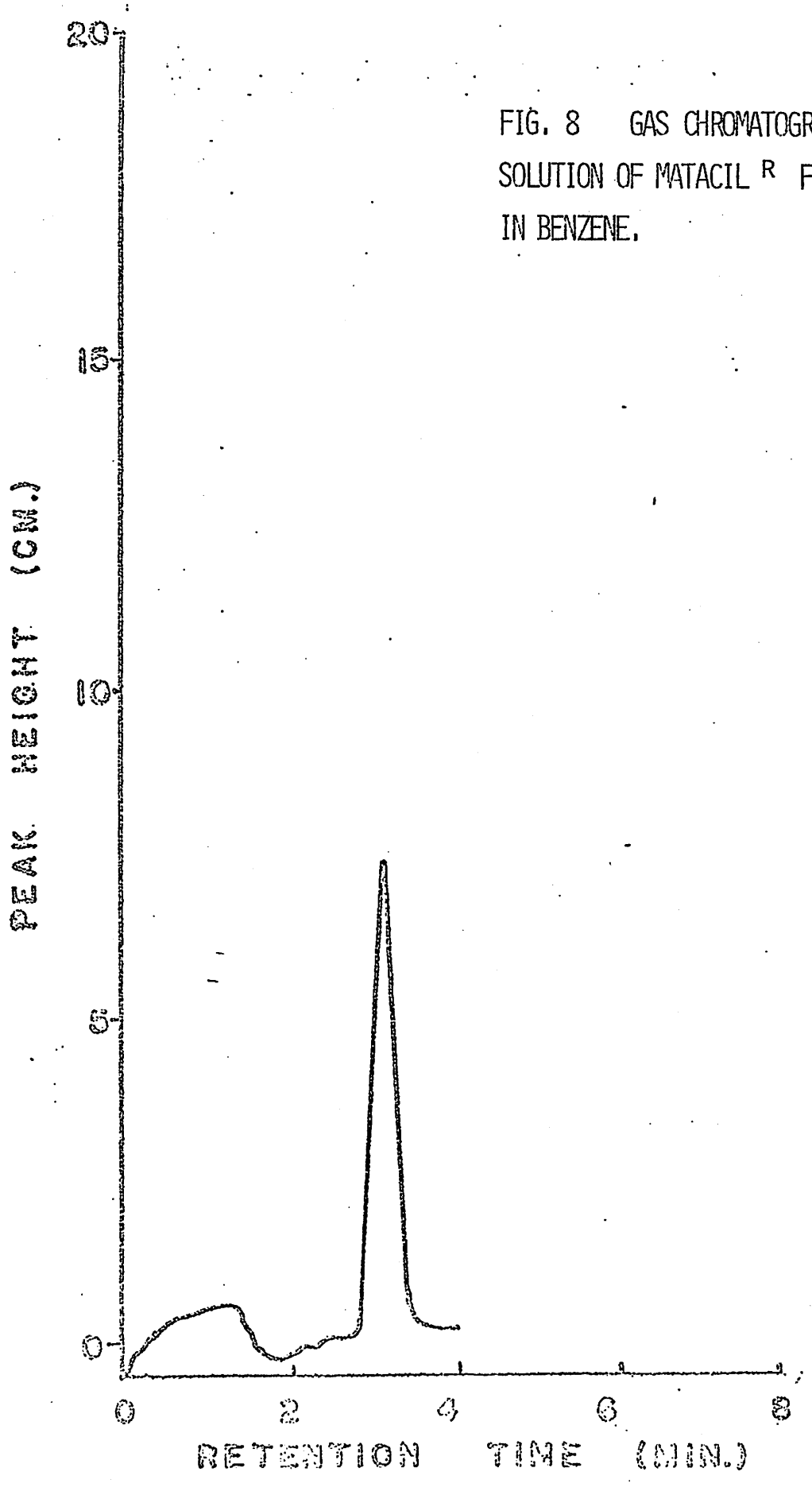


FIG. 8 GAS CHROMATOGRAM OF 2 UL SOLUTION OF MATACIL ^{R} FORMULATION IN BENZENE.

Table I

DESCRIPTION OF INSECTICIDE SAMPLES ANALYSED FOR EPS, QUEBEC REGION - 1976 SPRAY PROGRAM

INSECTICIDE	NO. OF TECHNICAL SAMPLES	NO. OF SPRAY MIXTURES	TOTAL
Fenitrothion	21	34	55
Matacil	-	31	31
Dimethoate	21	-	21
Phosphamidon	3	-	3
Totals:	45	65	110

Table II

ANALYSIS OF FENITROTHION SAMPLES RECEIVED FROM EPS, QUEBEC REGION - 1976 SPRAY PROGRAM

SERIAL NO.	C.C.R.I. IDENTIFICATION NUMBER	EPS - SAMPLE DESCRIPTION	FENITROTHION CONCENTRATION WEIGHT PERCENT
	19/76/200-209/220	Box # 1, Ten ("Folithion") Fenitrothion samples, 1975 stock [Ref. Letter May 10, 1976]	
1		Sample 1	88
2		Sample 2	85
3		Sample 3	89
4		Sample 4	85
5		Sample 5	85
6		Sample 6	86
7		Sample 7	86
8		Sample 8	86
9		Sample 9	86
10		Sample 10	87

Table II Continued

	19/76/210-213/18	Box # 2, Four samples of fenitrothion E.C., May 6, 1400 hrs, 1975 stock (1976 mix).	
11		Sample 1	89
12		Sample 2	6
13		Sample 3	5
14		Sample 4	7
	19/76/214-217/19	Box # 2, Four samples of fenitrothion E.C., May 6, 1000 hrs, 1975 stock.	
15		Sample 1	6
16		Sample 2	8
17		Sample 3	4
18		Sample 4	6
	19/76/218-220/17	Box # 2, Three samples of fenitrothion F2-16, May 6, noon, 1975 stock (1975 mixture)	
19		Sample 1	9
20		Sample 2	9
21		Sample 3	9

Table II Continued

	19/76/220,221/16	Box # 2, Two fenitrothion mixtures for use on block 109 (Env. Canada observation area) May 6, 1430 hrs 1975 stock (1976 mixture)	
22		Sample 1	8
23		Sample 2	8
	19/76/222,223/20	Box # 2, Two samples of "Arotex", May 6, 1400 hrs, 1975 stock	
24		Sample 1	0
25		Sample 2	0
	19/76/224-229/4-9	Box # 4, Six Fenitrothion samples of Mr Gabouri	
26		ASS: Fenitrothion pure	
		Sample 1	89
27		BSF: Fenitrothion pure	
		Sample 1	94
28		CE 76 EC (Fenitrothion & Arotex)	
		Sample 1	32
29		$DF_2$16: Mix (Fenitrothion & Arotex & Oil)	
		Sample 1	12

Table II Continued

30		$DF_2$12: Mix (Fenitrothion & Arotex & Oil)	
		Sample 1	17
31		Mix 109: Fenitrothion 3 oz	
		Sample 1	22
	19/76/230-237/221	Box # 5, Eight fenitrothion samples from Bonaventure, Quebec, Series 1 Chosen at random on tarmac.	
32		Sample 1	96
33		Sample 2	97
34		Sample 3	97
35		Sample 4	97
36		Sample 5	97
37		Sample 6	99
38		Sample 7	97
39		Sample 8	96
	19/76/238, 239/222	Box # 5, Two fenitrothion samples from Bonaventure, Quebec, Series 2	
40		Sample 1	17
41		Sample 2	17
	19/76/240, 241/223	Box # 5, Two fenitrothion samples from Bonaventure, Quebec, Series 3	
42		Sample 1	17
43		Sample 2	Bottle was empty

Table II Continued

	19/76/242, 243/224	Box # 5, Two fenitrothion samples from Bonaventure, Quebec, Series 4	
44		Sample 1	17
45		Sample 2	10
	19/76/244, 245/225	Box # 5, Two fenitrothion samples from Bonaventure, Quebec, Series 5	
46		Sample 1	14
47		Sample 2	12
	19/76/246-253/ 379-386	Box # 9, Eight fenitrothion samples from Bonaventure, Quebec.	
48		Bloc 403 residues boom 1 of 4 trips, 1st app.	14
49		Bloc 404 residues reservoir, 1st app.	6
50		Bloc 404 residues reservoir, 2nd app.	6
51		Bloc 403 residues reservoir, 2nd app.	11
52		Bloc 403 residues boom 1 of 4 trips, 2nd app.	11
53		Bloc 404 residues reservoir, 3rd app.	11
54		402 2nd app. of Bloc 402	14
55		406 2nd app. of Bloc 406	7

Table III

ANALYSIS OF DIMETHOATE SAMPLES RECEIVED FROM EPS, QUEBEC REGION - 1976 SPRAY PROGRAM

SERIAL NO.	C.C.R.I. IDENTIFICATION NUMBER	EPS - SAMPLE DESCRIPTION	FENITROTHION CONCENTRATION WEIGHT PERCENT
	19/76/254-258/199	Box # 1, Five Dimethoate Samples, [May 6, 1100 hrs, 1975 stock Quebec Gov. No. 099-686D]	
56		Sample 1	34
57		Sample 2	34
58		Sample 3	39
59		Sample 4	34
60		Sample 5	41
	19/76/259-263/31	Box # 3, Five Dimethoate Samples each from last 45 gal drums shipment May 6, 1000/1600 hrs 1975 stock	
61		Sample 1	35
62		Sample 2	43
63		Sample 3	41
64		Sample 4	36
65		Sample 5	37

Table III Continued

	19/76/264-273/21-30	Box # 3, Ten Dimethoate samples, each from first 45 gal drums in other storage shed (Bomarc base). See Box # 1 for details.	
66		Sample 1	36
67		Sample 2	33
68		Sample 3	35
69		Sample 4	36
70		Sample 5	37
71		Sample 6	33
72		Sample 7	39
73		Sample 8	37
74		Sample 9	38
75		Sample 10	41
		Box # 8, One Dimethoate sample.	
76		Sample 1	42

Table IV

ANALYSIS OF PHOSPHAMIDON SAMPLES FROM EPS, QUEBEC REGION - 1976 SPRAY PROGRAM

SERIAL NO.	C.C.R.I. IDENTIFICATION NUMBER	EPS - SAMPLE DESCRIPTION	PHOSPHAMIDON CONC. WT. PERCENT		
			TRANS	CIS	TOTAL
	19/76/275/226	Box # 6, St. Honoré, Barrel 530298M - 248			
77		Sample 1	21	64	85
	19/76/276/227	Box # 7, St. Honoré, Barrel 530298M - 903			
78		Sample 1	23	66	89
	19/76/277/228	Box # 7, St. Honoré, Barrel 530298M - 831			
79		Sample 1	22	66	88

Table V

ANALYSIS OF MATACIL ® SAMPLES FROM EPS, QUEBEC REGION - 1976 SPRAY PROGRAM

SERIAL NO.	C.C.R.I. IDENTIFICATION NUMBER	EPS - SAMPLE DESCRIPTION	PERCENT MATACIL ® CONC. (W/W)
	19/76/278-285/ 232-239	Box # 6, Eight Matacil ® Samples, Series 1	
80		Sample 1	16
81		Sample 2	16
82		Sample 3	16
83		Sample 4	16
84		Sample 5	16
85		Sample 6	16
86		Sample 7	16
87		Sample 8	16
	19/76/286-288/ 240-242	Box # 6, Three Matacil ® Samples, Series 2	
88		Sample 1	17
89		Sample 2	17
90		Sample 3	17

Table V Continued

	19/76/289-292/ 243-246	Box # 7, Four Matacil® Samples, Series 2	
91		Sample 1	7
92		Sample 2	7
93		Sample 3	7
94		Sample 4	7
	19/76/293-296/ 247-250	Box # 7, Four Matacil® Samples, Series 3	
95		Sample 1	7
96		Sample 2	7
97		Sample 3	7
98		Sample 4	7
	19/76/297-301/ 251-255	Box # 7, Five Matacil® Samples, Series 3	
99		Sample 1	6
100		Sample 2	5
101		Sample 3	7
102		Sample 4	6
103		Sample 5	6

Table V Continued

	19/76/302-303/ 350-351	Box # 8, Two Matacil® Samples, [305 mix, 2nd spray, 1 from tank and 1 from boom]	
104		Sample 1	7
105		Sample 2	7
	19/76/304-305/ 352-353	Box # 8, Two Matacil® Samples, [311 mix, 2nd app., 1 from tank and 1 from plane]	
106		Sample 1	7
107		Sample 2	7
	19/76/306-307/ 354-355	Box # 8, Two Matacil® Samples, [311 mix 4, 2nd app., 1 from tank and 1 from plane]	
108		Sample 1	7
109		Sample 2	7
		Box # 8, One Matacil® Sample, [308 mix - Tarmac]	
110		Sample 1	7

Table VI

MINOR DISCREPANCIES OBSERVED IN THE ANALYSIS OF FENITROTHION SAMPLES RECEIVED FROM EPS, QUEBEC REGION 1976 SPRAY PROGRAM

SERIAL NO.	C.C.R.I. IDENTIFICATION NUMBER	EPS - SAMPLE DESCRIPTION	PERCENT CONCENTRATION (W/W) OBSERVED AND CLAIMED (IN PARENTHESIS)		
	19/76/220-221/16	Box # 2, Two fenitrothion mixtures used in Block # 109, 1975 stock (1976 mixture)			
		Sample 1	8	(19)	
		Sample 2	8	(19)	
	19/76/210-213/18	Box # 2, Four samples of fenitrothion E.C., May 6, 1400 hrs, 1975 stock (1976 mixture)			
		Sample 1	89*	(28.25)	*Average for the four values 27%
		Sample 2	6*	(28.25)	
		Sample 3	5*	(28.25)	
		Sample 4	7*	(28.25)	
	19/76/214-217/19	Box # 2, Four fenitrothion E.C. Samples, May 6, 1000 hrs, 1975 stock (1976 mix)			
		Sample 1	6	(28)	
		Sample 2	8	(28)	
		Sample 3	7	(28)	
		Sample 4	6	(28)	

RESULTS AND DISCUSSION

Gas liquid chromatography (GLC) is one of the most rapid and efficient techniques for the quantitation of pesticide concentrates and has become an integral part of modern analytical laboratories for the absolute identification of the active chemical compounds present in various pest control materials and their residues in very many samples. Not only is it nearly universal in applicability but it is also rapid and extremely sensitive, capable of detecting subnanogram (10^{-9} g) to subpicogram (10^{-12} g) quantities. In the present study, the minimum detectable limit for the four insecticides present in the technical and formulated samples was found to be 0.20 ng and has been validated at this level throughout the analysis.

Tables II to V list the 45 insecticides and their 65 spray mixtures analysed using gas-liquid chromatography. The experimental results recorded in Tables II to V are the mean at least two repetitions with an average coefficient of variation as shown below:

Tech. Material	3.0
Spray Mixtures	2.0 to 1.0 (depending on the insecticide concentration; 2.0 for above 30% and 1.0 for below 30%).

Consequently, the error involved in the analysis ranged from 1 to 3% depending on the nature and concentration of the material analysed. The results are reproducible and the continuous use of GLC methods at this

laboratory for the past five years (Sundaram 1975) for the assay of insecticide formulations has yielded highly satisfactory results. The GLC methods described herein are sensitive, rapid (except Matacil®), easily managed and highly suitable for the four insecticides and the formulations.

The gas chromatograms for the four insecticide standards are given in Figs. 1 to 4. The peak shapes were symmetrical and the responses were adequate. The gas chromatograms of the four insecticide formulations are given in Figs. 5 to 8. As could be seen in the diagrams, no significant interferences from the admixed solvents and surfactants in the formulations were observed. There was no marked interference from the water present in some of the formulations but it is advisable to remove it prior to analysing by passing the sample through a column of anhydrous sodium sulphate.

Apart from some minor discrepancies observed between the values obtained and expected (Table VI), probably due to wrong mixing or insufficient information, no significant problems were encountered during the analysis. The monitoring program undertaken by the EPS (Quebec Region) for the insecticide spray mixtures used in 1976 Quebec spray operation, is a very useful venture and it is hoped that this program would be continued actively in the years to come.

SUMMARY

Although gas-liquid chromatography (GLC) is associated with the determination of pesticide residues, the technique is also useful for analysis of insecticides and their formulations. GLC methods have been developed and are described for the direct analysis of liquid formulations and spray mixtures of Matacil®, dimethoate, phosphamidon and fenitrothion used in the 1976 Quebec spray programs. The method consists of dissolving the sample, after weighing, in benzene; an aliquot of the diluted solution is injected into gas chromatographs fitted with suitable detectors and column packings. The methods reported are sensitive, reliable, rapid and free from interferences, from impurities or admixed solvents including surfactants and could be used conveniently for assaying the insecticides and their formulations. Analytical data and results from formulations and mixtures are presented to show the wide applicability of the method.

ACKNOWLEDGEMENTS

The authors are indebted to Messrs F. Leduc and G.M. Lévesque of EPS, Quebec Region, for collecting and providing them with the insecticides, their formulations and spray mixtures used in this investigation. The assistance, friendliness and resourcefulness of Mr G.M. Lévesque during sampling and discussions, are greatly appreciated by the senior author.

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