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SUFFIELD MEMORANDUM

NO. 1370

CANADIAN CONTRIBUTION TO THE 1990 UNITED NATIONS ROUND ROBIN ANALYTICAL VERIFICATION EXERCISE

PART I: CHROMATOGRAPHIC ANALYSIS

by

P.A. D'Agostino, J.R. Hancock, L.R. Provost and C.E. Lough

PART II: NMR ANALYSIS AND SYNTHESIS

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C.A. Boulet and A.S. Hansen

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ABSTRACT

Twenty-nine samples, reported to be taken during an inspection of a "Schedule 3" chemical industry, were received by Defence Research Establishment Suffield as part of a United Nations sponsored international round robin analytical exercise designed to evaluate laboratory capabilities. This report summarizes Canada's contribution to the round robin analytical verification exercise Part I provides the results of the chromatographic analyses (GC-MS, GC-FTIR, GC-FID and GC-FPD) and Part II provides the results of NMR analysis and synthesis of authentic standards. Canada confirmed Dichlorvos production and identified more than 20 compounds in the samples, including a group of previously unreported dioctyl methylphosphonates, which would be scheduled under the proposed Chemical Weapons Convention.

RÉSUMÉ

Le Centre de recherches pour la défense de Suffield a reçu 29 échantillons prélevés, signale-t-on, au cours de l'inspection d'une usine chimique inscrite à "l'annexe 3", dans le cadre d'une campagne d'analyses interlaboratoires menée à l'échelle internationale sous l'égide des Nations-Unies en vue d'évaluer la capacité des laboratoires. On résume dans ce rapport les travaux réalisés par le Canada dans le cadre de cette campagne de vérification de la capacité analytique des participants. La Partie I renferme les résultats des analyses chromatographiques (CG-SM, CG-IRTF, CG-DIF et CG-DPF), tandis que la Partie II contient les résultats des analyses RMN et de la synthèse d'étalons authentiques. Le Canada a confirmé la production de dichlorvos et un groupe de méthylphosphonates de dioctyle non encore signalés, qui seraient des substances désignées dans la Convention sur les armes chimiques que l'on se propose de mettre en application.

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INTRODUCTION

Twenty-nine samples, reported to be taken during an inspection of a "Schedule 3" chemical industry, were received by Defence Research Establishment Suffield (DRES) on November 5, 1990 as part of an international round robin analytical exercise designed to evaluate laboratory capabilities. The participating National Laboratories in Canada, Australia, China, Soviet Union, Finland (co-ordinating laboratory), France, Germany, India, The Netherlands, Norway, Sweden, Switzerland, Czechoslovakia, United Kingdom and United States of America were given the samples with no prior knowledge of their content and were asked to report in a semi-quantitative manner the presence of any scheduled compounds or degradation products.

DRES began analysis of the round robin samples on November 5, 1990. Solvent extracts of the cotton swab (FS1, FS2, FS3, AF, RV, PS1, PS2, WS1C), Tenax TA (WS1T), XAD resin (WS1X), charcoal (RC) and aqueous (WS2) samples were analysed by capillary column GC-MS (EI and ammonia CI), GC-FTIR, GC-FPD (phosphorus mode) and GC-FID. Confirmation of the principal sample components was usually possible by comparing acquired spectrometric data with that obtained for standards. Trimethylsilylation was performed on the samples (AF, WS1C, WS1X, WS2 and RC) thought to contain nonvolatile components. All chromatographic analyses were completed by the four analysts by November 14, 1990 (6.5 working days or 170 man hours). Report writing and figure preparation was undertaken by two persons on November 14, 1990 and was completed by November 20, 1990 (4.5 working days or 70 man hours).

The NMR analyses were undertaken to provide supplemental data to the GC, GC-FTIR and GC-MS analyses. Because NMR is a relatively insensitive method compared to the aforementioned techniques, these analyses were not intended to provide trace detection but done to give additional data for the unambiguous identification of chemicals present in the Round Robin samples. NMR analyses were performed from November 20-30, 1990.

DRES had expected to receive a number of soil and water samples along the lines of an allegation of use scenario. The samples provided were not as expected and were said to have been collected from a "Schedule 3" pesticide plant during an inspection. Clarification of the exercise objectives was required as insufficient guidance was provided with the samples. DRES drafted a set of objectives, which were reviewed and agreed to in principal by the co-ordinating laboratory, Finland. The set of samples was analysed with the following basic objectives in mind:

a) Indicate the identity of the major sample components in each of the samples provided. An estimate of major sample component concentration will be given as this would indicate to the Inspectorate if most of the sample taken can be accounted for by the extract components.

b) Scheduled compounds will be screened for in the sample extracts at reasonable levels, say 1% of the extractable organic content. DRES will not go to extraordinary lengths to look for the presence of a scheduled compound (e.g., Selected Ion Monitoring etc....).

c) A full report will be submitted by the end of November, based on about 1 week worth of analysis time (20 man days). Spectra, chromatograms and sample handing details will be well documented.

d) Very little emphasis will be placed on determining whether a violation has taken place, as this is the responsibility of the Inspectorate following review of all the laboratories data.

This report summarizes Canada's contribution to the round robin analytical exercise. Part I provides the results of the chromatographic analyses (GC-MS, GC-FTIR, GC-FID

and GC-FPD) and Part II provides the results of NMR analysis and synthesis of authentic standards. A number of compounds related to dichlorvos pesticide production were identified along with scheduled compounds, such as dioctyl methylphosphonates (Table I). The Experimental portion of each Part summarizes the instrumental methods used, the semi-quantitation method employed and the detection limits of the methods. The sample handling details, analytical results, compounds identified and amounts (major components) for the analysis of each sample are provided in the Results section of Parts I and II. Mass spectrometric and FTIR data for each of the compounds identified are provided in Annexes 1 to 21 of Part I. The chromatographic peak numbers, used in Figures 1 to 18 of Part I, for each sample component are the same as the Annex number for that compound. The compounds structures are given next to the chemical shift, δ (ppm) in Part II. The synthesis and NMR spectroscopic data of di-1-octyl and di-2-octyl methylphosphonate are also reported in Annexes 22-25. These compounds were prepared to provide authentic reference samples for NMR and GC-MS identification.

TABLE I: Compounds Identified during Round Robin Analysis

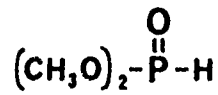
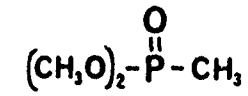
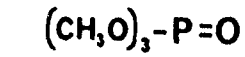
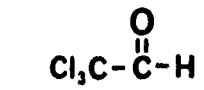
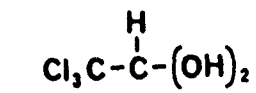
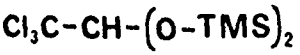
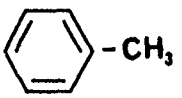
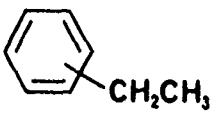
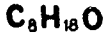
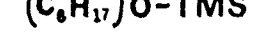
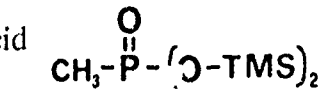
Peak No.[a]	Mol. Wt.	Compound Name	Structure
1[b,c]	124	Trimethyl phosphite	
2[b,c]	110	Dimethyl phosphite	
3[b,c]	124	Dimethyl methylphosphonate	
4	140	Trimethyl phosphate	
5	146	Trichloroacetaldehyde	
6[b]	164	2,2,2-Trichloro-1,1-ethanediol	
7	308	di-TMS derivative of 2,2,2-trichloro -1,1-ethanediol	
8[b]	92	Toluene	
9[b]	106	C_2-alkyl benzenes	
10[b]	130	C_8 Alcohols	
11	202	TMS derivative of C_8 alcohols	
12[c]	240	di-TMS derivative of methylphosphonic acid	

TABLE I (con't): Compounds Identified during Round Robin Analysis

Peak No.[a]	Mol. Wt.	Compound Name	Structure
13	314	tri-TMS derivative of phosphoric acid	$O{=}P\text{-}(O\text{-}TMS)_3$
14	186	Chloroethenyl dimethyl phosphates	$(CH_3O)_2\text{-}P(=O)\text{-}O\text{-}C_2H_2Cl$
15[b]	220	Dichlorvos	$(CH_3O)_2\text{-}P(=O)\text{-}O\text{-}CH{=}CCl_2$
16		Unknowns (chlorinated)	
17[b,c]	320	Dioctyl methylphosphonates	$(C_8H_{17}O)_2\text{-}P(=O)\text{-}CH_3$
18	198	TMS derivative of dimethyl phosphoric acid	$(CH_3O)_2\text{-}P(=O)\text{-}O\text{-}TMS$
19	298	tri-TMS derivative of phosphorous acid	$P\text{-}(O\text{-}TMS)_3$
20	226	di-TMS derivative of hydrogenphosphonic acid	$H\text{-}P(=O)\text{-}(O\text{-}TMS)_2$
21	256	di-TMS derivative of methyl phosphoric acid	$CH_3O\text{-}P(=O)\text{-}(O\text{-}TMS)_2$

[a] Refer to Figures 1 to 18 in Part I.

[b] Compounds contained in distributed samples.

[c] Chemical Weapons Convention scheduled compound.

PART I: CHROMATOGRAPHIC ANALYSIS

EXPERIMENTAL

Quantitation

A semi-quantitative estimate of the amount (mg) of each major component in each sample was calculated using the FID responses of toluene and triethyl phosphate. Triethyl phosphate response was used to provide estimates of organophosphorus component levels and toluene response was used for the other sample component levels.

Instrumental Conditions

TABLE II: GC-MS Conditions	
Country	Canada
Mass Spectrometer	VG 70/70E (double focusing MS)
Accelerating Voltage	6 kV
Mass Range/Scan Function	500 - 40 u (0.75 sec/decade; 0.25 sec ISD)
EI (source conditions)	70eV/100μA/10^{-6} Torr/ 200°C
CI (source conditions)	50eV/500μA/2x10^{-4} Torr/110-130°C
Detection Limit	EI: full scanning 1-5 ng/component
	CI: full scanning 3-10 ng/component
GC Parameters	
Instrument:	Varian 3700
Column:	15 m x 0.32 mm ID DB-1701 (0.25 μm)
Carrier Gas:	Helium approx. 100 cm/s
Temperature Program:	40°C (2 min) then 10°C/min to 280°C (4 min)
Injection Mode:	On-column at 40°C

TABLE III: GC-FTIR CONDITIONS	
Country	Canada
IR Spectrometer	Nicolet 730
Resolution	8 cm^{-1}
Light Pipe Dimensions	15 cm x 1 mm
Detector Type	MCT
Scan Rate	approx. 2 scans/s
Accumulated Scans/Spectrum	nominally 10 scans
Wavenumber Range	4000 to 600
Make-up Gas Flow Rate in Light Pipe	0.3 mL/min
Light Pipe Temperature	200°C
Detection Limit	approx. 50 ng/component
GC Parameters	
Instrument:	Hewlett Packard 5890
Column:	15 m x 0.25 mm ID DB-1701 (0.25 μm)
Carrier Gas:	Helium approx. 30 cm/s
Temperature Program:	40°C (2 min) then 10°C/min to 190°C (10 min)
Injection Mode:	On-column at 40°C
Comments Light pipe temperature set at 250°C for sample WS2	

TABLE IV: GC-FPD CONDITIONS	
Country:	Canada
Instrument:	Hewlett Packard 5890
Column:	15m x 0.53mm ID DB-1701 (1.0 μm)
Detector:	FPD (P)
Carrier Gas:	Helium 40 cm/s
Temperature Program:	40°C (2 min) then 10°C/min to 250°C
Injection Mode	On-column at 40°C
Detection Limit	20 pg/component

TABLE V: GC-FID Conditions	
Country:	Canada
Instrument:	Hewlett Packard 5890
Column:	15m x 0.32mm ID DB-1701 (0.25 μm)
Detector:	FID
Carrier Gas:	Helium approx. 40 cm/s
Temperature Program:	40°C (2 min) then 10°C/min to 280°C (4 min)
Injection Mode	On-column at 40°C
Detection Limit	1 ng/component

RESULTS

a) FS1 (Swab sample)

Sample Handling

The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring at the mid-point of the container. The container was broken into two and the swab and both pieces of glass were submersed in 10 mL of dichloromethane in a 16 x 125 mm screw-capped (Teflon lined) centrifuge tube. The centrifuge tube was placed in an ultrasonic bath for only 2 minutes to allow extraction of the organics with minimal extraction of the swab material. This extract was then removed and stored in a new centrifuge tube prior to capillary column GC analysis (extract code name FS1-901105-01M). Trimethylsilylation was not performed.

Results

Figure 1 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL and 0.25 μL aliquots respectively of the 10 mL dichloromethane extract of FS1. Most of the organic content was accounted for by the presence of the following sample components.

Compounds	Spectra	Quantity (mg)
Trimethyl phosphite	Annex 1	20
Dimethyl phosphite	Annex 2	11
Dimethyl methylphosphonate	Annex 3	0.4
Trimethyl phosphate	Annex 4	1

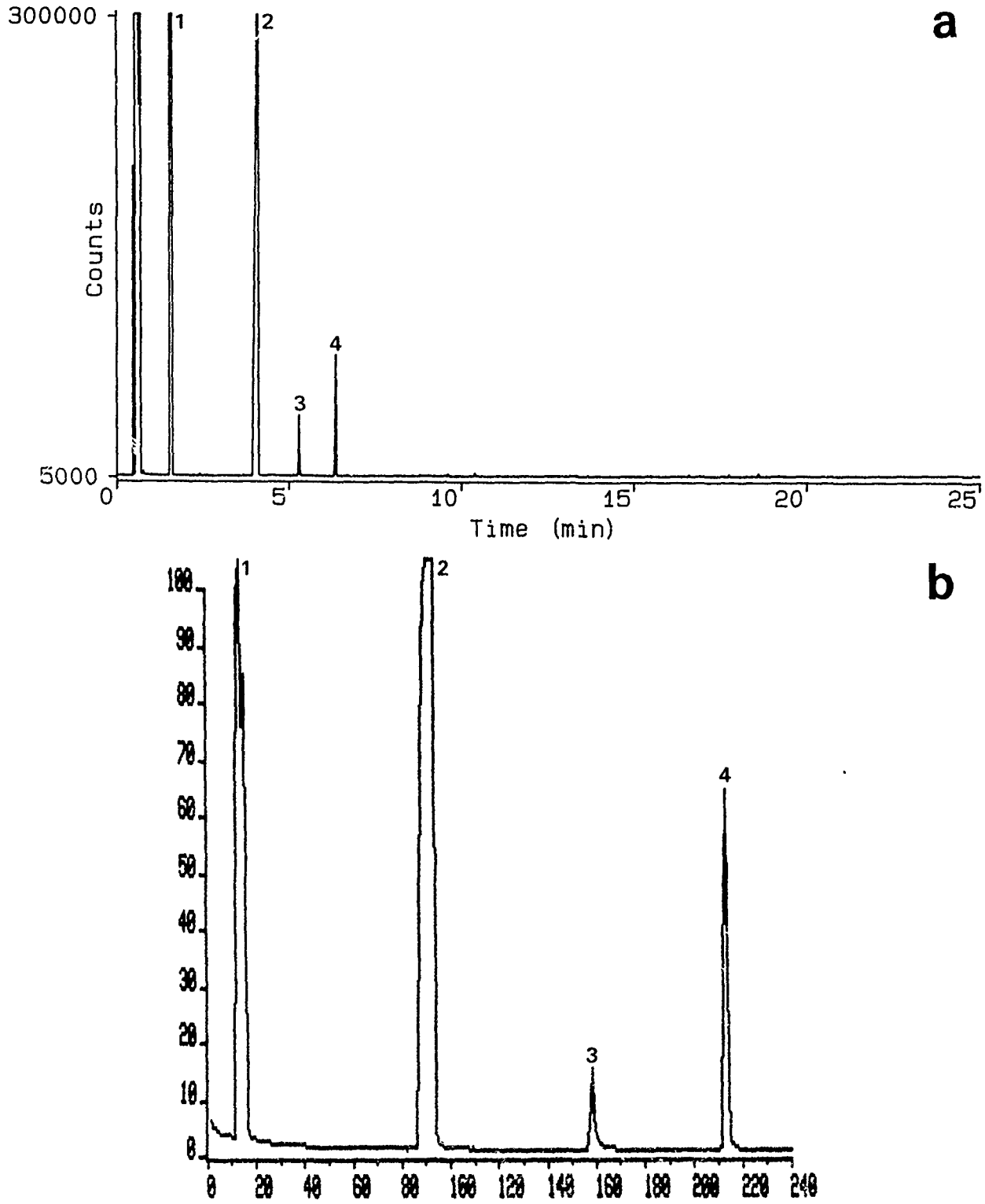


Figure 1: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of dichloromethane extract of FS1. Numbered peaks are identified in Table 1. Spectral data for numbered peaks appears in the Annex with the same number.

b) FS2 (Swab sample)

Sample Handling

The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring at the mid-point of the container. The container was broken into two and the swab and both pieces of glass were submersed in 10 mL of dichloromethane in a 16 x 125 mm screw-capped (Teflon lined) centrifuge tube. The centrifuge tube was placed in an ultrasonic bath for only 2 minutes to allow extraction of the organics with minimal extraction of the swab material. This extract was then removed and stored in a new centrifuge tube prior to capillary column GC analysis (extract code name FS2-901105-03M).

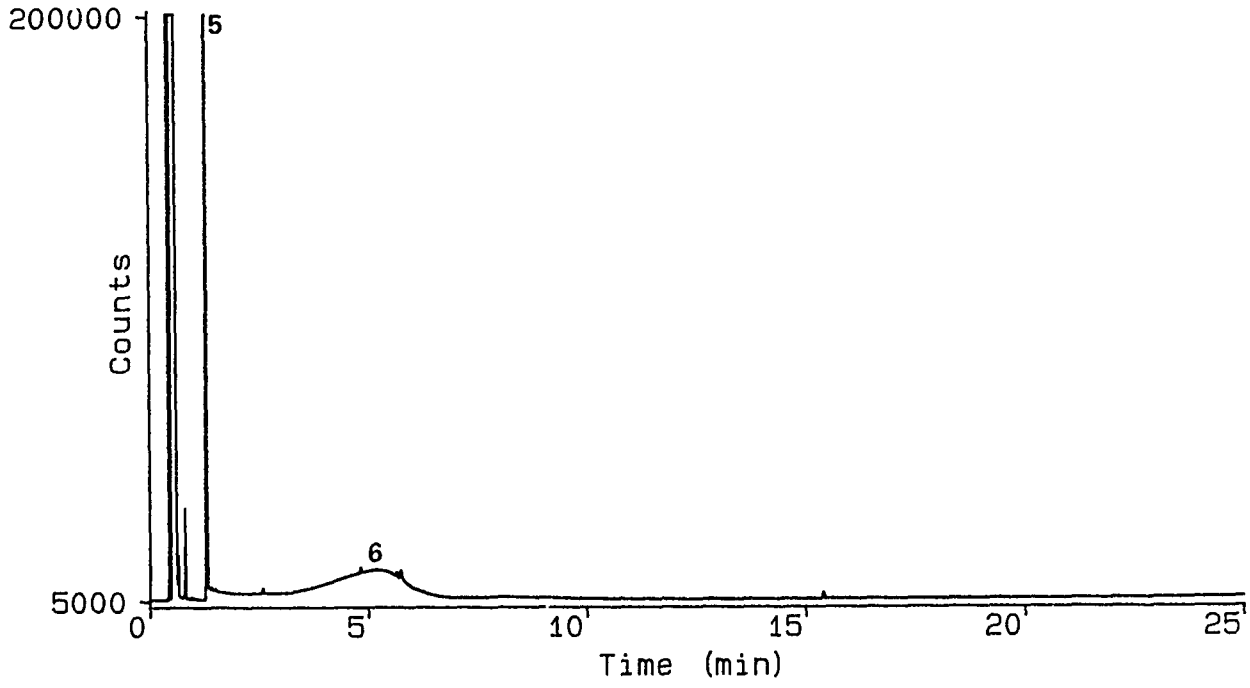
Trimethylsilylation (TMS) was performed by combining 100 μL BSTFA, 100 μL pyridine and 100 μL of the dichloromethane extract (above) in a 1.8 mL screw-capped (Teflon lined) glass vial. This sample was heated for 20 minutes at 60°C prior to analysis. Analysis was performed immediately after cooling to minimize degradation (extract code name FS2-901107-07TMS).

Results

Figure 2 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL and 0.25 μL aliquots respectively of the 10 mL dichloromethane extract of FS2. Most of the organic content was accounted for by the presence of the following sample components.

Compounds	Spectra	Quantity (mg)
Trichloroacetaldehyde	Annex 5	2.3
2,2,2-Trichloro-1,1-ethanediol	Annex 6	
di-TMS derivative of 2,2,2-trichloro-1,1-ethanediol	Annex 7	50

Chromatography of 2,2,2-trichloro-1,1-ethanediol was poor due to the presence of diol substitution. The presence of a diol was confirmed by TMS derivatization of the FS2 dichloromethane extract. Quantitation was done on the di-TMS derivative only. Spectrometric and chromatographic data for the di-TMS derivative of 2,2,2-trichloro-1,1-ethanediol (standard) were identical to that obtained for the principal sample component of FS2 (Annex 7). Figure 3 illustrate capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL of the TMS extract.



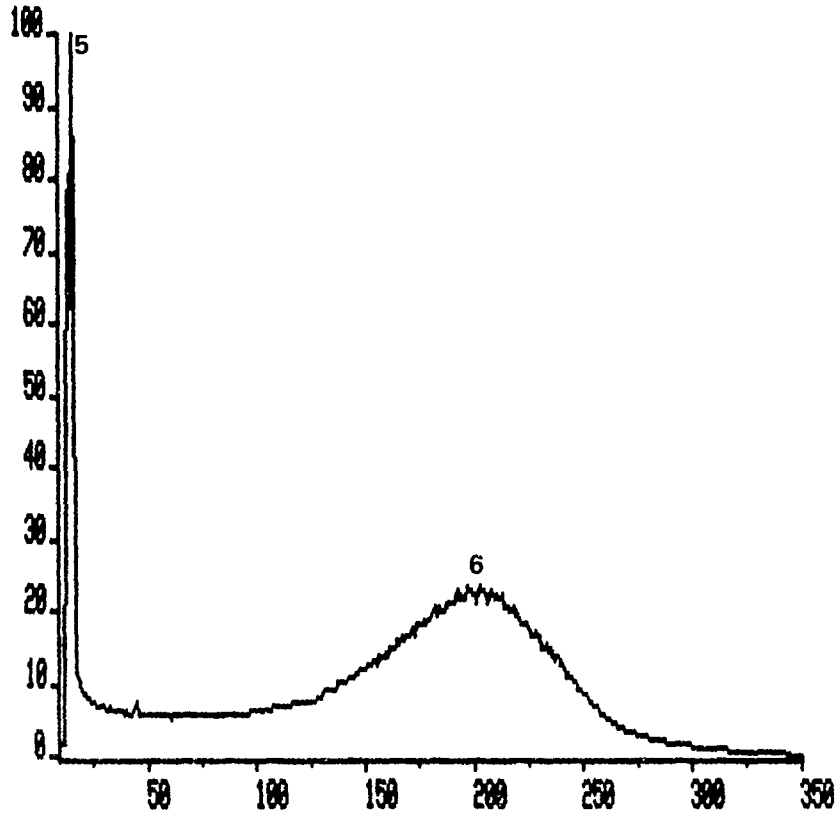


Figure 2: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of dichloromethane extract of FS2. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

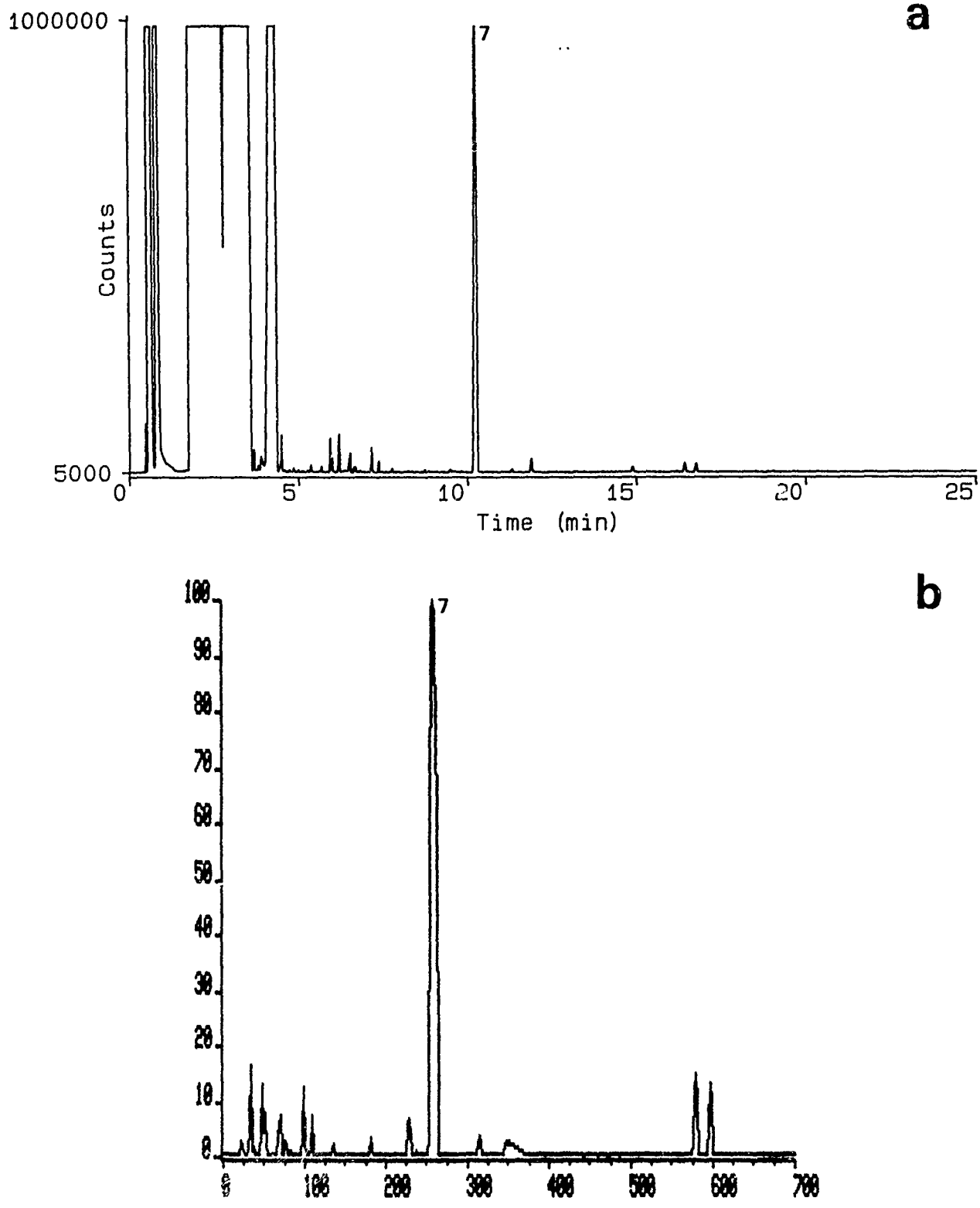


Figure 3: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of TMS derivative of dichloromethane extract of FS2. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

c) FS3 (Swab sample)

Sample Handling

The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring at the mid-point of the container. The container was broken into two and the swab and both pieces of glass were submersed in 10 mL of dichloromethane in a 16 x 125 mm screw-capped (Teflon lined) centrifuge tube. The centrifuge tube was placed in an ultrasonic bath for only 2 minutes to allow extraction of the organics with minimal extraction of the swab material. This extract was then removed and stored in a new centrifuge tube prior to capillary column GC analysis (extract code name FS3-901105-04M).

Trimethylsilylation was not performed.

Results

Figure 4 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL and 0.2 μL aliquots respectively of the 10 mL dichloromethane extract of FS3. Most of the organic content was accounted for by the presence of the following sample components.

Compounds	Spectra	Quantity (mg)
Toluene	Annex 8	14
C_2-alkyl benzenes	Annex 9	

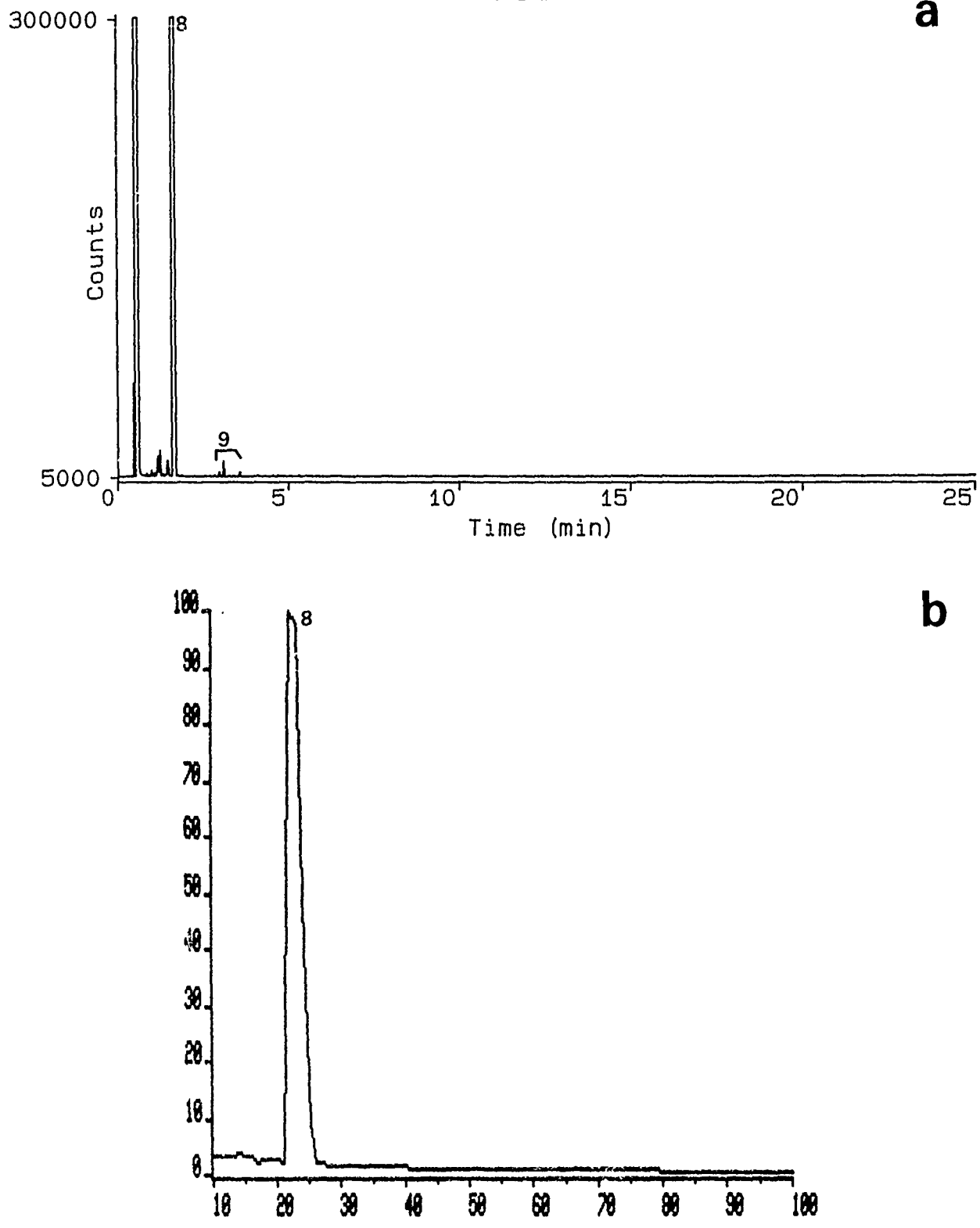


Figure 4: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of dichloromethane extract of FS3. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

d) AF (Swab sample)

Sample Handling

The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring at the mid-point of the container. The container was broken into two and the swab and both pieces of glass were submersed in 10 mL of dichloromethane in a 16 x 125 mm screw-capped (Teflon lined) centrifuge tube. The centrifuge tube was placed in an ultrasonic bath for only 2 minutes to allow extraction of the organics with minimal extraction of the swab material. This extract was then removed and stored in a new centrifuge tube prior to capillary column GC analysis (extract code name AF-901105-05M).

Trimethylsilylation (TMS) was performed by combining 100 μL BSTFA, 100 μL pyridine and 100 μL of the dichloromethane extract (above) in a 1.8 mL screw-capped (Teflon lined) glass vial. This sample was heated for 20 minutes at 60°C prior to analysis. Analysis was performed immediately after cooling to minimize degradation (extract code name AF-901107-08TMS).

A second trimethylsilylation (TMS) was performed after ultrasonic (2 minutes) extraction of the same swab and glass material with 10 mL of acetonitrile. The acetonitrile was taken to dryness and 100 μL BSTFA, 100 μL pyridine and 100 μL dichloromethane were added to the dried extract in a 1.8 mL screw-capped (Teflon lined) glass vial. This sample was heated for 20 minutes at 60°C prior to analysis. Analysis was performed immediately after cooling to minimize degradation (extract code name AF-901108-05TMS).

A third trimethylsilylation was carried out after ultrasonic extraction (2 minutes) of the second sample of AF with 1 mL acetonitrile in a similar fashion (extract code name AF-901109-01TMS).

Results

Figure 5 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL aliquots of the 10 mL dichloromethane extract of AF. Most of the organic content was accounted for by the presence of C_8 alcohols.

Figure 6 illustrates the capillary column GC-MS chromatogram for TMS derivatization of the dichloromethane extract of AF. TMS derivatives of the C_8 alcohols were formed (Annex 11), confirming the presence of hydroxyl substitution. A trace of two phosphorus acids, methylphosphonic acid (Annex 12) and phosphoric acid (Annex 13), as their TMS derivatives, were also detected. The same two acids were also detected in the TMS derivatized acetonitrile extracts. There was no evidence of organic compounds that would be a powder.

Compounds	Spectra	Quantity (mg)
C_8 alcohols	Annex 10	16
TMS derivatives of the C_8 alcohols	Annex 11	29
di-TMS derivative of methylphosphonic acid	Annex 12	
tri-TMS derivative of phosphoric acid	Annex 13	

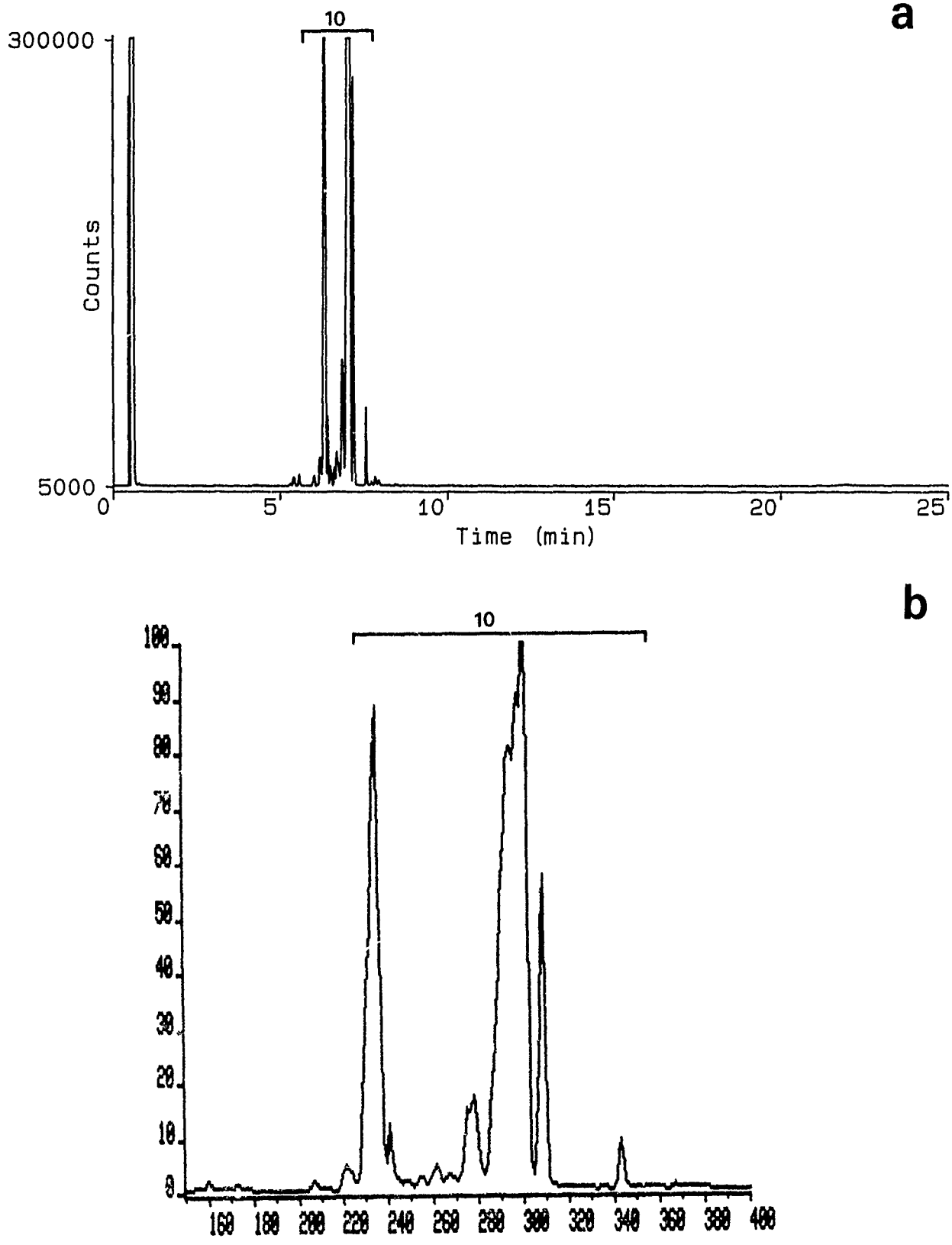


Figure 5: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of dichloromethane extract of AF. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

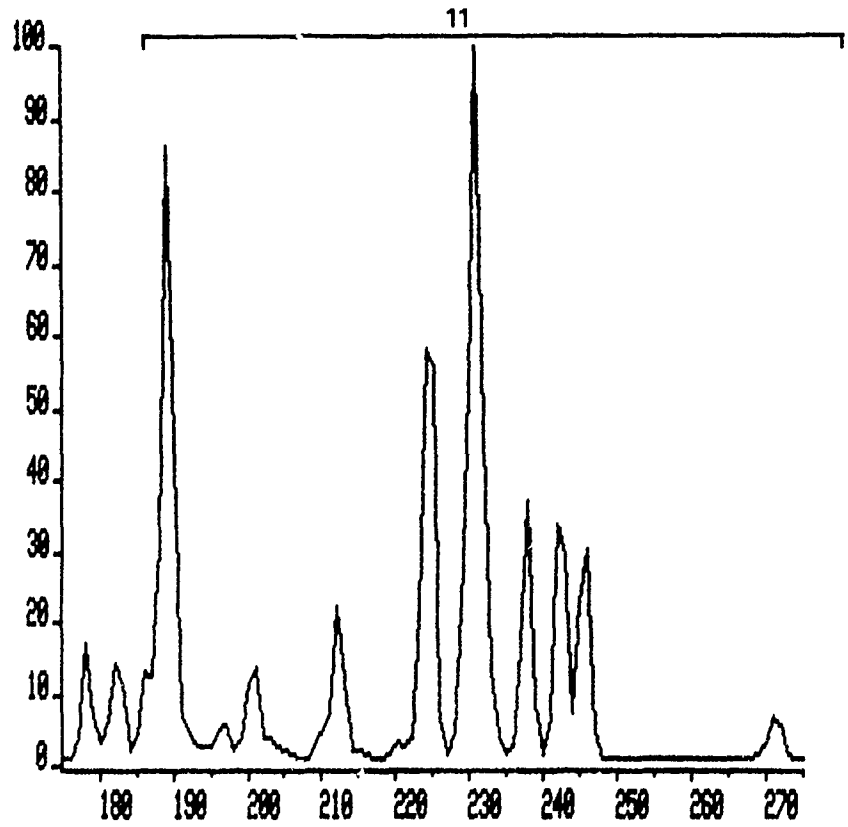


Figure 6: Capillary column GC-MS (EI) chromatogram of TMS derivative of dichloromethane extract of AF. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

e) RV (Swab sample)

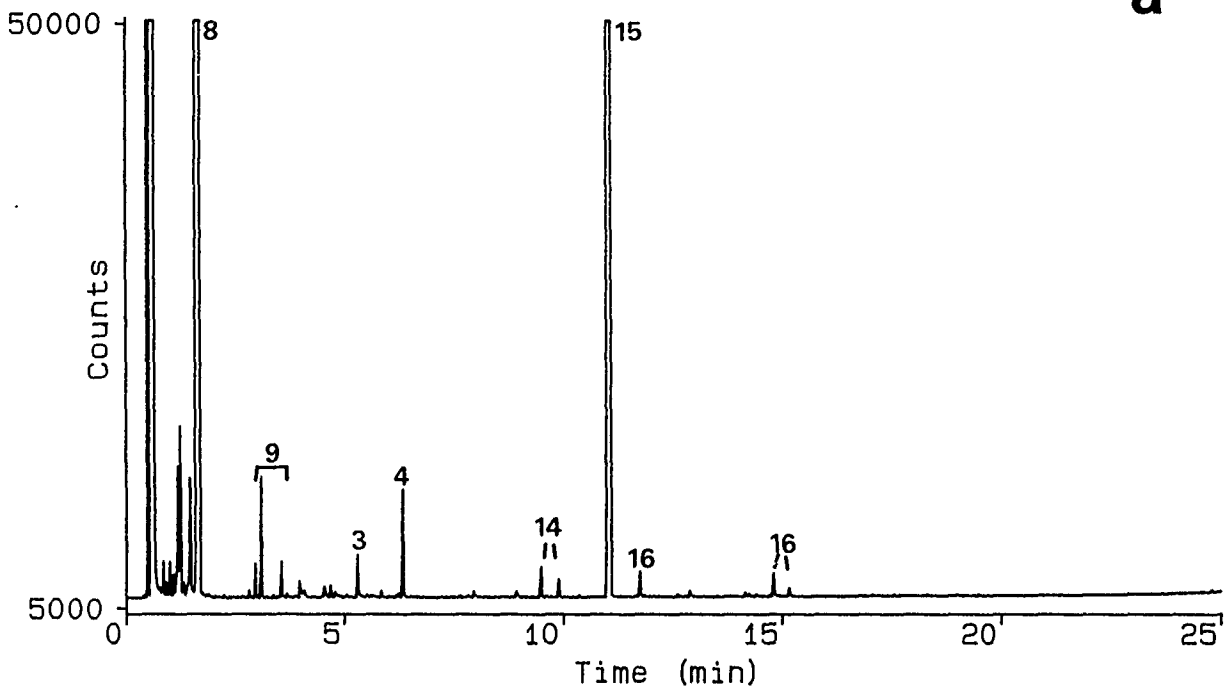
Sample Handling

The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring at the mid-point of the container. The container was broken into two and the swab and both pieces of glass were submersed in 10 mL of dichloromethane in a 16 x 125 mm screw-capped (Teflon lined) centrifuge tube. The centrifuge tube was placed in an ultrasonic bath for only 2 minutes to allow extraction of the organics with minimal extraction of the swab material. This extract was then removed and stored in a new centrifuge tube prior to capillary column GC analysis (extract code name RV-901105-07M). Trimethylsilylation was not performed.

Results

Figure 7 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL aliquots of the 10 mL dichloromethane extract of RV. Most of the organic content was accounted for by the presence of the following sample components.

Compounds	Spectra	Quantity (mg)
Dimethyl methylphosphonate	Annex 3	0.04
Trimethyl phosphate	Annex 4	0.09
Toluene	Annex 8	12
C_2-alkyl benzenes	Annex 9	
Chloroethenyl dimethyl phosphates	Annex 14	
Dichlorvos	Annex 15	5
Unknowns (chlorinated)	Annex 16	



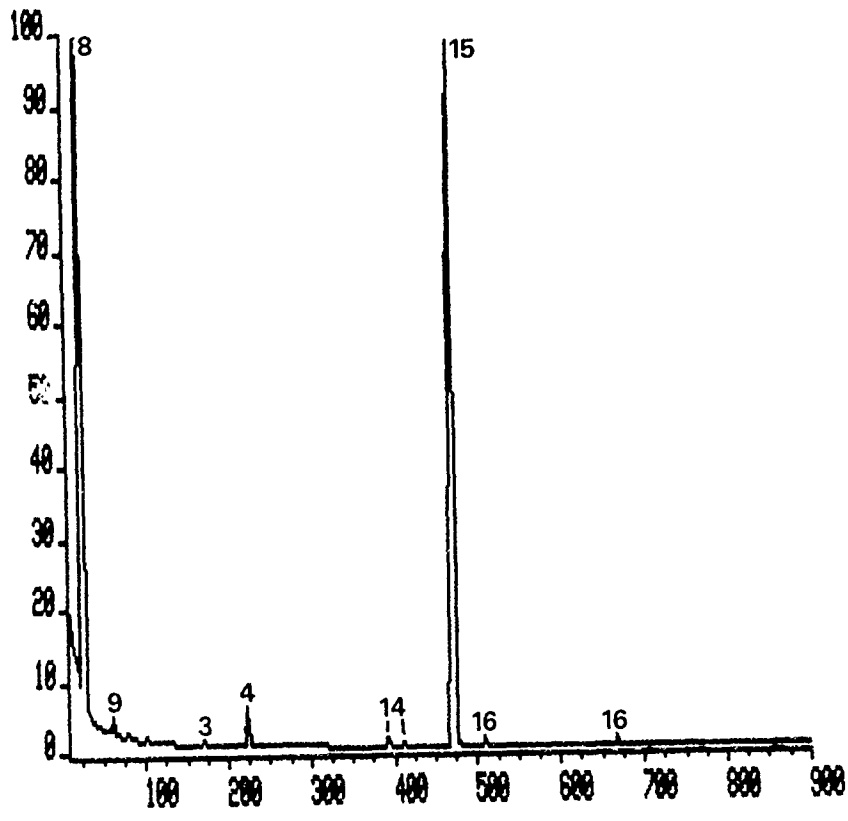


Figure 7: Capiliary column a) GC-FID and b) GC-MS (EI) chromatograms of dichloromethane extract of RV. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

f) PS1 (Swab sample)

Sample Handling

The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring at the mid-point of the container. The container was broken into two and the swab and both pieces of glass were submersed in 10 mL of dichloromethane in a 16 x 125 mm screw-capped (Teflon lined) centrifuge tube. The centrifuge tube was placed in an ultrasonic bath for only 2 minutes to allow extraction of the organics with minimal extraction of the swab material. This extract was then removed and stored in a new centrifuge tube prior to capillary column GC analysis (extract code name PS1-901105-08M).

Trimethylsilylation was not performed.

Results

Figure 8 illustrate capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL aliquots of the 10 mL dichloromethane extract of PS1. Most of the organic content was accounted for by the presence of the following sample components. No attempt was made to identify the chlorinated unknowns as their relevance to this exercise seemed limited.

Compounds	Spectra	Quantity (mg)
Dimethyl methylphosphonate	Annex 3	0.46
Trimethyl phosphate	Annex 4	0.62
Chloroethenyl dimethyl phosphates	Annex 14	
Dichlorvos	Annex 15	38
Unknowns (chlorinated)[1]	Annex 16	

[1] No attempt was made to identify these chlorinated unknowns as their relevance to this exercise seemed limited.

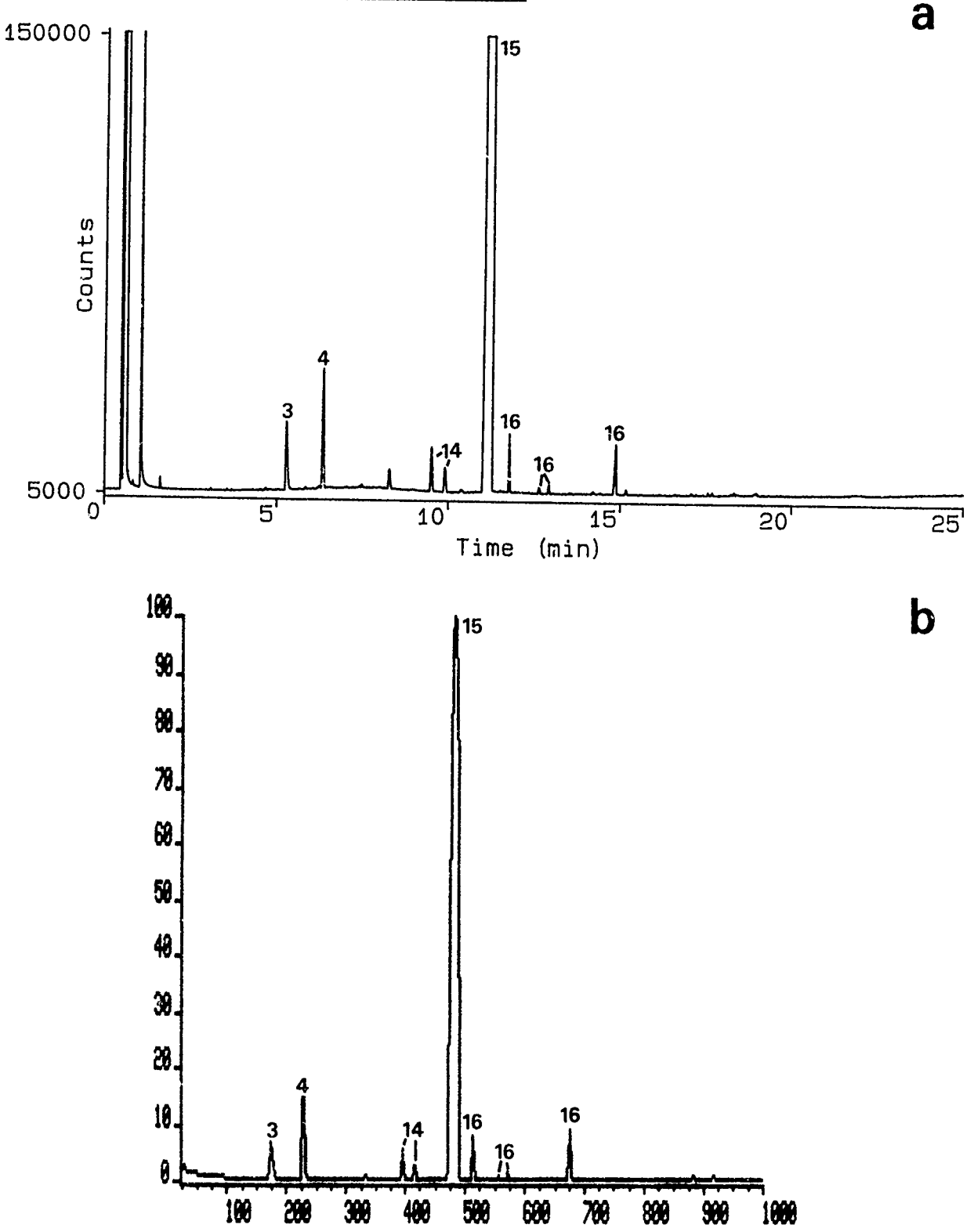


Figure 8: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of dichloromethane extract of PS1. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

g) PS2 (Swab sample)

Sample Handling

The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring at the mid-point of the container. The container was broken into two and the swab and both pieces of glass were submersed in 10 mL of dichloromethane in a 16 x 125 mm screw-capped (Teflon lined) centrifuge tube. The centrifuge tube was placed in an ultrasonic bath for only 2 minutes to allow extraction of the organics with minimal extraction of the swab material. This extract was then removed and stored in a new centrifuge tube prior to capillary column GC analysis (extract code name PS2-901105-09M). Trimethylsilylation was not performed.

Results

Figure 9 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL aliquots of the 10 mL dichloromethane extract of PS2. Most of the organic content was accounted for by the presence of the following sample components. No attempt was made to identify the chlorinated unknowns as their relevance to this exercise seemed limited.

Compounds	Spectra	Quantity (mg)
Dimethyl methylphosphonate	Annex 3	0.07
Trimethyl phosphate	Annex 4	0.38
Chloroethenyl dimethyl phosphates	Annex 14	
Dichlorvos	Annex 15	27
Unknowns (chlorinated)	Annex 16	
Dioctyl methylphosphonates	Annex 17	1.2

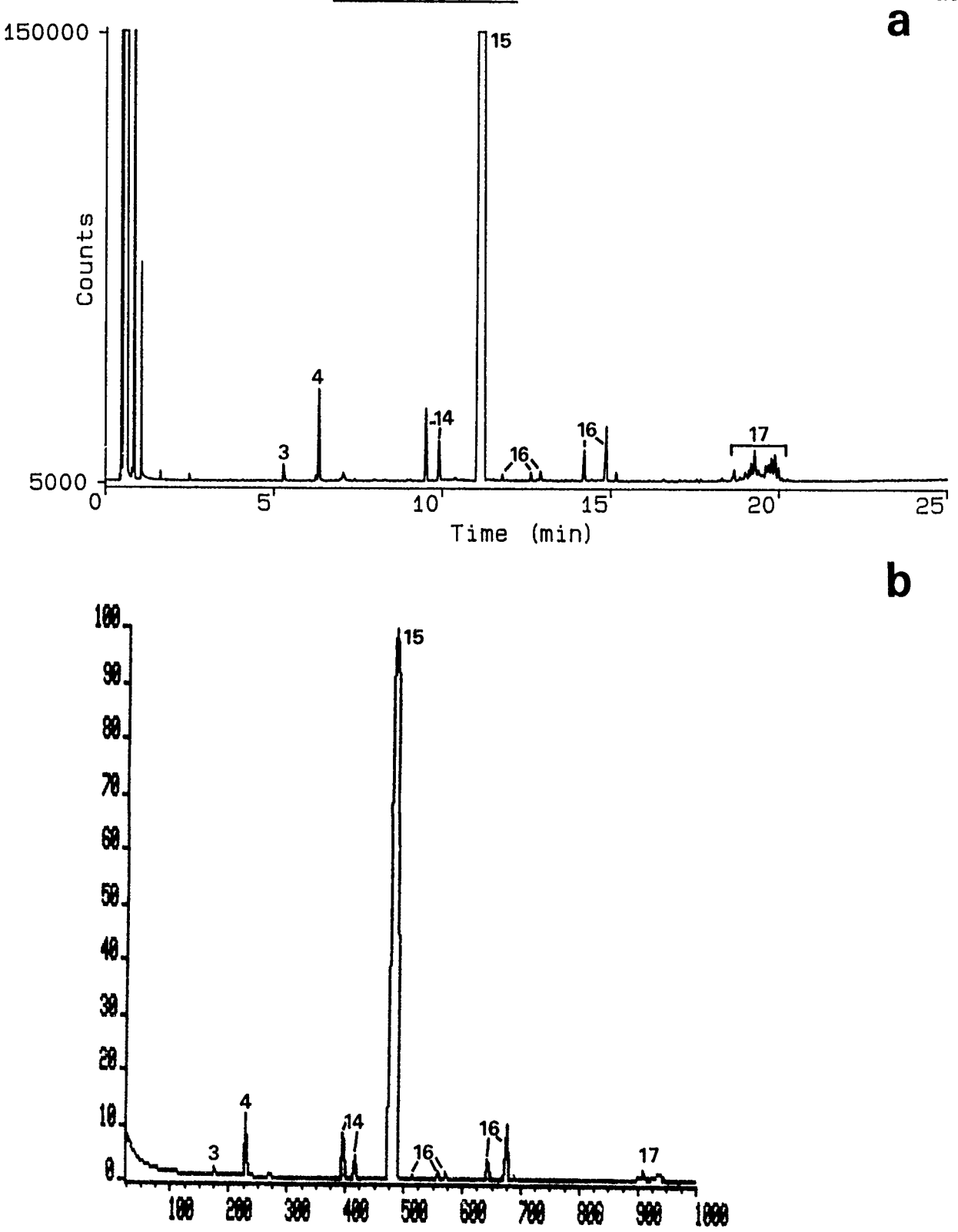


Figure 9: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of dichloromethane extract of PS2. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

h) WS1T (Tenax TA)

Sample Handling

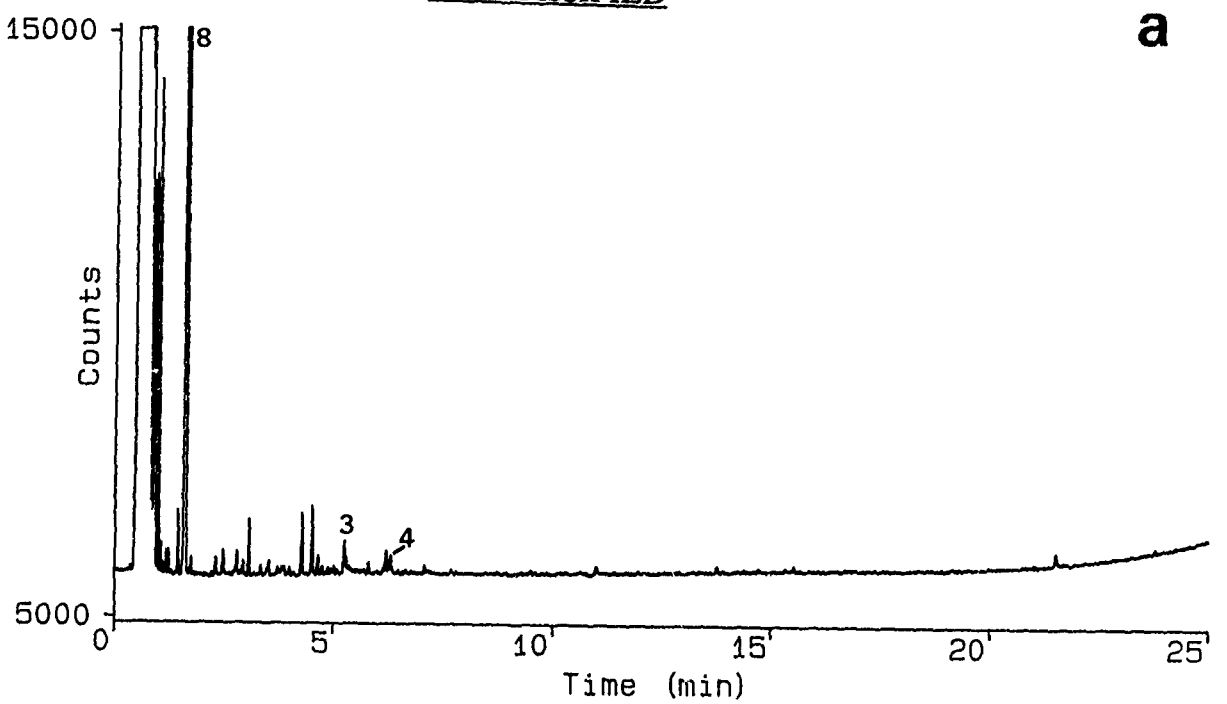
The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring near the top of the container. The Tenax TA was removed into a 6 mL vial and ultrasonic extracted for 5 minutes with 2 mL of hexane. This extract was allowed to settle then removed and stored in a centrifuge tube prior to capillary column GC analysis (extract code name WS1T-901106-07H).

Trimethylsilylation was not performed.

Results

Figure 10 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL aliquots of the 10 mL hexane extract of WS1T. Most of the organic content was accounted for by toluene with a trace of several other compounds.

Compounds	Spectra	Quantity (mg)
Dimethyl methylphosphonate	Annex 3	
Trimethyl phosphate	Annex 4	
Toluene	Annex 8	1.4
C_2-alkyl benzenes	Annex 9	



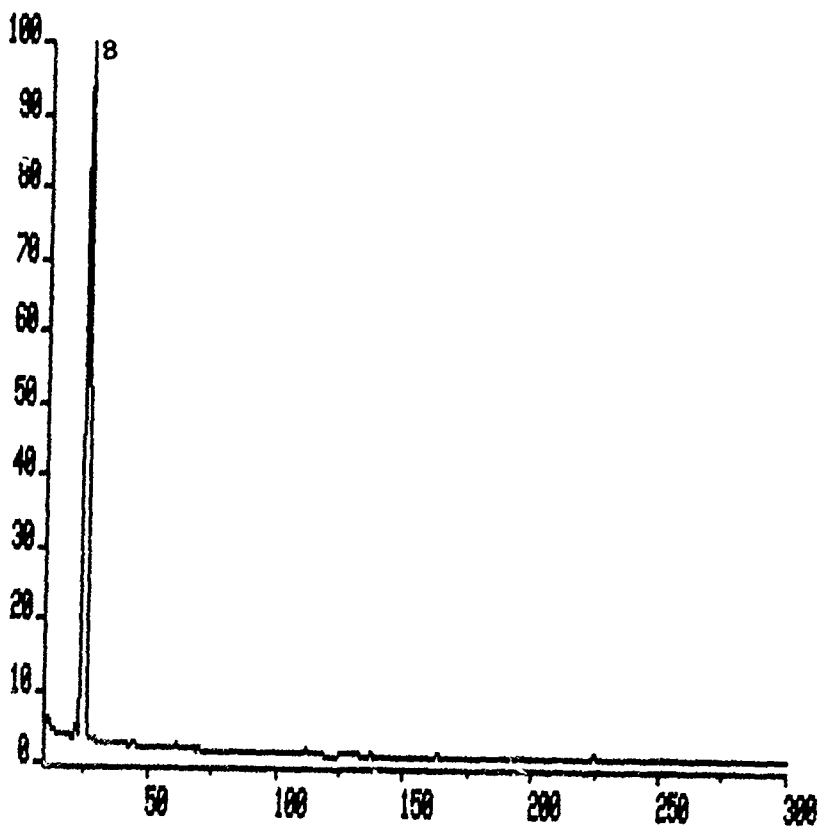


Figure 10: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of hexane extract of WS1T. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

i) WS1C (Swab sample)

Sample Handling

The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring at the mid-point of the container. The container was broken into two and the swab and both pieces of glass were submersed in 10 mL of dichloromethane in a 16 x 125 mm screw-capped (Teflon lined) centrifuge tube. The centrifuge tube was placed in an ultrasonic bath for only 2 minutes to allow extraction of the organics with minimal extraction of the swab material. This extract was then removed and stored in a new centrifuge tube prior to capillary column GC analysis (extract code name WS1C-901106-04M).

Trimethylsilylation was performed on a 1 mL acetonitrile extract of the second WS1C sample. The acetonitrile extract was taken to dryness by nitrogen blowdown and derivatized with 100 μL BSTFA, 100 μL pyridine and 300 μL dichloromethane at 60°C for 20 minutes (WS1C-901114-02TMS). Analysis was performed immediately after cooling to minimize degradation.

Results

Figure 11 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL aliquots of the 10 mL dichloromethane extract of WS1C. Figure 12 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL of the TMS extract of WS1C. Most of the organic content was accounted for by the presence of the following sample components.

Compounds	Spectra	Quantity (mg)
Dimethyl methylphosphonate	Annex 3	0.58
Trimethyl phosphate	Annex 4	0.38
Toluene	Annex 8	17
C_2-alkyl benzenes	Annex 9	
Dichlorvos	Annex 15	1.2
Dioctyl methylphosphonates	Annex 17	1.1
di-TMS derivative of methylphosphonic acid	Annex 12	0.04
tri-TMS derivative of phosphoric acid	Annex 13	0.05
TMS derivative of dimethyl phosphoric acid	Annex 18	0.1
tri-TMS derivative of phosphorous acid	Annex 19	1
di-TMS derivative of hydrogenphosphonic acid	Annex 20	0.07
di-TMS derivative of methyl phosphoric acid	Annex 21	0.02

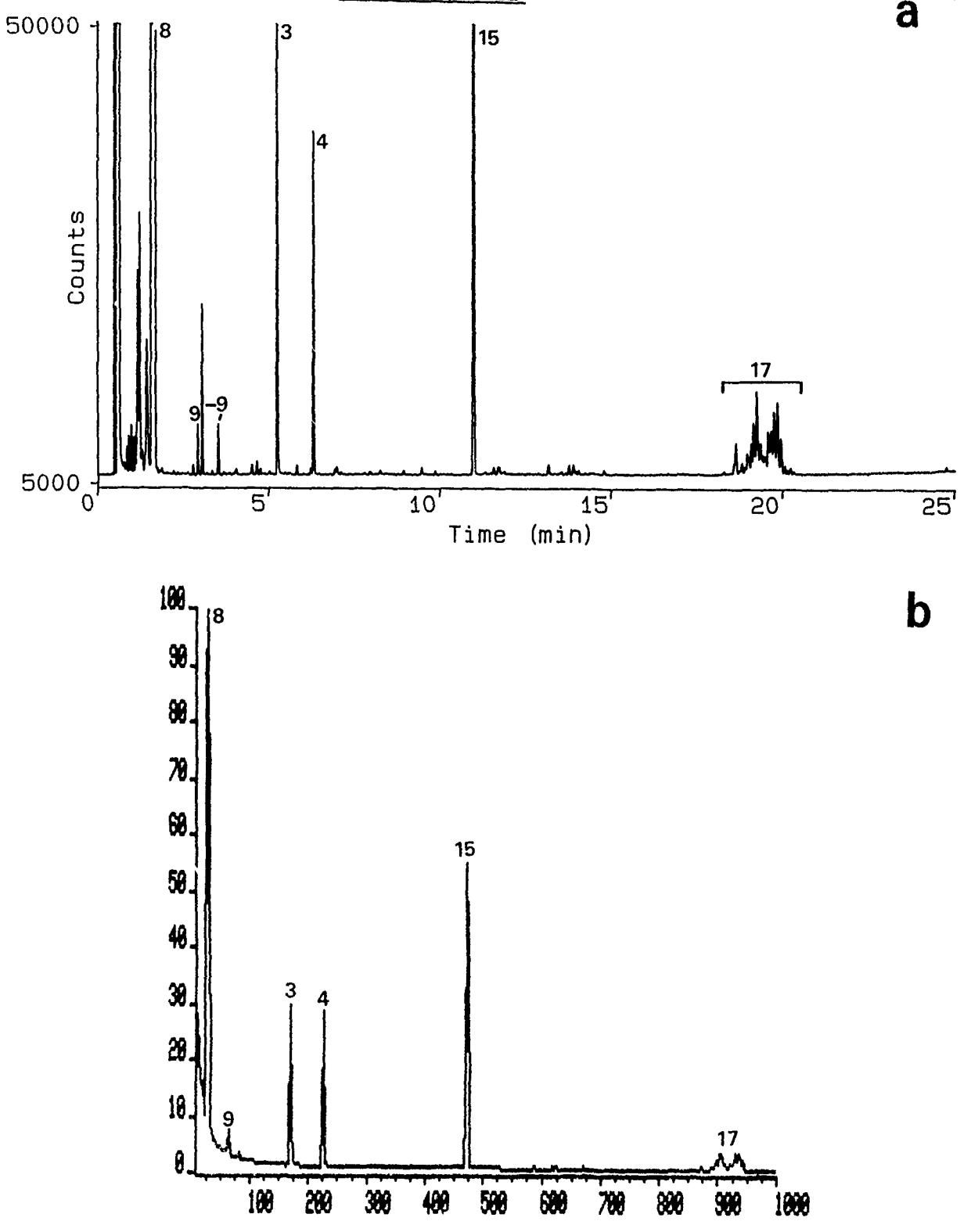


Figure 11: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of dichloromethane extract of WS1C. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

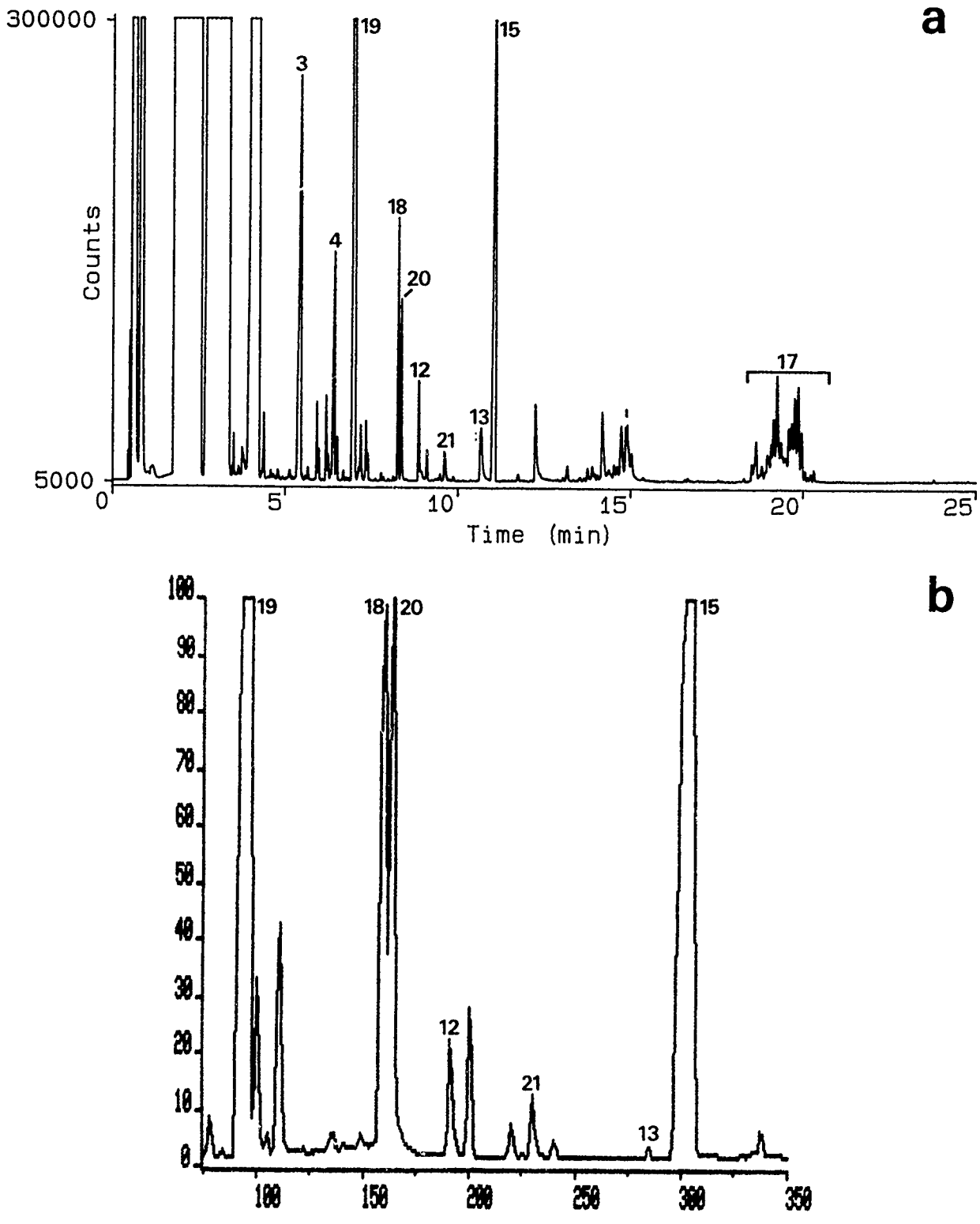


Figure 12: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of TMS derivative of acetonitrile extract of second WS1C. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

j) WS1X (XAD sample)

Sample Handling

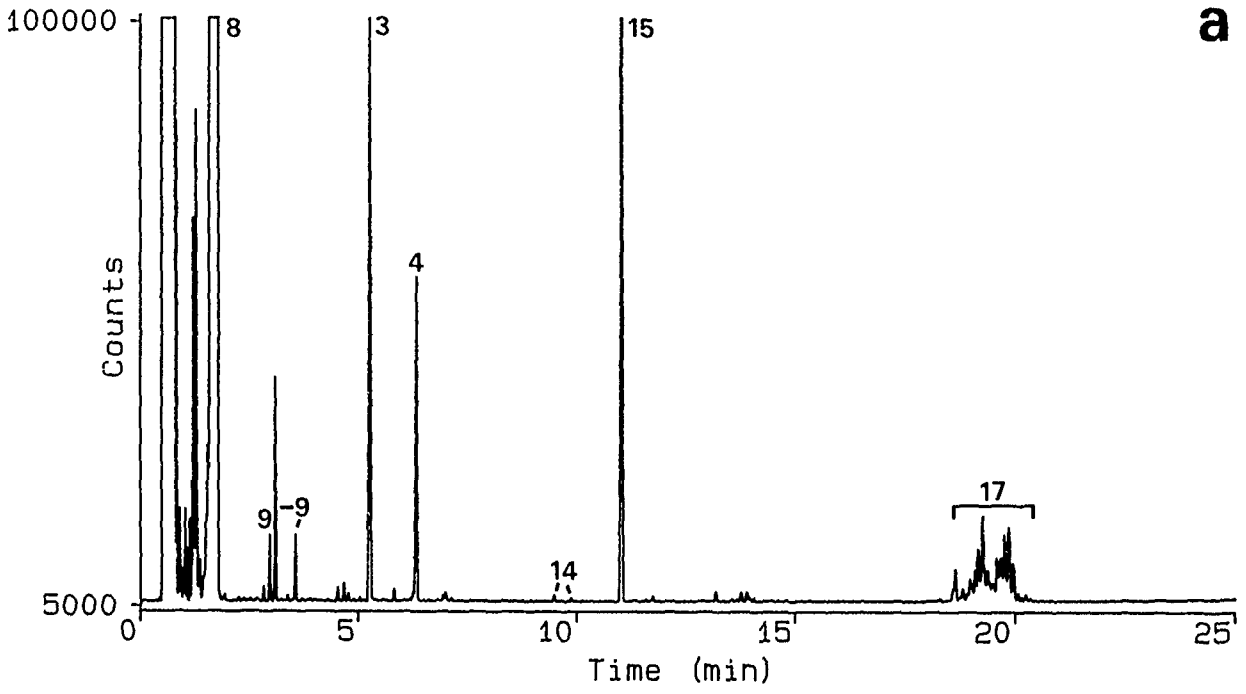
The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring at the top of the container. The XAD resin was removed into a 6 mL vial and ultrasonic extracted for 5 minutes with 2 mL of hexane. This extract was allowed to settle then removed and stored in a centrifuge tube prior to capillary column GC analysis (extract code name WS1X-901106-10M).

Trimethylsilylation was performed on the remaining XAD resin following ultrasonic extraction for 5 minutes with 1 mL of acetonitrile. The acetonitrile extract was taken to dryness under nitrogen and derivatized with 100 μL BSTFA, 100 μL pyridine and 300 μL dichloromethane at 60°C for 20 minutes (WS1X-901109-02TMS). Analysis was performed immediately after cooling to minimize degradation.

Results

Figure 13 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL aliquots of the 10 mL dichloromethane extract of WS1X. Figure 14 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL of the TMS extract of WS1X. Most of the organic content was accounted for by the presence of the following sample components.

Compounds	Spectra	Quantity (mg)
Dimethyl methylphosphonate	Annex 3	0.21
Trimethyl phosphate	Annex 4	0.12
Toluene	Annex 8	>5
C_2-alkyl benzenes	Annex 9	
Chloroethenyl dimethyl phosphates	Annex 14	
Dichlorvos	Annex 15	0.3
Dioctyl methylphosphonates	Annex 17	0.3
di-TMS derivative of methylphosphonic acid	Annex 12	0.017
tri-TMS derivative of phosphoric acid	Annex 13	0.023
TMS derivative of dimethyl phosphoric acid	Annex 18	0.07
tri-TMS derivative of phosphorous acid	Annex 19	0.25
di-TMS derivative of hydrogenphosphonic acid	Annex 20	0.021
di-TMS derivative of methyl phosphoric acid	Annex 21	0.006



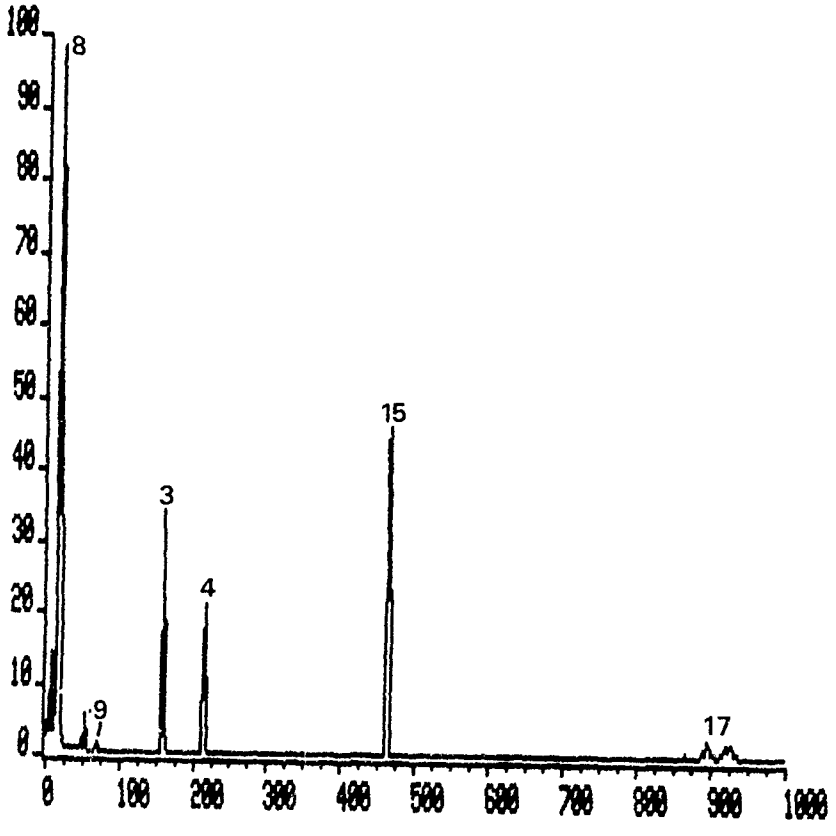


Figure 13: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of hexane extract of WS1X. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

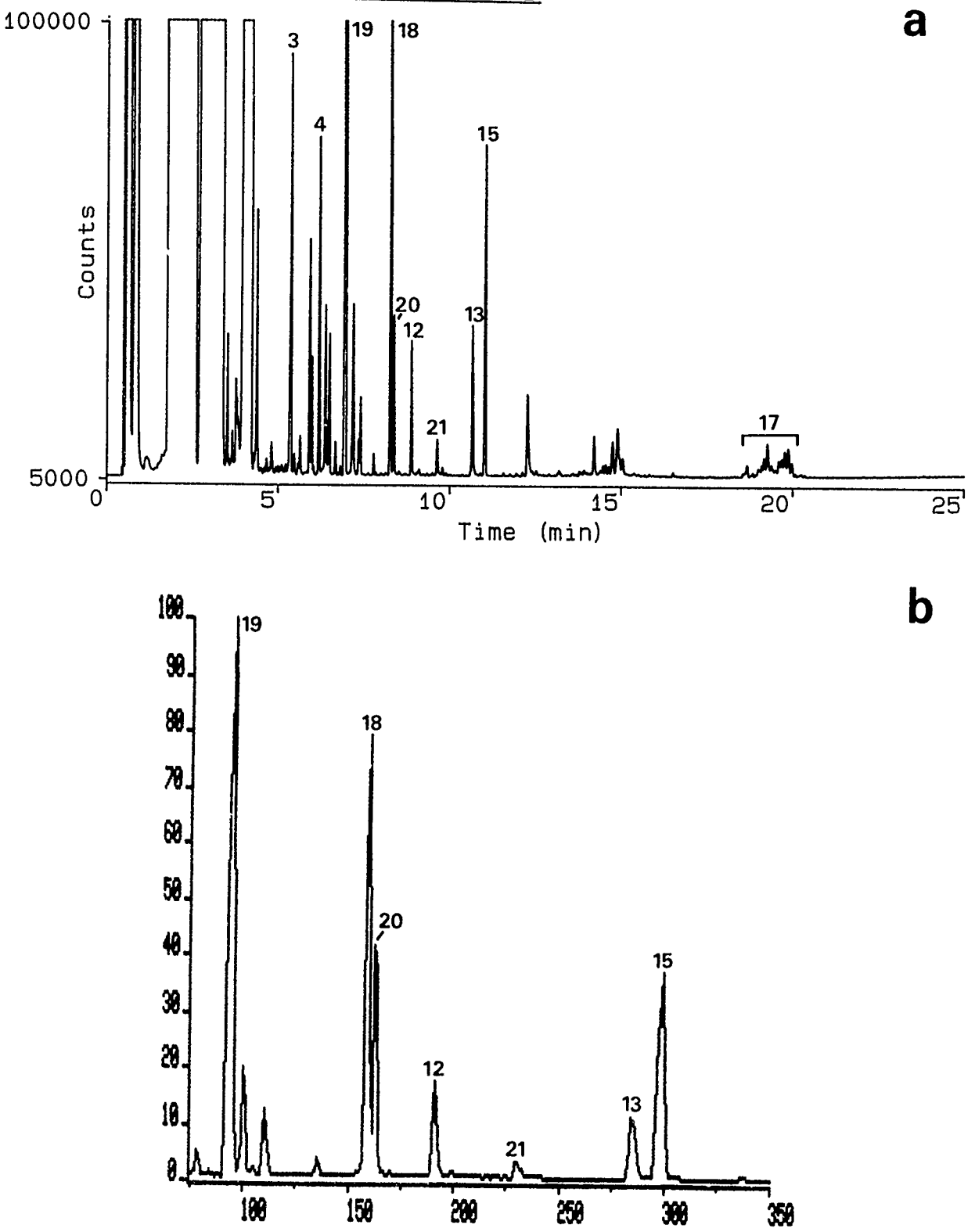


Figure 14: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of TMS derivative of acetonitrile extract of WS1X. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

k) WS2 (Aqueous sample)

Sample Handling

The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring at the top of the container. The aqueous sample was extracted with 2 x 1 mL of hexane in a 6 mL glass vial. This extract was then removed and stored in a centrifuge tube prior to capillary column GC analysis (extract code name WS2-901106-11H). A second extraction with 2 x 1 mL of dichloromethane was performed similarly (extract code name WS2-901106-12M).

Trimethylsilylation was performed after bringing the remaining aqueous sample to dryness under nitrogen. The sample was dissolved in 2 mL of acetonitrile. A 100 μL aliquot of the acetonitrile extract was dried and derivatized with 100 μL BSTFA, 100 μL pyridine and 100 μL dichloromethane at 60°C for 20 minutes (WS2-901108-01TMS). Analysis was performed immediately after cooling to minimize degradation.

Results

Figure 15 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 1 μL aliquots of the hexane extract of WS2. The dichloromethane extract was clean, indicating good hexane extraction. Figure 16 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 1 μL aliquots of the TMS extract of WS2. Most of the organic content was accounted for by the following sample components.

Compounds	Spectra	Quantity (mg)
C_8-alcohols	Annex 10	0.13
Dioctyl methylphosphonates	Annex 17	3
di-TMS derivative of methylphosphonic acid	Annex 12	
tri-TMS derivative of phosphoric acid	Annex 13	
TMS derivative of dimethyl phosphoric acid	Annex 18	0.14

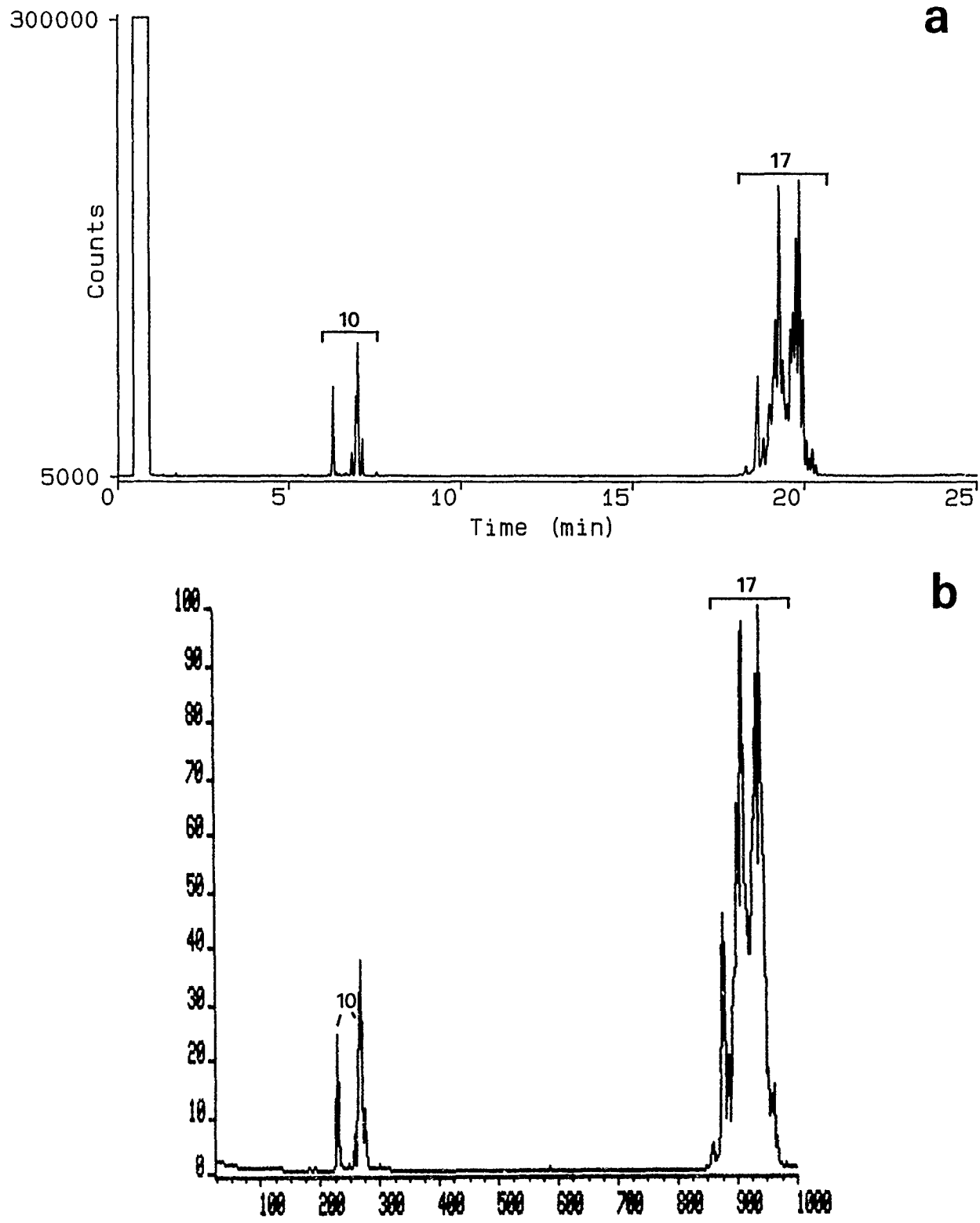


Figure 15: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of hexane extract of WS2. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

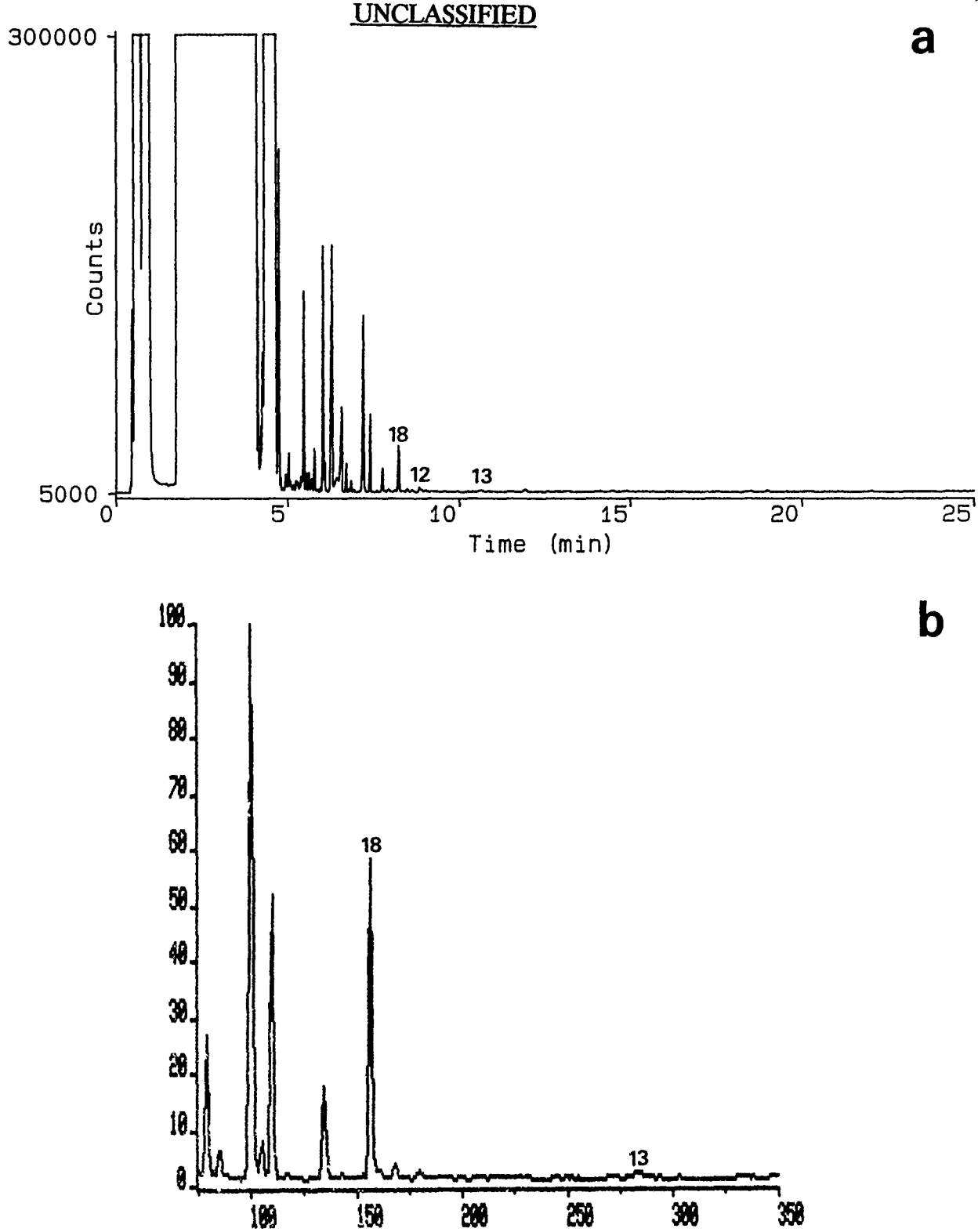


Figure 16: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of TMS derivative of dried WS2. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

l) RC (Charcoal sample)

Sample Handling

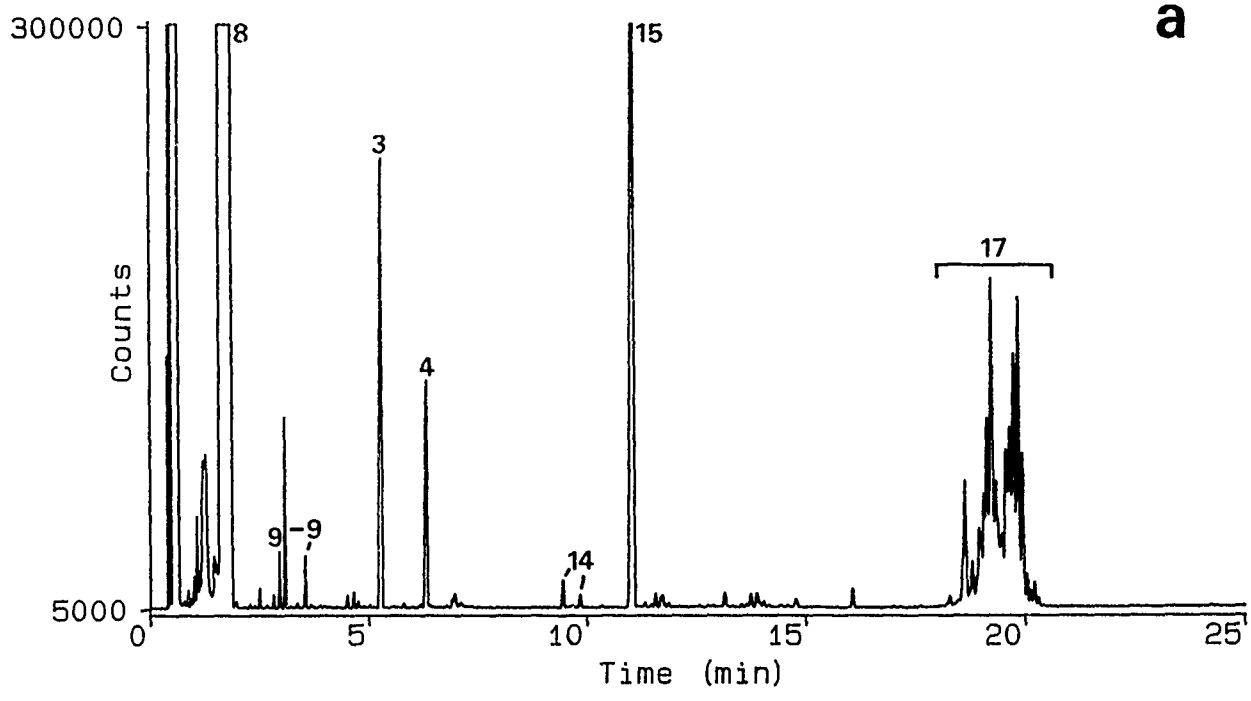
The label from the glass container was removed and the outer glass surface was cleaned with dichloromethane prior to scoring at the top of the container. The charcoal sample was removed, put in a 6 mL vial, and ultrasonic extracted for 5 minutes with 1 mL of dichloromethane. This extract was removed into a centrifuge vial and spun for 2 minutes at 2000 rpms prior to capillary column GC analysis (extract code name RC-901106-02M).

The dichloromethane extract (after GC analysis) was put in the vial containing the extracted charcoal and taken to dryness under nitrogen. This sample was then ultrasonic extracted for 2 minutes with 1 mL of acetonitrile. The extract was removed into a centrifuge vial and spun for 2 minutes at 2000 rpms, removed into a 1.8 mL vial, and taken to dryness under nitrogen. The sample was derivatized with 100 μL BSTFA, 100 μL pyridine and 100 μL dichloromethane at 60°C for 20 minutes (extract code name RC-901114-01TMS). Analysis was performed immediately after cooling to minimize degradation.

Results

Figure 17 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.6 μL and 0.25 μL aliquots respectively of the dichloromethane extract of RC. Figure 18 illustrates capillary column GC-FID and GC-MS chromatograms obtained during analysis of 0.5 μL aliquots of the TMS extract of RC. Most of the organic content was accounted for by the presence of the following sample components.

Compounds	Spectra	Quantity (mg)
Dimethyl methylphosphonate	Annex 3	0.36
Trimethyl phosphate	Annex 4	0.18
Toluene	Annex 8	>4
C_2-alkyl benzenes	Annex 9	
Chloroethenyl dimethyl phosphates	Annex 14	
Dichlorvos	Annex 15	0.9
Dioctyl methylphosphonates	Annex 17	2.3
di-TMS derivative of methylphosphonic acid	Annex 12	
TMS derivative of dimethyl phosphoric acid	Annex 18	0.28
di-TMS derivative of hydrogenphosphonic acid	Annex 20	
di-TMS derivative of methyl phosphoric acid	Annex 21	



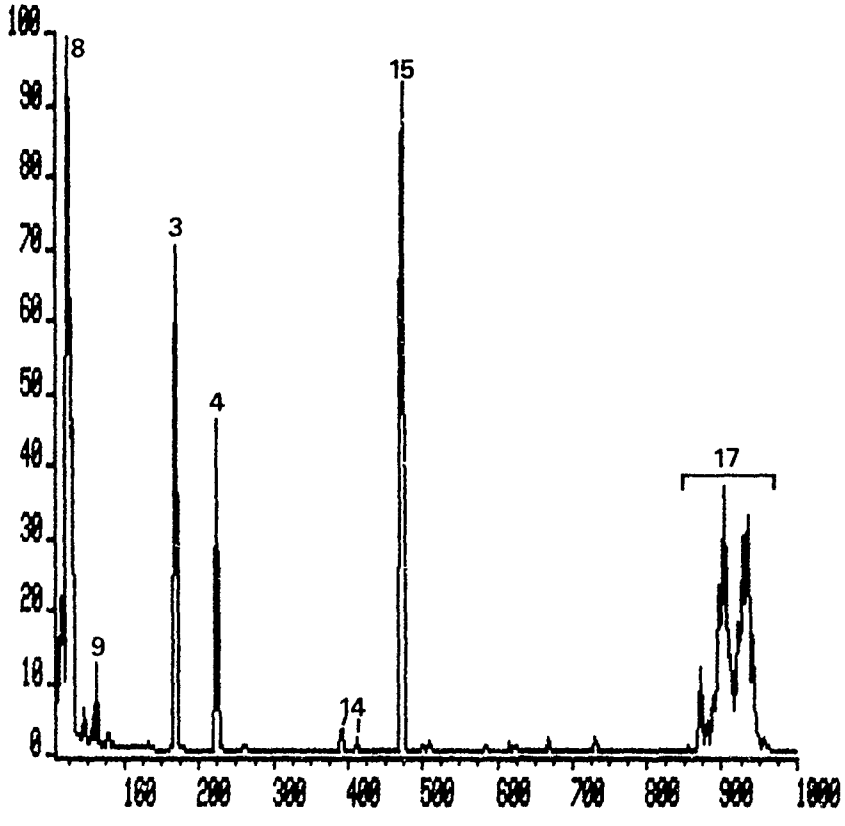


Figure 17: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of dichloromethane extract of RC. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

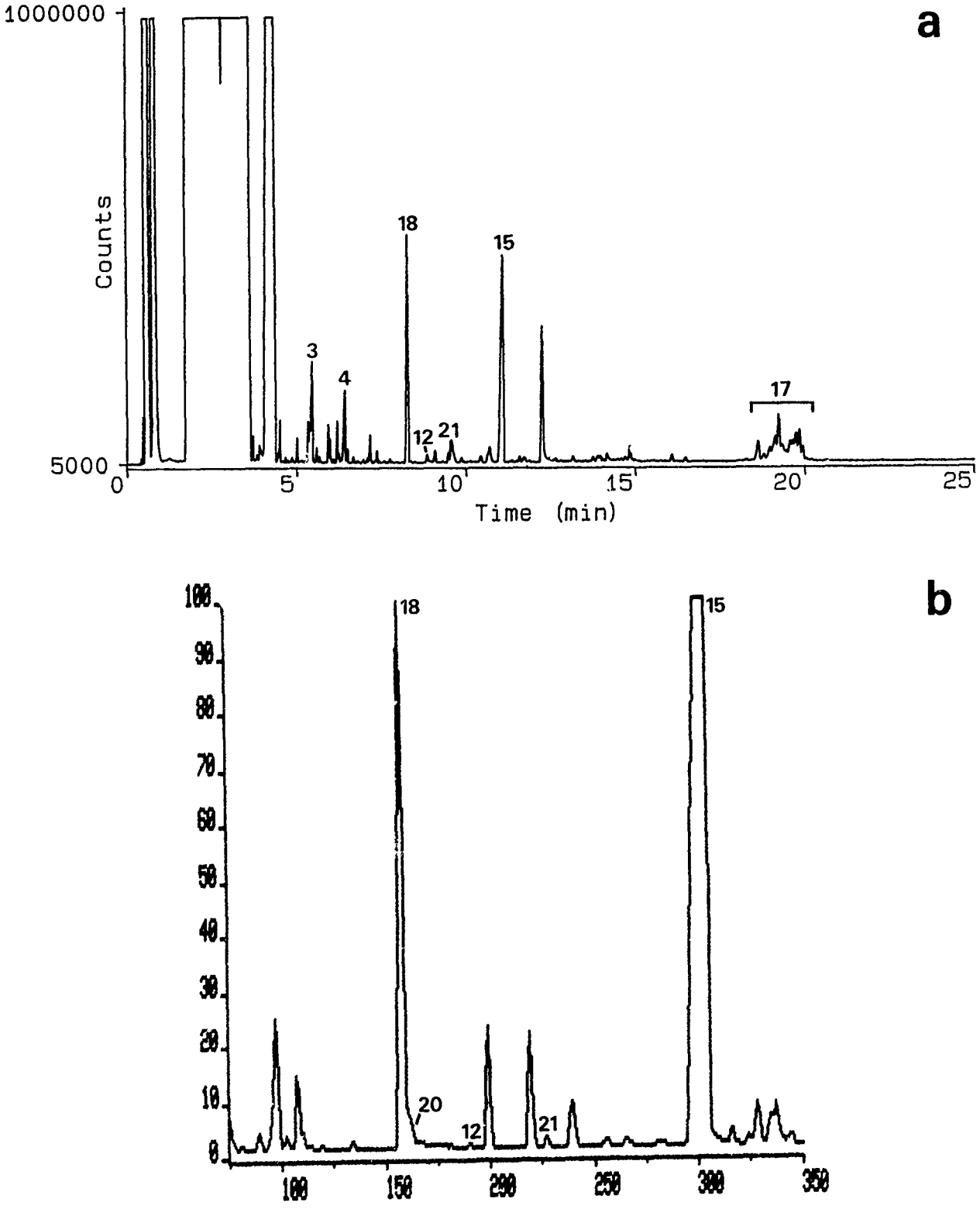


Figure 18: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of TMS derivative of acetonitrile extract of RC. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

DISCUSSION

DRES adopted the following general philosophy for the chromatographic analysis of the twenty-nine samples and blanks received for analysis. The following steps indicate the order of analysis at DRES:

a) Capillary column GC-FID screening of solvents (e.g., hexane, dichloromethane) used for extraction of samples.

b) Capillary column GC-FID (and when required GC-MS) screening of blank sample extracts to ascertain the levels of potential interference and the presence of any scheduled or unusual compounds.

c) One sample at a time was extracted with dichloromethane or hexane and analysed by capillary column GC with MS, FTIR, FID and FPD (phosphorus mode) detection. Once completed the next sample was subjected to extraction and analysis. The sample order was from feedstock to waste (i.e., FS1 to WS2).

d) Sample components were confirmed by comparison with standard data, comparison with library data or by interpretation of the spectrometric data acquired. The availability of standards or library data has been indicated in the captions of Annexes 1 to 21.

e) Trimethylsilylation of acetonitrile (or dichloromethane) sample extracts was performed on the samples thought to most likely contain nonvolatile degradation products.

f) All sample extract components though to possess a phosphorus atom were subjected to GC-FPD analysis to confirm this finding.

g) Capillary column GC-MS (EI) chromatograms of all the hexane and dichloromethane extracts of the samples were screened for the presence of the CW agents GB, GD, GA, GF, VX, H, Q and T using reconstructed ion current chromatograms. Minor or trace sample component EI mass spectra were checked to be sure that they did represent, in the best opinion of the laboratory, scheduled compounds.

h) A semi-quantitative estimate of major sample components was done using capillary column GC-FID data. In several instances integration saturation occurred. This has been indicated by the greater than symbol (>).

i) The duplicate samples provided were only analysed if required.

The solvent extracts of the blank media provided were fairly clean and free of potential interferences with the exception of the XAD resin. A small amount of toluene was detected following hexane extraction of the XAD resin blank (XB). The only other point worthy of consideration during blank analyses was the length of time used for swab extraction. Prolonged extraction with hexane or dichloromethane led to high levels of contamination. It was found that a fast (2 minute) extraction greatly minimized extraction of the swab materials and led to minimal contamination.

The compounds identified during chromatographic analysis of the samples are indicated in the Results section along with an estimate of amount. Compounds related to the production of the pesticide dichlorvos were detected along with several scheduled compounds, including a cluster of dioctyl methylphosphonates. The presence of two additional scheduled compounds in FS1, dimethyl phosphite and dimethyl methylphosphate,

is probably usual for a trimethyl phosphite feedstock, as both these compounds (as well as trimethyl phosphate) were detected in an unpurified DRES standard of trimethyl phosphite. Some of the phosphorus containing acids were likely due to degradation of this feedstock. Tables IX and X list the non-scheduled and scheduled compounds respectively identified in the samples. None of the CW agents screened for were detected during full scanning EI operation.

PART II: NMR ANALYSIS AND SYNTHESIS

INTRODUCTION

The samples of the Round Robin exercise were analyzed by NMR to provide additional data, such as ^{31}P chemical shift data, to support the identification of phosphorus compounds in Part I. Extracts, which had shown phosphorus containing compounds by GC/GC-MS analysis, were directly screened by phosphorus NMR without further sample handling (for details regarding sample handling see Part 1). The duplicate samples of PS-1 and PS-2 were extracted with a deuterated solvent ($CDCl_3$) for ^{1}H and ^{13}C NMR analysis and the duplicate sample of WS1X was extracted with CD_3CN for further ^{31}P analysis. The aqueous sample, WS2, was analyzed directly without extraction.

EXPERIMENTAL

General

All reactions, unless otherwise indicated were performed under a positive pressure of dry N2. All solvents employed were reagent grade or better; anhydrous solvents were prepared according to standard methods. Triethylamine (TEA) was distilled from NaOH. The term *in vacuo* refers to removal of solvent by Buchi Rotavapor at water aspirator vacuum followed by 0.1 mm Hg vacuum.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian VXR 300S NMR operating at the following frequencies (MHz); ^{1}H: 299.949, ^{13}C: 75.429, and ^{31}P: 121.421. ^{1}H and ^{13}C spectra are referenced using the solvent as internal reference; ^{1}H: δ 7.27 ($CHCl_3$); ^{13}C: δ 77.0 ($CDCl_3$). All ^{31}P NMR spectra are proton decoupled and were referenced to either external triethyl phosphate (TEP, δ -1.0) or external H_3PO_4 (δ 0.00). Standard Varian pulse sequences were employed using the conditions shown in Table 3. Temperature was regulated at 25°C throughout all acquisitions. Other acquisition parameters are shown in Table VII.

TABLE VII: NMR Conditions			
Country:	Canada		
Instrument:	Varian VXR 300 S		
Probe:	5 mm $^{1}H/^{19}F$, BB		
	Acquisition Parameters		
	^{1}H	^{19}F	^{31}P
np	29952	32000	59008
sw	4000	18000	38731
tpwr	62	60	55
pw	7.0	7.0	10
nt	as given on individual spectra		
solvent	as given on individual spectra		

Synthesis of Dioctyl methylphosphonates

Di-n-octyl methylphosphonate

1-Octanol (Fischer Tech. Grade, 0.02 mole, 2.60 g) and triethylamine (0.02 mole, 2.02 g) in toluene (15 mL) was added dropwise to stirred solution of methylphosphonodichloridate (0.01 mole, 1.32 g) in toluene (15 mL). The reaction mixture was heated to 80°C overnight. The precipitate was then removed by filtration and the filtrate concentrated *in vacuo.* The product was purified by Kugelrohr distillation (220°, 0.1 mm Hg) to give 2.45 g (76.6%) of a colourless oil. See Annexes 22 to 25 for NMR data.

Di-2-octyl methylphosphonate

Di-2-octyl methylphosphonate was prepared from technical grade 2-octanol as described above. The product was purified by Kugelrohr distillation (220°, 0.1 mm Hg) to give 2.35 g (73.4%) of a colourless oil. See Annexes 22 to 25 for NMR data.

RESULTS

Because of the large number of components present in these samples, the data is limited to the proton decoupled ^{31}P NMR data which minimizes the problem of overlapping signals which can occur in ^{1}H and ^{13}C NMR spectra. The identification of dichlorvos as the product of the pesticide production plant was confirmed from the ^{1}H and ^{13}C data (Table VIII, Figures 27, 28). This data, in addition to the GC-MS and GC-FTIR data previously reported, provides complete and unambiguous identification of this compound. Other compounds confirmed by NMR analysis are given in the figures.

The spectra and identification of compounds, based on comparison to either

authentic standards available in this laboratory, literature NMR data, or in some cases, newly synthesized compounds, are shown in Figures 19-28 . ^{31}P NMR spectra are shown with the largest component full-scale; in some instances minor components are reported in the list but are not evident in the spectrum. Baseline expansions for the ^{1}H analysis of PS-1 are given.

Two octyl methylphosphonates were synthesized to provide synthetic standards for both ^{31}P NMR analysis, as well as GC-FTIR and GC-MS analysis, and compound identification.

TABLE VIII: NMR analysis of Round Robin Samples.

EXTRACT CODE[2]	NMR ANALYSIS[3] (nucleus)					
	^{31}P[4]		^{1}H		^{13}C	
	CODE	FIG	CODE	FIG	CODE	
FS1-901105-01M	CAB221B	19				
RV-901105-07M	CAB221D	20				
PS1-901105-08M	CAB221E	21	CAB224A	27	CAB224C	28
PS2-901105-09M	CAB221G	22	CAB227h		CAB227C	
WS1C-901105-09M	CAB221H	23				
WS1X-901106-10M	CAB221J CAB222B	24 25				
WS2-901106-12M	CAB222A	26				

[2] For details regarding sample handling and extraction procedures, see Part I.

[3] Blank entries denote no NMR analysis performed (see text for explanation).

[4] All samples were run unlocked except for CAB222B.

TABLE VIII: NMR data of dichlorvos.

	^{1}H (CAB224A)		^{13}C (CAB224C)		^{13}C (lit.)[5]	
	δ (ppm)	J_{PH} (Hz)	δ (ppm)	J_{PC} (Hz)	δ (ppm)	J_{PC} (Hz)
1	7.00	2.4	133.63	4.38	132.50	3.3
2	--	--	114.03	14.33	111.80	13.9
3a,b	3.689	11.7	55.21	6.56	53.5	6.0

[5] G. Szalontai, Org. Magn. Resonance, **10**, 63 (1977).

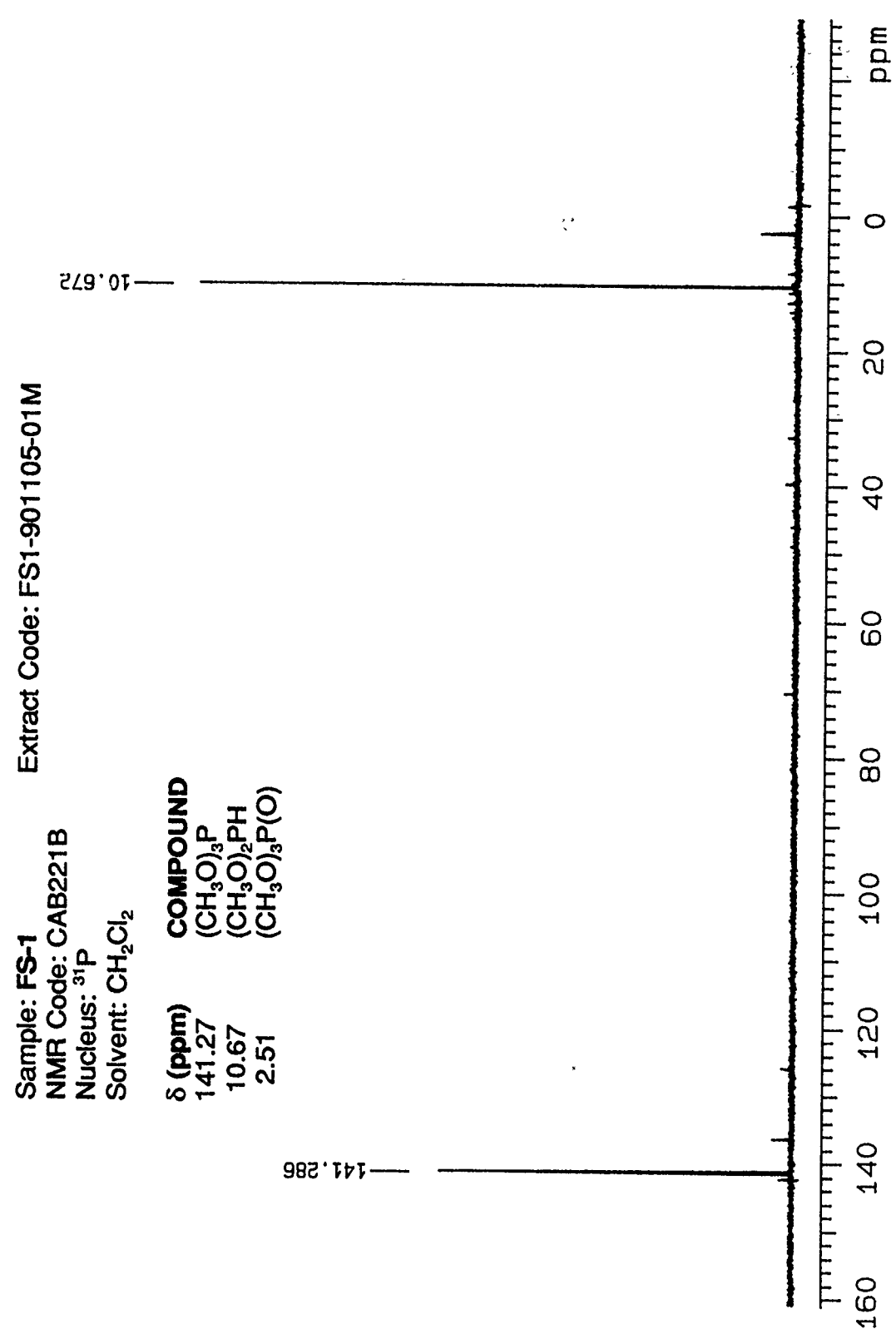


Figure 19: Proton decoupled ^{31}P NMR of FS-1 (nt = 512).

Sample: **RV** Extract Code: RV-901105-07M
NMR Code: CAB221D
Nucleus: ^{31}P
Solvent: CH_2Cl_2

δ (ppm)	COMPOUND
2.51	$(CH_3O)_3P(O)$
- 3.24	DICHLORVOS

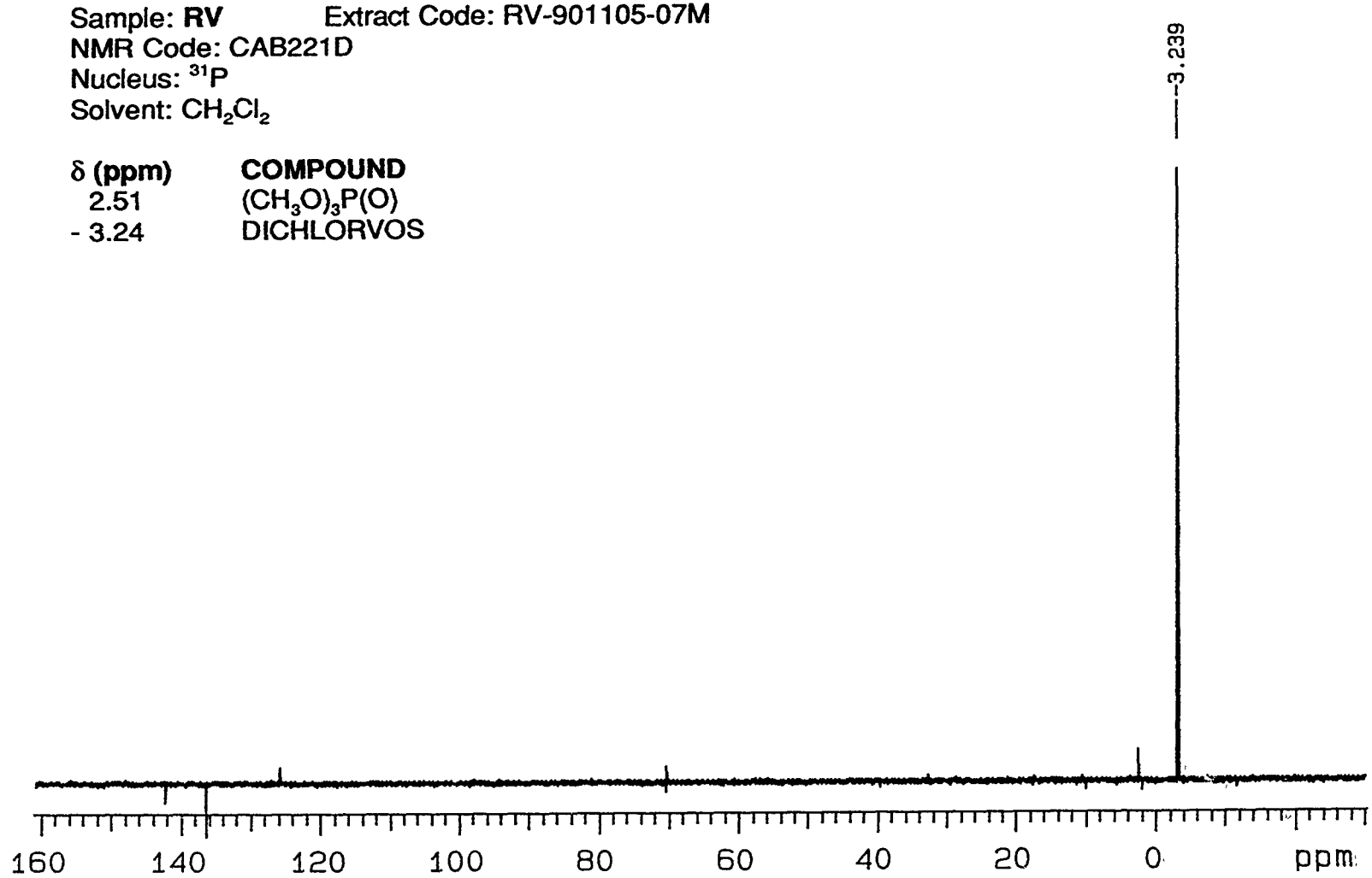


Figure 20: Proton decoupled ^{31}P NMR spectrum of RV (nt = 16384).

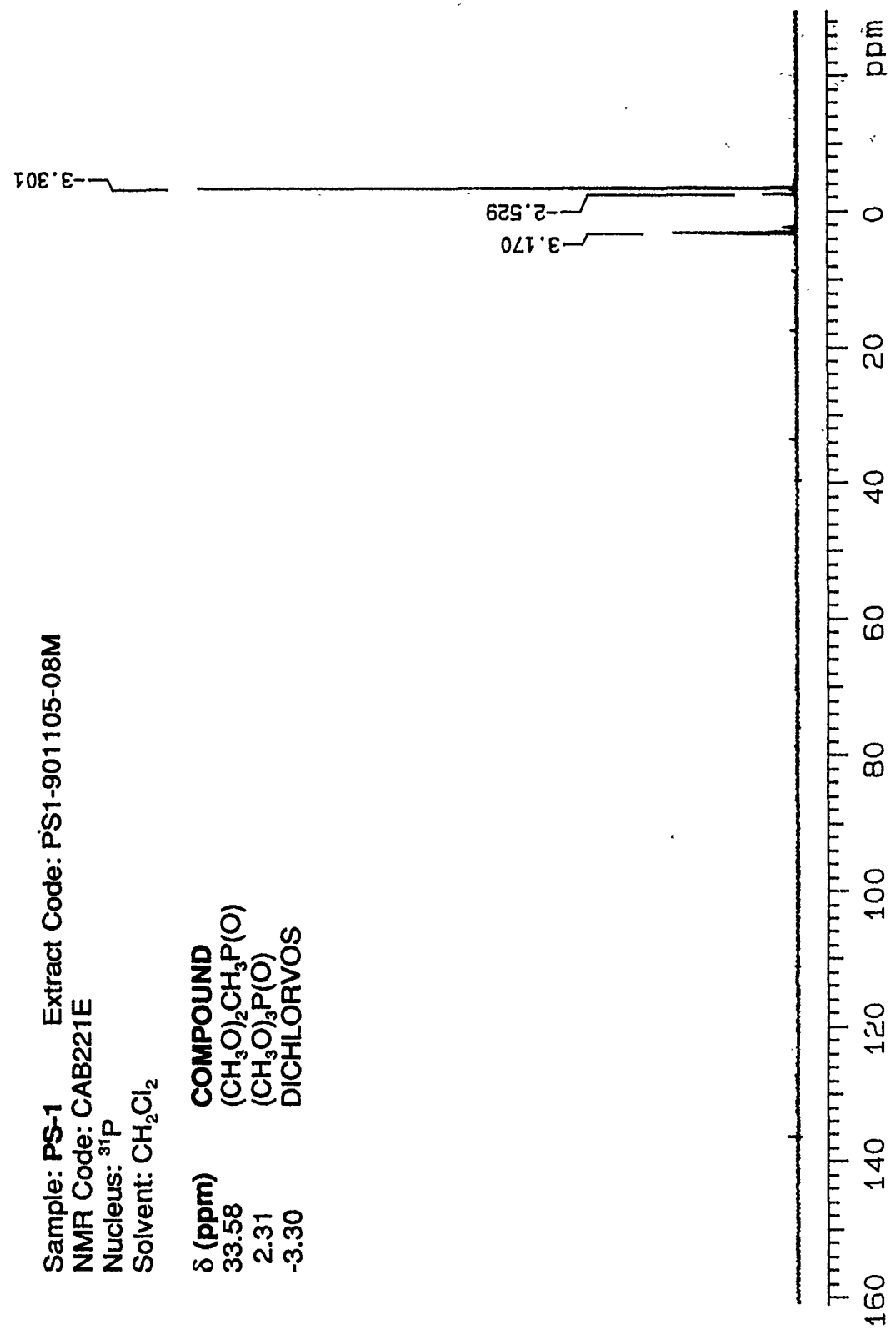


Figure 21: Proton decoupled ^{31}P NMR spectrum of PS-1 (nt = 4096).

Sample: **PS-2** Extract Code: PS2-901105-09M
NMR Code: CAB221G
Nucleus: P-31
Solvent: CH_2Cl_2
nt=4096

δ (ppm)	COMPOUND
39.71	
17.49	
4.57	$CH_3P(O)(OH)_2$
3.53	
2.46	$(CH_3O)_3P(O)$
-3.26	DICHLORVOS

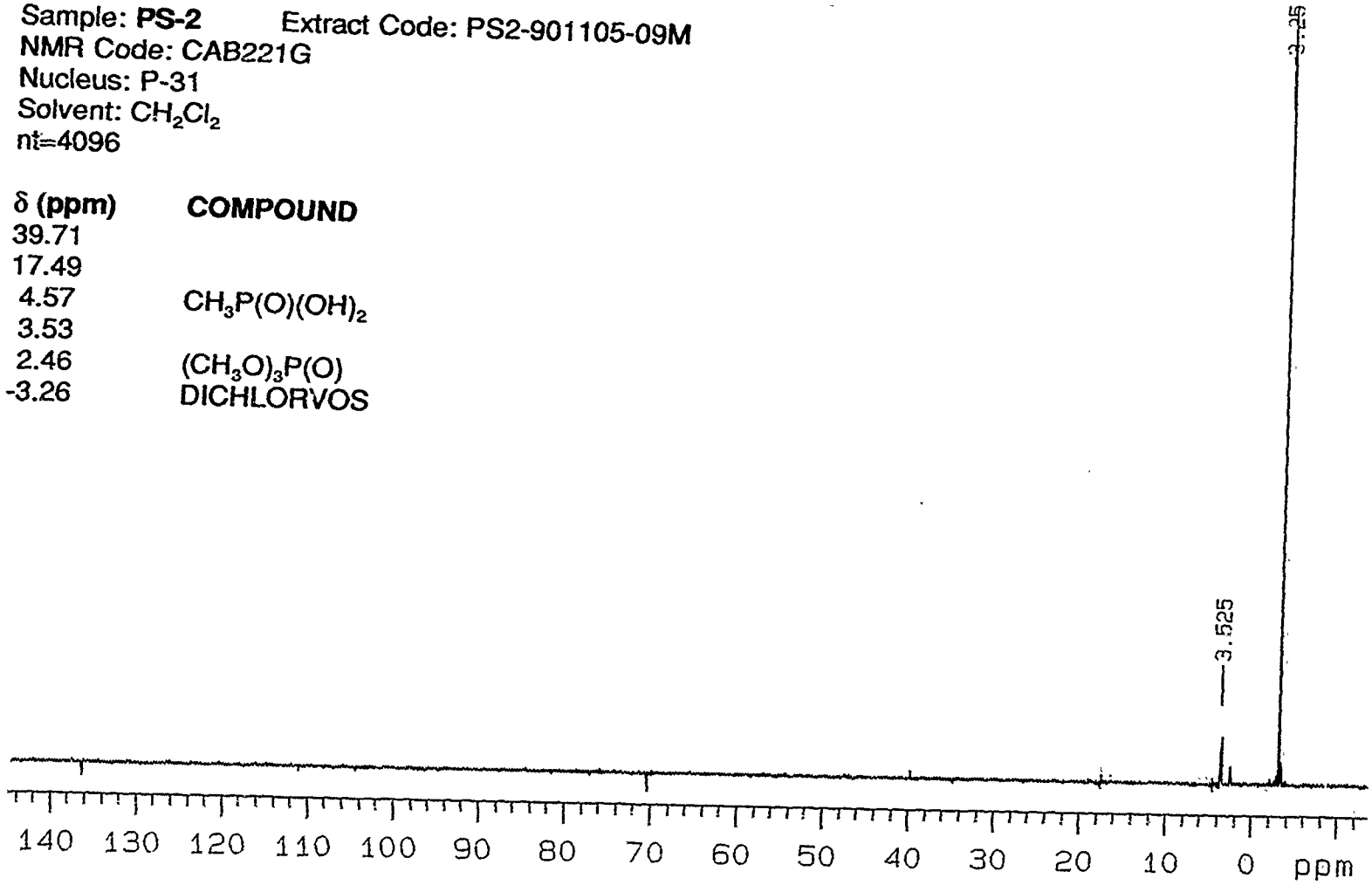


Figure 22: Proton decoupled ^{31}P NMR spectrum of PS-2 (nt = 4096).

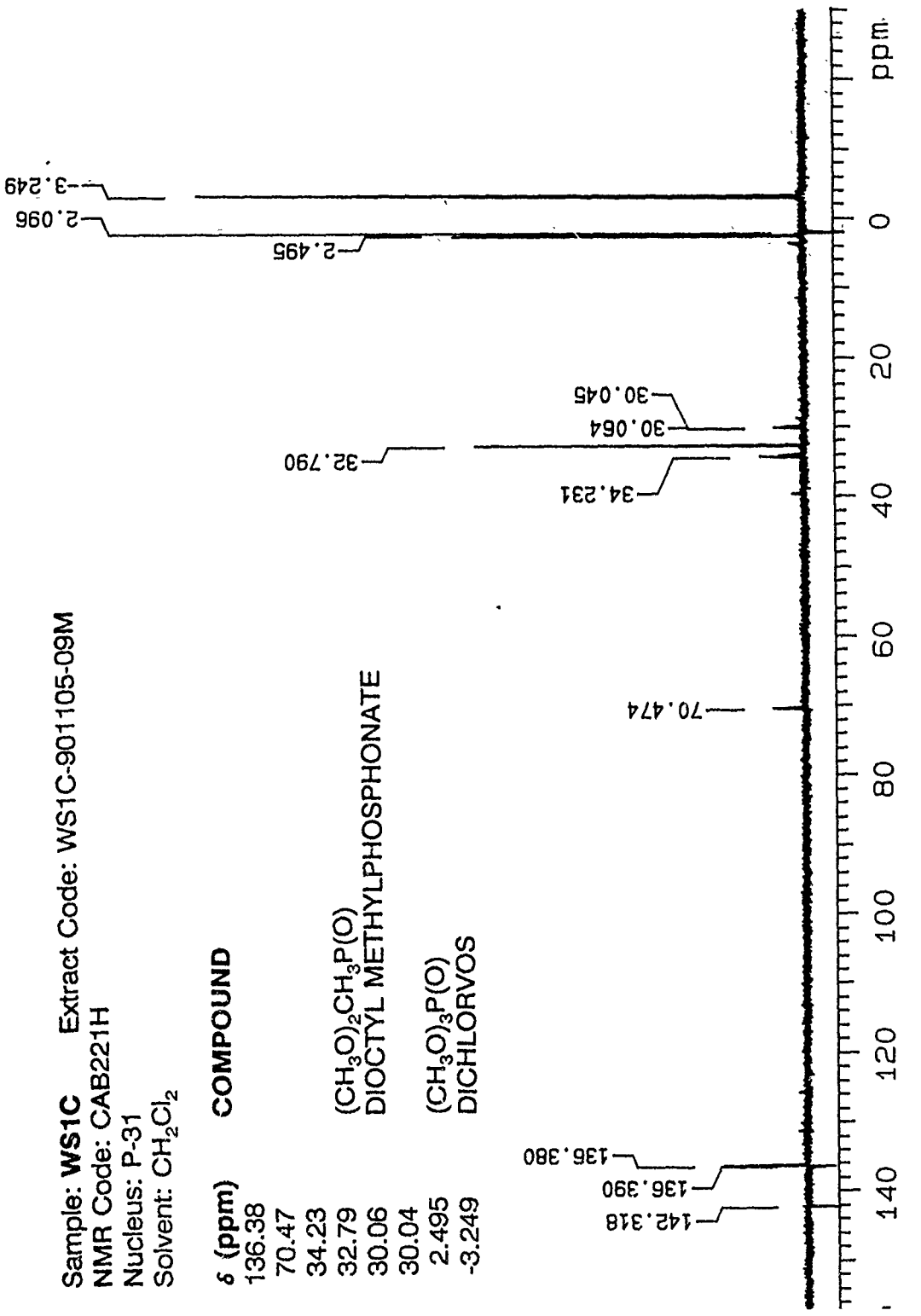


Figure 23: Proton decoupled ^{31}P NMR spectrum of WS1C (nt = 655356).

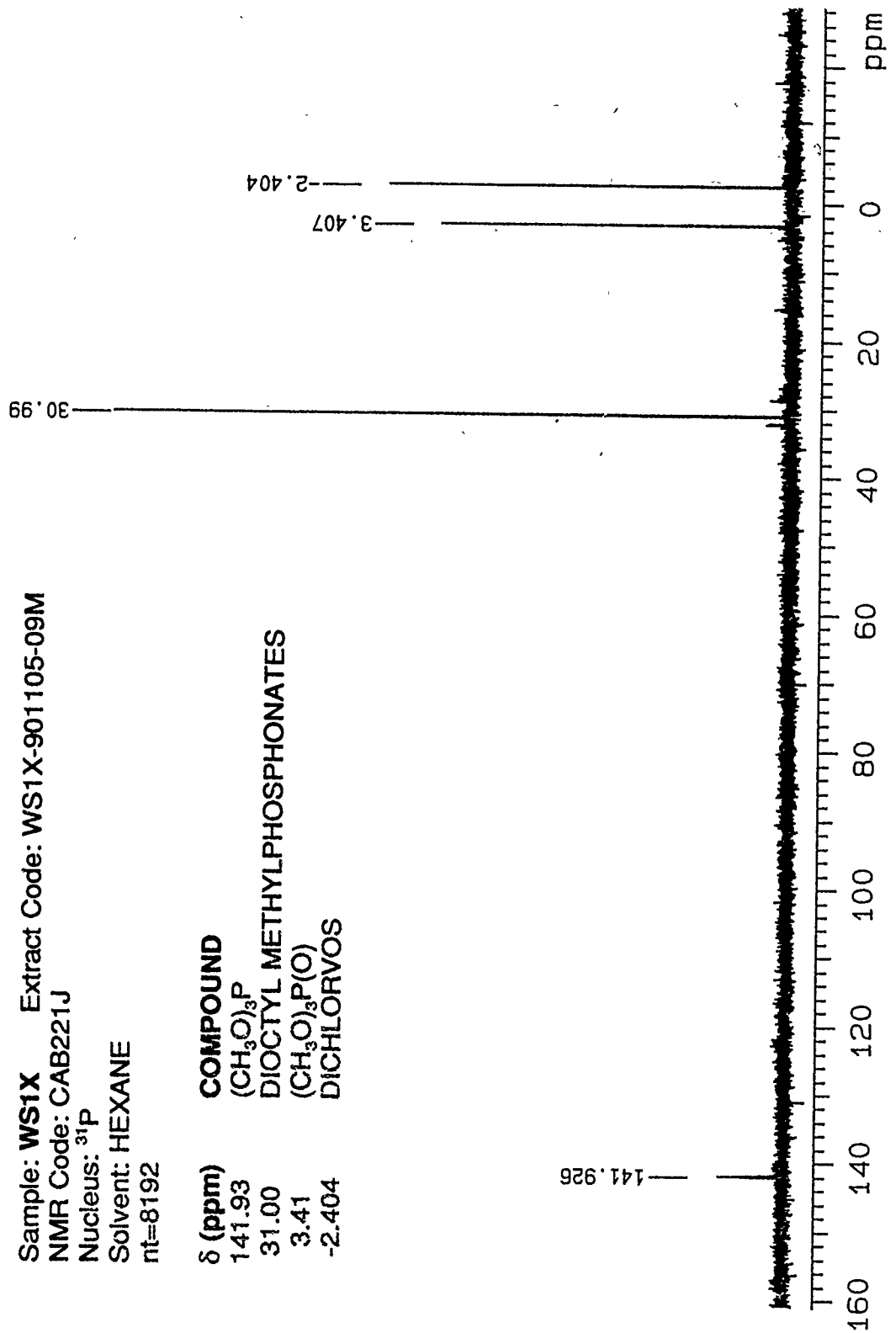


Figure 24: Proton decoupled ^{31}P NMR spectrum of WS1X (nt = 4096).

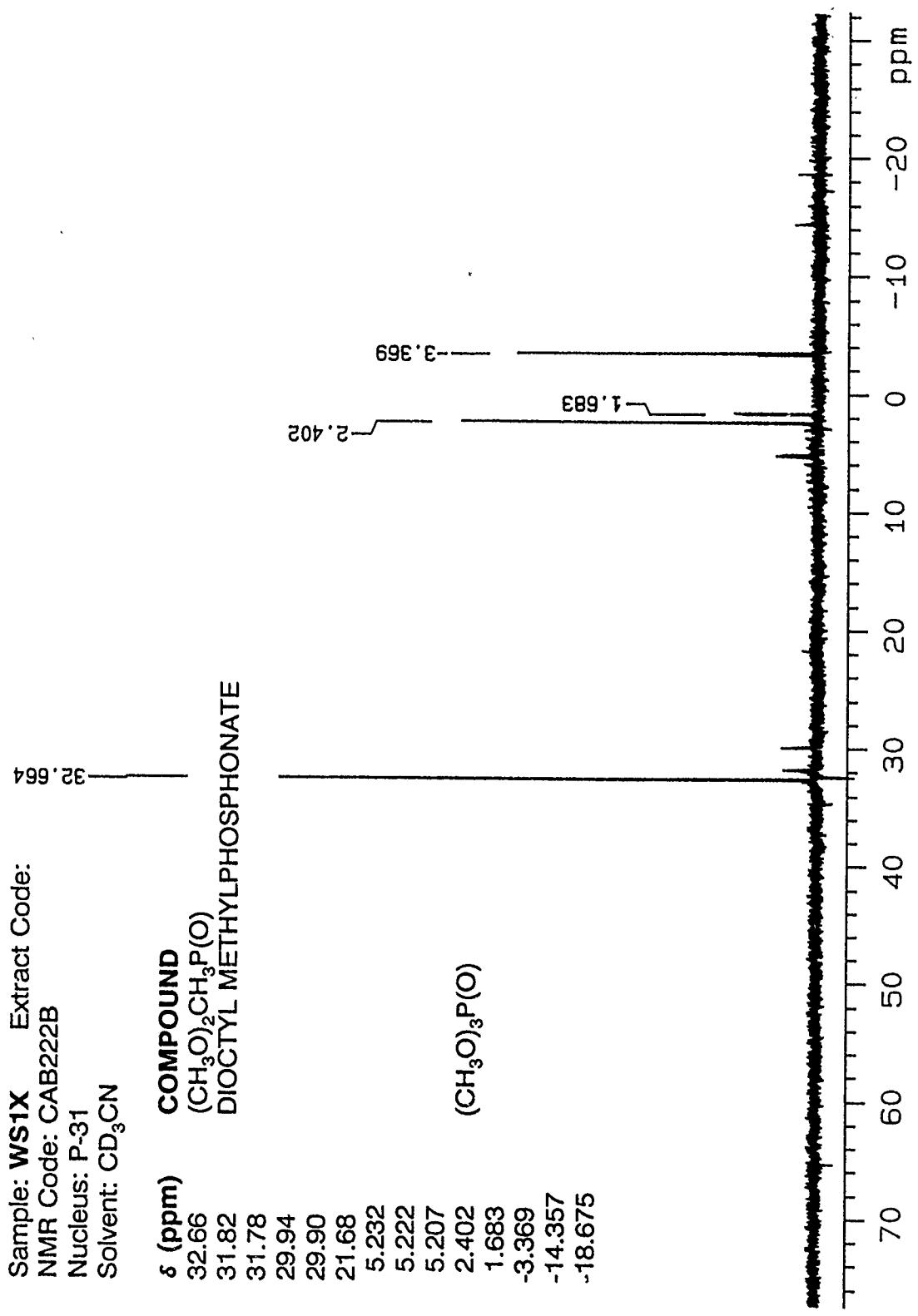


Figure 25: Proton decoupled ^{31}P NMR spectrum of WS1X (nt = 8192).

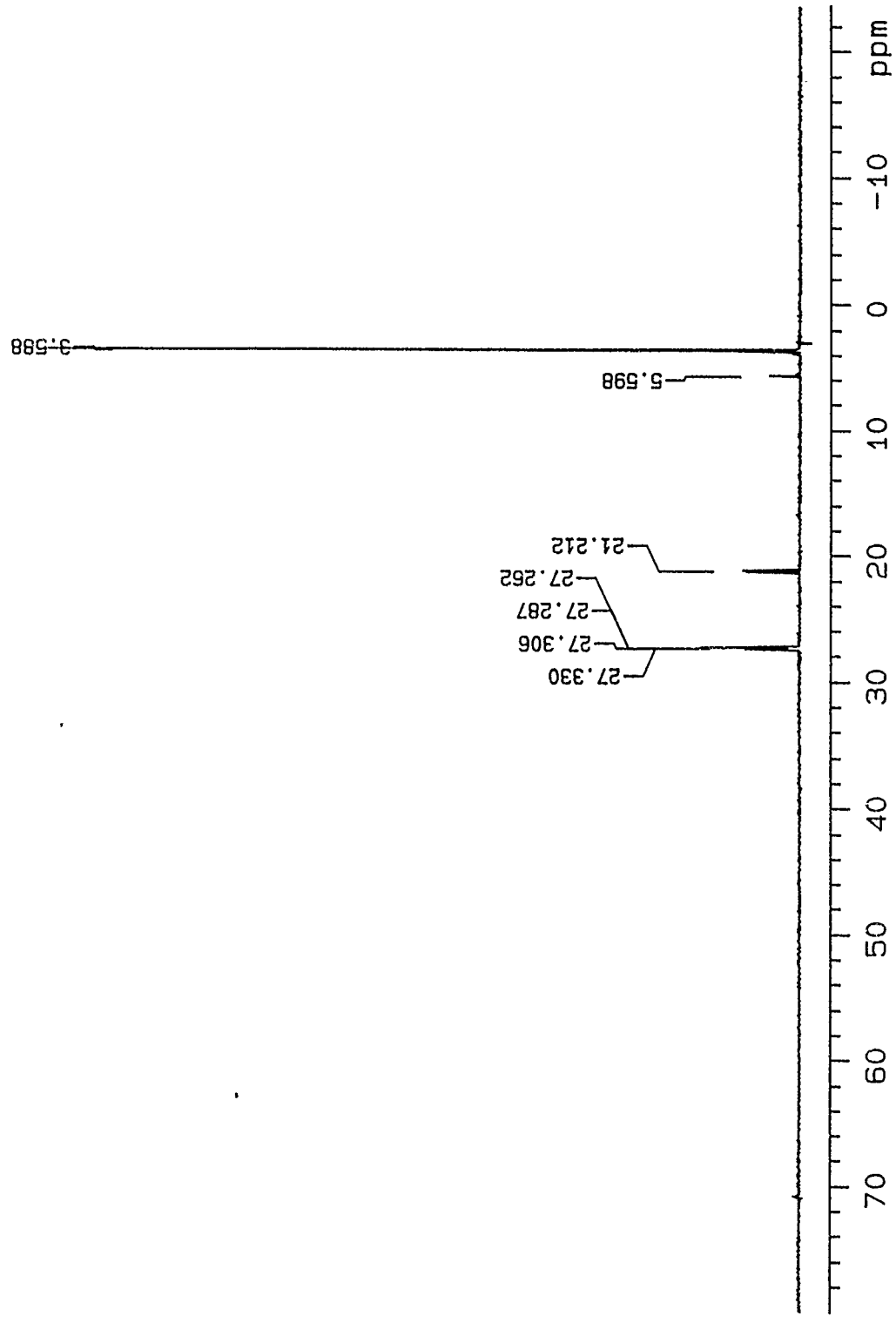


Figure 26: Proton decoupled ^{31}P NMR spectrum of WS2 (solvent: H_2O, nt = 8192).

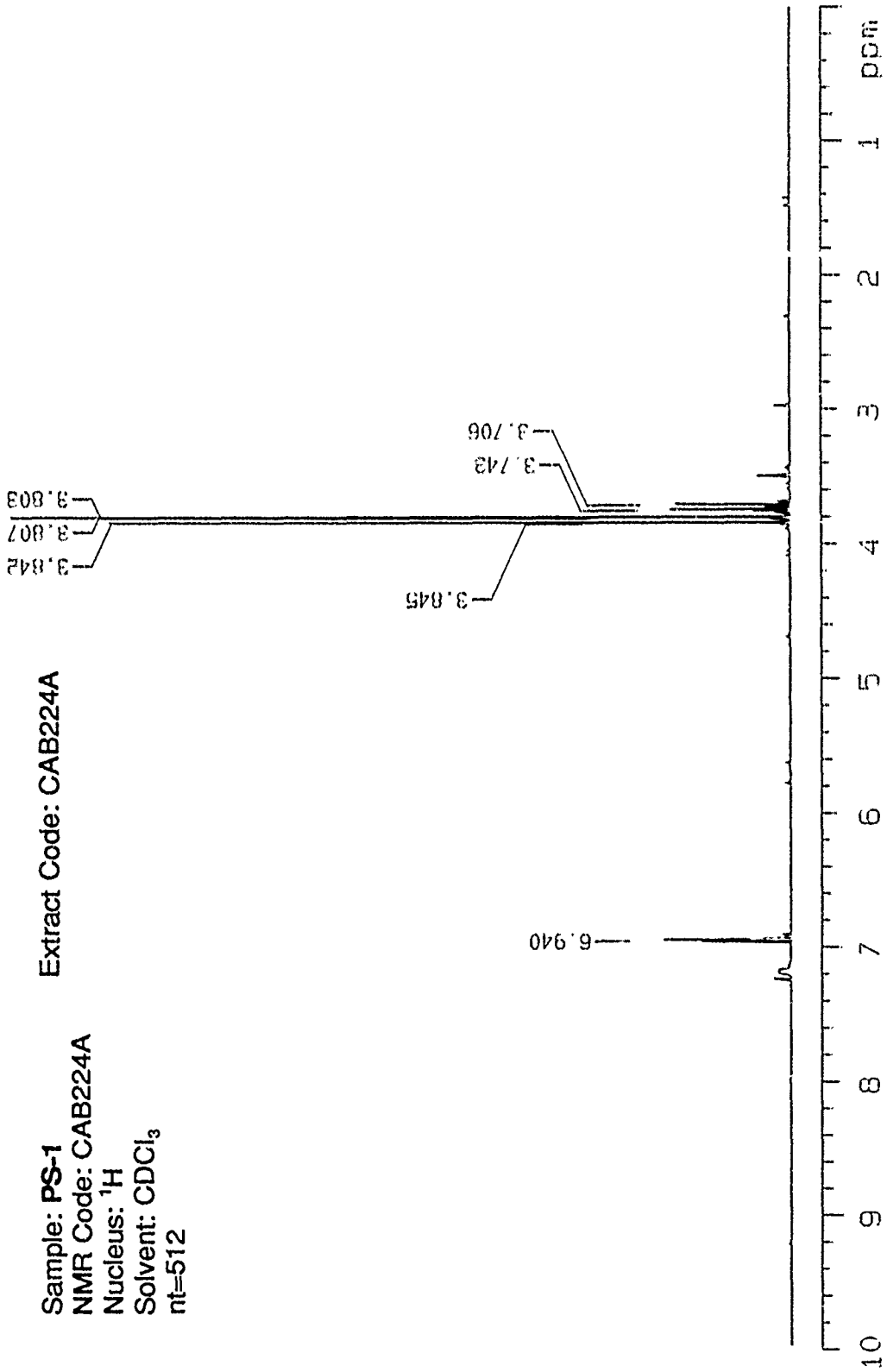


Figure 27: ^{1}H NMR of a $CDCl_3$ extract of PS-1 (nt = 512).

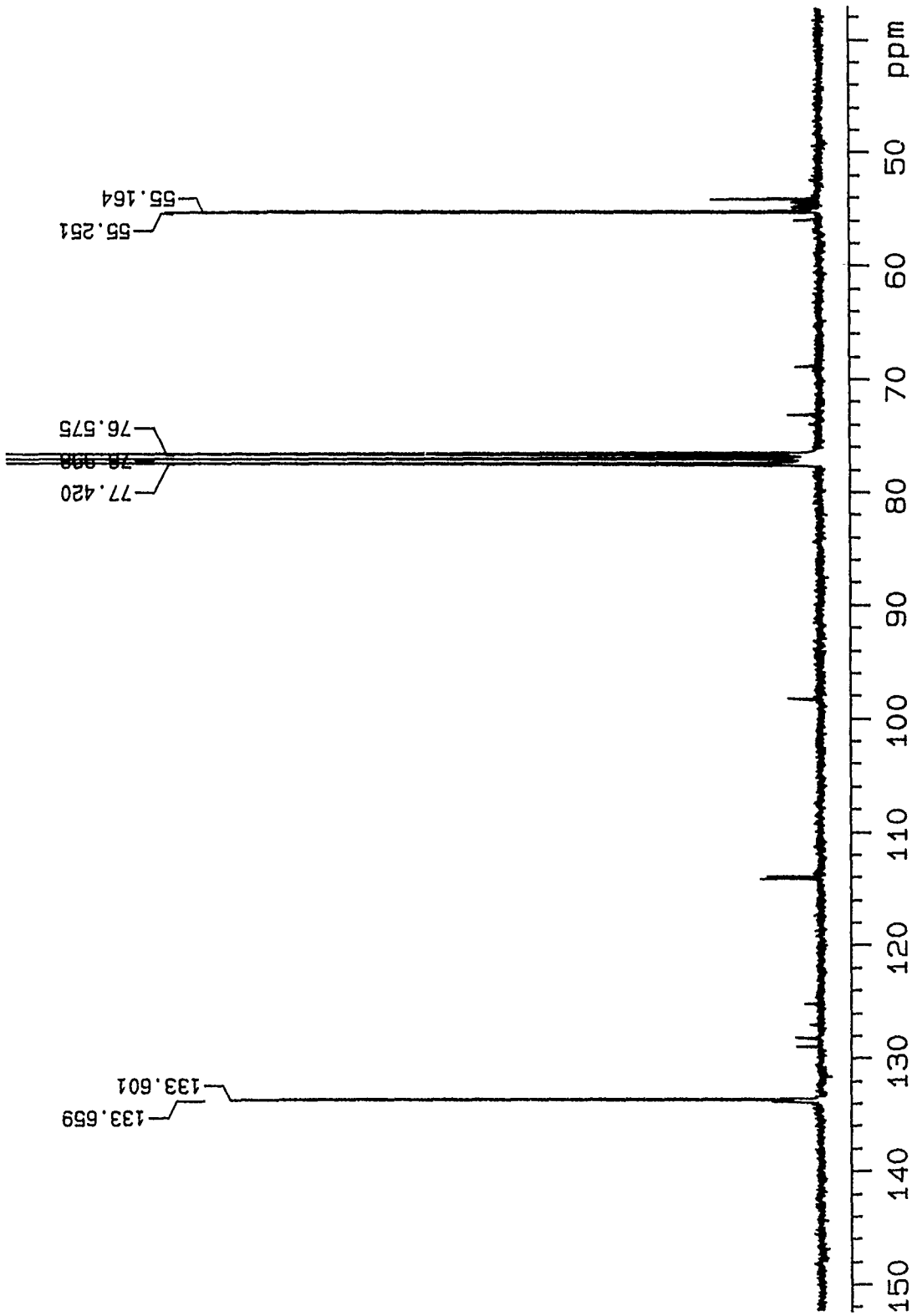


Figure 28: ^{13}C NMR of a $CDCl_3$ extract of PS-1.

CONCLUSIONS

The samples provided contained compounds related to the production of the pesticide dichlorvos and several scheduled compounds. Table IX summarizes the presence of those compounds that are not scheduled while Table X indicates the presence of scheduled compounds. It is the opinion of the Canadian analysts that, had these been the results of a real pesticide plant inspection, the presence of the dioctyl methylphosphonates (and the C_8 alcohols) would warrant an explanation. The other organophosphorus scheduled compounds detected are probably typical of an industry using a trimethyl phosphite feedstock.

Canada identified more than 20 compounds in the samples, including 5 compounds scheduled under the proposed CWC. Thirteen of the 16 participating National Laboratories (including Canada) identified the presence of the organophosphorus pesticide, dichlorvos, and detected the scheduled compounds, trimethyl phosphite, dimethyl phosphite and dimethyl methylphosphonate. Nine of the 16 laboratories (including Canada) identified the scheduled degradation product, methylphosphonic acid. Since these organophosphorus compounds would be expected at a dichlorvos plant, it is not likely that their presence would raise concerns under the proposed CWC. Only 5 of the 16 participating National Laboratories (including Canada) unambiguously identified the presence of dioctyl methylphosphonates. These scheduled compounds would not be associated with dichlorvos production, and would raise concerns under the proposed CWC. Two of these 5 laboratories also detected traces of octyl methylphosphonofluoridate, a potential CW agent, the presence of which would be a definite violation should the production of this Schedule 1 compound not be declared for this pesticide plant.

TABLE IX: Non-scheduled Compounds Identified during the Round Robin Analytical Exercise

Compound Name	Peak No.	SAMPLE CODE											
		FS1	FS2	FS3	AF	RV	PS1	PS2	WS1C	WS1X	WSIT	WS2	RC
Trimethyl phosphate	4	X				X	X	X	X	X	X		X
Trichloroacetaldehyde	5		X										
2,2,2-Trichloro-1,1- ethanediol	6		X										
di-TMS derivative of 2,2,2-trichloro-1,1-ethanediol	7		X										
Toluene	8			X		X			X	X	X		X
C_2-alkyl benzenes	9			X		X			X	X	X		X
C_8 Alcohols	10				X							X	
TMS derivative of C_8 alcohols	11				X								
tri-TMS derivative of phosphoric acid	13				X				X	X		X	
Chloroethenyl dimethyl phosphates	14					X	X	X		X			X
Dichlorvos	15					X	X	X					
Unknowns (chlorinated)	16					X	X	X					
TMS derivative of dimethyl phosphoric acid	18								X	X		X	X
tri-TMS derivative of phosphorous acid	19								X	X			
di-TMS derivative of hydrogenphosphonic acid	20								X	X			X
di-TMS derivative of methyl phosphoric acid	21								X	X			X

TABLE X: Scheduled Compounds Identified during the Round Robin Analytical Exercise

Compound Name	Peak No.	SAMPLE CODE											
		FS1	FS2	FS3	AF	RV	PS1	PS2	WS1C	WS1X	WSIT	WS2	RC
Trimethyl phosphite	1	X											
Dimethyl phosphite	2	X											
Dimethyl methylphosphonate	3	X				X	X	X	X	X	X		X
di-TMS derivative of methylphosphonic acid	12				X				X	X		X	X
Dioctyl methylphosphonates	17							X	X	X		X	X

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Figure 10: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of hexane extract of WS1T. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

Figure 11: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of dichloromethane extract of WS1C. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

Figure 12: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of TMS derivative of acetonitrile extract of second WS1C. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

Figure 13: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of hexane extract of WS1X. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

Figure 14: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of TMS derivative of acetonitrile extract of WS1X. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

Figure 15: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of hexane extract of WS2. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

Figure 16: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of TMS derivative of dried WS2. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

Figure 17: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of dichloromethane extract of RC. Numbered peaks are identified in

Table I. Spectral data for numbered peaks appears in the Annex with the same number.

Figure 18: Capillary column a) GC-FID and b) GC-MS (EI) chromatograms of TMS derivative of acetonitrile extract of RC. Numbered peaks are identified in Table I. Spectral data for numbered peaks appears in the Annex with the same number.

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with a standard).

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Annex 16 (con't): a) EI mass spectrum and b) ammonia CI mass spectrum of an unknown (chlorinated).

Annex 16 (con't): a) EI mass spectrum and b) ammonia CI mass spectrum of an unknown (chlorinated).

Annex 16 (con't): a) EI mass spectrum and b) ammonia CI mass spectrum of an unknown (chlorinated).

Annex 16 (con't): a) EI mass spectrum and b) ammonia CI mass spectrum of an unknown (chlorinated).

Annex 17: a) EI mass spectrum and b) ammonia CI mass spectrum of a typical dioctyl methylphosphonate (based on interpretation).

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Annex 17 (con't): EI mass spectra (100 to 350 u) of four dioctyl methylphosphonates (based on interpretation).

Annex 17 (con't): EI mass spectra (100 to 350 u) of four dioctyl methylphosphonates (based on interpretation).

Annex 17 (con't): EI mass spectra (100 to 350 u) of four dioctyl methylphosphonates (based on interpretation).

Annex 17 (con't): Ammonia CI mass spectra (100 to 350 u) of four dioctyl methylphosphonates (based on interpretation).

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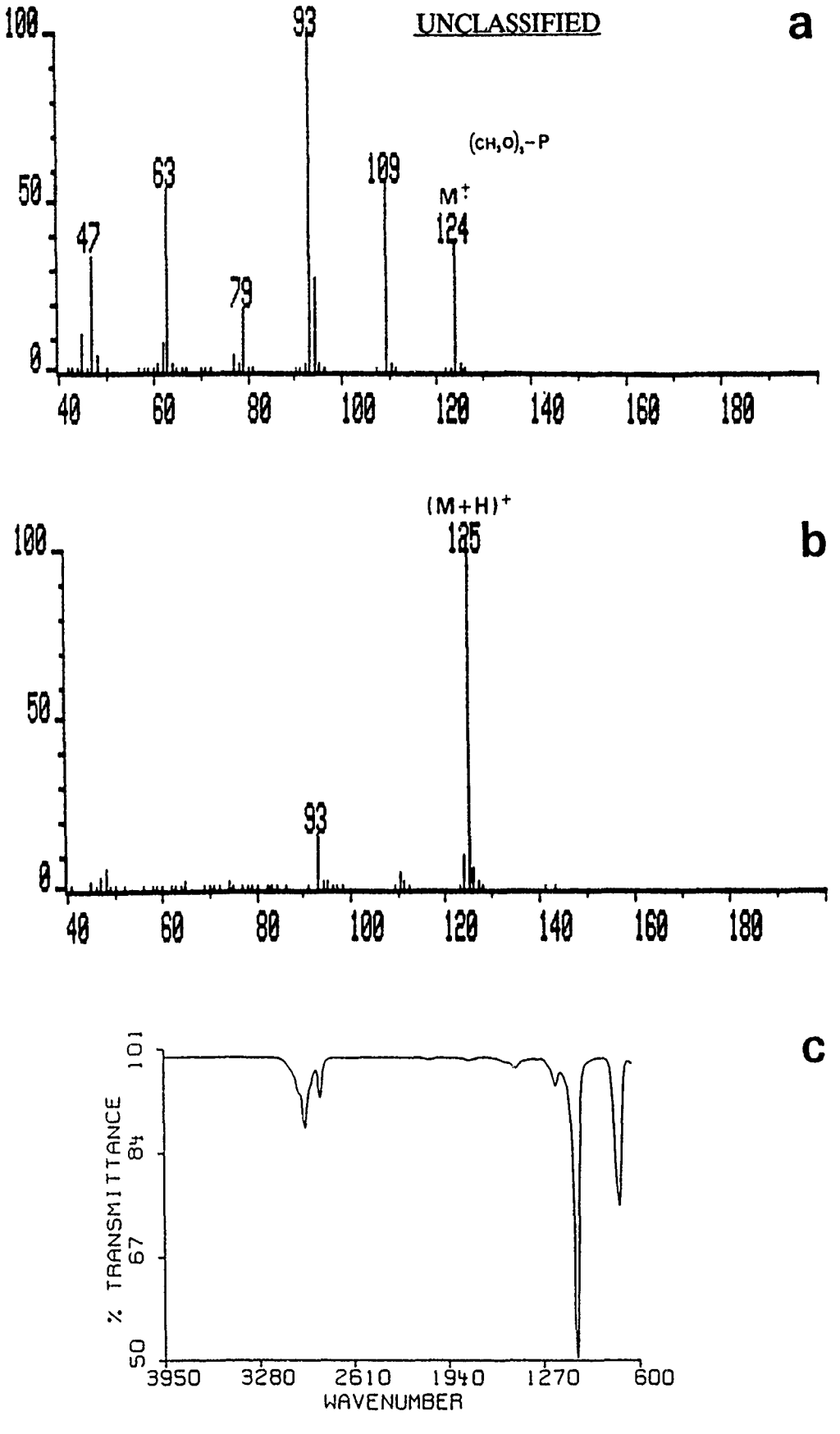
Annex 23: Comparison of the ^{1}H NMR spectra of di-n-octyl methylphosphonate (A) and di-2-octyl methylphosphonate (B).

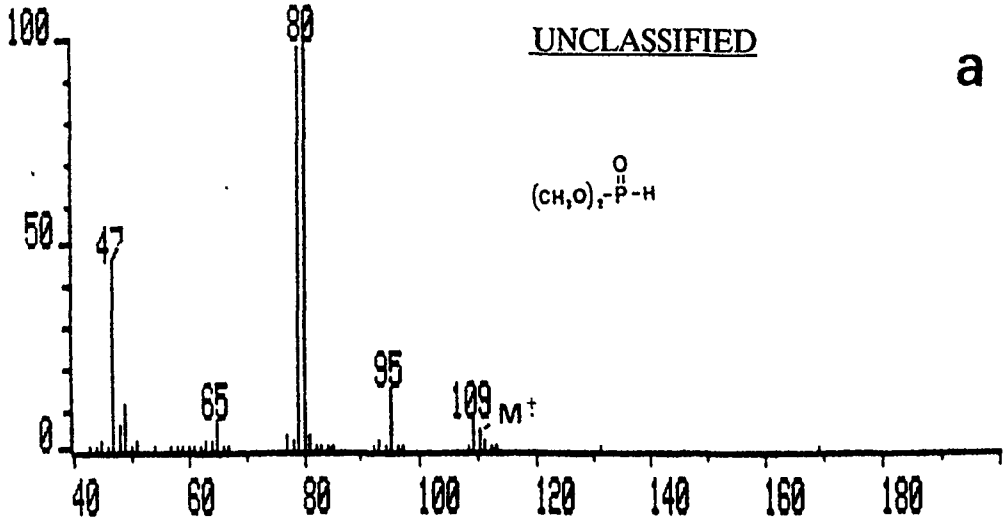
Annex 24: ^{13}C NMR spectrum of di-n-octyl methylphosphonate.

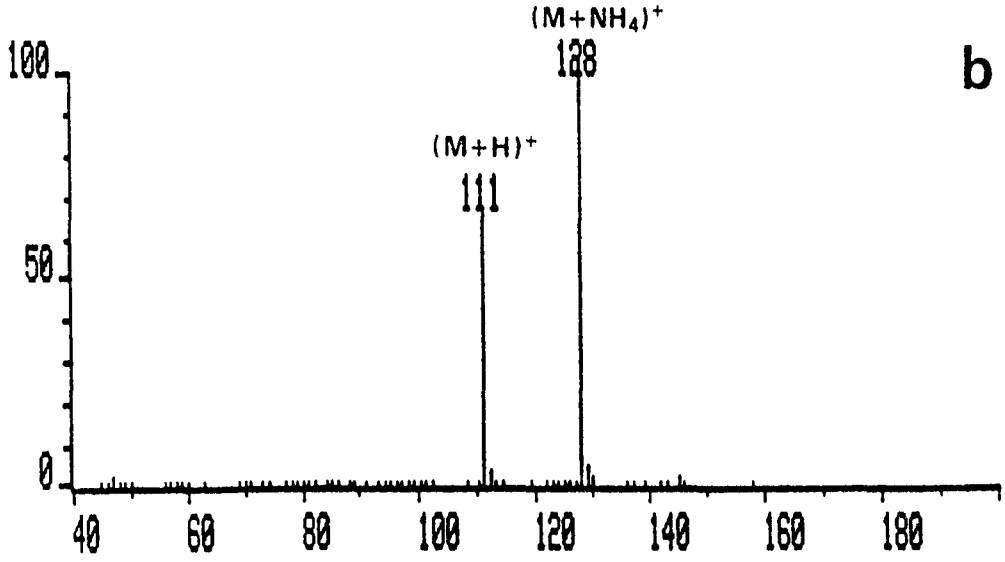
Annex 25: ^{13}C NMR spectrum of di-2-octyl methylphosphonate.

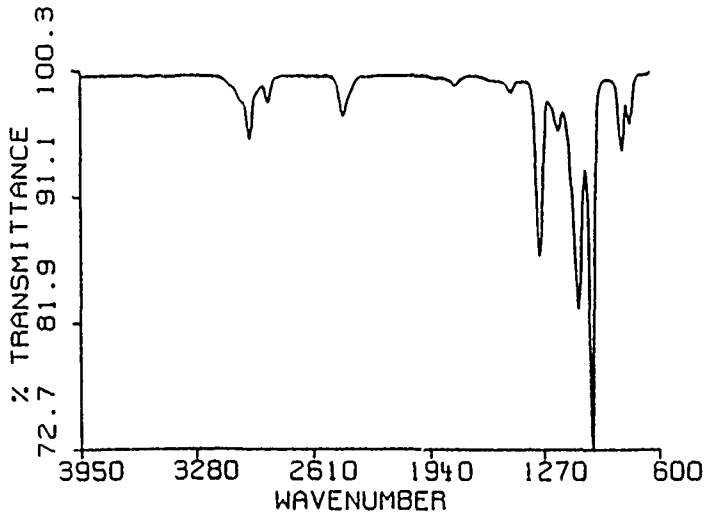
ANNEXES



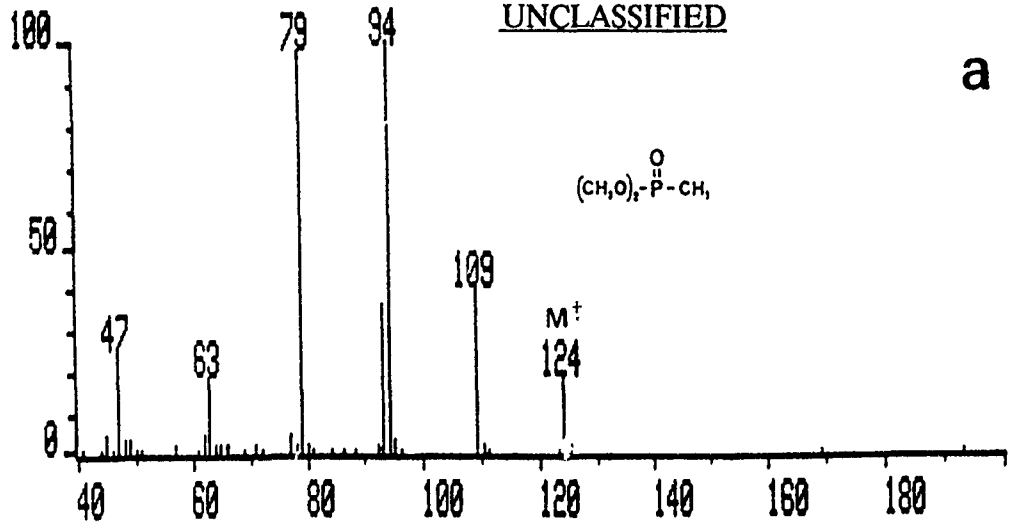
Annex 1: a) EI mass spectrum, b) ammonia CI mass spectrum and c) FTIR spectrum of trimethyl phosphite (confirmed with a standard).

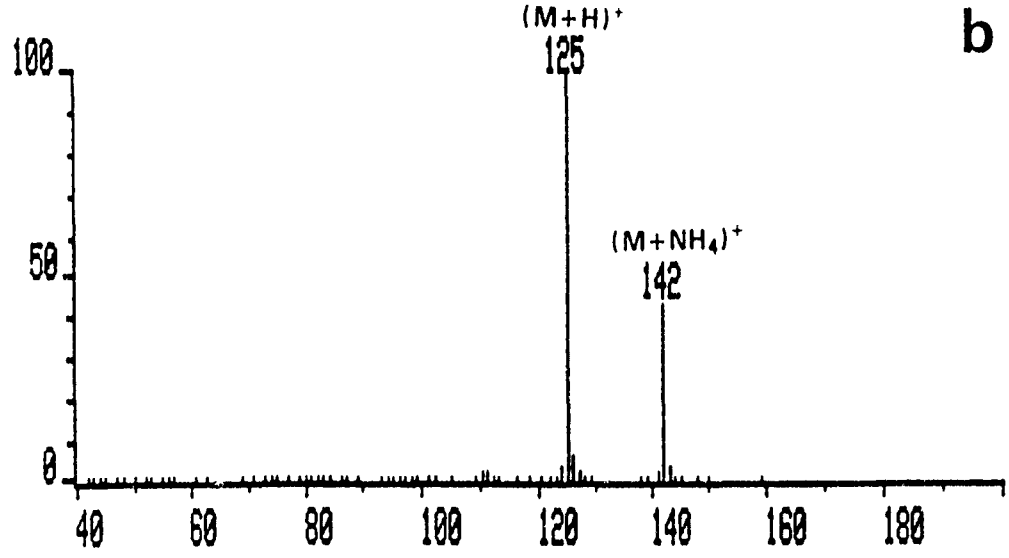


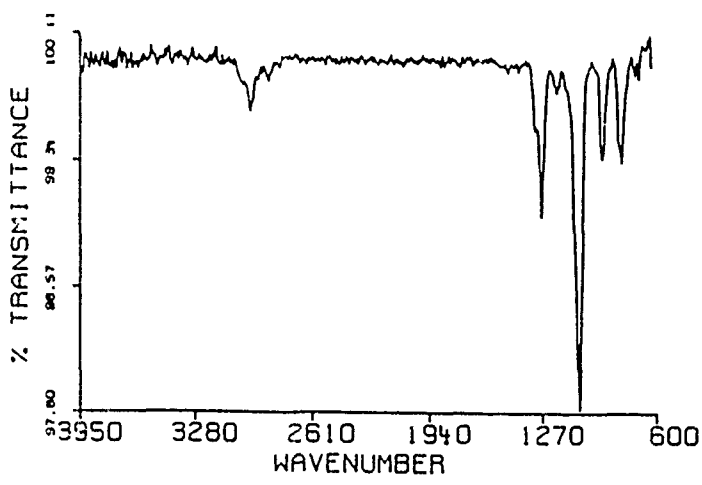




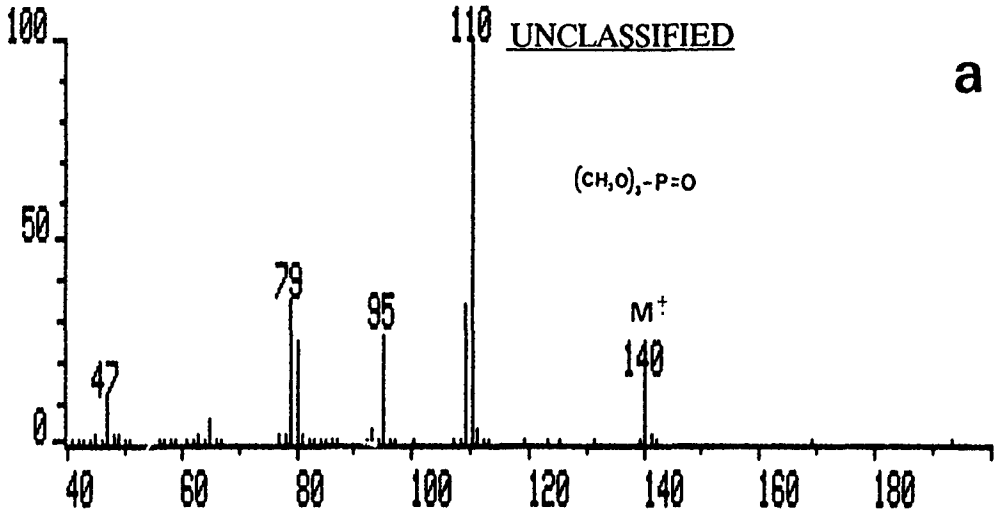
Annex 2: a) EI mass spectrum, b) ammonia CI mass spectrum and c) FTIR spectrum of dimethyl phosphite (based on library matches).

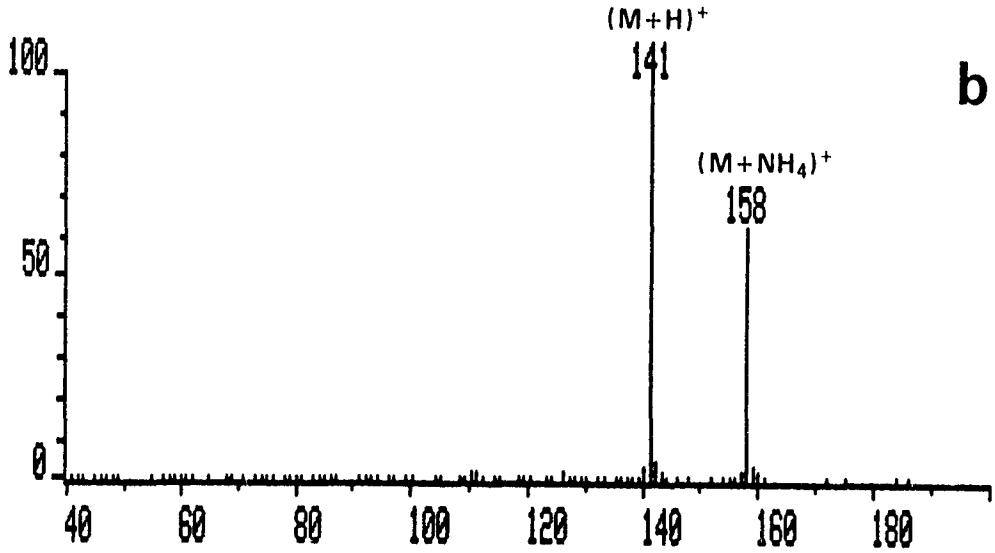


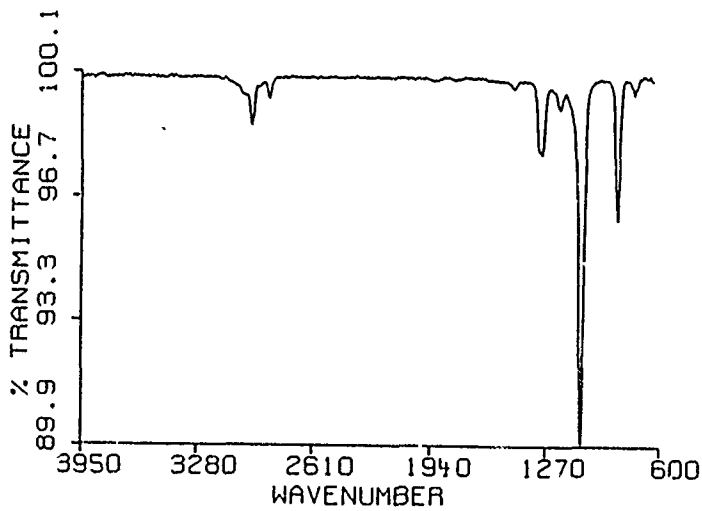




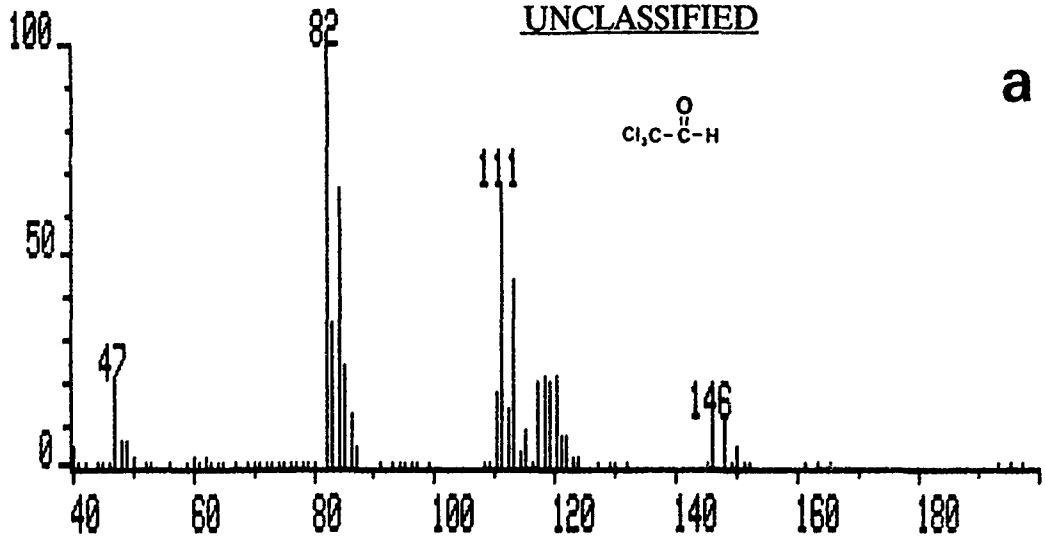
Annex 3: a) EI mass spectrum, b) ammonia CI mass spectrum and c) FTIR spectrum of dimethyl methylphosphonate (confirmed with a standard).

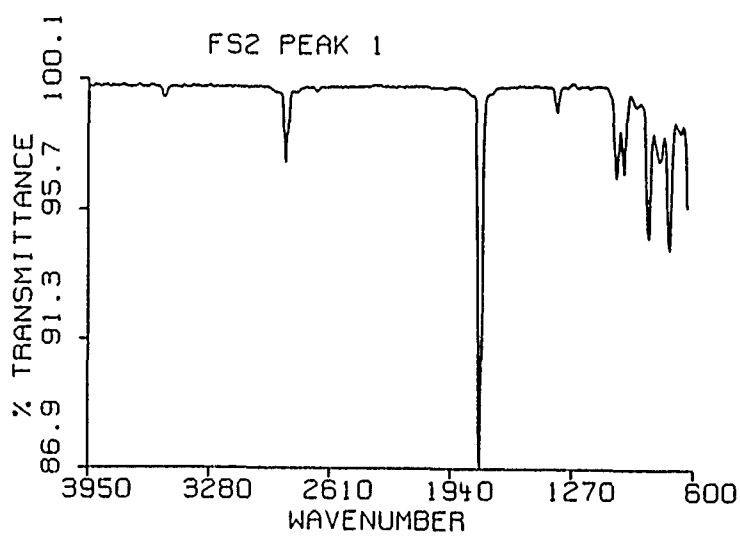




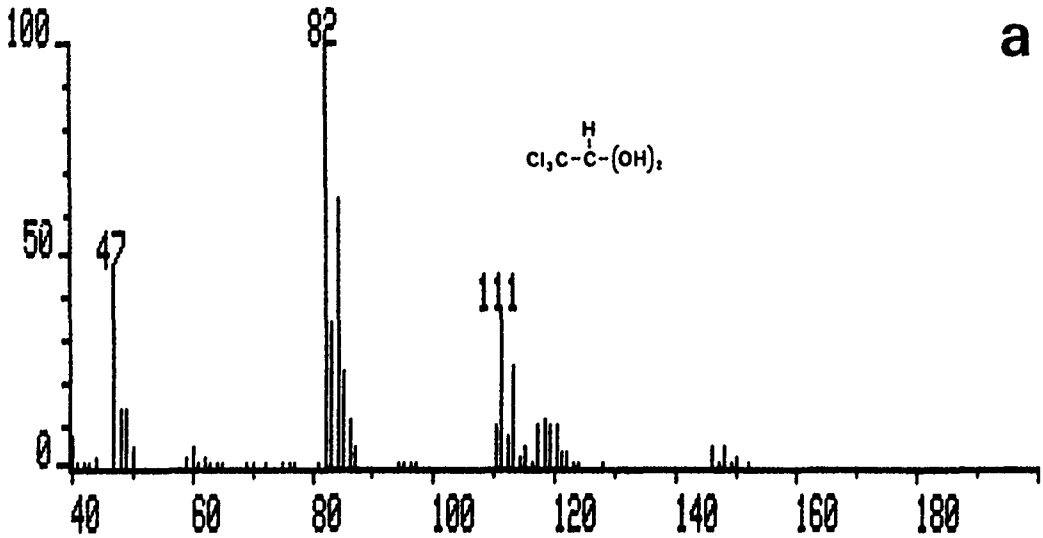


Annex 4: a) EI mass spectrum, b) ammonia CI mass spectrum and c) FTIR spectrum of trimethyl phosphate (confirmed with a standard).

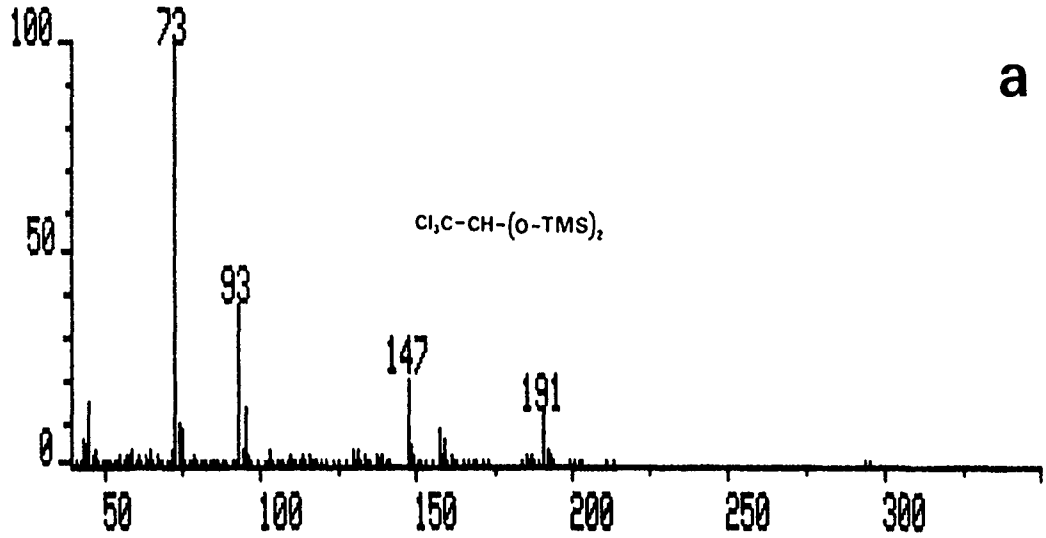


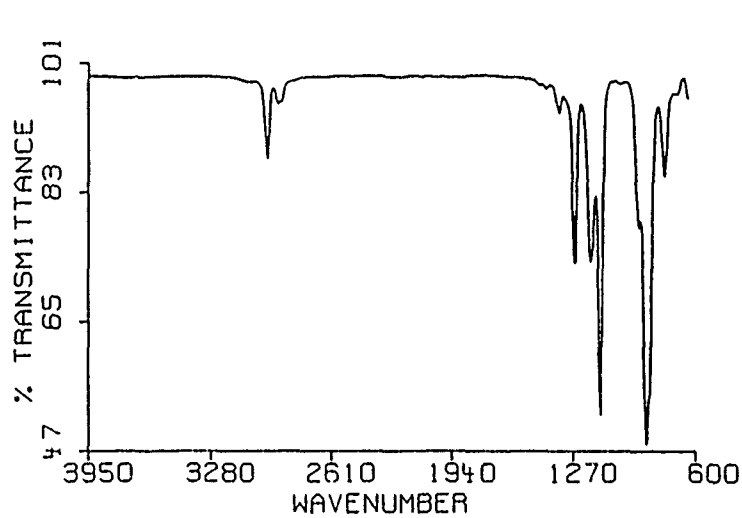


Annex 5: a) EI mass spectrum and b) FTIR spectrum of trichloroacetaldehyde (based on library matches).

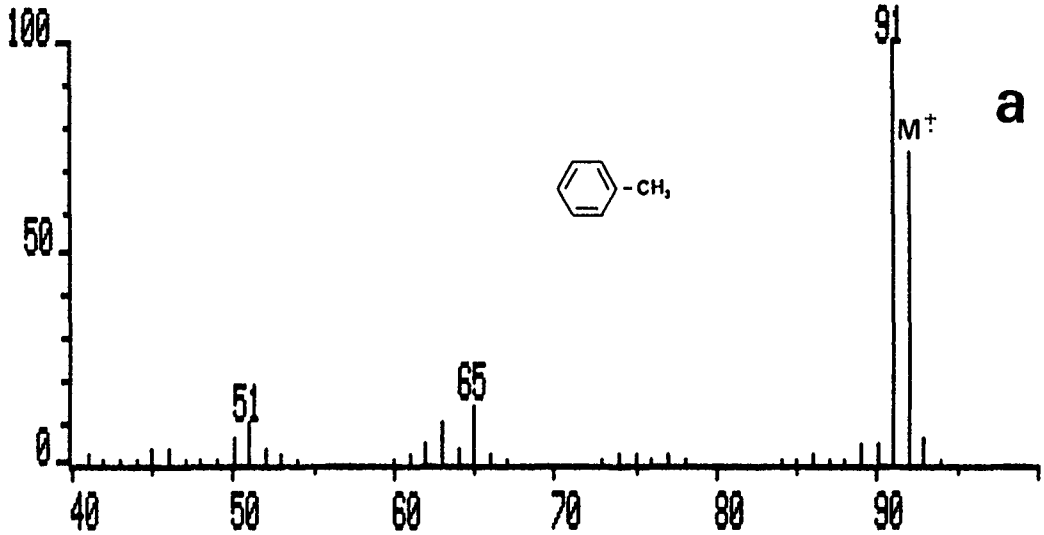


Annex 6: a) EI mass spectrum of 2,2,2-trichloro-1,1-ethanediol (confirmed with a standard).



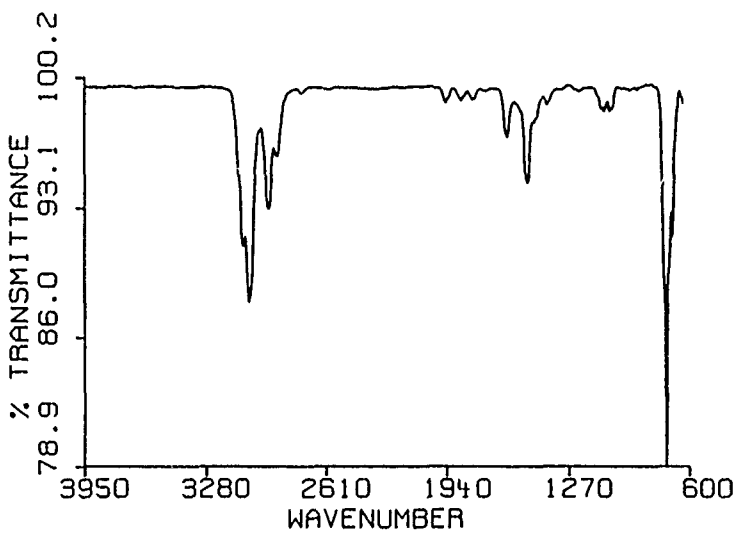


Annex 7: a) EI mass spectrum and b) FTIR spectrum of di-TMS derivative of 2,2,2-trichloro-1,1-ethanediol (confirmed with a standard).

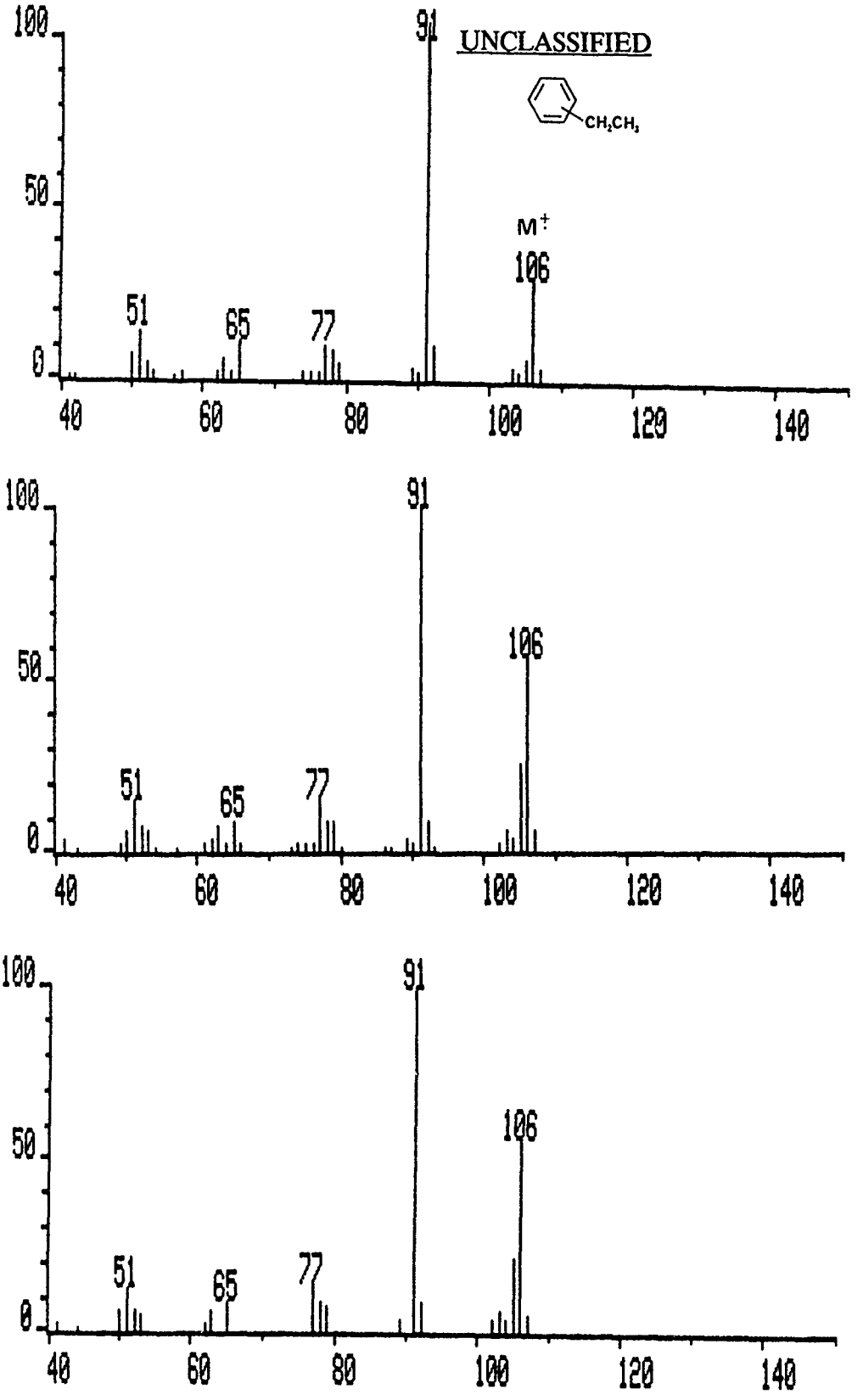


a

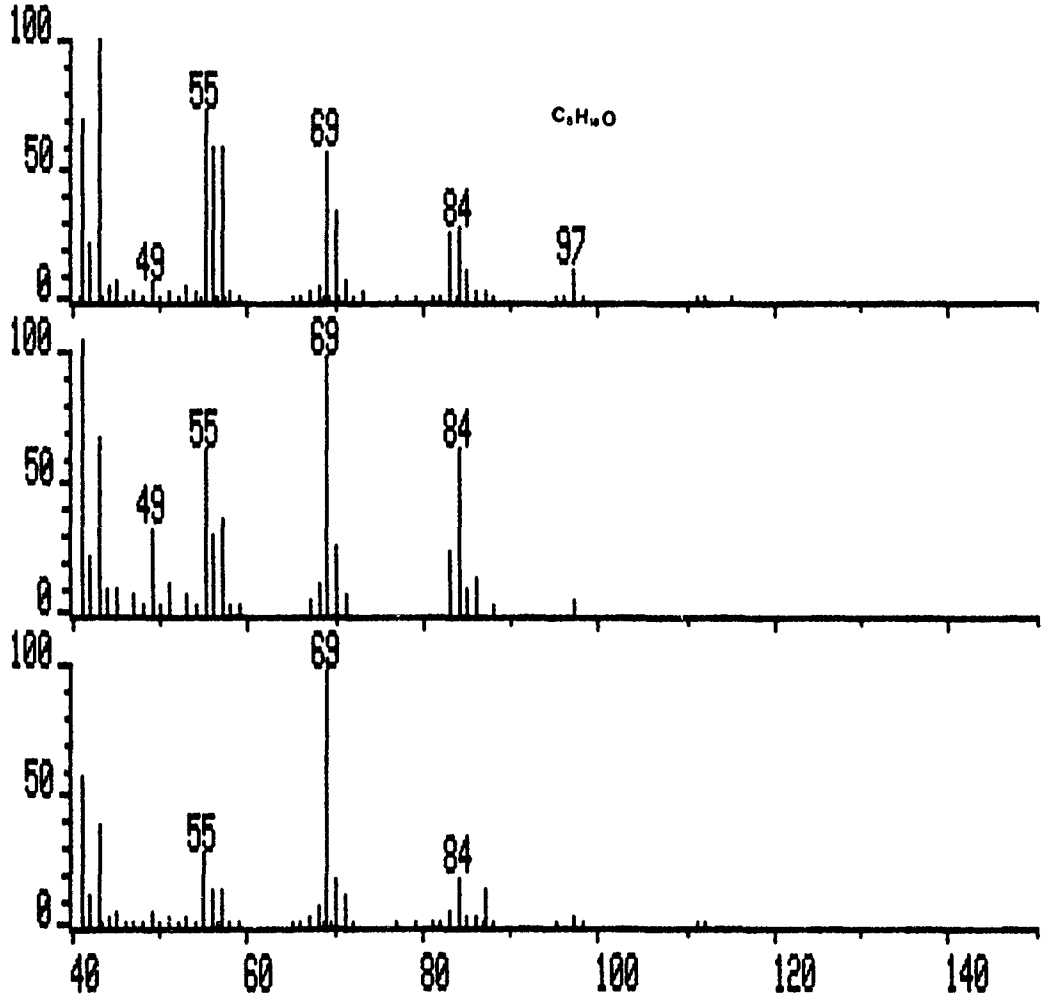
b



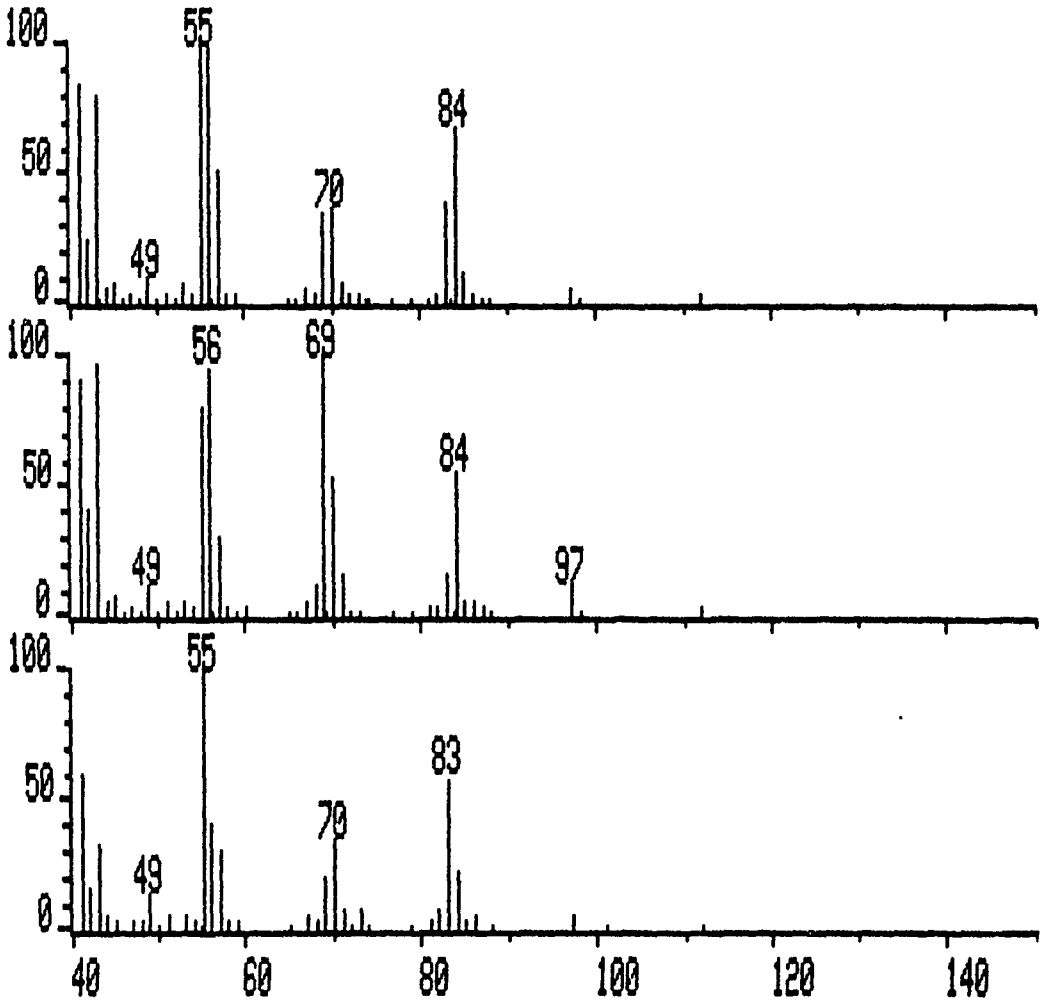
Annex 8: a) EI mass spectrum and b) FTIR spectrum of toluene (confirmed with a standard).



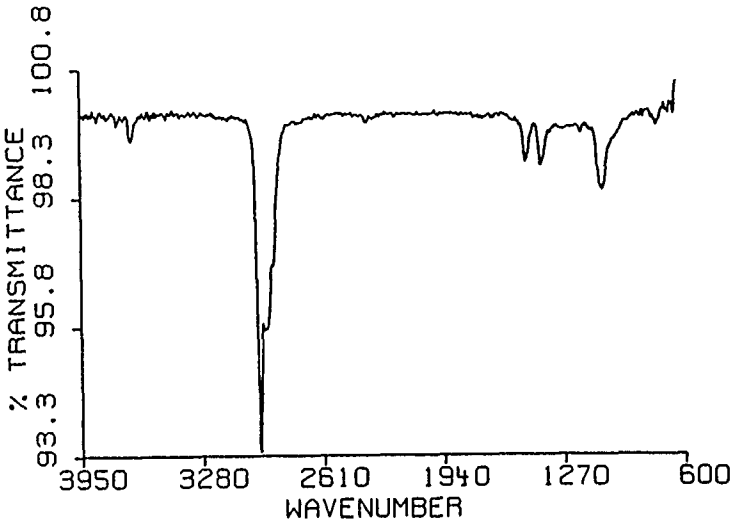
Annex 9: EI mass spectra of three C_2- alkyl benzenes (based on library matches).

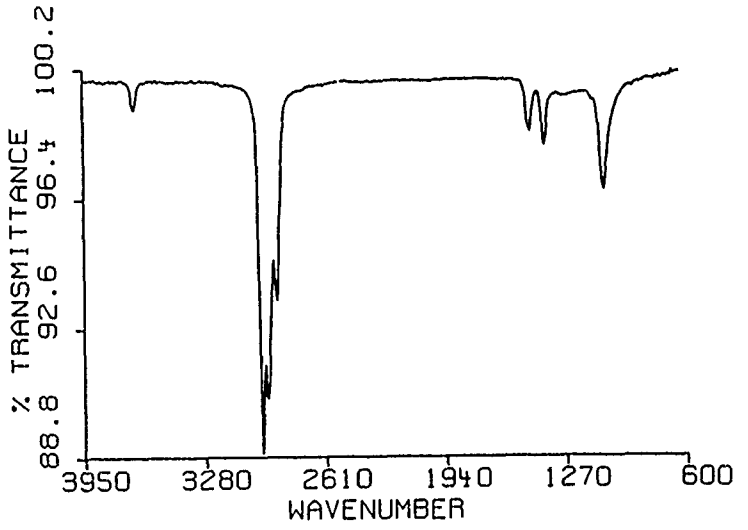


Annex 10: EI mass spectra of three C_8 alcohols (based on library matches).

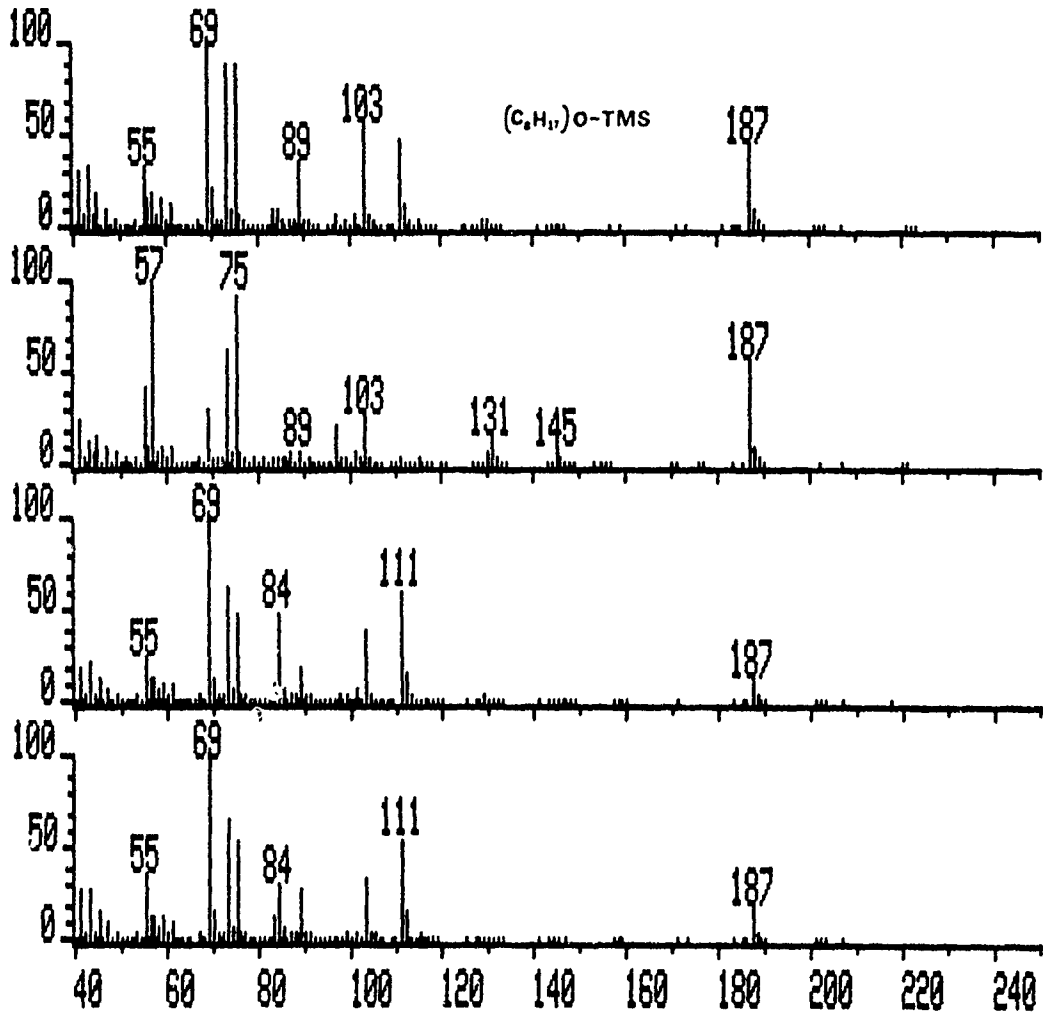


Annex 10 (con't): EI mass spectra of three C_8 alcohols (based on library matches).

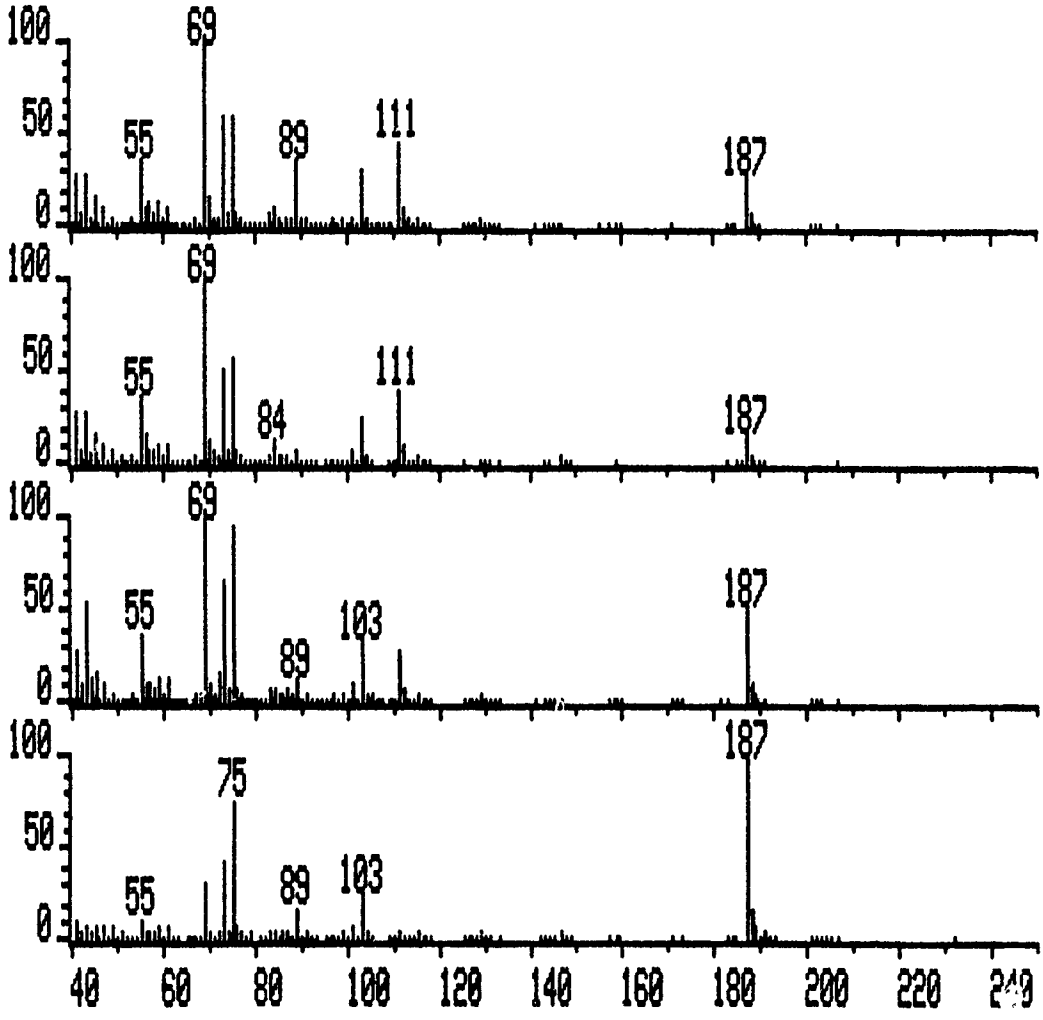




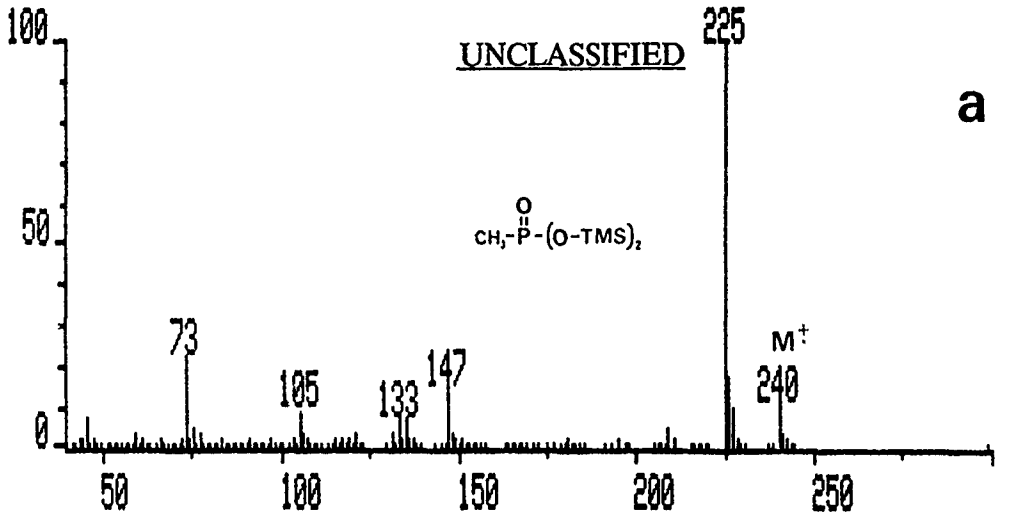
Annex 10 (con't): FTIR spectra of two C_8 alcohols (based on library matches).

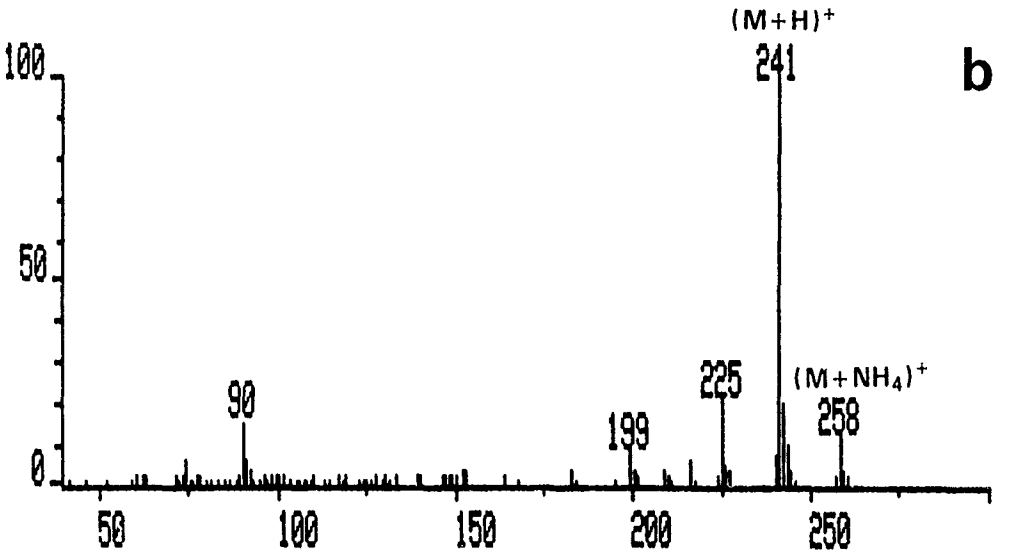


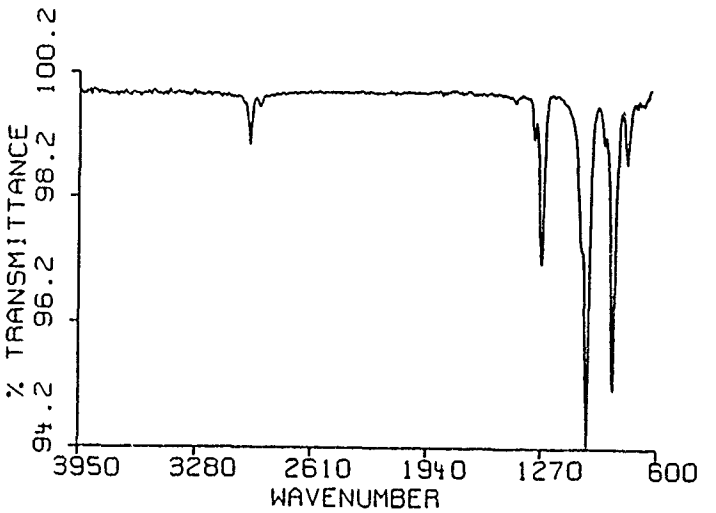
Annex 11: EI mass spectra of TMS derivatives of four C_8 alcohols (based on interpretation).



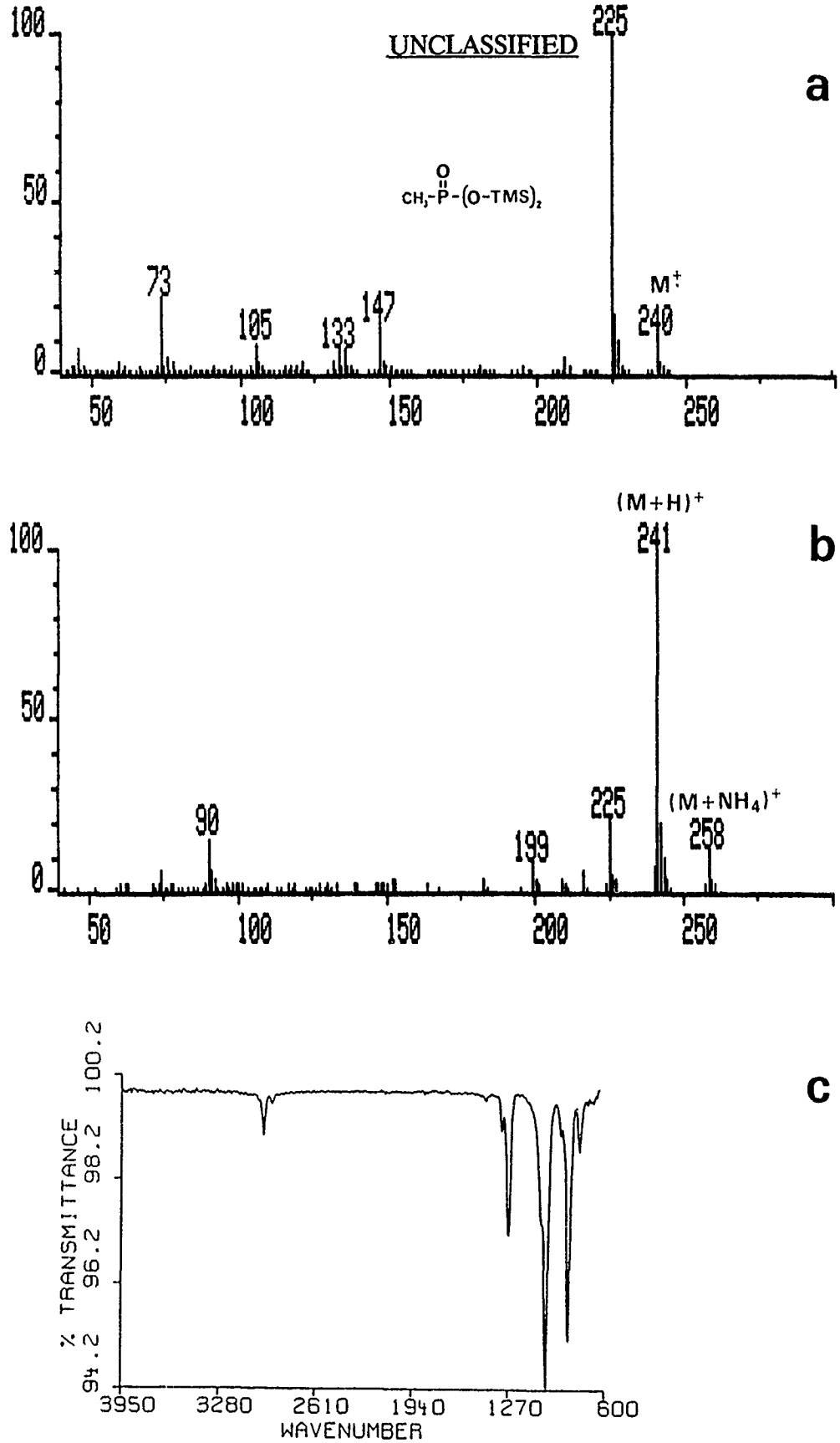
Annex 11 (con't): EI mass spectra of TMS derivatives of four C_8 alcohols (based on interpretation).



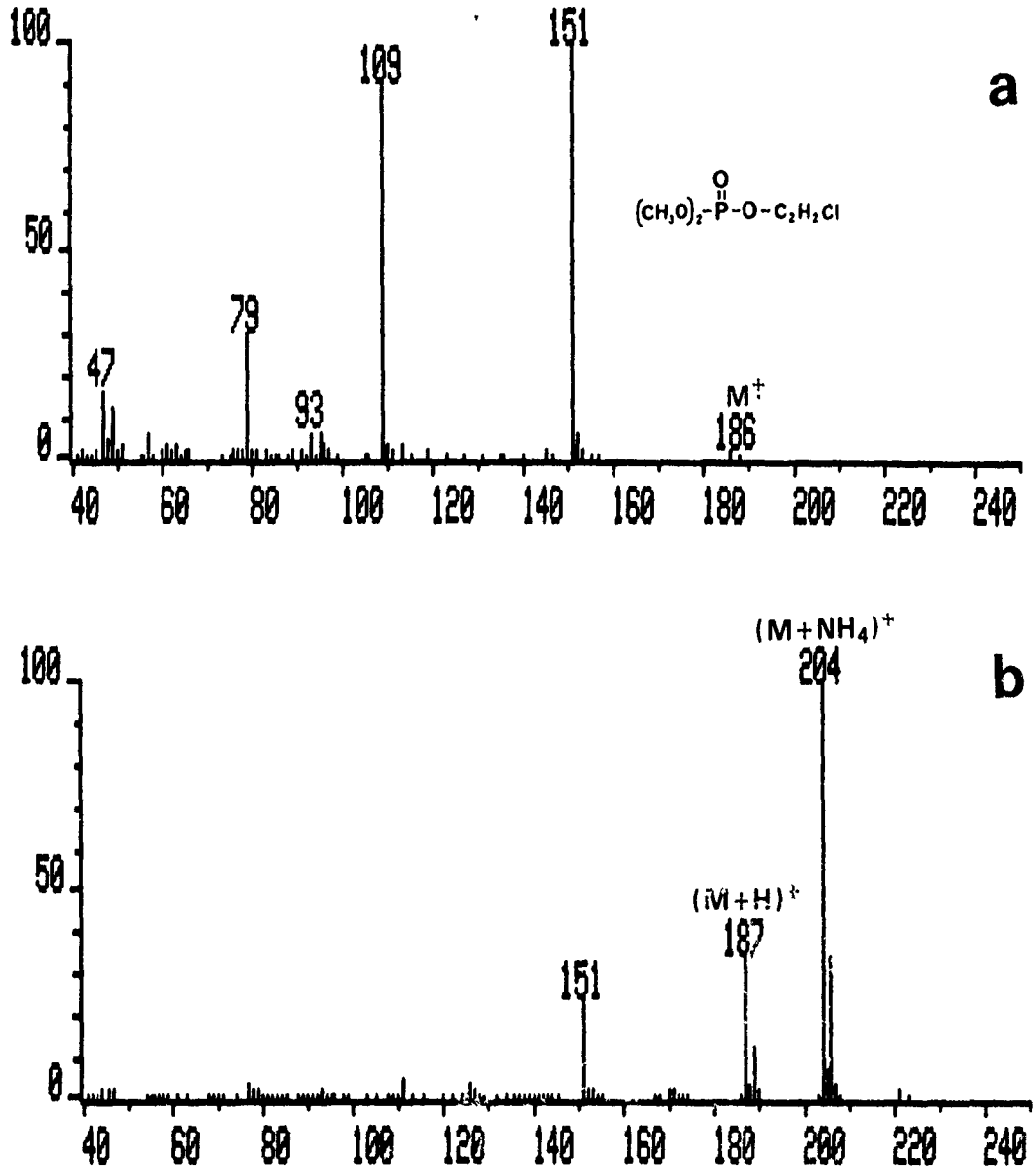




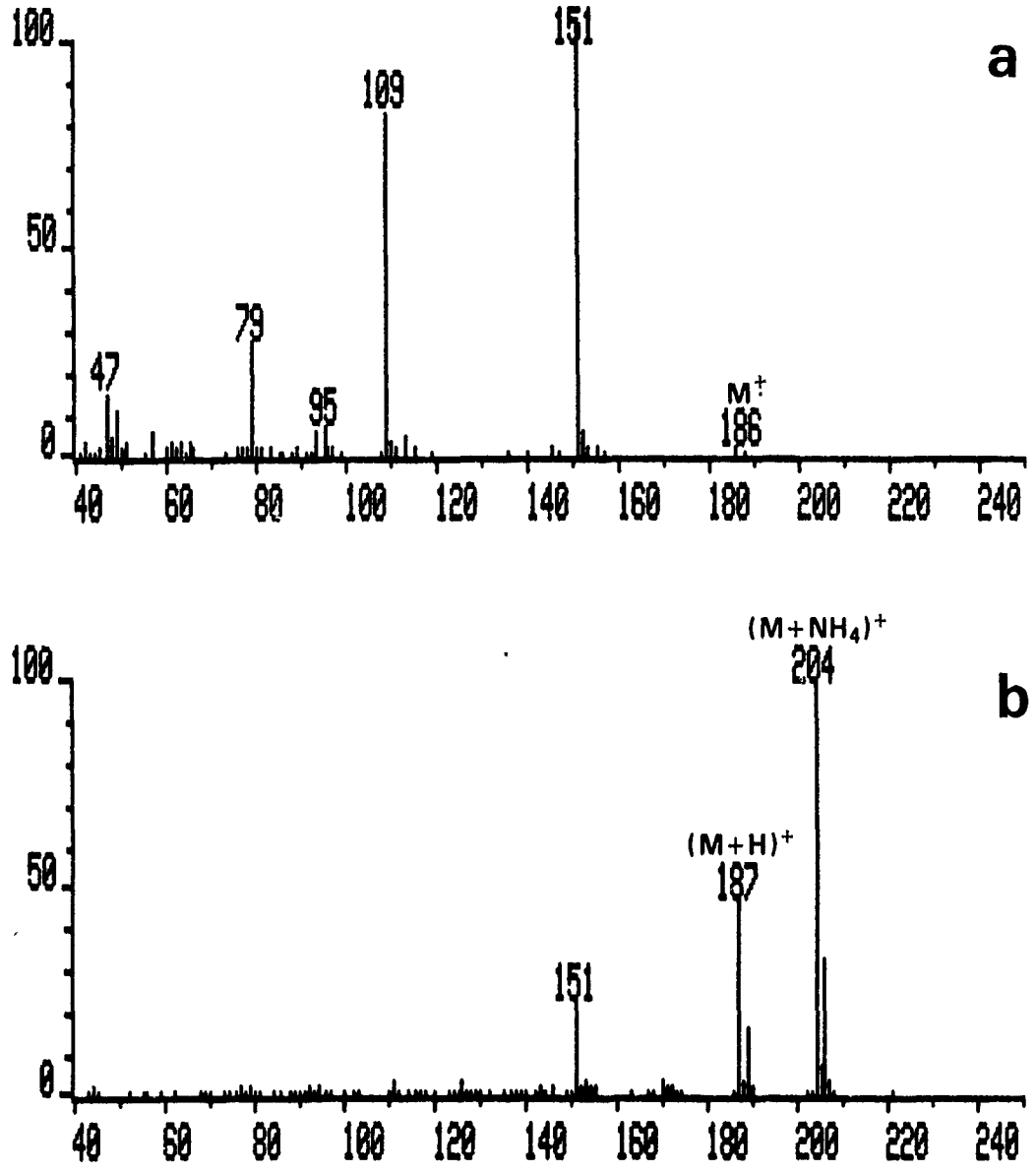
Annex 12: a) EI mass spectrum, b) ammonia CI mass spectrum and c) FTIR spectrum of di-TMS derivative of methylphosphonic acid (confirmed with a standard).



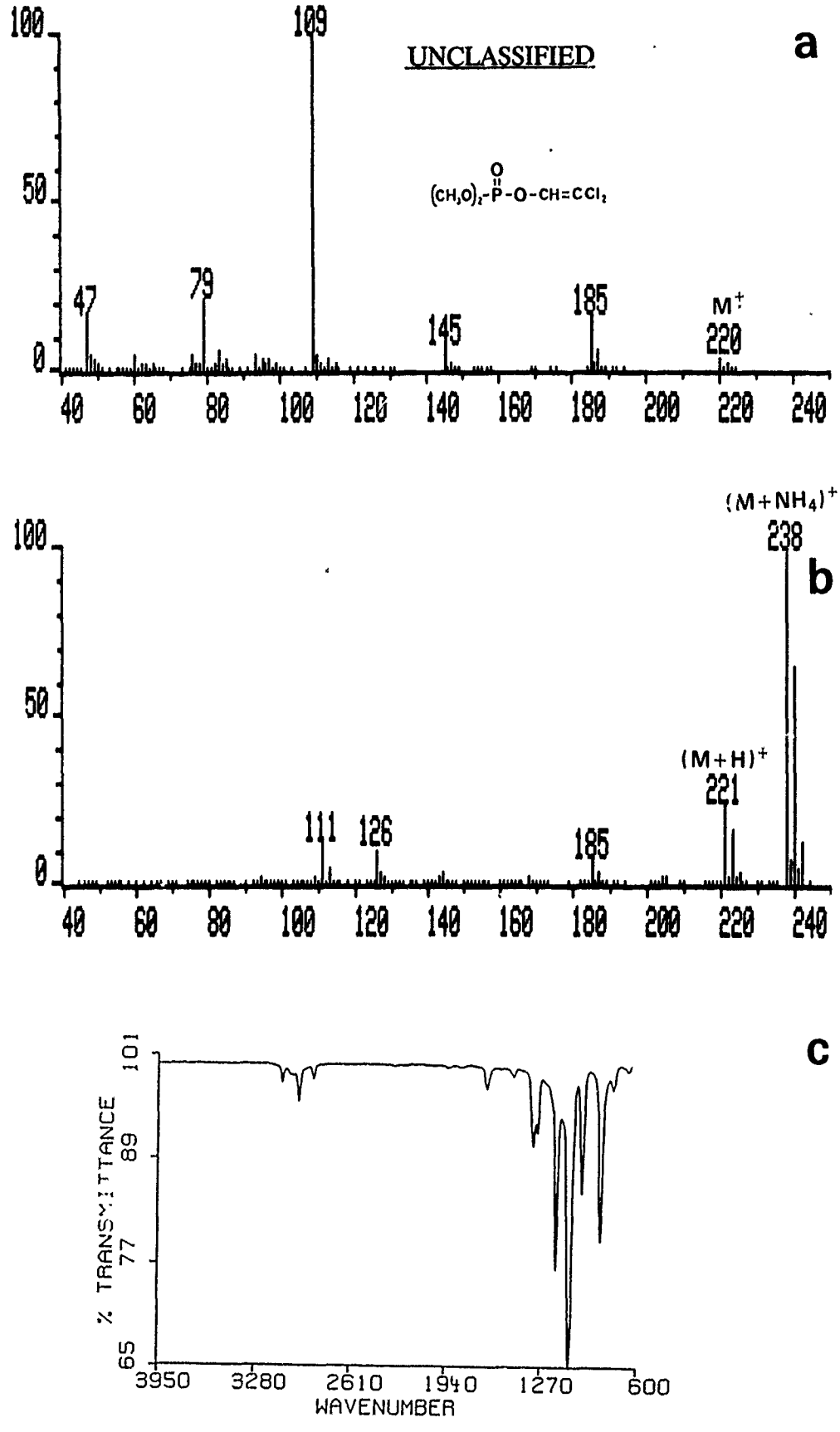
Annex 12: a) EI mass spectrum, b) ammonia CI mass spectrum and c) FTIR spectrum of di-TMS derivative of methylphosphonic acid (confirmed with a standard).



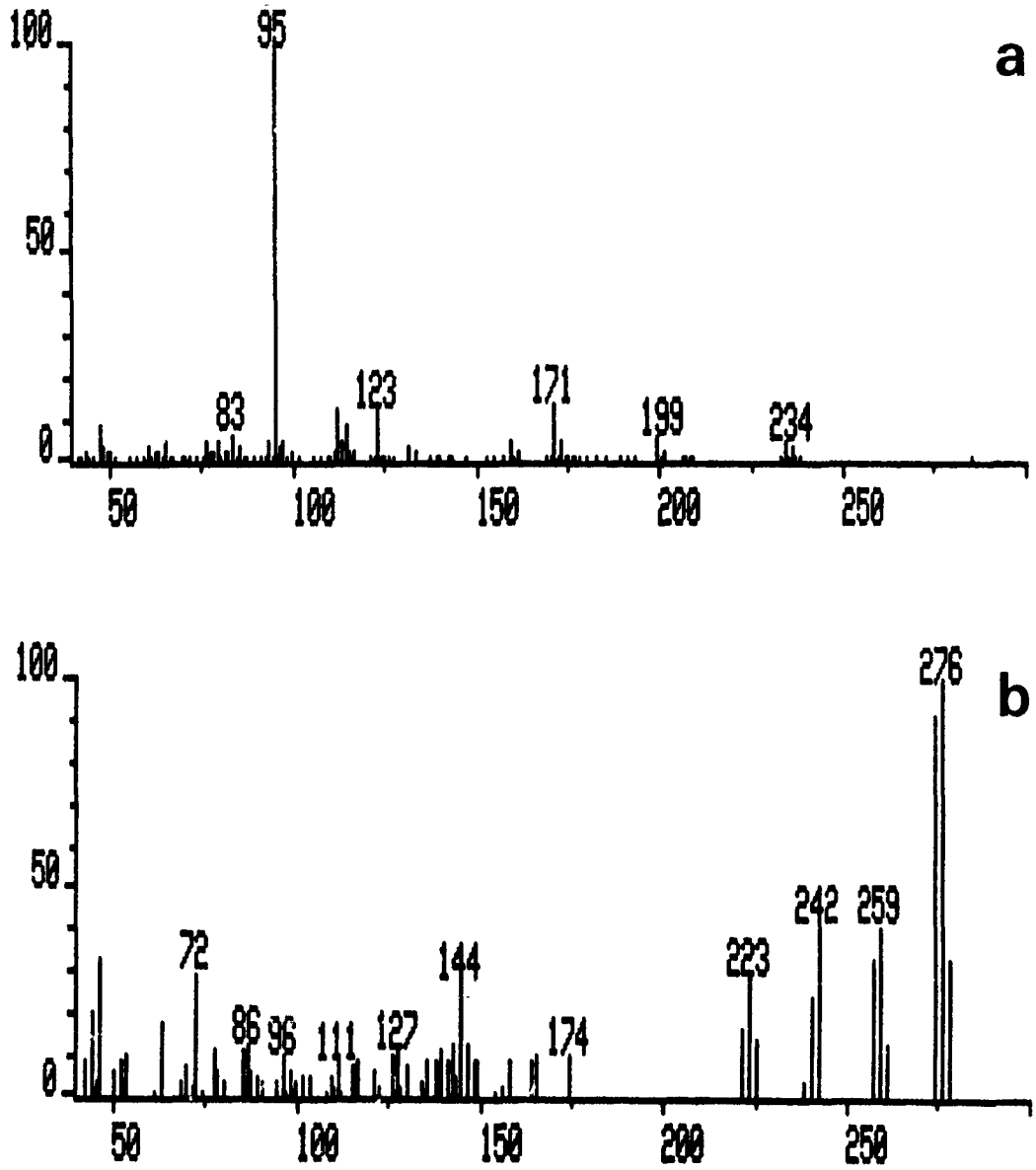
Annex 14: a) EI mass spectrum and b) ammonia CI mass spectrum of a chloroethenyl dimethyl phosphate (based on library match).



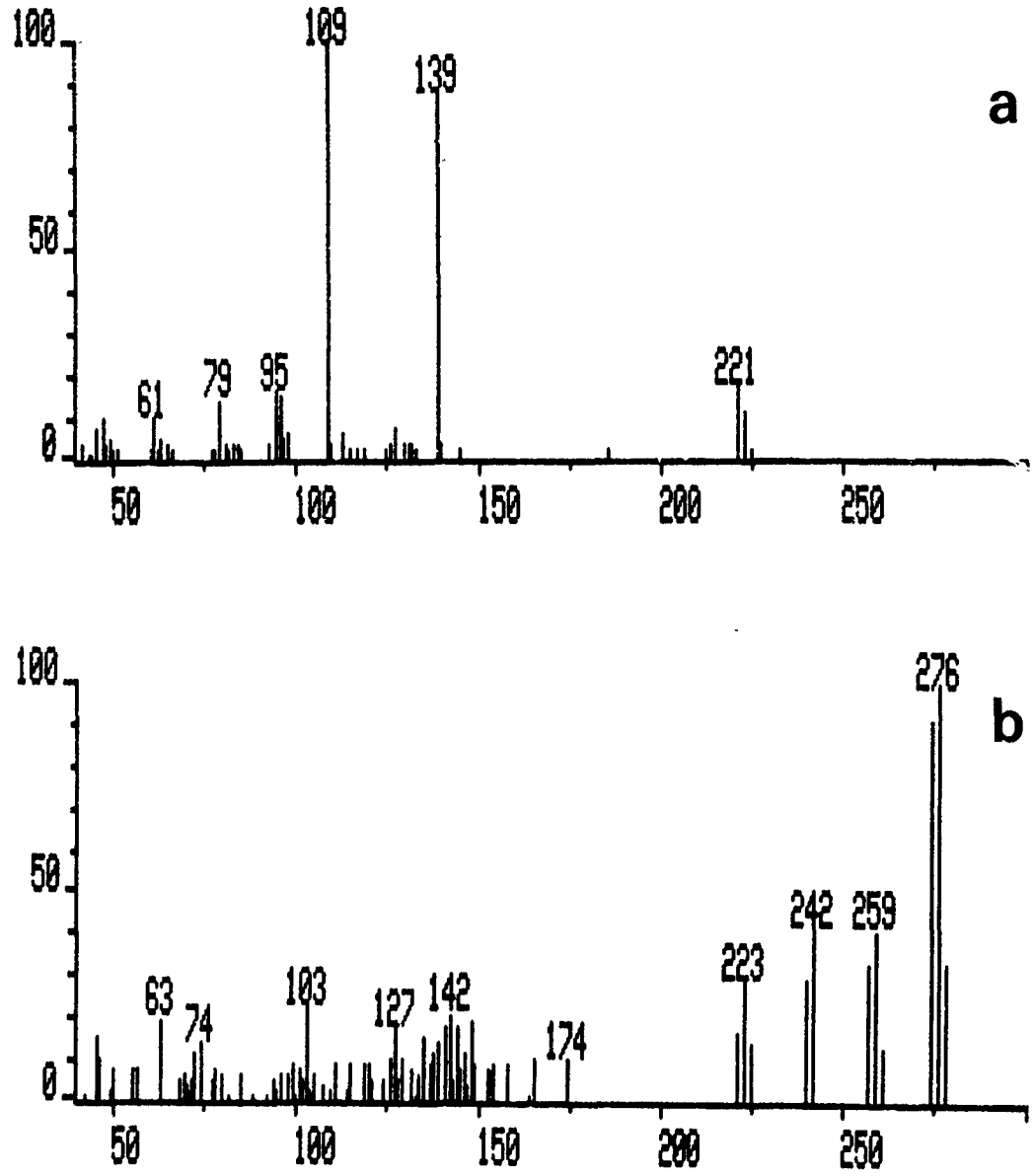
Annex 14 (con't): a) EI mass spectrum and b) ammonia CI mass spectrum of a chloroethenyl dimethyl phosphate (based on library match).



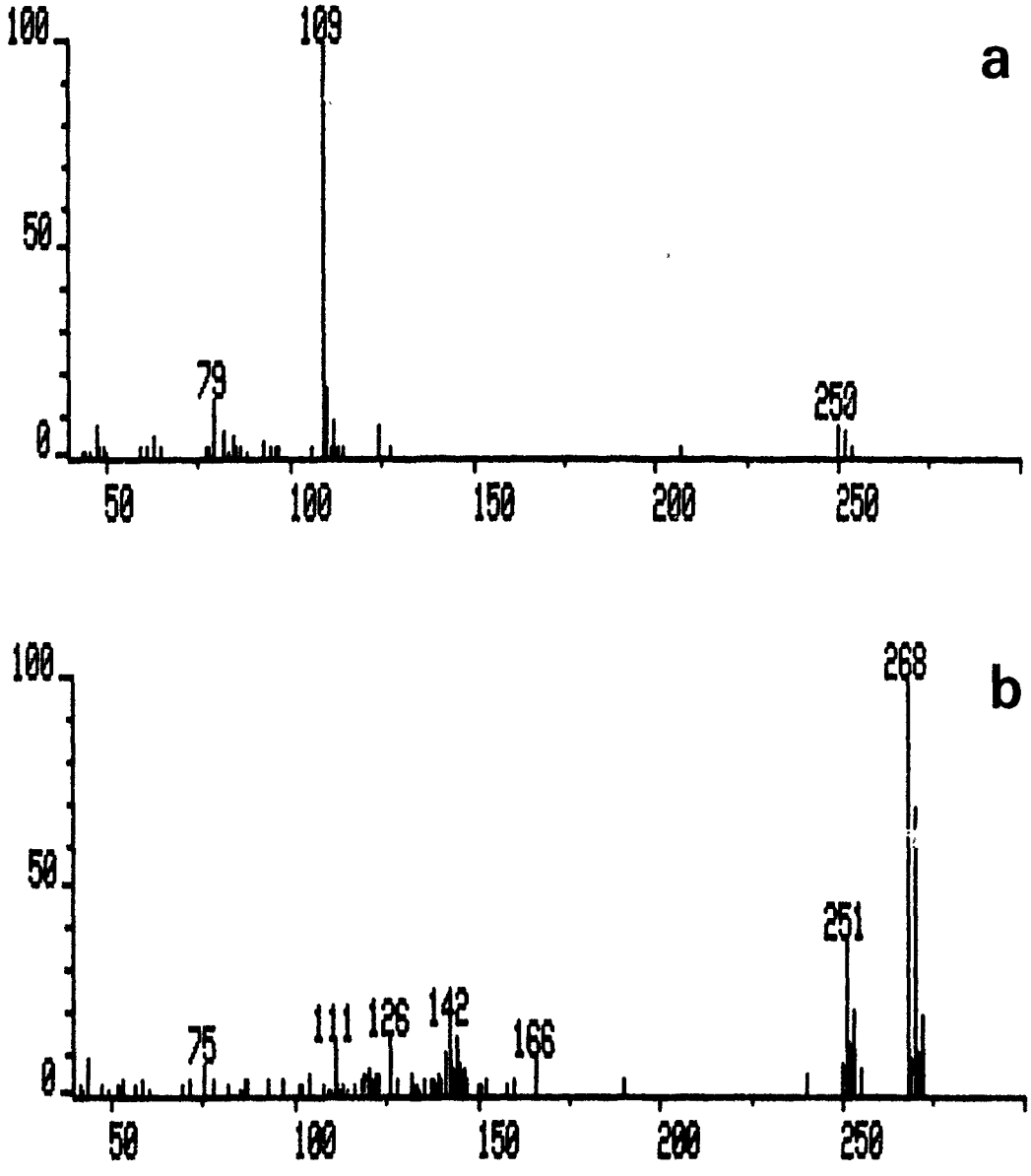
Annex 15: a) EI mass spectrum, b) ammonia CI mass spectrum and c) FTIR spectrum of dichlorvos (confirmed with a standard).



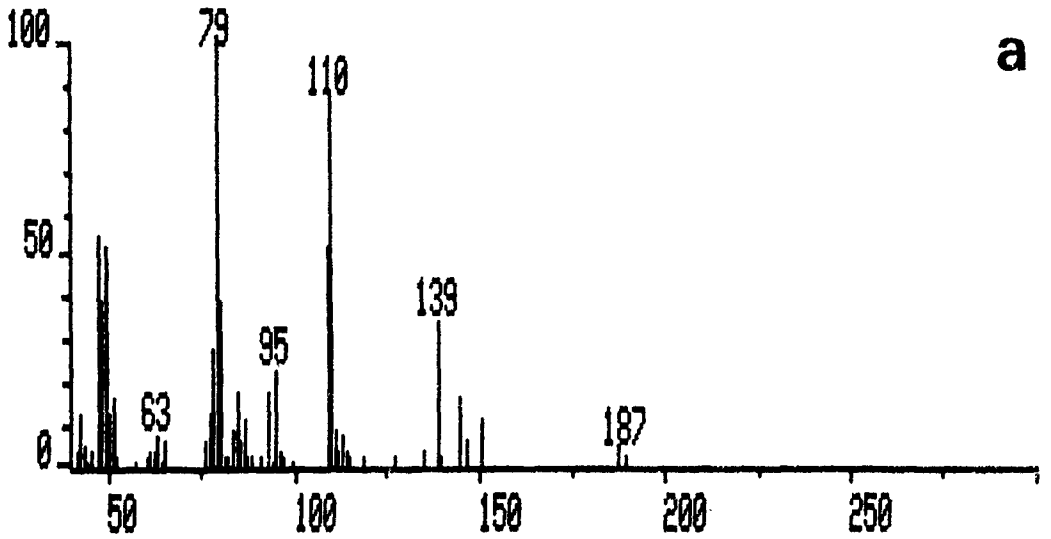
Annex 16: a) EI mass spectrum and b) ammonia CI mass spectrum of an unknown (chlorinated).

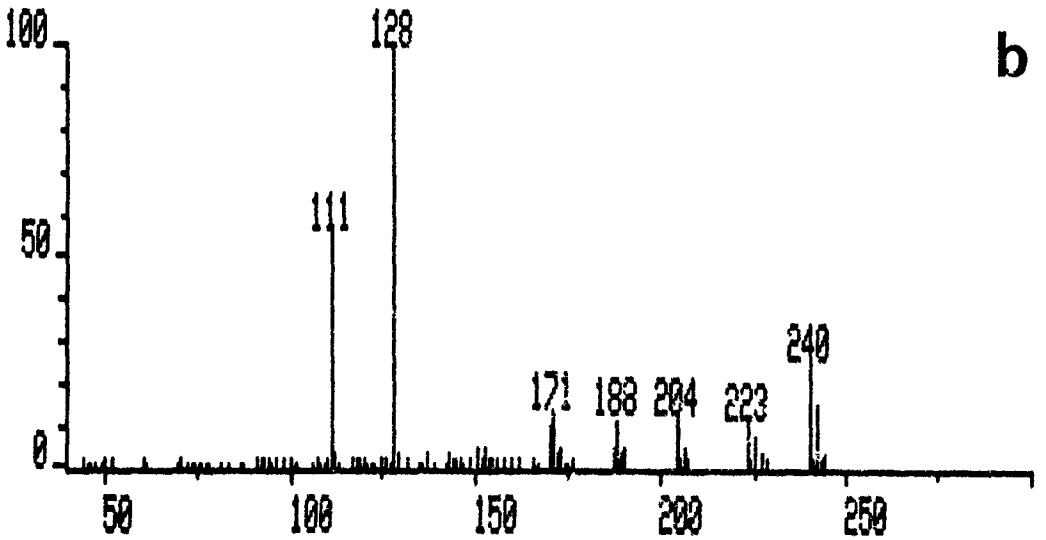


Annex 16 (con't): a) EI mass spectrum and b) ammonia CI mass spectrum of an unknown (chlorinated).

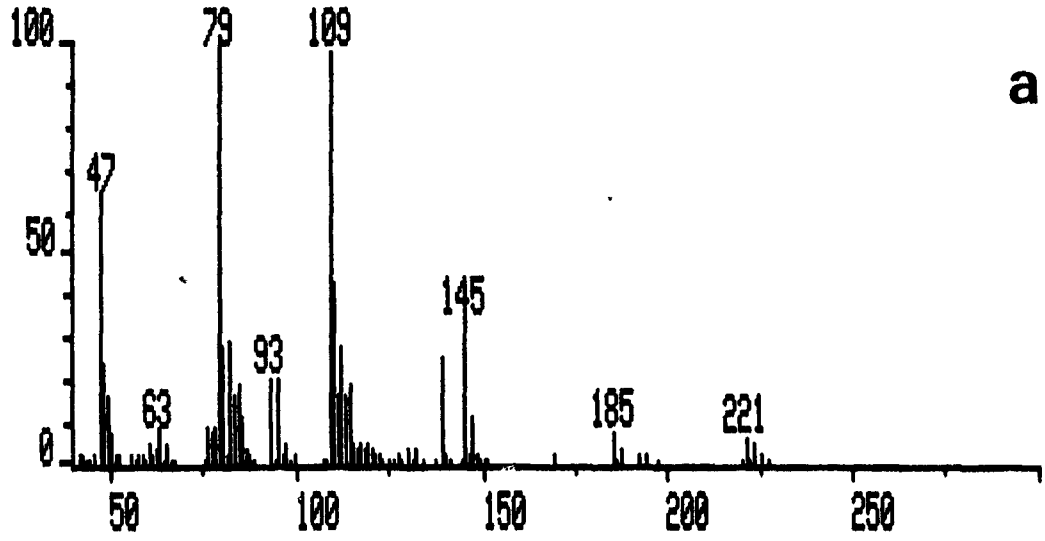


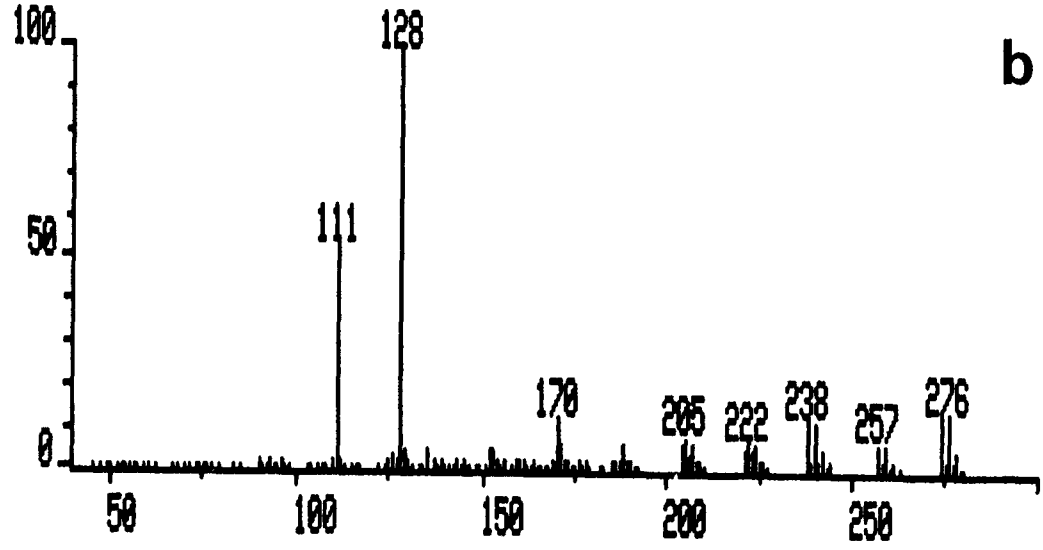
Annex 16 (con't): a) EI mass spectrum and b) ammonia CI mass spectrum of an unknown (chlorinated).



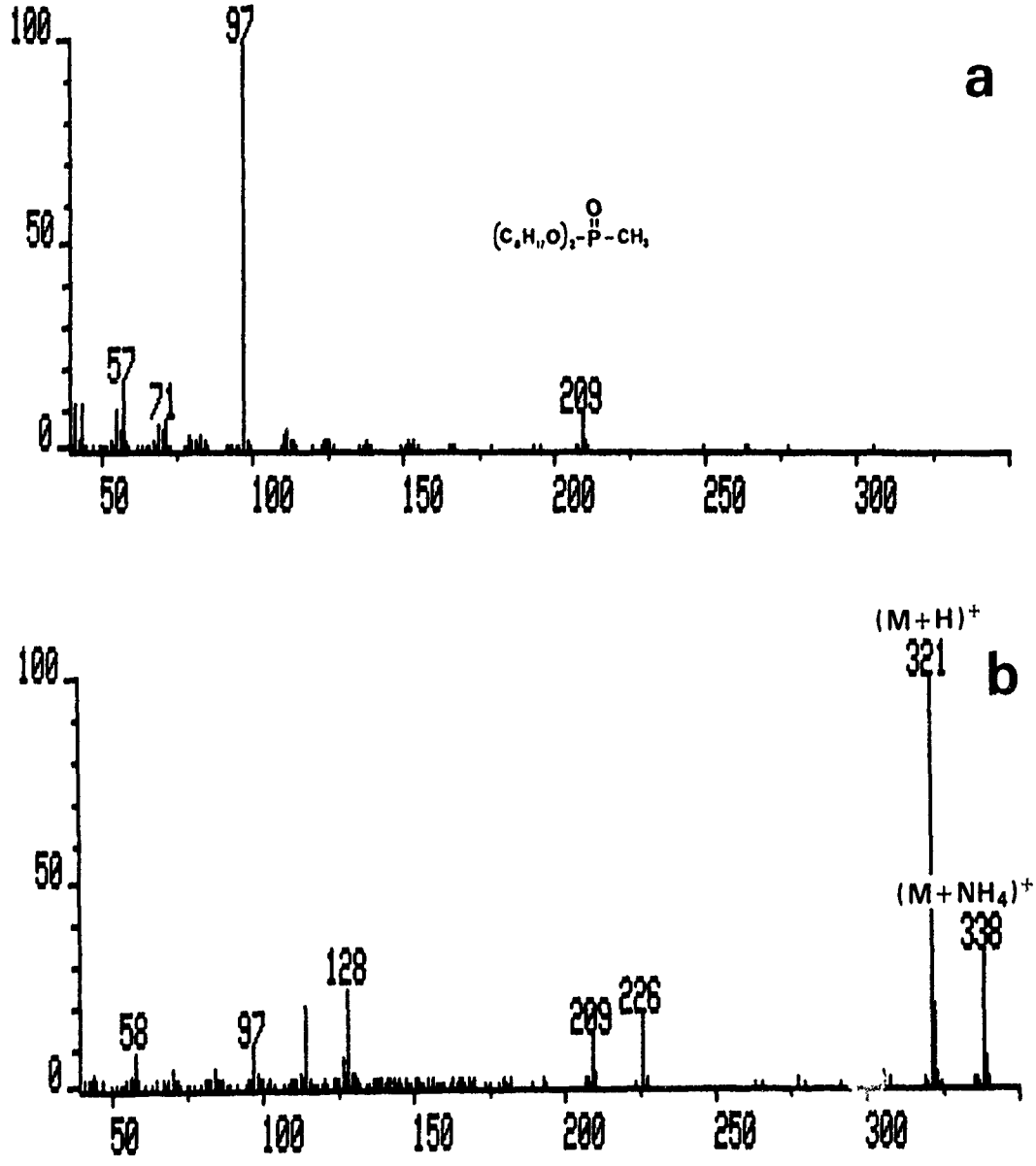


Annex 16 (con't): a) EI mass spectrum and b) ammonia CI mass spectrum of an unknown (chlorinated).

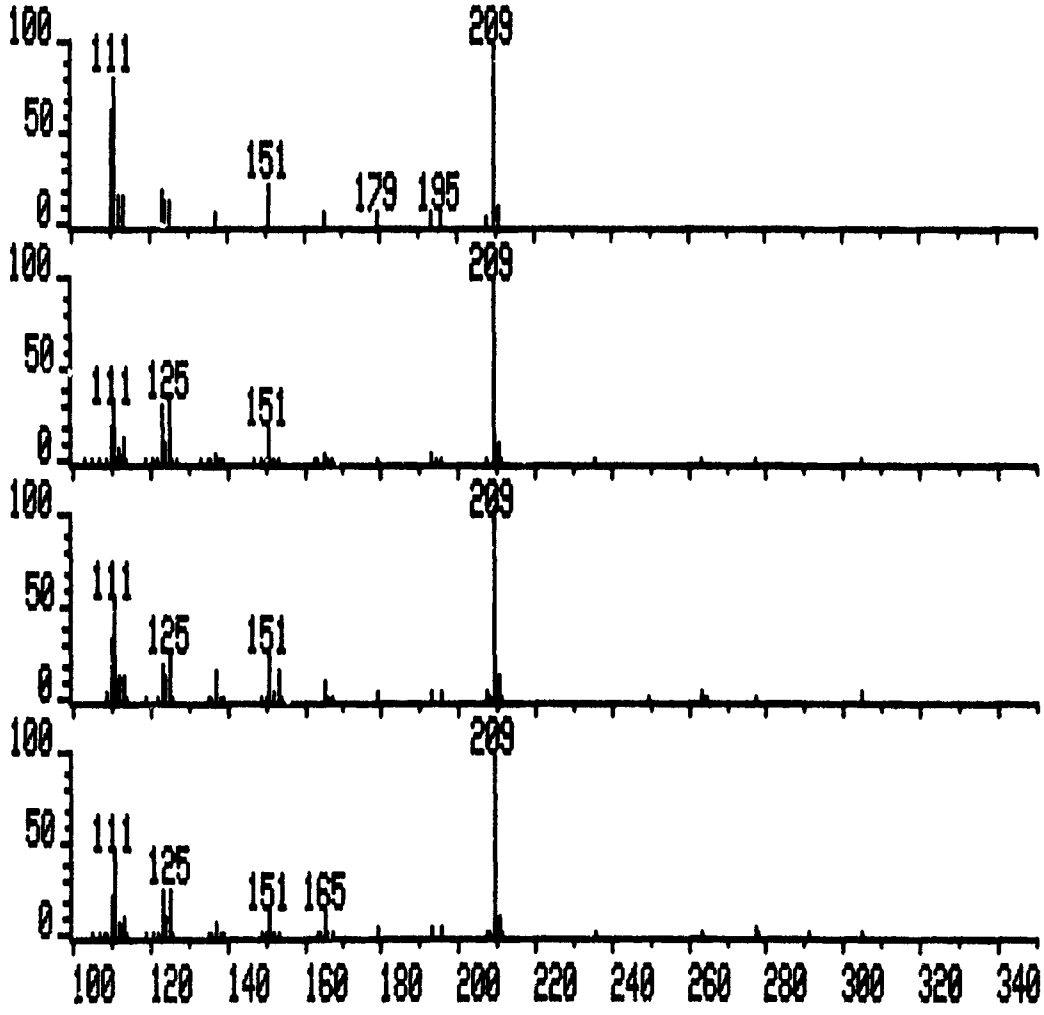




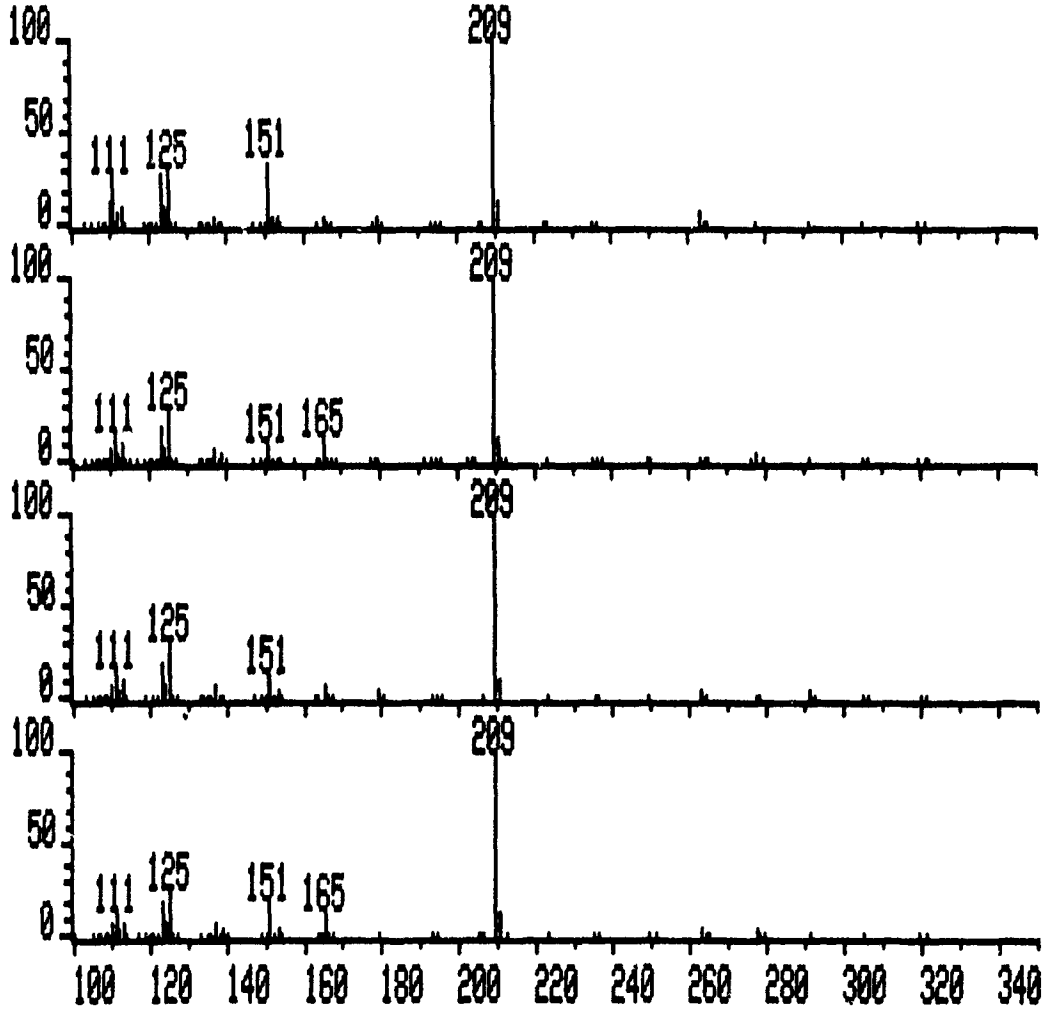
Annex 16 (con't): a) EI mass spectrum and b) ammonia CI mass spectrum of an unknown (chlorinated).



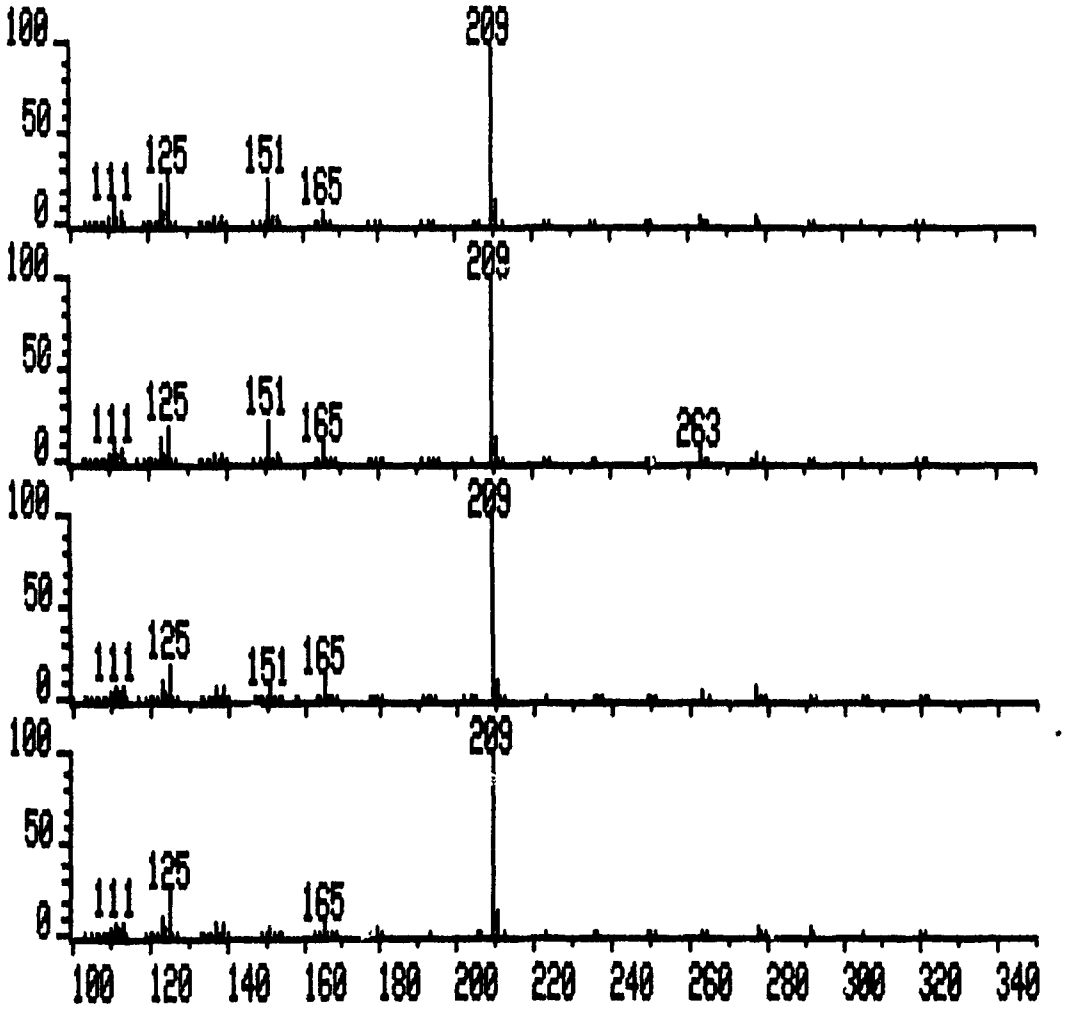
Annex 17: a) EI mass spectrum and b) ammonia CI mass spectrum of a typical dioctyl methylphosphonate (based on interpretation).



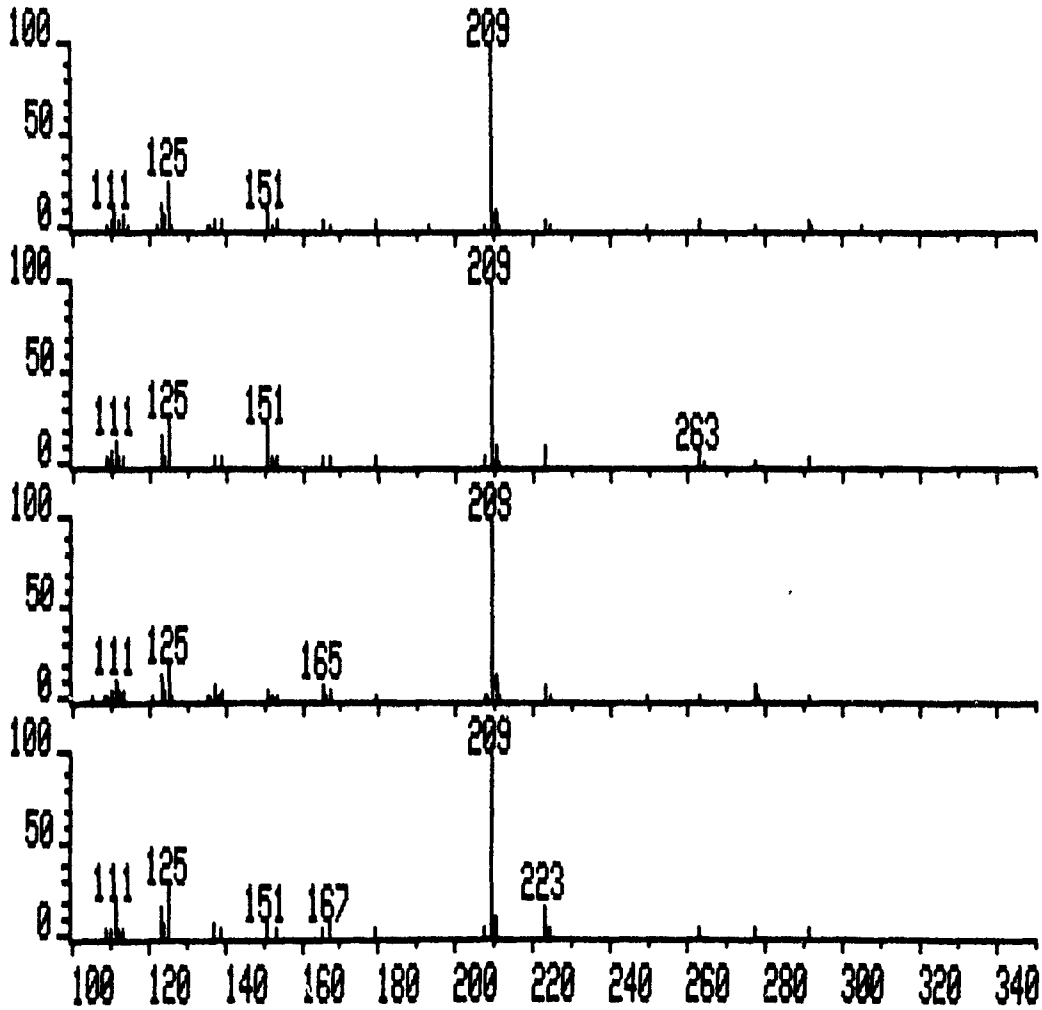
Annex 17 (con't): EI mass spectra (100 to 350 u) of four dioctyl methylphosphonates (based on interpretation).



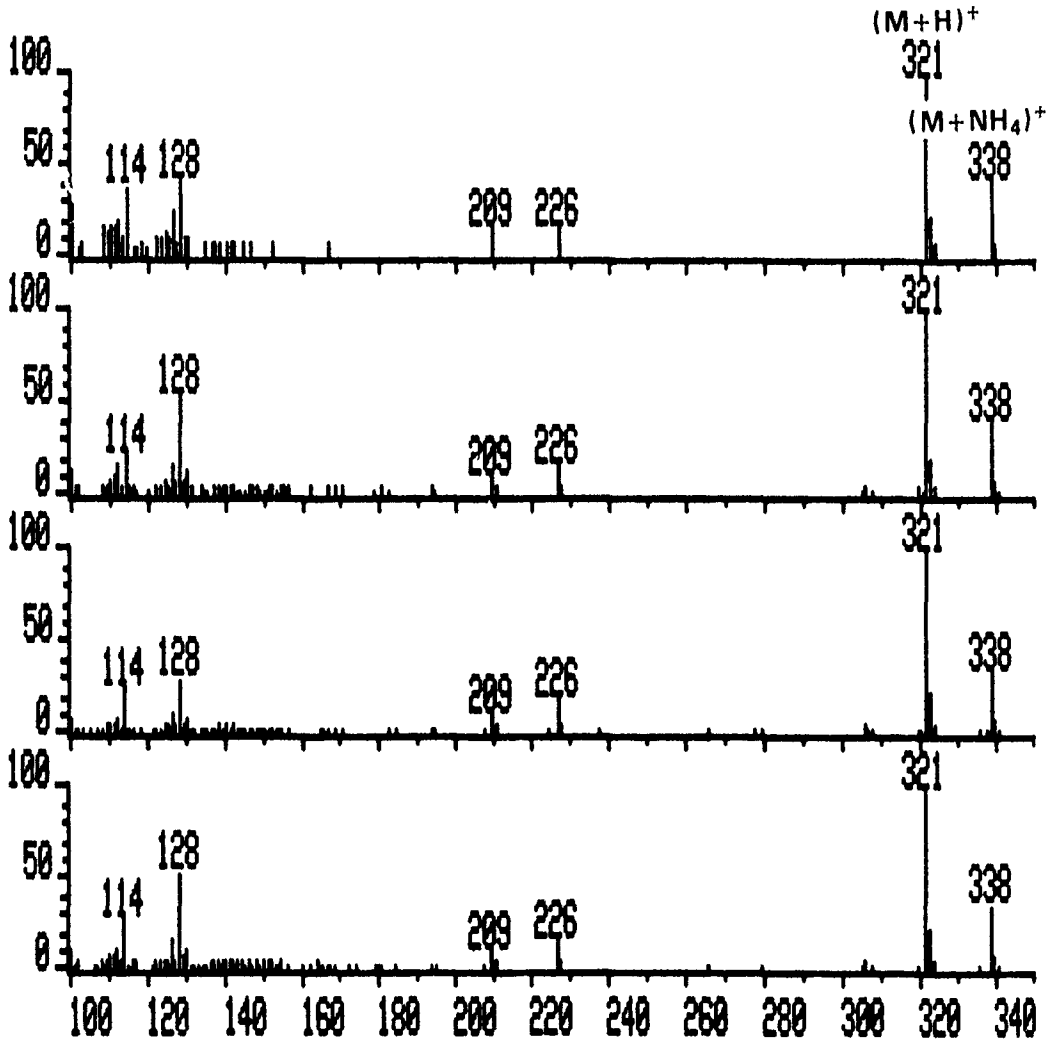
Annex 17 (con't): EI mass spectra (100 to 350 u) of four dioctyl methylphosphonates (based on interpretation).



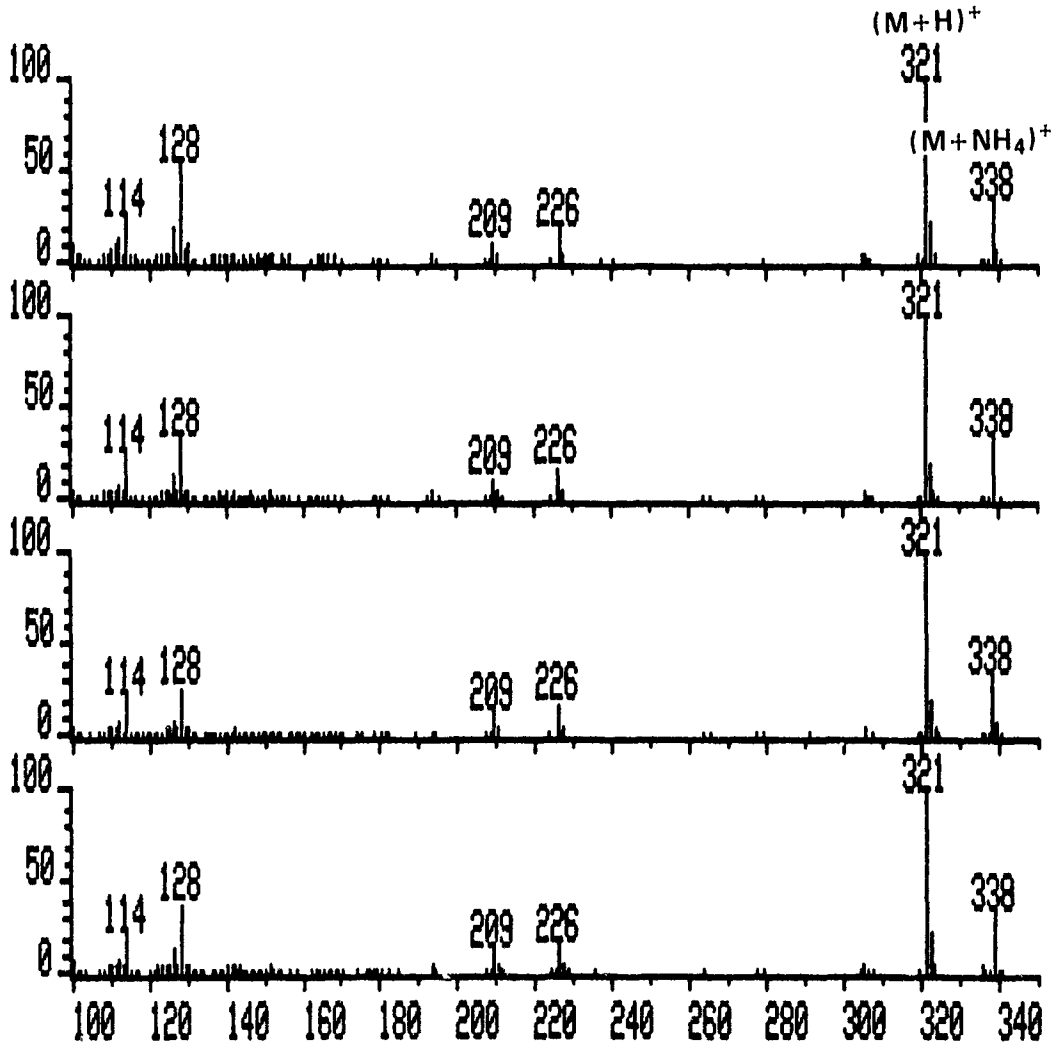
Annex 17 (con't): EI mass spectra (100 to 350 u) of four dioctyl methylphosphonates (based on interpretation).



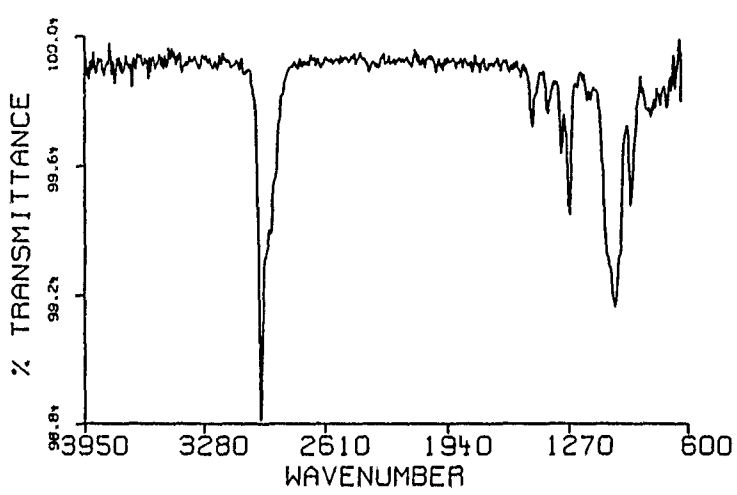
Annex 17 (con't): EI mass spectra (100 to 350 u) of four dioctyl methylphosphonates (based on interpretation).

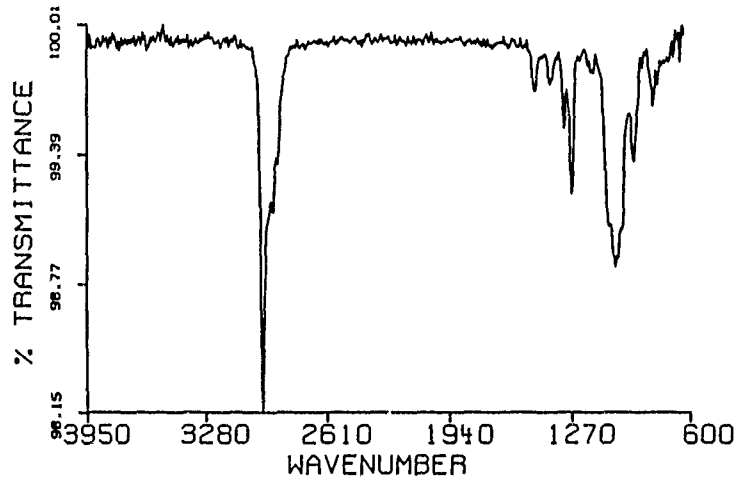


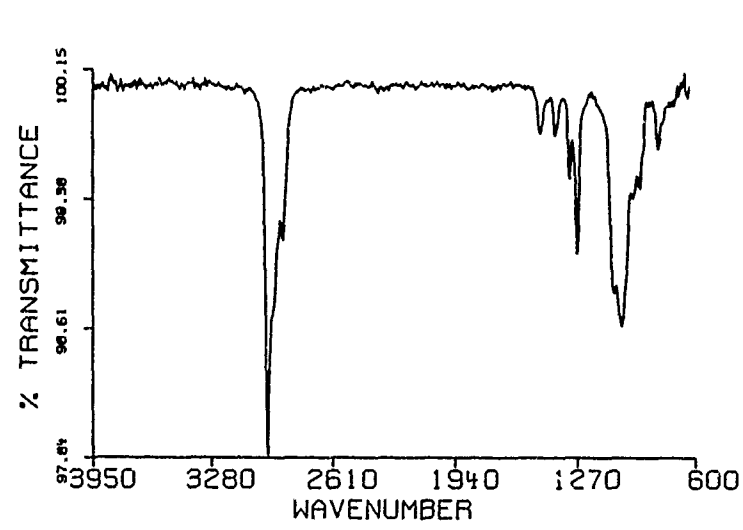
Annex 17 (con't): Ammonia CI mass spectra (100 to 350 u) of four dioctyl methylphosphonates (based on interpretation).



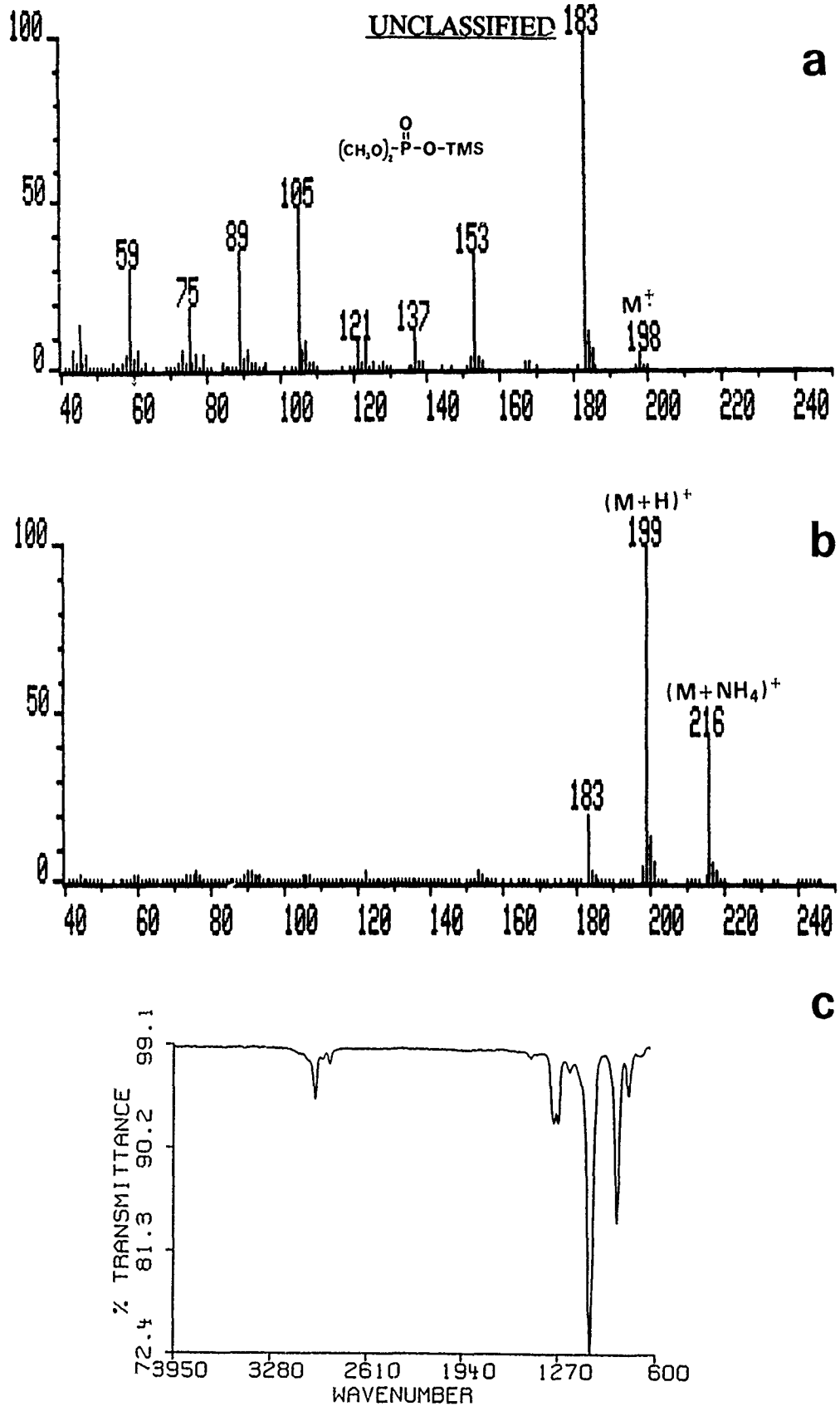
Annex 17 (con't): Ammonia CI mass spectra (100 to 350 u) of four dioctyl methylphosphonates (based on interpretation).



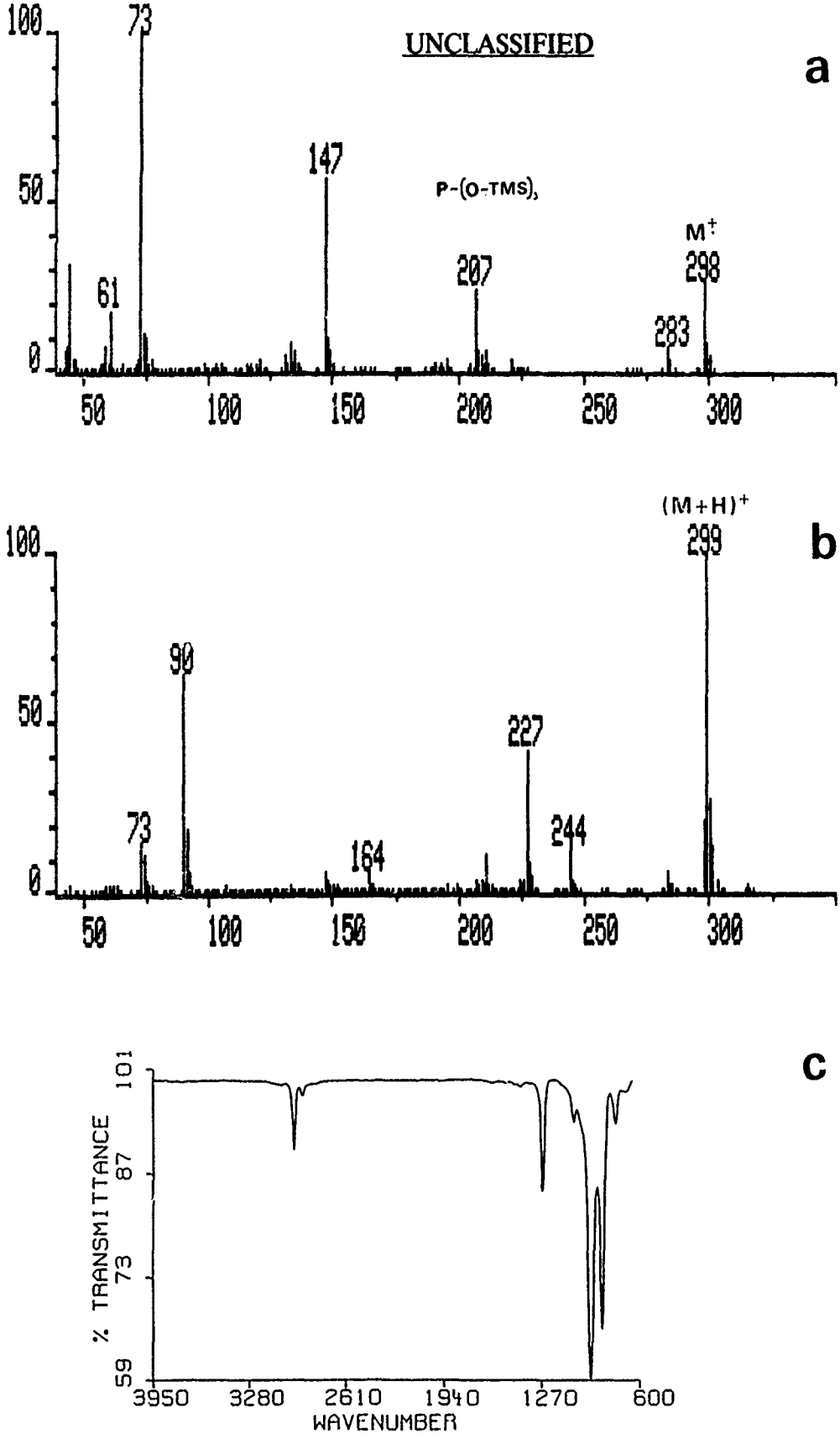




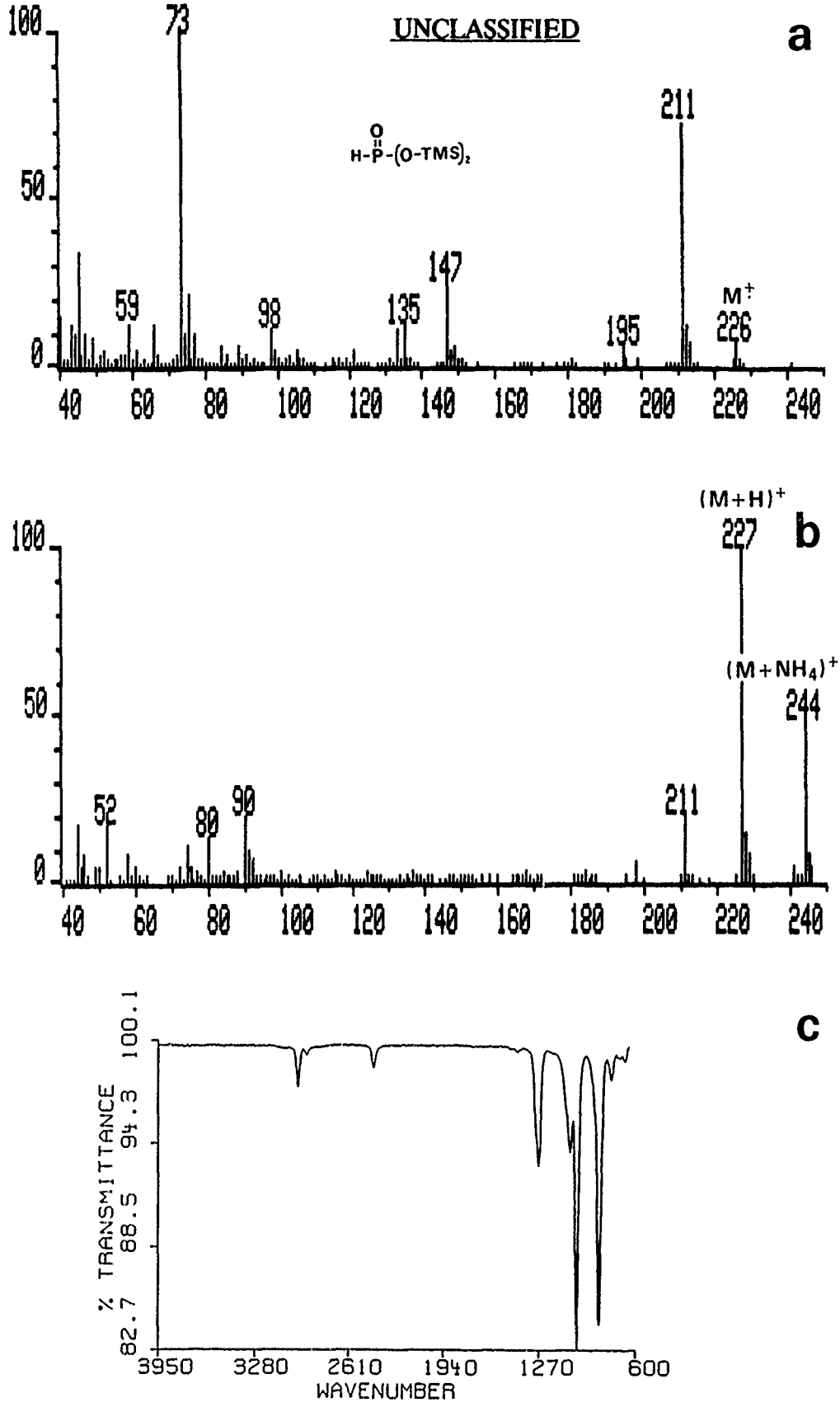
Annex 17 (con't): FTIR spectra of three dioctyl methylphosphonates (based on interpretation).



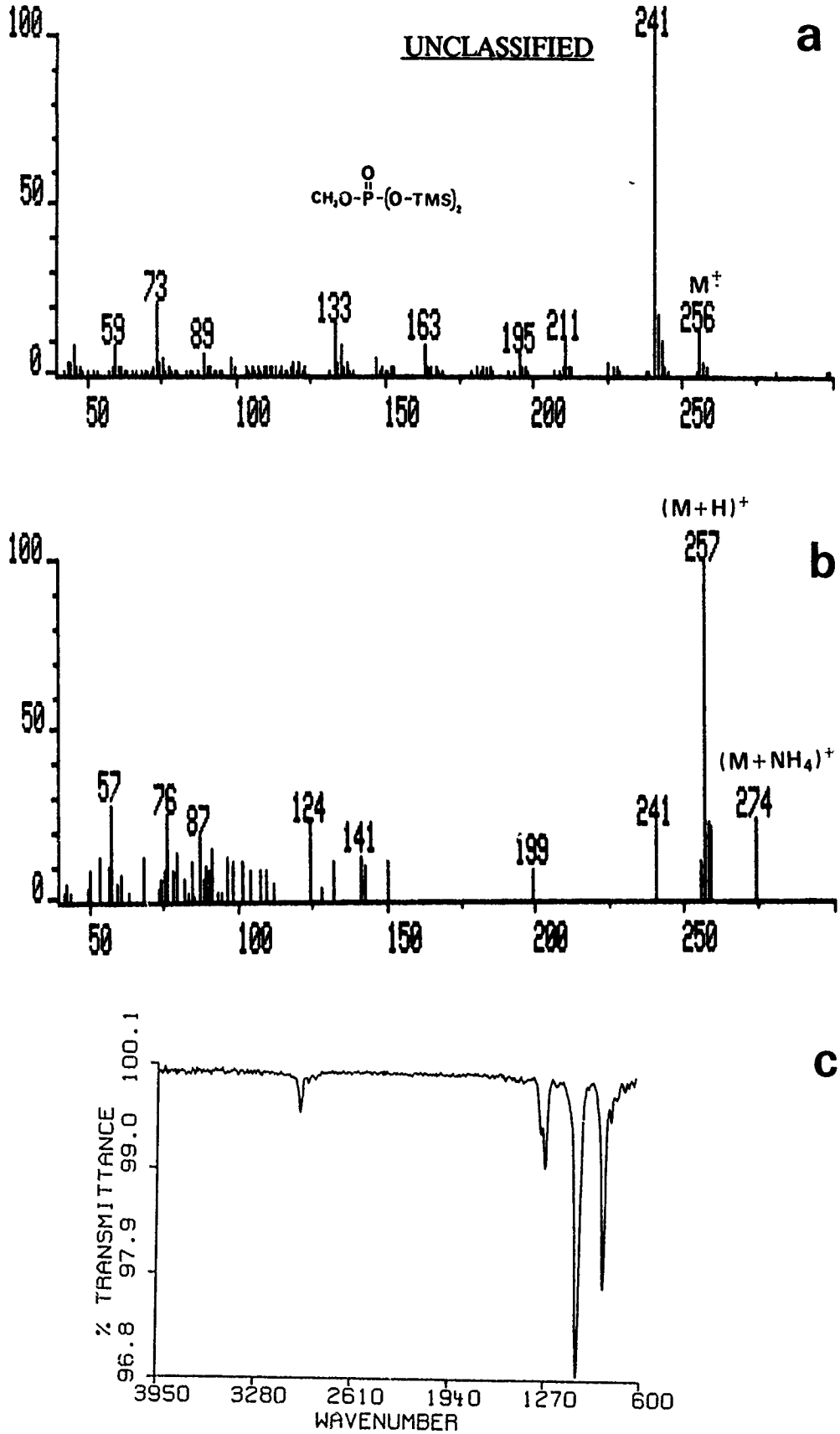
Annex 18: a) EI mass spectrum, b) ammonia CI mass spectrum and c) FTIR spectrum of TMS derivative of dimethyl phosphoric acid (based on interpretation).



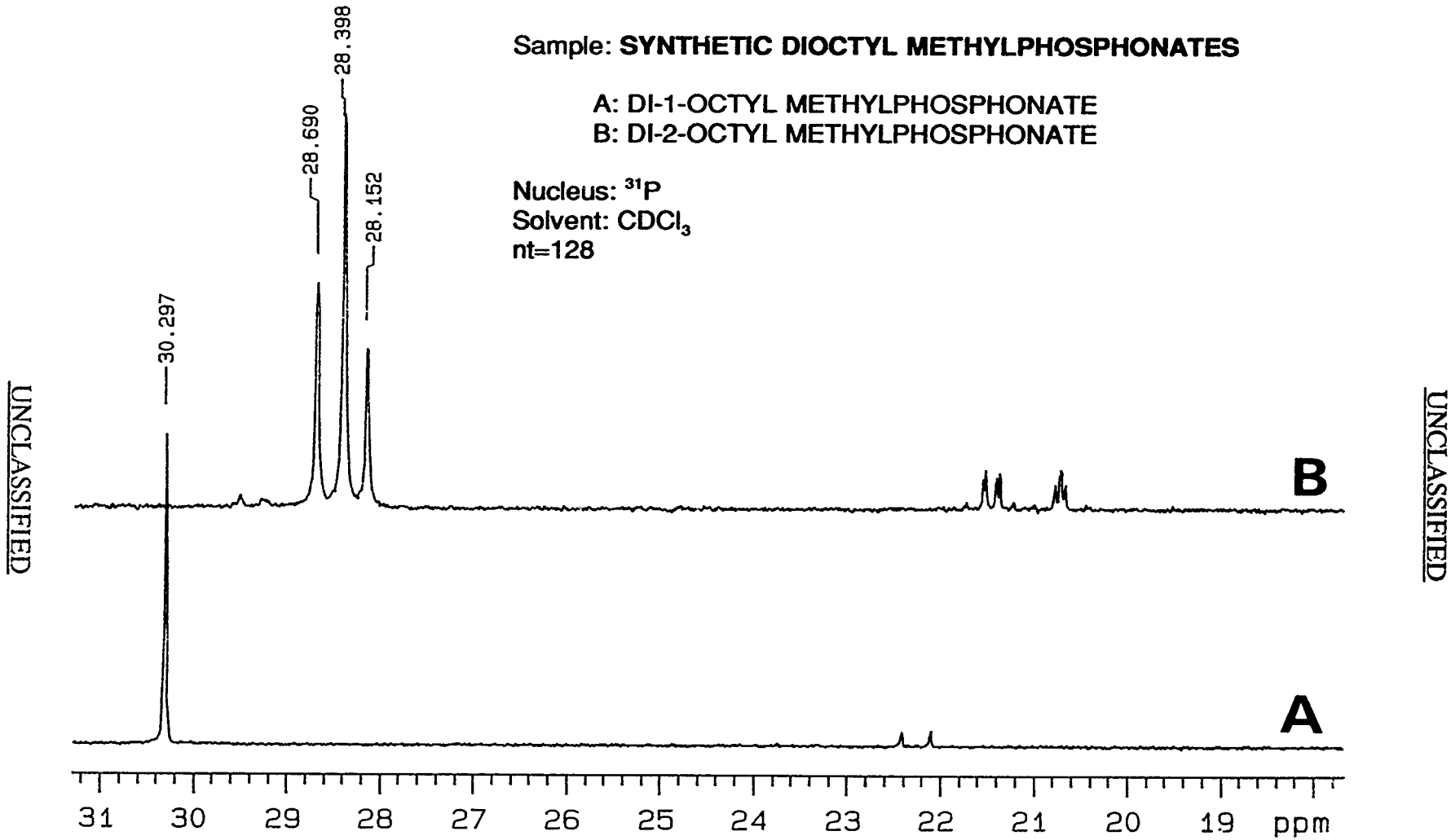
Annex 19: a) EI mass spectrum, b) ammonia CI mass spectrum and c) FTIR spectrum of tri-TMS derivative of phosphorous acid (based on interpretation).



Annex 20: a) EI mass spectrum, b) ammonia CI mass spectrum and c) FTIR spectrum of di-TMS derivative of hydrogenphosphonic acid (based on interpretation).



Annex 21: a) EI mass spectrum, b) ammonia CI mass spectrum and c) FTIR spectrum of di-TMS derivative of methyl phosphoric acid (based on interpretation).



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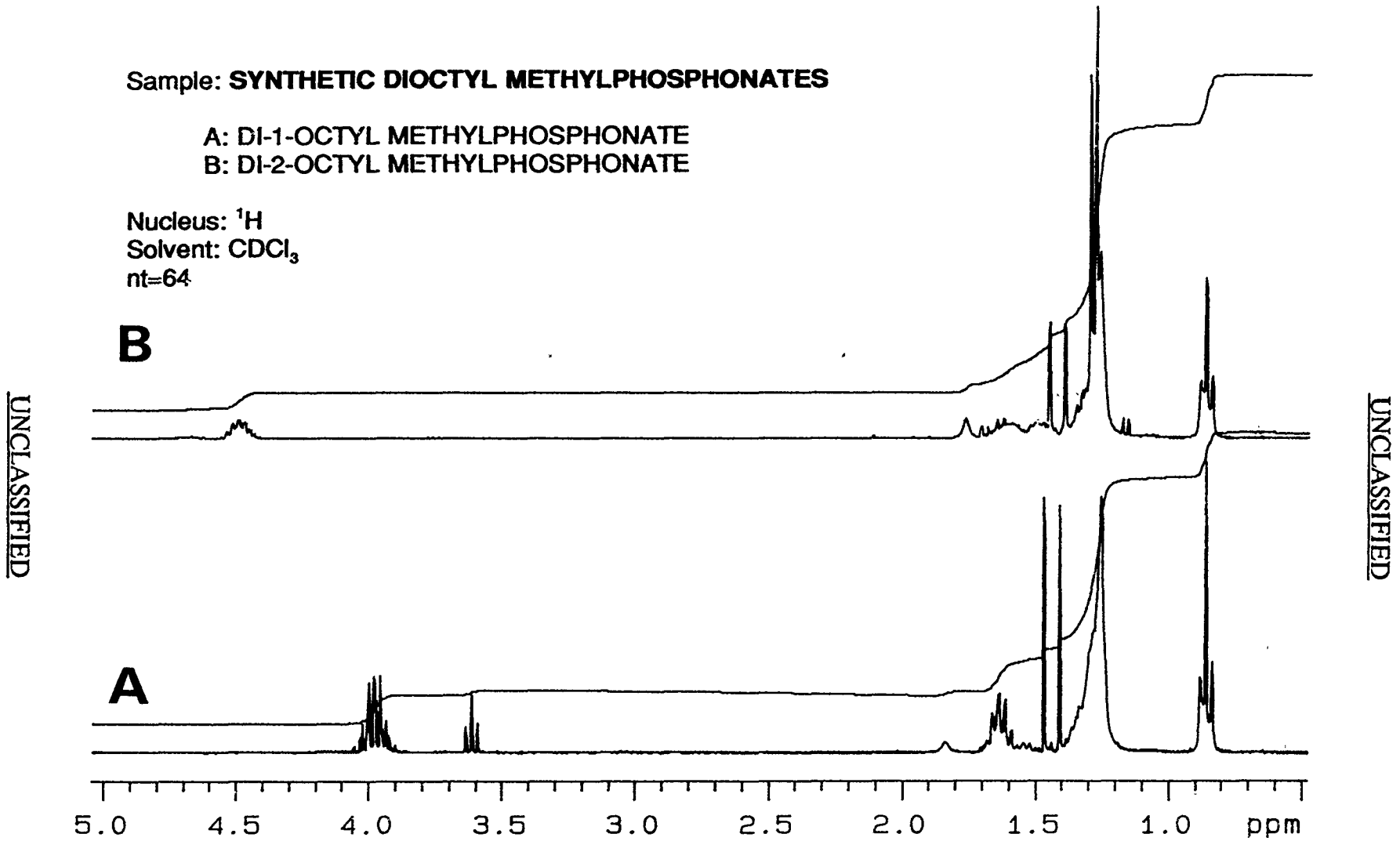
Annex 22: Comparison of the proton decoupled ^{31}P NMR spectra of di-n-octyl methylphosphonate (A) and di-2-octyl methylphosphonate (B). The use of technical grade 2-octanol gives rise to a number of 2-octyl isomers as seen in B.



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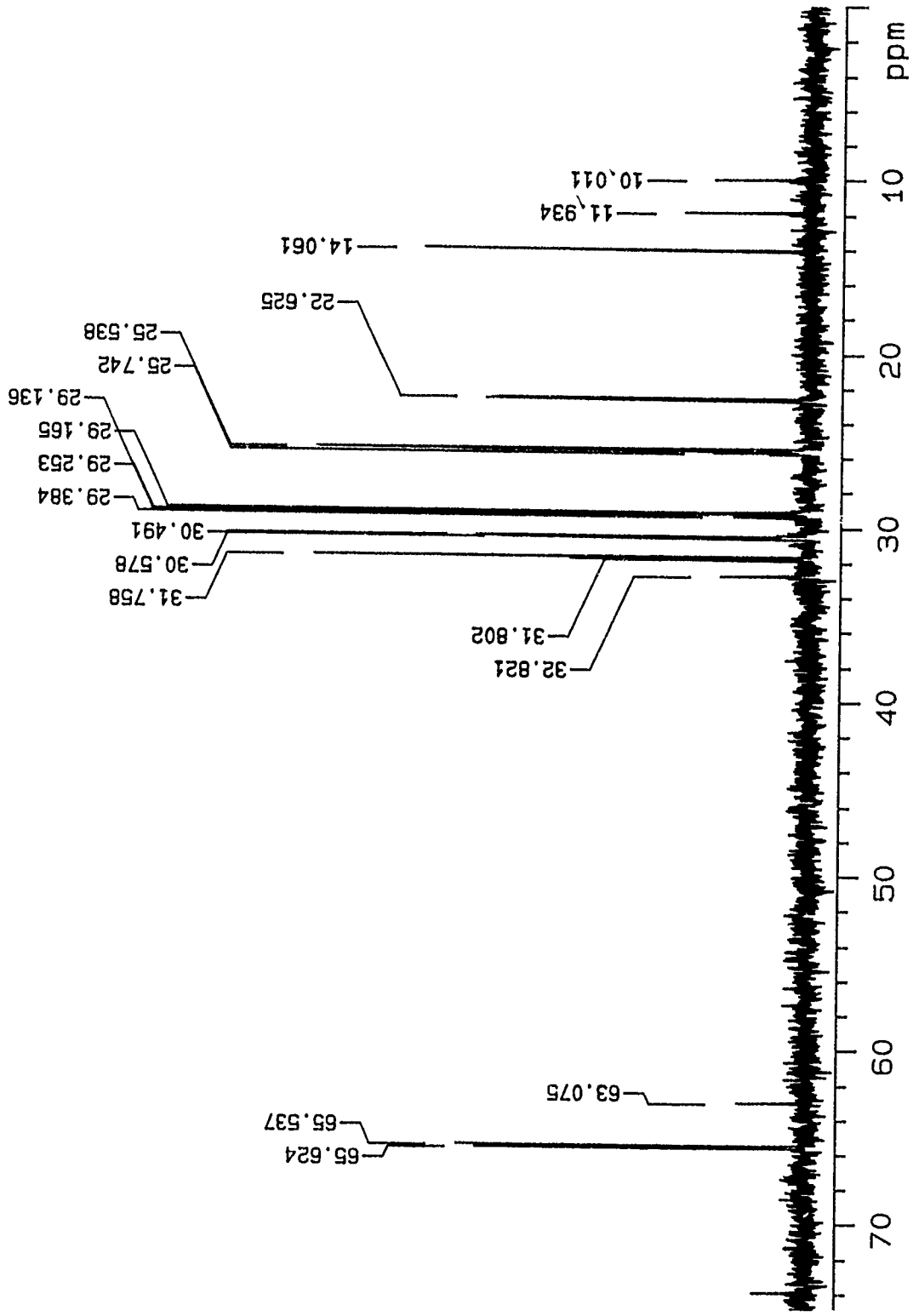
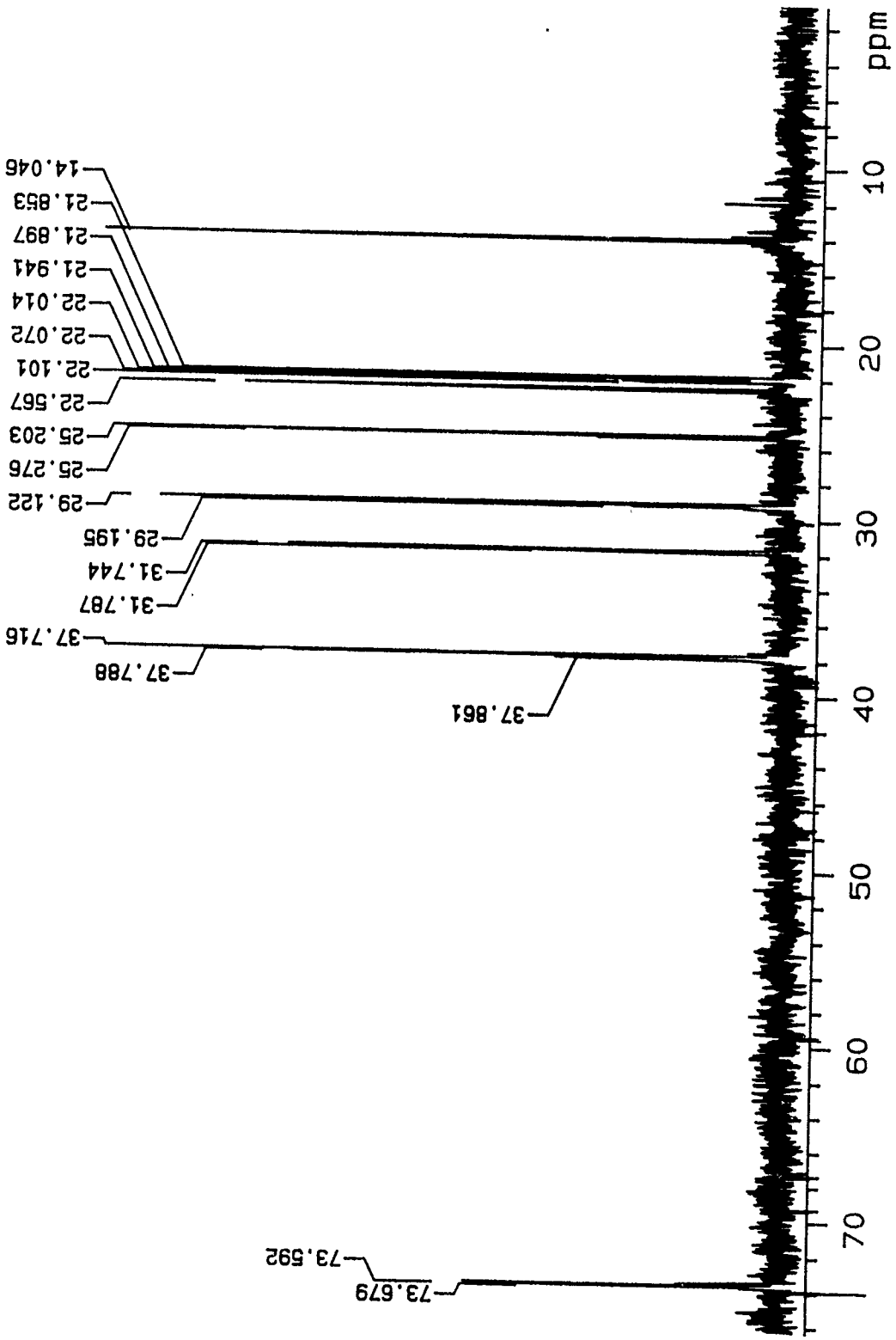
Annex 23: Comparison of the ^{1}H NMR spectra of di-n-octyl methylphosphonate (A) and di-2-octyl methylphosphonate (B).



Annex 24: ^{13}C NMR spectrum of di-n-octyl methylphosphonate.



Annex 25: ^{13}C NMR spectrum of di-2-octyl methylphosphonate.

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Twenty-nine samples, reported to be taken during an inspection of a "Schedule 3" chemical industry, were received by Defence Research Establishment Suffield as part of a United Nations sponsored international round robin analytical exercise designed to evaluate laboratory capabilities. This report summarized Canada's contribution to the round robin analytical verification exercise. Part I provides the results of the chromatographic analyses (GC-MS, GC-FTIR, GC-FID and GC-FPD) and Part II provides the results of NMR analysis and synthesis of authentic standards. Canada confirmed Dichlorvos production and identified more than 20 compounds in the samples, including a group of previously unreported dioctyl methylphosphonates, which would be scheduled under the proposed Chemical Weapons Convention.

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