GAS CHROMATOGRAPHIC ANALYSIS OF METHOXYCHLOR FORMULATIONS AND SPRAY MIXTURES

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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 spruce budworm, white pine weevil, hemlock looper, maple worm, balsam woolly aphid, tent caterpillar, aspen tortrix, sawflies, biting flies and elm bark beetles. A large number of synthetic organic insecticides are

dispersed sporadically in large volumes 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. This report describes a gas-liquid chromatographic (GLC) method developed and employed for determining quantitatively the methoxychlor isomers (*o,p* and *p,p'*) and the olefin metabolite present in seven commercial formulations and twelve operational spray mixtures used for white pine weevil control since 1972. 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 methoxychlor formulations.

MATERIALS AND METHODS

Insecticide Formulations

Table 1 lists the various commercial formulations (emulsifiable concentrates or solutions) and the spray mixtures used in the GLC analysis. The spray mixtures were prepared locally by adding aliquot amounts of either specific petroleum oil fractions and/or water to the commercial preparations to give the desired concentration levels of the insecticide.

Reagents

Benzene: Pesticide grade solvent distilled in glass obtained from the Caledon Laboratories.

Insecticides: Analytical grade samples of methoxychlor isomers (*o,p* and *p,p'*) and methoxychlor ethylene were obtained from the Agriculture Canada, Ottawa.

Apparatus

Gas Chromatograph

Hewlett-Packard (H.P.) Model 5750 Gas Chromatograph fitted with Ni 63 electron capture detector. Westronics Model MT-22 recorder with chart speed 0.25 inch per minute. GC column: 1.22 m x 6 mm i.d. borosilicate glass packed with 4% DC-200 + 6% QF1 on AW-DMCS treated 60-80 mesh Chromosorb W preconditioned at 230°C for 48 hours.

Operating Conditions

Carrier gas	Argon - methane (95/5%), 40 ml/min, 40 psi (rotometer setting 2.0)	
Temperature (^{o}C)	Column	220
	Detector	275
	Injection port	225
Electrometer range		10
Attenuation		16
Pulse		150

Calibration Curve

Stock solutions containing 10 mg of *p,p'*-MC, *o,p*-MC and MCE* were prepared in 100 ml of benzene (100 *u*g/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/*u*l) of the insecticides in the resulting standard solution were MCE 0.36, *o,p*-MC 0.54 and *p,p'*-MC 0.90 respectively. 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 (nano gram) of the insecticides on log-log paper

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* *p,p'*-MC : 2,2-*Bis* (*p*-methoxyphenyl)-1,1,1-trichloroethane
o,p-MC : 2,2-*Bis* (*o,p*-methoxyphenyl)-1,1,1-trichloroethane
MCE : 2,2-*Bis* (*p*-methoxyphenyl)-1,1-dichloroethylene

(see Fig 1). The instrument response was linear between 0.20 to 2 ng range (Fig 1), the peak shapes were good (Fig 2) providing adequate resolution and appropriate retention times and provided a 50% full-scale recorder deflection for 1.8 ng of *p,p'*-MC. The calibration of the instrument and its response was checked twice daily in the morning and in the afternoon during the course of the formulation analysis.

Analysis of Formulations and Spray Mixtures

Each formulation of methoxychlor or spray mixture was weighed accurately (20 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 so that a 4 ul 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 outlined earlier. Each peak height was measured and found to agree within 2% and the average peak heights for the two isomers (*o,p* and *p,p'*-MC) and the ethylene (MCE) were calculated. The amounts of insecticide (ng/*u*l) were read from the calibration curve using the peak heights and the weights of active materials (*o,p*-MC, *p,p'*-MC and MCE) present in 100 ml of the commercial formulations were calculated and their concentrations expressed as a percentage (weight/volume).

For spray mixtures, in addition to percent active ingredient, the content in ounces or pounds (avoirdupois) in one gallon (U.S.) were also calculated 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.

Table 1

Methoxychlor Formulations and Spray Mixtures Analysed

Serial No	Identification No	Source
1	1972 - F1	Green Cross (25 EC)
2	1972 - F2	DuPont (Tech 95)
3	1973 - F3	DuPont (Tech 95)
4	1973 - F4	Green Cross (25 EC)
5	1974 - F5	Green Cross (25 EC)
6	1974 - F6	Green Cross (25 EC)
7	1975 - F7	Green Cross (25 EC)
8	1972 - SM1	C.C.R.I. - 1 - 2.5 AI
9	1973 - SM2	C.C.R.I. - 1 - 2.5 AI
10	1973 - SM3	C.C.R.I. - 2 - 2.5 AI
11	1974 - SM4	C.C.R.I. - 1 - TS
12	1974 - SM5	C.C.R.I. - 2 - TB
13	1974 - SM6	C.C.R.I. - 3 - SC - B3 - 4 - 9
14	1974 - SM7	C.C.R.I. - 4 - SC - 5
15	1974 - SM8	C.C.R.I. - 5 - SC - 5 + OF
16	1974 - SM9	C.C.R.I. - 6 - SC - 7
17	1974 - SM10	C.C.R.I. - 7 - 8 + OF
18	1975 - SM11	C.C.R.I. - 1 - L1
19	1975 - SM12	C.C.R.I. - 2 - L2

Table 2

Percent Active Ingredients Present in Methoxychlor Formulations

Serial No	Identification No	Wt. percent in 100 ml of formulation			
		MCE	*o,p*-MC	*p,p'*-MC	Total
1	1972 - F1	0.4	1.2	22.1	23.7
2	1972 - F2	1.2	3.1	94.2	98.5 *
3	1973 - F3	1.8	4.7	93.4	97.9 *
4	1973 - F4	0.4	1.6	24.5	26.5
5	1974 - F5	0.2	1.3	23.6	25.1
6	1974 - F6	0.4	2.2	24.5	27.1
7	1975 - F7	0.4	1.2	24.9	26.5

* 100 g original sample

Table 3

Concentration of Methoxychlor Spray Mixtures

Serial No	Identification No	Wt. percent in 100 ml of spray mixture				Pounds per U.S. gallon			
		MCE	*o,p*-MC	*p,p'*-MC	Total	MCE	*o,p*-MC	*p,p'*-MC	Total
8	1972 - SM1	0.3	1.3	23.9	25.5	0.03	0.11	1.98	2.12
9	1973 - SM2	0.2	1.9	24.6	26.7	0.02	0.16	2.23	2.41
10	1973 - SM3	0.3	1.0	25.1	26.4	0.03	0.08	2.10	2.21
11	1974 - SM4	0.3	0.6	7.6	8.5	0.03	0.05	0.63	0.71
12	1974 - SM5	0.5	2.2	34.0	36.7	0.04	0.18	2.84	3.06
13	1974 - SM6	0.2	0.5	6.5	7.2	0.02	0.04	0.54	0.60
14	1974 - SM7	0.3	0.7	8.8	9.8	0.03	0.06	0.74	0.83
15	1974 - SM8	0.2	0.6	7.8	8.6	0.02	0.05	0.65	0.72
16	1974 - SM9	0.2	0.5	7.1	7.8	0.02	0.04	0.59	0.65
17	1974 - SM10	0.2	0.4	6.4	7.0	0.02	0.03	0.53	0.58
18	1975 - SM11	0.5	1.8	31.0	33.3	0.04	0.15	2.59	2.78
19	1975 - SM12	0.3	1.2	25.3	26.8	0.03	0.10	2.11	2.24

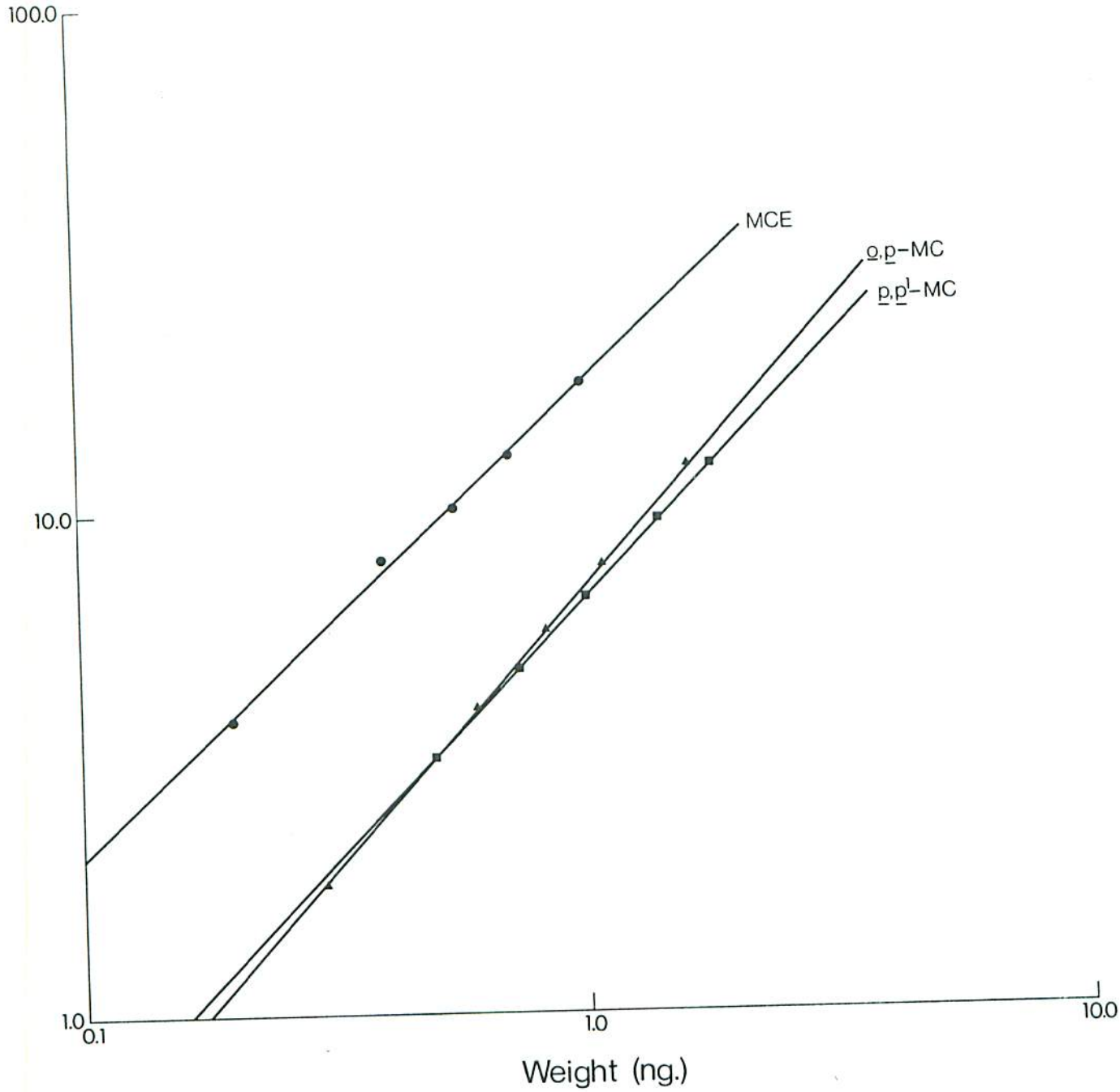

Fig. 1. Gas Chromatographic Calibration Curves for Methoxychlor Isomers and Methoxychlor Ethylene obtained with the HP 5750 Electron Capture Detector.

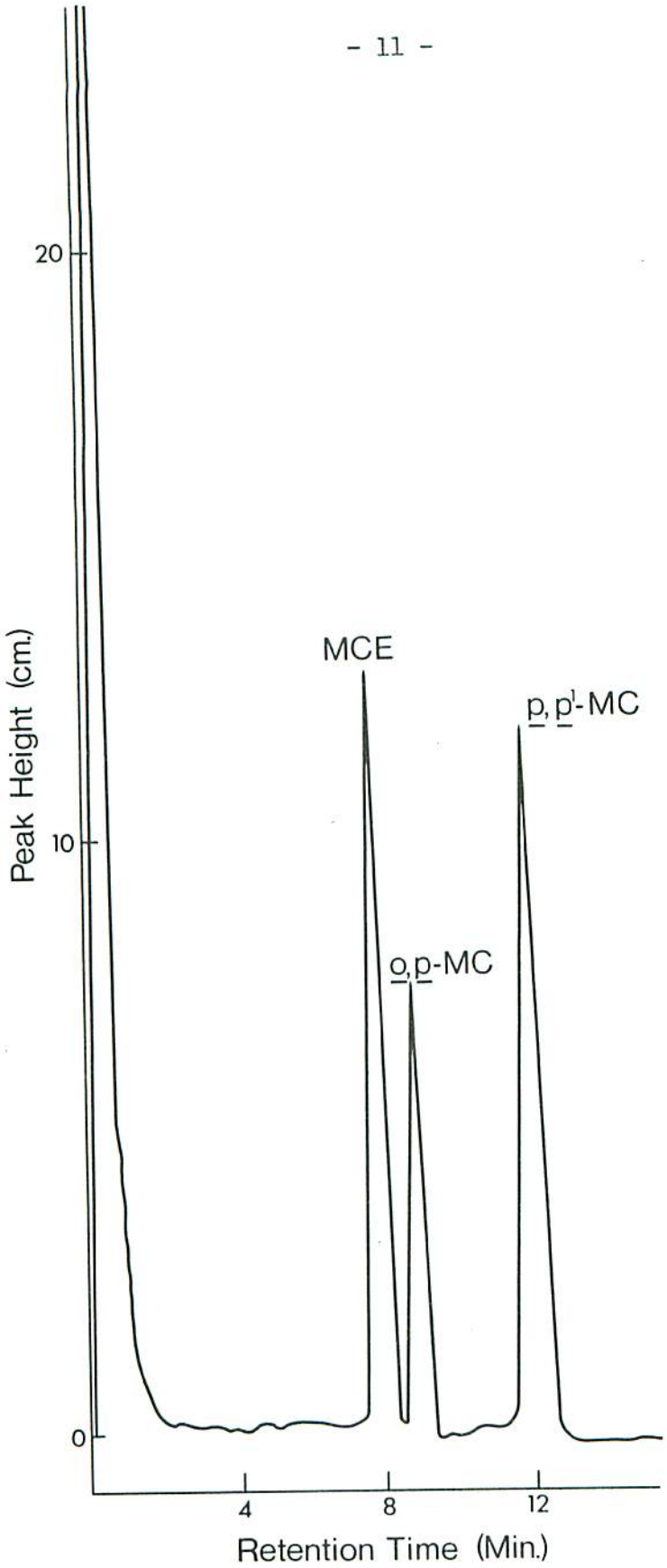

Fig. 2. Gas Chromatograph of 0.72 ng of MCE (RT = 8.4 min) 1.08 ng of *o,p*-MC (RT = 9.1 min) and 1.80 ng of *p,p'*-MC (RT = 12.0 min) standards.

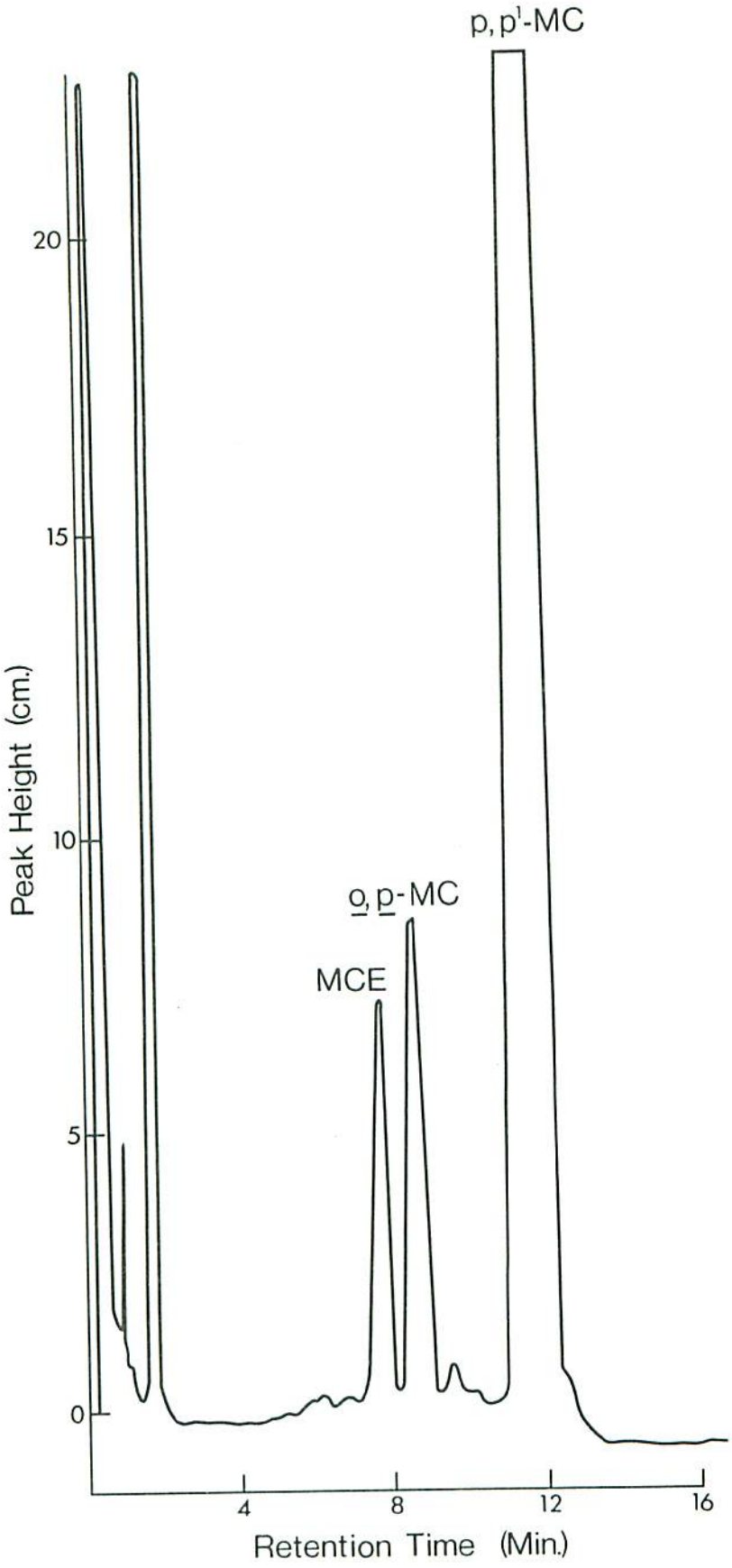

Fig. 3. Gas Chromatogram of a 2 ul solution of Methoxychlor Formulation prepared by dissolving 0.05 ug per ml of benzene.

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 methoxychlor isomers present in the technical and formulated samples was found to be 0.20 ng and has been validated at this level throughout the analysis.

Table 1 lists the seven methoxychlor formulations and twelve spray mixtures analysed using the HP-GLC unit fitted with an electron capture (EC) detector. The formulations analysed were from Green Cross and DuPont companies* in Canada and the spray mixtures used for white pine weevil control since 1972 were supplied by Dr R.F. DeBoo and his associates at this Institute. Percent of active methoxychlor ingredients (MCE, *o,p*-MC and *p,p'*-MC) present in the formulations and the concentrations of methoxychlor isomers and the ethylene metabolite are given in Tables 2 and 3 respectively. The EC-GLC responses for

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* Mention of trade names or commercial products does not constitute endorsement or recommendation for use either by the C.C.R.I. or by the author.

standard solutions of the three active ingredients were linear in the 0.20 to 2.0 ng range as shown by the straight line graphs obtained for them (Fig. 1) on plotting the peak heights against concentrations. The gas chromatograms for the three standards and their respective retention times are given in Fig. 2. The peak shapes were symmetrical and the resolution was adequate. The relative retention times taking the *p,p'*-MC isomer as 1.0, are 0.70 for MCE and 0.76 for the *o,p*-MC. The gas chromatogram of a typical methoxychlor formulation is given in Fig. 3. The GLC response for a 2 *ul* shot at the suitable dilution was good for the ethylene and the *o,p*- isomer but the *p,p'*- isomer went off the scale and required further dilution. As could be seen in the diagram, no significant interference from the admixed solvents and surfactants in the formulation was observed except for a large peak soon after the solvent front. There was no marked interference from water present in the aqueous formulations but it is advisable to remove it prior to analysing by passing the sample through a column of anhydrous sodium sulphate.

The experimental results recorded in Tables 2 and 3 are the mean of at least three repetitions with an average coefficient of variation within 2.5. The results are reproducible and the continuous use of this GLC method at this laboratory during the past four years for the assay of methoxychlor formulations has yielded highly satisfactory results. The formulations studied contained on average about 1.5% of MCE, 4.7% of *o,p*-MC and 93.8% of *p,p'*-MC whereas the spray mixtures had slightly more of the ethylene (1.9%) and the *o,p*-

isomer (5.7%). The content of *o,p-* isomer in the emulsifiable liquid formulations and spray mixtures was found to be lower than the value reported (*ca* 10%) in literature (Metcalf 1955).

Structurally, methoxychlor is related to DDT. Many analytical procedures developed for the latter compound are applicable, but selective methods like paper chromatographic, colorimetric, titrimetric and infrared spectrophotometric methods have been developed especially for dry methoxychlor formulations (Lowen *et al* 1964, AOAC 1970, Pease 1975). The GLC method described herein is sensitive, rapid, easily managed and highly suitable for liquid formulations of methoxychlor.

SUMMARY

Although gas-liquid chromatography (GLC) is associated with the determination of pesticide residues, the technique is also useful for analysis of commercial pesticide formulations. A GLC method has been developed and is described for the direct analysis of liquid formulations and spray mixtures of methoxychlor used in forest pest control programs. The method consists of dissolving the sample, after weighing, in benzene; an aliquot of the diluted solution is injected into a gas chromatograph fitted with an electron capture detector and a mixed column packed with 4% DC-200 and 6% QF1 on 60-80 mesh Chromosorb W. The method is sensitive, reliable, rapid and free from interferences from impurities or admixed solvents including surfactants and could be used conveniently for assaying any

methoxychlor formulation. Analytical data including graphs and results from formulations and mixtures are presented to show the wide applicability of the method.

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