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The Determination of Trichlorfon in Water

by V. Zitko
D. B. Sergeant

FISHERIES AND MARINE SERVICE
SERVICE DES PÊCHES ET DES SCIENCES DE LA MER

TECHNICAL REPORT No. **714**
RAPPORT TECHNIQUE N°

1977



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Department of the Environment
Fisheries and Marine Service
Research and Development Directorate

TECHNICAL REPORT NO. 714

(Numbers 1-456 in this series
were issued as Technical Reports
of the Fisheries Research Board of
Canada. The series name was changed
with report number 457.)

Ministère de l'Environnement
Service des Pêches et des Sciences de la mer
Direction de la Recherche et du
Développement

RAPPORT TECHNIQUE N^o. 714

(Les numéros 1-456 dans cette série
furent utilisés comme Rapports
Techniques de l'office des recherches
sur les pêcheries du Canada. Le nom
de la série fut changé avec le
rapport numéro 457.)

The Determination of Trichlorfon in Water

by V. Zitko and D.B. Sergeant

This is the one hundred and fourth
Technical Report from the
Research and Development Directorate
Biological Station
St. Andrews, New Brunswick

Ceci est le cent quatrième
Rapport Technique de la Direction de la
Recherche et du Développement
Station Biologique
St-Andrews, Nouveau Brunswick

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ABSTRACT

Zitko, V., and D.B. Sergeant. 1977. The determination of trichlorfon in water. Fish. Mar. Serv. Res. Dev. Tech. Rep. 714, 14 p.

Trichlorfon may be determined after conversion to DDVP at pH 10.0 with a detection limit of about 1 $\mu\text{g}/\ell$ in the original water sample.

Trichlorfon may also be determined intact, in a less time-consuming manner after trimethylsilylation. This method doubles the sensitivity over the hydrolysis method, could be of a greater analytical utility, and deserves further study.

The stability of trichlorfon in water samples was determined. The results indicate that samples should be immediately refrigerated and analyzed within a week after collection.

Key words: Organophosphate pesticides, analysis, fenitrothion, forest spraying

RÉSUMÉ

Zitko, V., and D.B. Sergeant. 1977. Le Dosage du Trichlorfon dans L'eau. Fish. Mar. Serv. Res. Dev. Tech. Rep. 714, 14 p.

Il est possible de doser le trichlorfon une fois sa transformation effectuée en DDVP au pH 10.0, avec un seuil de détection d'environ 1 $\mu\text{g}/\ell$ pour l'échantillon d'eau initial.

On peut également doser le trichlorfon, après une triméthylsilylation, ce qui est plus rapide. Cette dernière méthode s'avère deux fois plus sensible que le procédé d'hydrolyse; elle pourrait donc être d'un usage plus répandu pour les analyses et, de ce fait, mérite une étude plus poussée.

La stabilité du trichlorfon dans l'eau fut étudiée. Les résultats démontrent la nécessité de réfrigérer les échantillons immédiatement et de procéder à leur analyse en deçà d'une semaine après les prélèvements.

INTRODUCTION

This investigation was initiated when a number of samples were received for the determination of trichlorfon (Dylox^R, Dipterex^R, Neguvon^R, Tugon^R, ChlorophosTM; O,O-dimethyl 2,2,2-trichloro-1-hydroxyethyl phosphonate). It was suggested that, during the 1976 forest-spraying program for spruce budworm control near blueberry fields, a stream and a brook has become contaminated with trichlorfon causing a kill of some experimental caged aquatic insects (Symons, personal communication). Trichlorfon is used instead of fenitrothion in blueberry-growing areas due to its lower toxicity to bees (involved in pollination of blueberries). It has good budworm larval knockdown at 8 oz/acre dosage (Varty 1976).

Trichlorfon determinations had not been performed previously in this laboratory. The literature search yielded two references (El-Refai and Giuffrida 1965; Devine 1973), neither of which was available in our library, and a third paper (Pieper and Richmond 1976) was published just about the time we completed our analyses. Due to the fact that the samples had already been taken, we immediately set out to develop a method for trichlorfon determination.

Attempts to determine trichlorfon directly by the electron-capture detector (ECD) and the flame-photometric detector (FPD) were hampered by poor detector response. However, DDVP, the dehydrochlorination product of trichlorfon, had a conveniently short retention time and a good response under our analysis conditions. It was therefore decided to determine trichlorfon indirectly by converting it in the samples to DDVP.

Upon completion of the analyses we attempted to arrive at a more convenient way to determine trichlorfon by two derivatization procedures.

Methylation of trichlorfon with diazomethane did not improve the ECD response. On the other hand, the response of FPD to trimethylsilylated trichlorfon was very good and this approach may lead to the development of a faster and more sensitive technique for the determination of trichlorfon in water.

The original insecticide (trichlorfon and DDVP), dehydrochlorination, methylation and trimethylsilylation

products were characterized by GC/MS.

The following two sections provide some basic information on the toxicity and chemistry of trichlorfon and DDVP. For more details, the reader is referred to the original literature and the quoted reviews.

TOXICITY

A. Trichlorfon

Trichlorfon, an organophosphorus pesticide, inhibits cholinesterases and is poisonous if ingested or absorbed through the skin (WHO 1973). A summary of its toxicity is presented in Table 1. Tolerance levels for trichlorfon in agricultural products and animal products vary between countries (Table 2).

Trichlorfon induces tumors in Wistar-strain rats at a single dose of 15 mg/kg (Gibel and Lohs 1975), and is on EPA's dangerous pesticides list (Anon. 1976).

The LC50 of trichlorfon increases with water hardness (Edwards 1973). Growth of five species of marine plankton was prevented by trichlorfon (Ware and Roan 1970). Trichlorfon was 1800 times more toxic than lindane to *Daphnia magna*.

B. DDVP

Dichlorvos (DDVP), the dehydrochlorination product of trichlorfon, is also used as a pesticide and is generally more toxic than trichlorfon (Table 1).

Since DDVP is used in insect pest strips, the effects on man were studied. Zavon and Kindel (1966) indicated that DDVP is relatively harmless to humans in this form, and found no significant cholinesterase inhibition in the people studied.

LC50's for bluegill and rainbow trout at 24 hr were 1000 and 5000 mg/l, respectively, and at 96 hr was 480 mg/l for the bluegill (Edwards 1973). In continuous flow tests with juvenile spot (*Xanthus*), the mean lethal concentration for both 24 hr and 48 hr was 0.550 mg/l, the same as that of malathion (Edwards 1973).

Two recent reviews and a bibliography on the toxicity of trichlorfon and DDVP are available (Kaemmerer and Buntenkötter 1973; Vettorazzi and Miles-Vettorazzi 1975; Vettorazzi 1976).

Table 1. Toxicity of trichlorfon and dichlorvos (DDVP).

	Trichlorfon		DDVP
Mammals	LD50, mg/kg oral	450	4-80
Birds	" " "	-	8-11
	" " food, 2 wks	700-2000	>5000
Fish	LC50, mg/l	3.2-180	0.5-5000
Arthropods	" "	0.00018-0.32	0.00007-0.39

Table 2. Trichlorfon and DDVP tolerances.

<u>Pesticide</u>	<u>Country or Organization</u>	<u>Products</u>	<u>Tolerance level, mg/kg</u>		
Trichlorfon	WHO (1972)	Peppers	1		
		Bananas (pulp)	0.2		
		Fresh fruit, vegetables and grain	0.1		
		Meat	0.1		
		Milk	0.05		
		Sugar beet	0.05		
		USSR Melnikov and Shevchenko (1971)	Forage of lactating animals, egg-laying poultry, meat animals	2.0	
DDVP	USSR Melnikov and Shevchenko (1971)	All food stuffs	1.0		
	U.S.A.		0.2		
DDVP	Poland Stobiecki (1970)	Fruits and vegetables	0.5		
		Czechoslovakia Benes and Cerná (1970)	Fruits and vegetables	0.1	
	WHO (1972)	Coco beans	5.0		
		Grain	2.0		
		Milled grain	0.5		
		Mushrooms	0.5		
		Fresh vegetables	0.5		
		Lettuce	1.0		
		Meat	0.05		
		Milk	0.02		
		Eggs	0.05		
		Acceptable daily intake			
		Trichlorfon			0.01
DDVP			0.004		

APPLICATION

Trichlorfon is used for crop protection, ornamentals (Taylor 1975), on agricultural and industrial premises, forest protection, pest control and control of stock infestations (Thompson 1975). DDVP is used for protection of vegetable crops (Taylor 1975), live-stock protection, as an orchard insecticide, agricultural and industrial fumigant, and for control of a wide variety of common pests on agricultural premises (Thompson 1975). Period of protection is two to three weeks.

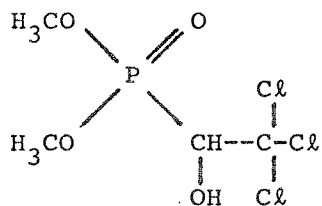
The concentration of trichlorfon in water after an aerial forest spraying at 1 lb/acre ranged from 12-52 µg/l on the day of spraying, 8-15 µg/l after 24 hr, and trichlorfon was not detectable in samples taken 7 days after spraying (Pieper and Richmond 1976).

- Properties:
- white crystalline powder
 - m.p. 73-74°C
 - b.p. 100°C at 0.1 mm Hg
 - water solubility: 12.3 g/100 g H₂O (Melnikov 1971)
 - 15.4 g/100 g H₂O at 25°C (Gunther et al. 1968)
 - slightly soluble in alcohols
 - soluble in aromatic solvents
 - soluble in ethylacetate

Trichlorfon is a phosphonic acid derivative and is thermally unstable (Devine 1973). It reacts differently under varying pH conditions. Under basic conditions it decomposes to DDVP (Melnikov 1971; Lorenz et al. 1955; Faust and Suffet 1966), while hydrolysis occurs in an acid solution (Arthur and Casida 1957; Faust and Suffet 1966).

CHEMISTRY

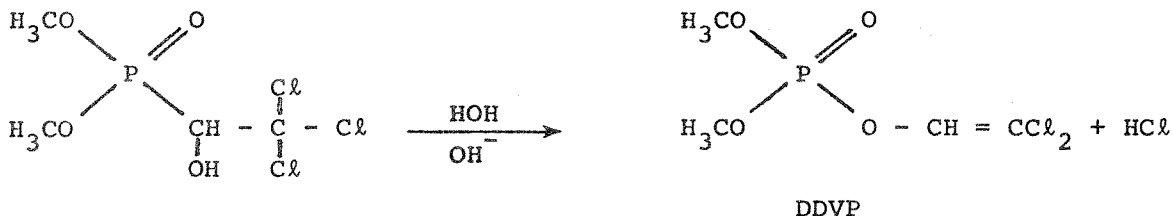
A. Trichlorfon



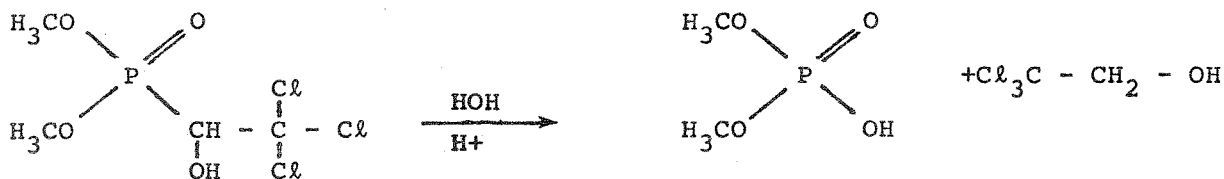
(C₄H₈O₄Cl₃P) M.W. 256

O,O-dimethyl 1-hydroxy-2,2,2-trichloroethyl phosphonate.

BASIC:



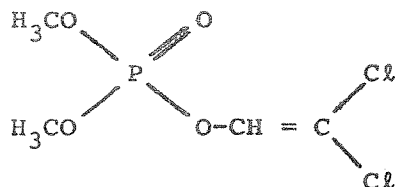
ACIDIC:



The half-life of trichlorfon is 63, 386, and 5340 minutes at pH 8, 7, 6, respectively (Metcalf et al. 1959).

Trichlorfon is a good methylating agent (methylates potassium iodide to methyl iodide (Melnikov 1971), and this property may have toxicological implications.

B. DDVP:



(C₄H₇O₄Cl₂P) M.W. 220

O,O-dimethyl-O-2,2-dichlorovinyl phosphate.

Properties: - colourless liquid
- b.p. 74°C at 1 mm Hg
- Solubility in water: 10% (Melnikov 1971)
- highly soluble in most organic solvents

The half-life of DDVP is 301, 462, 2100 and 4620 minutes at pH 8, 7, 6, and 5.4, respectively (Metcalf et al. 1959).

DDVP adds Cl and Br at the double bond to form other compounds with insecticidal properties.

C. Analytical methods

A colorimetric method for trichlorfon is available and was used, for example, for the determination of residues on cherries (Benes and Cerná 1970). All other methods (Devine 1973) are based on gas chromatography. Trichlorfon is decomposed in a hot injector block and the resulting dimethyl phosphite is measured. Due to this decomposition reaction, the instrument parameters are extremely critical (Brun, EMS, Moncton, New Brunswick, personal communication). The determination of DDVP, on the other hand, presents no difficulties.

EXPERIMENTAL

Reagents:

Pesticide-grade solvents and reagent-grade chemicals were utilized throughout this work. Trichlorfon and

DDVP were from a Pesticide Kit (Chem Service, Media, Pennsylvania).

Apparatus:

a) Perkin Elmer Model 990 gas chromatograph equipped with a Melpar flame-photometric detector (FPD) operating in the P mode was utilized to quantitate DDVP. A 6' x 1/4" O.D., coiled-glass column packed with 3% OV-1 on Chromosorb W, HP, 80/100 mesh was used. Flow rate of nitrogen carrier was 55 ml/min, hydrogen and air-flow rates were 170 ml/min and 80-90 ml/min, respectively.

Temperature programming was utilized to speed up elution of late-eluting peaks. The starting temperature was 120°C and was increased at a rate of 6°C/min, starting 1 min after injection, to a maximum of 190°C.

b) Varian Model 600D gas chromatograph with a ³H electron-capture detector (ECD) was also used. Equipped with a 5' x 1/8" glass column packed with 4% SE-30 on Chromosorb W, HP, 100/200 mesh, at a nitrogen flow rate of 70 ml/min, it was operated isothermally at various temperatures during the experiment.

c) The GC/MS System consisted of:

(1) Finnigan Model 9500 gas chromatograph, injector 200°C, column 120°C, temperature programming at 4°C/min to 190°C starting at scan 20.

Column - 4' x 1/4" O.D., U-shaped glass column packed with 3% OV-1 on Chromosorb W, HP, 80/100 mesh.

(2) Finnigan Model 1015D mass spectrometer. The mass range 50-500 a.m.u. was scanned every 5 sec.

(3) Finnigan 6100 Data System.

Hydrolysis of trichlorfon to DDVP and quantitation

Initial tests were run at various concentrations of trichlorfon and DDVP to determine their response on the FPD and ECD systems. Having determined that the FPD gave the best results, it was used in all subsequent experiments.

A reaction time test was performed to determine the length of time to completely hydrolyze trichlorfon to DDVP. Five millilitres of 2.0 mg/ml trichlorfon in acetone were added to 1 l

of distilled water. The pH of this solution was then brought to 9.7 by the addition of a diluted sodium hydroxide solution at 21°C. Samples were taken at 0.5, 1.5, and 18 hr and immediately made slightly acidic by diluted sulfuric acid. Fifty grams of anhydrous sodium sulfate (sodium chloride may be substituted, but the amount required will be greater to obtain the same extraction efficiency) were added to the sample and successive extractions with 20 and 10 ml of ethyl acetate were performed. Extracts were then evaporated under a stream of nitrogen and the concentration of DDVP was determined by gas chromatography.

The method of sample analysis was derived from the above experiments:

- a) Measure out 400 ml of sample
- b) Bring pH to 9.7-10.0
- c) React sample for 1.75 hr at 20-25°C
- d) Terminate the reaction by adding a few drops of 1:10 sulfuric acid until sample is slightly acidic
- e) Add 50 g anhydrous sodium sulfate, or saturate
- f) Add 20 ml ethyl acetate and extract 0.75 hr in a 500-ml volumetric flask on a magnetic stirrer (Vortex mixing method)
- g) Bring ethyl acetate into the neck of the flask by adding distilled, organic-free water (or separate layers in a separatory funnel) and remove ethyl acetate layer to a 50-ml round-bottom flask
- h) Evaporate extract to 1-2 ml and transfer with washings to a 15-ml centrifuge tube
- i) Adjust the volume in the centrifuge tube to 0.5-10 ml depending on the expected concentration.

The recovery of trichlorfon was determined by analyzing spiked distilled and natural water samples.

No cleanup of the extracts of the environmental samples was necessary. One of the samples was subjected to GC/MS analysis to confirm the trichlorfon to DDVP conversion and to identify a well resolved, but unknown peak in the chromatogram.

A sample of commercial Dylox Emulsifiable Concentrate, supplied by Forest Protection Limited, was diluted and chromatographed both before and after the treatment with alkali to determine the amount of DDVP initially present and then the amount of trichlorfon.

To determine the stability of

trichlorfon in water samples, tap water was spiked to contain trichlorfon at 100, 25, and 5 µg/l. One set of samples was left at room temperature and the other stored at 4°C. Aliquots were withdrawn at intervals and analyzed up to the end of the experiment at 16 days.

METHYLATION EXPERIMENTS

1. Diazomethane (4.0 ml) was added to 100 µl of 20 mg/10 ml trichlorfon in acetone and the mixture was allowed to react at 40°C for 1 hr. Another such mixture was left to react at 20°C for 24 hr.
2. Diazomethane (7.0 ml) was added to 100 µl of 20 mg/10 ml trichlorfon in acetone and allowed to react in the dark for 4 hr at 0°C (trichlorfon and diazomethane both brought to 0°C prior to reaction).
3. The mixtures were examined by chromatography with ECD and FPD to determine their analytical utility and reaction products were characterized by mass spectrometry.

TRIMETHYLSILYLATION EXPERIMENTS

1. Trichlorfon (100 µl of 20 mg/10 ml in acetone) was silylated with 200 µl of TRI-SIL reagent. This was the reference standard.
2. Trichlorfon (100 µl of 20 mg/10 ml) was added to 400 ml distilled water. Anhydrous sodium sulfate (100 g) was added and the solution was extracted with 20 ml ethyl acetate followed by 2 x 10 ml ethyl acetate extractions. The combined extracts were evaporated to 2 ml, which was then transferred with washings to 15 ml centrifuge tube. Sample volume was brought to 1.0 ml under dry nitrogen on a water bath at 35°C. 200 µl of TRI-SIL were added and the sample reacted for 1 hr at room temperature.
3. The reference and extracted samples were then chromatographed in the FPD system. Final volumes were about 10.0 ml. Samples were examined by GC/MS.

RESULTS AND DISCUSSION

A. Trichlorfon to DDVP Conversion

A reasonable ECD response was obtained on the Varian 600D for a 2 ng/µl trichlorfon in hexane standard solution. However, due to the close

proximity of the trichlorfon peak to the solvent peak, samples would probably require extensive cleanup to prevent masking of this region of the chromatogram. Difficulties of extracting trichlorfon from water with chloroform (trichlorfon region masked badly) and hexane (did not extract it but contained some extraneous peaks), combined with solvent peak nearness and tailing of the trichlorfon peak led us to try the FPD system.

Poor response to 2.0 mg/ml was obtained on the FPD system, but a good response was obtained for DDVP at the 10 ng/μl level. This offered a possibility to decompose trichlorfon to DDVP and to determine the trichlorfon concentration indirectly.

The response factor (peak height/ng) of the FPD to DDVP was examined by injection of different concentrations of DDVP and was 0.12.

The rate of conversion of trichlorfon to DDVP (Table 3) indicates that the hydrolysis is essentially complete after 1.5 hr at 21°C and pH 9.7. Some degradation of DDVP then takes place over the next 16.5 hr. A reaction time of 1.75 hr was chosen as 100% hydrolysis (allowing slightly more time to ensure complete reaction, but not allowing any hydrolysis of the DDVP products to begin).

Table 3. Hydrolysis of trichlorfon to DDVP versus time.

Time, hr	Recovery as DDVP, % of Nominal
0	-
0.5	85.65
1.5	113.15
18	85.14

B. Recovery

Table 4 gives the percent recovery over a range of trichlorfon concentrations in spiked distilled water. From Table 4 it would appear that the detection limit of trichlorfon is about 1 μg/l. Relative standard deviation of 6.2% was obtained for a normal day's run of 7 standards, scattered amongst the samples (mean peak height, 9.19 cm).

Table 4. Recovery of trichlorfon from spiked distilled water.

Trichlorfon* μg/l		
Added	Found	% Recovery
2500	2958	118.4
1250	1447	115.8
625	722	115.6
100	142	142
50	64	128
25	34.5	138
10	10.8	108
10	13.3	133
5	7.0	140
1	0.823	82.3

* Converted from [DDVP] to [TRICHLORFON] by multiplying the DDVP concentration by 1.165.

The recovery of trichlorfon from natural water samples is given in Table 5. The results indicate a good recovery. Analysis of a blank showed no peaks in the DDVP region of the chromatogram. At the same time duplicate analyses of 3 samples yielded an average difference of ±3.2% for two determinations per sample.

The commercial sample of trichlorfon contained 2.75% of DDVP and 39.47% of trichlorfon. Nigam (1973) quotes a value of 29% Dylox in EC formulation from Chemagro.

Table 5. Recovery of trichlorfon from natural water.

Sample	Trichlorfon, μg/l			
	Initially Present	Added	Found	% Recovery
1	206	200	442	109
2	63	200	331	126
3	4	200	280	137

Table 6. Percentage recovery of trichlorfon from stored water samples.

Concentration ($\mu\text{g}/\text{l}$)	Temp. ($^{\circ}\text{C}$)	Storage time, days					
		0	1	2	4	8	16
100	21	100	72	91	79	87	40.5
	4	100	88.5	78	93	-	82
25	21	100	100	97	86	100	59
	4	100	100	69	76	79	85
5	21	100	114	100	71	86	29
	4	100	100	114	129	-	114

C. Stability of trichlorfon on storage of water samples

The concentration of trichlorfon decreases during the storage of water samples (Table 6). The loss of trichlorfon depends on the initial concentration, the highest loss occurring for the most concentrated sample (20%) and no loss at the lowest concentration. Losses for the samples stored at room temperature (temperature ranged from 20 to 26 $^{\circ}\text{C}$) were much more severe (loss of 59.5% at 100 ppb level, loss of 41% at 25 ppb, and loss of 71% at 5 ppb). This shows the necessity of refrigerating samples immediately after collection to prevent losses of trichlorfon. Hydrochloric acid may be added as a preservative (Pieper and Richmond 1976).

Trichlorfon and DDVP were examined by GC/MS. The mass spectrum of trichlorfon is presented in Fig. 1. The molecular ion ($m/e = 256$) is not detectable, but the (M-35) ion ($m/e = 221$) is clearly visible and so is the ion formed by further dehydrochlorination ($m/e = 185$). The intense ion at $m/e = 145$ is probably $\text{C}_2\text{H}_7\text{O}_3\text{PCl}$ and is formed by fragmentation and rearrangement of the molecular ion. The ion $m/e = 139$ is probably $\text{C}_3\text{H}_8\text{O}_4\text{P}$, formed by the loss of CCl_3 or CCl_2 from the molecular or from the (M-35) ion, respectively. The latter fragment is quite prominent ($m/e = 82$). $m/e = 109$, 110, and 79 are the characteristic methyl phosphate ions $\text{C}_2\text{H}_6\text{O}_3\text{P}$, $\text{C}_2\text{H}_7\text{O}_3\text{P}$, and $\text{CH}_4\text{O}_2\text{P}$, respectively.

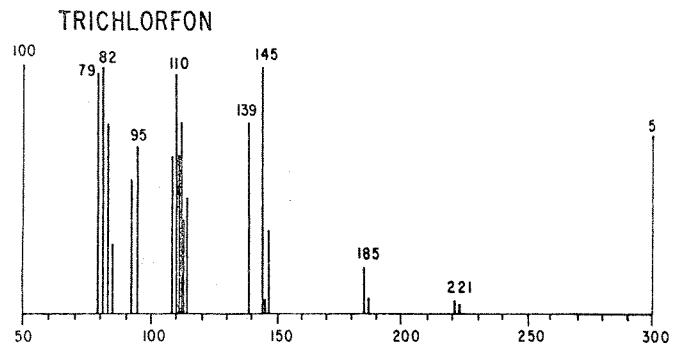


Fig. 1. Mass spectrum of trichlorfon.

The molecular ion is detectable in the mass spectrum of DDVP ($m/e = 220$, Fig. 2). The remaining ions in the spectrum are probably the same as those discussed above.

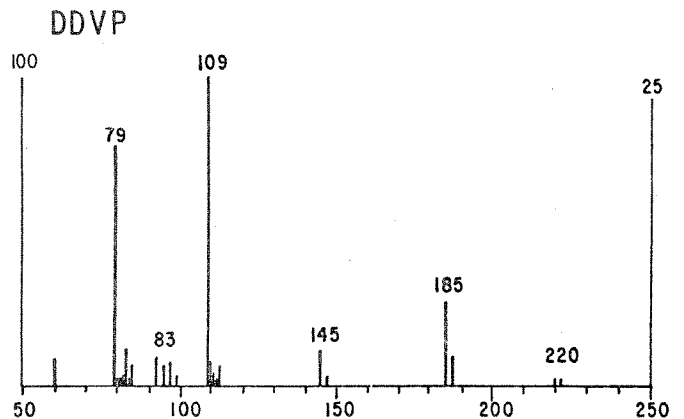


Fig. 2. Mass spectrum of DDVP

The presence of DDVP in sample 3 (Table 5) was confirmed by GC/MS. This sample was chosen for confirmation because it contained, in addition to DDVP, another phosphorus-containing peak, and several more peaks can be seen on the reconstructed gas chromatogram (Fig. 3). The other phosphorus-containing peak (F) is fenitrothion.

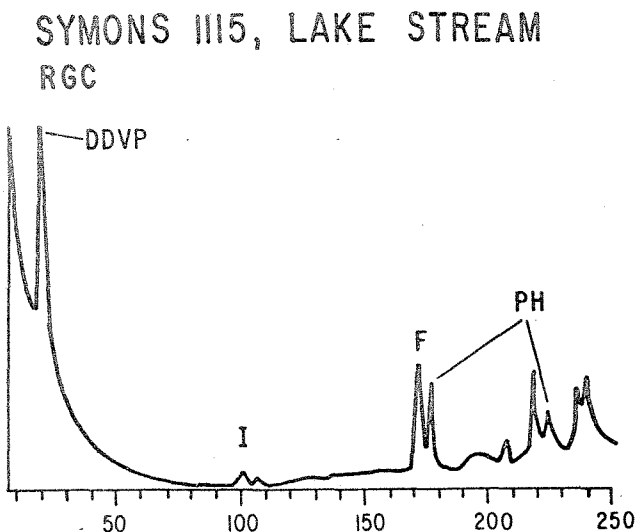


Fig. 3. RGC of sample Symons 1115, taken on June 2, 1976, from Lake Stream.

GC/MS conditions: Separator 223°C, Analyzer 90°C, Transfer line 221°C, Injector 225°C.

Column temperature 100 C and increased 4°C/min, starting at scan 20 (5 sec/scan).

DDVP generated from trichlorfon
F = fenitrothion, positive identification
PH = probably phthalates
I = unidentified, see Fig. 4 for MS

Unmarked peaks unidentified, probably paraffins or aliphatic compounds with >C₅ paraffinic moieties.

For the identification of the remaining peaks, see the caption of Fig. 3. The mass spectrum of the unidentified peak I is reproduced in Fig. 4 for future reference.

SYMONS 1115
101

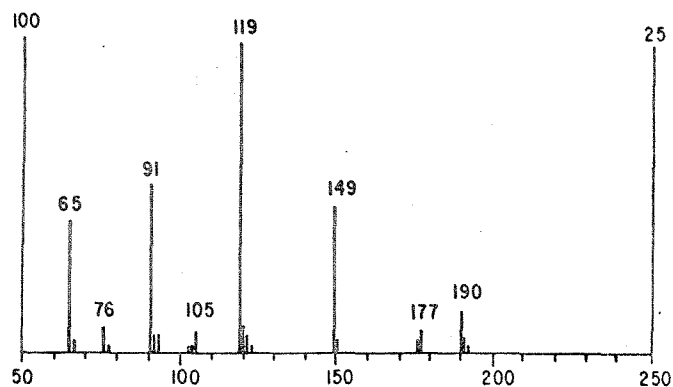


Fig. 4. Mass spectrum of unidentified component I (see Fig. 3). Probably an aromatic compound.

D. Reaction of trichlorfon with diazomethane

The reconstructed gas chromatograms of products formed on treatment of trichlorfon with diazomethane at 0, 20, and 40°C are given in Figs. 5-7, respectively.

DIA-5. 0C

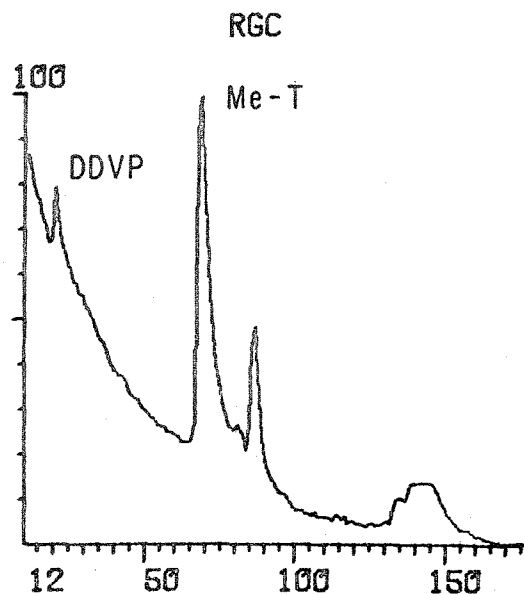


Fig. 5. RGC of trichlorfon methylation products (0°C, 1 hr).

Me - T = methyl trichlorfon (see Fig. 8)

Scan 87 = ethyl p-toluene sulfonate

Scan 135 = N-methyl-p-toluene sulfonamide

Scan 142 = unidentified (see Fig. 10)

DIA-2 DIAZOMETHANE REACTION 2
RGC

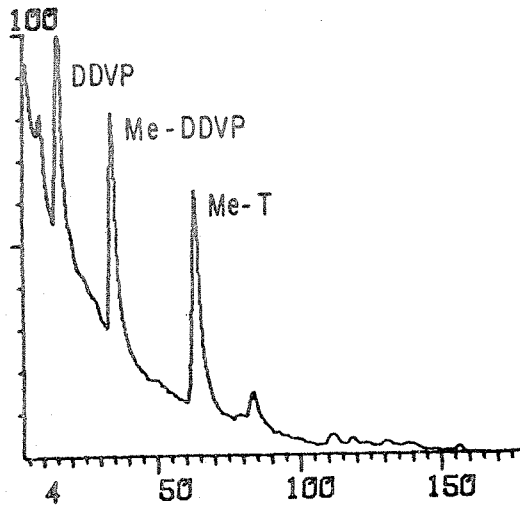


Fig. 6. RGC of trichlorfon methylation products (20°C, 24 hr).
Me-DDVP = methoxyDDVP (see Fig. 9)
Scan 112 = N,N-dimethylsulfonamide

DIA-4, 40C
RGC

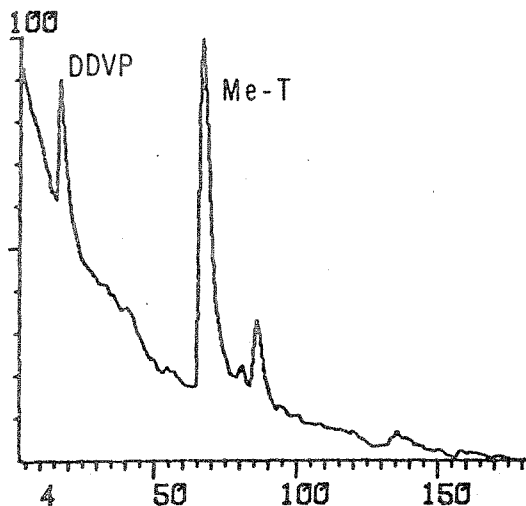
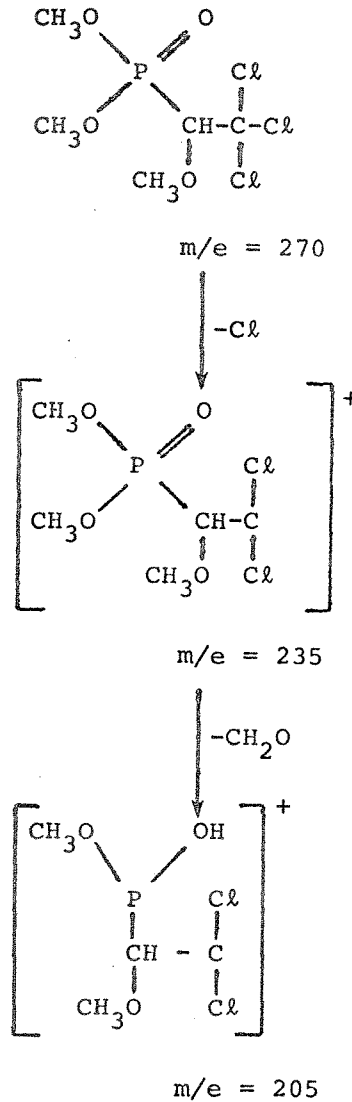


Fig. 7. RGC of trichlorfon methylation products (40°C, 1 hr).
Scan 80 = unidentified, probably a chlorinated phosphate (see Fig. 11)

According to the mass spectra, the desired product, "methyl trichlorfon" (Me-T, O,O-dimethyl 1-methoxy-2,2,2-trichloroethyl phosphonate) is the peak

number 65-70. The mass spectrum of Me-T is presented in Fig. 8, and the fragmentation patterns are given below.



The ions m/e = 161 and 126 are $[\text{CH}_3\text{OCHCCl}_3]^+$ and $[\text{CH}_3\text{OCHCCl}_2]^+$, respectively.

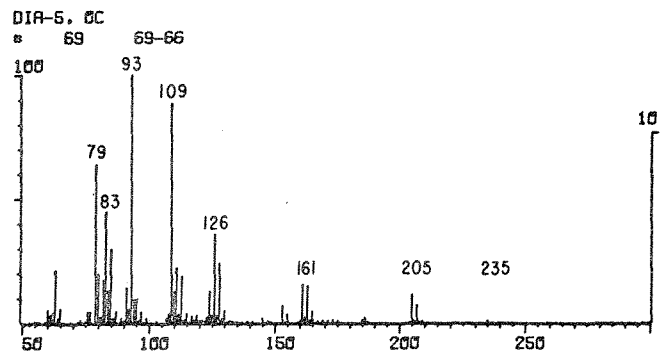


Fig. 8. Mass spectrum of methyl trichlorfon.

An additional major product formed in the reaction of trichlorfon with diazomethane at 20°C (Fig. 6, scan number 34) and its mass spectrum is presented in Fig. 9. According to the spectrum, this compound is "methoxyDDVP" (O,O-dimethyl 1-methoxy-2,2-dichloroethylene phosphonate). The fragmentation is given below.

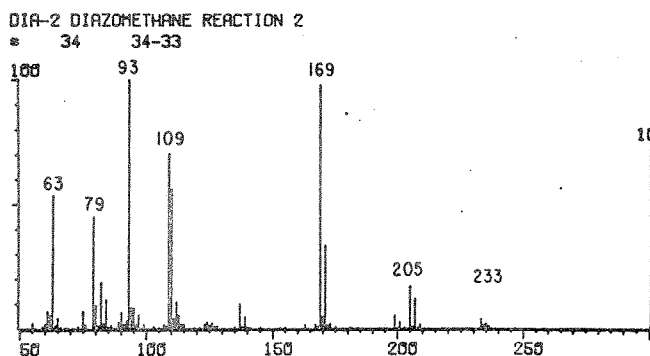
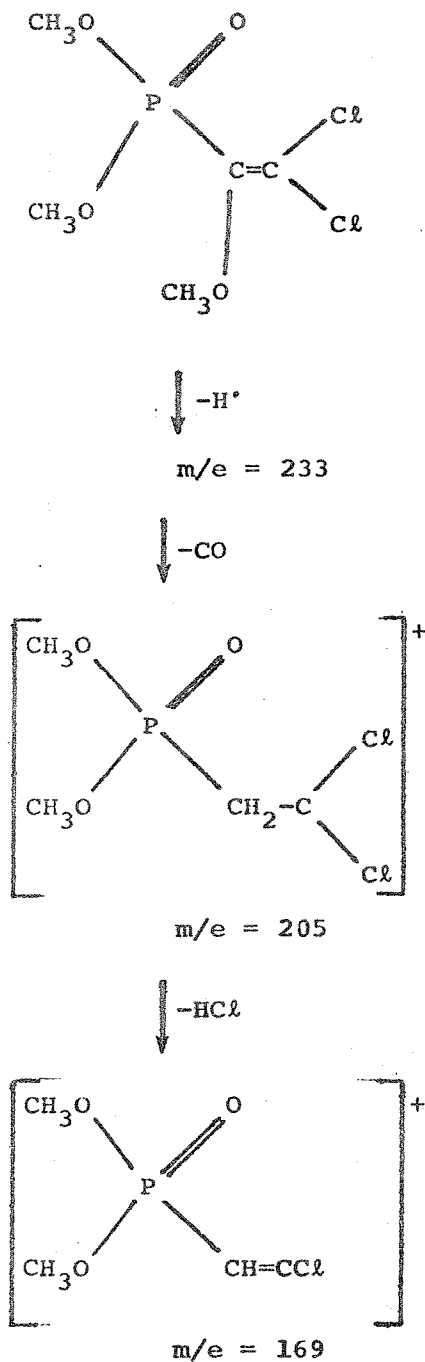


Fig. 9. Mass spectrum of methoxyDDVP.

The peak number 83-87 (Figs. 5-7) is ethyl p-toluene sulfonate, a reaction by-product from the generation of diazomethane from Diazald^R (N-methyl-N-nitroso-p-toluene sulfonamide). The peaks numbers 112 and 135 are N,N-dimethyl- and N-methyl-p-toluene sulfonamide, respectively.

The peak number 142 (Fig. 5) remains unidentified and its mass spectrum is reproduced in Fig. 10 for future reference. The spectrum indicates a chlorine-containing dimethyl phosphate.

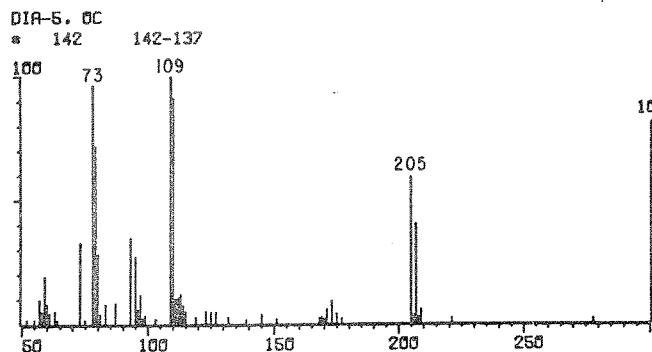


Fig. 10. Mass spectrum of the unidentified component, Fig. 5, Scan 142.

Similarly, the minor component of the reaction at 0 and 40°C, peak number 80 is an unidentified chlorinated phosphate (Fig. 11). It could be possibly O,O-dimethyl-O-(1-methoxy)-2,2,2-trichloroethyl phosphate, which might yield the ions m/e = 175 and 147 [C₃H₂O₂Cl₃]⁺ and [C₂H₂OCl₃]⁺, respectively.

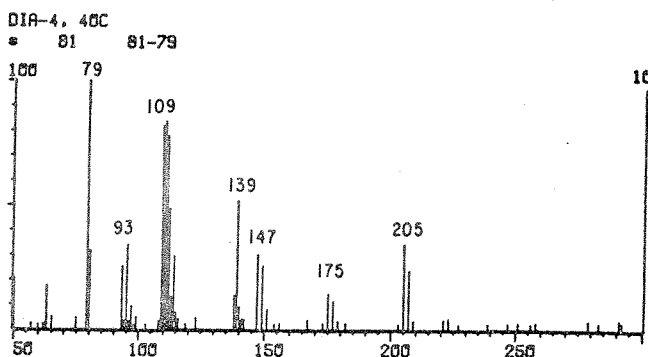


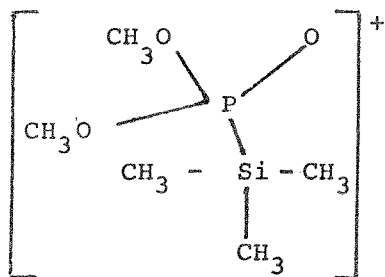
Fig. 11. Mass spectrum of the unidentified component, Figs. 5, 7, scan 80.

The variety of products formed from trichlorfon and diazomethane complicates the utilization of this reaction for analytical purposes.

E. Trimethylsilylation of trichlorfon

The reconstructed gas chromatogram of the trimethylsilylation products of trichlorfon is presented in Fig. 12. According to the mass spectrum, peak number 97 is TMS-trichlorfon (Fig. 13). The molecular ion ($m/e = 328$) is not detectable, but the ($M-15$) ion, $m/e = 313$ is quite prominent. The chlorine-containing ions $m/e = 219$ and 137 are probably $[C_5H_{10}OCl_3Si]^+$ and $[C_4H_{10}OClSi]^+$, respectively.

The $m/e = 182$ ion is probably formed by fragmentation and rearrangement:



$m/e = 182$

This ion then loses a methyl group and forms the base peak at $m/e = 167$.

The only other chlorinated compound in the mixture is contained in peak number 11. It appears to be trimethylsilylated and may have a molecular weight of 254 (Fig. 14).

TMSDY=TMS-DYLOX.10.9.
RGC

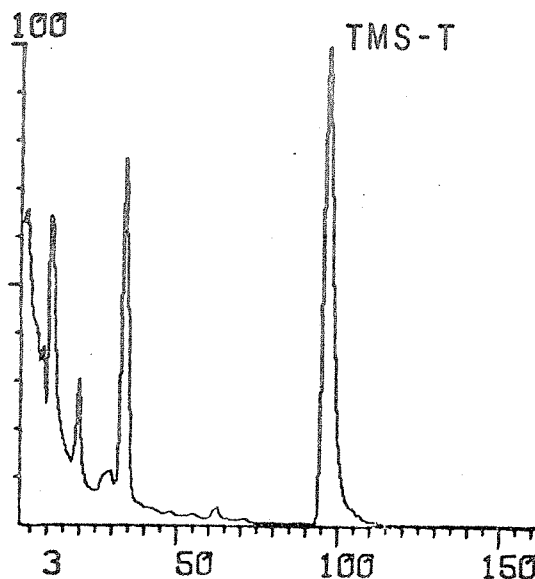


Fig. 12. RGC of trichlorfon trimethylsilylation products.
TMS-T = trimethylsilyl trichlorfon (see Fig. 13)
Scan 11 = unidentified (see Fig. 14)
Scan 20 = unidentified (see Fig. 15)
Scan 34 = unidentified (see Fig. 16)
Scan 29 = tris(trimethylsilyl) glycerol.

Compounds in the remaining peaks do not contain chlorine. The mass spectra of peaks number 20 and 34 are presented in Figs. 15 and 16 for future reference.

The peak number 29 contains tris(trimethylsilyl)glycerol.

The response of TMS - trichlorfon was roughly twice that of DDVP on the FPD. Therefore, from a sensitivity and detection limit point of view, extraction and silylation would be the preferred method over the conversion to DDVP, and should be investigated further.

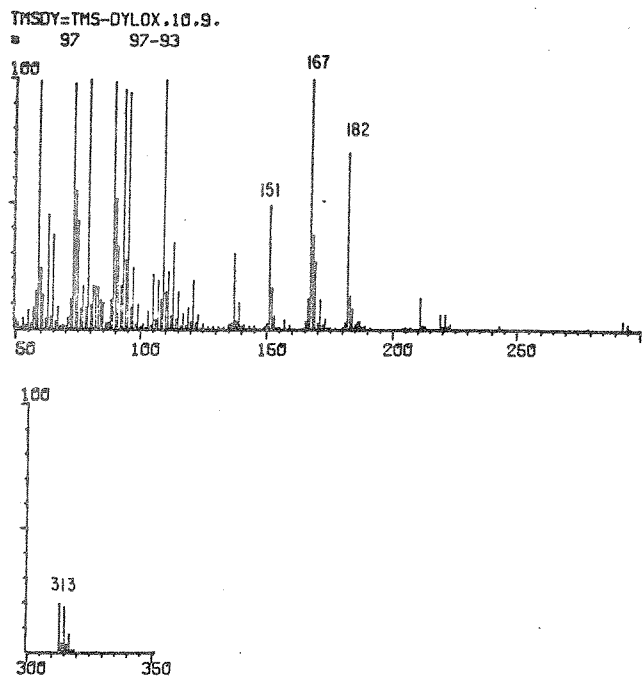


Fig. 13. Mass spectrum of trimethylsilyl trichlorfon.

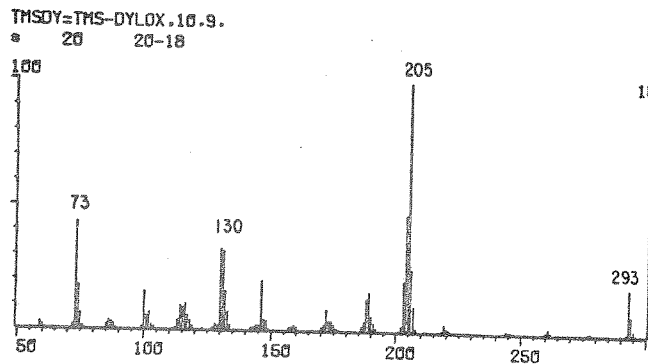


Fig. 15. Mass spectrum of the unidentified component, scan 20 (Fig. 12).

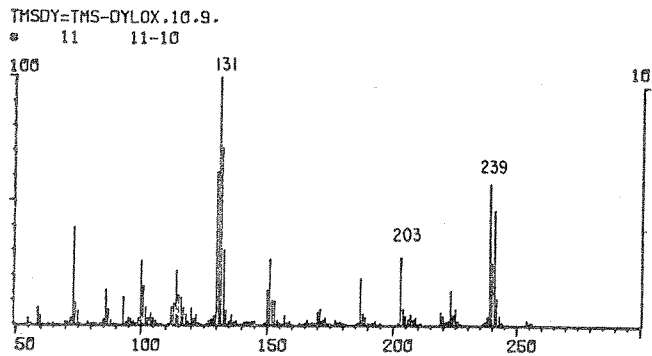


Fig. 14. Mass spectrum of the unidentified component, scan 11 (Fig. 12).

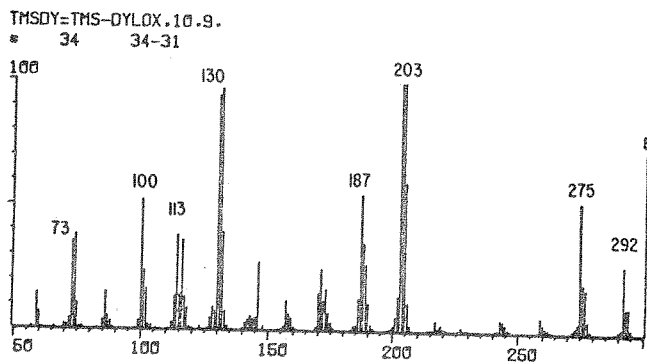


Fig. 16. Mass spectrum of the unidentified component, scan 34 (Fig. 12).

ACKNOWLEDGMENTS

We thank Mrs. Madelyn M. Irwin for typing the manuscript, and Drs. R.H. Peterson and D.W. McLeese for comments.

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