Interim Report R&D Project 215

Methodology for Organics Analysis
Progress report: April 1991 - March 1992
Appendices

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Project 215

METHODOLOGY FOR ORGANICS ANALYSIS - APPENDICES

Progress report: April 1991 - March 1992

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EXECUTIVE SUMMARY

The aim of the project is to examine the extent to which some recently introduced analytical techniques can be applied to the determination of Red List compounds in a variety of aqueous and water-related matrices.

The Red List compounds of interest may be conveniently considered as two groups - volatile organochlorines (VOCl's) and pesticides, the latter comprising organophosphorous compounds, organo-nitrogen compounds (triazines) and organochlorine pesticides (e.g. the "drins").

Two methods are being explored for the VOCl's, and it appears likely that the purge and trap method which utilises mass spectrometry (MS) for detection will prove to be the most satisfactory, particularly in terms of detection limits.

Although gas chromatography (GC) with specific detectors (such as electron capture (ECD) or nitrogen phosphorous (NPD) detectors) provides a satisfactory detection/quantification techniques for standard solutions of the Red List pesticides and potential interferences, for sample extracts the certainty of detection for Red List compounds may be low, particularly for "dirty" samples. It is therefore suggested that mass spectrometry is probably essential to provide confidence in the analytical results.

Unfortunately it seems that with the most widely used solid phases (C_{18}, C_8), recoveries of some of the compounds of interest using solid phase extraction discs (SPEDs) were low and the reproducibility was poor. It does not appear likely that a single solid phase extraction will be suitable for all of the Red List pesticides, and currently liquid liquid extraction provides a better alternative.

KEY WORDS

Red List, Organic Analysis, Solid Phase Extraction, Gas Chromatography, Mass Spectrometry, GCMS, Purge and Trap, Method Development.

Interim Report 215/6/T

1. INTRODUCTION

The broad aim of this project is to investigate the extent to which some of the more recently introduced techniques for organics analysis are applicable to the determination of Red List compounds in a variety of aqueous and water-related matrices. The NRA has a statutory obligation to monitor these substances in controlled waters, and it is desirable to be able to do this as effectively and efficiently as possible.

This progress report describes all of the work undertaken in the second year of the contract. Work undertaken during the first half of this year has already been reported (NRA Interim Report 215/3/T), and where appropriate is incorporated into this current report.

Work carried out during the first year (April 1990 - March 1991) was reported in NRA report NR 2746 (March 1991). The contract is scheduled to end in March 1993.

1.1 Overall project objective

To improve Red List analytical methodology, with the aim of increasing sample throughput and reducing cost through time and manpower savings, and to produce methods for the unambiguous identification of Red List organics.

1.2 Specific objectives

- To develop solid phase extraction (SPE) methods for Red List organics in treated sewage, river water and saline samples;
- To develop robot-compatible extraction methods for fish tissues, sediments and sewage sludge for Red List compounds;
- To investigate mass spectrometry for unambiguous identification of Red List organics;

- To determine the cost benefit of any new analytical methodology as a result of the research.

2. SUMMARY OF WORK

2.1 Introduction

The interim progress report (NRA Interim Report 215/3/T) described progress during the period April 1991 - September 1991. This work, and work undertaken during the period October 1991 - March 1992, is covered in this present report.

During the course of this year, an additional ten compounds were added to the UK Red List organic compounds (originally totalling nineteen organic compounds and compound classes). The Red List now comprises the compounds and compound classes listed in Table 2.1, the 1991 additions being highlighted in bold type. One effect of this increase in determinands to be analysed was that some work carried out during the course of the first year of the project, had to be repeated (e.g. the development of a single-column GC method).

2.2 Activity schedule

Following discussions with the NRA Project Leader, the originally planned schedule was revised to accommodate the increased number of compounds to be analysed. As noted above, this included the necessity to reinvestigate some of the methodology developed during the first year of the contract. The modified schedule was as shown in Table 2.2.

Table 2.1 UK Red List Organic Compounds

Aldrin	Organochlorines
DDT	
Dieldrin	
Endosulfan	
Endrin	
γ-Hexachlorocyclohexane (Lindane)	
Hexachlorobenzene (HCB)	
PCB's (Polychlorinated biphenyls)	
Pentachlorophenol	
Trifluralin	
Carbon tetrachloride	Volatile organochlorines (VOCl's)
Chloroform	
1,2-Dichloroethane	
Hexachlorobutadiene	
Tetrachloroethylene	
Trichlorobenzene	
Trichloroethane	
Trichloroethylene	
Atrazine	Triazines
Simazine	
Azinphos-ethyl	Organophosphorus
Azinphos-methyl	
Dichlorvos	
Fenitrothion	
Fenthion	
Malathion	
Parathion-ethyl	
Parathion-methyl	
Others (not considered)	
Tributyltin compounds	
Triphenyltin compounds	
Dioxins	

Table 2.2 Activity schedule for period 1.7.91 - 31.3.92

1. Optimisation of Single Column/Dual Detection GC system
2. Quarterly Report (1.7.91)
3. Assessment of alternative manufactured solid phase extraction discs (SPEDs)
4. Complete set-up of MID methods on Trio-1 system
5. Optimisation of 1 (above) with inclusion of additional Red List organophosphorus compounds
6. Interim Report (31.8.91)
7. Method details of SPEDs for clean water samples
8. Use of SPEDs
9. Use of GPC clean-up for Sludge/Paper Pulp effluent
10. Interim Report (31.10.91)
11. Interim Report (31.12.91)
12. Examination by GCMS of suitable extracts form activities 8 and 9 (above)
13. Confirmatory GC column study
14. Investigation of MSMS on Trio-3 system to provide more sensitive and specific identification
15. Method details of (i) GC technique for volatile chlorinated compounds, and (ii) all compounds by GCMS, to include Purge and Trap/GC-ITD methodology for volatile compounds
16. Annual report (31.3.92)

2.3 Gas Chromatography (GC) methods

All of the Red List compounds under consideration are amenable to analysis using gas chromatography (GC). They may be conveniently classified into organochlorine compounds (which are detectable by an electron capture detector (ECD)), organophosphorus and triazine compounds (which are detectable by a nitrogen-phosphorous detector (NPD)) and volatile organochlorines (VOCl's) (detectable using ECD). Detection using mass spectrometry (MS) may also be used for all of the compounds of concern.

MS potentially provides greater specificity of detection than either ECD or NPD. However, the specificity of GC-ECD or GC-NPD can be improved by carrying out the analysis of extracts on two different GC columns, so that the provisional detection of a compound based on its retention time on one column can be confirmed by the detection of a peak at the correct retention time on the second column.

In the interests of sample throughput, it is preferable to be able to analyse for as many of the compounds of interest as possible in a single GC run. By splitting the effluent from the GC column, it is possible to simultaneously use two selective detectors (e.g. ECD and NPD). However, one potential disadvantage of this approach may be a reduction in the confidence of detection if some of the compounds of interest and potential interferences co-elute or have retention times which differ by only a few seconds. As noted above, in practice two GC runs may be necessary.

The initial investigations for this work involved attempting to establish suitable GC conditions to allow all of the Red List organochlorine and organophosphorus compounds to be analysed on a single GC column fitted with a dual detector system, and on ascertaining the most appropriate MS techniques for their unambiguous detection. The analysis of the volatile chlorinated compounds (VOCl's) was considered separately.

2.3.1 Single column with dual detectors

The previous conditions using a single capillary column and two detectors for the analysis of the combined standard mixture of organophosphorus and organochlorine insecticides and the Red List triazines were reported in report NR 2746.

The expansion of the Red List to include four additional organophosphorus compounds required a reappraisal of the initially developed conditions, to ensure that the newly added compounds did not co-elute with either existing Red List compounds or potential interferences. The new combined standard mixture for the GC evaluation contained a total of 59 compounds. These comprised thirty one Red List compounds (including 6 PCB congeners), three internal standards, and twenty-five potential interferences (e.g. other organophosphorus compounds and several pyrethrins).

It was found that although for the majority of the compounds, there were no co-elution problems with the additional organophosphates when GC retention times were checked using the originally developed GC conditions, parathion ethyl co-eluted with one of the PCB's (C101). It was also noted that the retention times of lindane and disulphoton (the latter added as a potential interference) were very close, and could lead to doubt as to which had been detected.

The elution order of the compounds in the new standard mixture on a DB 1701 capillary column was as given in Table 2.3.

The GC conditions employed were as follows:

GC Column:	DB 1701, 60 m x 0.32 mm ID, 0.25 µm film thickness.
Column temperature:	Initially 160 °C, held for 2 minutes, linearly programmed at 1.5 °C/min to 190 °C, then at 5 °C/min to 280 °C. This final temperature was held for 30 minutes.
Injection temperature:	170-320 °C, programmed at 90 °C/min, final temperature held for 2 minutes.
Column effluent splitter:	Valco metallic splitter, volume split 50:50.
Detectors:	Electron capture detector (ECD) and nitrogen/phosphorous detector (NPD) at 340 °C.

Precision data (within batch relative standard deviation) relating to the detector response of the Red List compounds, relative to the internal standard, were presented in NRA report NR 2746. However, due to the increased number of Red List compounds, it was necessary to repeat these for the compounds detectable using the NPD detector. These results are given in Table 2.4. As all of the relevant additional Red List compounds were organophosphates (NPD detectable), the data obtained for the ECD detectable compounds were unaffected and remain as reported in report NR 2746. However, for the sake of completeness, they are presented in this report in Table 2.5.

Table 2.3 Order of elution of Red List organic compounds and potential interferences on DB 1701 capillary column.

1. *Dichlorvos
2. *Hexachlorobenzene (HCB)
3. Demeton-S-methyl
4. *Trifluralin
5. Phorate
6. α-HCH
7. Omethoate
8. Diazinon
9. Fonofos
10. *γ-HCH (Lindane)
11. Disulfoton
12. *Atrazine
13. *Simazine
14. Propetamphos
15. *PCB-28
16. Heptachlor
17. Pirimicarb (int. standard for OP's/ON's)
18. Dimethoate
19. *PCB-52
20. *Aldrin
21. Primiphos
22. β-HCH
23. Chlorpyriphos
24. *Parathion-methyl/ Isodrin
25. *Fenthion
26. *Malathion
27. *Fenitrothion
28. cis-Heptachlor epoxide
29. trans-Heptachlor epoxide (int. standard for OCl's)
30. *Parathion-ethyl/*PCB-C101
31. o,p'-DDE
32. *α-Endosulfan
33. Chlorfenvinphos
34. p,p'-DDE
35. *Dieldrin
36. o,p'-DDD
37. PCB-C118
38. *Endrin
39. *o,p'-DDT
40. *PCB-C153
41. p,p'-DDD
42. *PCB-C138
43. *β-Endosulfan
44. *p,p'-DDT
45. Triazinon
46. *PCB-C180
47. cis-Permethrin
48. Phosalone
49. trans-Permethrin
50. *Azinphos-methyl
51. *Azinphos-ethyl
52. Decachlorobiphenyl (int. standard for PCB's)
53. Cypermethrin (4 isomers)
54. Fenvalerate (2 isomers)
55. Deltamethrin

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* - Red List compounds

Table 2.4 Precision of the single column GC method with NPD detection for standard solutions.

Compound	Mean response relative to internal standard	Relative standard deviation (%)
*Dichlorvos	1.768	3.8
Demeton-S-methyl	1.591	4.4
Phorate	1.760	5.1
Omethoate	0.881	3.4
Diazinon	1.988	3.5
Fonofos	2.113	3.8
Disulfoton	1.928	4.3
*Simazine	0.676	4.2 (n=6)
*Atrazine	0.553	7.5
Dimethoate	1.524	3.2
Pirimiphos	2.010	3.5
Chlorpyrifos	1.614	3.9
*Parathion-methyl	1.431	3.4
*Fenthion	1.362	3.4
*Malathion	1.495	3.4
*Fenitrothion	1.244	3.7
*Parathion-ethyl	1.585	4.2
Chlorfenvinphos	1.127	3.9
Phosalone	0.545	3.6
*Azinphos-methyl	0.439	4.0
*Azinphos-ethyl	0.796	3.9

* - Red List compounds

The standard solution contained 250µg l^{-1} of each compound; the number of replicate injections (n) was 10, unless otherwise noted.

Table 2.5 Precision of the single column GC method with ECD detection for standard solutions

Compound	Conc. (μg l^{-1})	Mean response relative to int. standard	Relative standard deviation(%)
*Dichlorvos	250.00	0.511	6.2
*HCB	13.48	0.588	4.0
*Trifluralin	9.96	0.349	4.8
Phorate	250.00	0.371	4.0
α-HCH	8.84	0.515	3.6
Omethoate	250.00	0.149	5.3
Diazinon	250.00	0.439	3.0
Fonofos	250.00	3.816	2.6
*Lindane (γ-HCH)	6.95	0.408	5.2
*PCB-C28	40.00	0.844	3.3
Heptachlor	7.97	0.509	3.9
Dimethoate	250.00	1.442	2.9
*PCB-C52	39.00	0.521	2.4
*Aldrin	7.96	0.492	2.4
β-HCH	27.06	0.634	3.4
Chlorpyrifos	250.00	4.653	1.4
*Malathion	250.00	0.899	4.0 (n=9)
*Fenitrothion	250.00	2.486	2.7
cis-HCE^{+}	5.00	0.261	3.4
trans-HCE^{+}	0.01	1.948	2.3
*PCB-C101	41.40	0.768	2.6
o,p'-DDE	15.21	0.750	3.0
*α-Endosulfan	9.96	0.463	3.4
Chlorfenvinphos	250.00	4.215	2.6
Isodrin	10.00	0.169	12.8
p,p'-DDE	17.40	0.792	2.0
*Dieldrin	15.95	0.742	2.8
o,p'-DDD	13.15	0.353	3.0
*PCB-C118	41.76	0.777	2.5
*Endrin	15.02	0.579	3.7
*o,p'-DDT	12.94	0.370	3.0
*PCB-C153	49.56	0.940	2.6
p,p'-DDD	16.35	0.551	3.4
*PCB-C138	39.36	0.998	3.4
*β-Endosulfan	10.24	0.434	2.7 (n=6)
*p,p'-DDT	15.76	0.529	2.3
*PCB-C180	39.84	1.267	2.3
Phosalone	250.00	2.779	3.3
trans-Permethrin	79.12	0.292	1.8
Cypermethrin-1	159.89	0.467	3.1
Cypermethrin-2	159.89	0.310	9.0
Cypermethrin-3	159.89	0.389	5.7
Cypermethrin-4	159.89	0.239	6.6

Table 2.5 continued

Compound	Conc. ($\mu g\ l^{-1}$)	Mean response relative to int. standard	Relative standard deviation (%)
Fenvalerate-1	80.22	0.434	3.0
Fenvalerate-2	80.22	0.269	9.8
Deltamethrin	81.38	0.375	3.3

The number of measurements (n) was 10, unless otherwise stated.
* - Red List compounds
$^+$ - HCE = Heptachlor epoxide

Generally the retention times of most of the compounds in the new standard mixture were found to be column dependent, so although the elution order did not change when a new DB 1701 GC column was installed, there were slight differences in absolute retention times. This suggests that reliance on retention times as the only criterion of detection may lead to unreliable results, particularly as it is known that for sample extracts which contain significant quantities of interferences GC retention times may vary depending on the types and levels of the interferences.

2.3.2 Confirmatory GC column

Initially, investigation of suitable confirmatory GC columns suggested that a DB 5-625 column could be appropriate. However, it has since been found that due to coalition of chlorpyriphos and aldrin, trans-heptachlor epoxide and chlorfenvinphos, and p,p'-DDD and o,p-DDT, this GC column may not be suitable. Additional work is required to either optimise the GC conditions using the DB 5-625 column to ensure that co-elution does not occur, or other GC columns need to be investigated.

2.4 Volatile organochlorines (VOCl's) - GC method

Two methods for the analysis of VOCl's have been investigated. The first is based on solvent extraction with pentane and examination of the pentane extract using GC with ecd detection, and is described below. The second involves a purge and trap procedure with detection using GCMS and progress is outlined in Section 2.7.3.

The Red List VOCl's are listed in Table 2.6, together with some additional halogenated compounds which are known to be frequently present in surface waters at low levels and could be considered as potential interferences. The listing in Table 2.6 is in order of increasing retention times on the GC column used (DB 624) for the analysis of the solvent extracts.

Table 2.6 Elution order of Red List VOCl's and some potential interferences on a DB 624 GC column.

*Chloroform ($CHCl_3$)
*1,1,1-Trichloroethane (1,1,1-$C_2H_3Cl_3$)
*Carbon Tetrachloride (CCl_4)
*1,2-Dichloroethane (1,2-$C_2H_4Cl_2$)
*Trichloroethene (Trichloroethylene) (C_2HCl_3)
Bromodichloromethane ($CHCl_2Br$)
*1,1,2-Trichloroethane (1,1,2-$C_2H_3Cl_3$)
*Tetrachloroethene (Tetrachloroethylene) (C_2Cl_4)
Chlorodibromomethane ($CHBr_2Cl$)
Chlorobenzene (C_6H_5Cl)
1,2-Dibromopropane (Internal standard)
Bromoform ($CHBr_3$)
1,3-Dichlorobenzene (1,3-$C_6H_4Cl_2$)
1,4-Dichlorobenzene (1,4-$C_6H_4Cl_2$)
1,2-Dichlorobenzene (1,2-$C_6H_4Cl_2$)
*1,3,5-Trichlorobenzene (1,3,5-$C_6H_3Cl_3$)
*1,2,4-Trichlorobenzene (1,2,4-$C_6H_3Cl_3$)
*Hexachlorobutadiene (C_4Cl_6)
*1,2,3-Trichlorobenzene (1,2,3-$C_6H_3Cl_3$)

* - Red List compounds

The procedure for the solvent extraction method was as follows:

A screw-top glass vial (30 ml capacity) was slowly filled to overflowing with the sample. A teflon-faced silicon rubber septum was then carefully placed onto the vial, and the vial cap secured, ensuring that no air bubbles were trapped in the vial. A syringe needle was inserted through the septum, and pentane (10 ml) added via a syringe. (This addition of pentane expels an equivalent volume of sample via the initially inserted syringe needle.) The vial was shaken for 30 minutes, and an aliquot (c. 1 ml) of the pentane was removed using a syringe, and this extract analysed by GC with ecd detection. Dibromopentane was used as an internal standard.

The GC conditions used were as follows:

GC Column: DB 624, 30 m, 0.32 mm ID, 1.8 µm film thickness
Column temperature: Initially 45 °C, held for 2 minutes, linearly programmed at 5 °C/min to 65 °C, then linearly programmed at 7.5 °C/min to 200 °C and held for 5 minutes.
Injection temperature: 40-200 °C at 100 °C/min, held for 2 minutes.
Sample volume: 2.0 µl
Detector: Electron capture detector (ecd).

The results of a series of spiking experiments carried out in duplicate, to establish the performance characteristics of the method are given below in Table 2.7.

Table 2.7 Performance data of solvent extraction/GC-ECD method from spiking experiments with Red List VOCl's and potential interferences.

Compound	Concentration ($\mu g\ l^{-1}$)	Total standard deviation (%)	Number of pairs of duplicates
*$CHCl_3$	5.97	10.2	10
	14.92	8.1	10
*1,1,1-$C_2H_3Cl_3$	5.96	9.4	10
	14.90	11.5	10
*CCl_4	2.00	8.9	10
	5.00	8.9	10
*1,2-$C_2H_4Cl_2$	49.97	37.0	7
*C_2HCl_3	5.97	12.8	10
	14.93	15.4	10
$CHBrCl_2$	3.96	14.5	10
	9.90	8.0	9
*1,1,2-$C_2H_3Cl_3$	6.04	12.1	10
	15.11	15.8	7
*C_2Cl_4	2.02	13.4	10
	5.04	17.0	10
$CHBr_2Cl$	6.13	12.8	10
	15.32	11.2	10
C_6H_5Cl	300	12.3	7
	750	10.9	6
$CHBr_3$	5.79	21.4	10
	14.47	14.3	10
1,3-$C_6H_4Cl_2$	20.10	18.0	8
	50.26	13.2	8
1,4-$C_6H_4Cl_2$	50.08	29.8	6
1,2-$C_6H_4Cl_2$	19.97	17.8	8
	49.04	17.2	8
*1,3,5-$C_6H_3Cl_3$	21.09	6.4	5
	52.73	10.2	5
*1,2,4-$C_6H_3Cl_3$	21.39	5.2	5
	53.46	7.4	5
*C_4Cl_6	10.50	5.6	5
	26.26	11.4	5
*1,2,3-$C_6H_3Cl_3$	20.97	5.0	5
	52.41	8.4	5

* - Red List compounds

The limits of detection, at normal sensitivity settings, were calculated from between batch standard deviations of low standards. The limit of detection (LOD) was taken as 2ts, where _t_ is single sided. (LOD's calculated in this way are likely to be overestimated.) The LOD's found are given in Table 2.8

Table 2.8 Limits of detection (LOD's) for VOCl's by solvent extraction/GC-ECD method.

Compound	LOD (µg l^{-1})	° of freedom
*Chloroform	0.57	10
Bromodichloromethane	0.39	10
Chlorodibromomethane	0.79	10
Bromoform	0.58	10
*1,1,1-Trichloroethane	0.50	10
*Carbon tetrachloride	0.19	10
*Trichloroethylene	0.44	10
*1,1,2-Trichloroethane	2.48	10
*Tetrachloroethylene	0.17	10
Chlorobenzene	105	5
1,2-Dichlorobenzene	13.0	10
1,3-Dichlorobenzene	8.98	9
1,4-Dichlorobenzene	47.9	7
1,2-Dichloroethane	24.0	6
*1,3,5-Trichlorobenzene	0.72	9
*1,2,4-Trichlorobenzene	0.84	9
*Hexachlorobutadiene	0.35	9
*1,2,3-Trichlorobenzene	1.23	9

* - Red List compounds

2.5 Robot compatible clean-up methods

The gel-permeation chromatography (GPC) clean-up developed for fish livers, where the main interferences were lipids, was reported in report NR 2746. Alternatives to GPC clean-up for sewage sludge extracts were investigated, as in addition to lipids, other expected interferences were elemental sulphur and humic/fulvic material.

The results of these investigations (*viz.* the use of tetrabutyl ammonium hydrogen sulphate (TBAS) treatment for sulphur removal, and aminopropyl solid phase cartridges for the removal of humics/fulvics) were reported in NRA Report 215/T/3. Briefly, various combinations of TBAS, aminopropyl cartridges and GPC treatments were used serially with sewage sludge extracts, and the effectiveness of the clean-up assessed by measuring the UV absorbance (at 450 nm) after each clean-up stage. The conclusion of this work was that a clean-up utilising GPC alone is as effective as the various combinations of TBAS, aminopropyl cartridges and GPC.

Due to equipment problems (which have now been resolved), it has not yet been possible to apply the GPC clean-up to other types of extracts. However, its use for clean-up of river water extracts will be investigated in the near future.

2.6 Solid phase extraction discs (SPEDs)

At the commencement of this work, a decision was taken to investigate the use of SPEDs as an alternative to liquid-liquid extraction. SPEDs were chosen in preference to solid phase cartridges as it was believed that the former would be more appropriate for samples matrices likely to contain particulate matter and would offer more scope for increasing sample volumes (>500 ml). It was known that an EPA method existed (Method No. 525) which used SPEDs to extract a range of organic compounds from clean waters prior to GCMS samples.

In order to provide a reference against which to compare the performance of SPEDs a liquid-liquid extraction procedure employing sequential hexane and dichloromethane (DCM) extraction was used.

Initially, the EPA specified procedure for SPEDs (C_{18}) was followed. This involved precleaning the SPED with an ethyl acetate/DCM (1:1) mixture, passage of the sample (1 litre; groundwater spiked with the compounds of interest) through the SPED, and extraction of the adsorbed compounds using ethyl acetate/DCM (1:1).

At the time this work was carried out, the additional organophosphorus compounds had not been placed on the Red list, so the data produced refers to the original Red List compounds and the suite of potential interferences. The results obtained are given in Tables 2.9 (NPD responsive compounds, present in the samples at 375 ng $^{1-1}$) and 2.10 (ECD responsive compounds, present in the samples at concentrations of 10-60 ng l^{-1}, with the exception of cypermethrin and trans-permethrin at 120 and 240 ng l^{-1} respectively).

Table 2.9 Recovery data for selected NPD responsive compounds from C_{18} SPEDs, with ethyl acetate/DCM (1:1) as elution solvent.

Compound	% Recovery
*Dichlorvos	13.9
Demeton-S-methyl	31.7
Phorate	35.6
Omethoate	n/r
Diazinon	46.3
Disulphoton	26.4
*Atrazine	28.0
*Simazine	n/r
Dimethoate	n/r
Pirimiphos methyl	45.6
Chlorpyriphos	35.0
*Malathion	47.9
*Fenitrothion	42.9
Phosalone	45.3
*Azinphos methyl	n/r
Chlorfenvinphos	50.3
Fonofos	44.0

* - Red List compounds

n/r - not recovered; the concentration of each compound in the spiked sample was 375 ng l^{-1} of each.

Table 2.10 Recovery data for selected ECD responsive compounds from C_{18} SPEDs, with ethyl acetate/DCM as elution solvent.

Compound	% Recovery
*Hexachlorobenzene	11.5
α-HCH	45.2
*γ-HCH	32.6
Heptachlor	10.3
β-HCH	40.0
cis-Heptachlorepoxide	35.9
*α-Endosulphan	31.7
p,p'-DDE	11.9
*Dieldrin	30.3
p,p'-DDD	24.3
*PCB-C138	21.5
*p,p'-DDT	18.6
*PCB-C180	22.0
trans-Permethrin	22.2
Cypermethrin	20.6

* - Red List compounds
The concentrations of the compounds ranged between 10 and 60 ng l^{-1}, with the exception of cypermethrin and trans-permethrin, which were 120 and 240 ng l^{-1} respectively

Recoveries ranged from nil (for simazine and azinphos-methyl) to 20-40% (for organochlorine Red List compounds). These were very much lower than expected, and as it was thought that the adsorption of the various compounds from water onto the SPEDs was effective, it was decided to investigate different solvents and solvent combinations for the elution of the adsorbed compounds from the SPEDs. The first new elution solvent mixture used was DCM/hexane (1:1), and as the additional organophosphorus compounds had been incorporated into the Red List, the recoveries of the NPD responsive compounds using ethyl acetate/DCM were repeated in order to obtain comparable data. Liquid liquid extraction (LLE) was also carried out.

The results of the recovery experiments (SPEDs extraction with DCM/hexane elution, and LLE) are given in Tables 2.11 and 2.12. Generally, recoveries of Red List compounds from the SPEDs using DCM/hexane as the eluting solvent

(20-80%) were higher than when ethyl acetate/DCM was used for the elution (6-70%). However, LLE gave higher recoveries (70-100%) than either of the SPEDs extractions. The reason for the extreme variability found for the NPD responsive compounds (cf. Tables 2.9 and 2.11) when the SPEDs extraction using ethyl acetate/DCM for elution was repeated, is not known but is of some concern. The possibility of misidentification of some compounds cannot be ruled out, as identification was based only on GC retention time.

Table 2.11 Comparison of recovery data of NPD responsive compounds using C_{18} SPEDs, with elution with ethyl acetate/DCM (1:1) and hexane:DCM (1:1), and using liquid liquid extraction

Compound	% Recovery SPEDs with ethyl acetate/DCM	SPEDs with hexane/DCM	LLE
*Dichlorvos	23.2	30.4	85.9
Demeton-S-methyl	n/r	2.5	43.3
Phorate	3.5	22.2	52.5
Omethoate	n/r	6.7	n/r
Diazinon	56.0	73.7	90.9
Fonofos	44.0	61.4	92.7
Disulphoton	n/r	n/r	41.5
*Atrazine	46.1	72.6	82.6
*Simazine	35.6	53.2	78.5
Propetamphos	48.9	75.8	90.9
Dimethoate	7.5	6.0	40.5
Pirimiphos methyl	52.3	68.1	92.7
Chlorpyriphos	41.8	60.0	92.7
*Parathion-methyl	58.0	72.0	92.7
*Fenthion	5.9	22.7	69.6
*Malathion	50.6	70.9	88.3
*Fenitrothion	55.7	72.0	92.7
*Parathion-ethyl	53.3	68.1	90.9
Chlorfenvinphos	58.0	75.8	90.9
Triazinon	56.3	81.8	93.6
Phosalone	55.5	77.3	94.5
*Azinphos-methyl	69.8	78.8	101.7
*Azinphos-ethyl	56.9	78.0	96.3

* - Red List compounds
n/r - not recovered

Table 2.12 Comparison of recovery data of ECD responsive compounds using C_{18} SPEDs, with elution with ethyl acetate/DCM (1:1) and hexane/DCM (1:1) and using liquid liquid extraction

Compound		% Recovery	
	SPEDs with ethyl acetate/DCM	SPEDs with hexane/DCM	LLE
*HCB	11.5	19.4	79.2
α-HCH	45.2	60.2	84.2
*γ-HCH	32.6	40.2	79.2
Heptachlor	10.3	23.6	66.1
β-HCH	40.0	65.3	76.9
cis-HCE+	35.9	52.8	87.5
*α-Endosulphan	31.7	56.3	78.8
p,p'-DDE	11.9	52.8	76.1
*Dieldrin	30.3	60.2	76.6
p,p'-DDD	24.3	60.2	81.8
*PCB-C138	21.5	63.0	93.6
*p,p'-DDT	22.0	65.3	83.4
trans-Permethrin	22.2	67.5	77.8
Cypermethrin	20.6	64.7	87.7

* - Red List compounds
\+ - cis-Heptachlor epoxide

A second type of solid phase (C_8) became available as SPEDs during the course of this year, and as it was considered that these might offer a slightly different extraction selectivity their performance was compared to C_{18} SPEDs. Elution of the adsorbed compounds from both types of SPEDs was also investigated using hexane and DCM sequentially, rather than as a 1:1 mixture. The results of these investigations are given in Tables 2.13 (NPD detectable compounds) and 2.14 (ECD detectable compounds)

Table 2.13 Comparison of recoveries from C_8 SPEDs and C_{18} SPEDs, with separate hexane (a) and DCM (b) elutions for NPD responsive compounds.

Compound	%Recovery					
	C_8 SPEDs			C_{18} SPEDs		
	a	b	a+b	a	b	a+b
*Dichlorvos	0	27.6	27.6	0	61.7	61.7
Demeton-S-methyl	0	44.1	44.1	0	91.5	91.5
Phorate	4.2	76.4	80.6	2.2	74.7	76.9
Diazinon	2.4	110	112.4	0	105	105
Fonofos	4.5	98.9	103.4	0	94.6	94.6
Disulfoton	7.6	82.3	89.9	4.6	87.4	92
*Atrazine	0	84.7	84.7	0	92.9	92.9
Propetamphos	4.1	132	136.1	3.1	109	112.1
Dimethoate	0	3.2	3.2	0	12.5	12.5
Pirimiphos-methyl	3.8	114	117.8	3.4	127	130.4
Chlorpyriphos	9.9	87.2	97.1	4.7	98.7	103.4
*Parathion-methyl	5.3	117	122.3	3.8	113	116.8
*Fenitrothion	9.0	123	132	3.8	123	126.8
*Parathion-ethyl	6.4	111	117.4	4.2	112	116.2
Chlorfenvinphos	3.7	112	115.7	2.5	118	120.5
Triazinon	3.6	121	124.6	0	193	103
Phosalone	5.3	99.2	104.5	0	106	106
*Azinphos-methyl	0	104	104	0	98.8	98.8
*Azinphos-ethyl	7.2	109	116.2	0	110	110

* - Red List compounds

Table 2.14 Comparison of recoveries from C_8 SPEDs and C_{18} SPEDs, with separate hexane (a) and DCM (b) elutions for ECD responsive compounds.

Compound	%Recovery					
	C_8 SPEDs			C_{18} SPEDs		
	a	b	a+b	a	b	a+b
*HCB	8.5	32.4	40.9	7.3	29.2	36.5
α-HCH	5.5	49.4	54.9	4.3	44.6	48.9
*γ-HCH	6.1	57.0	63.1	4.4	54.7	59.1
Heptachlor	3.9	9.3	13.2	0	23.2	23.2
β-HCH	5.0	18.7	23.7	6.3	76.5	82.8
*β-Endosulfan	7.3	62.2	69.5	3.1	78.1	81.2
cis-Heptachlor epoxide	9.1	49.6	58.7	3.1	66.4	69.5
p,p'-DDE	13.1	35.6	48.7	10.0	42.8	52.8
*Dieldrin	14.0	55.9	69.9	7.2	69.9	77.1
p,p'-DDD	13.0	50.2	63.2	10.6	68.5	79.1
*PCB-C138	13.6	34.8	48.4	11.6	51.6	63.2
*p,p'-DDT	16.2	78.0	94.2	19.3	90.7	110
*PCB-C180	14.5	35.3	49.8	12.8	54.0	66.8
trans-Permethrin	19.3	46.0	65.3	17.8	90.3	108.1
Cypermethrin	18.3	44.3	62.6	15.4	66.1	81.5

* - Red List compounds

In an effort to maximise the generally poor recoveries from SPEDs, some work was carried out to investigate the possibility that a combination of C_8 and C_{18} SPEDs might provide improved recoveries. Hexane and DCM were used serially for elution of the compounds of interest from the SPEDs. The results are given in Tables 2.15 and 2.16.

Table 2.15 Recoveries from combined C_8+C_{18} SPEDs with separate hexane and DCM elutions for NPD responsive compounds.

Compound		%Recovery	
	Hexane	DCM	Total
*Dichlorvos	10.5	29.6	40.1
Demeton-S-methyl	9.1	86.1	95.2
Phorate	9.6	71.8	81.4
Diazinon	8.5	96.6	105.1
Fonofos	8.5	92.6	101.1
Disulfoton	10.5	78.5	89
*Atrazine	0	73.7	73.7
Propetamphos	9.2	107	116.2
Dimethoate	0	15.3	15.3
Pirimiphos	9.4	108	117.4
Chlorpyriphos	15.3	84.5	99.8
*Parathion-methyl	10.0	109	119
*Fenitrothion	9.9	117	126.9
*Parathion-ethyl	10.7	111	121.7
Chlorfenvinphos	9.0	104	123
Triazinon	9.8	100	109.8
Phosalone	9.0	92.0	101
*Azinphos-methyl	0	89.7	89.7
*Azinphos-ethyl	0	98.7	98.7

Table 2.16 Recoveries from combined C_8+C_{18} SPEDs with separate hexane and DCM elutions for ECD responsive compounds.

Compound		%Recovery	
	Hexane	DCM	Total
*HCB	10.5	29.6	40.1
α-HCH	10.0	45.2	55.2
*γ-HCH	11.5	51.1	62.6
Heptachlor	9.3	17.1	26.4
β-HCH	10.4	75.2	85.6
*β-Endosulfan	12.6	64.5	77.1
cis-Heptachlor epoxide	13.5	59.5	73
p,p'-DDE	19.7	32.5	52.2
*Dieldrin	14.7	55.8	70.5
p,p'-DDD	18.2	47.5	65.7
*PCB-C138	20.5	30.7	51.2
*p,p'-DDT	24.2	40.0	64.2
*PCB-C180	20.5	31.1	51.6
trans-Permethrin	27.9	42.8	70.7
Cypermethrin	24.8	44.7	69.5

* - Red List compounds

In spite of the considerable effort spent on investigating the use of SPEDs, it appears that the recoveries of most of the Red List compounds are significantly lower than when liquid liquid extraction is used. Although this does not necessarily rule out the routine use of SPEDs, where low limits of detection are sought poor recoveries will have an adverse effect. Of more concern is the poor reproducibility that has been noted.

It is suggested that for future work liquid liquid extraction is used as it does not appear to be possible to resolve the outstanding problems with SPEDs within the timescale of the project.

2.7 Mass Spectrometry (MS)

A principal objective of this contract is to investigate mass spectrometry (MS) for the unambiguous identification of Red List organic compounds. This section describes progress in this area.

2.7.1 Programme of work

The approach planned for the research was as follows:

1. Set up optimised multiple ion detection (MID) methods on a VG Trio-1 bench top mass spectrometer using the data obtained from the VG Trio-3 investigations, (NRA Report NR 2746) so as to provide MID, positive electron impact (+EI) and negative chemical ionisation (-CI), methods for routine application to most Red List organics with the exception of the VOCls which would be analysed by a purge and trap technique.

2. Investigate the use of purge and trap methodology linked to a GC-Ion Trap Detector (ITD) MS system to determine Red List volatile organic compounds.

3. Commence the investigation of the use of MS-MS techniques in the analysis of Red List organic compounds using the VG Trio-3 MS system.

4. Analysis of sample extracts produced from the SPED and robot-compatible sample preparation techniques using the MS methods developed in 1. above.

2.7.2 Development of VG Trio-1 MID methods

GCMS analysis was carried out using a Hewlett Packard 5890 GC equipped with a cool on-column injector and a Hewlett Packard autosampler model number 7673A. The GC was connected to a VG Trio-1 MS via a heated direct interface. The MS was operated with either a dedicated EI or a dedicated CI source.

The following operating conditions were employed.

1. GC conditions:

Column:	DB1701, 60 m, 0.32 mm ID, 0.25 µm film thickness
Column temperature:	150 °C held for four minutes 150-280 °C at 4 °C/min ramp, held for 15 minutes
Injection volume:	1 µl

2. MS conditions:

	EI	CI
Filament trap current, µamps	150	350
Electron energy, eV	70	70
Source temperature, °C	200	200
Full scan mass range, amu	33-550	30-500

Tuning and mass calibration for both +EI and -CI was carried out using heptacosa (perfluorotributylheptacosamine) which was bled into the source via a heated septum inlet.

3. MID conditions:

	EI	CI
Sampling time, ms	80	80
Stabilisation time, ms	20	20
MS peak width, amu	1	1

4. Materials

Helium (Research Grade 99.99% supplied by BOC Ltd) was used as a carrier gas at a flow rate of 1 ml/min.

Methane (Research Grade 99.99% supplied by BOC Ltd) was used as the CI reagent gas at a gas line pressure of 8 psi (it was not possible to measure the source pressure on the Trio-1).

Acetone, decane and cyclohexane (glass distilled grade supplied by Rathburns).

Stock standard solutions were made up in acetone at a concentration of 100 µg ml^{-1} for the following compounds:

Solution 1: α- and β-endosulfan
2: aldrin, dieldrin, endrin, trifluralin
3: malathion, dichlorvos, fenitrothion
4: atrazine and simazine
5: hexachlorobenzene
6: o,p- and p,p-DDT
7: o,p- and p,p-DDD
8: o,p- and p,p-DDE
9: α- and γ-HCH
10: β-HCH
11: hexachloro-1,3-butadiene
12: $^{13}C_6$-d_6-γ-HCH
13: d_{14}-trifluralin
14: d_5-atrazine
15: d_8-p,p-DDT
16: d_{10}-malathion
17: $^{13}C_4$-dieldrin

Stock standard solutions were made up in acetone at a concentration of 200 µg ml^{-1} for the following compounds:

Solution 18: fenthion
19: parathion-methyl
20: parathion-ethyl
21: azinphos-methyl
22: azinphos-ethyl

Stock standard solutions were made up in methanol for the following compounds:

Solution 23:	1,3,5-trichlorobenzene	1.15 mg ml^{-1}
24:	1,2,4-trichlorobenzene	2.0 mg ml^{-1}
25:	1,2,3-trichlorobenzene	1.0 mg ml^{-1}
26:	d_3-1,2,4-trichlorobenzene	1.57 mg ml^{-1}

Individual standard solutions of the PCB congeners C28, C52, C101, C118, C138, C153 and C180 in cyclohexane (supplied by Greyhound Chromotography and Allied Chemicals) were diluted in a ratio of 1:10 using decane to produce a mixed PCB stock standard solution (Solution: 27) of 10 µg ml^{-1} of each congener.

Two sets of composite calibration standard solutions (Set A and Set B) were prepared in decane from the stock solutions 1-7, 9, 10, 13-17 and 27. For the +EI mode (Set A), the concentrations were 0.05, 0.1, 0.5, 1.0 and 2 µg ml^{-1}, with the internal standards (d_{14}-trifluralin, d_5-atrazine and d_8-p,p-DDT) at 5 µg ml^{-1} in each. For the -CI mode Set B), the concentrations were 0.02, 0.05, 0.1, 0.5, and 1 µg ml^{-1}, with the internal standards (d_{14}-trifluralin, d_{10}-malathion and $^{13}C_4$-dieldrin) at 1 µg ml^{-1} in each.

Composite calibration solution C was prepared in decane at a concentration of 10 µg ml^{-1} from stock solutions 8, 11-15 and 18-26.

5. Methods

The composite calibration standard solutions A, B and C were analysed by GCMS using +EI and -CI ionization techniques, and full scan mass spectra were acquired. Compound retention time windows were determined and suitable quantification ions were selected for MID acquisitions.

Calibration curves based on triplicated injections of standard solutions A and B were obtained for +EI and -CI ionization techniques using MID conditions. Internal standards were used to determine peak area ratios for each Red List compound analysed and GCMS instrument precision data, including means, standard deviations and relative standard deviations based on the peak area ratio results, were calculated.

Replicate sewage sludge extracts which had been prepared to evaluate the reproducibility of the robot-compatible sample preparation methods using GC-NPD and GC-ECD were also analysed by GCMS. The primary purpose of these GCMS analyses was to evaluate the +EI and -CI MID methods which had been developed with standard solutions using the VG Trio-1 GCMS system. Replicate decane extracts (100 µl) of sewage sludge and sample preparation procedural blanks were spiked prior to GCMS analysis at 0.1 and 1 µg ml^{-1} with Red List compounds 1-7, 9, 10, 13-17 and 27, as summarized in Table 2.17

Calibration standards and extracts were analysed by both +EI and -CI ionization techniques using GCMS in MID mode. The calibration standard (1 µg ml^{-1}) was reanalysed after analysis of the extracts by +EI and again after analysis of the extracts by -CI.

Table 2.17 Summary of extracts analysed by +EI and -CI GCMS

Extract type	Spike concentration of the extract (µg ml^{-1})	Number of replicates analysed
Procedural Blank	Unspiked	2
Procedural Blank	0.1	3
Procedural Blank	1	3
Sewage Sludge	0.1	5
Sewage Sludge	1	5

Notes: Calibration standard solutions for +EI were 0.05, 0.1, 0.5, 1.0 and 2 µg ml^{-1}.
Calibration standard solution for -CI were 0.02, 0.05, 0.1, 0.5 and 1 µg ml^{-1}.

6. Results

Data have been compiled as an appendix in a separate volume to the main body of this report. The appendix contains the following information for both +EI and -CI MID methods:

- method parameter summary tables derived from standard solutions A, B and C. Examples of these are given as Tables 2.18, 2.19 and 2.20 in this report;
- full scan mass spectra for each compound;
- mass chromatogram traces for each compound;
- summary tables showing instrumental precision for Red List compounds in standard solutions A and B.

The results of the +EI and -CI MID GCMS analyses of spiked sewage sludge and procedural blank extracts are summarized in Tables 2.21 and 2.22 for the +EI analyses and Table 2.23 and 2.24 for the -CI analyses. These data were evaluated on the basis of the following analytical criteria:

- instrumental precision which was obtained by calculating the mean, standard deviation and relative standard deviation for the peak area ratios for each Red List compound analysed;

- analytical accuracy which was obtained by calculating the mean concentration of each analyte in the extracts using the relevant +EI or -CI standard calibration curves and comparing the results to the known concentrations spiked into the extracts prior to GCMS analysis.

- matrix effects which were identified by comparing the data obtained for the sewage extracts with that obtained for the procedural blank extracts;

- chromatographic effects which were identified by comparing the data obtained for the calibration standard (1 µg ml^{-1}) which was re-analysed at the end of each +EI and -CI analytical batch with the appropriate calibration curve.

An initial review of the data revealed that unlike previous standard calibration data the +EI and -CI calibration data obtained was significantly curved and the curvature increased as the mass-to-charge ratio (m/z) of the quantification ion increased. This suggested that there was a problem with the performance of the VG Trio-1. The most obvious reason for this was thought to be contamination of the quadrupole assembly, and it appeared that it would need to be cleaned or replaced.

Although the problem with the quadrupole significantly degraded the quality of the analytical data obtained for the extracts and complicated its evaluation, nevertheless, some useful information was obtained as summarized below.

The +EI data appeared to show that o,p-DDT and p,p-DDT were unstable in extracts if allowed to remain at ambient conditions on a GC autosampler for more than approximately three hours.

The -CI data appeared to indicate that the use of intense but non-specific ions such as m/z 71 for quantification of α-, β- and γ-HCH may result in the reporting of false positives or misleadingly high results because of the susceptibility of this ion to interferences.

The overall GCMS sensitivity was significantly decreased for all compounds after the analysis of the sewage sludge extracts.

Conclusions

d_8-p,p-DDT may not be a useful internal standard for +EI acquisitions because of its sensitivity to light and/or heat.

Although -CI is a more sensitive ionization technique than +EI for the determination of HCH isomers, data obtained from -CI monitoring of lower mass ions may not be as reliable as data obtained by +EI because of the greater possibility of interferences. The use of more specific high mass ions results in lower sensitivity.

Analytical batches of extracts should be kept small in order to minimise exposure to light and/or heat which can affect certain Red List compounds such as o,p- and p,p-DDT.

Analysis of sewage sludge extracts causes rapid deterioration of chromatographic and MS performance and therefore GCMS instrument performance must be checked frequently when this and similar types of extracts are being analysed.

Table 2.18 Summary of MID method parameters for Red List compounds in solution A, analysed by +EI GCMS

Peak	Compound	Relative reference peak	Ions monitored m/z	Retention time (min)
1	Hexachlorobenzene	2	284, 286	20.49
2	d_{14}-trifluralin	-	267, 315	20.92
3	Trifluralin	2	264, 306	21.17
4	α-hexachlorocyclohexane	6	183, 219	22.86
5	d_{10}-phenanthrene	-	160, 188	24.19
6	d_5-atrazine	-	205, 220	24.83
7	Atrazine	6	200, 215	24.90
8	Simazine	6	186, 201	25.07
9	Lindane	6	183, 219	25.07
10	PCB-C28	6	186, 256	25.49
11	PCB-C52	6	220, 292	27.25
12	β-hexachlorocyclohexane	6	183, 219	28.79
13	o,p-DDD	16	165, 235	34.81
14	o,p-DDT	16	165, 235	35.54
15	p,p-DDD	16	165, 235	37.05
16	d_8 p,p-DDT	-	173, 243	37.77
17	p,p-DDT	16	165, 235	37.91
19	Azinphos-methyl	16	77, 160	47.70
20	Decachlorobiphenyl	-	428, 498	51.50

Note: In most cases, the ion underlined is the most intense ion in the mass spectrum and was therefore selected as the quantification ion. A second ion which for some compounds may be more specific than the quantification ion has been selected to provide increased analytical confidence.

Table 2.19 Summary of MID method parameters for Red List compounds in Solution B, analysed by −CI GCMS

Peak	Compound	Relative reference peak	Ions monitored m/z	Retention time (min)
1	d_6-Dichlorvos	-	131, 136	10.53
2	Dichlorvos	3	125, 134	10.68
3	d_{14}-trifluralin	-	319, 349	21.06
4	Trifluralin	3	305, 335	21.32
5	α-hexachlorocyclohexane	3	71, 73	23.06
6	Lindane	3	71, 73	25.24
7	Aldrin	15	235, 237	27.75
8	β-hexachlorocyclohexane	3	71, 73	28.96
9	d_{10}-malathion	-	157, 182	30.08
10	Malathion	9	157, 172	30.38
11	Fenitrothion	9	141, 168	30.70
12	PCB-C101	9	256, 325	31.71
13	α-endosulfan	9	240, 242	32.70
14	Dieldrin	15	235, 237	34.50
15	$^{13}C_4$-dieldrin	-	239, 241	34.52
16	o,p-DDD	15	71, 246	34.96
17	PCB-C118	9	324, 326	35.10
18	Endrin	15	238, 272	35.56
19	o,p-DDT	15	71, 246	35.71
20	PCB-C153	9	360, 362	35.78
21	p,p-DDD	15	71, 73	37.21
22	PCB-C138	9	360, 362	37.50
23	β-endosulfan	9	240, 242	37.87
24	p,p-DDT	15	71, 73	38.07
25	PCB-C180	9	394, 396	40.95
26	Decachlorobiphenyl	-	464, 498	50.14

Note: In most cases, the ion underlined is the most intense ion in the mass spectrum and was therefore selected as the quantification ion. A second ion which for some compounds may be more specific than the quantification ion has been selected to provide increased analytical confidence.
At the present time d_6-dichlorvos and decachlorobiphenyl are not being used as MS internal standards.

Table 2.20 Summary of MID method parameters for Red List compounds in solution C, analysed by +EI GCMS

Peak	Compound	Ions monitored (m/z)	Retention time (min)
1	1,3,5-trichlorobenzene	180, 182	6.81
2	d_3-1,2,4-trichlorobenzene	183, 185	7.56
3	1,2,4-trichlorobenzene	180, 182	7.60
4	Hexachloro-1,3-butadiene	223, 225	7.71
5	1,2,3-trichlorobenzene	180, 182	8.42
6	d_{14}-trifluralin	267, 315	19.93
7	d_{10}-phenanthrene	188, 160	23.17
8	d_5-atrazine	205, 220	23.78
9	$^{13}C_6$-d_6-γ-hexachlorocyclohexane	191, 230	23.85
10	o,p-DDE	246, 248	30.68
11	p,p-DDE	246, 248	32.27
12	d_8-p,p-DDT	173, 243	36.74
13	decachlorobiphenyl	428, 498	49.70

Table 2.21 Summary of results of analyses of spiked blank extracts by +EI GCMS

Compound	Quantification ion	Peak area ratio Relative Std Dev (%)		Mean concentration obtained (μg ml^{-1})	
		for 0.1 μg ml^{-1} spike	for 1 μg ml^{-1} spike	for 0.1 μg ml^{-1} spike	for 1 μg ml^{-1} spike
Hexachlorobenzene	286	7	4	0.24	1.65
Trifluralin	264	NR	7	0.14	0.88
α-HCH	183	13	3	0.17	1.08
Atrazine	200	22	2	0.12	0.95
Simazine	201	41	5	0.15	0.97
γ-HCH	183	21	3	0.18	1.05
PCB-C28	256	11	2	0.15	1.11
PCB-C52	220	15	3	0.18	0.96
β-HCH	183	27	4	0.19	0.89
o,p-DDD	235	15	3	0.13	0.94
o,p-DDT	235	30	2	0.14	0.89
p,p-DDD	235	11	2	0.13	0.92
p,p-DDT	235	26	3	0.10	0.88

Notes: Relative Std Dev = Relative Standard Deviation

Table 2.22 Summary of results of analyses of spiked sludge extracts by +EI GCMS

Compound	Quantification ion	Peak area ratio Relative Std Dev (%)		Mean concentration obtained (µg ml^{-1})	
		for 0.1 µg ml^{-1} spike	for 1 µg ml^{-1} spike	for 0.1 µg ml^{-1} spike	for 1 µg ml^{-1} spike
Hexachlorobenzene	286	27	11	0.12	1.58
Trifluralin	264	31	9	0.14	1.52
α-HCH	183	14	8	0.23	3.69
Atrazine	200	34	14	0.13	1.25
Simazine	201	41	12	0.17	1.53
γ-HCH	183	18	33	0.22	2.87
PCB-C28	256	18	7	0.20	2.93
PCB-C52	220	7	11	0.19	2.17
β-HCH	183	34	13	0.20	2.00
o,p-DDD	235	NR	NR	NR	NR
o,p-DDT	235	NR	NR	NR	NR
p,p-DDD	235	NR	NR	NR	NR
p,p-DDT	235	NR	NR	NR	NR

Notes: Relative Std Dev = Relative Standard Deviation
NR = No result

Table 2.23 Summary of results of analyses of spiked blank extracts by -CI GCMS

Compound	Quantification ion	Peak area ratio Relative Std Dev (%)		Mean concentration obtained ($\mu g\ ml^{-1}$)	
		for 0.1 $\mu g\ ml^{-1}$ spike	for 1 $\mu g\ ml^{-1}$ spike	for 0.1 $\mu g\ ml^{-1}$ spike	for 1 $\mu g\ ml^{-1}$ spike
Dichlorvos	125	10	3	0.11	1.21
Trifluralin	305	5	2	0.11	0.16
α-HCH	71	2	10	0.22	2.86
γ-HCH	71	1	13	0.19	2.32
Aldrin	237	5	5	0.09	0.69
β-HCH	71	2	10	0.16	2.07
Malathion	172	1	14	0.07	0.54
Fenitrothion	168	7	13	0.07	0.43
PCB-C101	256	5	10	0.05	0.38
α-endosulfan	242	13	6	0.05	0.53
Dieldrin	237	6	4	0.12	1.07
o,p-DDD	71	6	10	0.10	1.12
PCB-C118	326	1	13	0.18	1.83
Endrin	272	12	8	0.10	1.07
o,p-DDT	71	8	10	0.13	1.33
PCB-C153	360	1	11	0.24	2.61
p,p-DDD	71	7	8	0.09	1.34
PCB-C138	360	7	12	0.25	2.53
β-endosulfan	242	4	8	0.11	1.25
p,p-DDT	71	3	10	0.15	1.56
PCB-C180	394	3	8	0.18	1.29

Notes: Relative Std Dev = Relative Standard Deviation

Table 2.24 Summary of results of analyses of spiked sludge extracts by -CI GCMS

Compound	Quantification ion	Peak area ratio Relative Std Dev (%)		Mean concentration obtained (µg ml^{-1})	
		for 0.1 µg ml^{-1} spike	for 1 µg ml^{-1} spike	for 0.1 µg ml^{-1} spike	for 1 µg ml^{-1} spike
Dichlorvos	125	15	14	0.09	0.96
Trifluralin	305	10	4	0.12	1.24
α-HCH	71	13	6	0.32	3.99
γ-HCH	71	11	6	0.29	3.40
Aldrin	237	29	8	0.08	0.53
β-HCH	71	13	7	0.28	3.46
Malathion	172	15	10	0.06	3.74
Fenitrothion	168	8	12	0.09	0.72
PCB-C101	256	30	17	0.03	0.40
α-endosulfan	242	10	5	0.06	0.71
Dieldrin	237	5	5	0.14	1.03
o,p-DDD	71	12	18	0.09	1.43
PCB-C118	326	12	9	0.18	1.51
Endrin	272	9	18	0.04	1.78
o,p-DDT	71	16	NR	0.11	NR
PCB-C153	360	7	8	0.27	2.33
o,p-DDD	71	14	17	0.13	2.05
PCB-C138	360	7	12	0.28	2.52
β-endosulfan	242	9	12	0.07	1.39
p,p-DDT	71	NR	NR	NR	NR
PCB-C180	394	13	14	0.14	0.98

Notes: Relative Std Dev = Relative Standard Deviation
NR = No result

2.7.3 Development of purge and trap GC-ITD method

Purge and trap GCMS analysis was carried out using a Chrompack Purge and Trap Injector with cryogenic focusing. The injector was interfaced with a Hewlett Packard 5890 GC which was connected to a Finnigan Ion Trap (ITD 700) via a short heated transfer line. The ITD was operated using +EI ionisation only.

The following operating conditions were used:

1. Purge and trap conditions:

Cooling bath temperature for moisture condenser	-15 °C
Cold trap for cryogenic focusing	-110 °C
Sample purge temperature	60 °C
Sample purge time at 60 °C	20 minutes
Cold trap desorbtion temperature	200 °C
Cold trap desorbtion time at 200 °C	15 minutes

2. GC conditions:

Column:	Chrompack CP-Sil 13CB, 50 m, 0.32 mm ID and 1.2 µm film thickness.
Column temperature:	40 °C held for 10 minutes 40-210 °C at 8 °C/min ramp, held for 5 minutes
Sample size:	10 ml

3. ITD conditions:

Filament current	On
Electron energy	70 eV
Ion trap manifold temperature	250 °C

Tuning and mass calibration was carried-out using heptacosa (perfluorotributylheptacosamine) which was bled into the ion-trap via a solenoid valve controlled inlet.

4. MID conditions 33-300 amu

5. Materials

Helium (Research Grade 99.99% supplied by BOC Ltd) was used as carrier gas at a flow rate of 1 ml min^{-1}.

Methanol (glass distilled grade supplied by Rathburns)

Stock standard solutions were made up in methanol for the following compounds as shown below:

Solution 1:	hexachloro-1,3-butadiene	100 µg ml^{-1}
2:	1,3,5-trichlorobenzene	1.15 mg ml^{-1}
3:	1,2,4-trichlorobenzene	2.0 mg ml^{-1}
4:	1,2,3-trichlorobenzene	1.0 mg ml^{-1}
5:	1,2-dichloroethane	1.196 mg ml^{-1}
6:	carbontetrachloride	0.996 mg ml^{-1}
7:	chloroform	1.0 mg ml^{-1}
8:	1,1,1-trichloroethane	1.172 mg ml^{-1}
9:	trichloroethylene	1.16 mg ml^{-1}
10:	1,1,1,2-tetrachloroethane	1.12 mg ml^{-1}
11:	1,1,2,2-tetrachloroethane	1.156 mg ml^{-1}
12:	tetrachloroethylene	1.0 mg ml^{-1}
13:	d_3-1,1,1-trichloroethane	25 mg ml^{-1}
14:	d_3-1,2,4-trichlorobenzene	1.57 mg ml^{-1}
15:	d_5-chlorobenzene	25 mg ml^{-1}

A composite stock solution was made up in methanol at a concentration of 10 µg ml^{-1} from the individual stock solutions 1-15. Using this composite stock solution, a composite working standard was made up daily in water to give a concentration of 5 ng ml^{-1}.

6. Methods

Composite calibration standard solution D was analysed by purge and trap GC ITD using +EI ionization. Various combinations of purge times (10 and 20 minutes) and purge temperatures (ambient, 40 °C, 50 °C and 60 °C) were evaluated in order to optimise the purging efficiency of the compounds of interest. The GC column temperature programme was optimized in order to obtain chromatographic baseline separation of all the compounds within the shortest possible analysis time.

Standard solution D was analysed using these optimized analysis conditions and full scan mass spectra were acquired. Compound retention times were determined and suitable quantification ions were selected for MID acquisitions.

7. Results

Full scan mass spectra and mass chromatogram traces have been compiled as an appendix in a separate volume to the main body of this report. Retention time and quantification ion data have been summarized and they are reported here in Table 2.25.

Table 2.25 Summary of MID method parameters for Red List compounds analysed using purge and trap GC-ITD method

Peak	Compound	Ions monitored (m/z)	Retention time (min)
1	Chloroform	47, 83, 85,	7.22
2	d_3-1,1,1-trichloroethane	63, 100, 102	8.21
3	1,1,1-trichloroethane	61, 97, 99	8.31
4	Carbontetrachloride	47, 82, 117, 119	9.20
5	1,2-dichloroethane	49, 62, 64	9.43
6	Trichloroethylene	47, 60, 95, 130	12.04
7	Tetrachloroethylene	82, 94, 131, 166	17.24
8	1,1,1,2-tetrachloroethane	95, 117, 131, 133	19.26
9	1,1,2,2-tetrachloroethane	60, 83, 85, 133	21.49
10	1,3,5-trichlorobenzene	74, 84, 109, 180	27.30
11	d_3-1,2,4-trichlorobenzene	76, 148, 183, 185	28.44
12	1,2,4-trichlorobenzene	74, 145, 180, 182	28.46
13	Hexachlorobutadiene	118, 190, 225, 260	29.12
14	1,2,3-trichlorobenzene	180, 182	29.46

Note: In most cases, the ion underlined is the most intense ion in the mass spectrum and therefore it was selected as the quantification ion. Secondary ions have also been selected to provide increased analytical confidence.

2.7.4 MS-MS techniques

Some preliminary work has been carried out on the VG Trio-3 to look for useful daughter ions and neutral losses in both +EI and -CI modes. The triazines and some of the organochlorine and organophosphorus compounds have been examined.

The data obtained are being evaluated.

3. FUTURE WORK

Future work will focus on the following:

- **o** evaluation of liquid-liquid extraction for river water analysis;
- **o** development of GPC clean-up for river water extracts, and investigation of GPC clean-up for sediment extracts;
- o validate GC-MS (MID; +EI and -CI) procedures for river water extracts (following clean-up), and final sewage effluent extracts;
- o complete work for VOCl's, to include compilation of instrumental precision data for purge and trap GCMS method, and application to river waters; particular attention will be paid to 1,2-dichloroethane.

4. FACTORS AFFECTING COMPLETION OF WORK

The targets listed in Section 3 (Future work) will be met.

It is obviously vital that an effective clean-up is developed, and much of the progress for the pesticides included in the Red List depends on the success of this step.

5. CONCLUSIONS

For the volatile Red List compounds (the VOCl's) two methods have been investigated and although further work remains to be done on the purge and trap GCMS method, due to the lower limits of detection that can be achieved (when compared with the alternative solvent extraction-GC ECD method), it is likely that this will be the method of choice.

For the remaining Red List compounds of interest, it is apparent from the work on GC methods with selective detectors (ECD; NPD) that their specificity is not sufficiently high to provide adequate certainty of detection with "dirty" samples - difficulties have been encountered in this respect with river waters, which represent relatively clean samples. Although an effective clean-up technique may still allow GC ECD/NPD to be used for clean samples, it is suggested that GCMS is more appropriate for sediment and sewage effluent samples.

In spite of the considerable effort expended on the investigation of SPEDs as an alternative to solvent extraction it appears that C_{18} and C_8 SPEDs are not satisfactory when the Red List pesticides are treated as one group. Recoveries for some compounds are poor, and the reproducibility is not good. Although it is likely that splitting these compounds into several groups and developing different SPEDs-based extractions for each group could lead to satisfactory methods, this is currently considered considered to be undesirable. Future work for these Red List compounds will therefore be based on solvent extraction.

APPENDIX

CONTENTS

APPENDIX

SECTION 1

Table A1-1

Summary of MID Method Parameters for Red List Compounds in Solution (A) Analysed Using +EI GCMS

Peak	Compound	Relative reference peak	Ions Monitored m/z	Retention time (min)
1	Hexachlorobenzene	2	284, 286	20.49
2	d14-trifluralin	-	267, 315	20.92
3	Trifluralin	2	264, 306	21.17
4	α-hexachlorocyclohexane	6	183, 219	22.86
5	d10-phenanthrene	-	160, 188	24.19
6	d5-atrazine	-	205, 220	24.83
7	Atrazine	6	200, 215	24.90
8	Simazine	6	186, 201	25.07
9	Lindane	6	183, 219	25.07
10	PCB-C28	6	186, 256	25.49
11	PCB-C52	6	220, 292	27.25
12	β-hexachlorocyclohexane	6	183, 219	28.79
13	o,p-DDD	16	165, 235	34.81
14	o,p-DDT	16	165, 235	35.54
15	p,p-DDD	16	165, 235	37.05
16	d8 p,p-DDT	-	173, 243	37.77
17	p,p-DDT	16	165, 235	37.91
18	Azinphos-methyl	16	77, 160	47.70
19	Decachlorobiphenyl	-	428, 498	51.50

Note

In most cases, the ion underlined is the most intense ion in the mass spectrum and therefore it was selected as the quantitation ion. A second ion, which may be more unique than the quantitation ion for some compounds, has been selected as a confirmatory ion.

TABLE A1-2

SUMMARY OF INSTRUMENTAL PRECISION FOR RED LIST COMPOUNNDS

IN STANDARD SOLUTIONS ANALYSED USING +EI GCMS

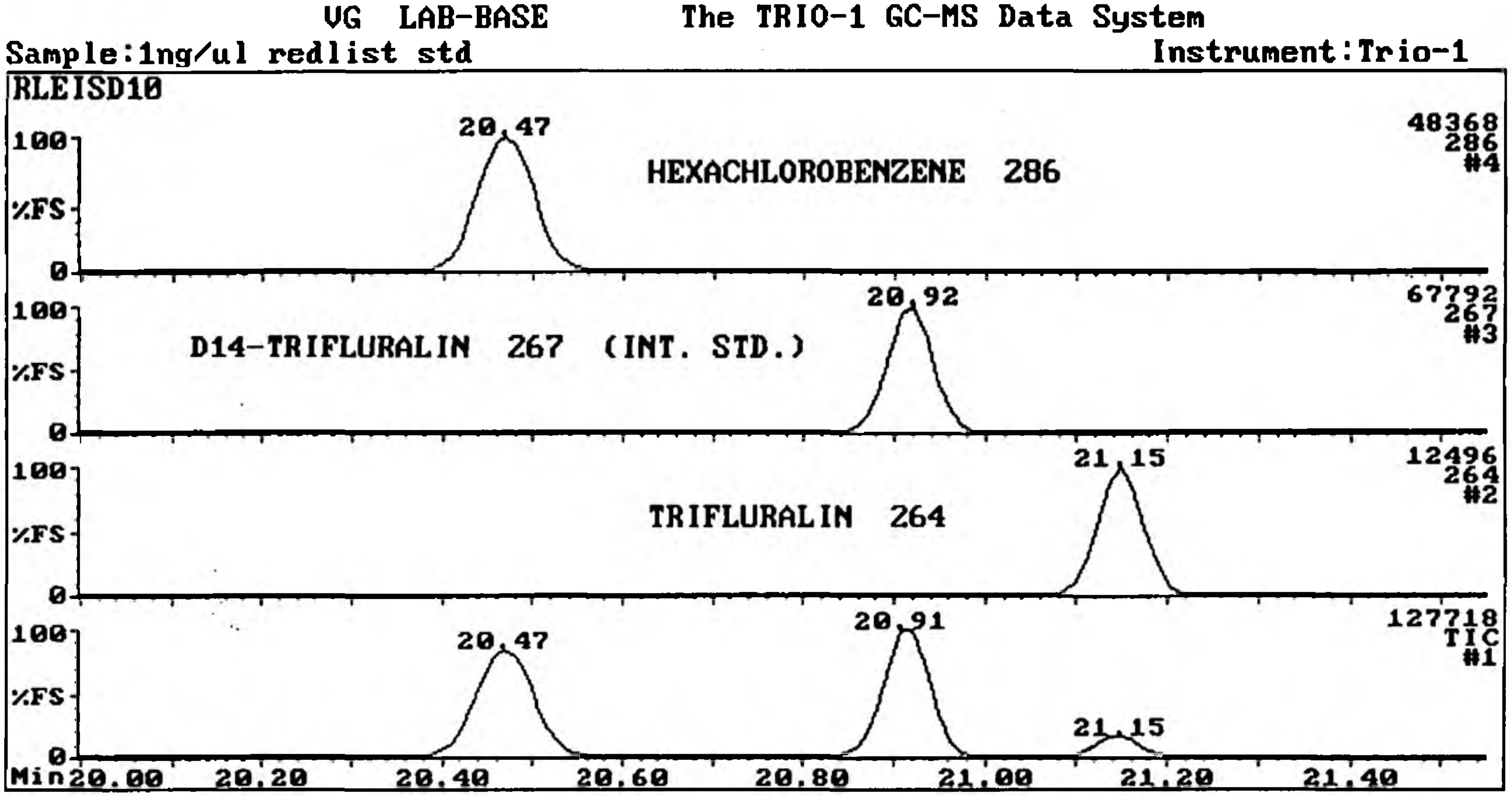
COMPOUND	PEAK AREA RATIO	STANDARD SOLUTION CONCENTRATION (ug/ml)				
	STATISTIC	0.05	0.10	0.50	1.00	2.00
HEXACHLORO-BENZENE	MEAN	0.129	0.327	2.518	5.543	11.06
	STANDARD DEVIATION	0.010	0.016	0.176	0.272	0.160
	REL.STD.DEV.(%)	7.8	4.8	7.0	4.9	1.5
TRIFLURALIN	MEAN	0.004	0.049	0.042	0.917	2.213
	STANDARD DEVIATION	0.004	0.025	0.006	0.003	0.018
	REL.STD.DEV.(%)	94.7	50.1	15.5	0.4	0.8
α-HCH	MEAN	0.010	0.038	0.312	0.718	1.681
	STANDARD DEVIATION	0.006	0.011	0.030	0.025	0.035
	REL.STD.DEV.(%)	64.0	29.0	9.5	3.5	2.1
ATRAZINE	MEAN	0.037	0.087	0.545	1.237	2.886
	STANDARD DEVIATION	0.007	0.017	0.011	0.008	0.013
	REL.STD.DEV.(%)	19.9	19.1	2.1	0.6	0.5
SIMAZINE	MEAN	0.010	0.039	0.298	0.748	1.926
	STANDARD DEVIATION	0.005	0.011	0.016	0.009	0.035
	REL.STD.DEV.(%)	52.9	27.7	5.3	1.1	1.8
LINDANE	MEAN	0.013	0.041	0.304	0.705	1.637
	STANDARD DEVIATION	0.006	0.005	0.021	0.016	0.035
	REL.STD.DEV.(%)	46.2	11.2	7.0	2.3	2.2
PCB-C28	MEAN	0.053	0.145	1.081	2.303	5.325
	STANDARD DEVIATION	0.003	0.012	0.005	0.030	0.007
	REL.STD.DEV.(%)	6.5	8.1	0.4	1.3	0.1
PCB-C52	MEAN	0.037	0.130	0.920	2.024	4.757
	STANDARD DEVIATION	0.003	0.013	0.012	0.025	0.021
	REL.STD.DEV.(%)	6.9	10.1	1.3	1.2	0.4
β-HCH	MEAN	0.028	0.090	0.739	1.735	4.138
	STANDARD DEVIATION	0.003	0.029	0.039	0.038	0.011
	REL.STD.DEV.(%)	12.4	32.7	5.3	2.2	0.3
o,p-DDD	MEAN	0.105	0.268	1.931	4.276	9.735
	STANDARD DEVIATION	0.032	0.042	0.067	0.143	0.081
	REL.STD.DEV.(%)	30.7	15.6	3.5	3.4	0.8
o,p-DDT	MEAN	0.064	0.145	1.080	2.428	5.760
	STANDARD DEVIATION	0.036	0.033	0.059	0.023	0.049
	REL.STD.DEV.(%)	56.7	22.6	5.5	0.9	0.9

(Table A1-2 continued)

COMPOUND	PEAK AREA RATIO STATISTIC	STANDARD SOLUTION CONCENTRATION (ug/ml)				
		0.05	0.10	0.50	1.00	2.00
p,p-DDD	MEAN STANDARD DEVIATION REL.STD.DEV.(%)	0.062 0.019 6.2	0.132 0.010 7.2	0.927 0.039 4.2	2.081 0.034 1.7	4.657 0.022 0.5
p,p-DDT	MEAN STANDARD DEVIATION REL.STD.DEV.(%)	0.041 0.020 4.1	0.082 0.008 10.3	0.462 0.036 7.8	0.961 0.012 1.2	2.181 0.016 0.7
	MEAN STANDARD DEVIATION REL.STD.DEV.(%)					

Notes :-

Statistical data in this table was based on triplicate analyses of each compound at each concentration. For each compound, the peak area ratio was calculated by dividing the area of the peak for that compound by the area of the peak for the most appropriate internal standard.



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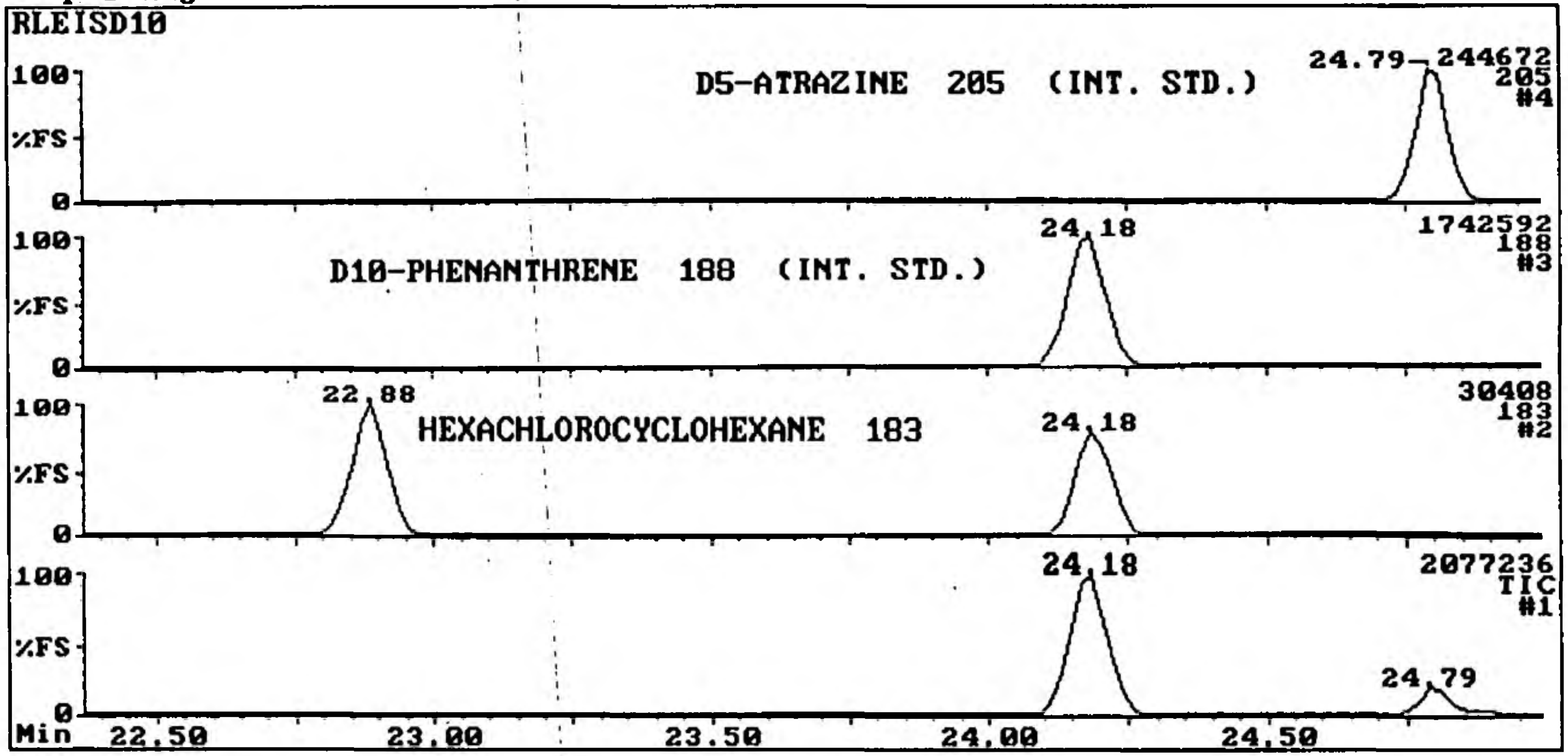
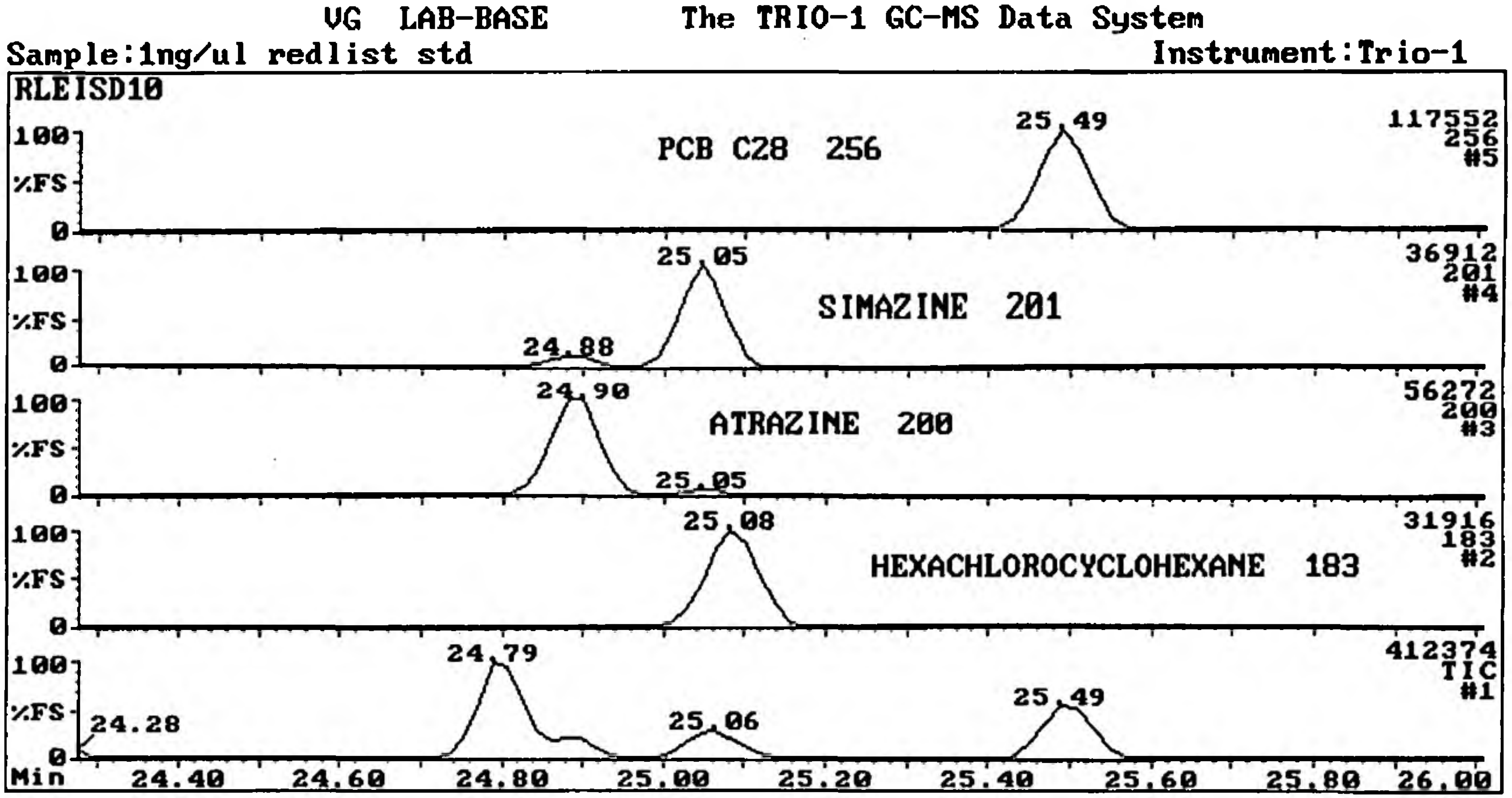
Instrument:Trio-1

VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:1ng/ul redlist std Instrument:Trio-1





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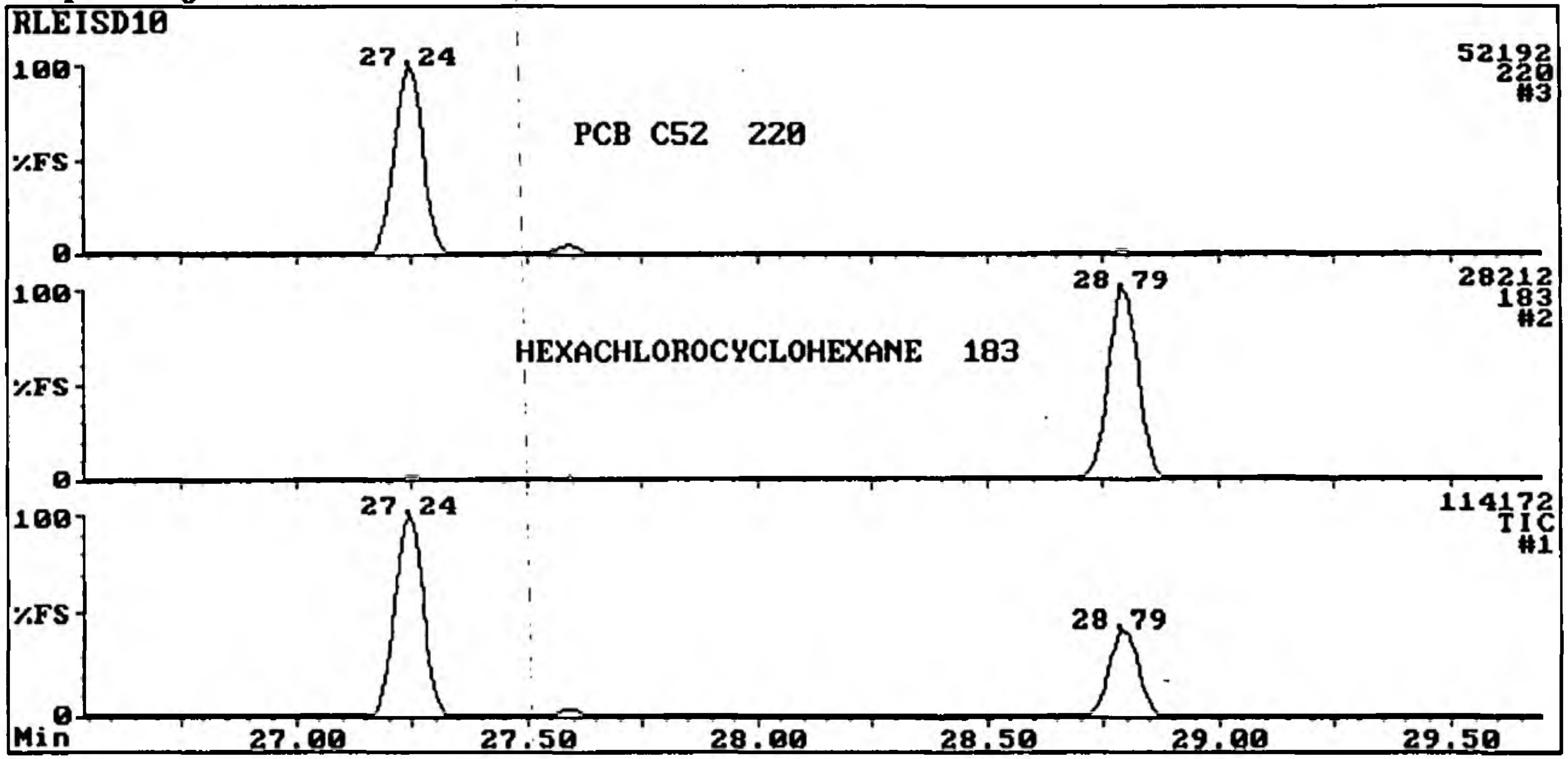

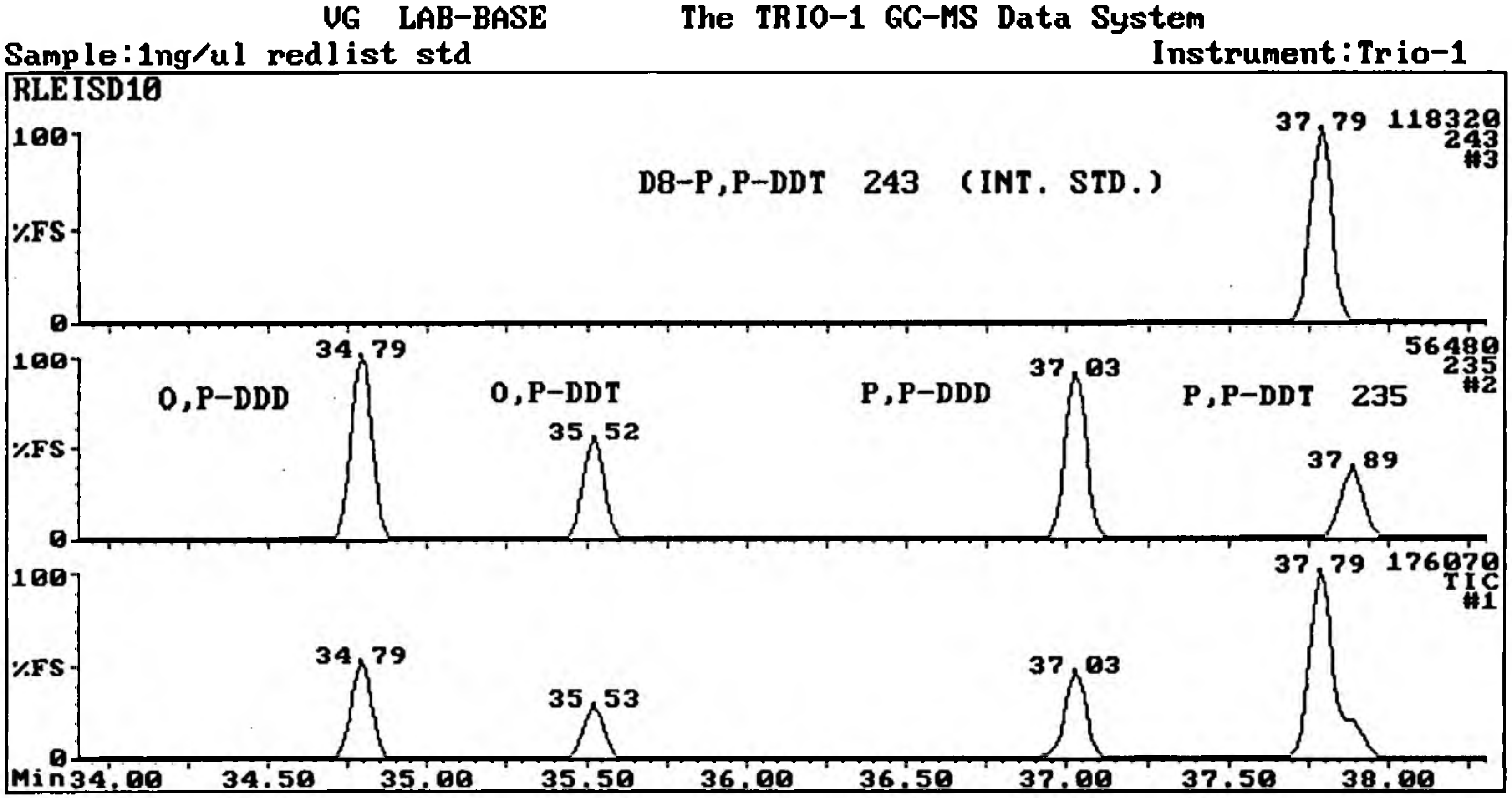

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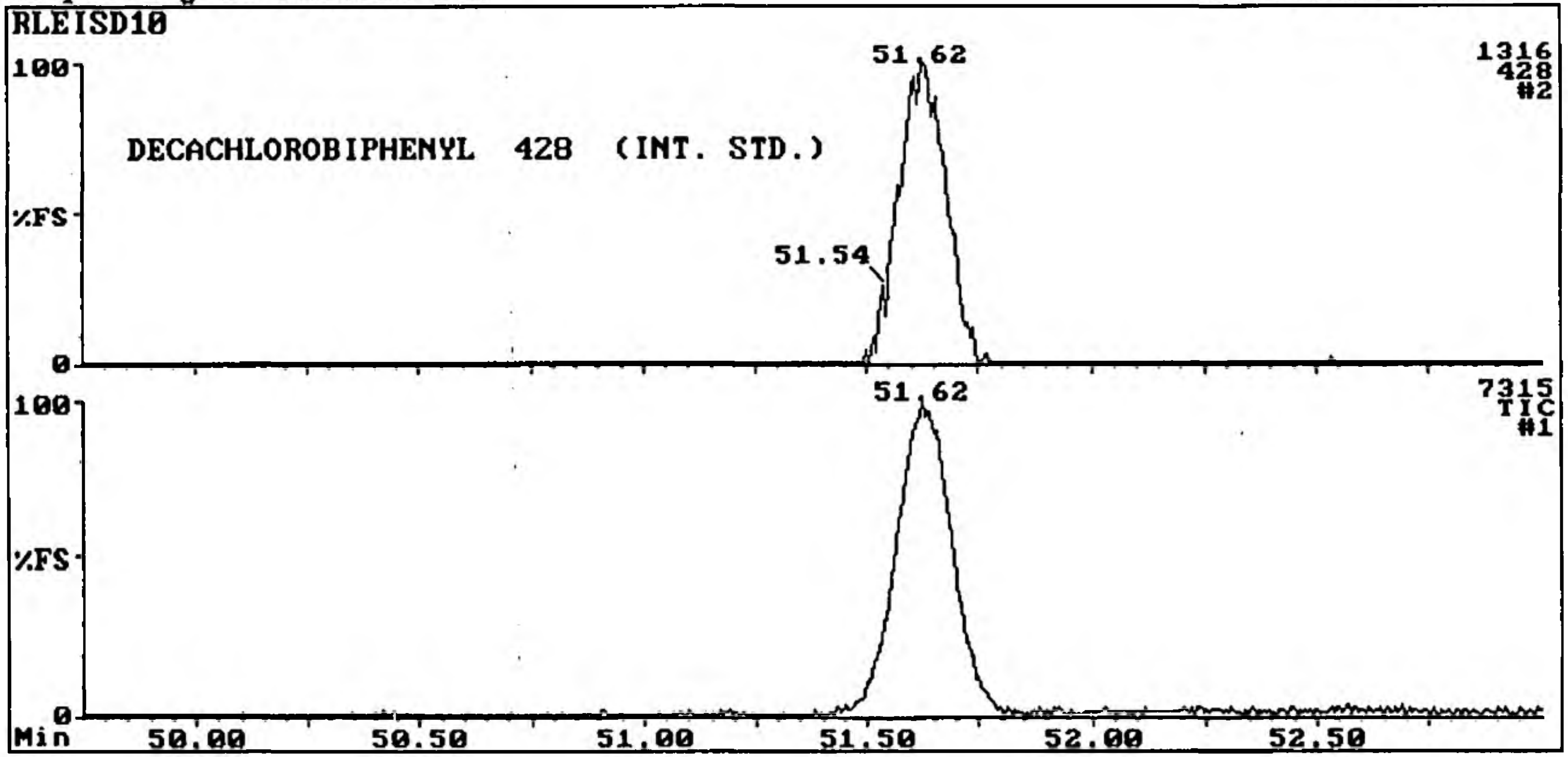

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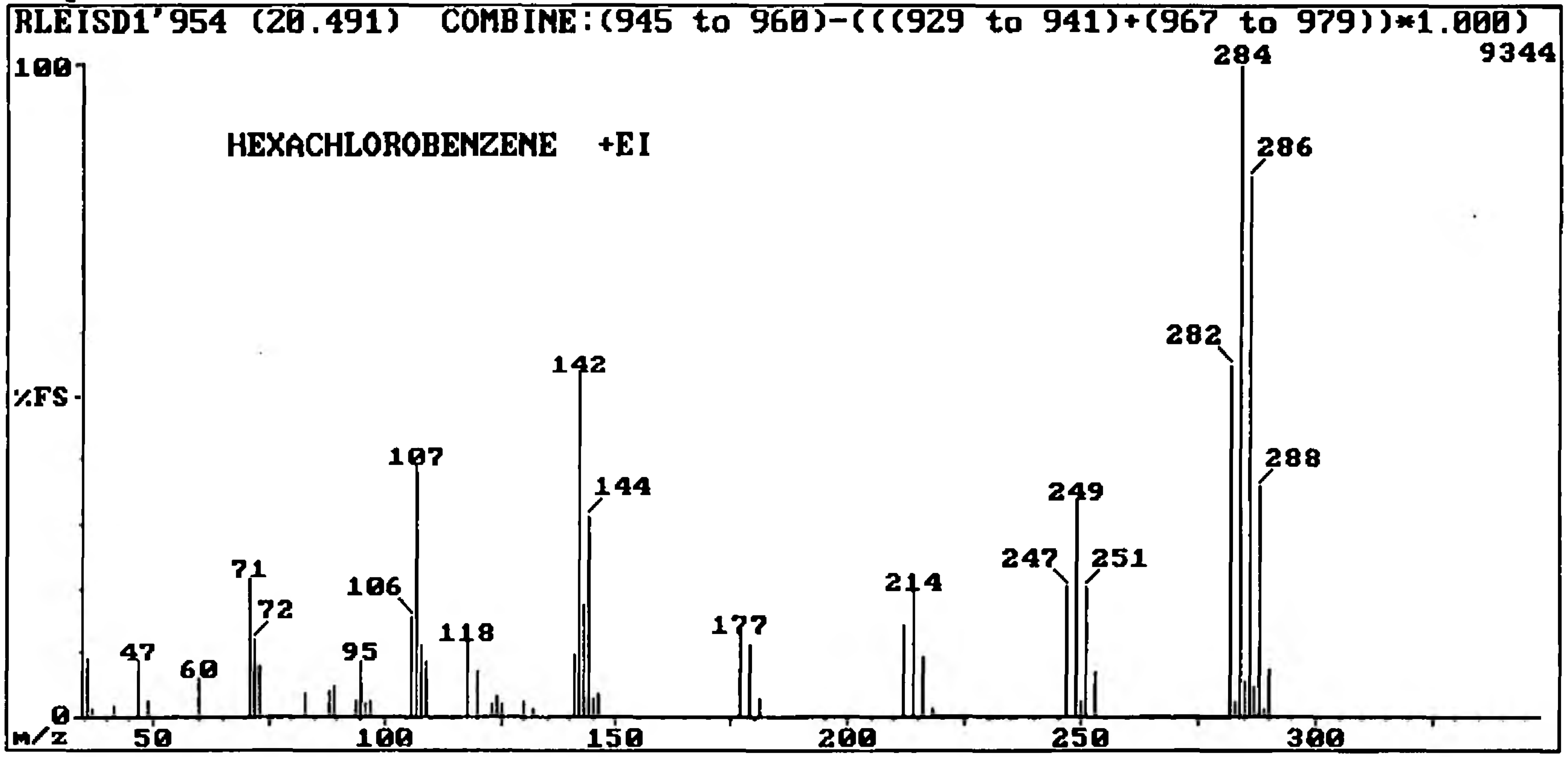

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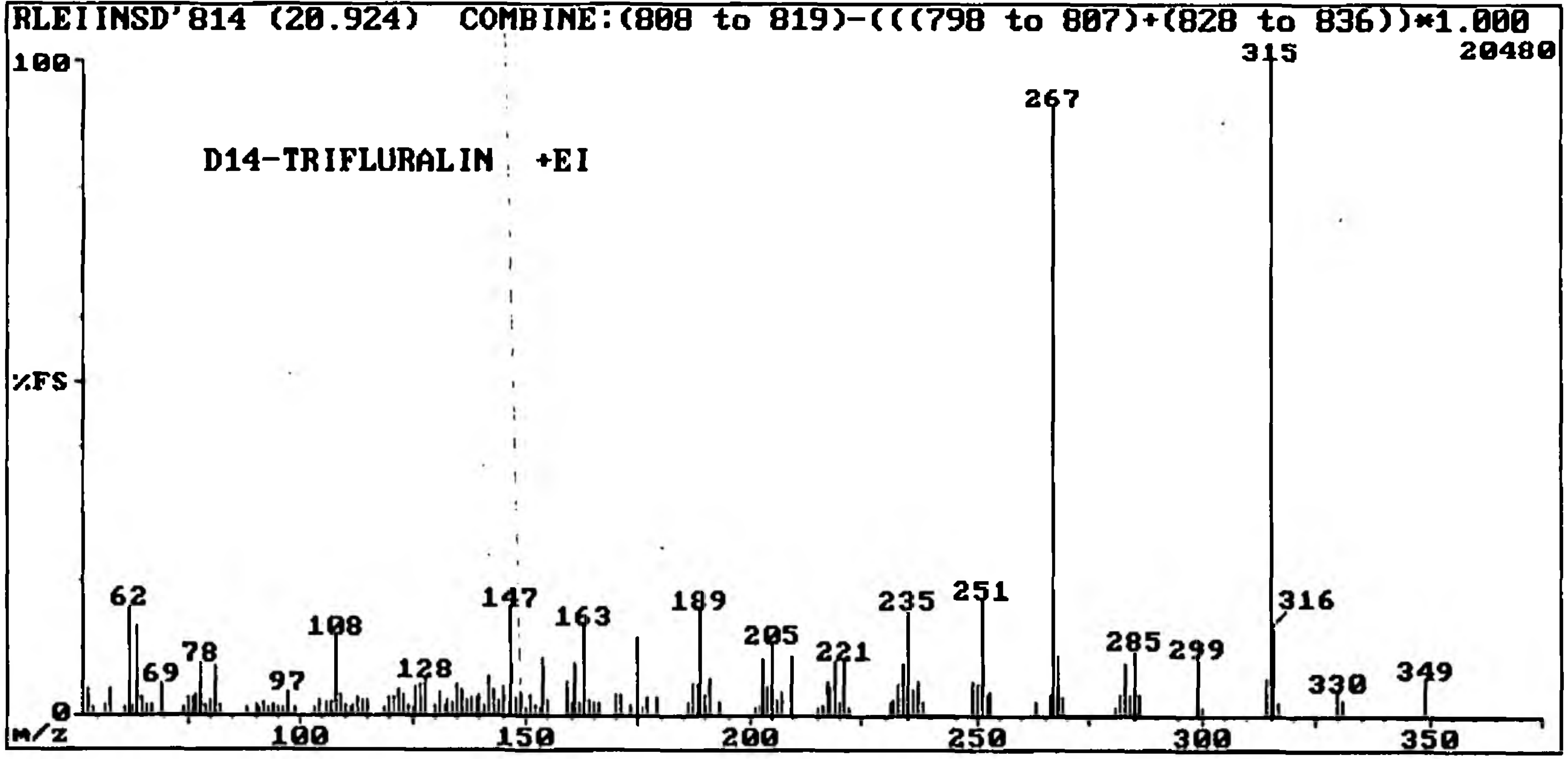
Sample:red list +ei int stds Instrument:Trio-1



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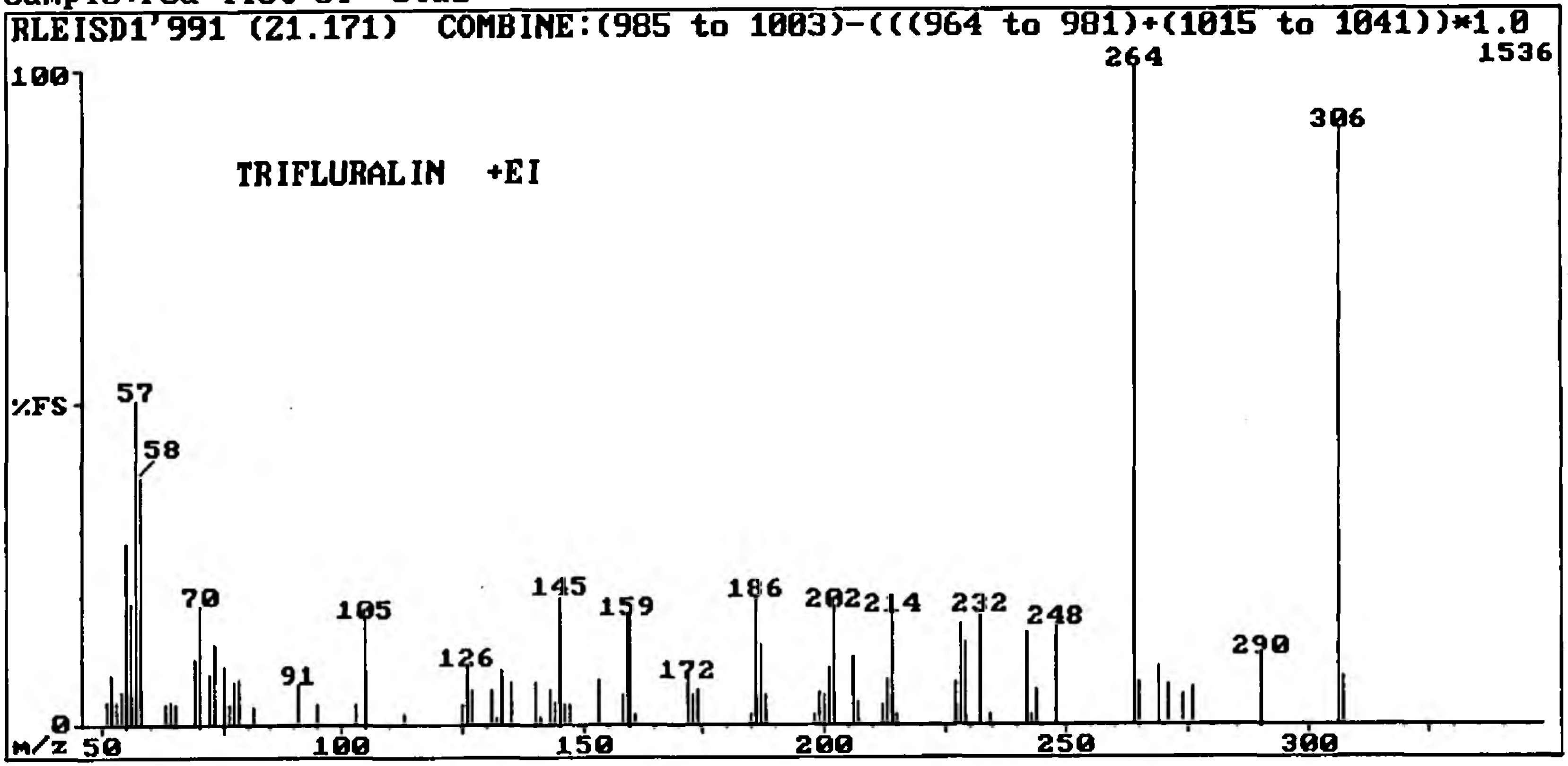

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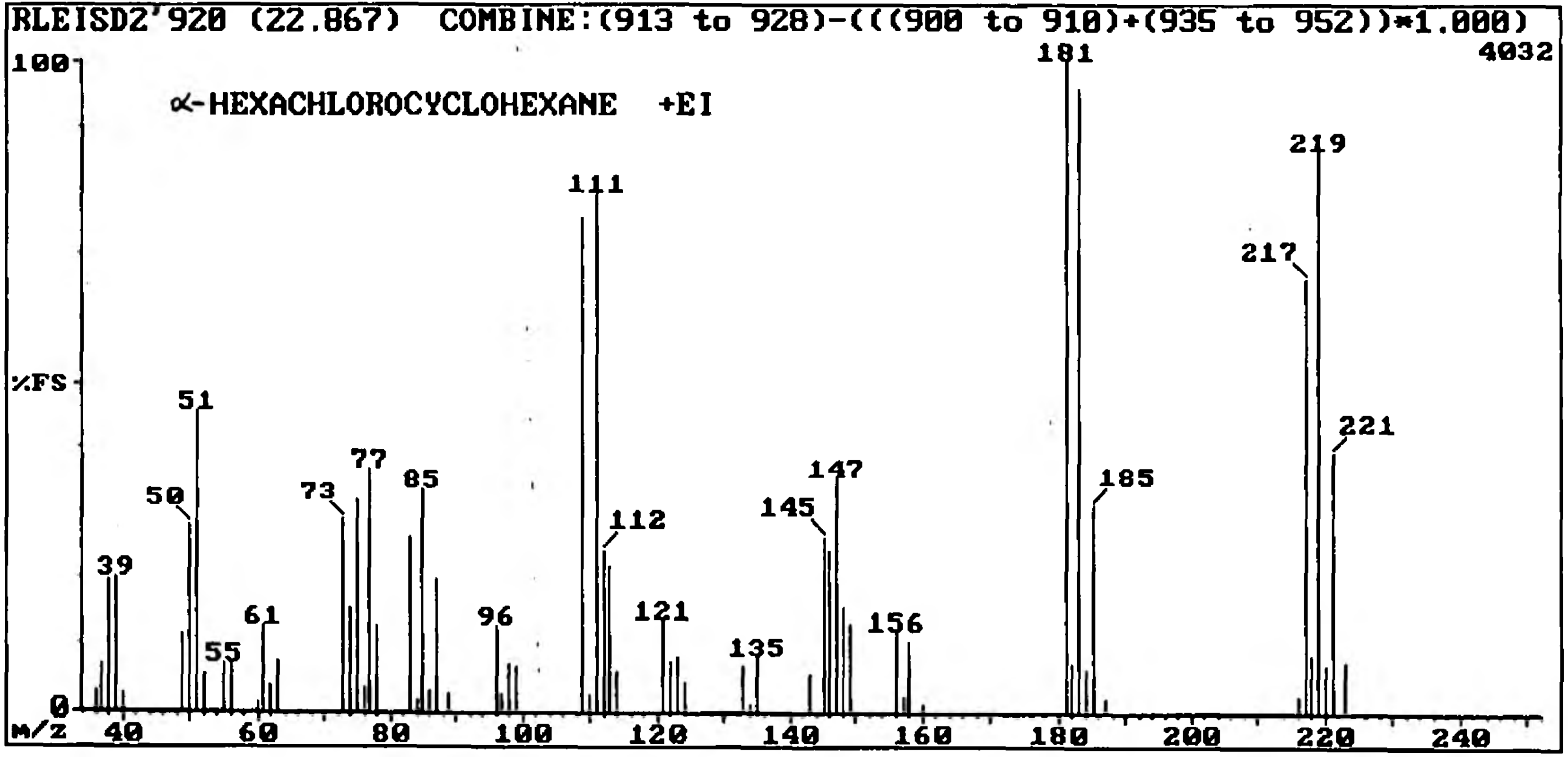
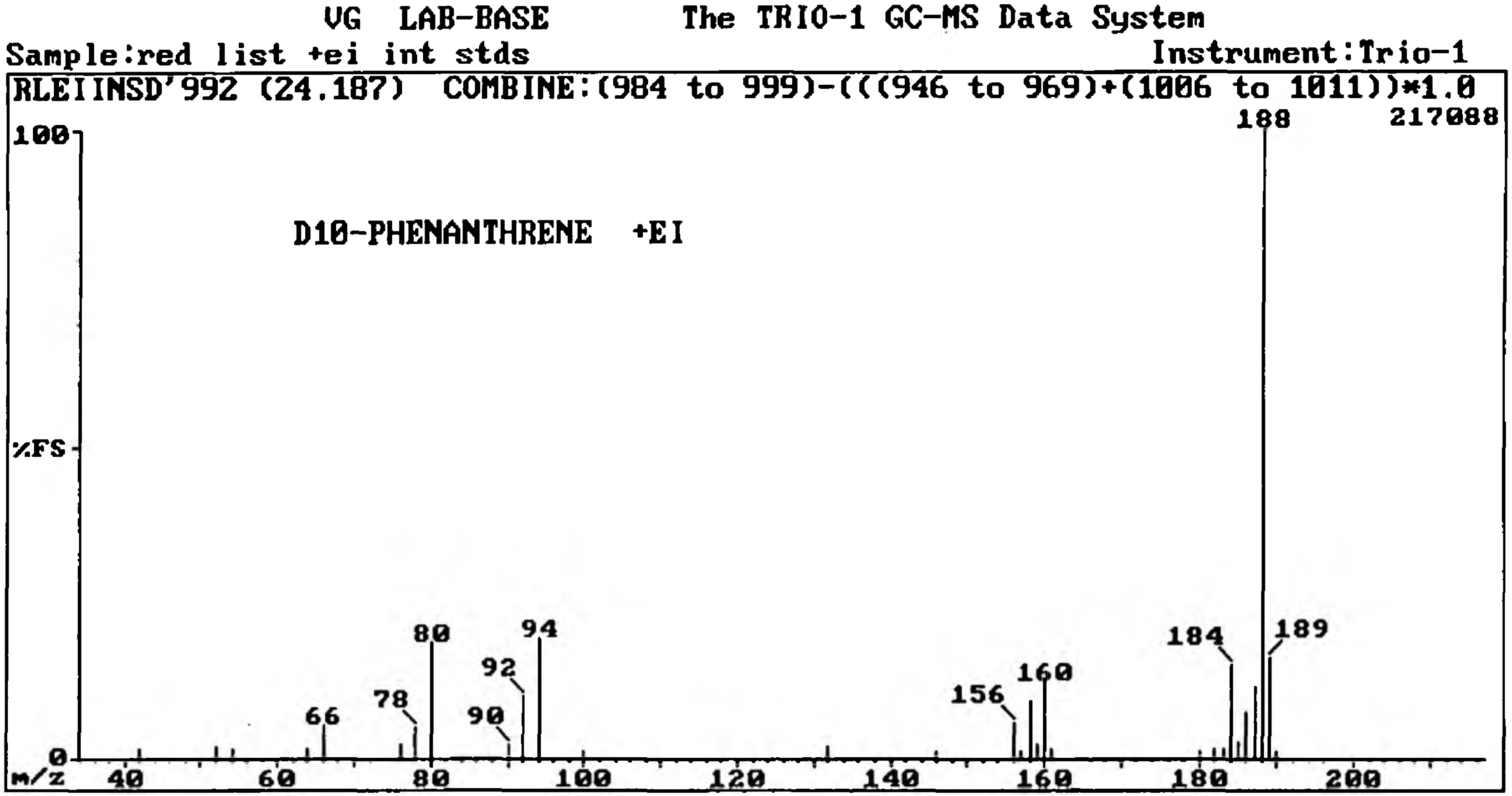
Sample:red list ei+ std2 Instrument:Trio-1





VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:red list +ei int stds Instrument:Trio-1

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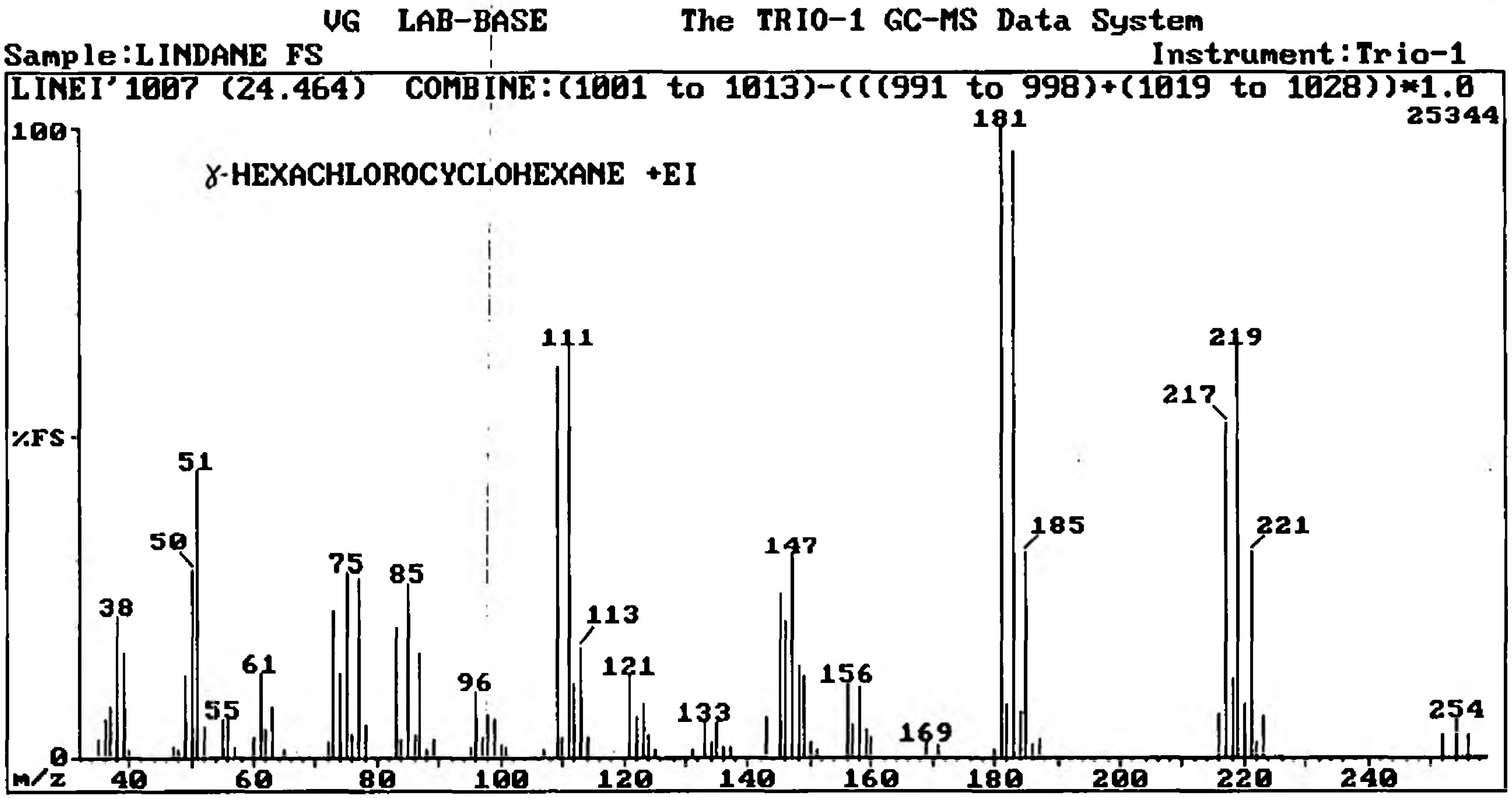


VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:LINDANE FS Instrument:Trio-1

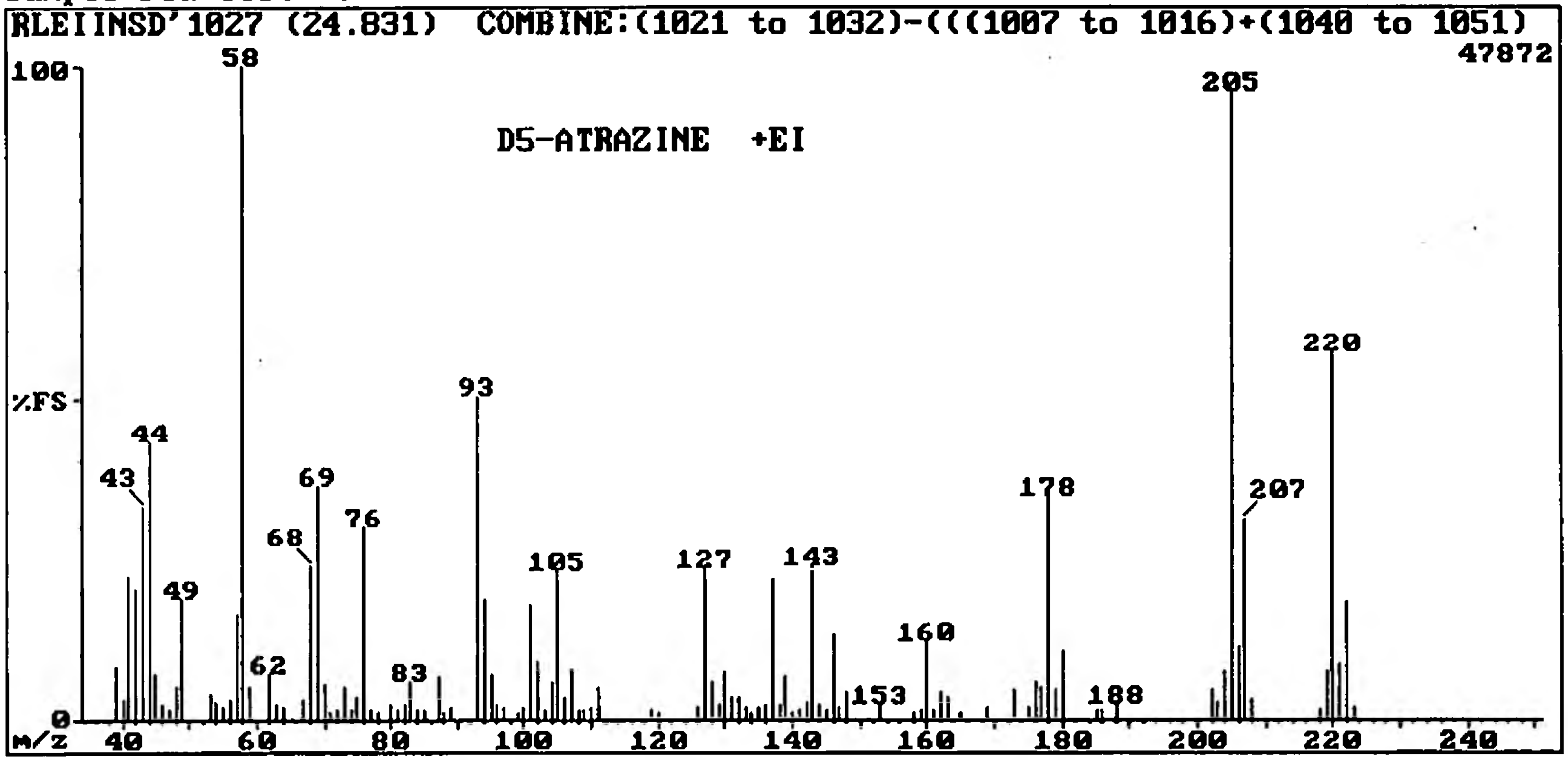
LINEI'1007 (24.464) COMBINE:(1001 to 1013)-(((991 to 998)+(1019 to 1028))*1.0

25344

γ-HEXACHLOROCYCLOHEXANE +EI

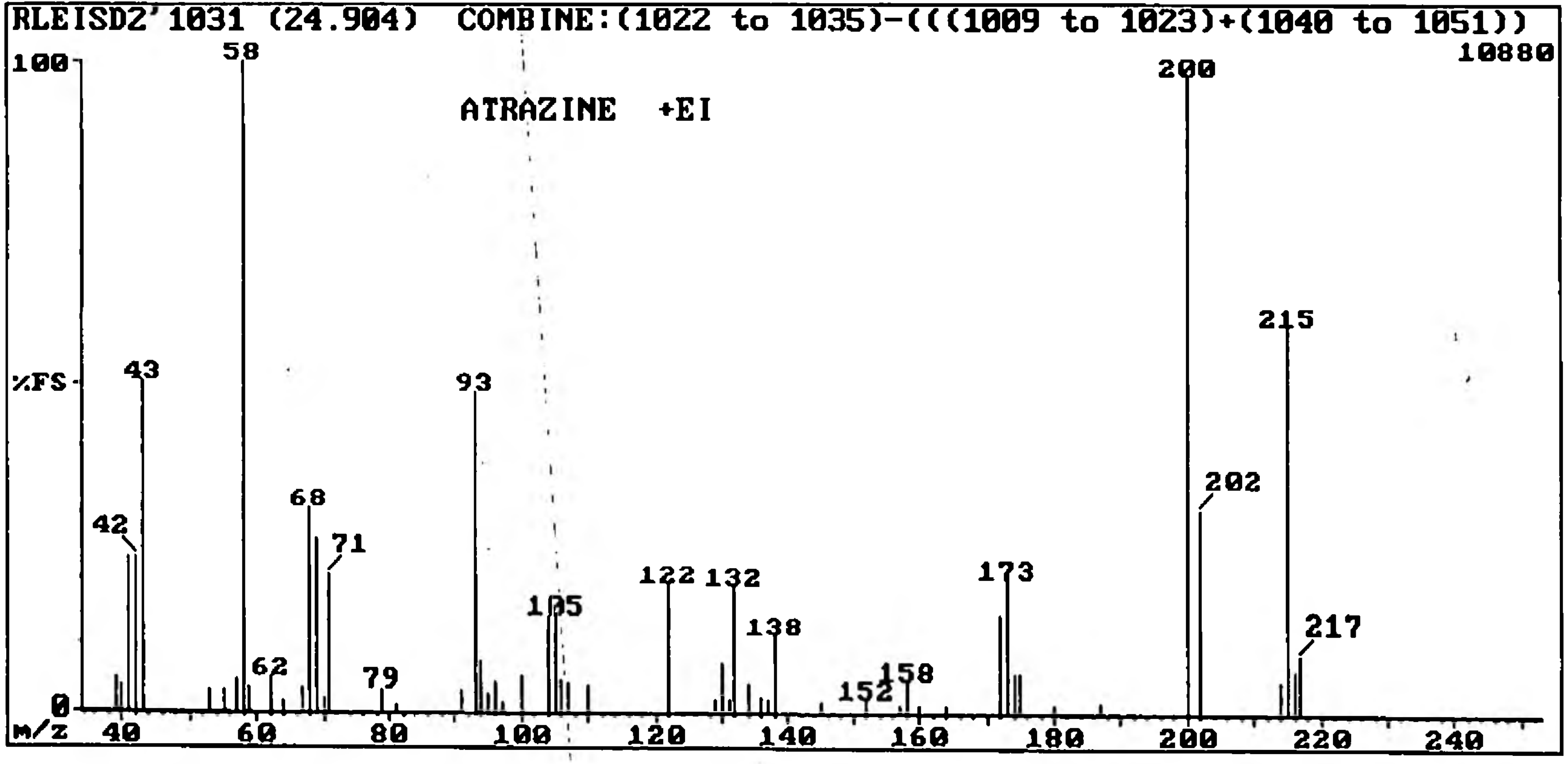
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:red list +ei int stds Instrument:Trio-1



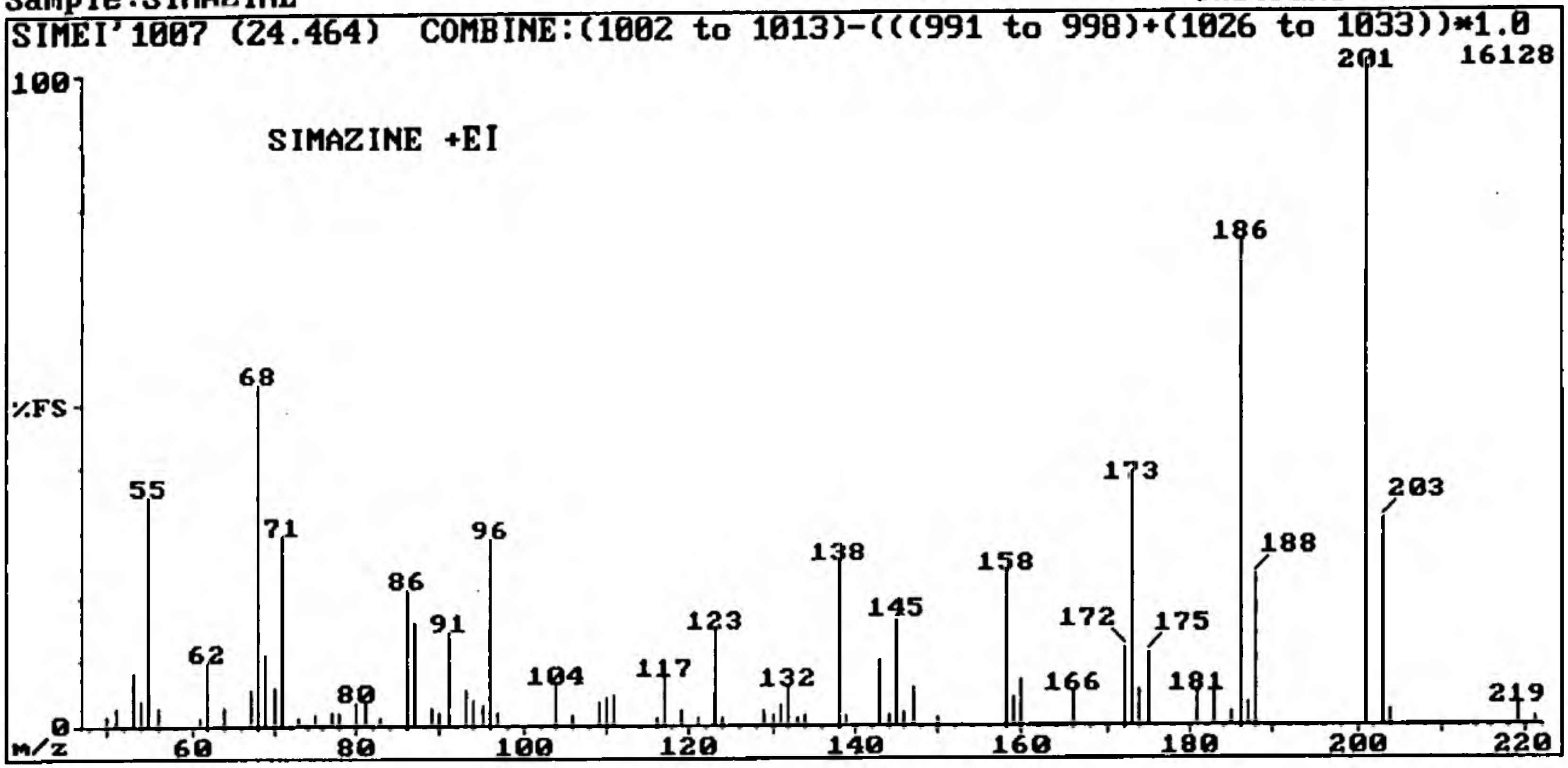
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:red list ei+ std2 Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:SIMAZINE Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:red list ei+ std2 Instrument:Trio-1

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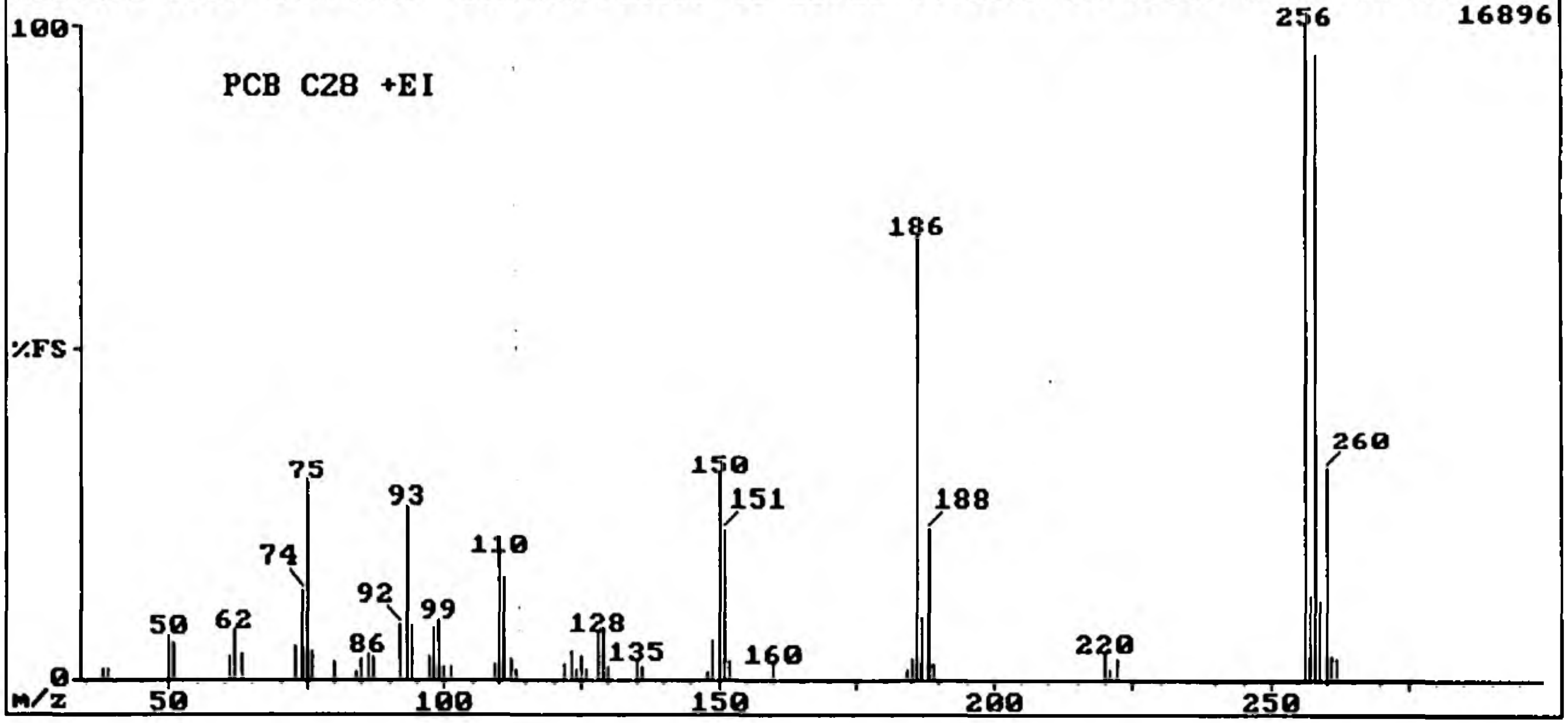

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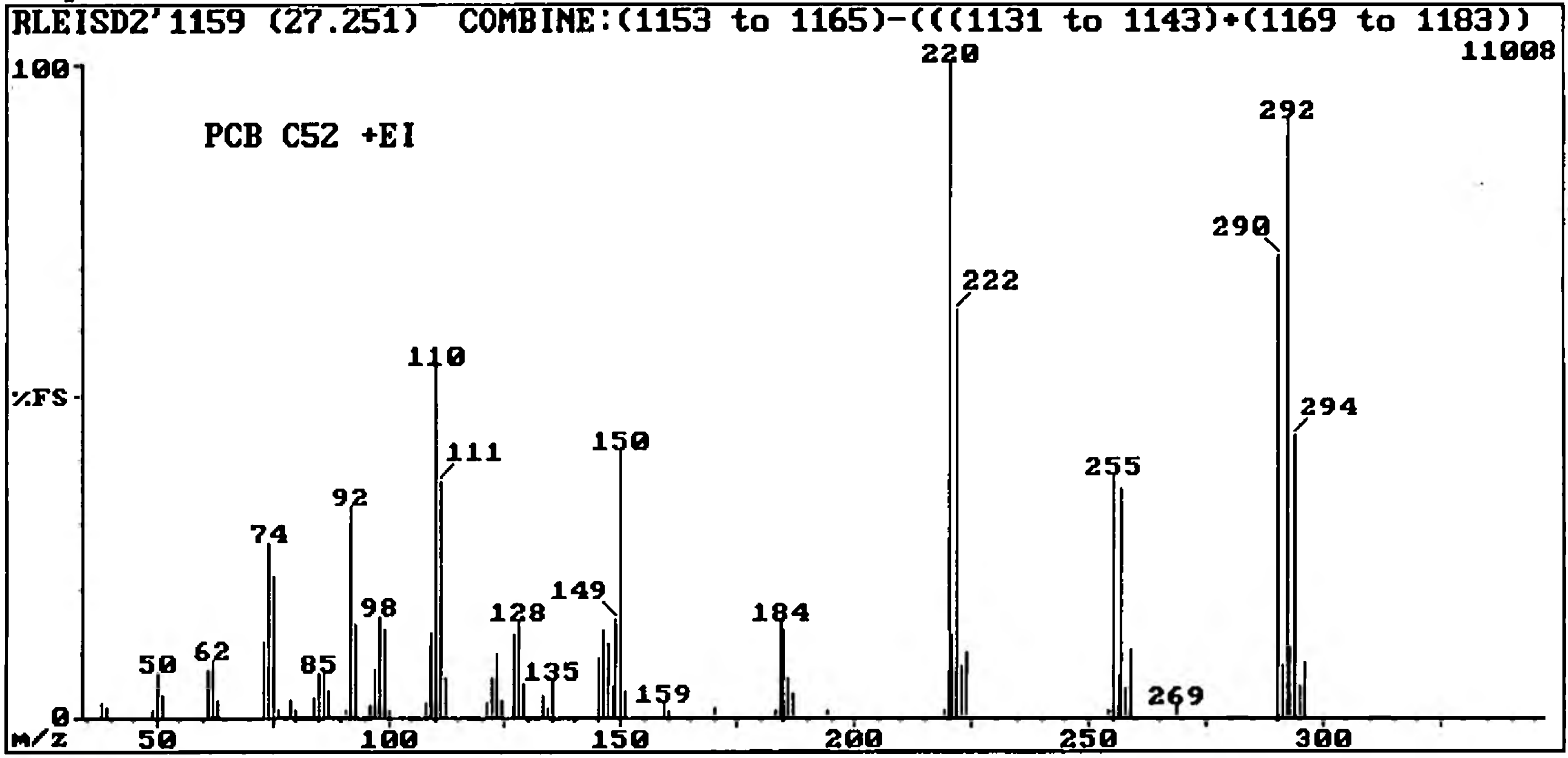
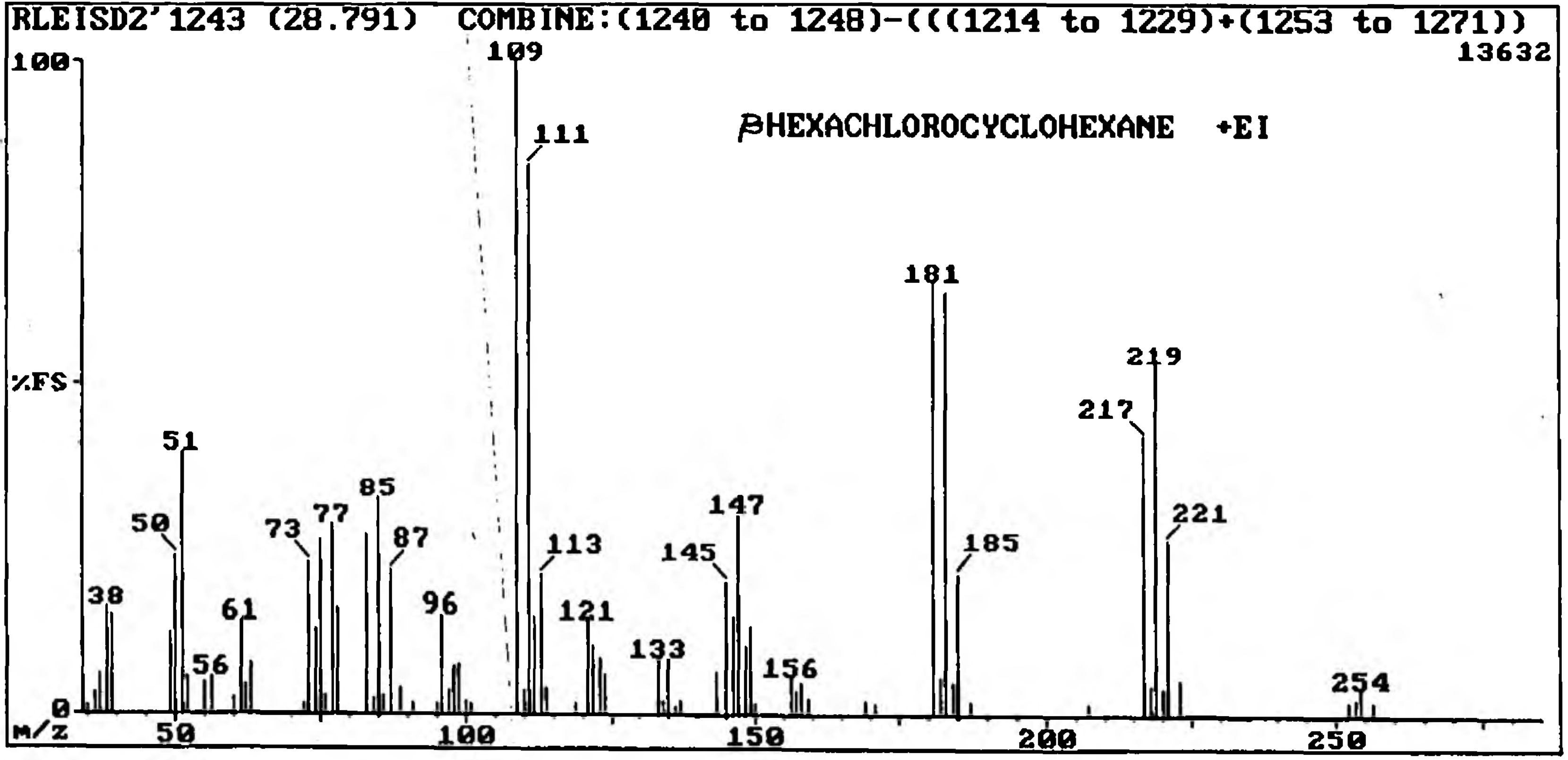


VG LAB-BASE The TRIO-1 GC-MS Data System

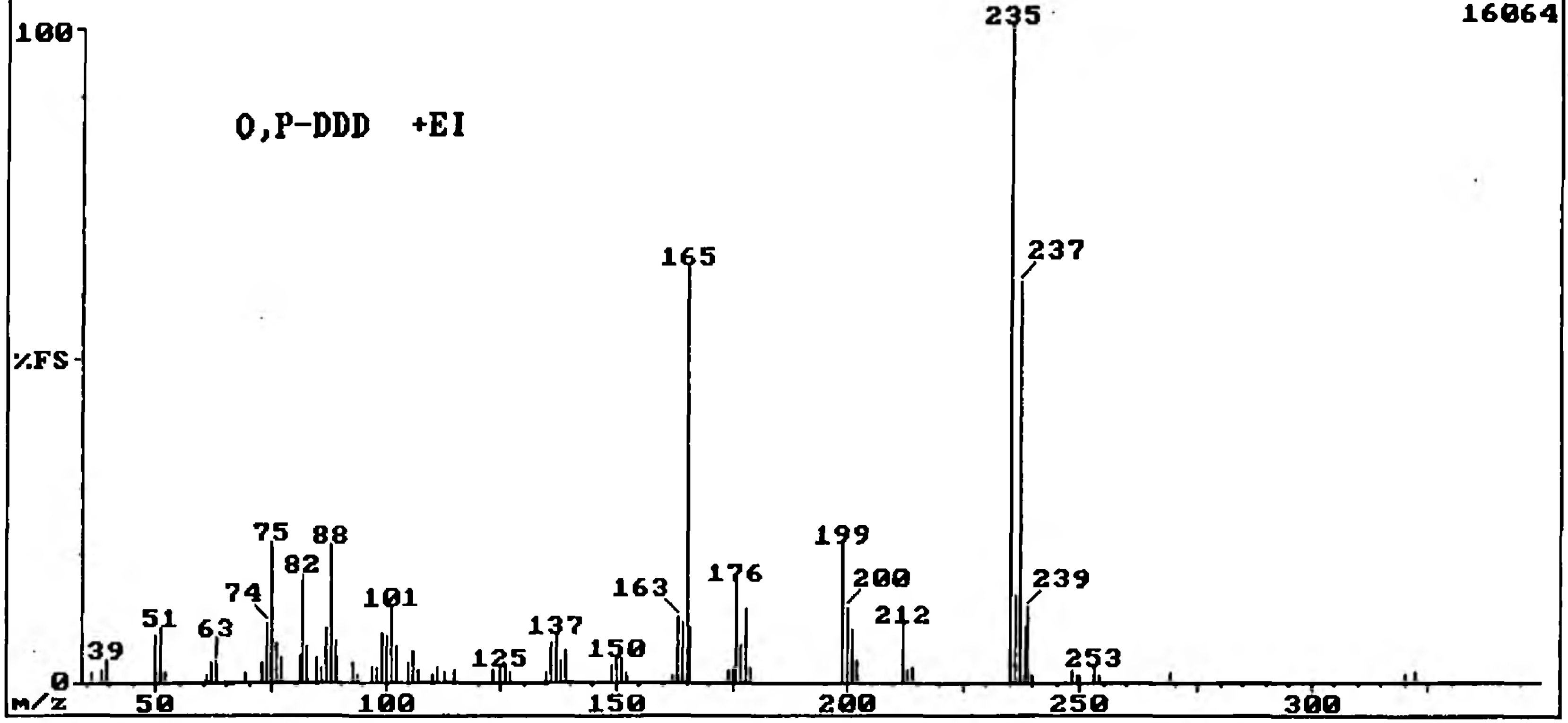
Sample:red list ei+ std2 Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

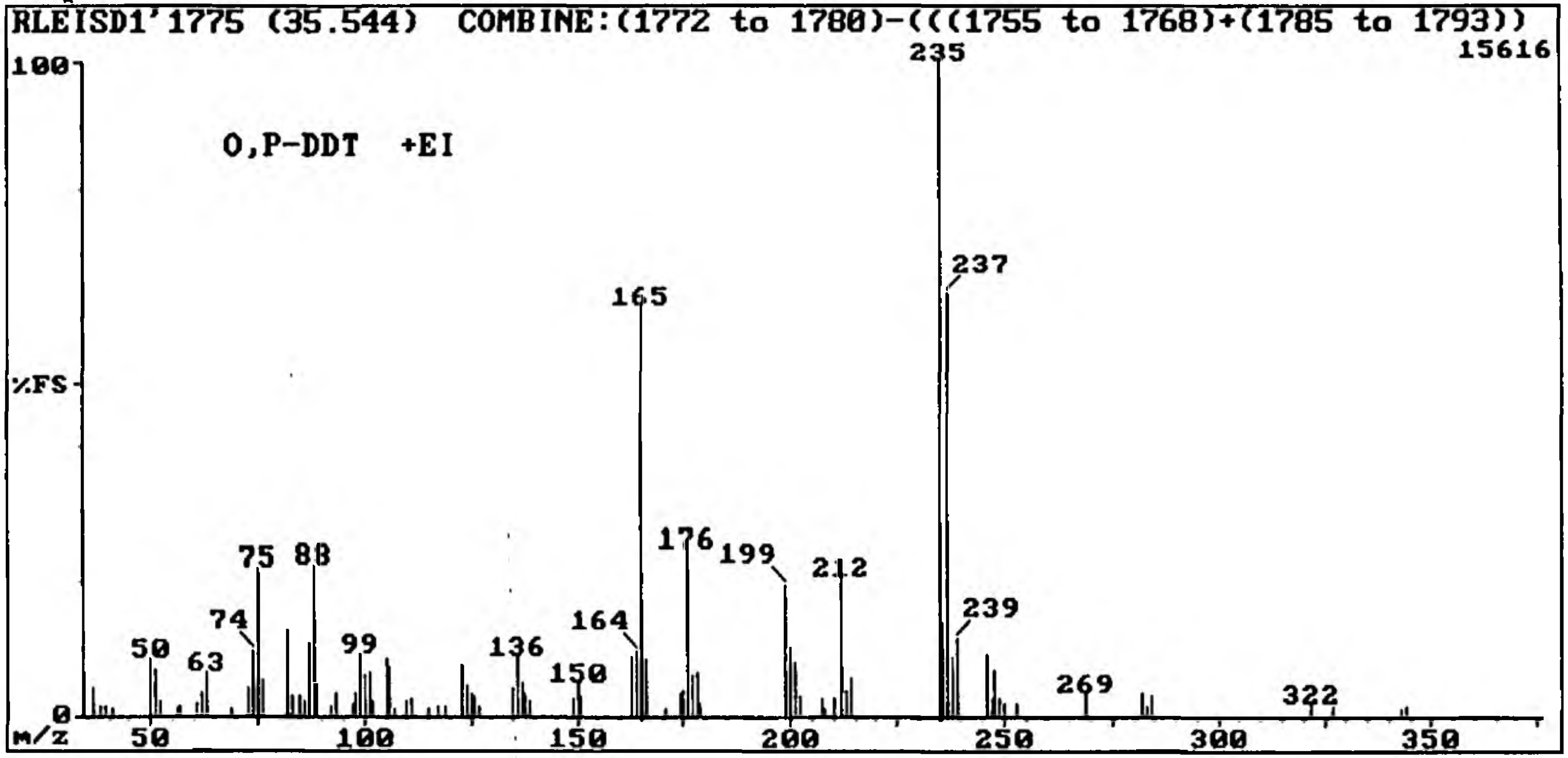
Sample:red list ei+ std1 Instrument:Trio-1

RLEISD1'1735 (34.811) COMBINE:(1728 to 1741)-(((1719 to 1726)+(1744 to 1751))

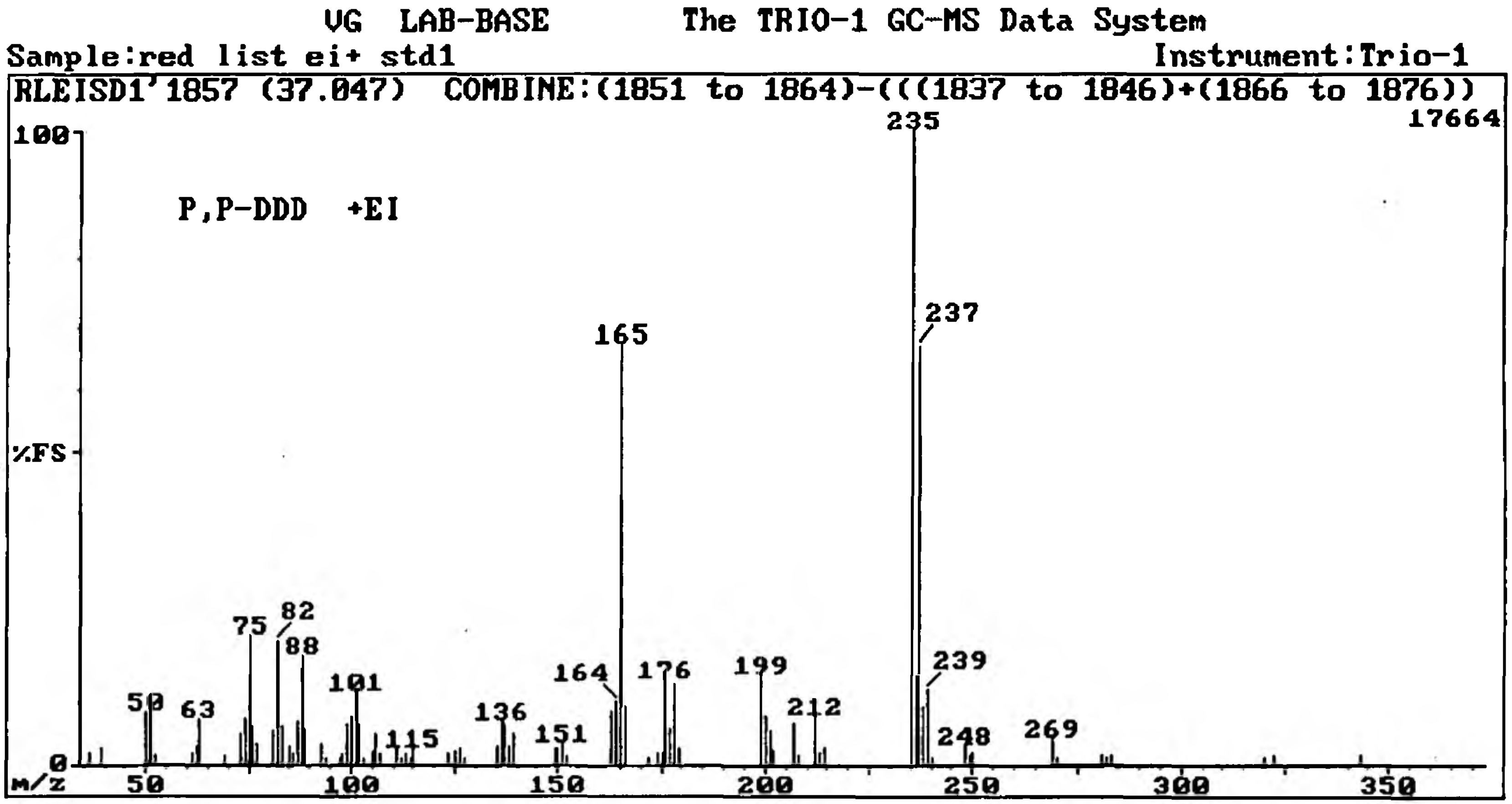


VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:red list ei+ std1 Instrument:Trio-1



RLEISD1'1775 (35.544) COMBINE:(1772 to 1780)-(((1755 to 1768)+(1785 to 1793))



VG LAB-BASE The TRIO-1 GC-MS Data System

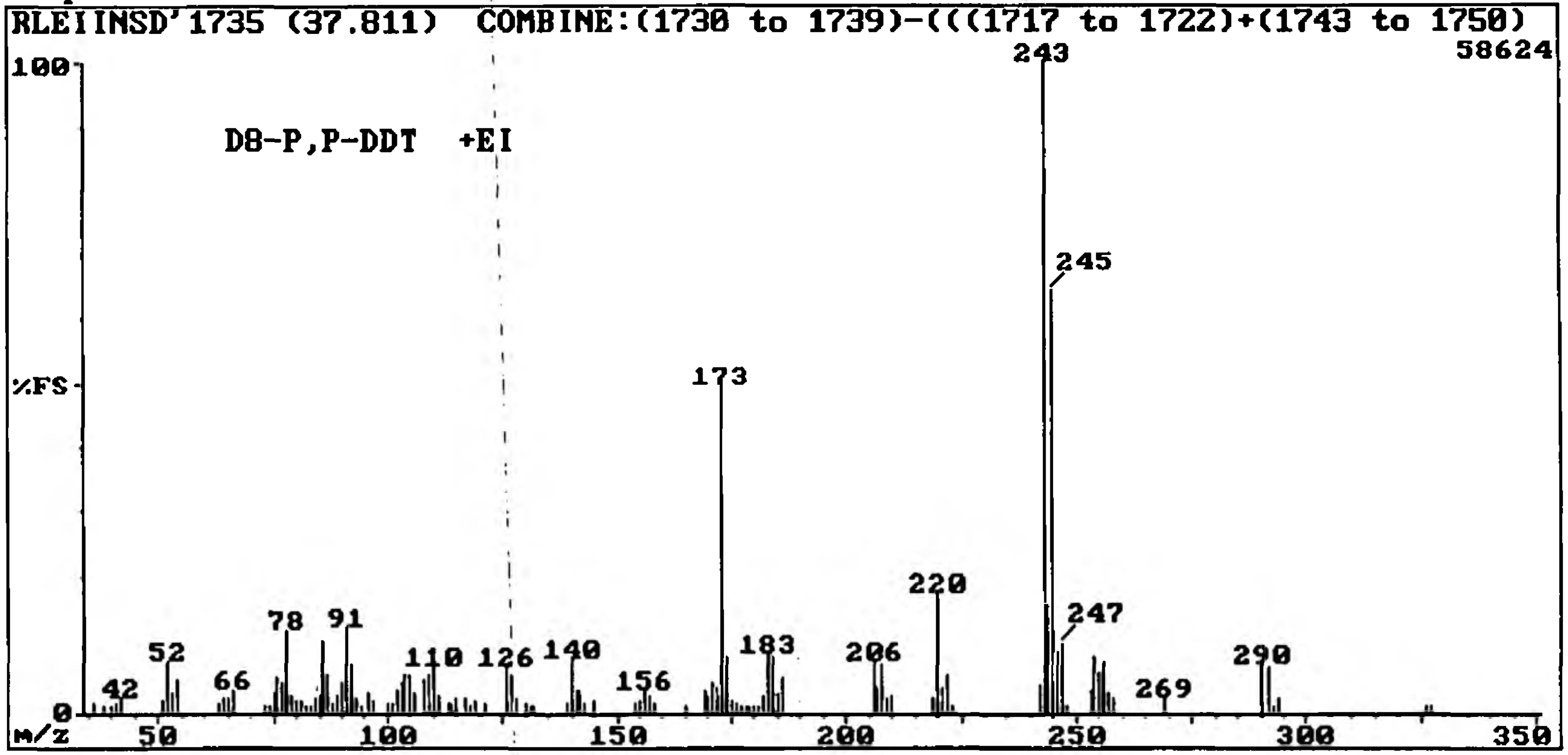
Sample:red list ei+ std1 Instrument:Trio-1

RLEISD1'1857 (37.047) COMBINE:(1851 to 1864)-(((1837 to 1846)+(1866 to 1876))

P,P-DDD +EI

VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:red list +ei int stds Instrument:Trio-1

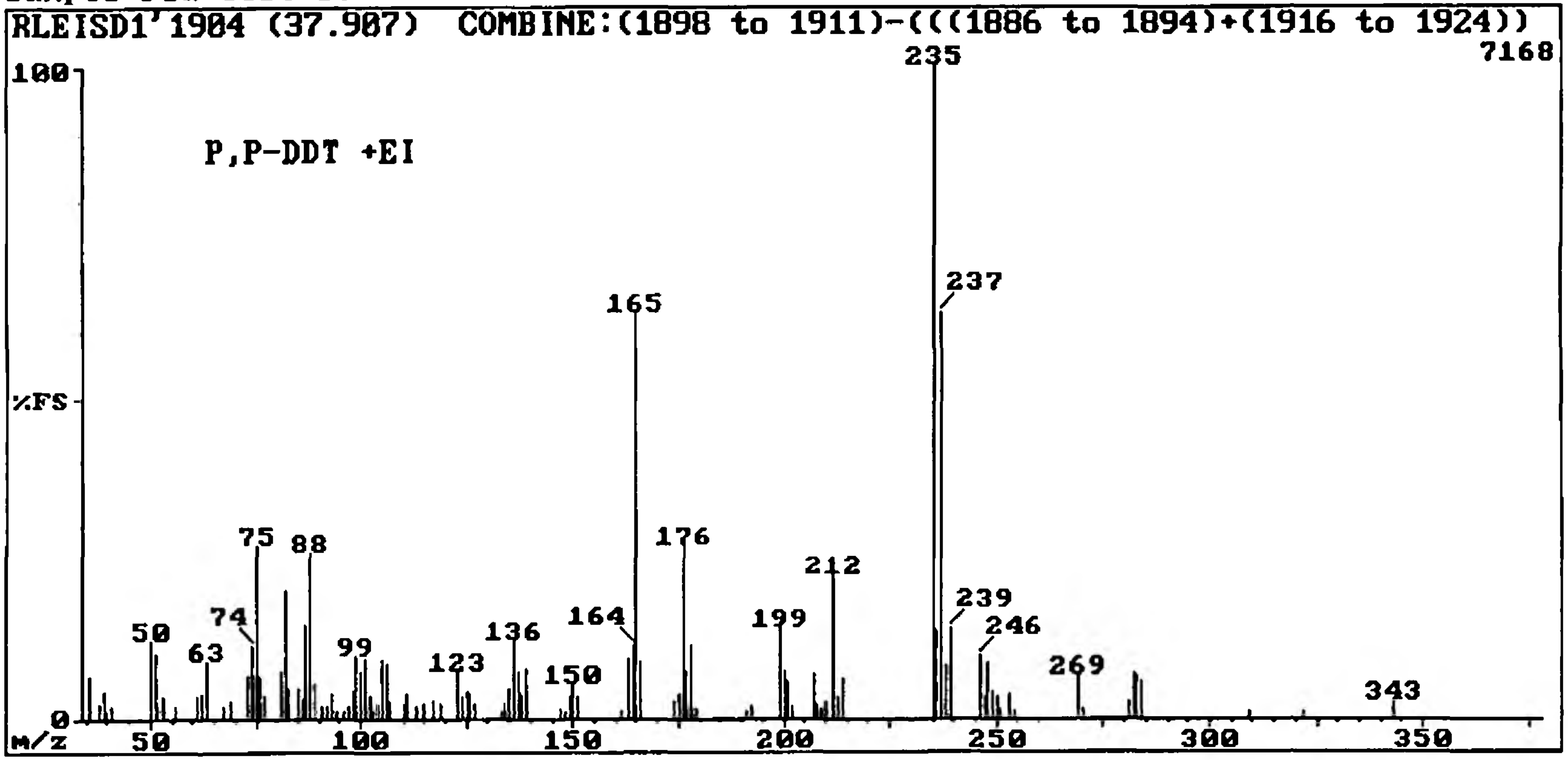


RLEIINSD'1735 (37.811) COMBINE:(1730 to 1739)-(((1717 to 1722)+(1743 to 1750)

D8-P,P-DDT +EI

VG LAB-BASE The TRIO-1 GC-MS Data System

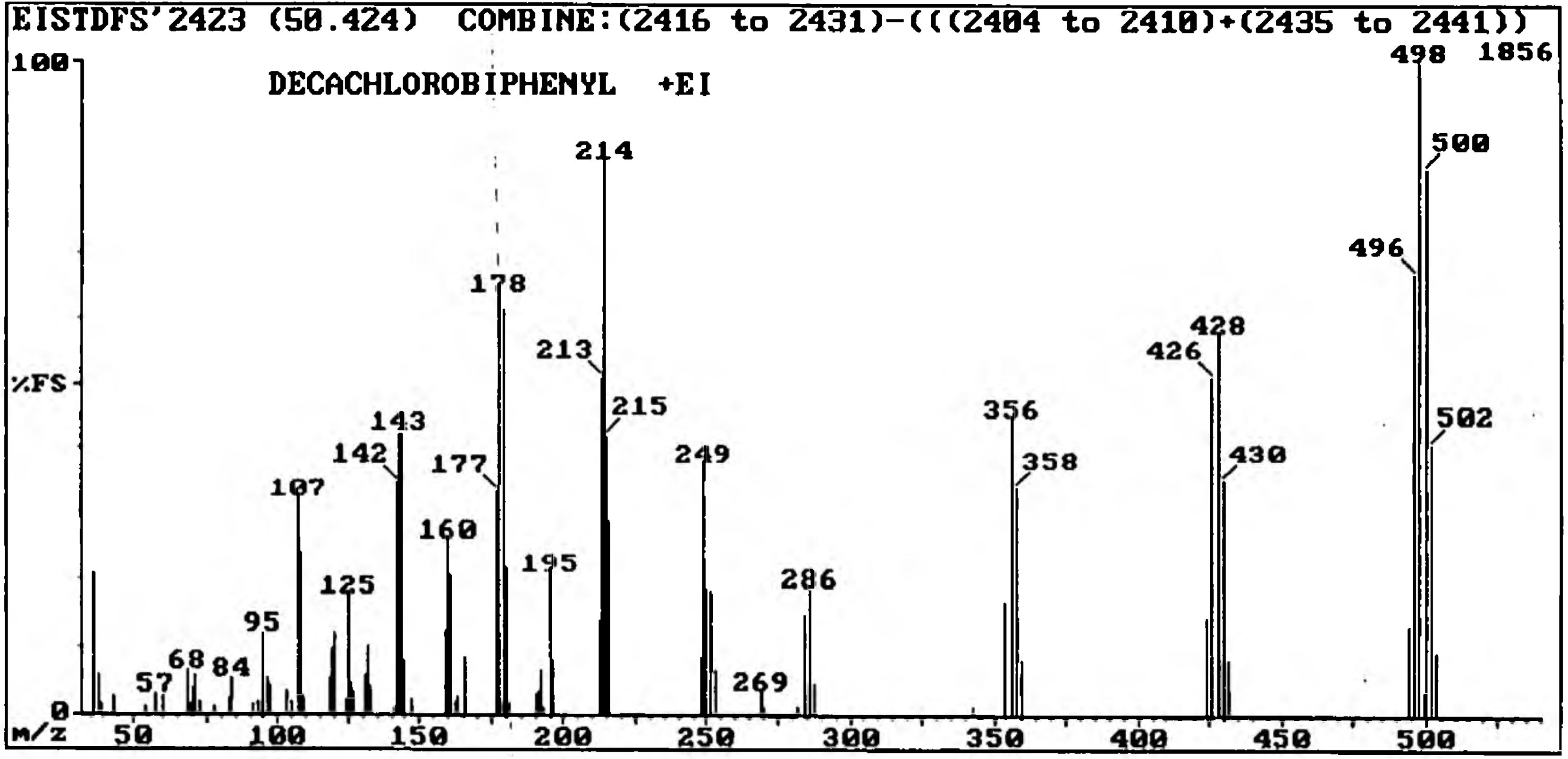
Sample:red list ei+ std1 Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:STD FS

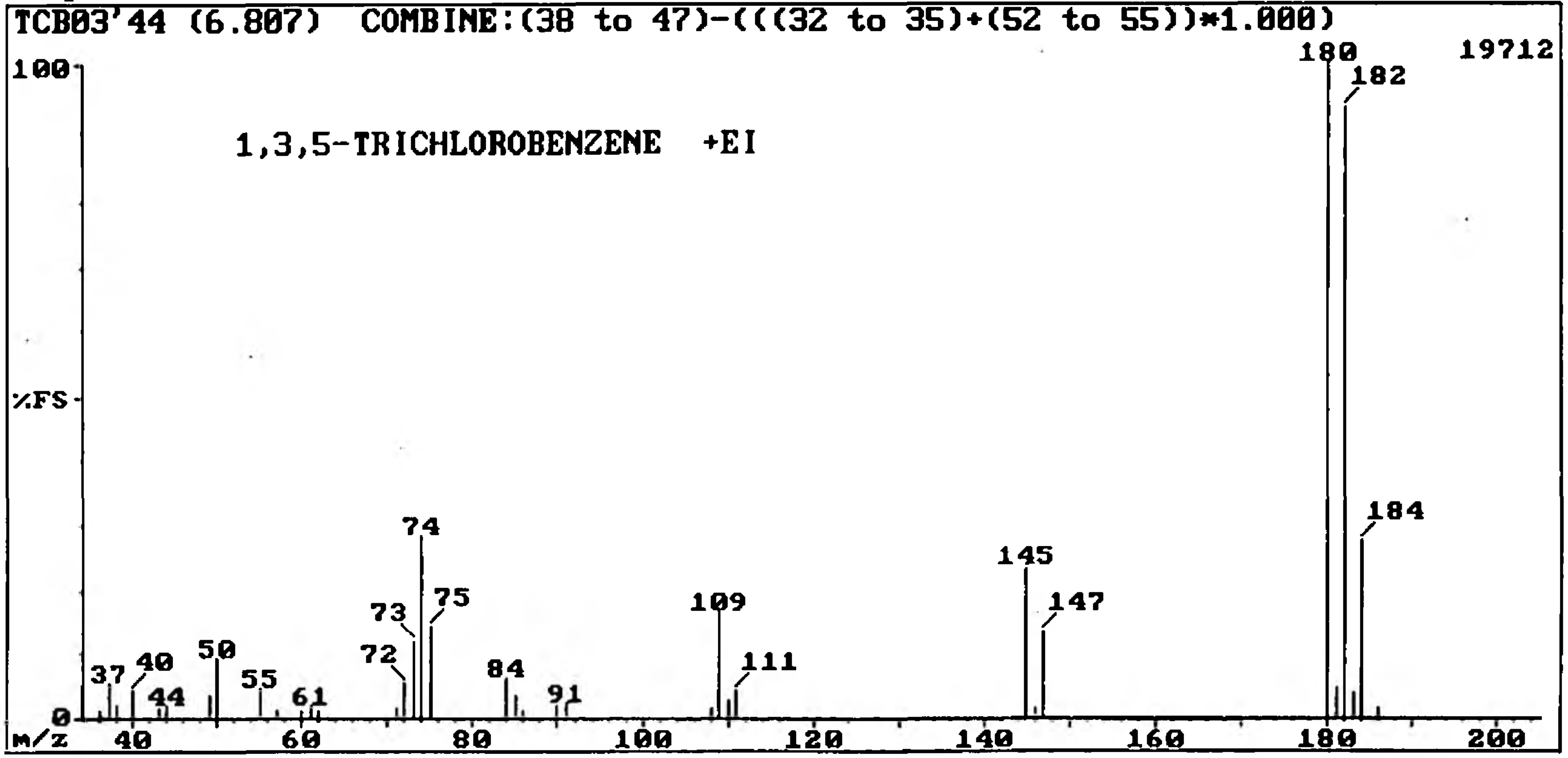
Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

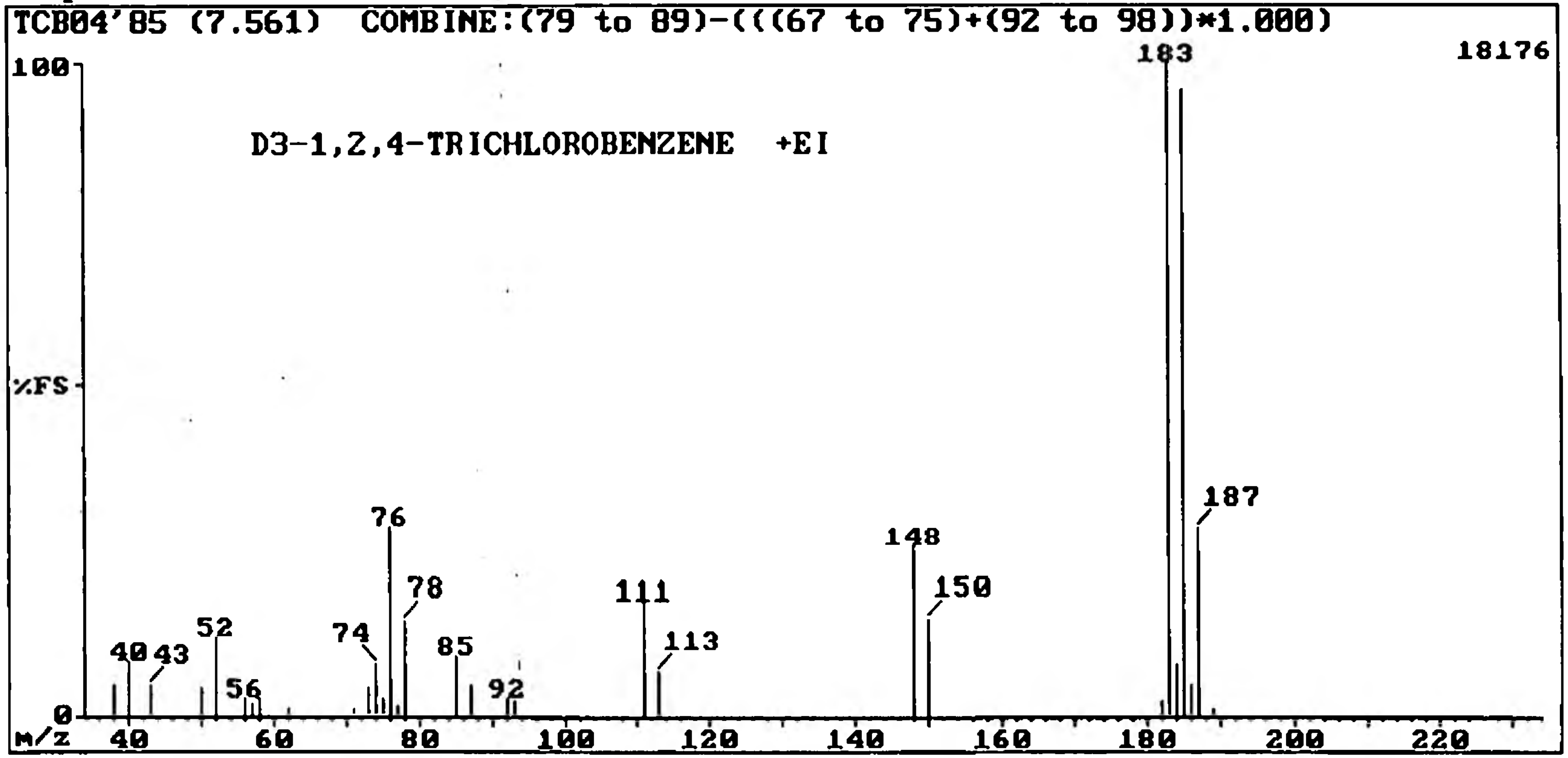
Sample:TRICHLOROBENZENE Instrument:Trio-1

TCB03'44 (6.807) COMBINE:(38 to 47)-(((32 to 35)+(52 to 55))*1.000)



VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:TRICHLOROBENZENE Instrument:Trio-1

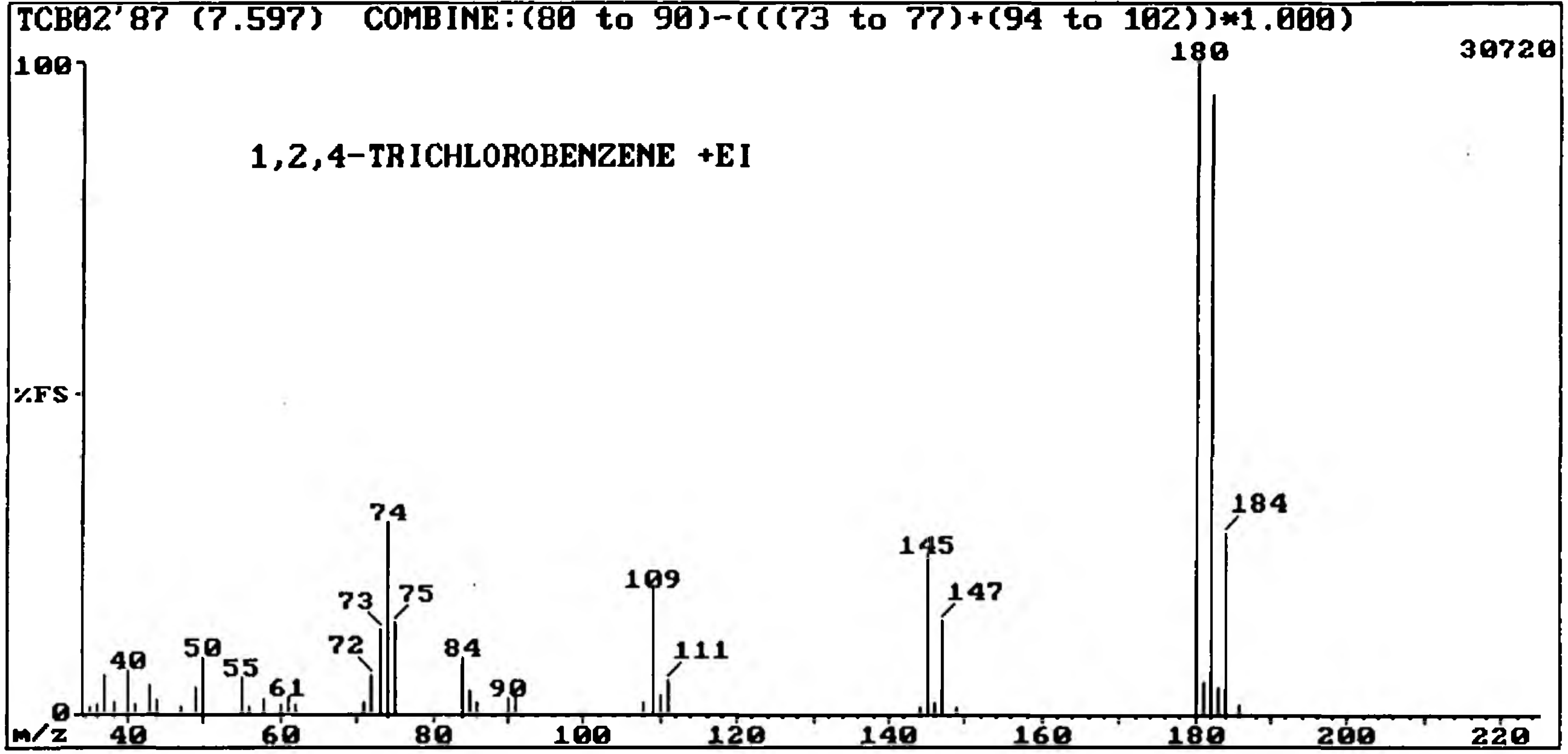

TCB04'85 (7.561) COMBINE:(79 to 89)-(((67 to 75)+(92 to 98))*1.000)

D3-1,2,4-TRICHLOROBENZENE +EI

VG LAB-BASE The TRIO-1 GC-MS Data System

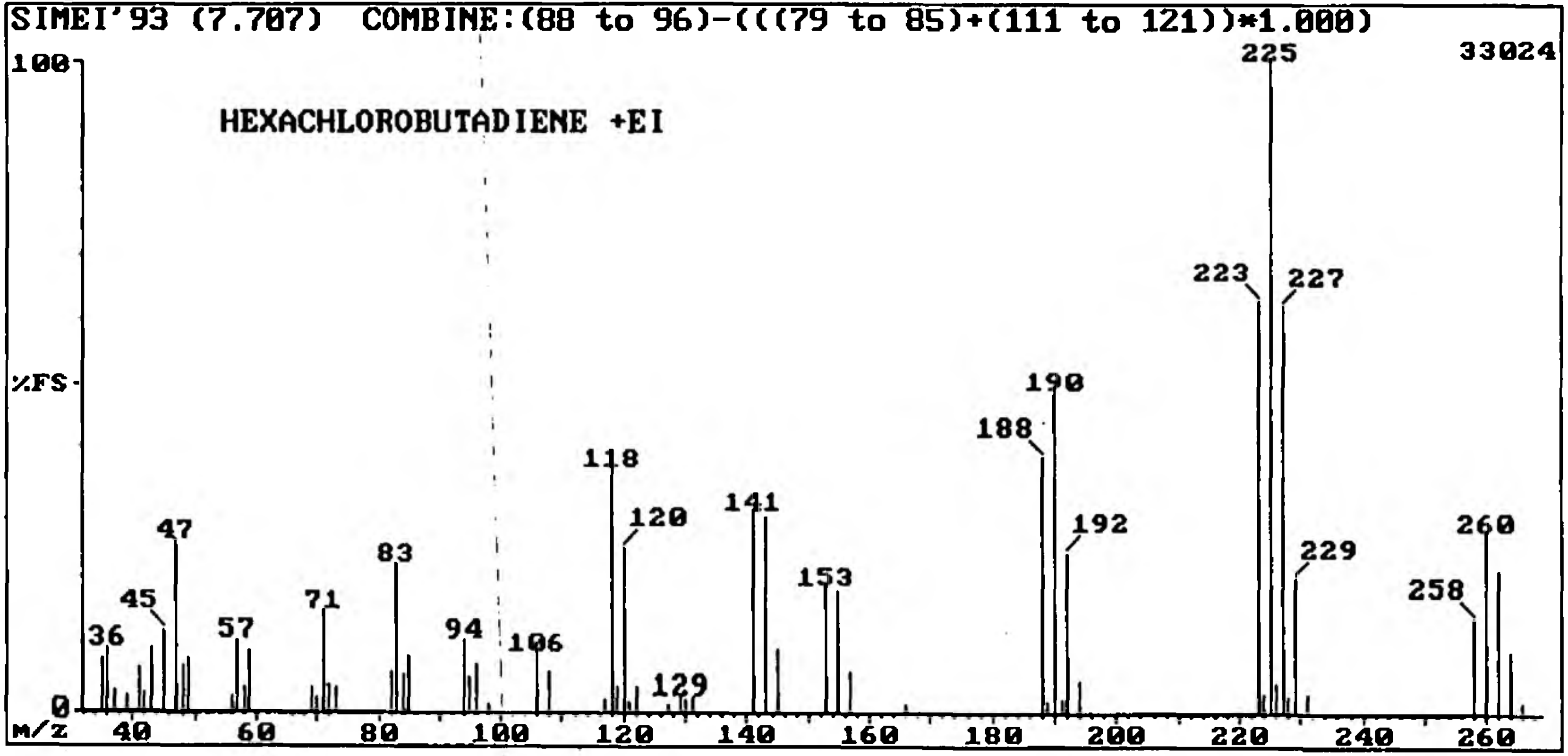
Sample:TRICHLOROBENZENE Instrument:Trio-1

TCB02'87 (7.597) COMBINE:(80 to 90)-(((73 to 77)+(94 to 102))*1.000)



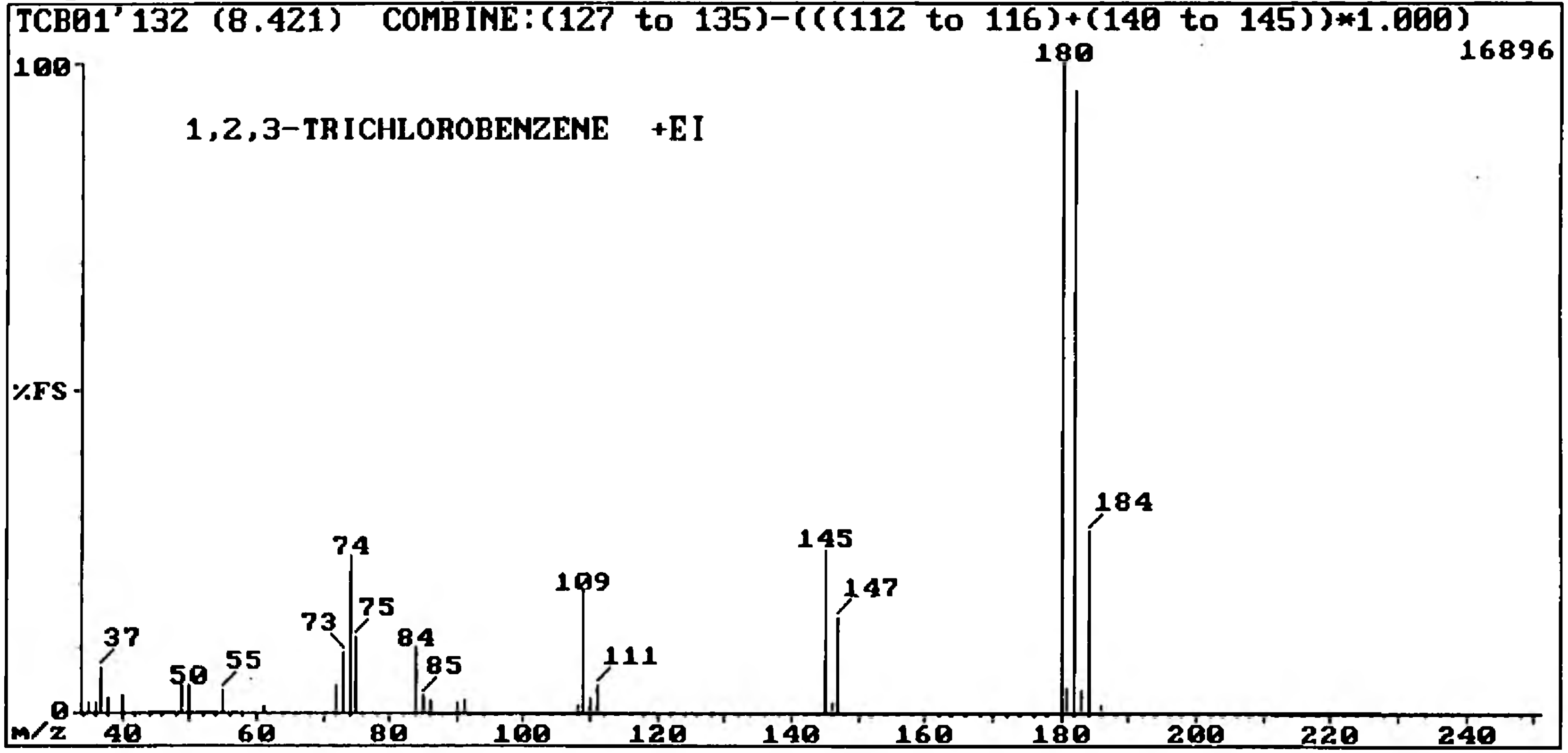
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:SIMAZINE Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

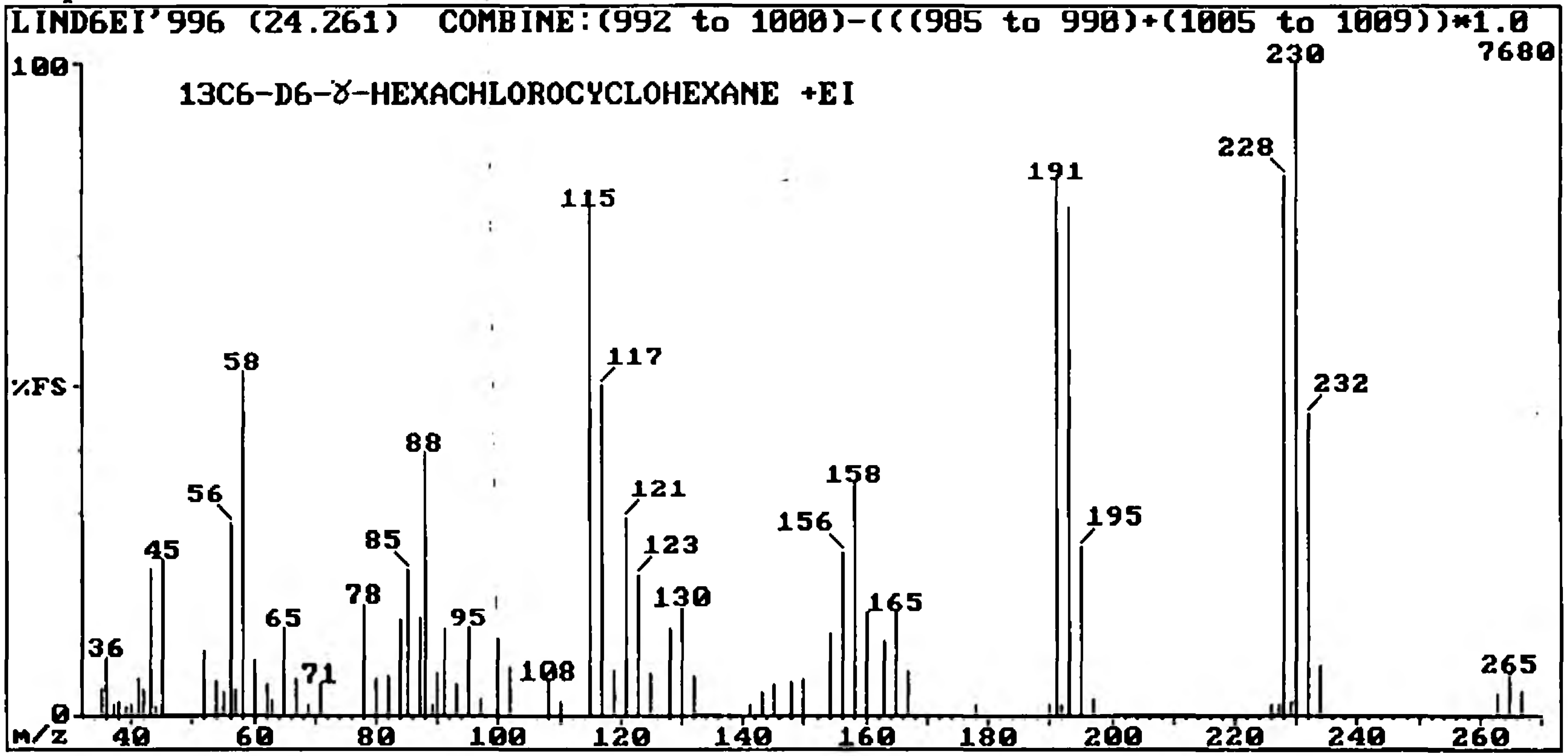
Sample:TRICHLOROBENZENE Instrument:Trio-1



TCB01'132 (8.421) COMBINE:(127 to 135)-(((112 to 116)+(140 to 145))*1.000)

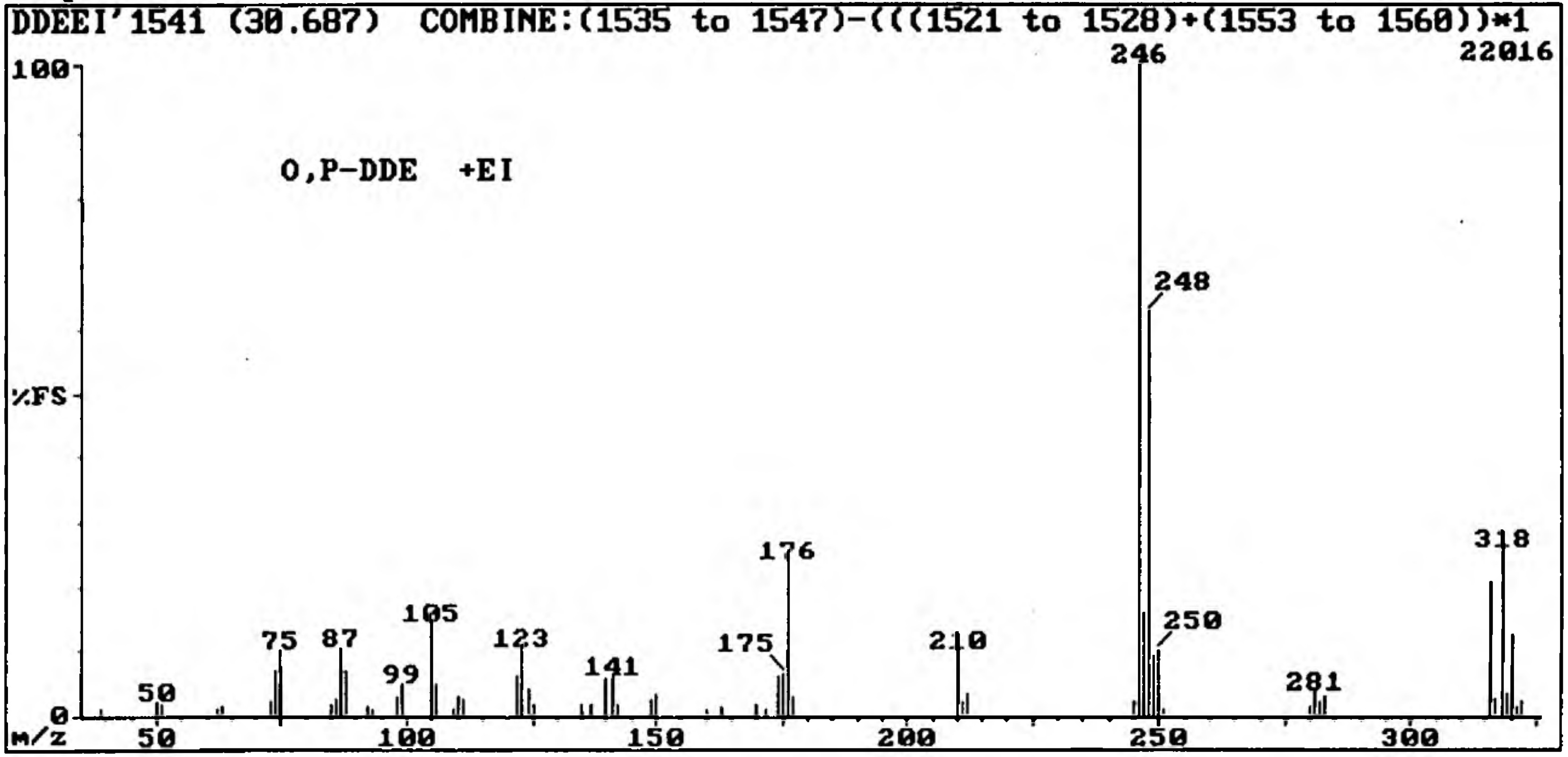
VG LAB-BASE   The TRIO-1 GC-MS Data System

Sample:d6 lindane +ei   Instrument:Trio-1



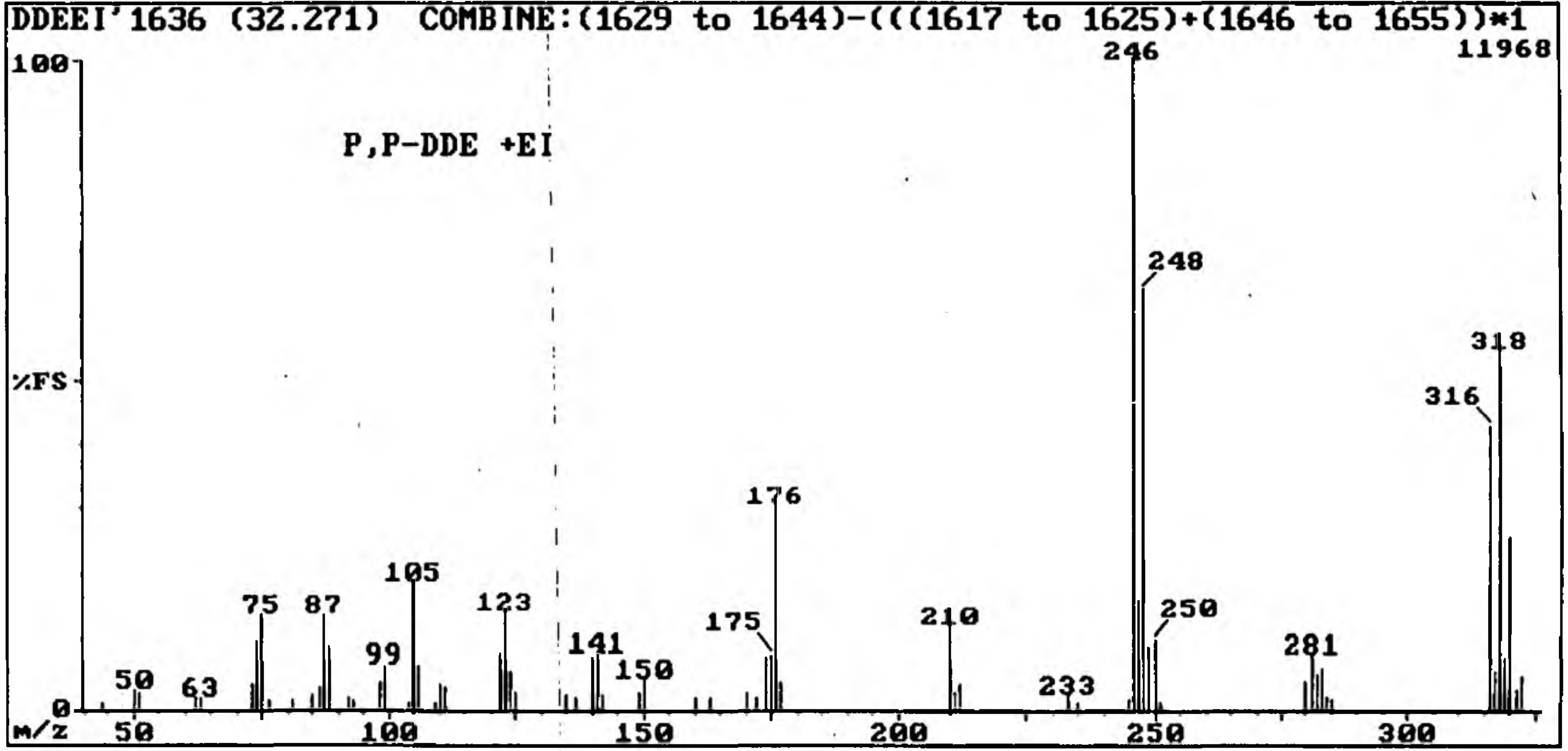
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:Inlet Level HP5890A GC Editor Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

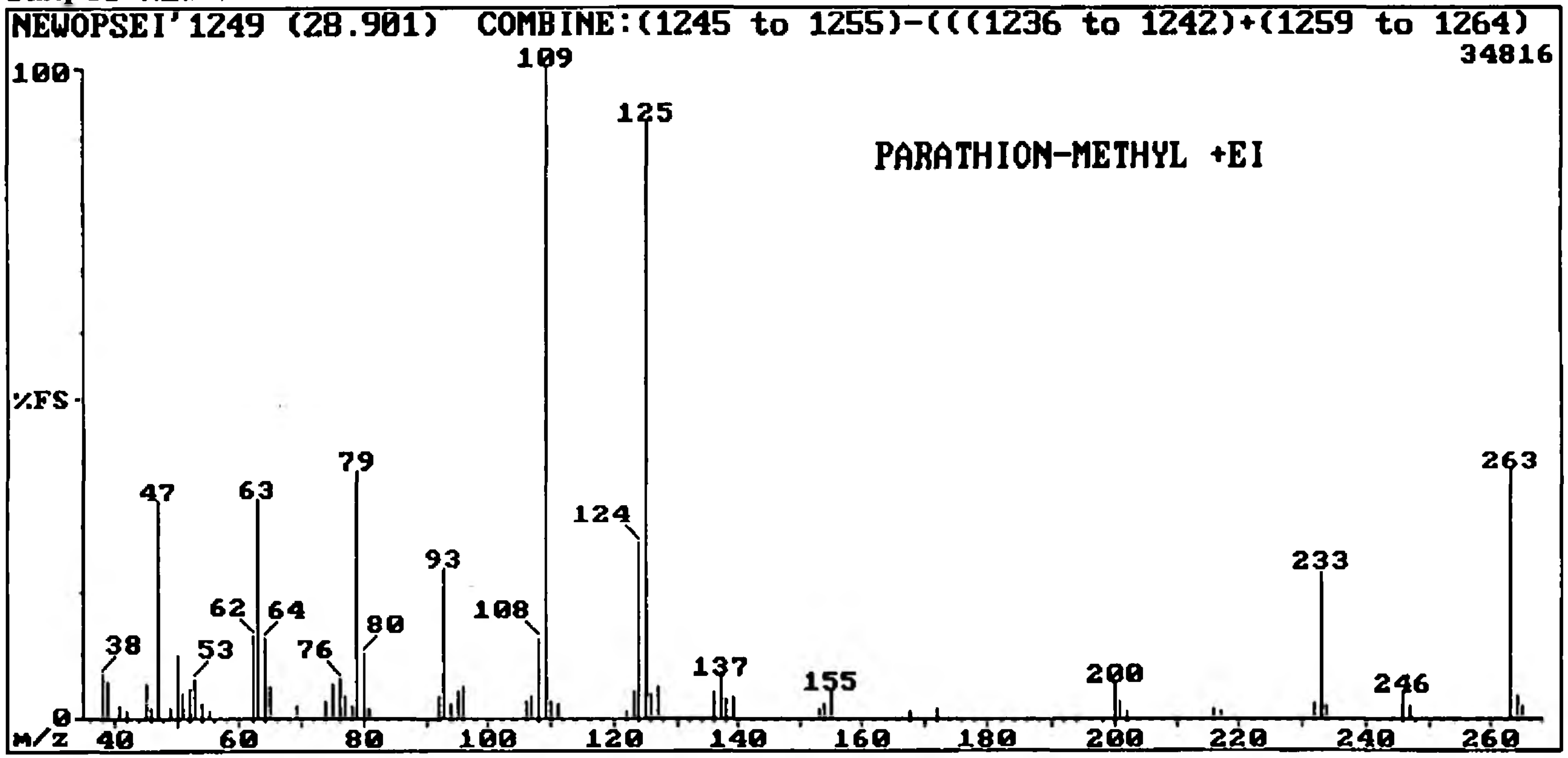
Sample:Inlet Level HP5890A GC Editor Instrument:Trio-1

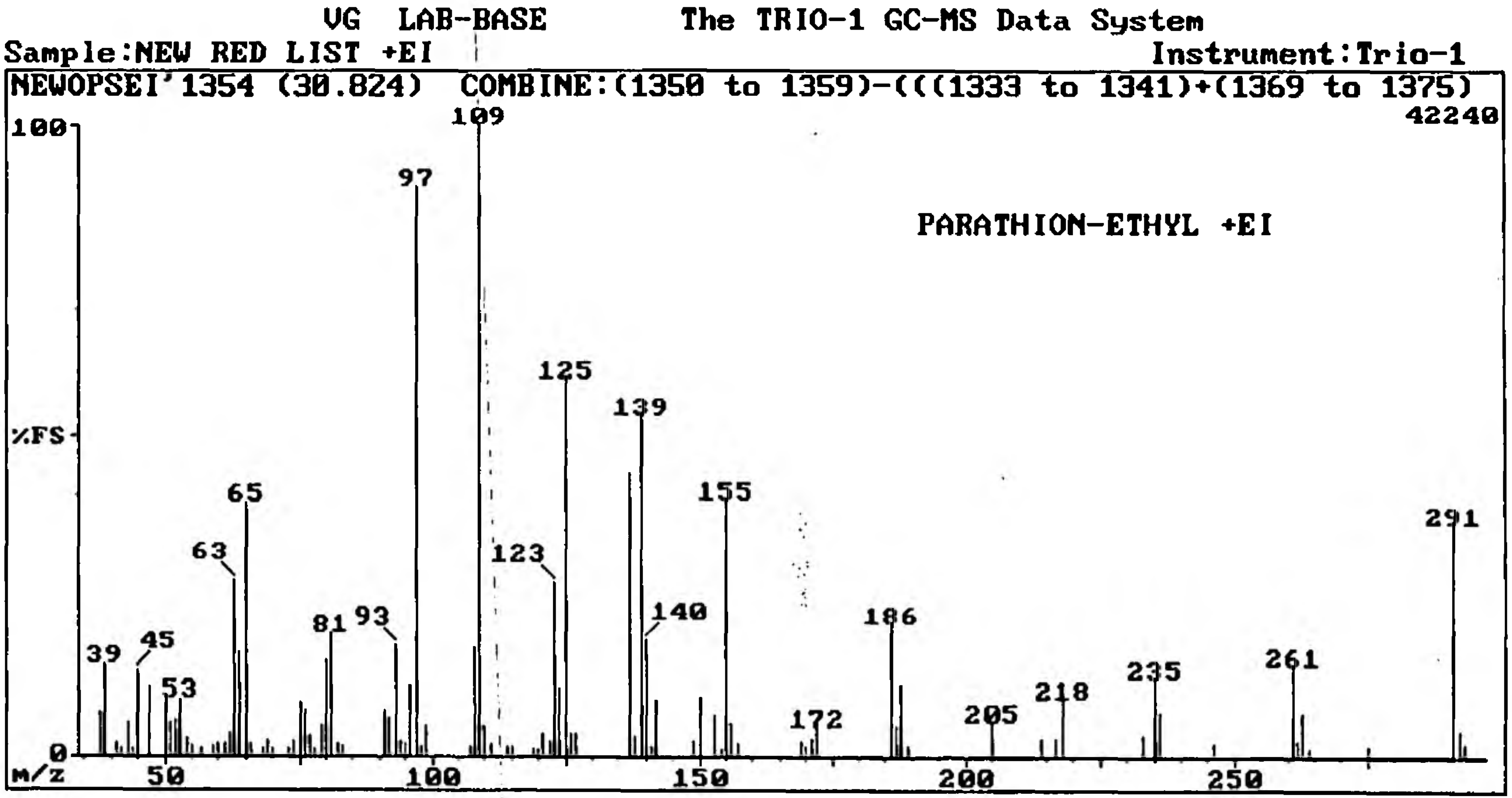


DDEEI'1636 (32.271) COMBINE:(1629 to 1644)-(((1617 to 1625)+(1646 to 1655))*1

VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:NEW RED LIST +EI Instrument:Trio-1





VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:NEW RED LIST +EI Instrument:Trio-1

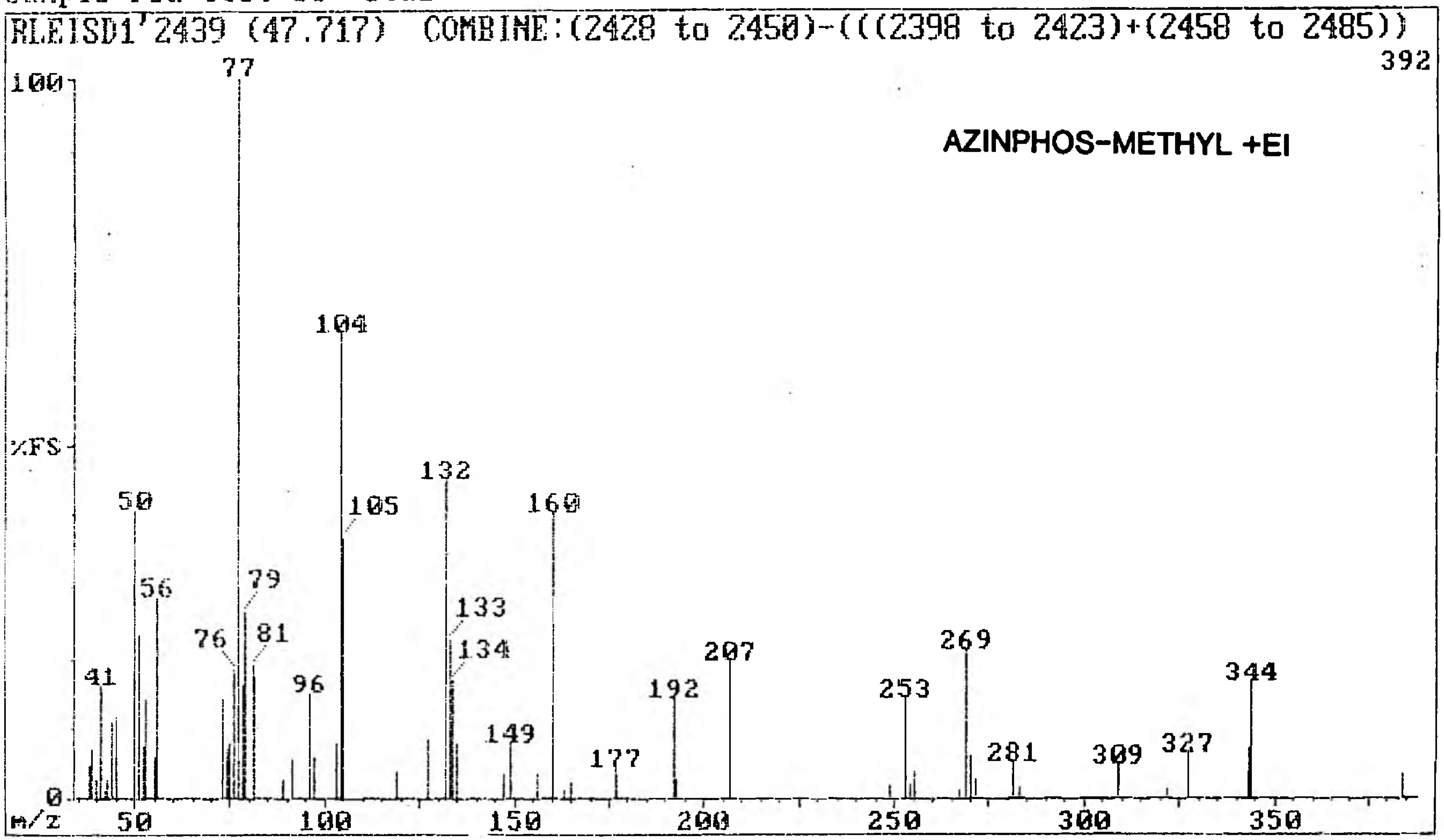
NEWOPSEI'1354 (30.824) COMBINE:(1350 to 1359)-(((1333 to 1341)+(1369 to 1375)

42240

PARATHION-ETHYL +EI

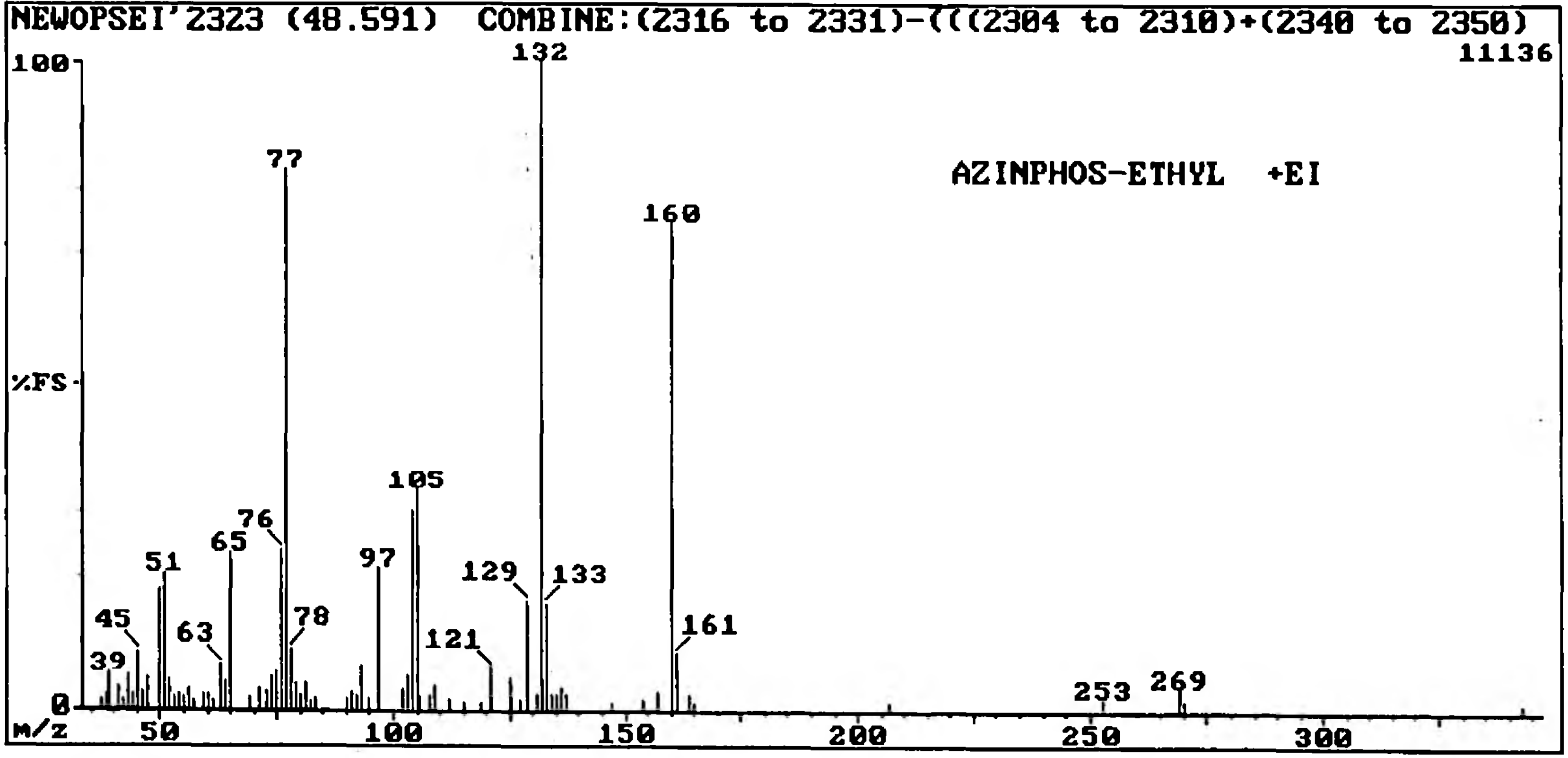
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:red list ei+ std1 Instrument:Trio-1



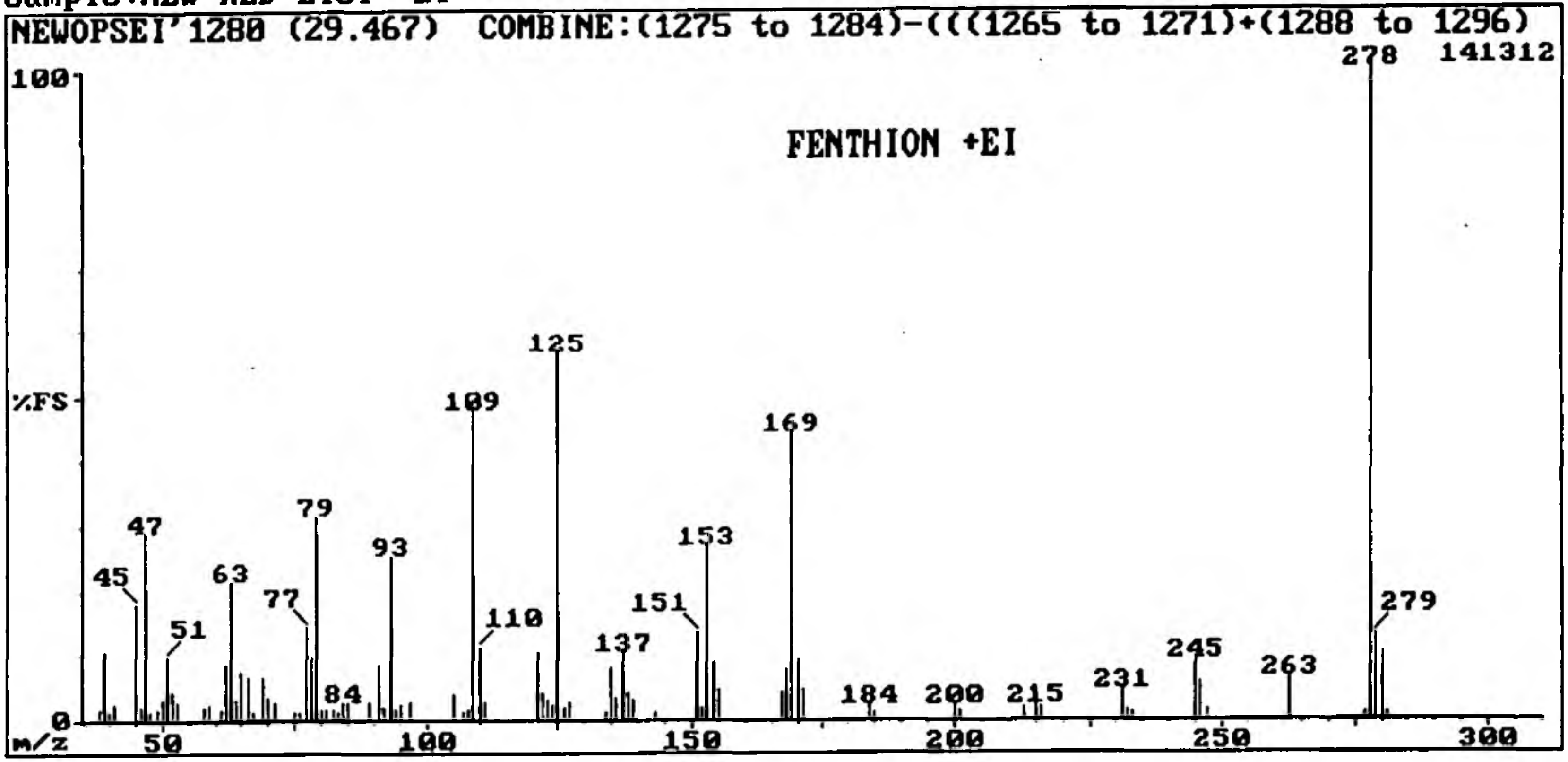
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:NEW RED LIST +EI Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:NEW RED LIST +EI Instrument:Trio-1



APPENDIX

SECTION 2

Table A2-1

Summary of MID Method Parameters for Red List Compounds in Solution (B) Analysed by -CI GCMS

Peak	**Compound**	**Relative reference peak**	**Ions Monitored m/z**	**Retention time (min)**
1	d6-dichlorvos	-	$\underline{131}$, 136	10.53
2	Dichlorvos	3	$\underline{125}$, 134	10.68
3	d14-trifluralin	-	$\underline{319}$, 349	21.06
4	Trifluralin	3	$\underline{305}$, 335	21.32
5	α-hexachlorocylohexane	3	$\underline{71}$, 73	23.06
6	Lindane	3	$\underline{71}$, 73	25.24
7	Aldrin	15	235, $\underline{237}$	27.75
8	β-hexachlorocyclohexane	3	$\underline{71}$, 73	28.96
9	d10-malathion	-	157, $\underline{182}$	30.08
10	Malathion	9	157, $\underline{172}$	30.38
11	Fenitrothion	9	141, $\underline{168}$	30.70
12	PCB-C101	9	$\underline{256}$, 325	31.71
13	α-endosulfan	9	240, $\underline{242}$	32.70
14	Dieldrin	15	235, $\underline{237}$	34.50
15	13C4-dieldrin	-	239, $\underline{241}$	34.52
16	o,p-DDD	15	$\underline{71}$, 246	34.96
17	PCB-C118	9	324, $\underline{326}$	35.10
18	Endrin	15	238, $\underline{272}$	35.56
19	o,p-DDT	15	$\underline{71}$, 246	35.71
20	PCB-C153	9	$\underline{360}$, 362	35.78
21	p,p-DDD	15	$\underline{71}$, 73	37.21
22	PCB-C138	9	$\underline{360}$, 362	37.50
23	β-endosulfan	9	240, $\underline{242}$	37.87
24	p,p-DDT	15	$\underline{71}$, 73	38.07
25	PCB-C180	9	$\underline{394}$, 396	40.95
26	Decachlorobiphenyl	-	464, $\underline{498}$	50.14

Note

In most cases, the ion underlined is the most intense ion in the mass spectrum and therefore it was selected as the quantitation ion. A second ion, which may be more unique than the quantitation ion for some compounds, has been selected as a confirmatory ion.

TABLE A2-2

SUMMARY OF INSTRUMENTAL PRECISION FOR RED LIST COMPOUNDS IN STANDARD SOLUTIONS ANALYSED USING -CI GCMS

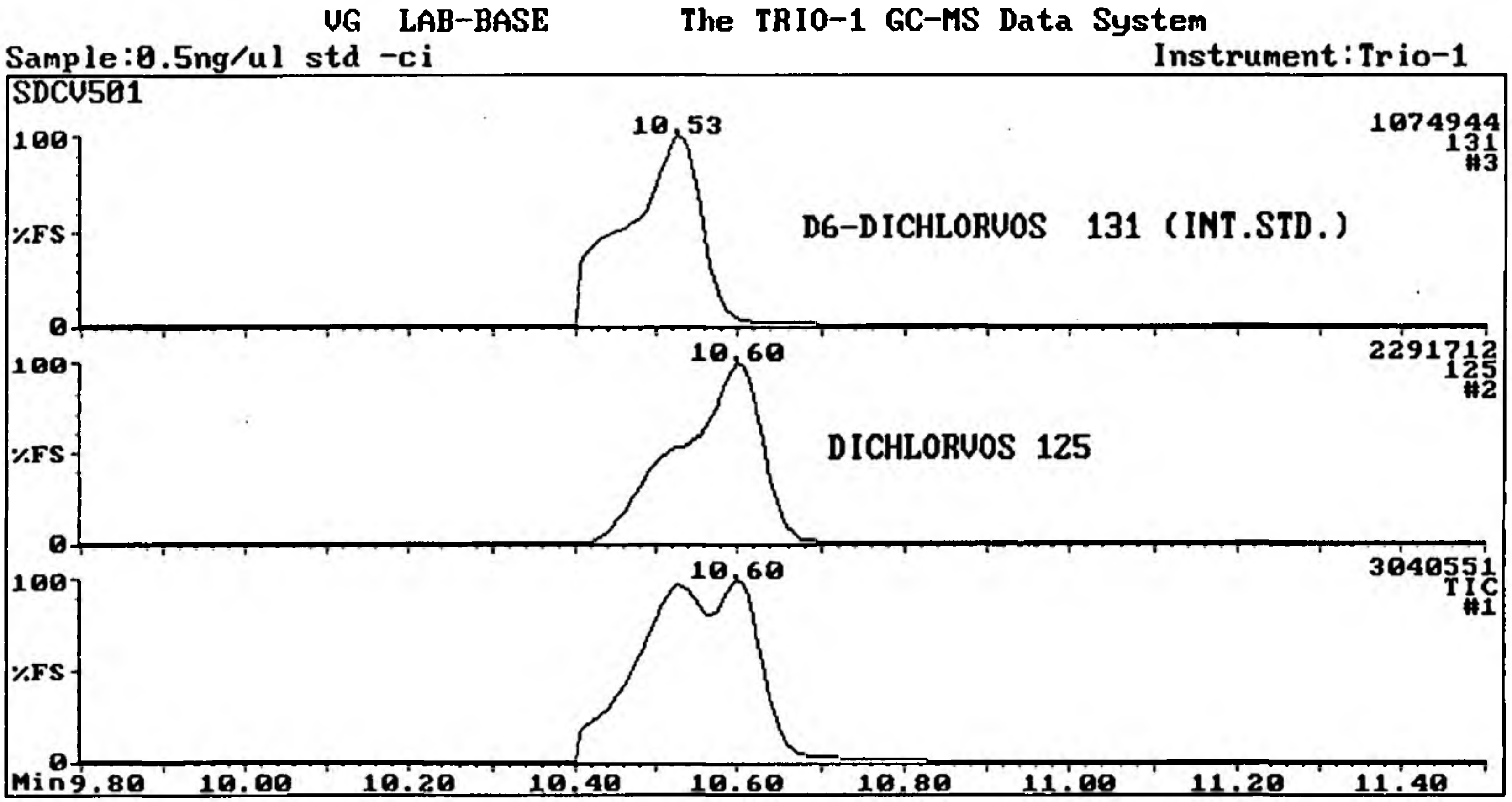
COMPOUND	PEAK AREA RATIO STATISTIC	STANDARD SOLUTION CONCENTRATION (ug/ml)				
		0.02	0.05	0.10	0.50	1.0
DICHLORVOS	MEAN	0.041	0.080	0.149	0.772	1.465
	STANDARD DEVIATION	0.010	0.004	0.004	0.016	0.073
	REL.STD.DEV.(%)	23.3	5.3	2.4	2.1	5.0
TRIFLURALIN	MEAN	0.014	0.040	0.079	0.424	0.825
	STANDARD DEVIATION	0.001	0.001	0.002	0.004	0.013
	REL.STD.DEV.(%)	4.0	1.8	2.7	0.9	1.5
α-HCH	MEAN	0.416	0.875	1.501	7.115	12.90
	STANDARD DEVIATION	0.020	0.093	0.019	0.112	0.524
	REL.STD.DEV.(%)	4.8	10.6	1.3	1.6	4.1
LINDANE	MEAN	0.494	1.015	1.695	7.789	14.20
	STANDARD DEVIATION	0.028	0.058	0.038	0.148	0.628
	REL.STD.DEV.(%)	5.8	5.8	2.3	1.9	4.4
ALDRIN	MEAN	0.136	0.356	0.647	2.975	5.101
	STANDARD DEVIATION	0.007	0.025	0.014	0.150	0.099
	REL.STD.DEV.(%)	5.2	7.0	2.2	5.1	2.0
β-HCH	MEAN	0.182	0.342	0.577	2.627	4.805
	STANDARD DEVIATION	0.014	0.016	0.019	0.034	0.165
	REL.STD.DEV.(%)	7.9	4.6	3.3	1.3	3.4
MALATHION	MEAN	0.024	0.061	0.120	0.632	1.305
	STANDARD DEVIATION	0.001	0.002	0.002	0.009	0.040
	REL.STD.DEV.(%)	4.2	3.5	1.9	1.5	3.0
FENITROTHION	MEAN	0.054	0.156	0.264	1.199	2.133
	STANDARD DEVIATION	0.009	0.002	0.021	0.043	0.047
	REL.STD.DEV.(%)	15.9	1.4	7.9	3.6	2.2
PCB-C101	MEAN	0.001	0.002	0.004	0.020	0.033
	STANDARD DEVIATION	0.001	0	0.001	0.001	0
	REL.STD.DEV.(%)	86.6	0	13.3	2.8	0
α-ENDOSULPHAN	MEAN	0.109	0.240	0.386	1.659	2.752
	STANDARD DEVIATION	0.003	0.011	0.038	0.093	0.045
	REL.STD.DEV.(%)	2.3	4.4	9.9	5.6	0
o,p-DDD	MEAN	0.139	0.223	0.365	1.668	3.006
	STANDARD DEVIATION	0.016	0.016	0.008	0.028	0.109
	REL.STD.DEV.(%)	11.2	7.0	2.2	1.7	3.7

(Table A2-2 continued)

COMPOUND	PEAK AREA RATIO	STANDARD SOLUTION CONCENTRATION (ug/ml)				
	STATISTIC	0.02	0.05	0.10	0.50	1.0
PCB-C118	MEAN	0.003	0.010	0.020	0.119	0.234
	STANDARD DEVIATION	0	0.001	0.001	0.006	0.011
	REL.STD.DEV.(%)	0	7.4	5.7	5.1	4.7
ENDRIN	MEAN	0.017	0.025	0.043	0.203	0.404
	STANDARD DEVIATION	0.005	0.001	0.002	0.016	0.014
	REL.STD.DEV.(%)	27.0	2.9	3.6	7.9	3.5
o,p-DDT	MEAN	0.113	0.179	0.285	1.384	2.374
	STANDARD DEVIATION	0.020	0	0.017	0.066	0.072
	REL.STD.DEV.(%)	24.7	0	5.8	4.8	3.0
PCB-C153	MEAN	0.002	0.007	0.015	0.084	0.163
	STANDARD DEVIATION	0.001	0	0.001	0.005	0.013
	REL.STD.DEV.(%)	34.6	0	6.7	5.0	7.8
p,p-DDD	MEAN	0.284	0.446	0.756	3.425	6.378
	STANDARD DEVIATION	0.037	0.022	0.040	0.074	0.350
	REL.STD.DEV.(%)	13.0	4.9	5.3	2.2	5.5
PCB-C138	MEAN	0.002	0.008	0.017	0.092	0.175
	STANDARD DEVIATION	0.001	0.001	0.002	0.006	0.013
	REL.STD.DEV.(%)	24.7	9.4	12.0	6.6	7.8
β-ENDOSULPHAN	MEAN	0.163	0.305	0.482	1.862	3.200
	STANDARD DEVIATION	0.008	0.016	0.052	0.088	0.025
	REL.STD.DEV.(%)	4.6	5.3	10.8	4.7	0.8
p,p-DDT	MEAN	0.408	0.885	1.520	7.55	15.38
	STANDARD DEVIATION	0.022	0.058	0.046	0.678	0.898
	REL.STD.DEV.(%)	5.4	6.6	3.1	9.0	5.8
PCB-C180	MEAN	0.127	0.461	1.016	5.164	10.14
	STANDARD DEVIATION	0.055	0.010	0.011	0.188	0.689
	REL.STD.DEV.(%)	43.2	2.2	1.1	3.6	6.8
DIELDRIN	MEAN	ND	0.065	0.117	0.514	0.892
	STANDARD DEVIATION	ND	0	0.002	0.003	0.008
	REL.STD.DEV.(%)	ND	0	1.48	0.58	0.85

Notes :-

Statistical data in this table was based on triplicate analyses of each compound at each concentration. For each compound, the peak area ratio was calculated by dividing the area of the peak for that compound by the area of the peak for the most appropriate internal standard.
ND = Not Detected.



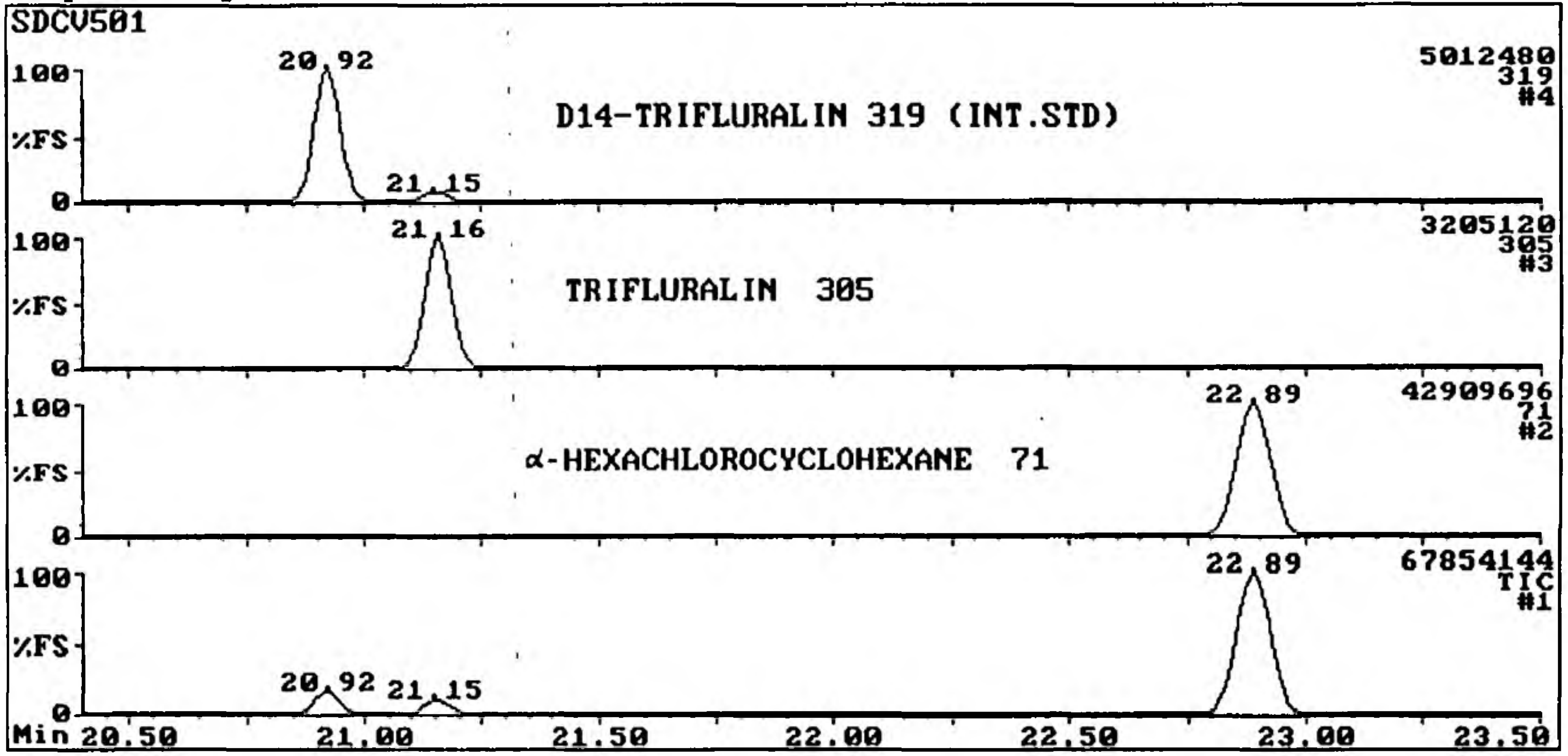
VG LAB-BASE The TRIO-1 GC-MS Data System

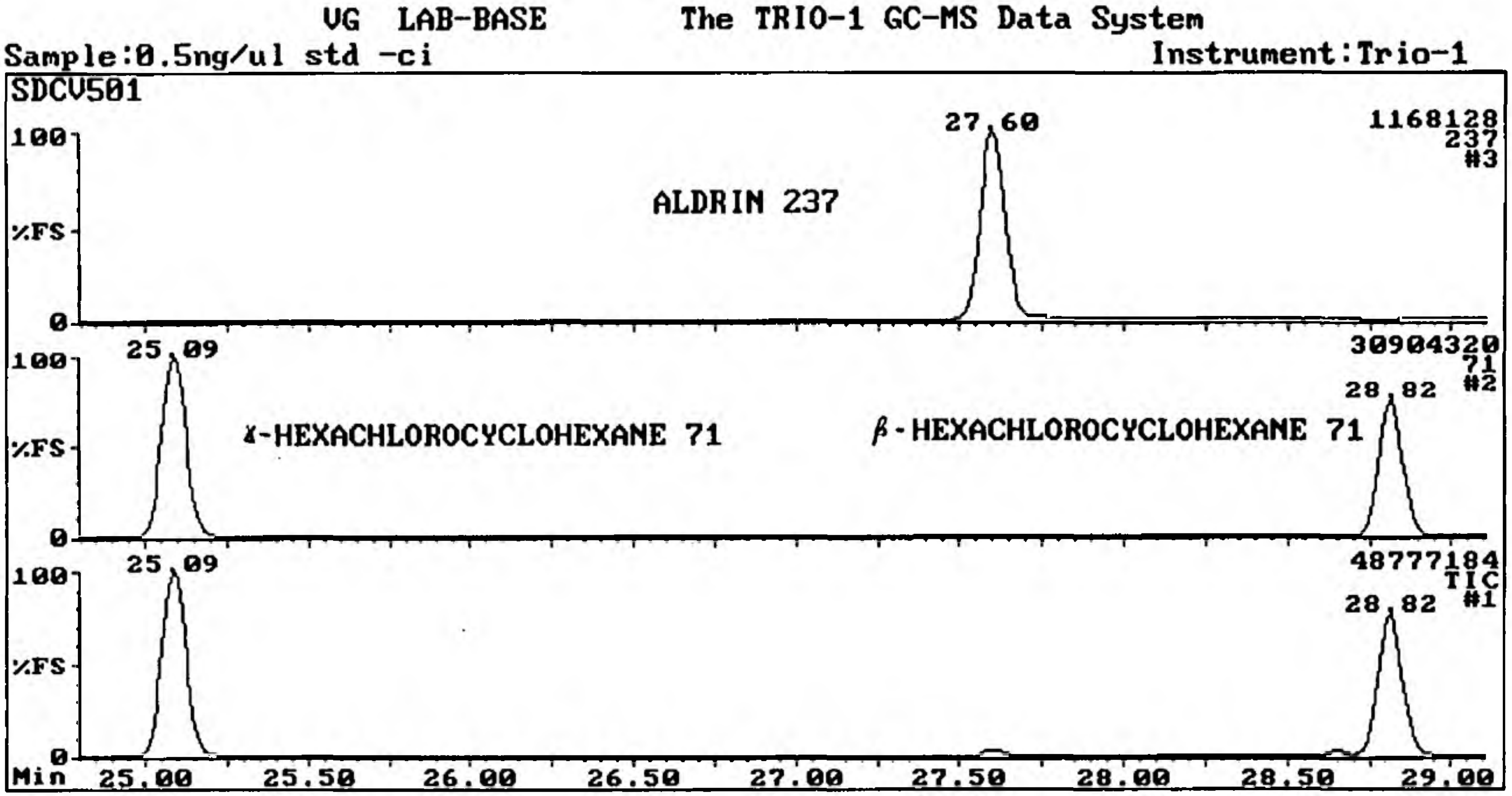
Sample:0.5ng/ul std -ci

Instrument:Trio-1

VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:0.5ng/ul std -ci Instrument:Trio-1





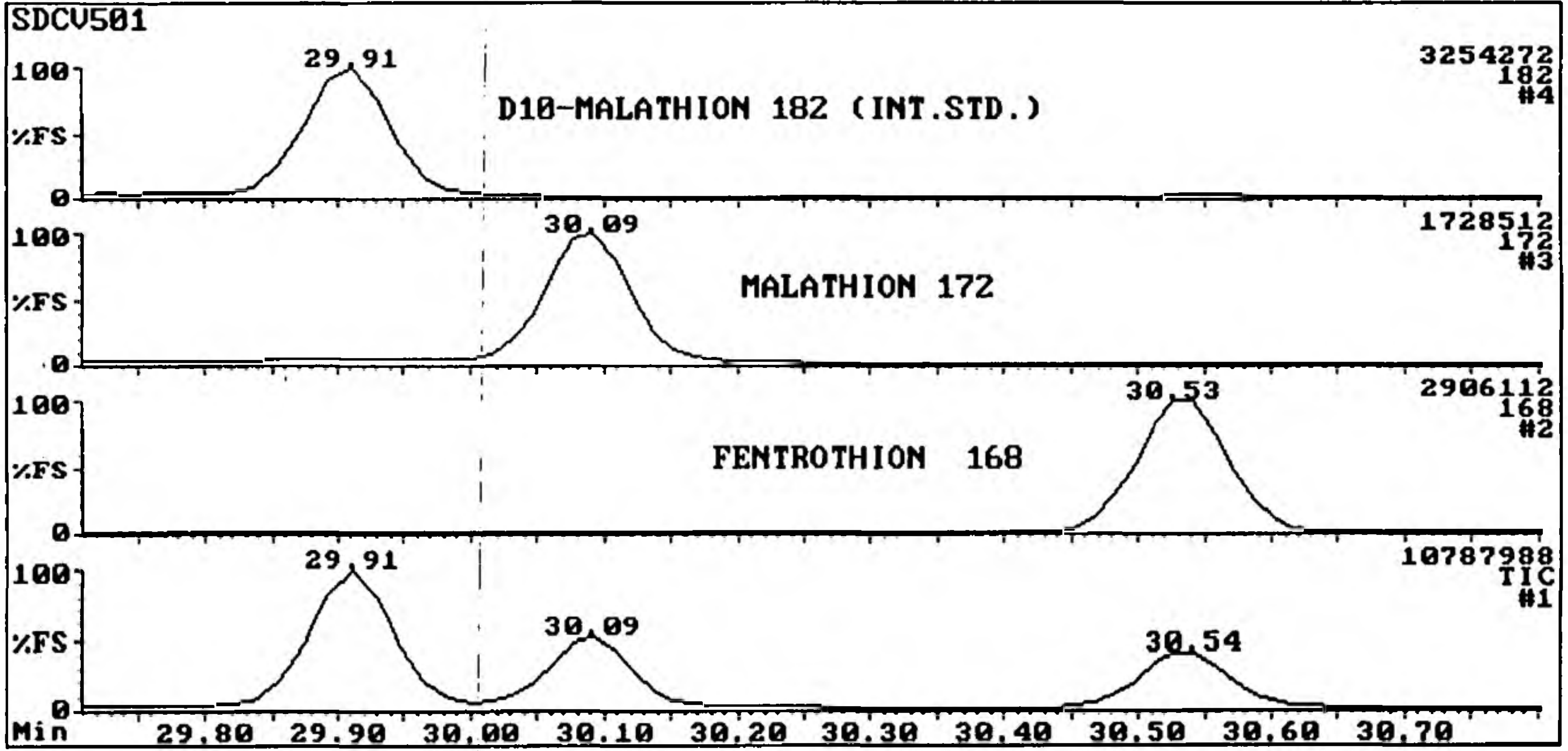
VG LAB-BASE The TRIO-1 GC-MS Data System

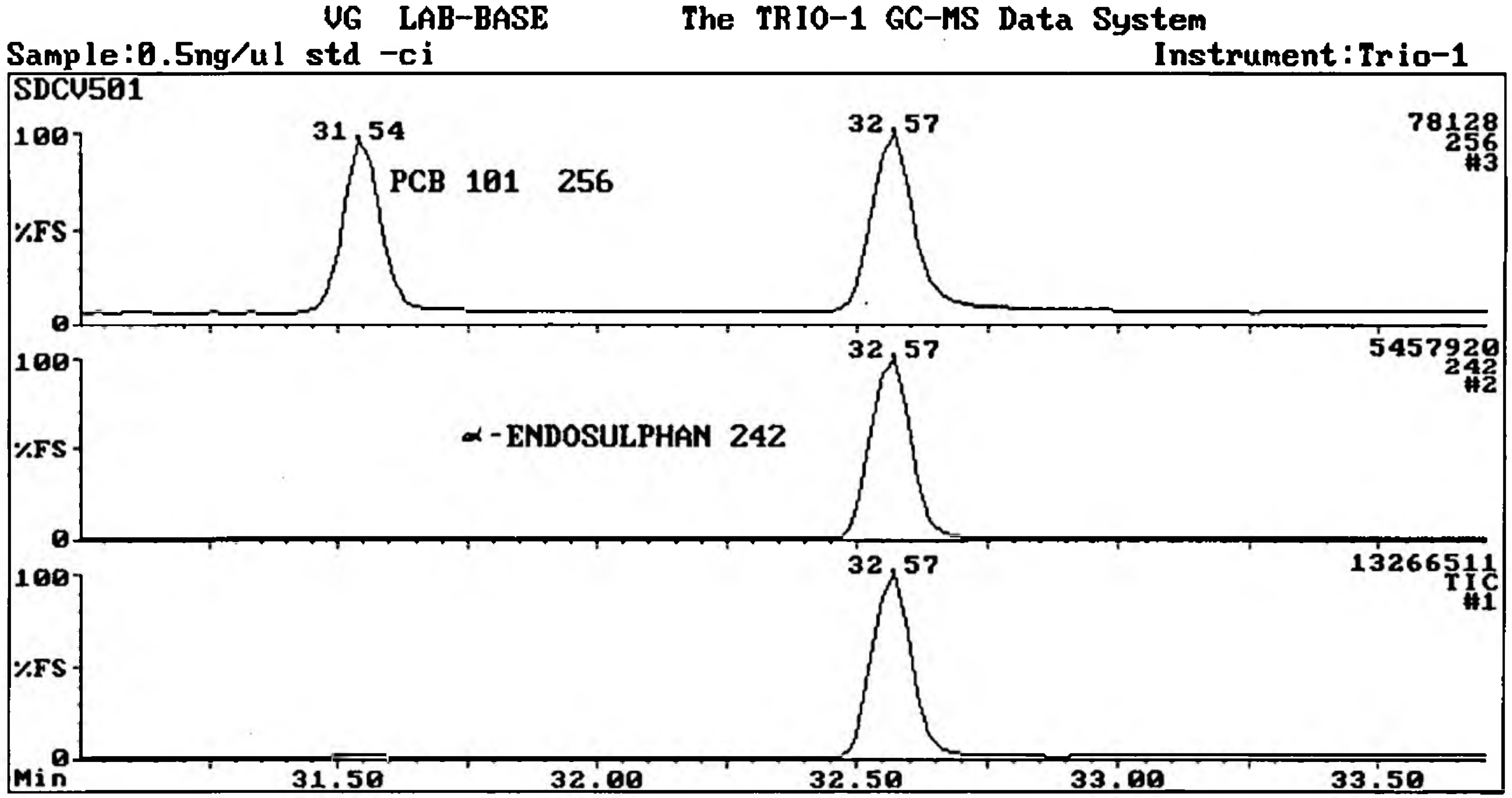
Sample:0.5ng/ul std -ci

Instrument:Trio-1

VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:0.5ng/ul std -ci Instrument:Trio-1





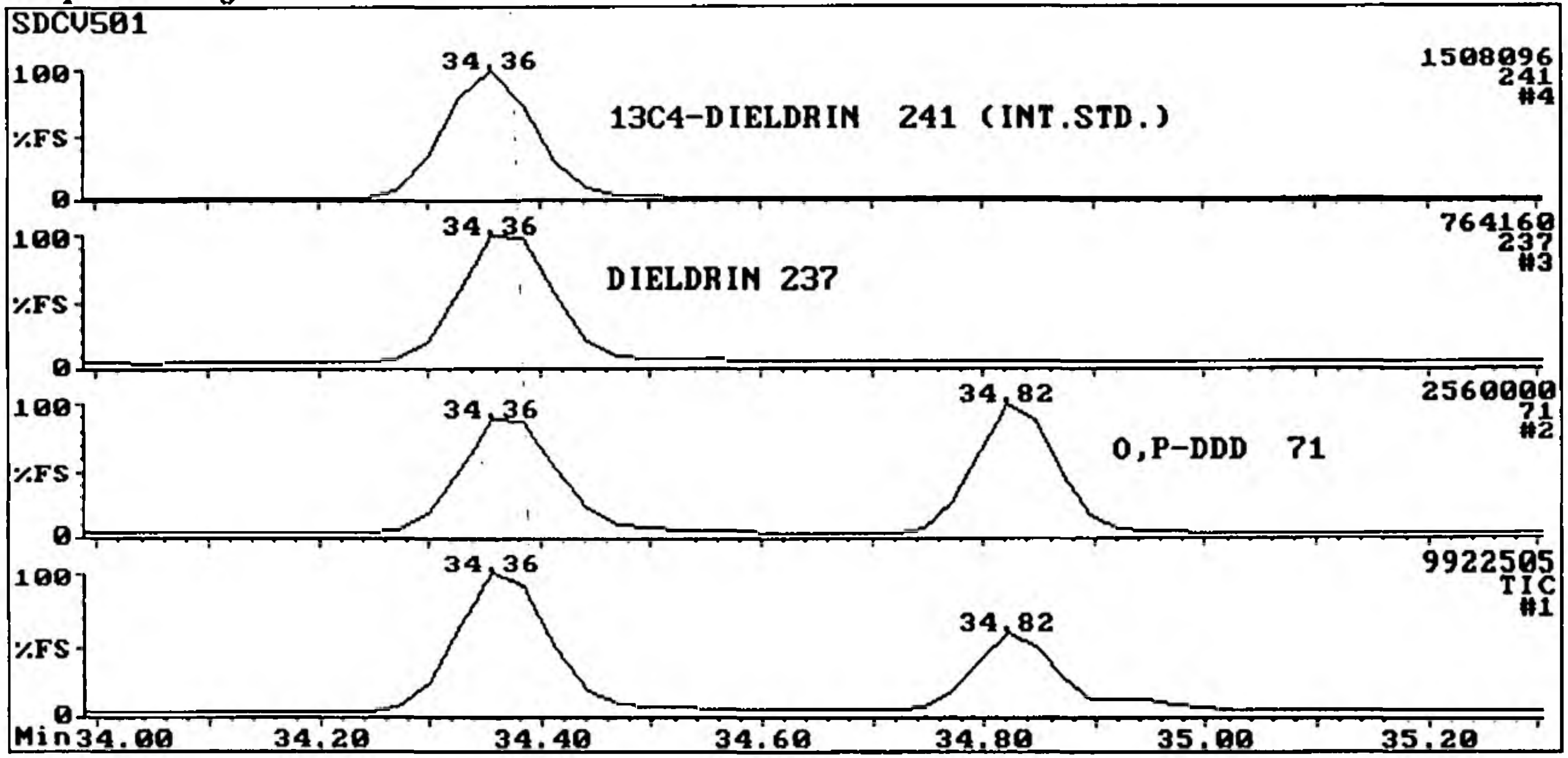
VG LAB-BASE The TRIO-1 GC-MS Data System

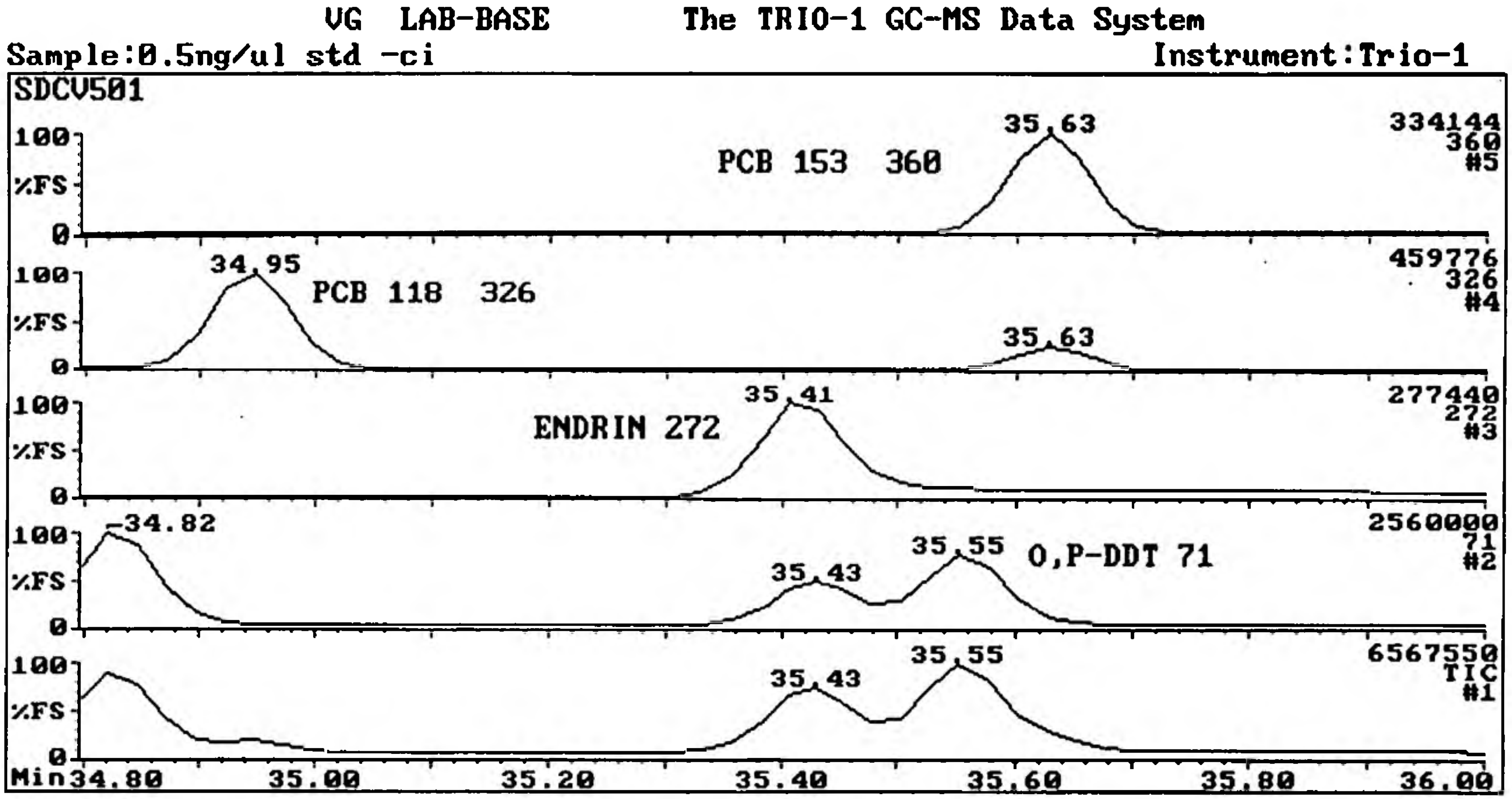
Sample:0.5ng/ul std -ci

Instrument:Trio-1

VG LAB-BASE The TRIO-1 GC-MS Data System

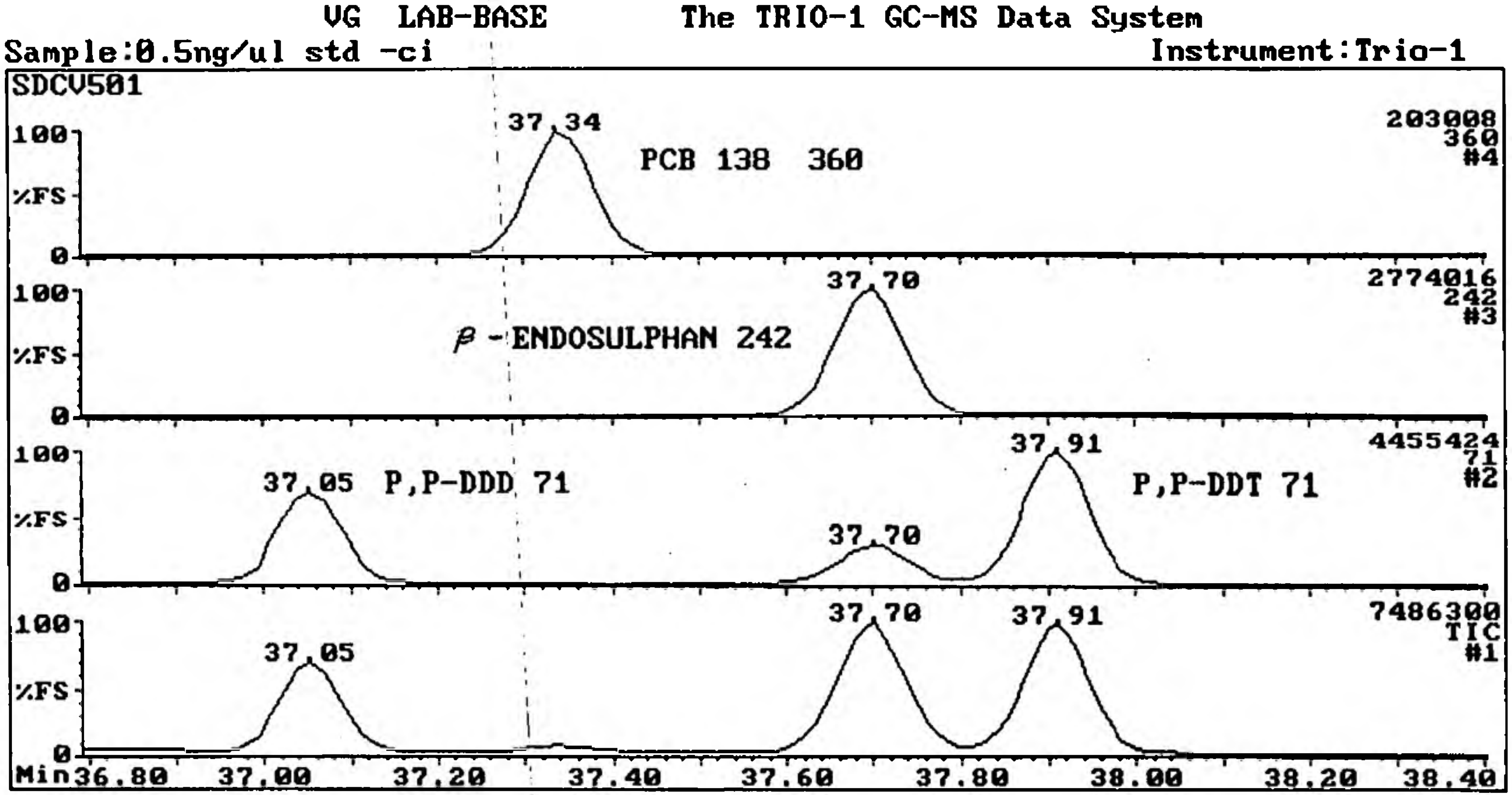
Sample:0.5ng/ul std -ci Instrument:Trio-1





VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:0.5ng/ul std -ci Instrument:Trio-1

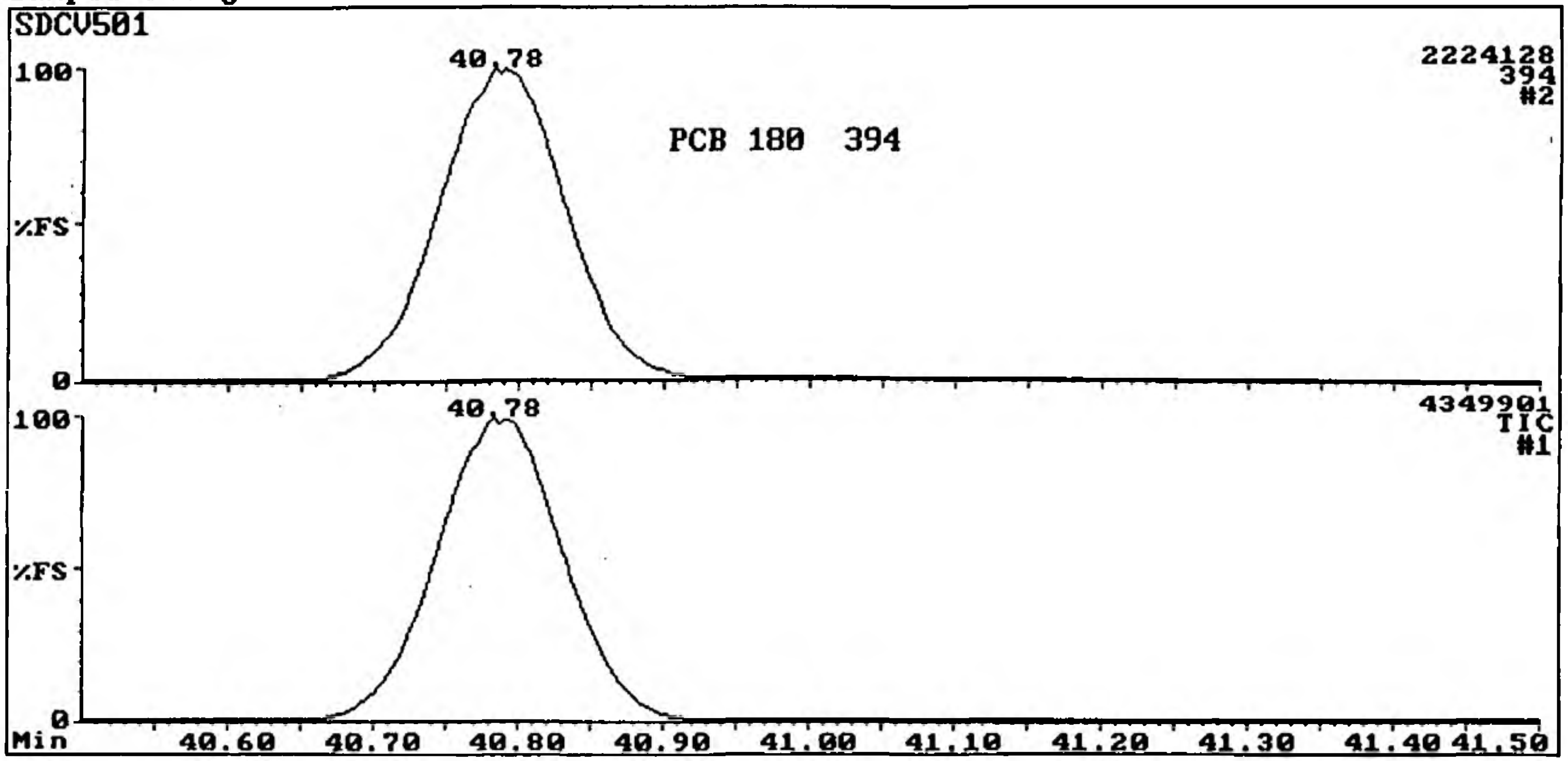


VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:0.5ng/ul std -ci Instrument:Trio-1

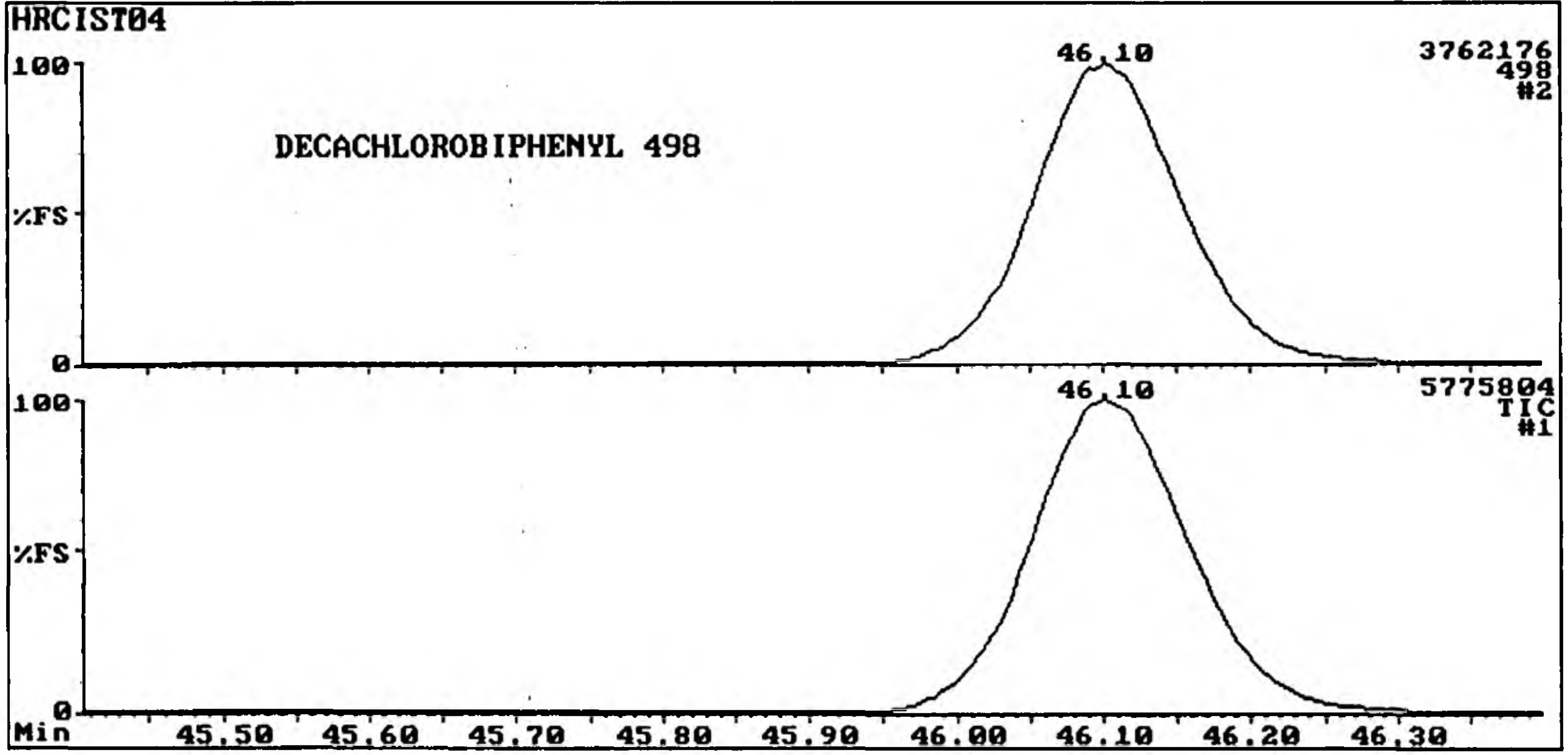
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:0.5ng/ul std -ci Instrument:Trio-1



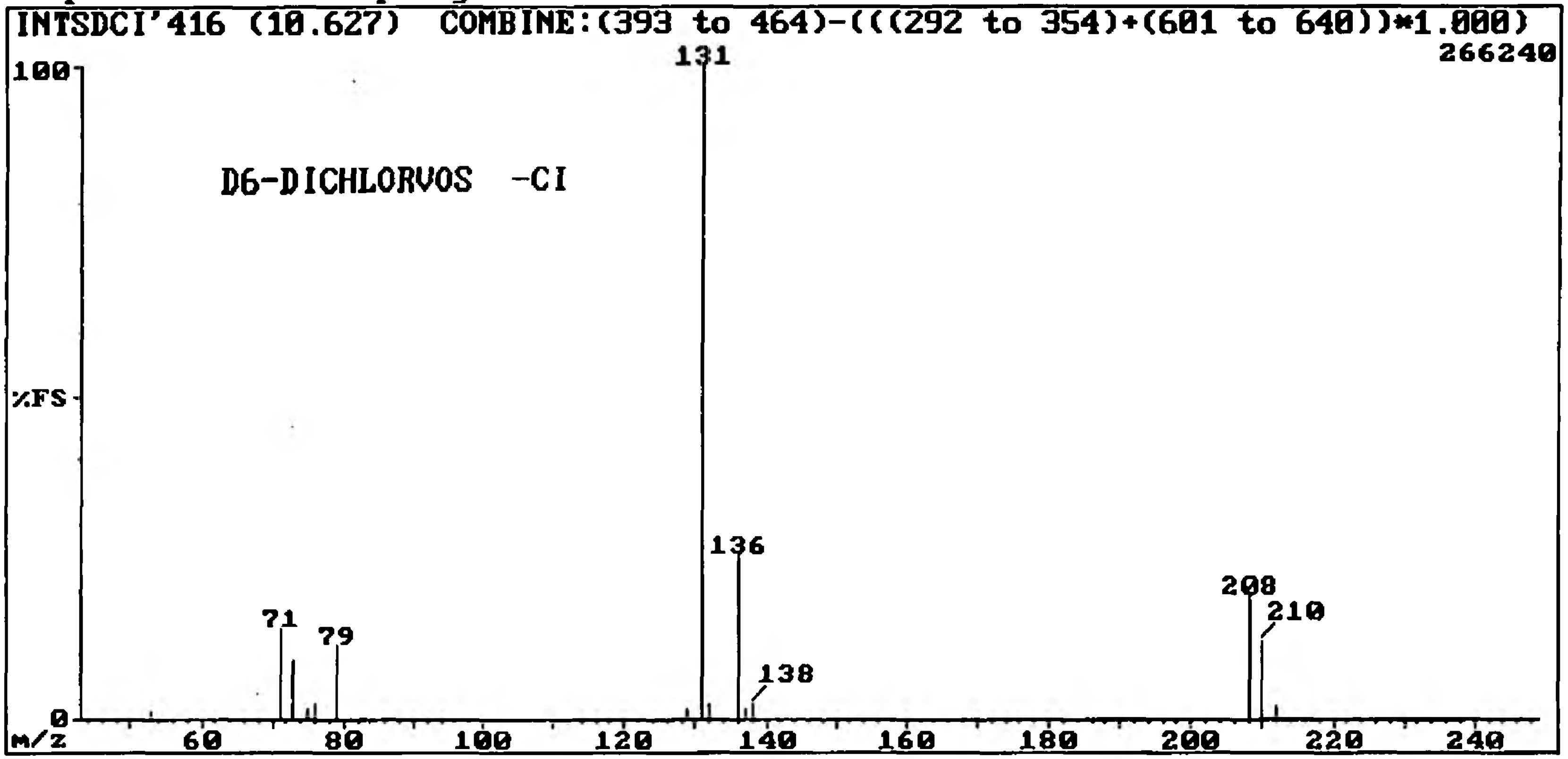
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:ci std 0.5ng/ul Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

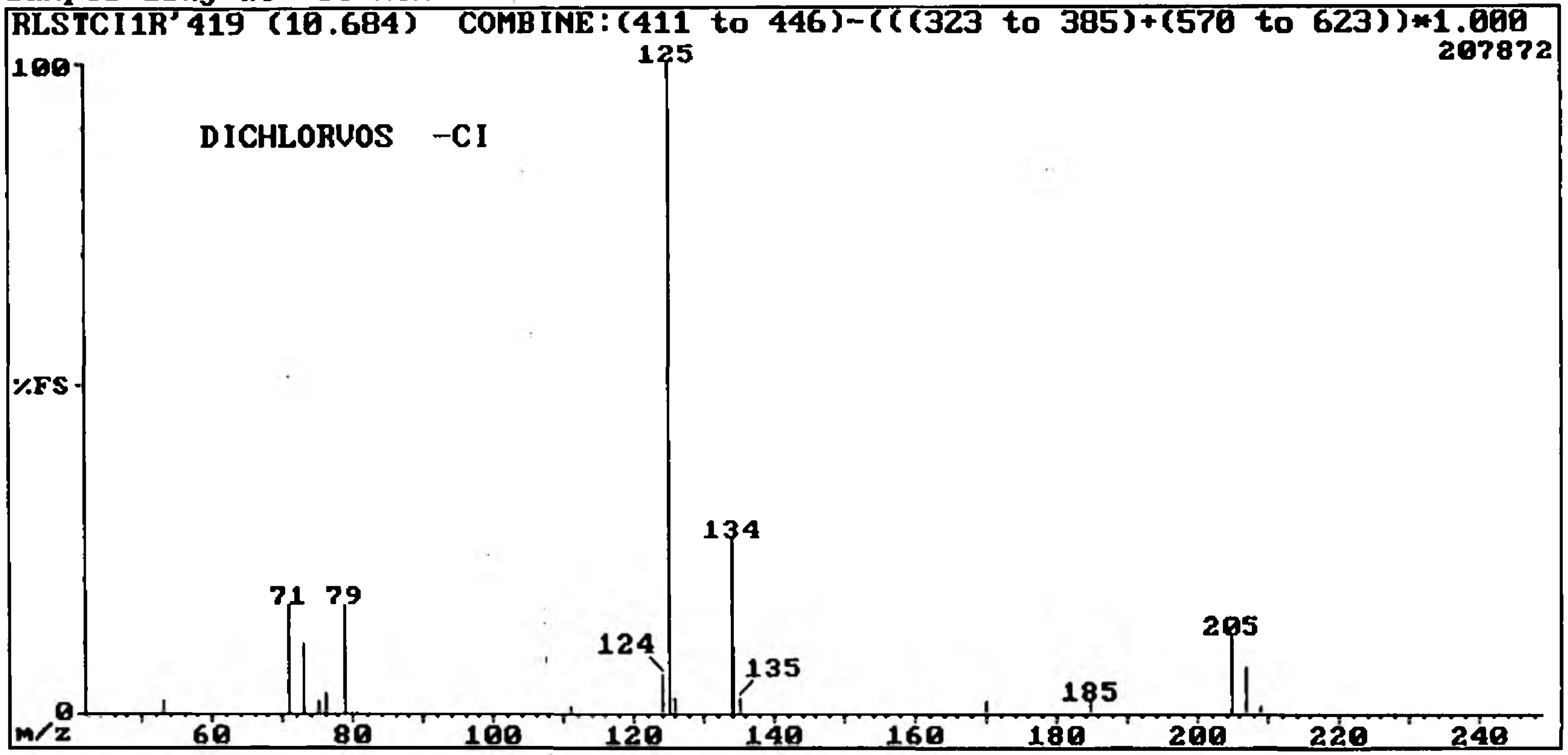
Sample:decachlorobiphenyl d6 dichlorvos -ci Instrument:Trio-1



INTSDCI'416 (10.627) COMBINE:(393 to 464)-(((292 to 354)+(601 to 640))*1.000)

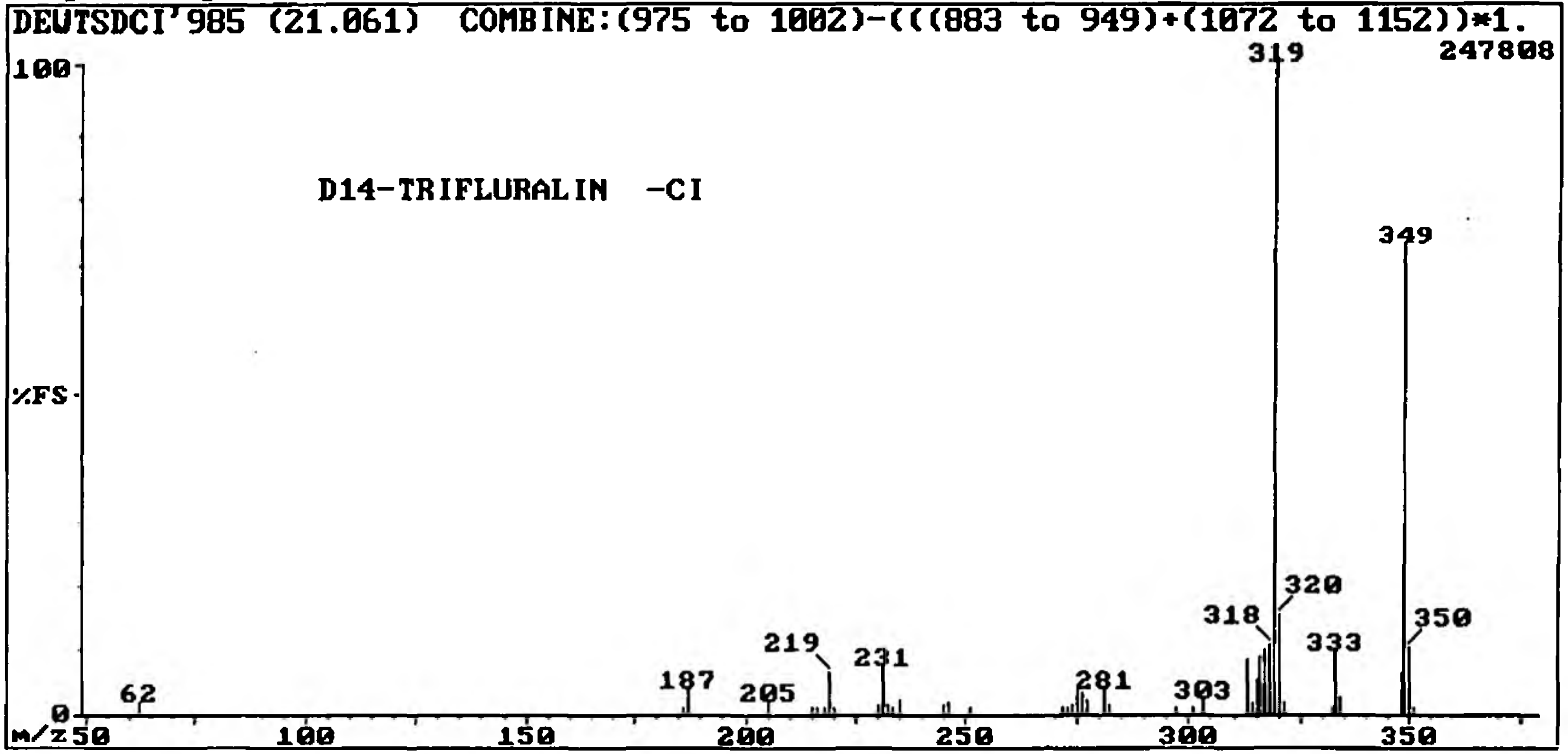
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul -ci mix Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

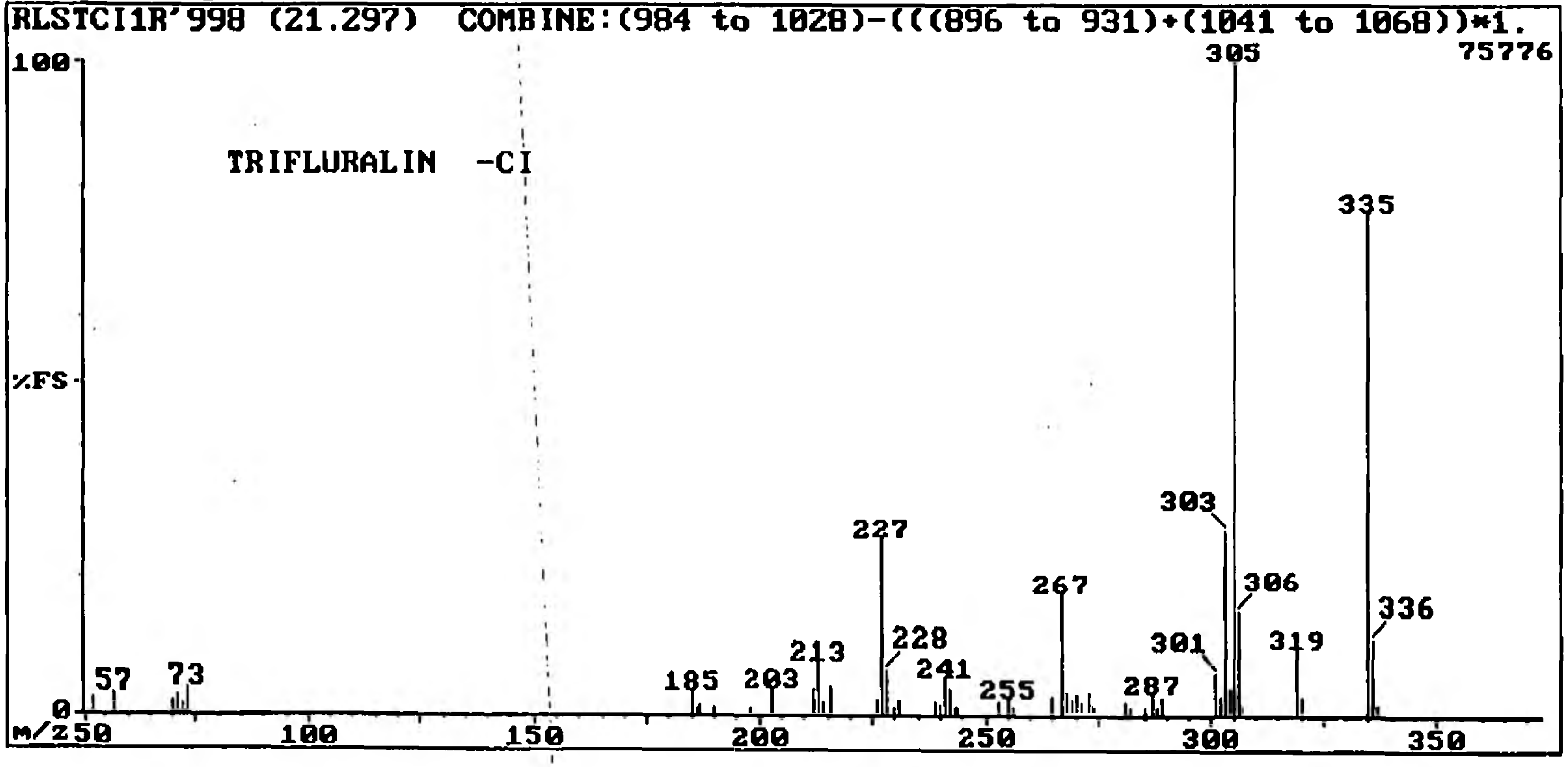
Sample:10ng/ul deut -ci mix Instrument:Trio-1



DEUTSDCI'985 (21.061) COMBINE:(975 to 1002)-(((883 to 949)+(1072 to 1152))*1.

VG LAB-BASE The TRIO-1 GC-MS Data System

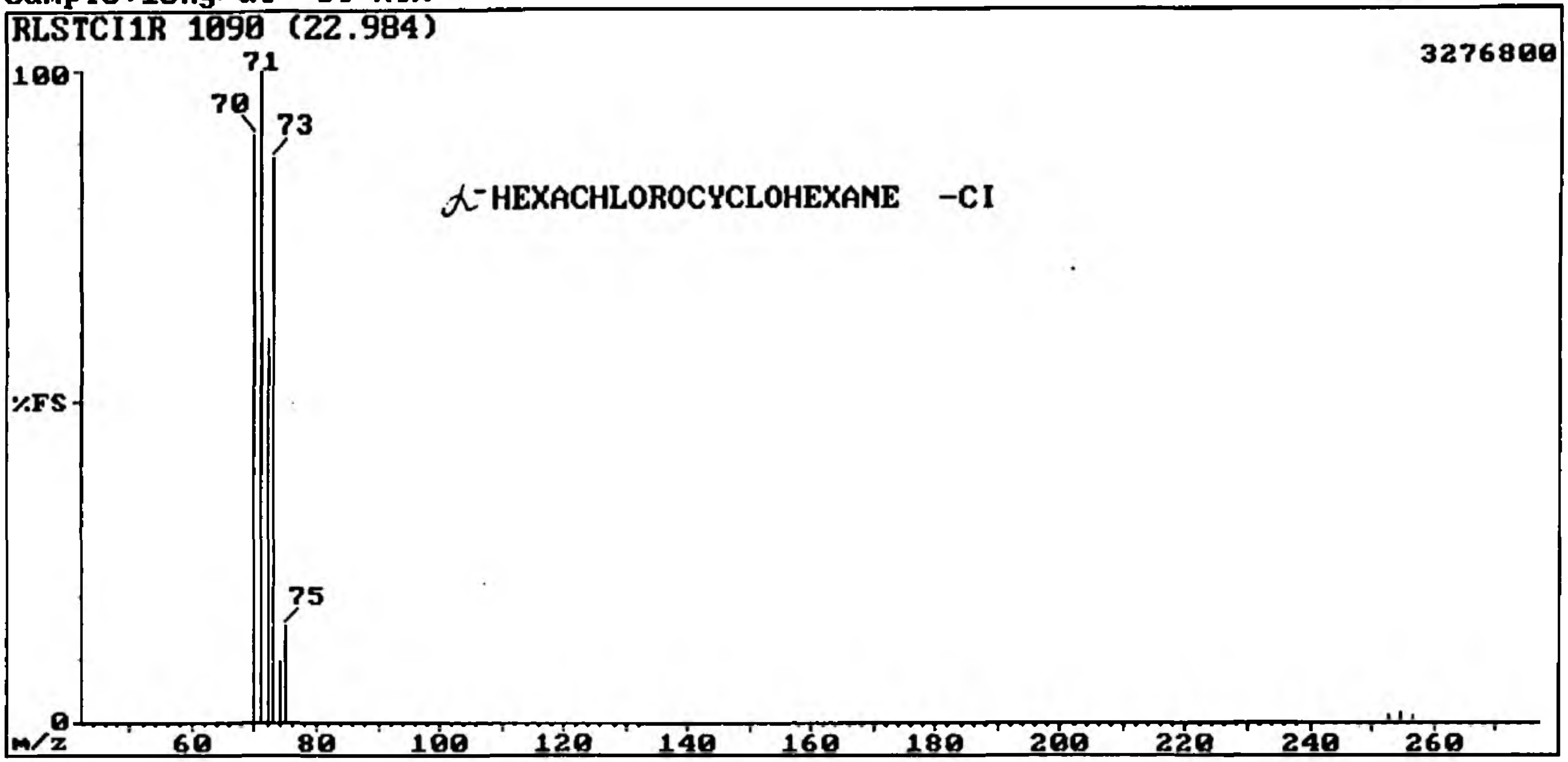
Sample:10ng/ul -ci mix Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

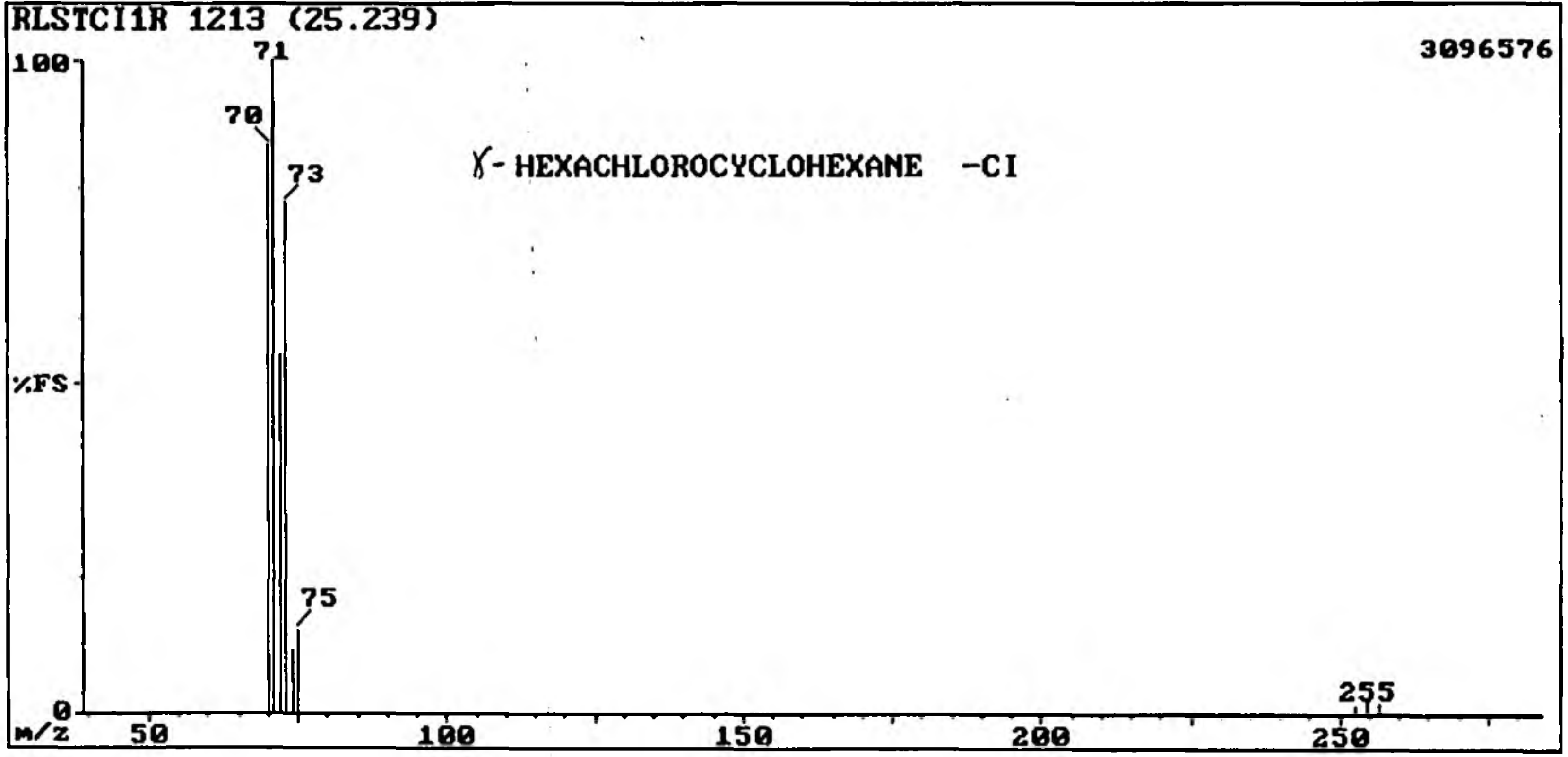
Sample:10ng/ul -ci mix

Instrument:Trio-1



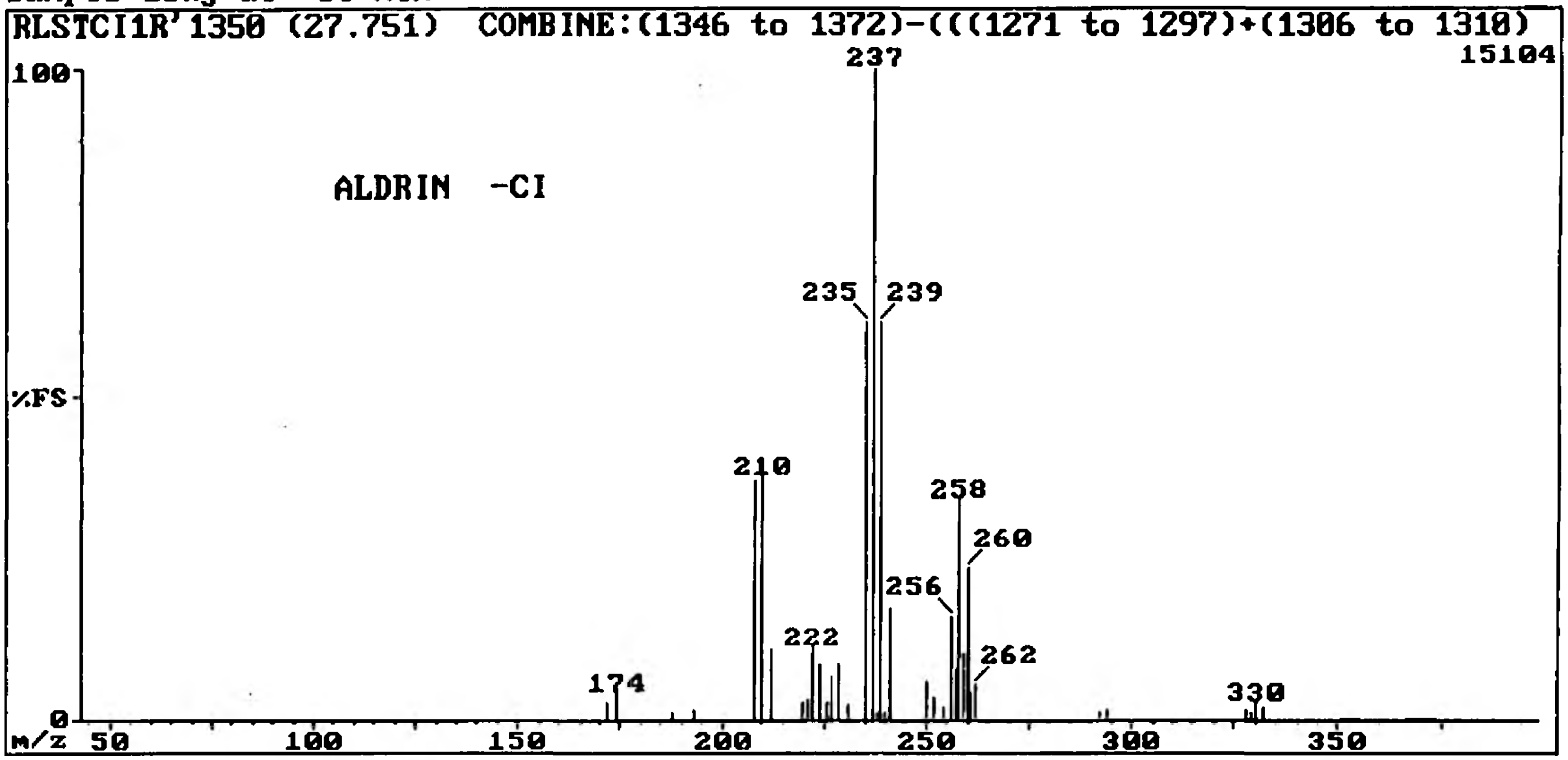
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul -ci mix Instrument:Trio-1



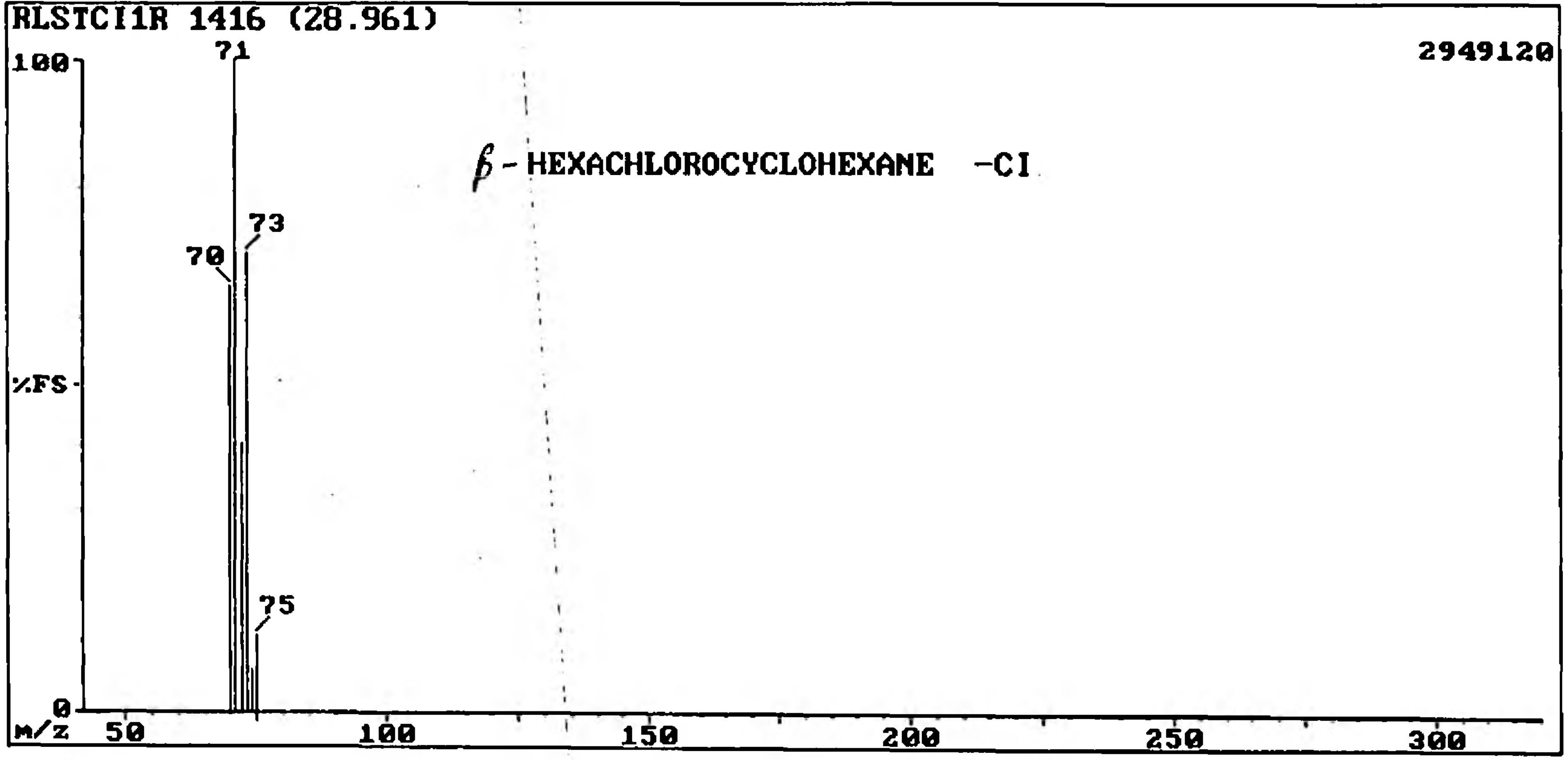
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul -ci mix Instrument:Trio-1



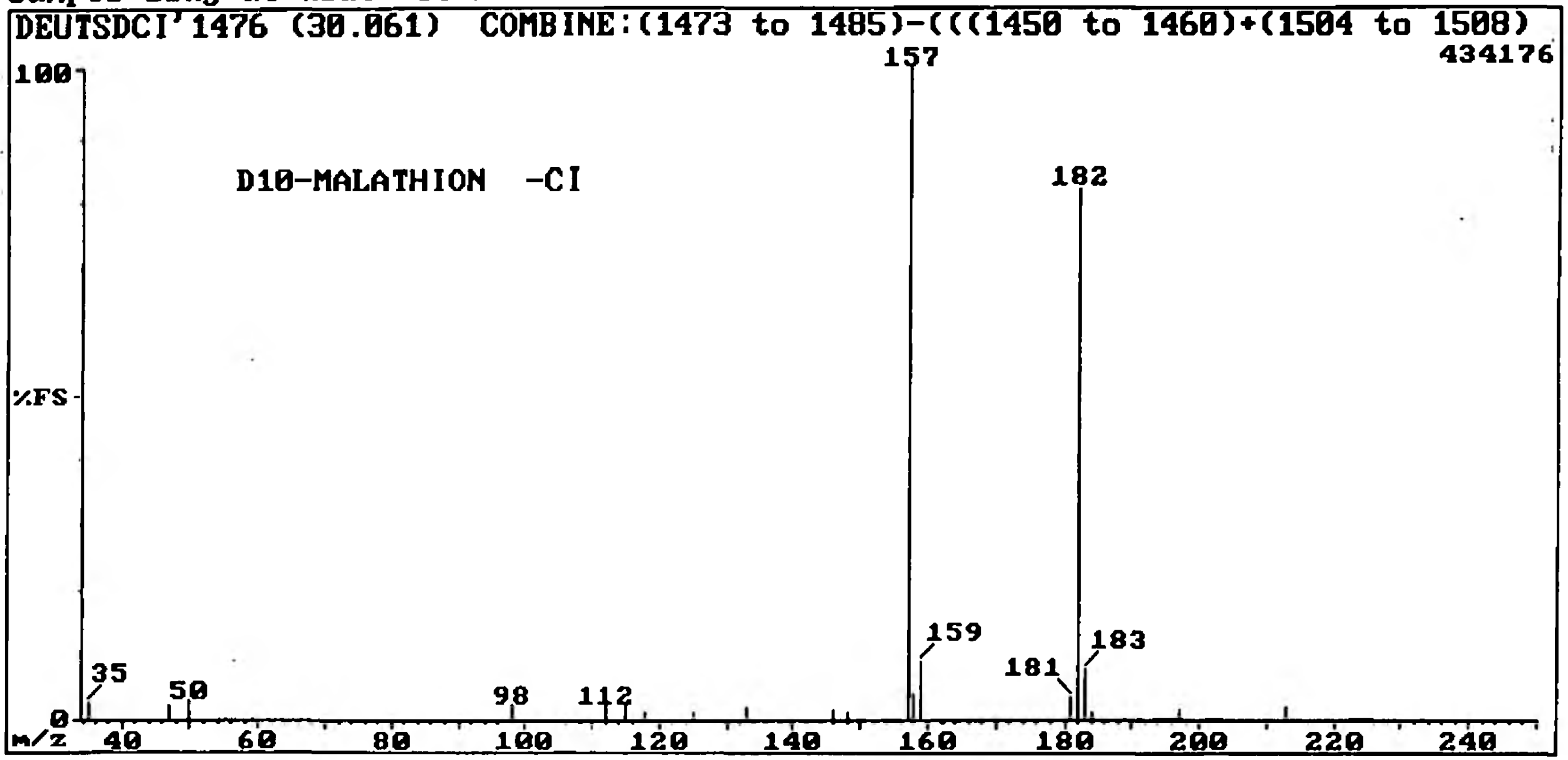
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul -ci mix Instrument:Trio-1



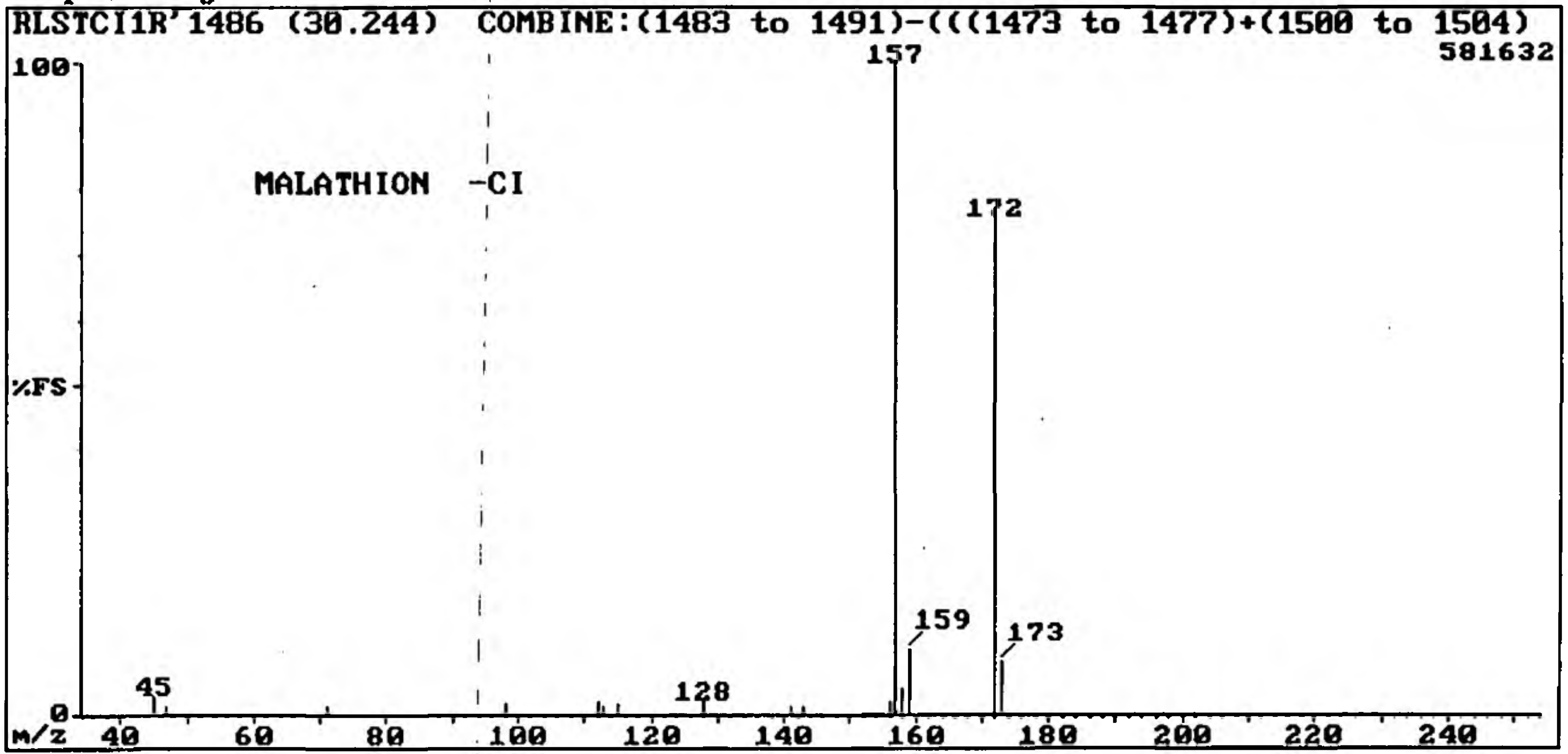
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul deut -ci mix Instrument:Trio-1



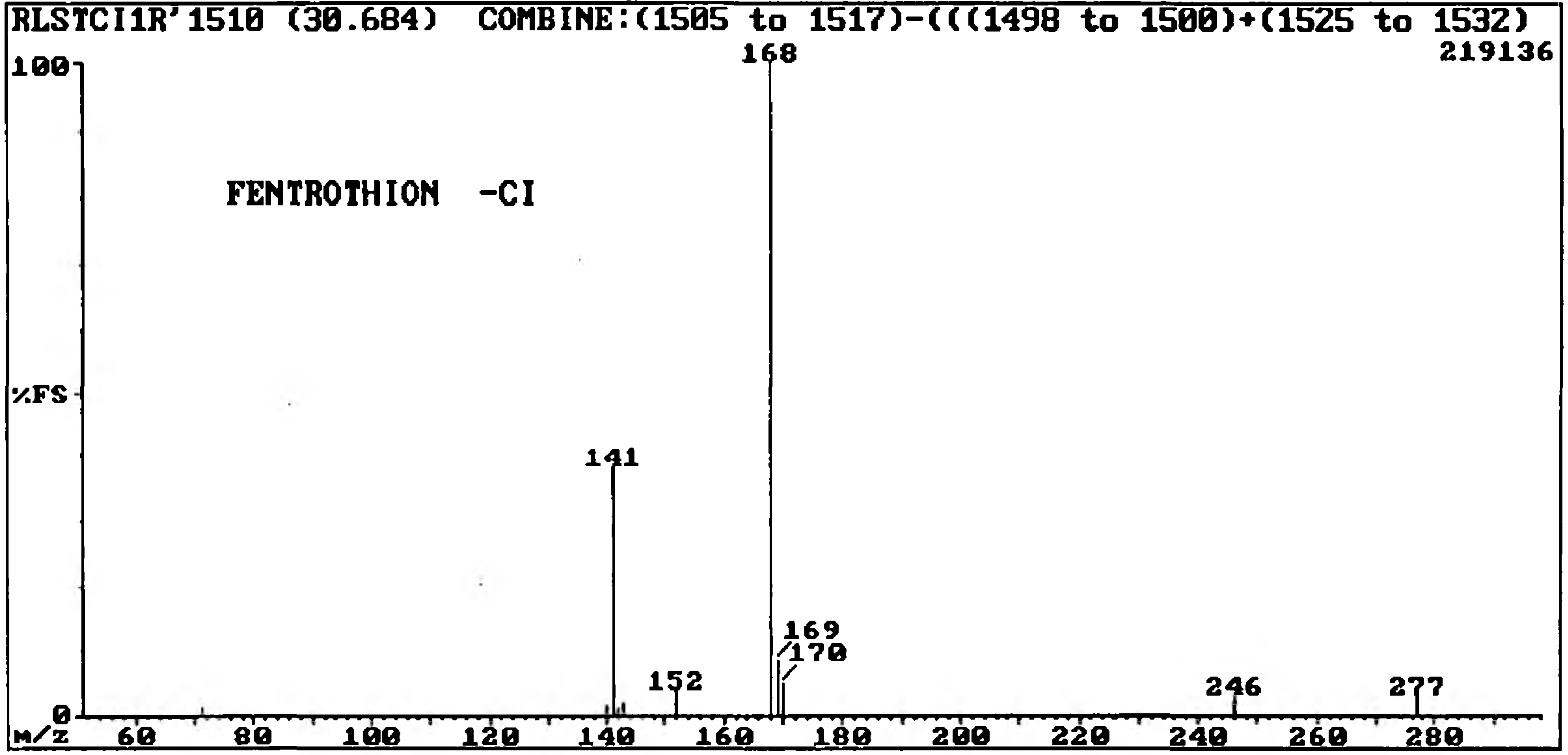
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul -ci mix Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

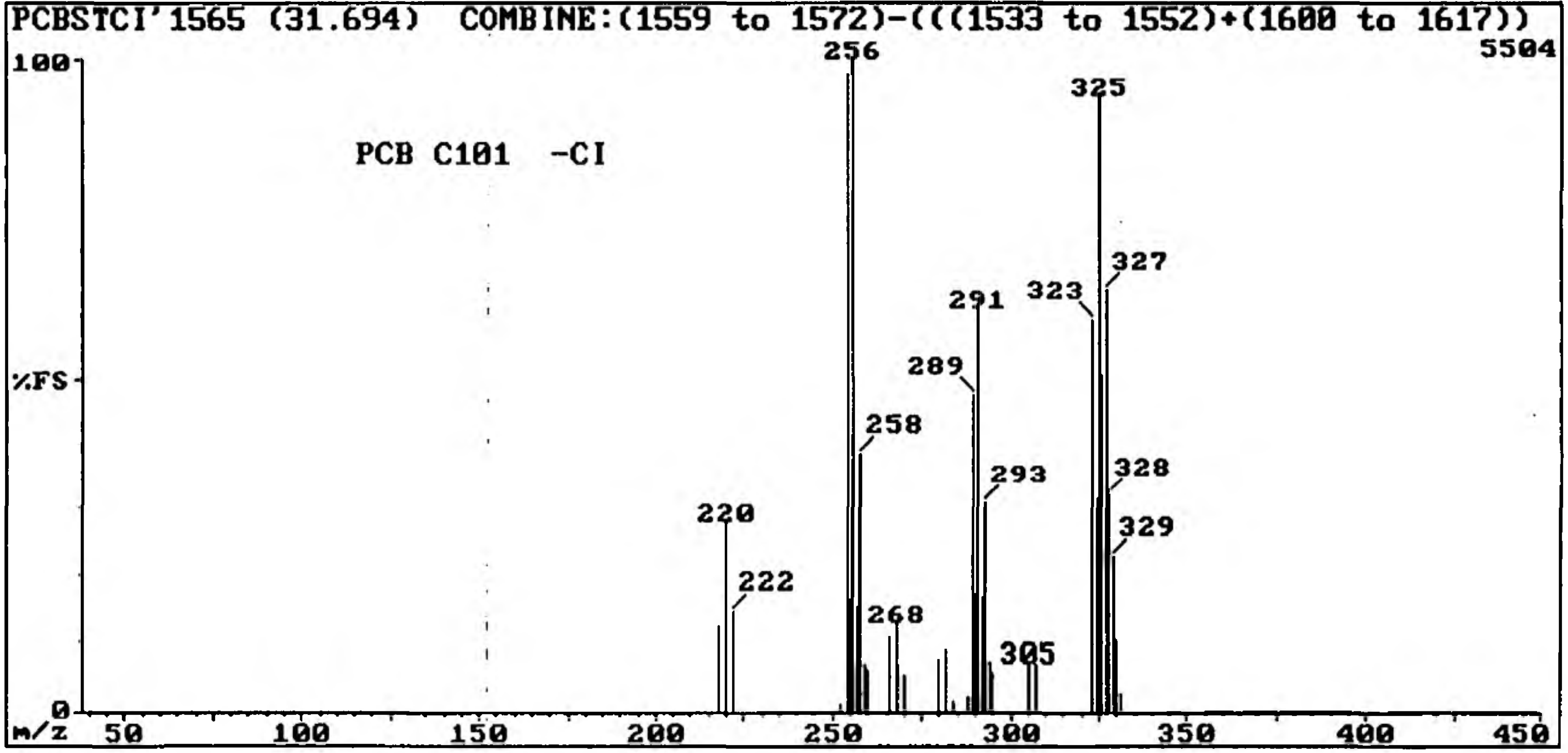
Sample:10ng/ul -ci mix Instrument:Trio-1



RLSTCI1R'1510 (30.684) COMBINE:(1505 to 1517)-(((1498 to 1500)+(1525 to 1532)

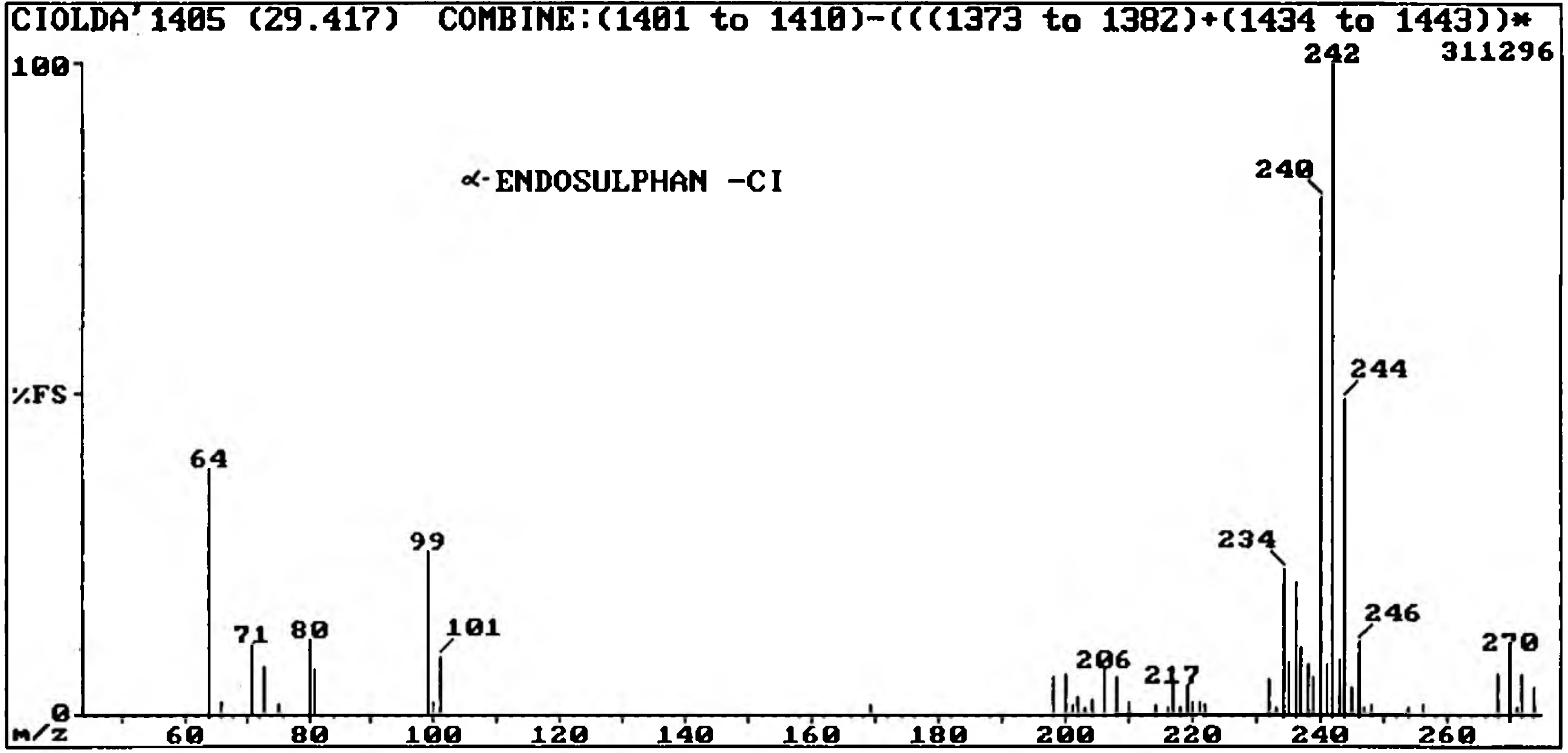
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul deut -ci mix Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

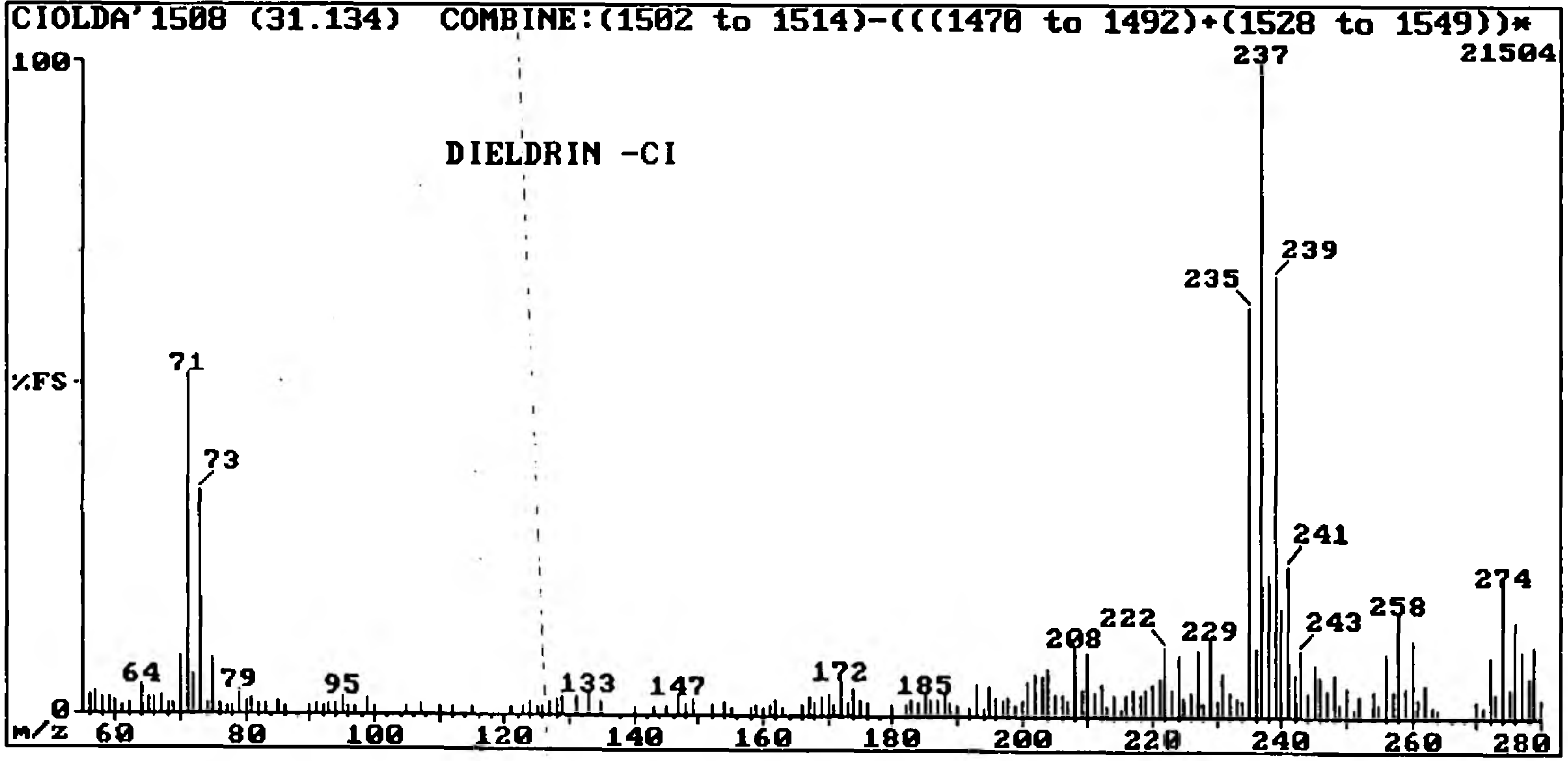
Sample:-CI NEW RED LIST Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

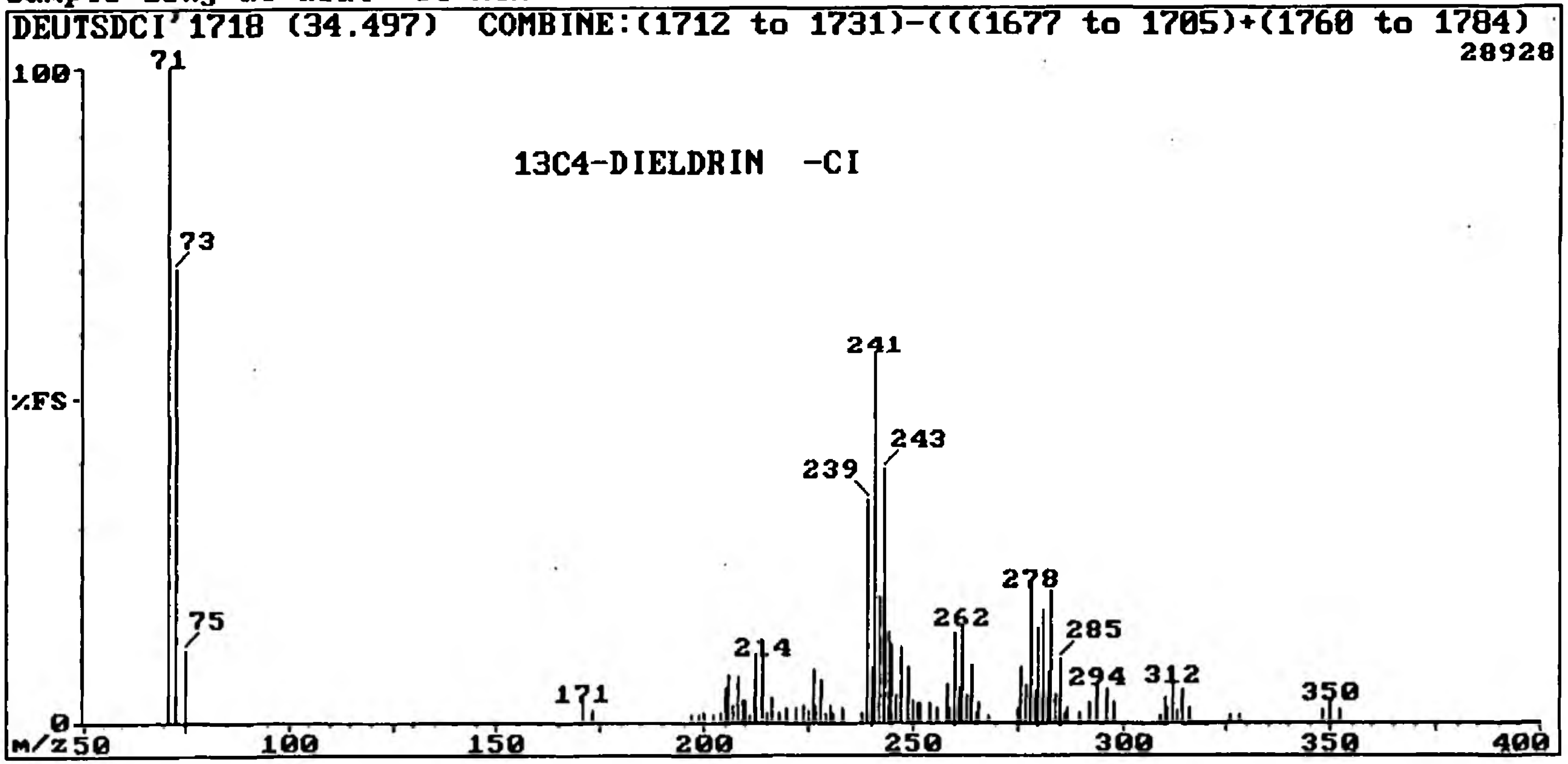
Sample:-CI NEW RED LIST

Instrument:Trio-1



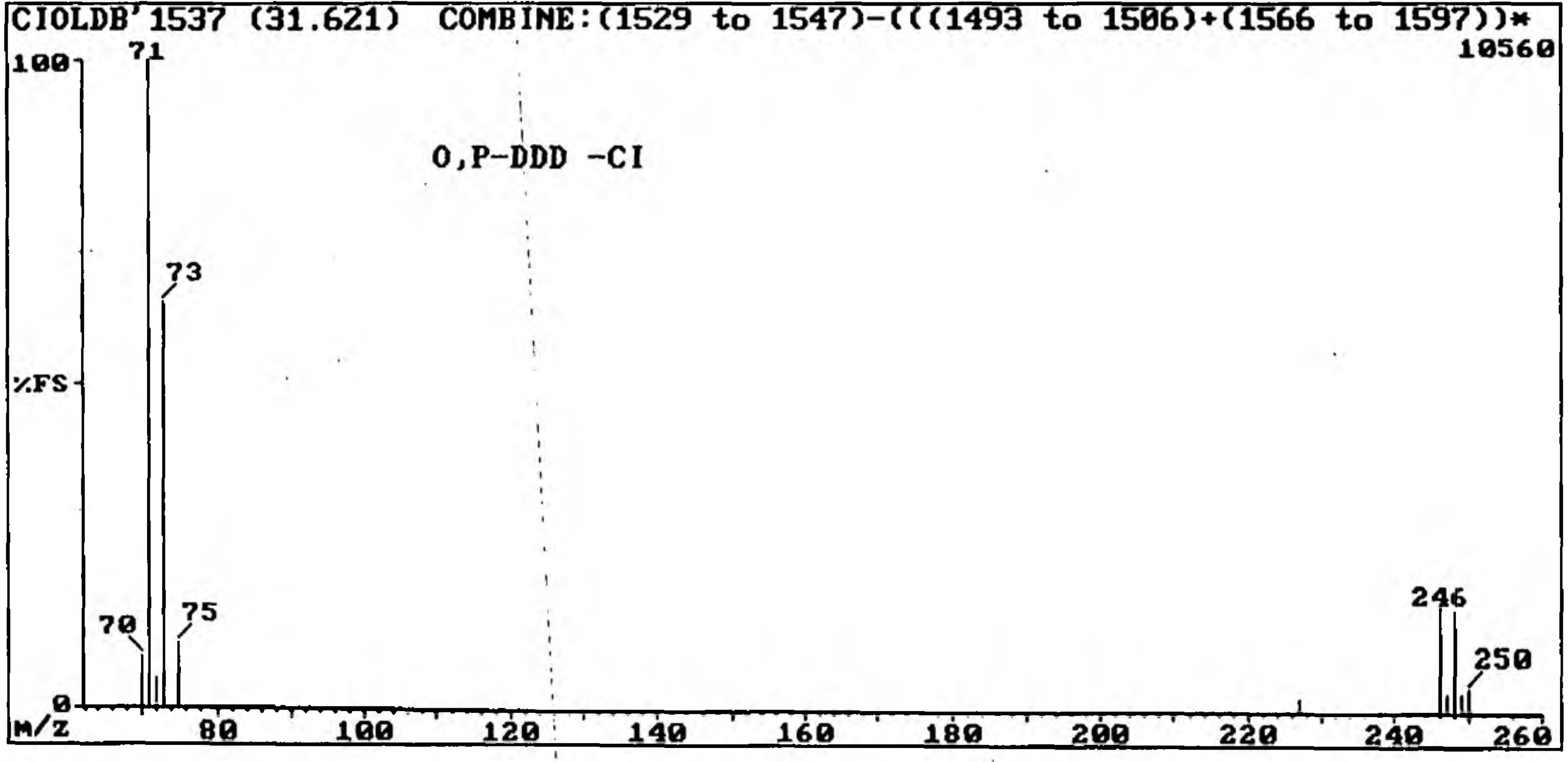
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul deut -ci mix Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

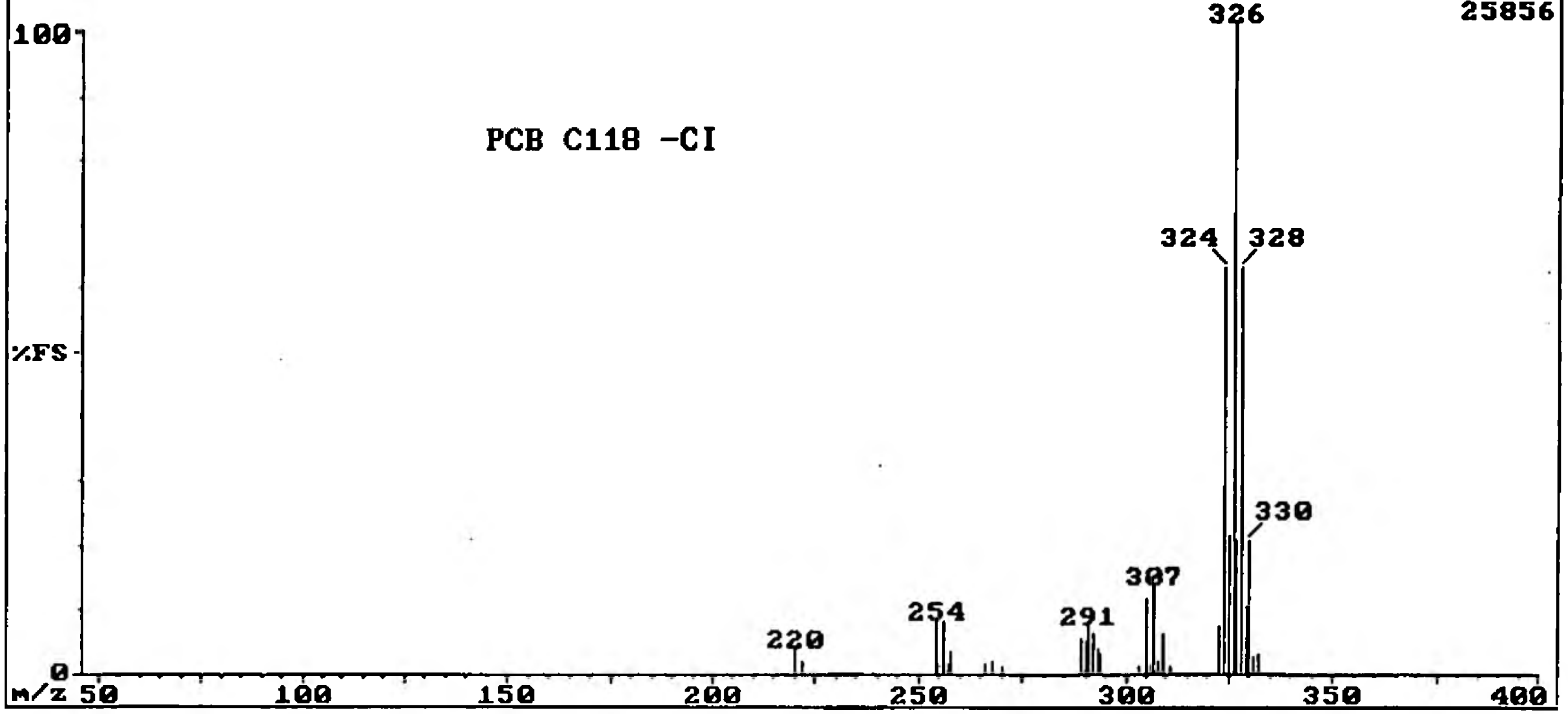
Sample:-ci old red list b Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul deut -ci mix Instrument:Trio-1

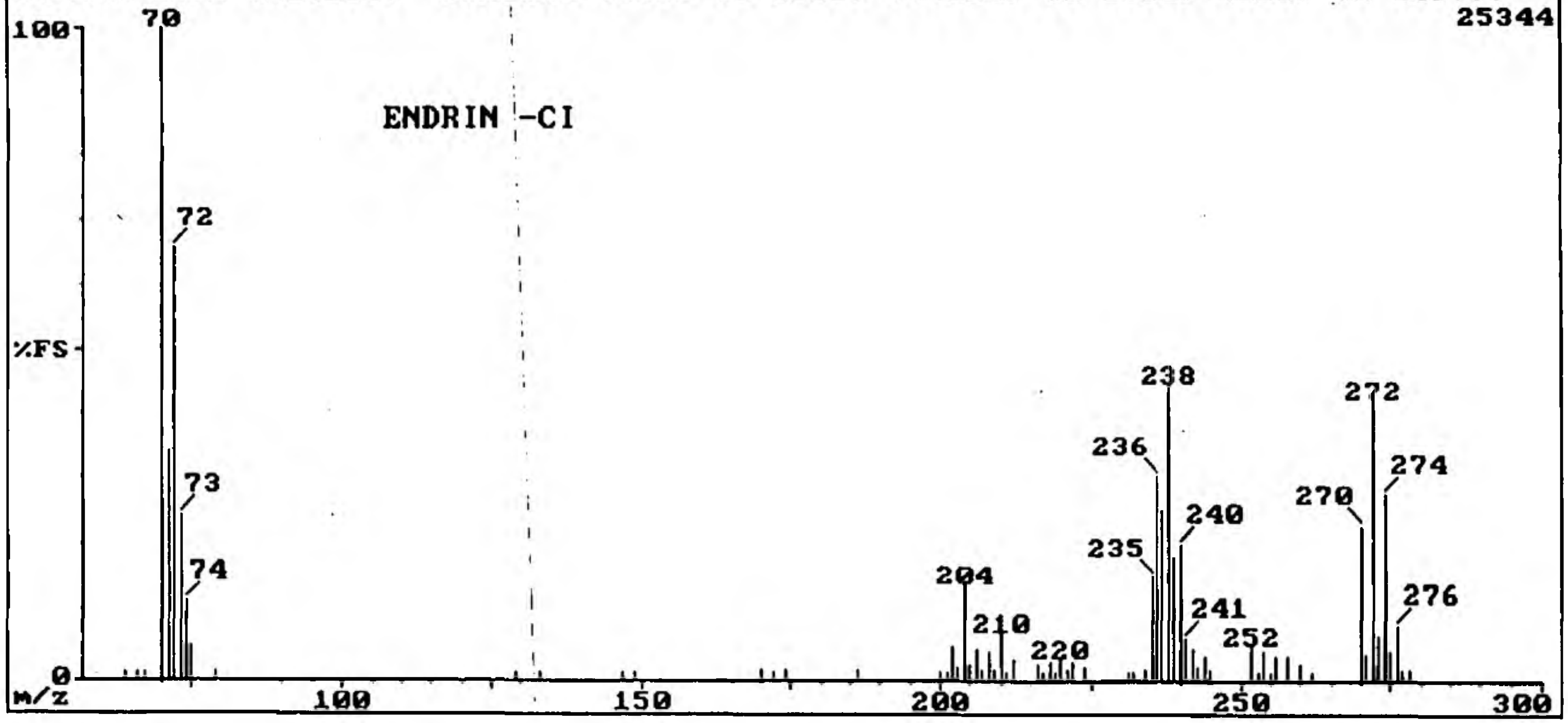
PCBSTCI'1751 (35.104) COMBINE:(1745 to 1762)-(((1723 to 1737)+(1771 to 1779))



VG LAB-BASE The TRIO-1 GC-MS Data System

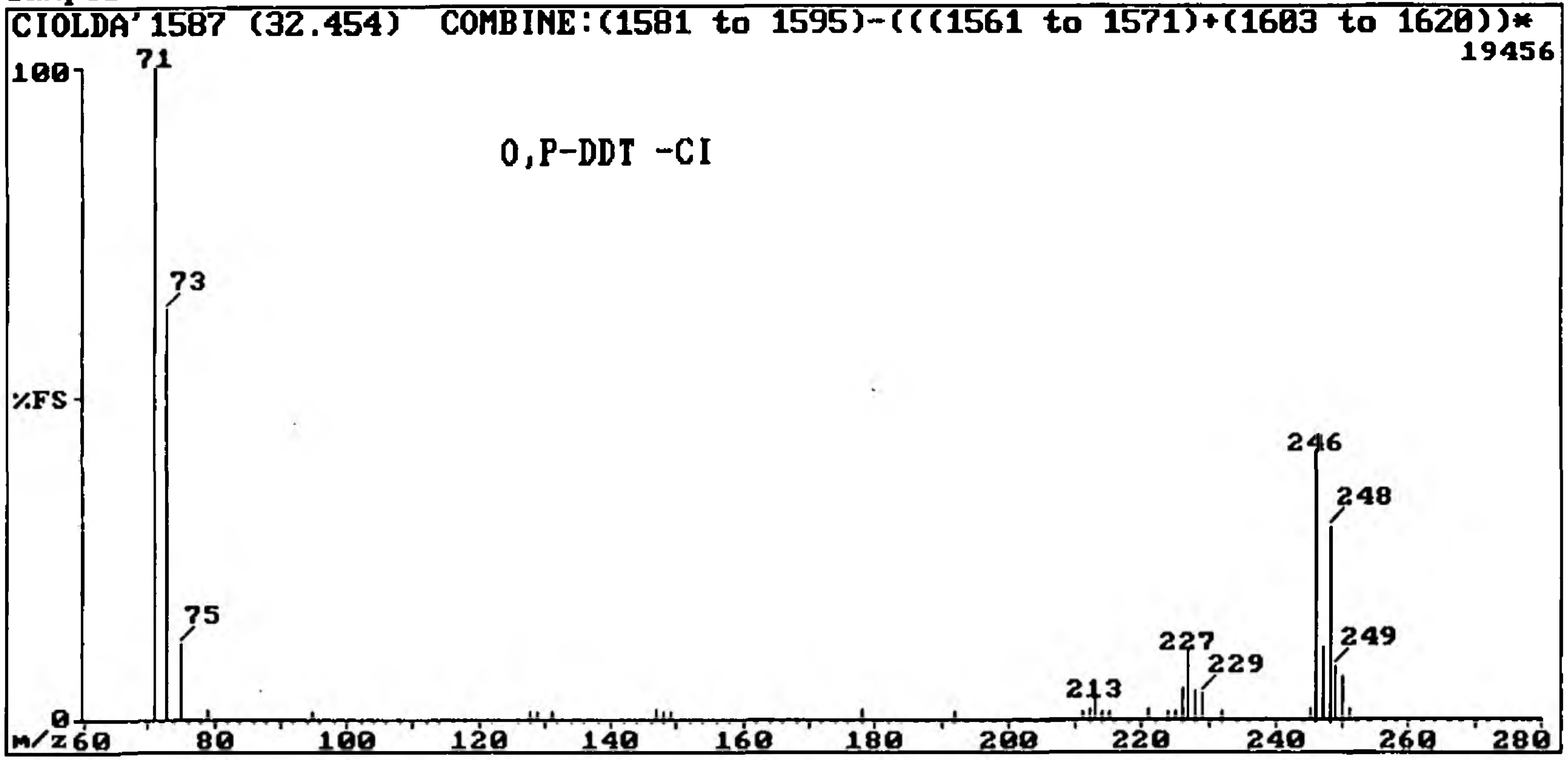
Sample:-CI NEW RED LIST Instrument:Trio-1

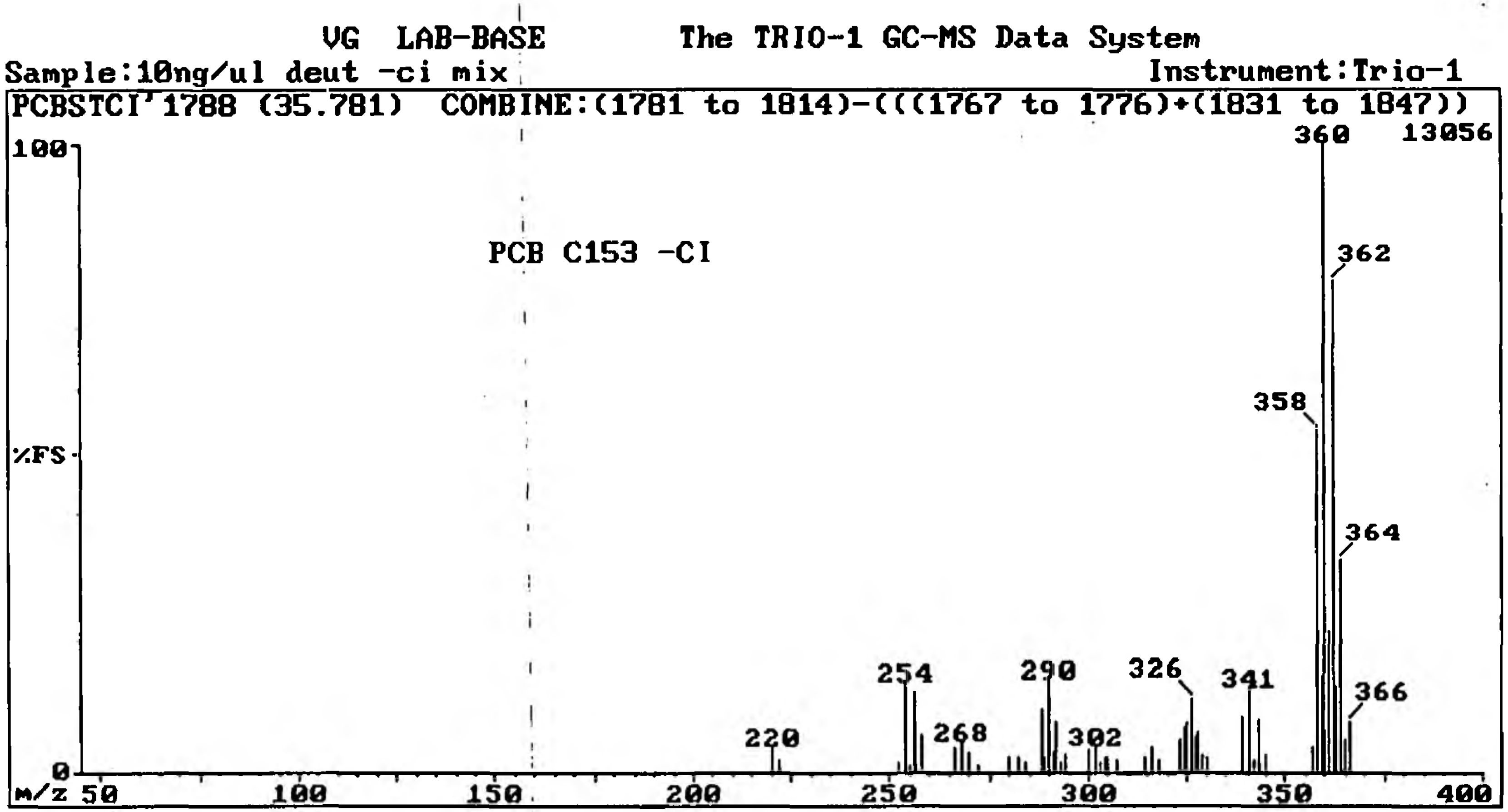
CIOLDA'1572 (32.204) COMBINE:(1565 to 1581)-(((1549 to 1561)+(1587 to 1597))*



VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:-CI NEW RED LIST Instrument:Trio-1





VG LAB-BASE The TRIO-1 GC-MS Data System

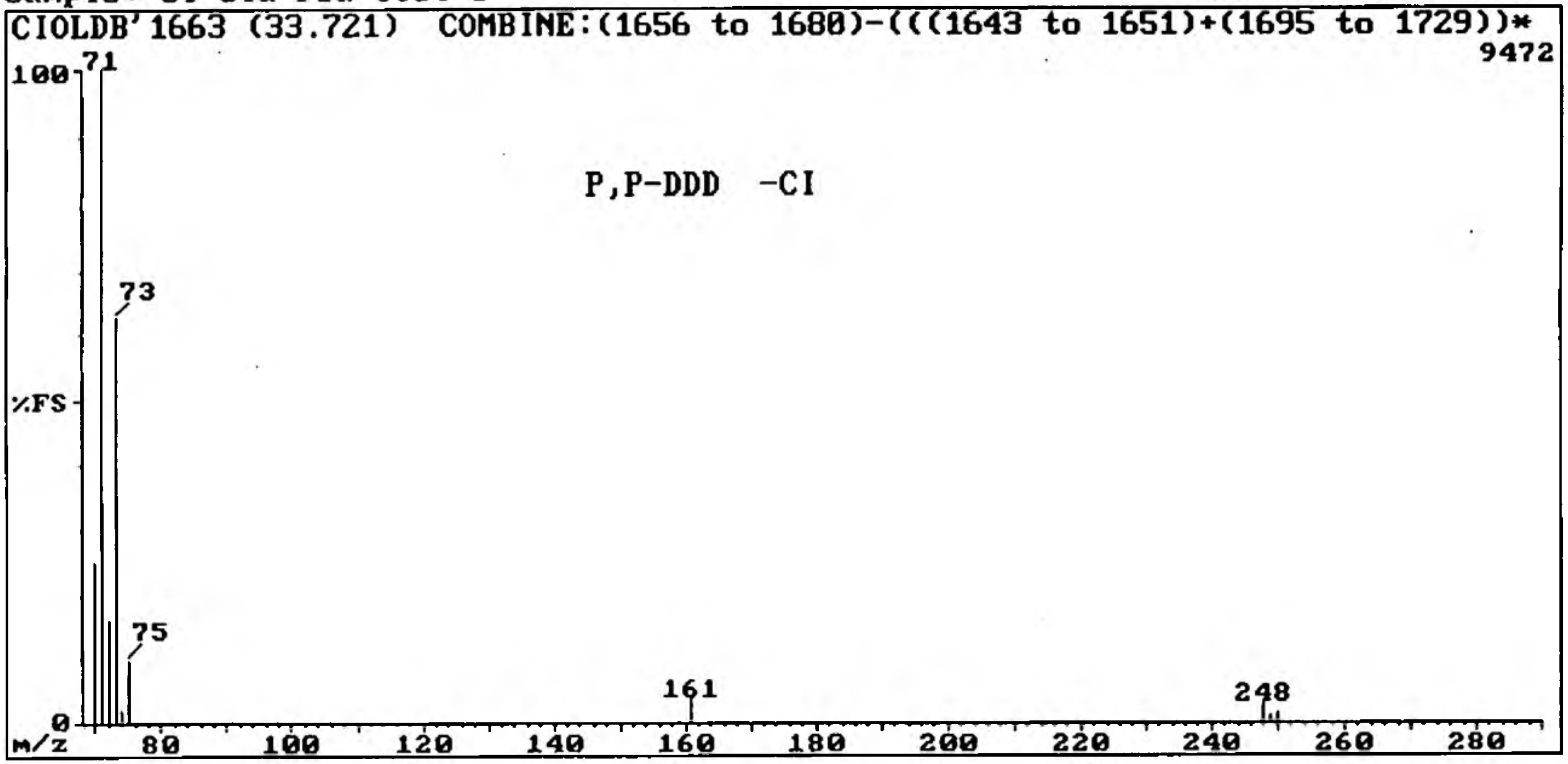
Sample:10ng/ul deut -ci mix Instrument:Trio-1

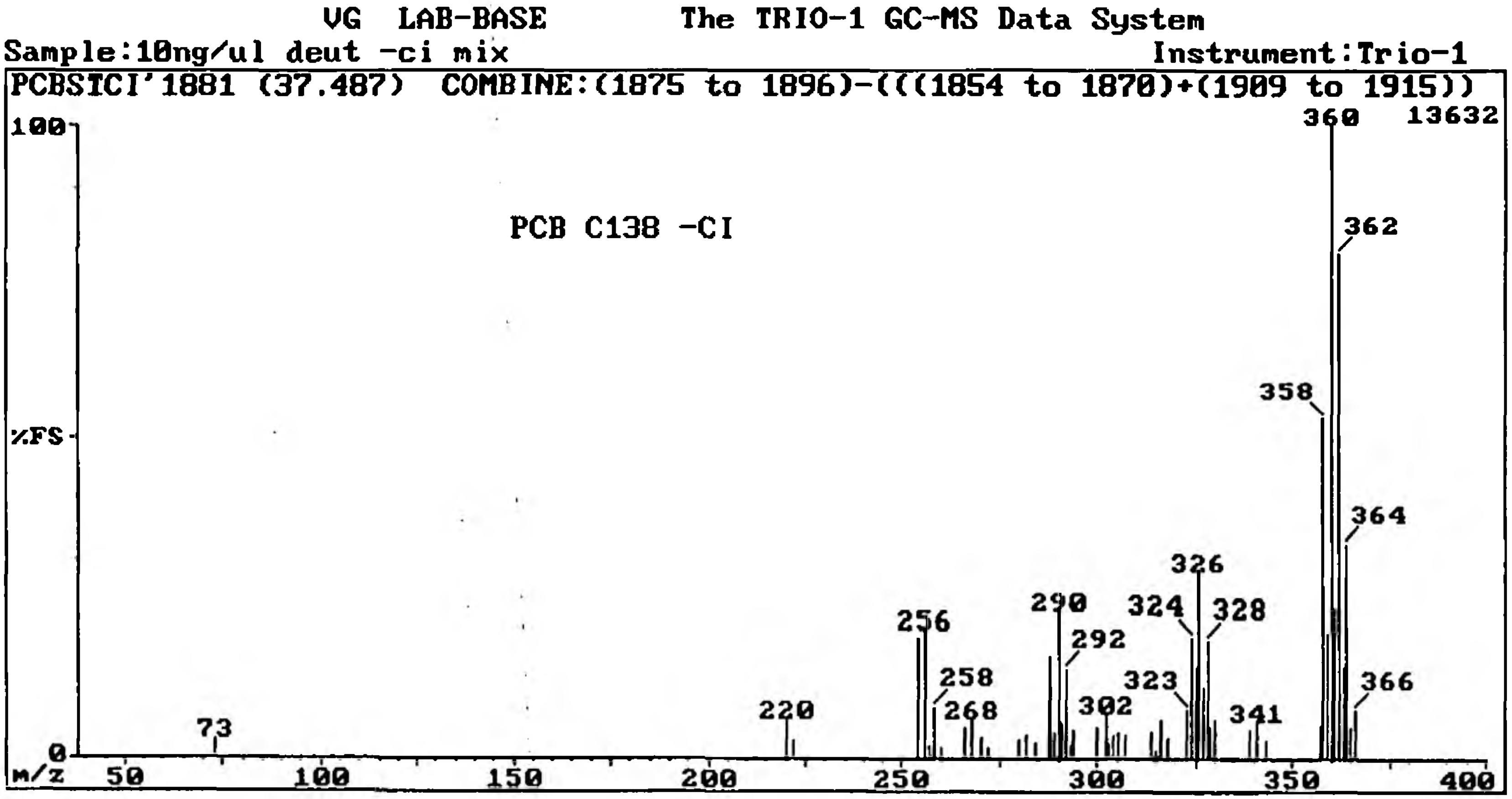
PCBSTCI'1788 (35.781) COMBINE:(1781 to 1814)-(((1767 to 1776)+(1831 to 1847))

PCB C153 -CI

VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:-ci old red list b Instrument:Trio-1



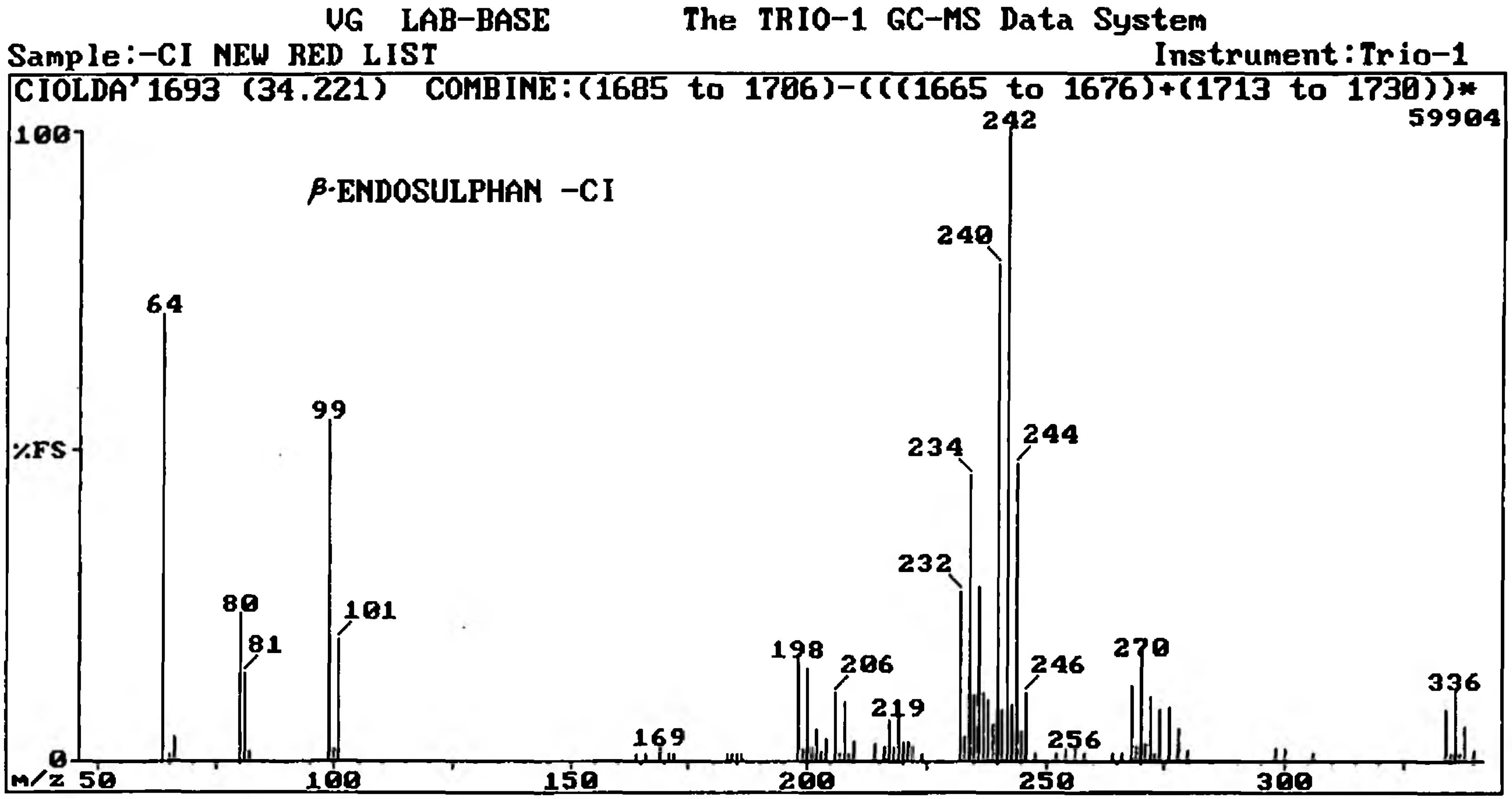


VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul deut -ci mix Instrument:Trio-1

PCBSICI'1881 (37.487) COMBINE:(1875 to 1896)-(((1854 to 1870)+(1909 to 1915))

PCB C138 -CI



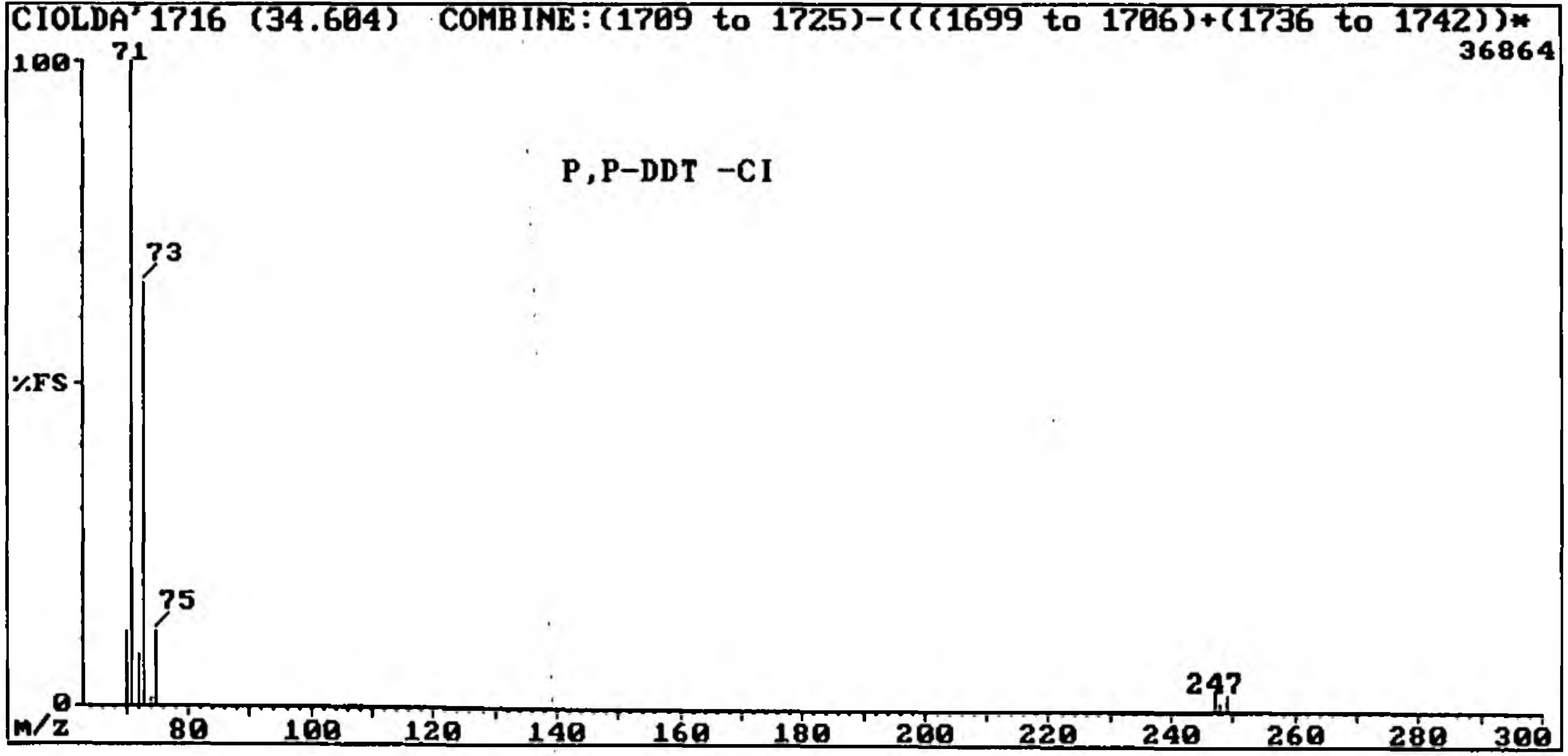
VG LAB-BASE The TRIO-1 GC-MS Data System

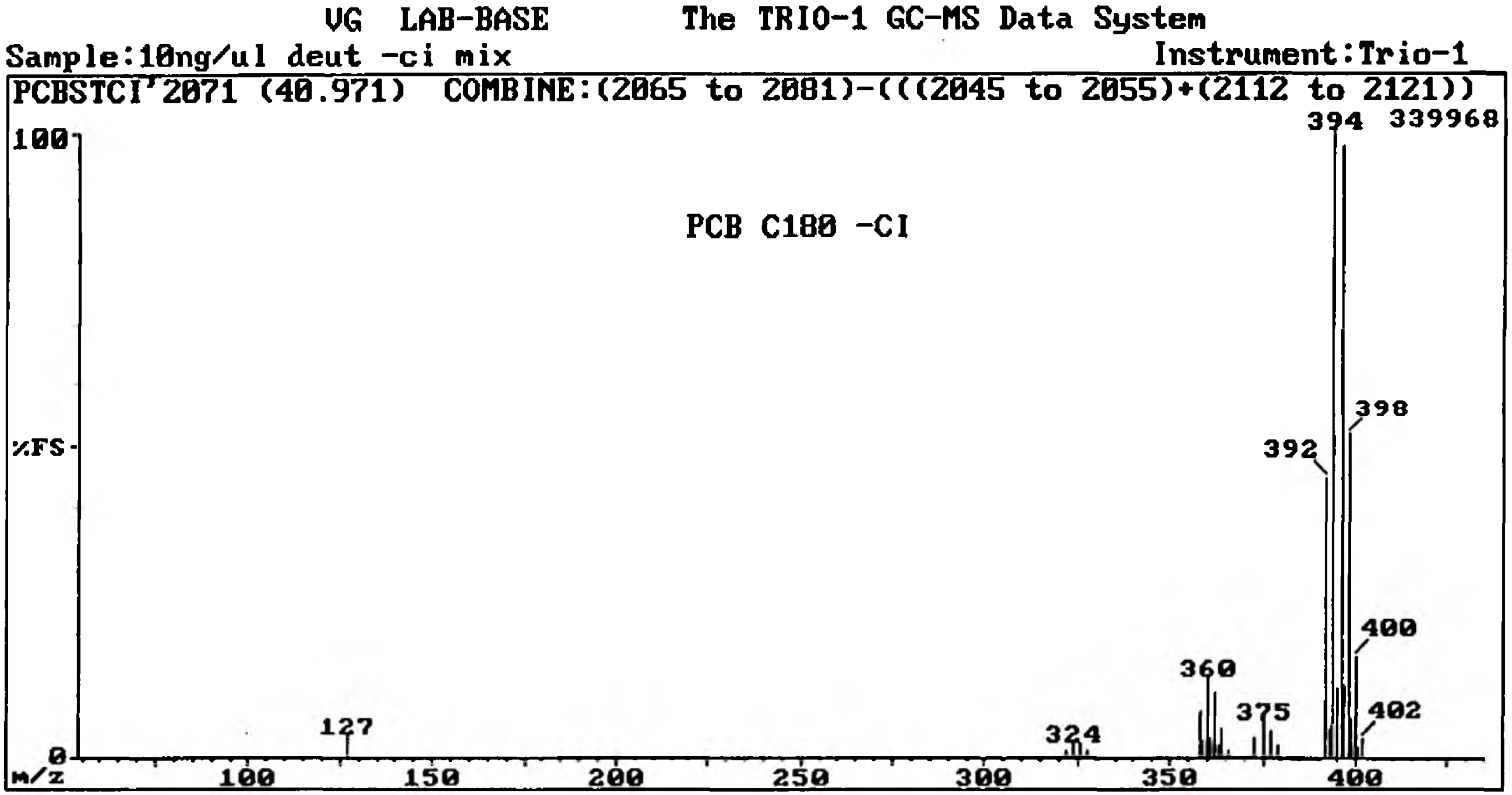
Sample:-CI NEW RED LIST Instrument:Trio-1

CIOLDA'1693 (34.221) COMBINE:(1685 to 1706)-(((1665 to 1676)+(1713 to 1730))*

VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:-CI NEW RED LIST Instrument:Trio-1





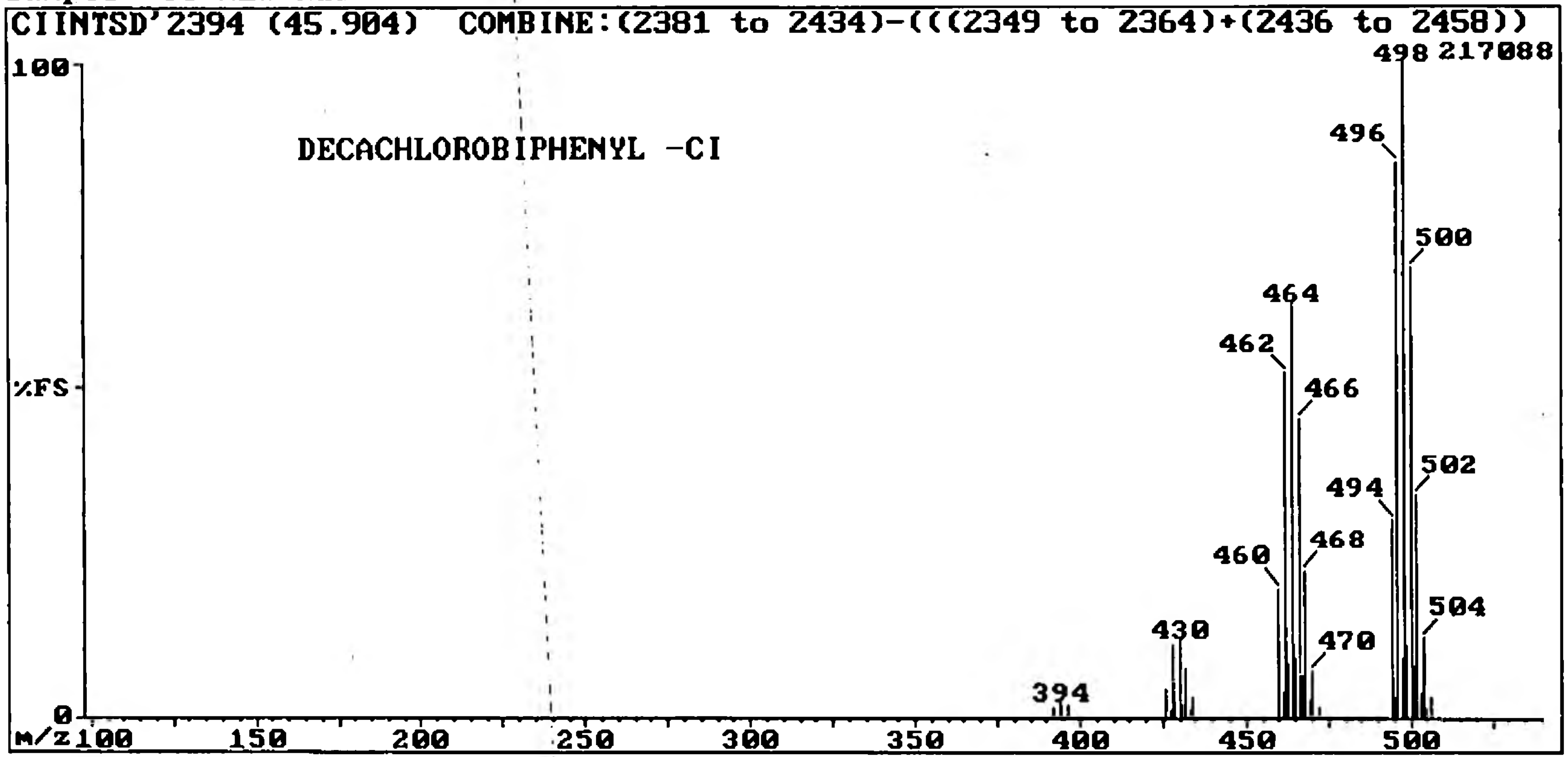
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul deut -ci mix Instrument:Trio-1

PCBSTCI'2071 (40.971) COMBINE:(2065 to 2081)-(((2045 to 2055)+(2112 to 2121))

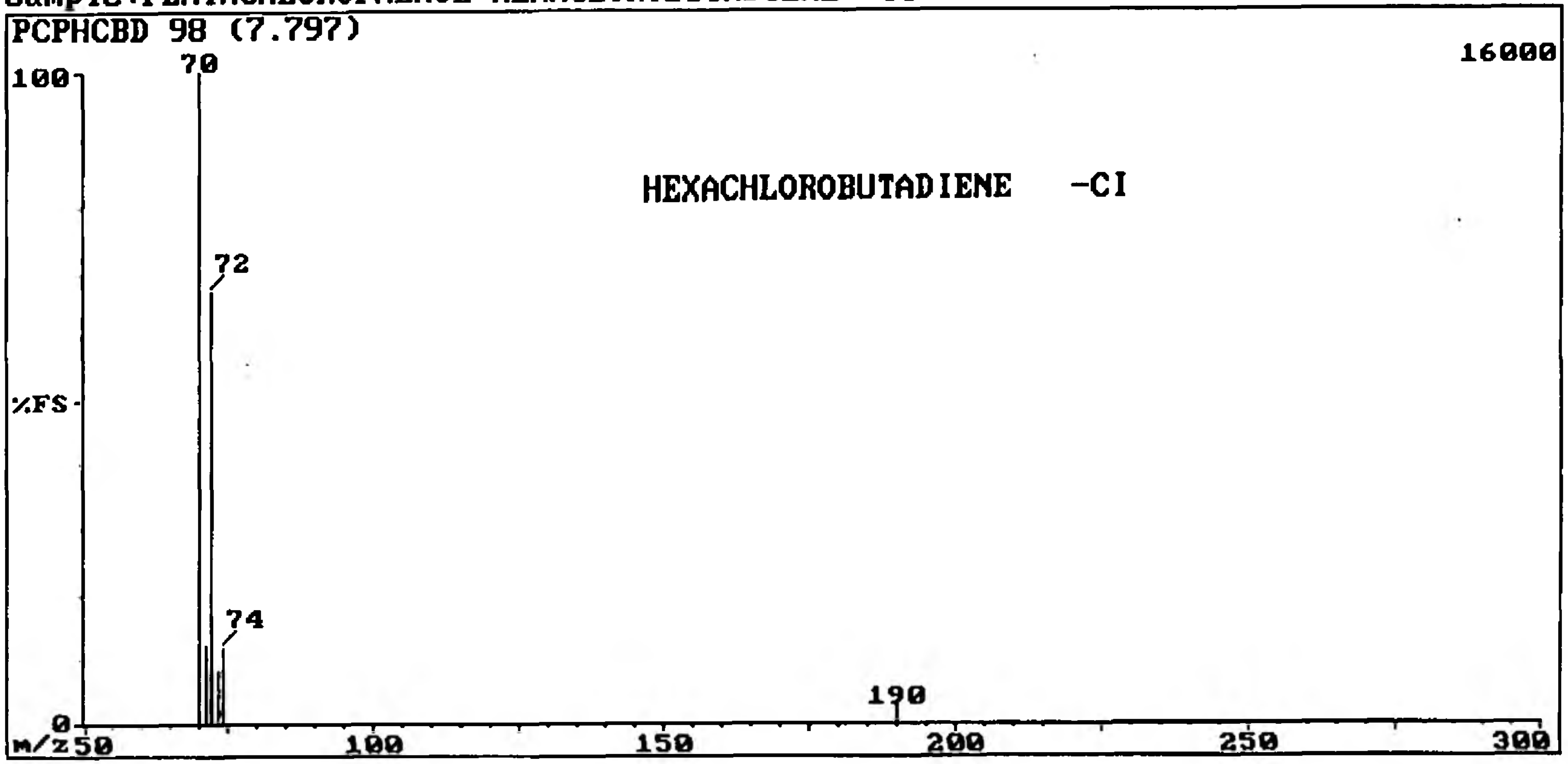
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:-CI NEW RED LIST Instrument:Trio-1



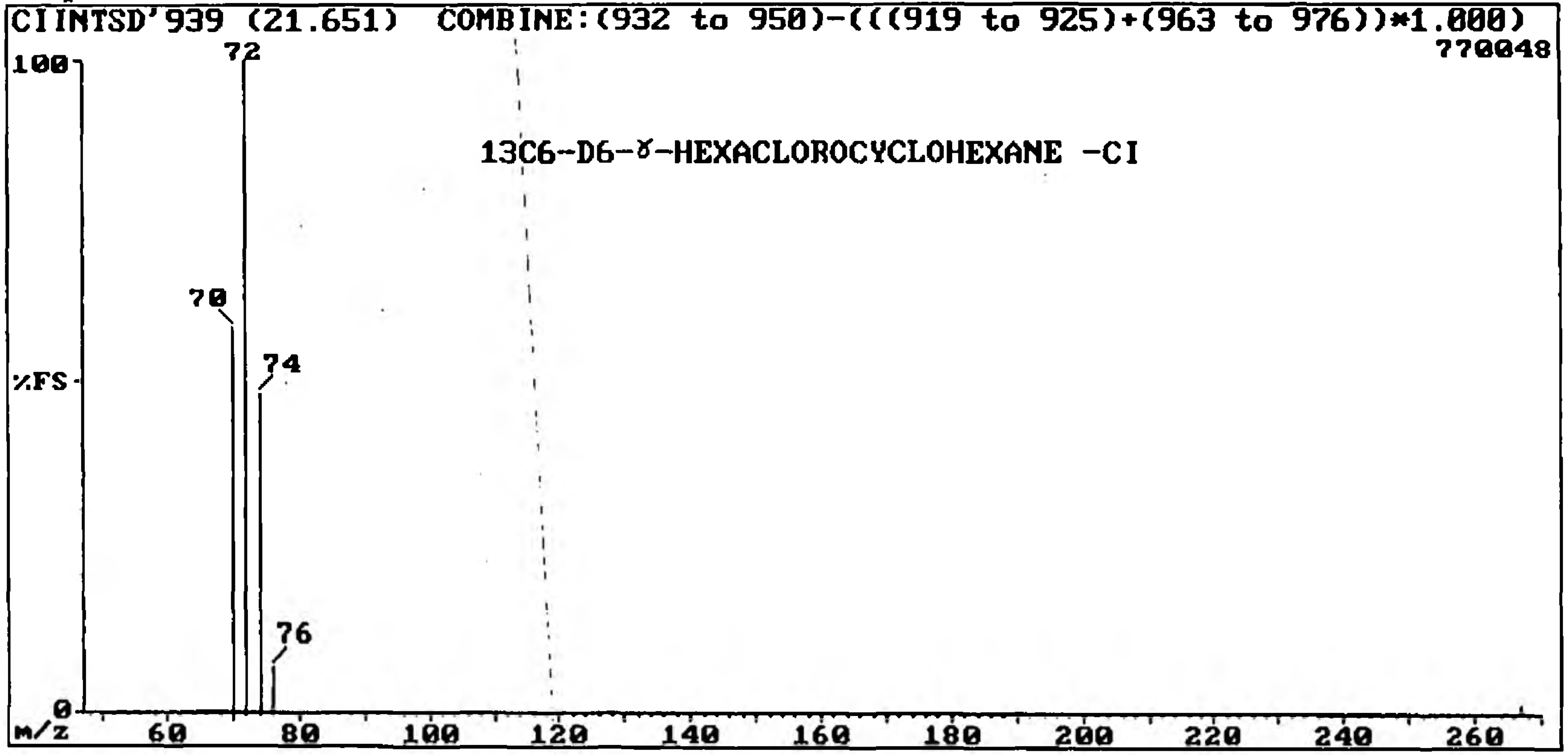
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:PENTACHLOROPHENOL HEXACLOROBUTADIENE -CI Instrument:Trio-1



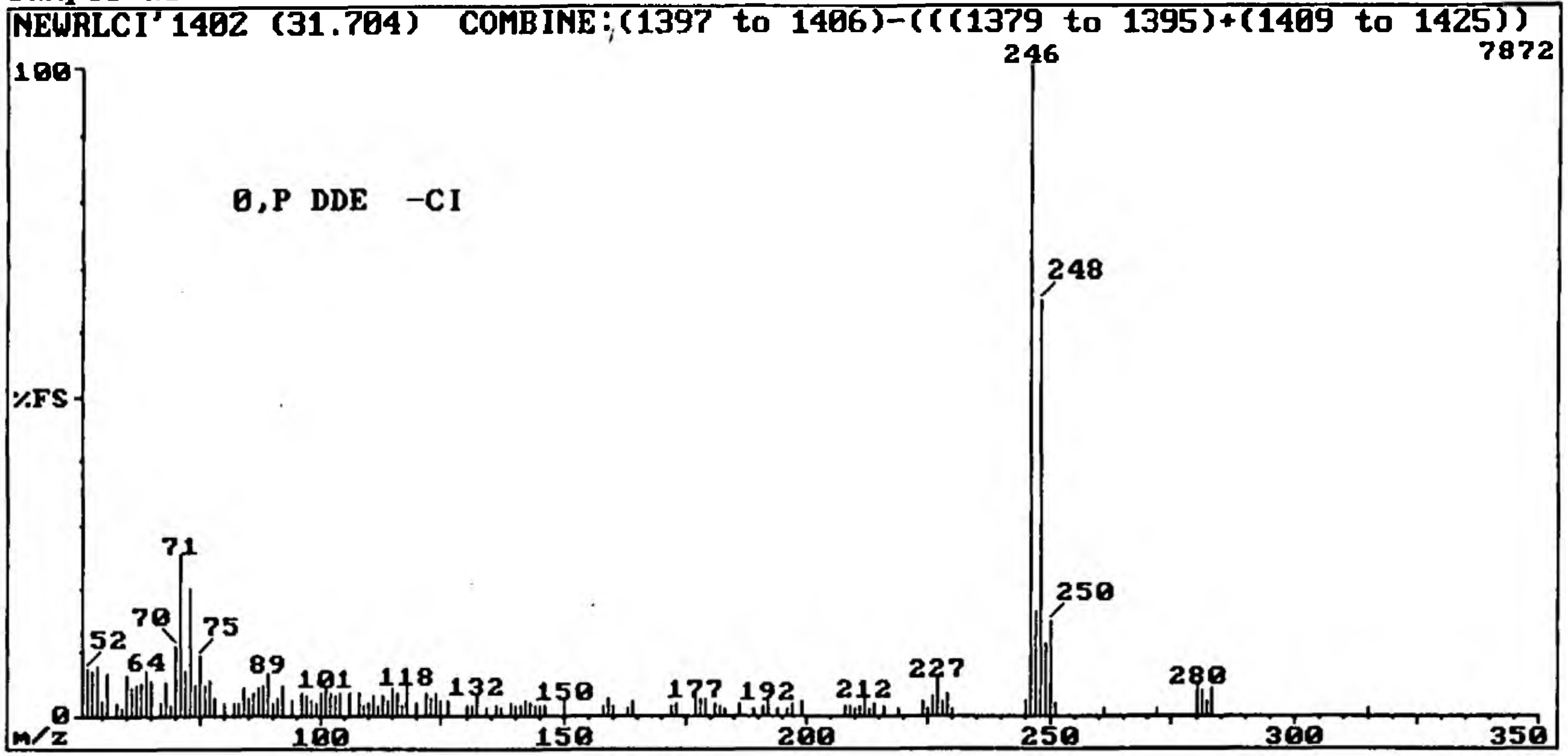
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:-CI NEW RED LIST Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

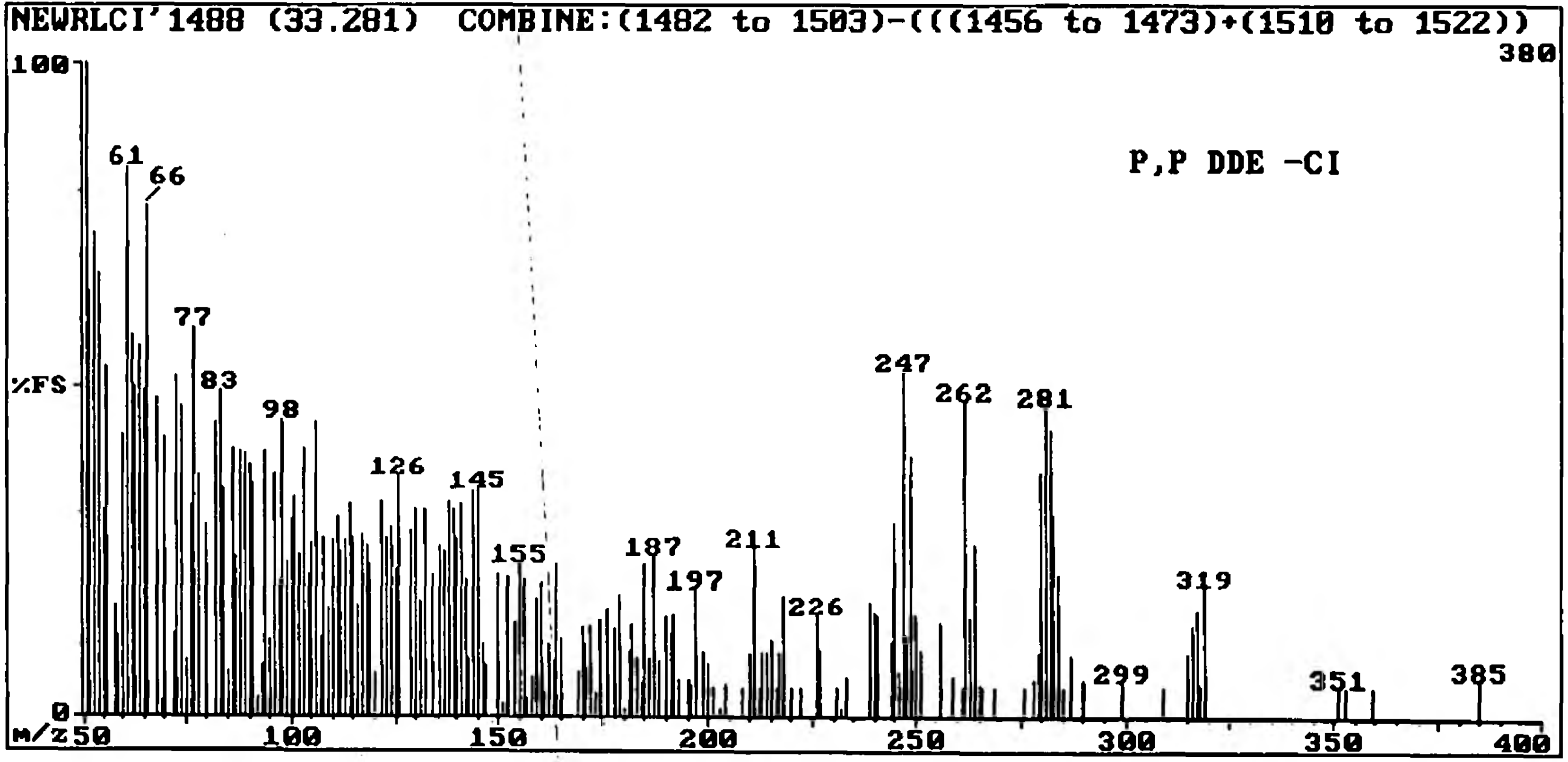
Sample:new red list stds -ci Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

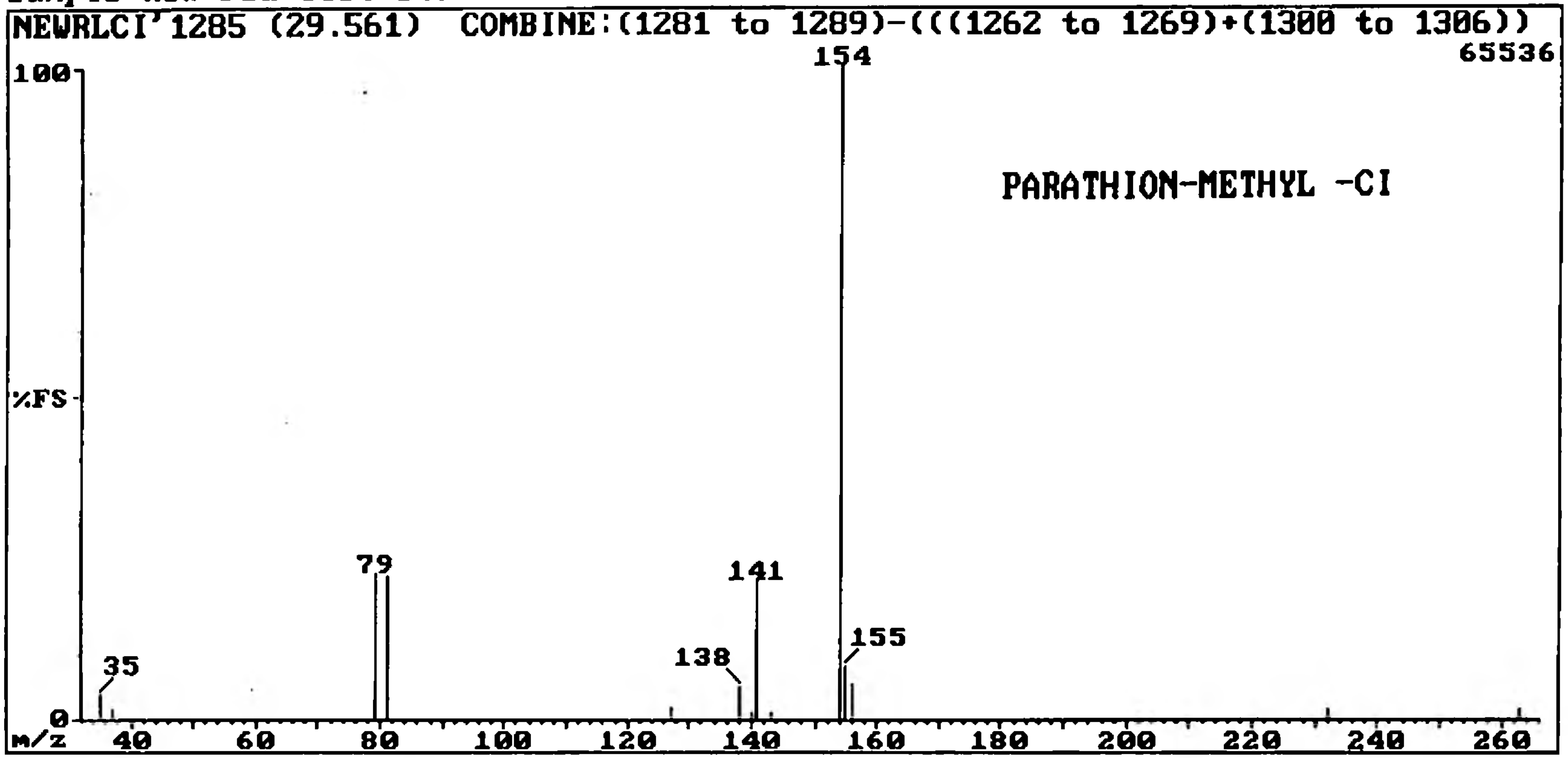
Sample:new red list stds -ci

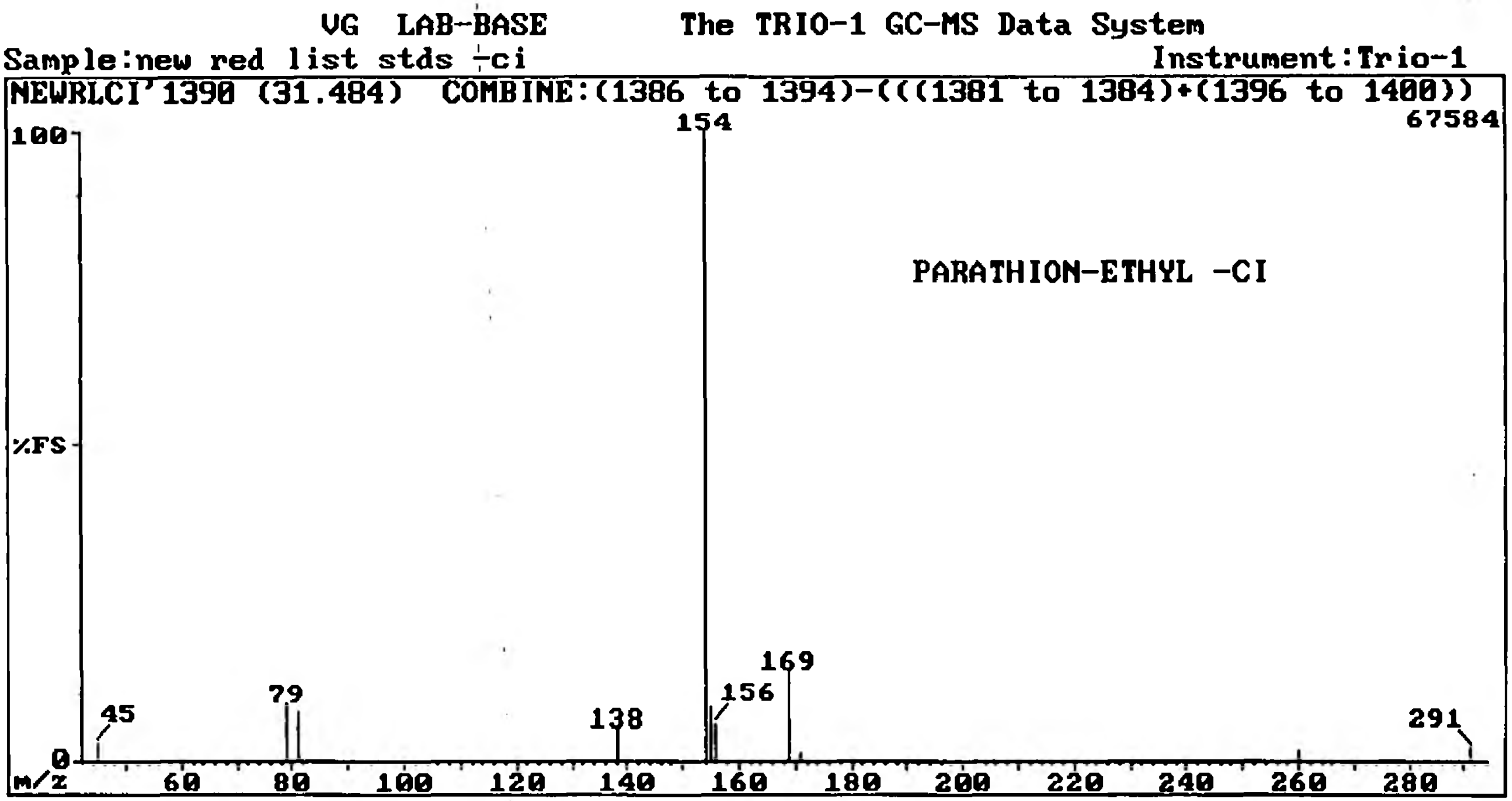
Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:new red list stds -ci Instrument:Trio-1





VG LAB-BASE The TRIO-1 GC-MS Data System

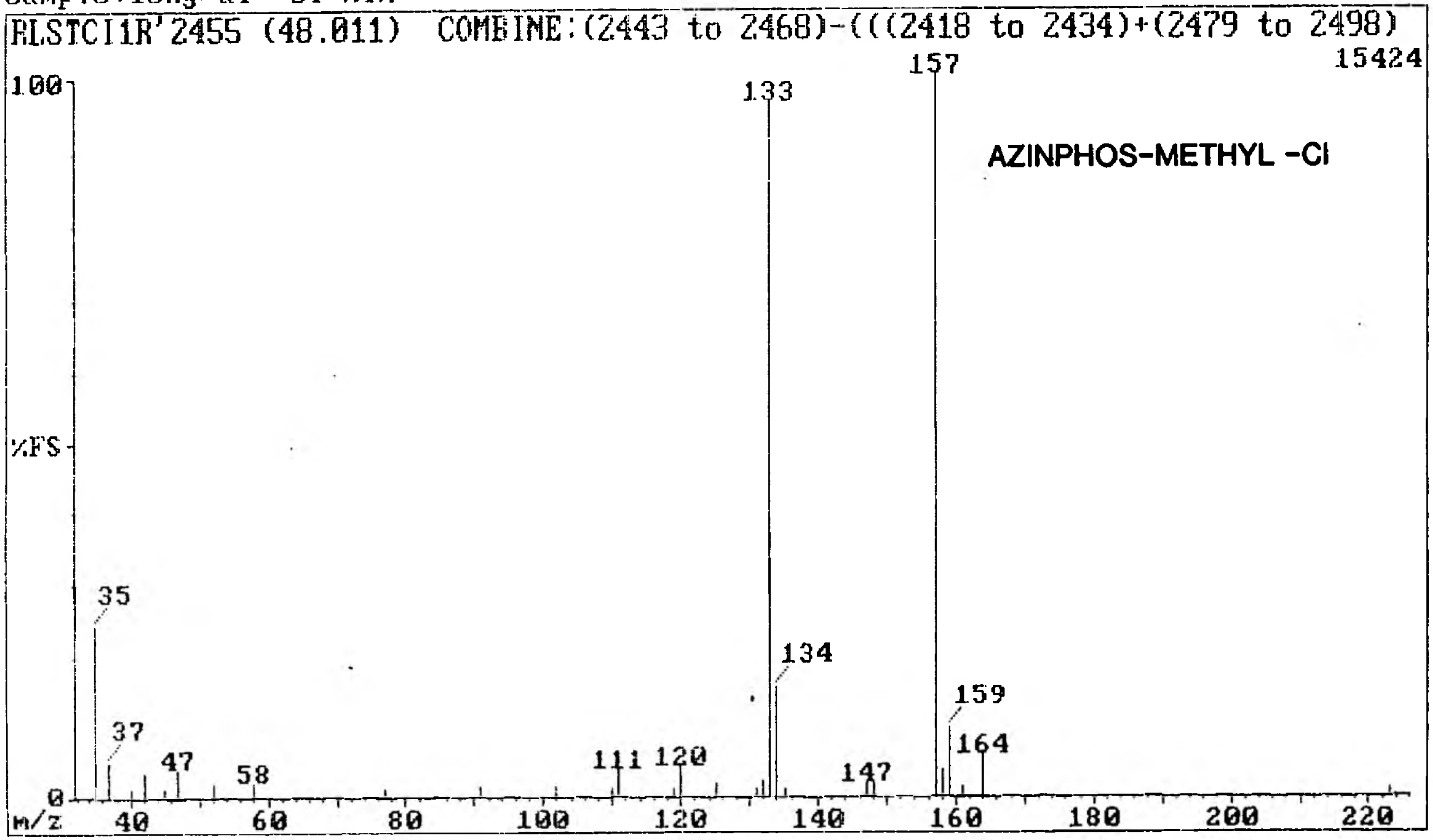
Sample:new red list stds -ci Instrument:Trio-1

NEWRLCI'1390 (31.484) COMBINE:(1386 to 1394)-(((1381 to 1384)+(1396 to 1400))

PARATHION-ETHYL -CI

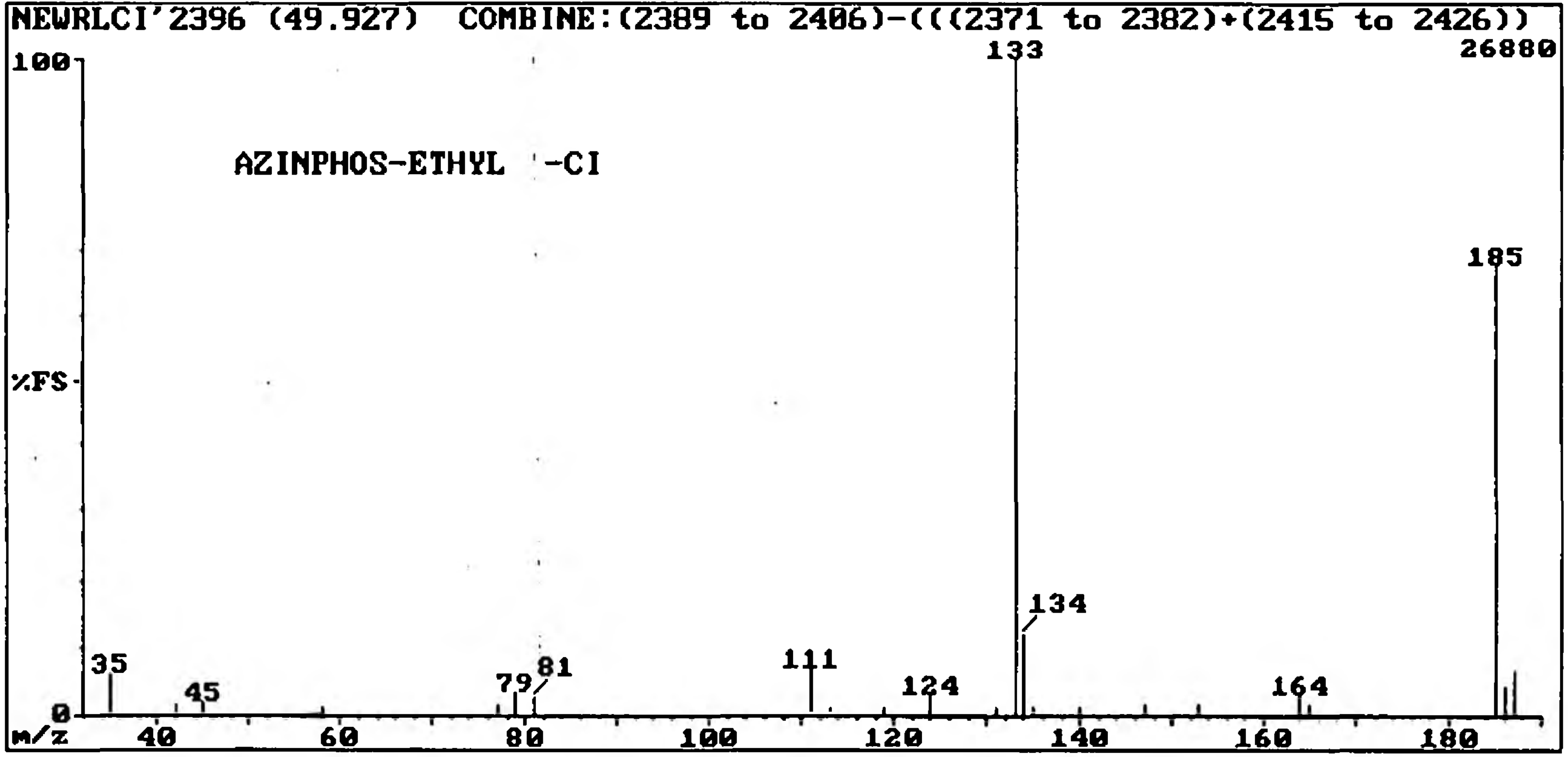
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:10ng/ul -ci mix Instrument:Trio-1



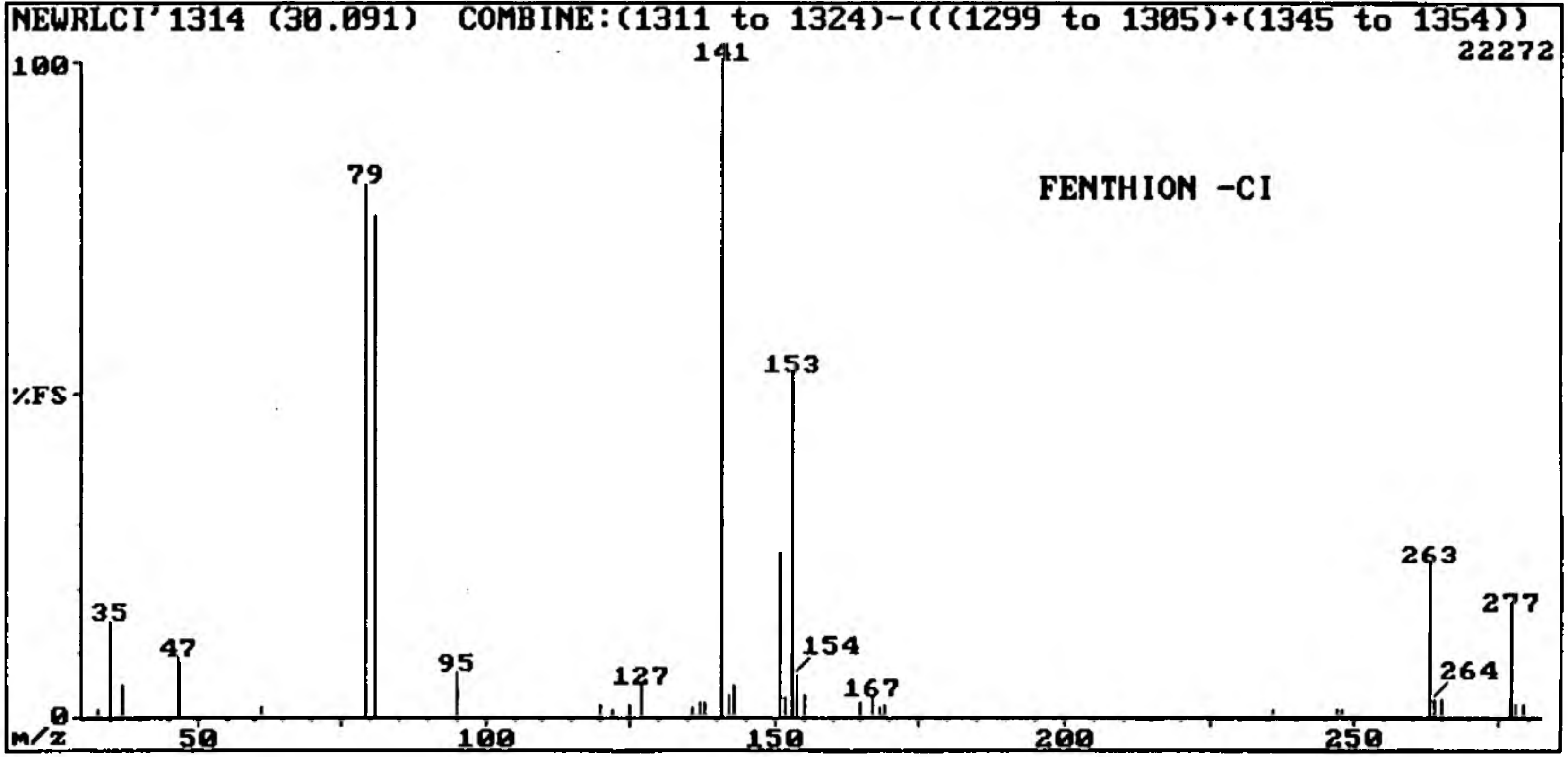
VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:new red list stds -ci Instrument:Trio-1



VG LAB-BASE The TRIO-1 GC-MS Data System

Sample:new red list stds -ci Instrument:Trio-1



APPENDIX

SECTION 3

Table A3-1

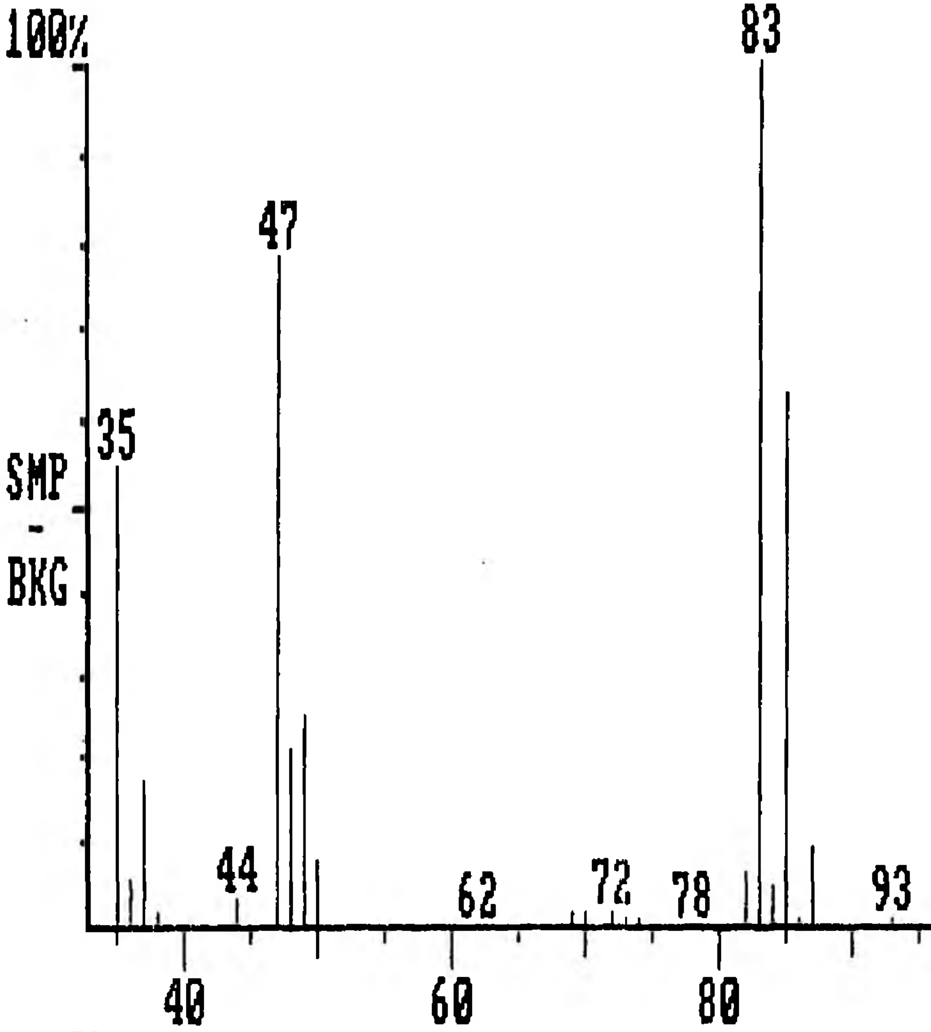
Summary of MID Method Parameters for Red List Compounds Analysed by Purge and Trap GCMS

Peak	Compound	Ions Monitored m/z	Retention Time (min)
1	Chloroform	47, 83, 85	7.22
2	d3-1,1,1-trichloroethane	63, 100, 102	8.21
3	1,1,1-trichloroethane	61, 97, 99	8.31
4	Carbontetrachloride	47, 82, 117, 119	9.20
5	1,2-dichloroethane	49, 62, 64	9.43
6	Trichloroethylene	47, 60, 95, 130	12.04
7	Tetrachloroethylene	82, 94, 131, 166	17.24
8	1,1,1,2-tetrachloroethane	95, 117, 131, 133	19.26
9	1,1,2,2-tetrachloroethane	60, 83, 85, 133	21.49
10	1,3,5-trichlorobenzene	74, 84, 109, 180	27.30
11	d3 1,2,3-trichlorobenzene	76, 148, 183, 185	28.44
12	1,2,4-trichlorobenzene	74, 145, 180, 182	28.46
13	Hexachlorobutadiene	118, 190, 225, 260	29.12
14	1,2,3-trichlorobenzene	180, 182	29.46

Note

In most cases, the ion underlined is the most intense ion in the mass spectrum and therefore it was selected as the quantitation ion. Secondary ions, which may be more unique than the quantitation ion for some compounds, have been selected as confirmatory ions.

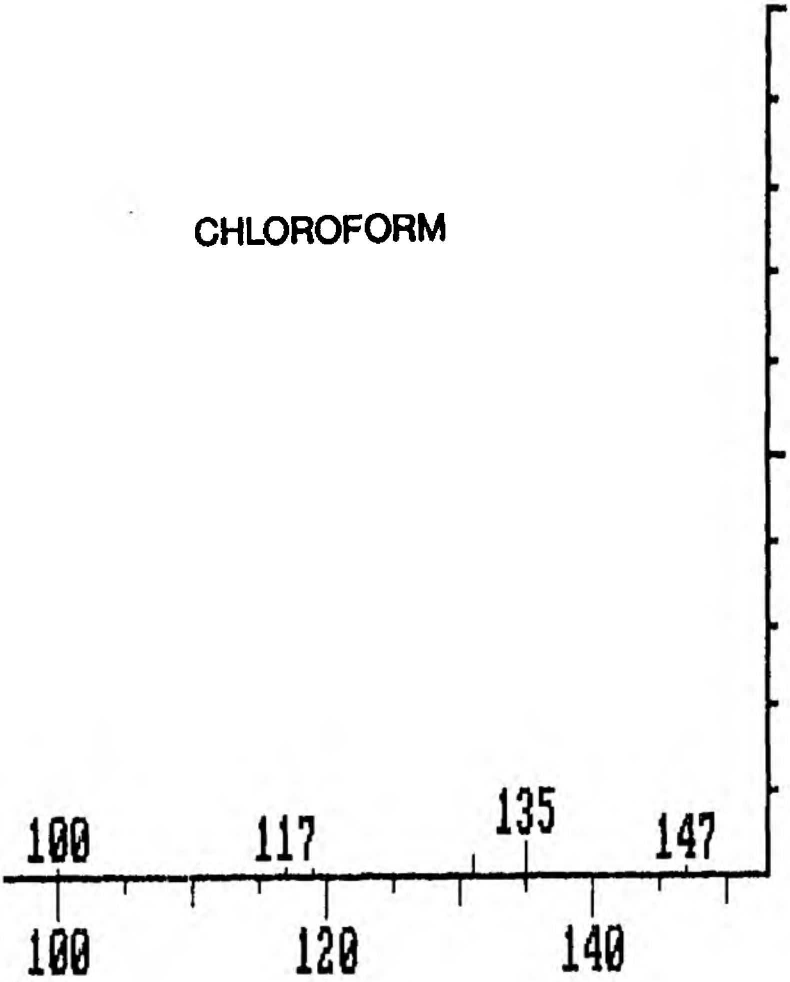
```
Background Subtract    Filename: REDLIST3
Comment: RED LIST STDS TEST 3
Average of: 429 to 440  Minus: 445 to 453
```



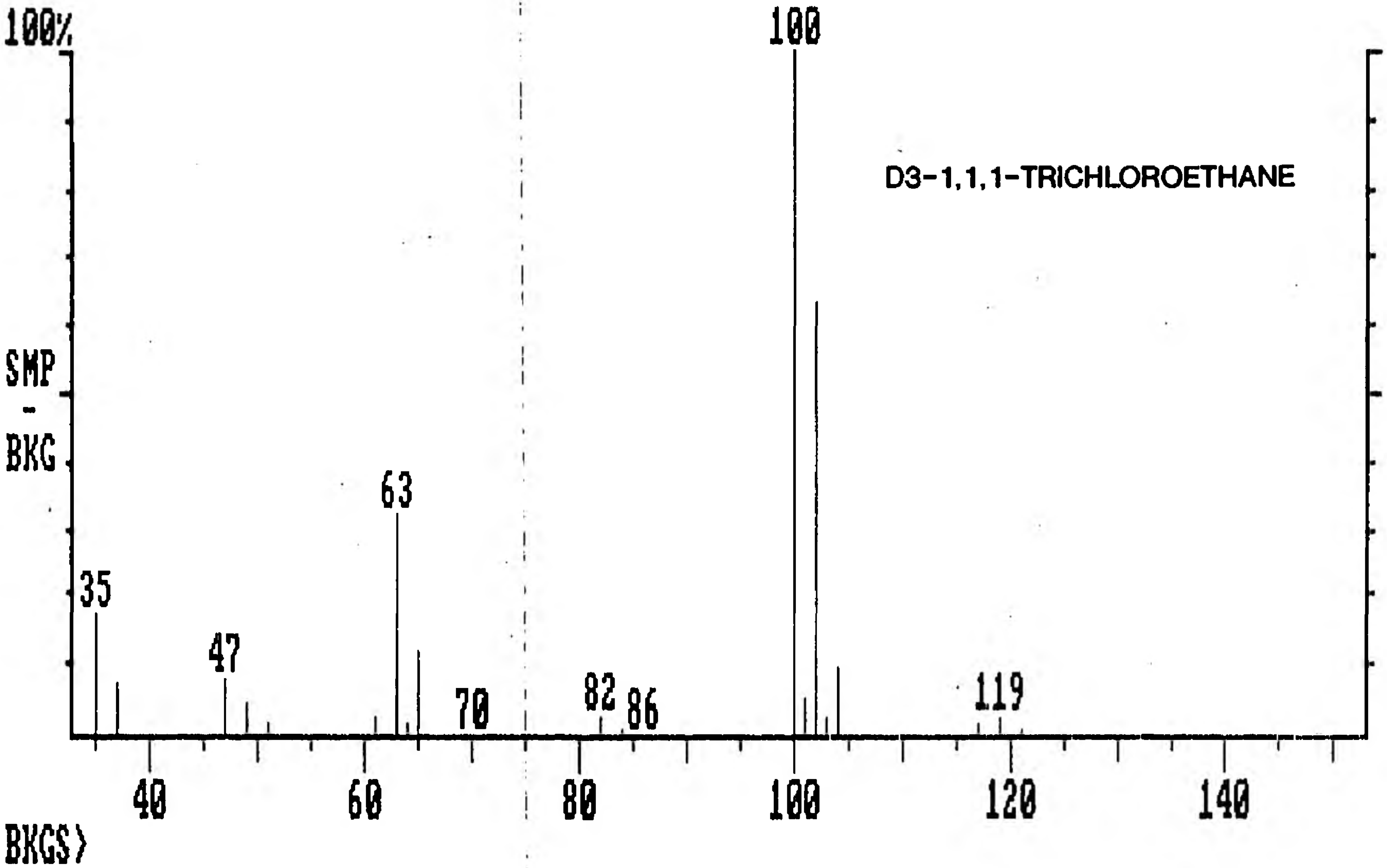
```
BKGS>
```

Acquired: Jan-04-1980 03:43:48

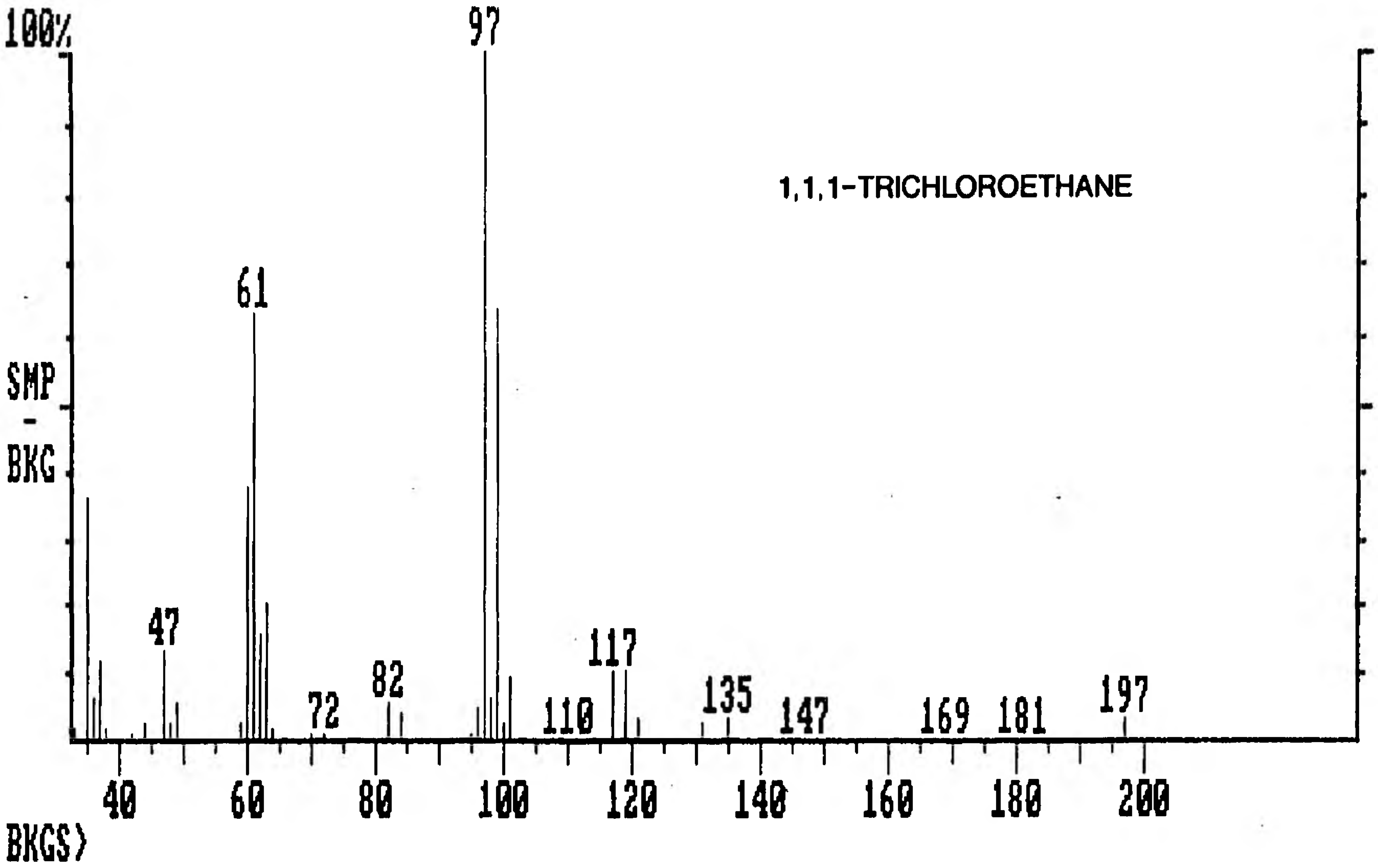
100% = 1433



Background Subtract   Filename: REDLIS23   Acquired: Jan-01-1980 03:41:01
Comment: RED LIST TEST STD 20MIN PURGE AT 60C
Average of: 498 to 510 Minus: 516 to 527   100% = 5385

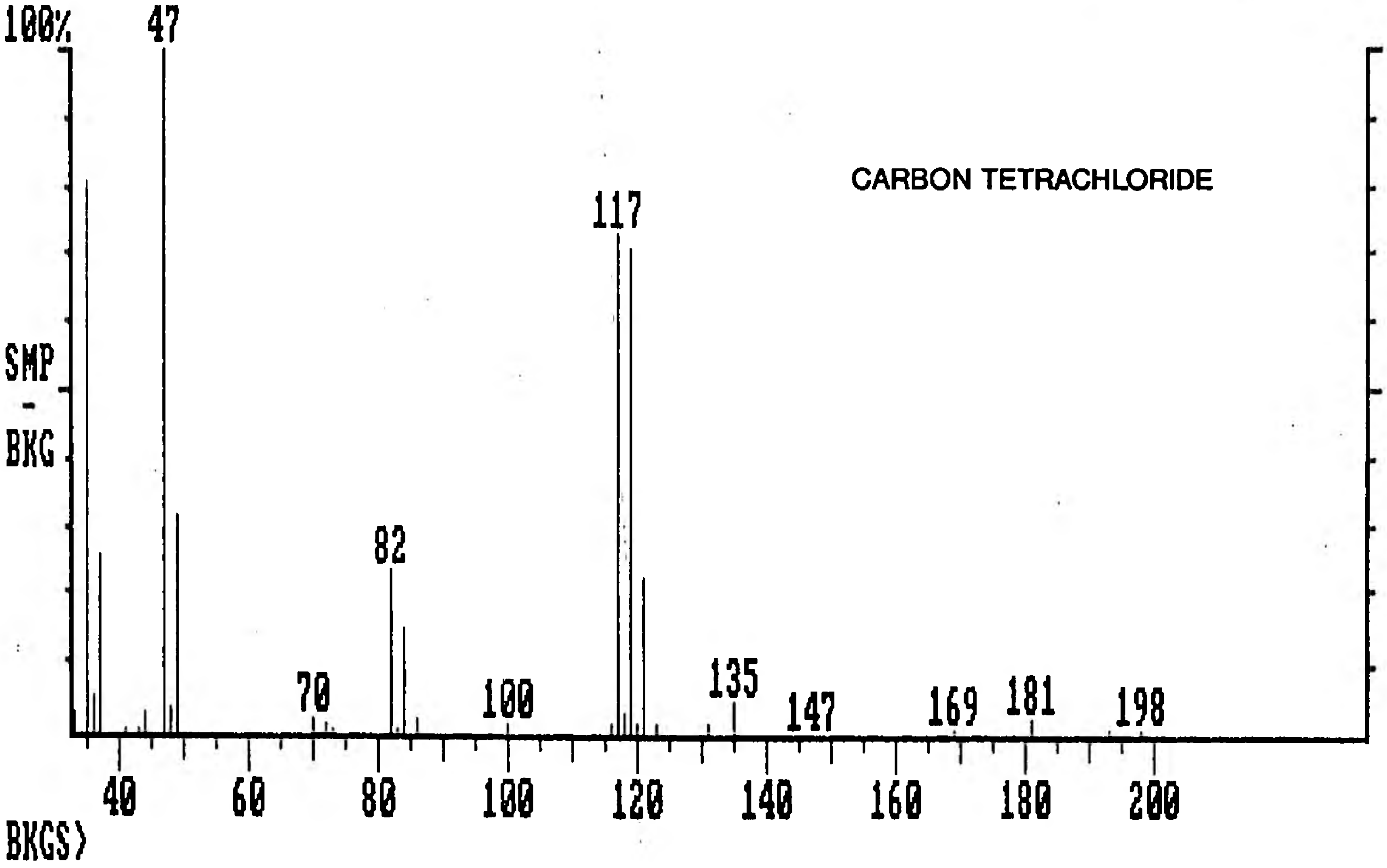


Background Subtract Filename: REDLIST3 Acquired: Jan-04-1980 03:43:48
Comment: RED LIST STDS TEST 3
Average of: 499 to 512 Minus: 515 to 527 100% = 1323



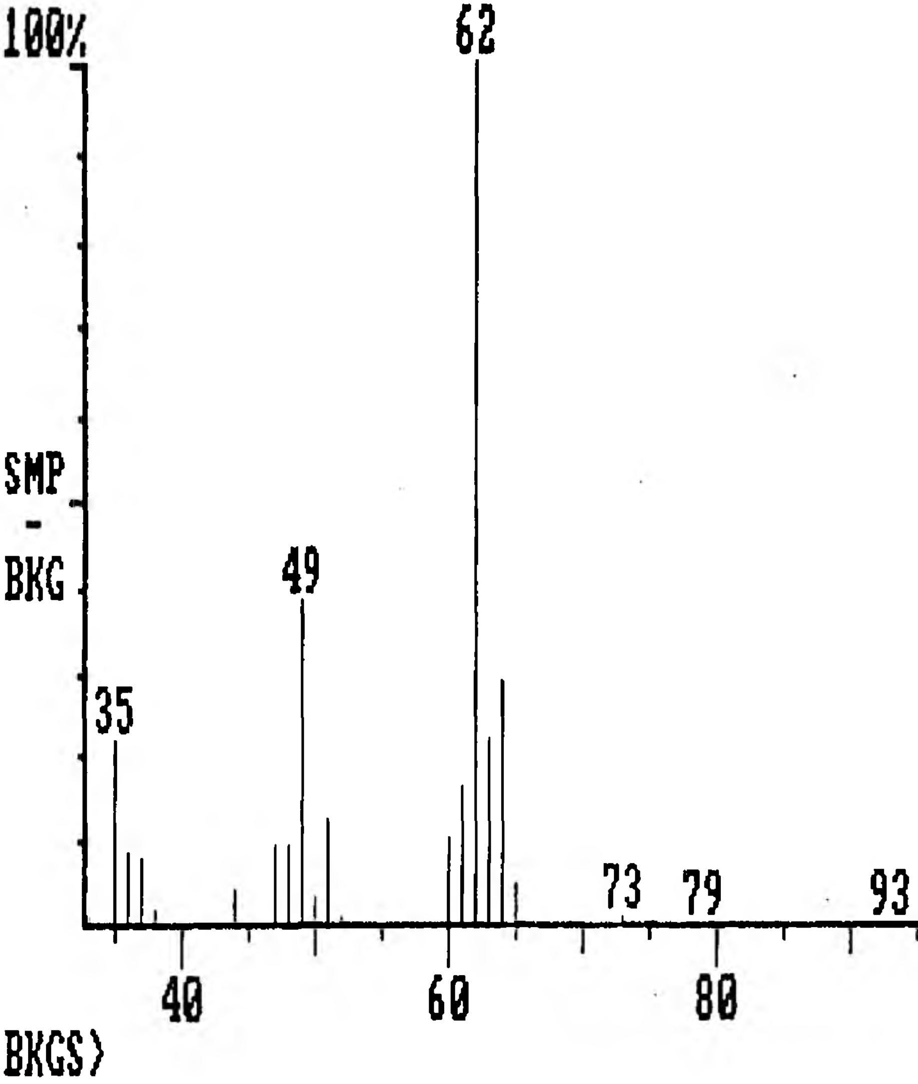
1,1,1-TRICHLOROETHANE

```
Background Subtract     Filename: REDLIST3        Acquired: Jan-04-1980  03:43:48
Comment: RED LIST STDS TEST 3
Average of: 546 to 559  Minus: 562 to 568                        100% = 1158
```



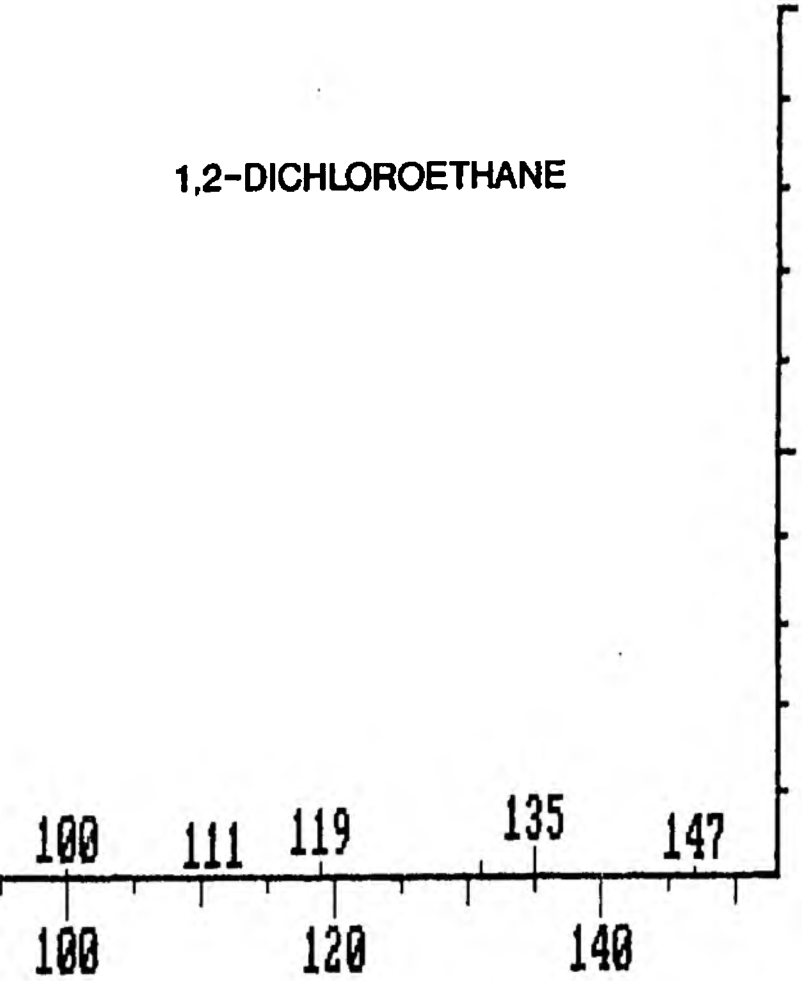
CARBON TETRACHLORIDE

Background Subtract   Filename: REDLIST3
Comment: RED LIST STDS TEST 3
Average of: 569 to 580 Minus: 583 to 595

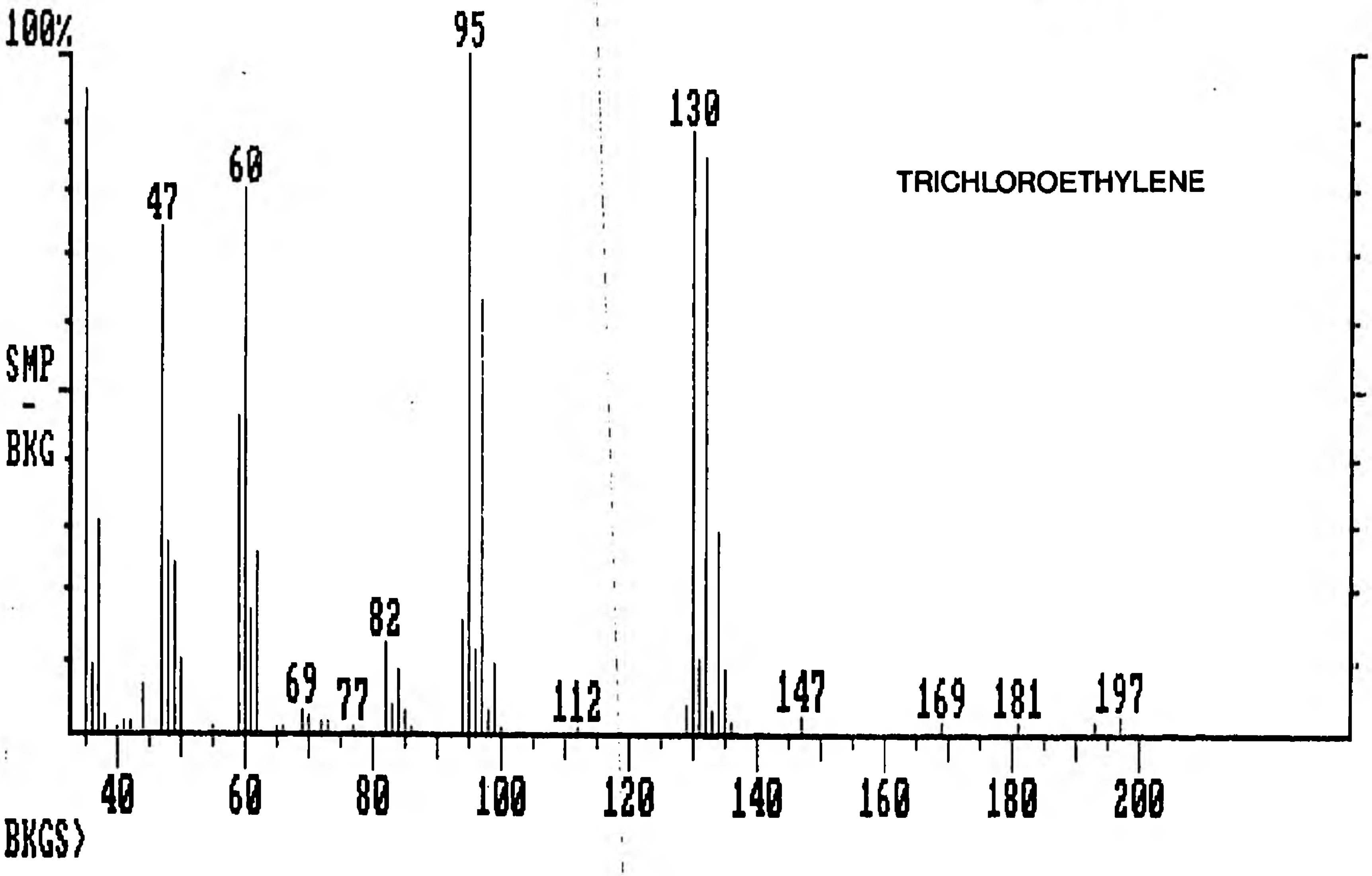


Acquired: Jan-04-1980 03:43:48

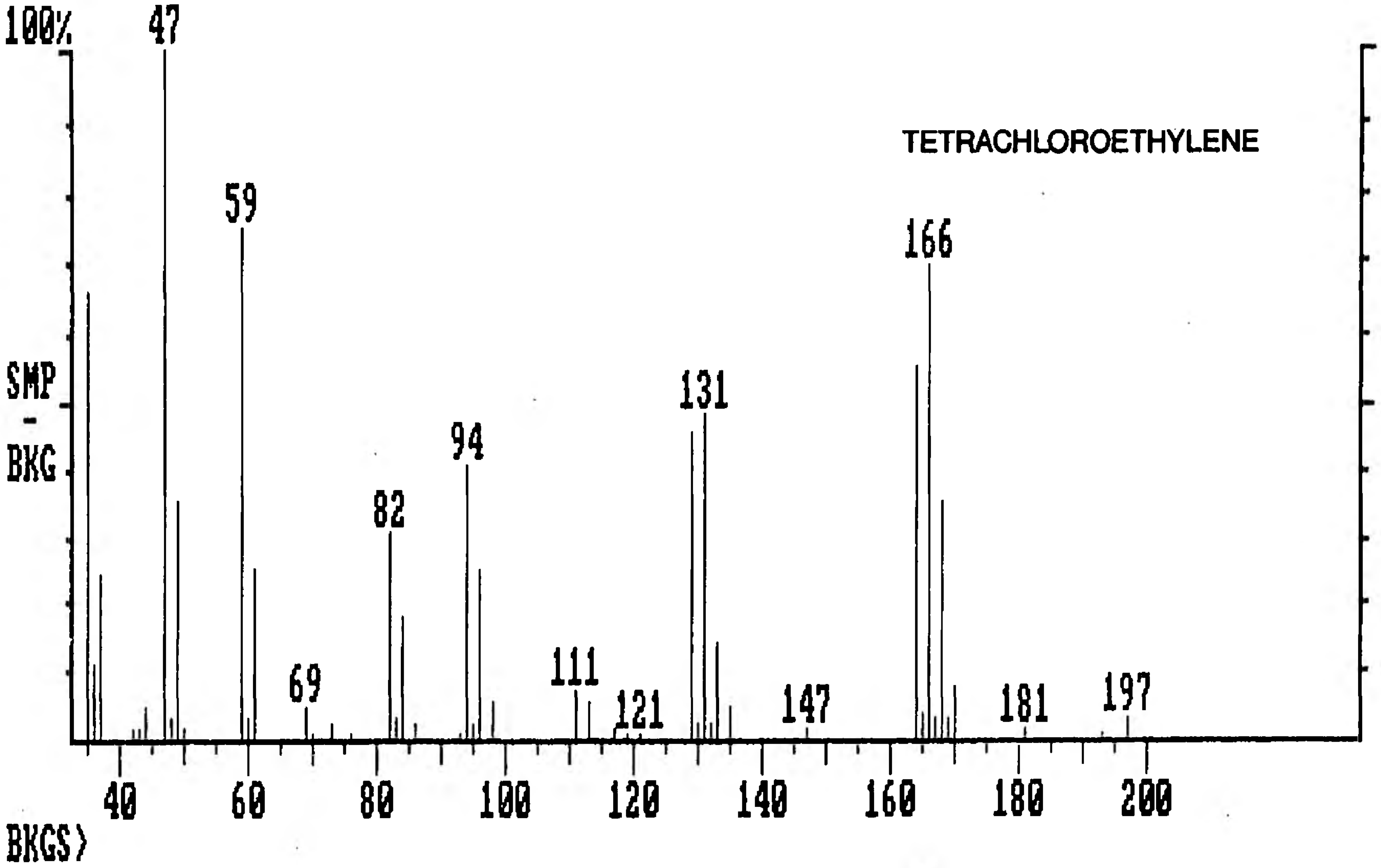
100% = 831



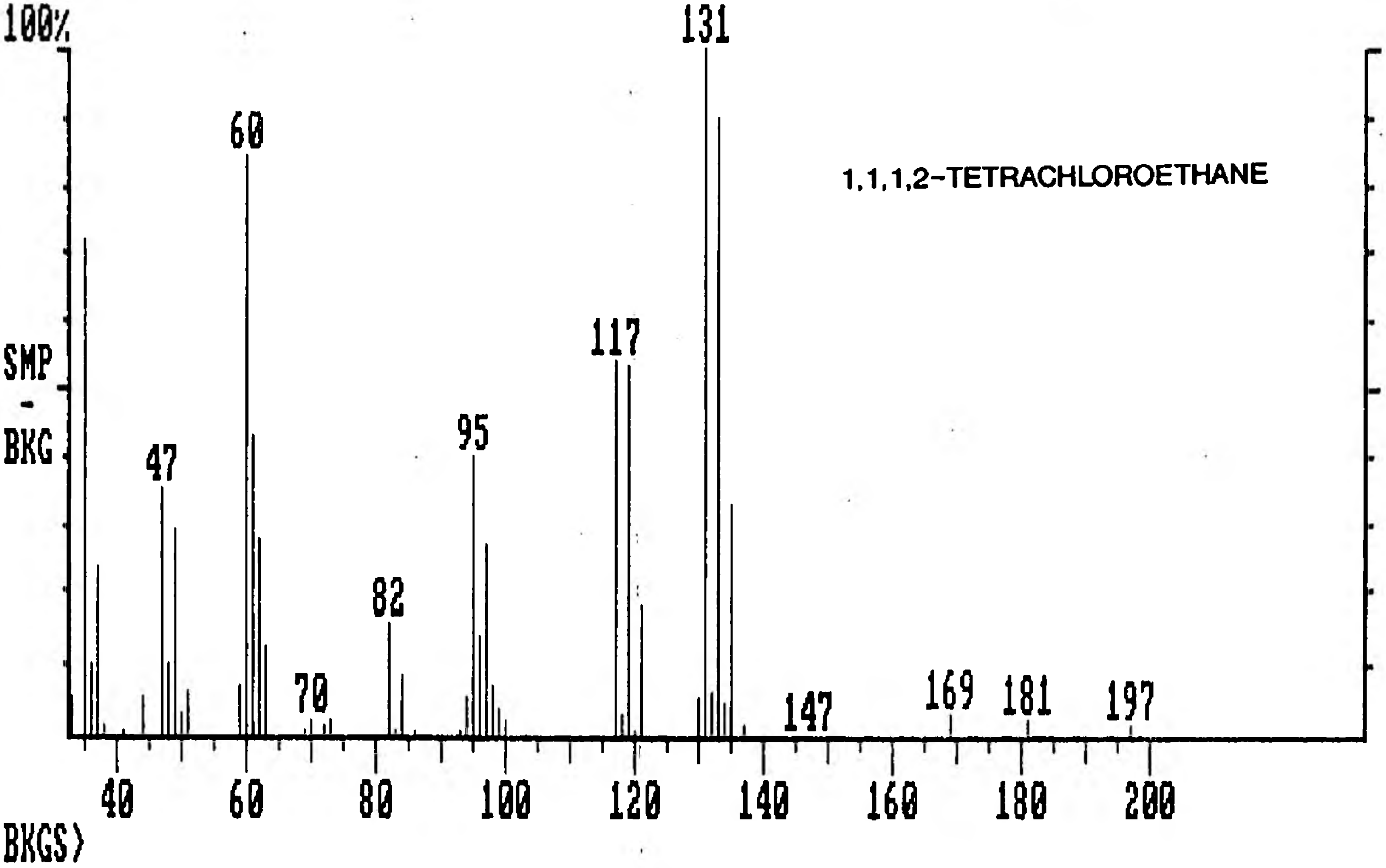
Background Subtract   Filename: REDLIST3   Acquired: Jan-04-1980 03:43:48
Comment: RED LIST STDS TEST 3
Average of: 711 to 723 Minus: 727 to 739   100% = 832



Background Subtract   Filename: REDLIST3   Acquired: Jan-04-1980 03:43:48
Comment: RED LIST STDS TEST 3
Average of: 1031 to 1042 Minus: 1045 to 1055   100% = 743

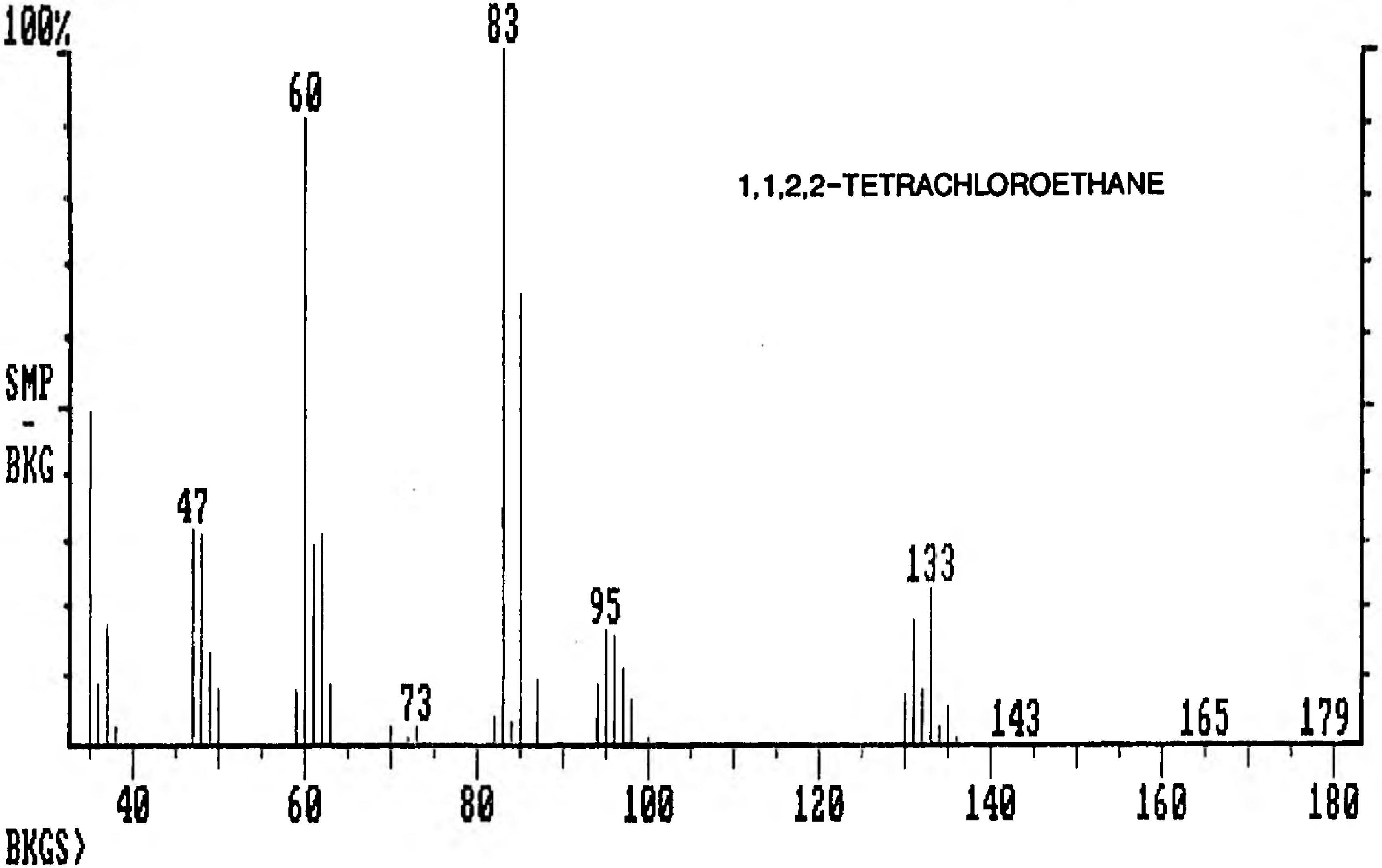


Background Subtract Filename: REDLIST3 Acquired: Jan-04-1980 03:43:48
Comment: RED LIST STDS TEST 3
Average of: 1156 to 1163 Minus: 1167 to 1179 100% = 837



1,1,1,2-TETRACHLOROETHANE

Background Subtract Filename: REDLIS17 Acquired: Feb-26-1992 17:38:53
Comment: RED LIST TEST STD 10MIN PURGE AT 60C\
Average of: 1308 to 1317 Minus: 1320 to 1327 100% = 438



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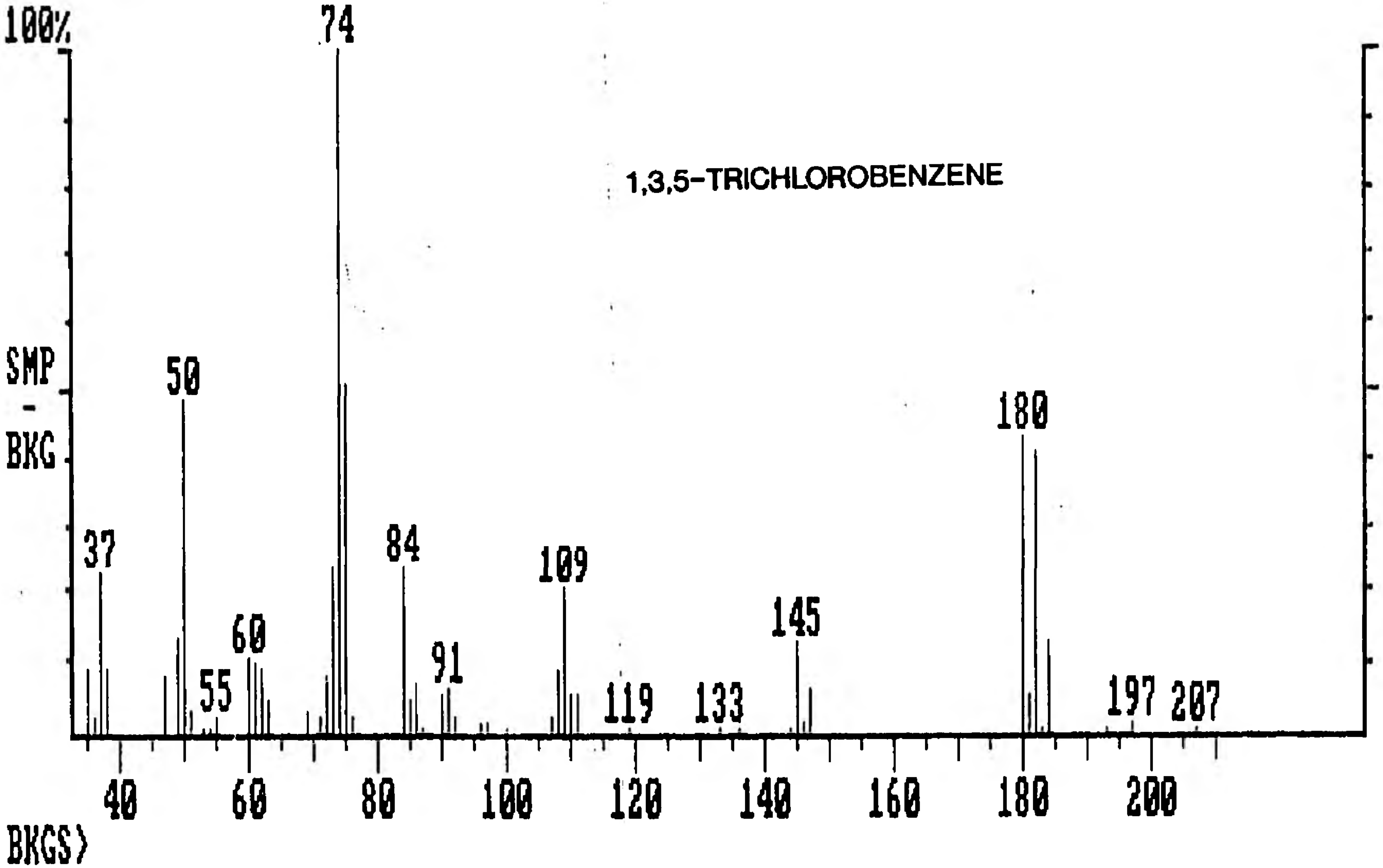
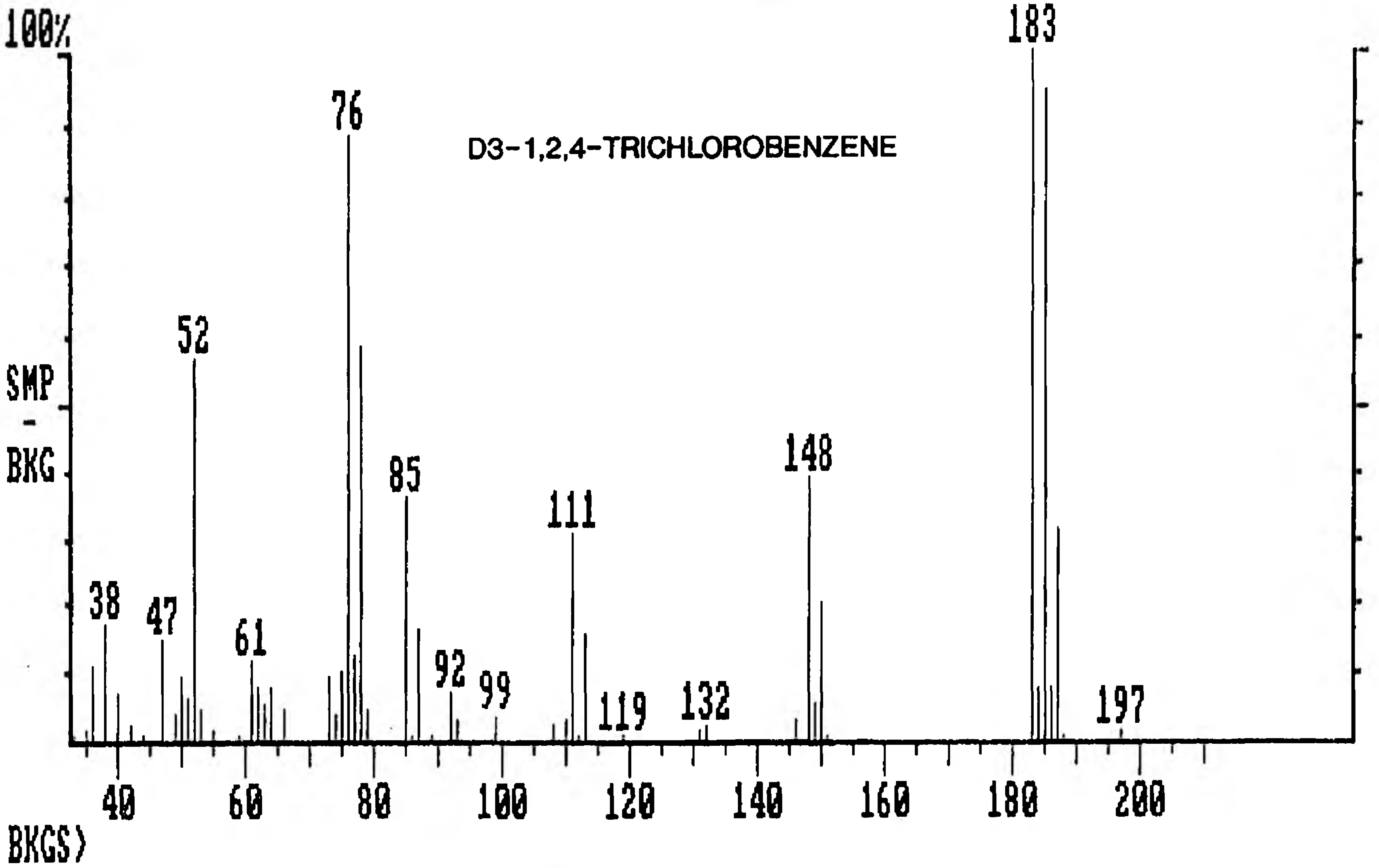
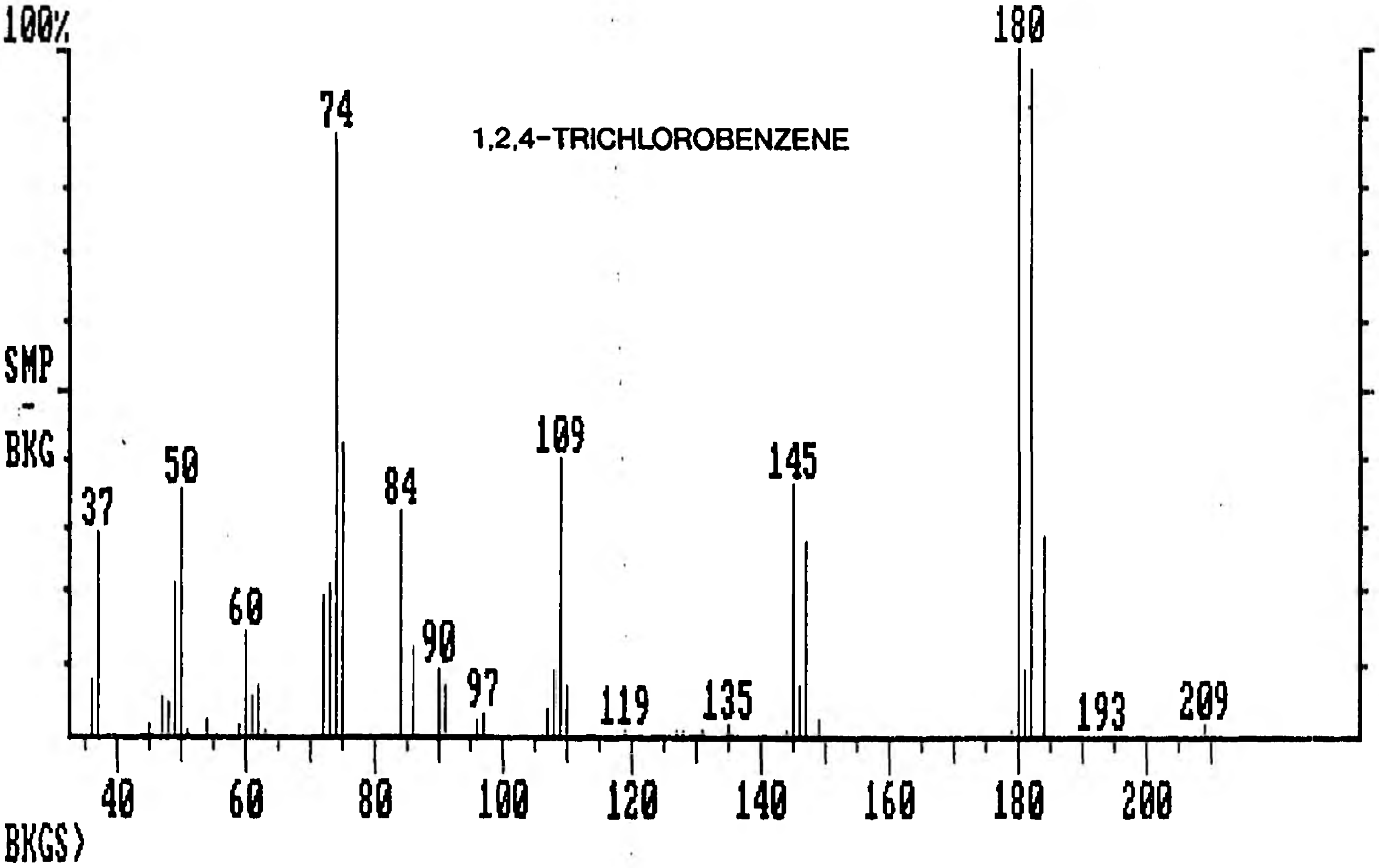
Background Subtract     Filename: REDLIS17       Acquired: Feb-26-1992  17:38:53
Comment: RED LIST TEST STD 10MIN PURGE AT 60C\
Average of: 1648 to 1657  Minus: 1665 to 1673              100% = 252
```


1,3,5-TRICHLOROBENZENE

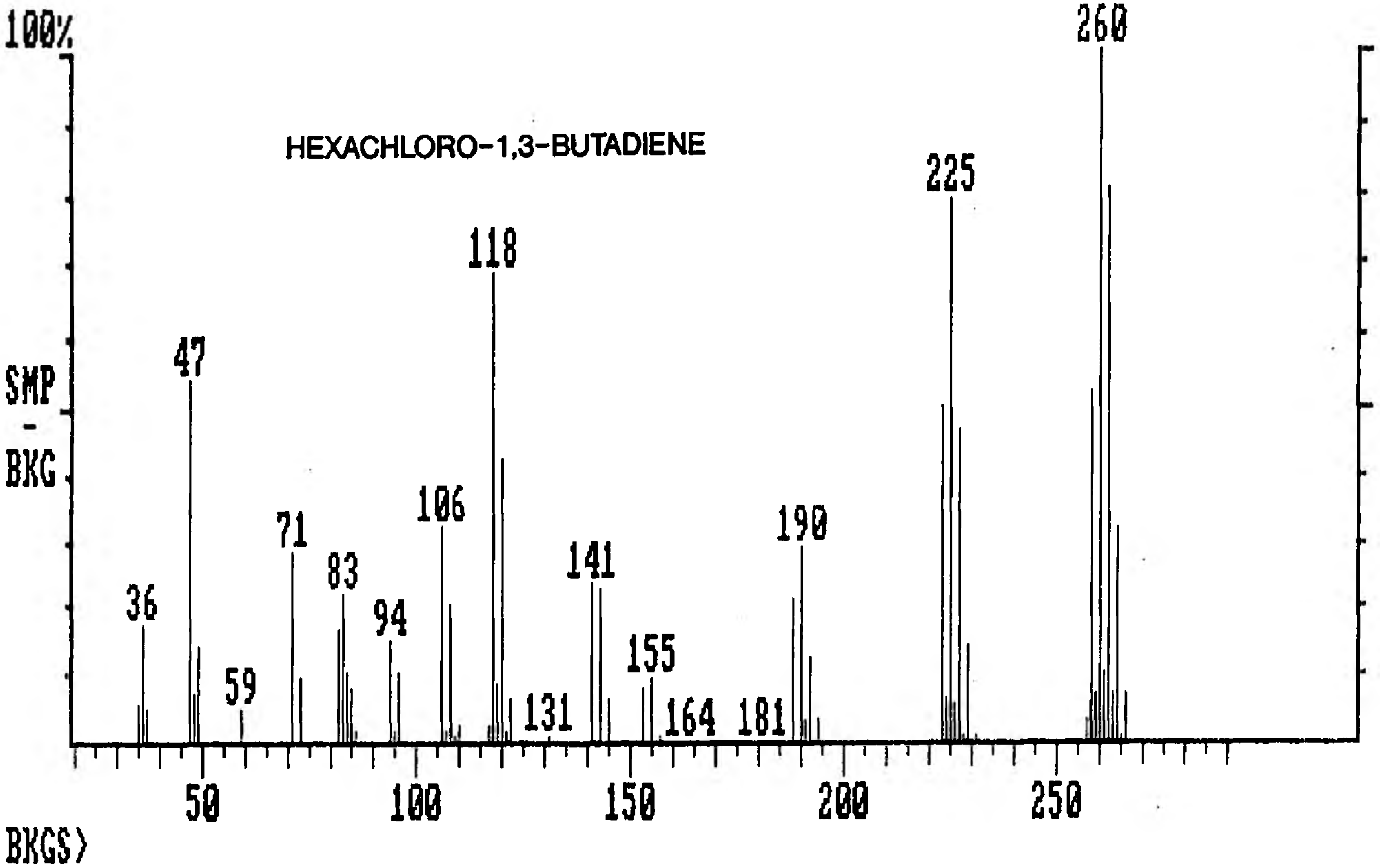
Background Subtract Filename: REDLIS19 Acquired: Feb-27-1992 10:13:28
Comment: RED LIST TEST STD 10MIN PURGE AT 60C\
Average of: 1724 to 1729 Minus: 1730 to 1737 100% = 366


D3-1,2,4-TRICHLOROBENZENE

Background Subtract   Filename: REDLIS20   Acquired: Feb-27-1992 11:54:21
Comment: RED LIST TEST STD 10MIN PURGE AT 60C\
Average of: 1728 to 1733 Minus: 1723 to 1728   100% = 469


1,2,4-TRICHLOROBENZENE

Background Subtract   Filename: REDLIS23   Acquired: Jan-01-1980 03:41:01
Comment: RED LIST TEST STD 20MIN PURGE AT 60C
Average of: 1748 to 1756 Minus: 1759 to 1768   100% = 1421



```
Background Subtract     Filename: REDLIS21       Acquired: Feb-27-1992  14:21:08
Comment: RED LIST TEST STD 10MIN PURGE AT 60C\
Average of: 1785 to 1793  Minus: 1798 to 1809                   100% = 35
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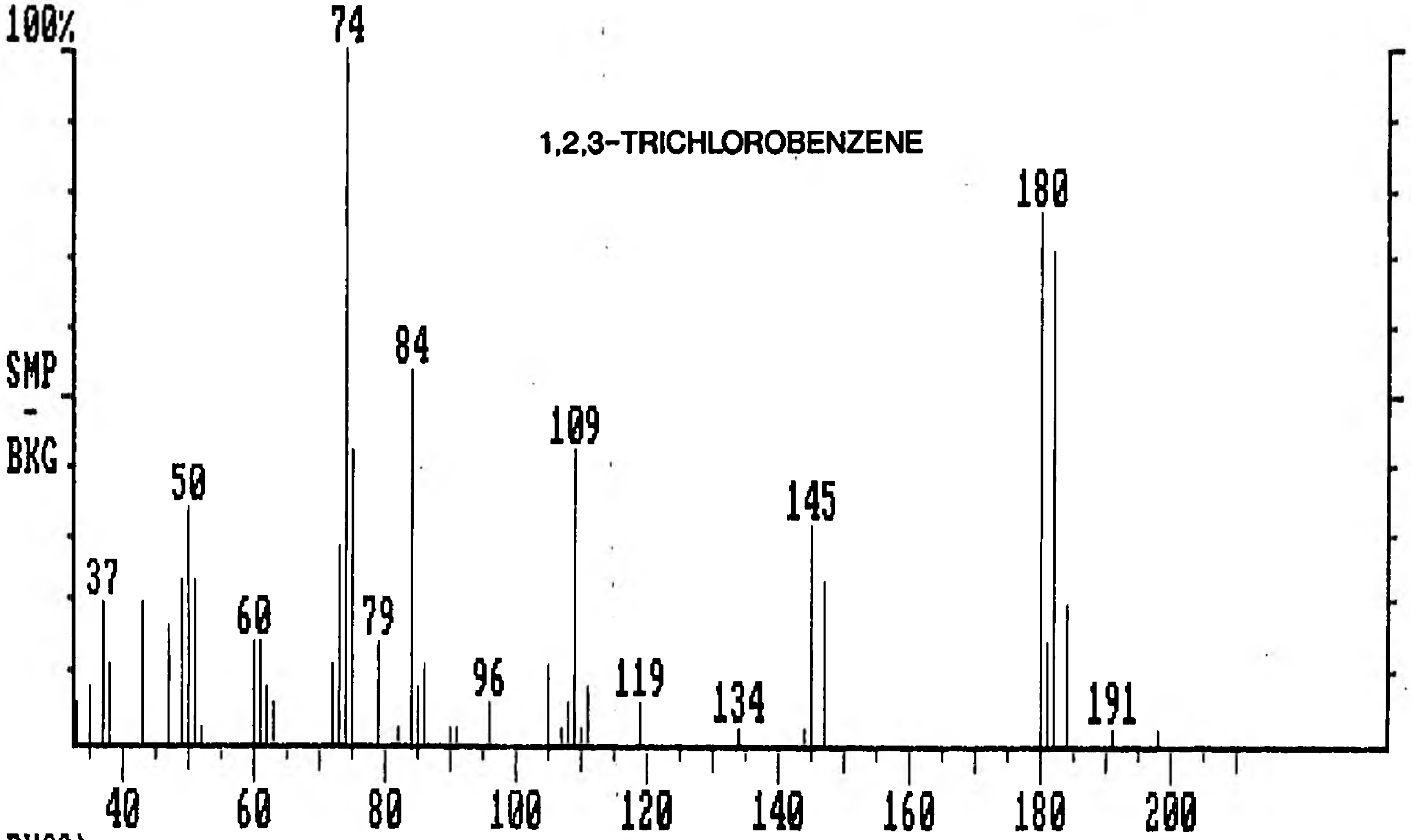

1,2,3-TRICHLOROBENZENE

```
BKGS>
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Background Subtract Filename: RLBLANK3 Acquired: Mar-15-1992 13:58:50
Comment: RED LIST BLANK + 1NG/L INT STDS 15-03-92
Average of: 1149 to 1157 Minus: 1160 to 1167 100% = 1915