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## GAS CHROMATOGRAPHIC ANALYSIS OF INSECTICIDAL PREPARATIONS USING CARBON DIOXIDE PROPELLANTS

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### SUMMARY

A technique for the sampling and analysis of solutions or organic compounds for consumer use such as insecticides in liquid carbon dioxide is described.

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### INTRODUCTION

Little attention has been directed towards the use of carbon dioxide solutions despite its potential as a solvent in the liquefied form<sup>1</sup>. Commonwealth Industrial Gases (Australia), has recently introduced a range of products which employ compressed carbon dioxide as a unique solvent-propellant system<sup>2</sup> for the aerosol dispensation of a variety of commercially significant substances which are collectively referred to as Envirosol gases. The four products in this range are Pestigas-P, (0.4% pyrethrin insecticide), Insectigas-D [5% 2,2-dichlorovinyl dimethylphosphate (DDVP) insecticide], Insectigas-F (5% Fenithrothion insecticide), Deodourgas (1% odour absorber). These products have found wide acceptance for insect or odour control and are dispensed either by a hand held spray gun or by automatically controlled piped systems where large areas require regular treatment.

In applications such as these, where the solute may be a complex organic mixture, a convenient analytical method is required for product control.

Pestigas-P<sup>®</sup> is a pyrethrin based insecticide, the concentrate consists of 3.2% (w/w) pyrethrins, 16% (w/w) piperonyl butoxide and balance Shellsol T<sup>®</sup>. The required amount of this concentrate is filled into cylinders to give a final cylinder product composition as follows: 0.4% (w/w) pyrethrins, 2.0% (w/w) piperonyl butoxide, 10% (w/w) Shellsol T and balance carbon dioxide.

Insectigas-D<sup>®</sup> is based on the organophosphorus insecticide dichlorvos (2,2-dichlorovinyl dimethyl phosphate.) The technical grade dichlorvos has a minimum purity of 95% (w/w) and a specific gravity of 1.42. Insectigas-D is made up of 5% (w/w) technical dichlorvos and balance carbon dioxide.

Insectigas-F® is based on the organophosphorus insecticide Fenitrothion (O,O-dimethyl O-(3 methyl-4-nitrophenyl)phosphorothiate). The concentrate consists of 25% (w/w) technical Fenitrothion and 75% (w/w) acetone. The required amount of this concentrate is filled into cylinders to give a final cylinder product composition as follows: 5% (w/w) Fenitrothion, 15% (w/w) acetone and balance carbon dioxide.

Deodourgas® is based on a concentrate consisting of a proprietary mixture of odour absorbing compounds in acetone. The nominal composition of Deodourgas in cylinders is: 1% (w/w) Haurmann and Reimer Odour Absorber HR3107, 2% (w/w) acetone and balance carbon dioxide.

The analysis of the active materials employed have been extensively reported using gas chromatography with a considerable emphasis on the determination of residues in a wide variety of products at widely varying concentration levels. Chromatography has been readily conducted using both non-polar stationary phases, the latter including polyethylene glycols, polyesters and cyanoalkyl siloxanes.

Typical analysis for the active agents *i.e.* pyrethrins<sup>3-6</sup>, piperonyl butoxide<sup>7,8</sup>, dichlorvos<sup>9-18</sup> and Fenitrothion<sup>14-18</sup> are widely available as are general reviews<sup>19,20</sup>. The analysis of products using carbon dioxide as propellant would appear to be limited to a recent work with the same products<sup>21</sup> using high-performance liquid chromatography. A high-pressure sample injection valve was incorporated into the chromatograph such that pressurization of the solution diminished the effects of nucleate boiling and gasification within the liquid phase.

The present work reports a method for the quantitative determination of the composition of the preparations indicated using gas chromatography and a simple sampling system.

## EXPERIMENTAL

### Sampling

A stainless-steel Whitey sample cylinder of approximately 150 cm<sup>3</sup> water capacity was used to sample the liquid carbon dioxide envirosol mixture from the filled cylinders according to the following procedure.

The sample cylinder was flushed with carbon dioxide then weighed accurately ( $W_1$ ). With the sample cylinder supported vertically and connected as shown in Fig. 1 (valve B shut), the cylinder valve was opened then valve A allowing some of the envirosol product mixture to decant to the sample cylinder. Allowing a few minutes for establishing equilibrium, the cylinder valve and the valve A were shut and the sample cylinder disconnected and weighed accurately ( $W_2$ ). A metal cap on the outlet of valve was fitted, through which a 0.2-mm orifice was drilled. Holding the sample cylinder vertically, valve B was opened to vent the carbon dioxide off, the 0.2-mm orifice will restrict the vent rate regardless how far valve B is opened and hence achieving consistency in the vent rate. When no more carbon dioxide is vented off the cylinder is re-weighed ( $W_3$ ). The concentration of the envirosol concentrate in the sample was then determined as follows:

$$\% \text{ Envirosol concentrate} = \frac{W_3 - W_1}{W_2 - W_1} \times 100$$

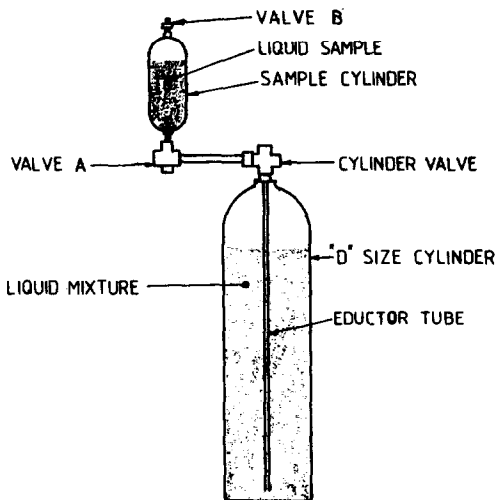


Fig. 1. Envirosol sampling system.

A sample of this concentrate would then be taken for chromatographic analysis for identification and purity determination. The Envirosol sampling system is shown in Fig. 1.

### Chromatography

The pyrethrin products were examined using a Packard 427 instrument with flame ionisation detection and glass columns (3 ft.  $\times$  1/8 in. O.D.). The conditions are shown in Table I.

Dichlorvos and its impurities were examined using *n*-decane as an internal standard and carbon disulphide as solvent, standard solutions were prepared as follows: 20 ml of carbon disulphide were pipetted into a sample tube to which 0.1 ml *n*-decane and 0.2 ml dichlorvos are added. The final composition was 1.0925% (w/w) dichlorvos, 0.285% (w/w) *n*-decane and balance carbon disulphide.

The analytical conditions for both concentrated and trace levels using both flame ionization and electron-capture detection are shown in Table II.

TABLE I

ANALYTICAL CONDITIONS FOR EXAMINATION OF PYRETHRIN PRODUCTS

Column packing	3% SE-30 in Gas-Chrom Q	2% Neopentylglycol succinate on Chromosorb W HP
Column temperature	Isothermal at 190°C	Linearly programmed Initial 150°C Final 225°C Rate 2°C/min
Injection temperature	200°C	230°C
Detector temperature	220°C	235°C
Carrier gas	Helium at 40 ml/min	Helium at 40 ml/min
Sample size	0.4 $\mu$ l	0.4 $\mu$ l

TABLE II  
ANALYTICAL CONDITIONS FOR EXAMINATION OF DICHLORVOS AND ITS IMPURITIES

Chromatograph	Packard 427	Packard 27	Hewlett Packard 5840A
Detector	Flame ionization	Flame ionization	Electron capture
Column material	Glass, 1.2 m × 4 mm O.D.	PTFE, 5 ft. × 1/8 in. O.D.	PTFE, 5 ft. × 1/8 in. O.D.
Column packing	5% DC-200 on Gas-Chrom Q	5% DC-200 on Gas-Chrom Q	5% DC-200 on Gas-Chrom Q
Column temperature	150°C	135°C	120°C
Injection temperature	160°C	225°C	130°C
Carrier gas	Nitrogen 50 ml/min	Helium 40 ml/min	5% Methane in argon 75 ml/min
Sample volume	1 μl	2 ml (syringe injection)	0.2 ml (syringe injection)

Fenitrothion was successfully examined using gas chromatography. With methyl stearate as an internal standard, solutions of Fenitrothion in chloroform were successfully analyzed using the following conditions: chromatograph, Packard 429; detector, flame ionization; column, glass 3 ft. × 1/8 in. O.D.; column packing, 10% SE-30 on Chromosorb W HP; column temperature, 215°C; injector and detector temperatures, 275°C; carrier gas, helium at 30 ml/min; sample volume, 1 μl.

Deodourgas was estimated using the following conditions: chromatograph, Packard 429; detection, flame ionization; column, glass 1 m × 2 mm I.D.; column packing, 3% SE-30 on Gaschrom Q; column temperature, 200°C; injector temperature, 250°C; carrier gas, Helium 30 ml/min; sample volume 1 μl.

## RESULTS AND DISCUSSION

The pyrethrins\* extract comprises approximately 71% pyrethrin (I and II), 2% cinerin (I and II) and 7% jasmolin (I and II). Chemically pyrethrins are organic esters formed by the combination of two carboxylic acids and three keto alcohols. They are unstable in sunlight and are rapidly hydrolysed by alkalies but this is delayed by the addition of synergists such as piperonyl butoxide.

A refined pyrethrum extract of known pyrethrins content as determined by the A.O.A.C. method<sup>22</sup> was used as a standard. Solutions of standard and unknown were prepared in chloroform. When these solutions are chromatographed, the peak area of each component is calculated and the total area response for pyrethrin I and

\* The composition of the pyrethrin compounds is as follows: pyrethrin I, C<sub>21</sub>H<sub>28</sub>O<sub>3</sub>, 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid 2-methyl-4-oxo-3-(2,4-pentadienyl)-2-cyclopenten-1-yl ester, chrysanthemummonocarboxylic acid pyrethrolone ester; pyrethrin II, C<sub>22</sub>H<sub>28</sub>O<sub>5</sub>, 3-(3-methoxy-2-methyl-3-oxo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid 2-methyl-4-oxo-3-(2,4-pentadienyl)-2-cyclopenten-1-yl ester, chrysanthemumdicarboxylic acid monomethyl ester pyrethrolone ester; cinerin I, C<sub>20</sub>H<sub>28</sub>O<sub>3</sub>, 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid 3-(2-butenyl)-2-methyl-4-oxo-2-cyclopenten-1-yl-ester; cinerin II, C<sub>21</sub>H<sub>28</sub>O<sub>5</sub>, 3-(3-methoxy-2-methyl-3-oxo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid 3-(2-butenyl)-2-methyl-4-oxo-2-cyclopenten-1-yl ester; jasmolin I, C<sub>21</sub>H<sub>30</sub>O<sub>3</sub>, 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylic acid 2-methyl-4-oxo-3-(2-pentenyl)-2-cyclopenten-1-yl ester, 4',5'-dihydropyrethrin I; jasmolin II, C<sub>22</sub>H<sub>30</sub>O<sub>5</sub>, 3-(3-methoxy-2-methyl-3-oxo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid 2-methyl-4-oxo-3-(2-pentenyl)-2-cyclopenten-1-yl ester, 4',5'-dihydropyrethrin II.

TABLE III

COMPARISON OF A.O.A.C. AND GAS CHROMATOGRAPHIC METHODS FOR PYRETHRIN ANALYSIS

Method	Pyrethrins I (%)	Pyrethrins II (%)	Total (%)
A.O.A.C. method	30.33	20.10	50.43
Gas chromatograph	29.70	20.70	50.40

pyrethrin II related to the A.O.A.C. analysis by the area response of the standard. Using computing integrators and piperonyl butoxide as an internal standard excellent agreement was obtained with A.O.A.C. standard as shown in Table III. The composition of the standard pyrethrins are as follows: pyrethrin I: cinerin I (6.8%), jasmolin I (3.1%) and pyrethrin I (19.8%) (total 29.7%); pyrethrin II: cinerin II (7.6%), jasmolin II (4.2%) and pyrethrin II (8.9%) (total 20.7%). Chromatograms of the separations using both stationary phases are shown in Figs. 2 and 3.

Technical grade dichlorvos is pesticidally active material containing not less than 96% of 2,2-dichlorovinyl dimethyl phosphate. It is readily hydrolyzed in alkaline solutions yielding predominantly dichloroacetaldehyde and dimethylphosphoric acid. The hydrolysis rate in buffer solutions is shown in Table IV.

Due to the limited stability it is essential that the purity of the dichlorvos be determined at regular intervals. The tolerance limits for dichlorvos in the atmosphere is very small (0.1 ppm). Therefore regular checks on the atmosphere surrounding the disposal and filling systems must be carried out.

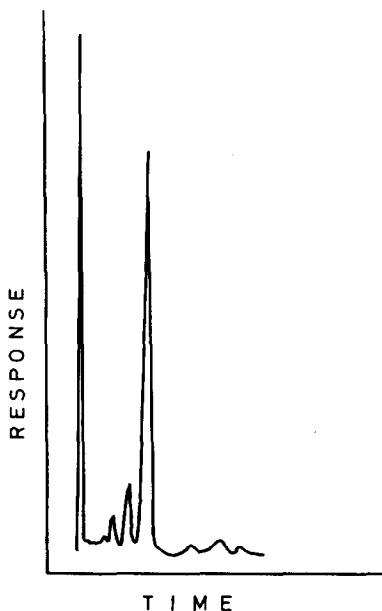


Fig. 2. Separation of pyrethrins on SE-30.

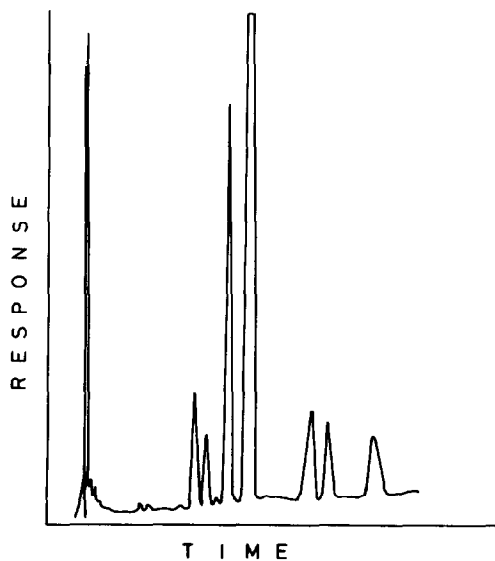


Fig. 3. Separation of pyrethrins on neopentylglycol succinate.

TABLE IV

## HYDROLYSIS RATE OF TECHNICAL GRADE DICHLORVOS AT DIFFERENT pH VALUES

<i>pH</i>	<i>Half life (min)</i>
8	301
7	462
6	2100
5.4	4620

Analysis of very low levels of DDVP can be achieved using gas chromatography employing either a flame ionization or electron-capture detector. The flame ionization detector, while being sensitive is probably best used above 0.5 ppm. The electron-capture detector, on the other hand, is excellent for lower concentration but too sensitive for concentrations above 10 ppm.

Sampling injection using a gas loop was found to be totally inadequate due to adsorption on the tubing. For example, a gas sample taken by syringe immediately

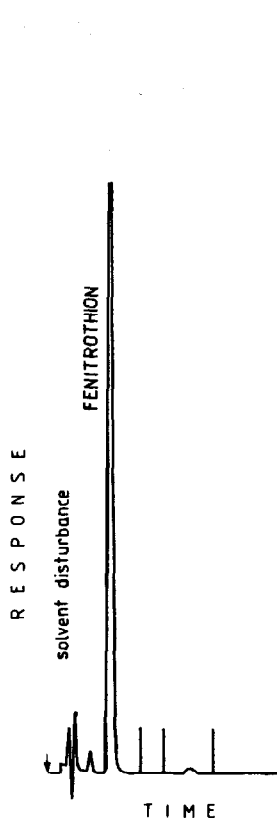


Fig. 4. Separation of Fenitrothion on SE-30.

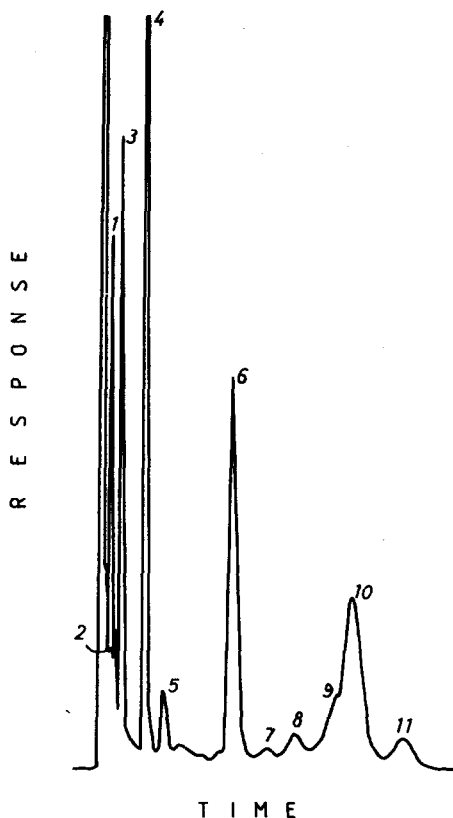


Fig. 5. Separation of Deodourgas on SE-30.

TABLE V  
CONCENTRATION OF FENITHROTHION DURING A SIX MONTH TEST PERIOD

Time (days)	Cylinder 1 (room temp.)	Cylinder 2 (40°C)	Cylinder 2 (40°C)
Initial	5.30	5.25	5.18
28	5.38	5.32	5.26
75	5.34	5.32	5.36
131	5.26	5.32	5.22
184	5.32	5.20	5.20

above a saturator folled with DDVP showed a ten-fold increase in concentration as compared to a sample taken 2 ft. from the saturator (stainless-steel tubing used).

Due to the low vapour pressure of DDVP ( $1.2 \cdot 10^{-2}$  mmHg at 20°C) a standard gas mixture could not be prepared accurately. The calibration, therefore, was obtained by bubbling dry nitrogen at a very low flow (*ca.* 30 ml/min) through a saturator filled with DDVP. The exit gas was then assumed to be saturated at that temperature, *i.e.* 15.8 ppm DDVP at 20°C.

Fenitrothion is prepared by the reaction of O,O-dimethyl phosphorochloridothioate and 3-methyl-4-nitrophenolate in the presence of an alkali metal. It is a brownish yellow liquid, b.p. 140 to 145°C at 0.1 torr, with decomposition. It is practically insoluble in water but soluble in most organic solvents but of low solubility in aliphatic hydrocarbons. It is hydrolysed by alkali, the half life in 0.01 *N* sodium hydroxide at 30°C being 272 min. It is a contact insecticide, particularly effective against rice stem borers and red spider mites. Fig. 4 shows the chromatogram of the separation achieved on SE-30 while quantitative values are shown in Table V using three accurately prepared cylinder samples, two of which were kept at 40°C for 6 months while the other was left at room temperature for the whole period. Sampling was carried out at 28, 75, 131 and 184 days.

Fig. 5 shows a chromatogram of *ca.* 1% (w/w) Deodourgas concentrate with 0.1% (w/w) methyl stearate as an internal standard (peak 6). Peak 4 as numbered on the chromatogram, although unidentified, was used for quantitation since its sensitivity is far greater than any other and the peak is reasonably symmetrical.

## CONCLUSION

Methods for the routine analysis of Commonwealth Industrial Gases products employing carbon dioxide as the solvent-propellant system were achieved using gas-liquid chromatography.

Dichlorvos was successfully quantitated on a 5% DC-200 on Gas-Chrom Q column. Trace analysis was successfully achieved using the same column and an electron capture detector. The separation and quantitation of pyrethrins was achieved on a 3% SE-30 dimethylpolysiloxane on Gas-Chrom Q column; an accuracy of  $\pm 5\%$  was obtained when compared with a standard analyzed using the A.O.A.C. method. The analysis and quantitation of Fenetrothion was also accomplished using a 10% SE-30 on Chromosorb W HP column and methyl stearate as an internal standard.

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