DIOXATHION ANALYTICAL METHOD
SW846 METHOD 8141

FOR

HERCULES, INCORPORATED
HATTIESBURG, MS

BY

BONNER ANALYTICAL TESTING COMPANY
2703 OAK GROVE ROAD
HATTIESBURG, MS 39402
601-264-2854

BONNER ANALYTICAL TESTING COMPANY
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"Testing Your World for a Safer Tomorrow"

August 3, 1999

MS State Hand Chemistry Lab
112 Hand Lab
Morillo Road
MS State, MS 39762
Attn: Dr. Larry G. Lane
Director IAS Division

Dear Dr. Lane:

I am submitting some data that we have developed at our laboratory in Hattiesburg while attempting to run a dioxathion MDL study for Hercules, Incorporated. After you have had an opportunity to look at this data, please let me know what you think. The following is an overview of our findings:

1. We used Method 8141 with an FPD detector and an RTX-5 Megabore column. I believe that is the same column you are using. Our carrier gas flow rates probably are not exactly the same as yours so we will rely on RRTs to make comparisons.

2. What we have found is this. We are getting 2 peaks in the standard that you supplied to us.

3. The first peak (RRT = 0.670) appears to be the same as the peak that your lab found (see chromatogram supplied by your lab).

4. The second peak (RRT = 2.47) did not show up in your chromatogram, but did in our analysis. We found the second peak at a retention time at 32 minutes.

5. We have analyzed the standard a number of times and find that both peaks are reproducible.

6. We have submitted some mass spec data for both peaks. We did this on an HP quadrupole. The NBS Library is calling peak #2 dioxathion. Note that both the Library mass spectrum and the standard mass spectrum do not exhibit a molecular weight ion.

7. We also ran some experiments at injection port temperatures of 140°C, 190°C, and 220°C. What we see is that peak #1 is about 1.5% of peak #2 at 140°C, but at 220°C, peak #1 is about 15% of peak #2. It looks like peak #1 may be degradation product.

8. We have also analyzed a new sample from MW4. We ran at an injection port temperature of 140°C and 220°C. Interestingly, we found peak #1 but not peak #2 in the well sample. We also spiked a MW4 sample with standard dioxathion. We found peak #2 in the spiked sample.

9. We have previously reported dioxathion, or an organo-phosphate compound that matches it, in MW4 at levels around 30 ppb. We have quantitated on peak #2 in our work.

Our next step is to perform an MDL study. At this point it appears that peak #2 is the appropriate peak to evaluate. Before we go forward with our study, I would like to know what your thoughts are. If you have any questions regarding the data I have sent, please give me a call.

Sincerely,

Michael S. Bonner, Ph.D.

cc: Tony Russell, MDEQ
Charlie Jordan, Hercules – Hattiesburg, MS
Frank Carlin, Consultant
Tim Hassett, Hercules

TABLES

TABLE 1

DIOXATHION STANDARD PEAK AREA AS A FUNCTION OF INJECTION PORT TEMPERATURE USING A 100PPM STANDARD

	8:86 min Peak Area Injtemp (140°)	8:86 min Peak Area State (190°)	8:86 min Peak Area StateB (220°)	32:75 min Peak Area Injtemp (140°)	32:75 min Peak Area State (190°)	32:75 min Peak Area StateB (220°)
Run						
A	3,661,503	26,835,902	38,271,410	211,997,570	223,039,399	251,926,013
B	3,309,698	26,943,578	36,997,275	220,528,545	223,581,528	248,093,036
C	3,596,355	24,704,408	35,980,523	224,749,442	227,063,957	252,268,801
D	3,400,280	25,851,068		229,224,594	228,092,392	
E	3,179,532	24,262,766		231,234,855	231,778,415	
F	3,472,164	25,228,732		233,495,837	232,701,733	
G	3,519,928	24,982,250		235,144,114	234,932,804	
AVERAGE	3,448,494	25,544,101	37,083,069	226,624,994	228,741,461	250,762,617
STDDEV	166747.4495	1039515.296	1147850.736	8189816.301	4575538.254	2318269.097

Chlorpyrifos Surrogate Peak Areas

Chlorpyrifos Peak Area Injtemp (140°)	Chlorpyrifos Peak Area State (190°)	Chlorpyrifos Peak Area StateB (220°)
4,321,251	4,748,962	5,005,377
4,455,198	4,662,562	5,221,548
4,524,343	4,667,440	5,181,867
4,457,611	4,921,065	
4,517,534	4,927,239	
4,633,435	4,740,706	
4,258,214	4,773,053	
AVERAGE 4,452,512	4,777,290	5,136,264
STDDEV 127236.6969	108431.4734	115074.7606

TABLE 2

HERCULES MW#4 WATER ANALYSIS AT INJECTION PORT TEMPERATURES OF 140° AND 220°

							Dioxathion							
SAMPLE	Recovery 140°	Recovery 220°	Chlorpyrifos Area 140°	PPB 140°	Chlorpyrifos Area 220°	PPB 220°	8:71 Peak Area 140°	PPB 140°	8:71 Peak Area 220°	PPB 220°	32.66 Peak Area 140°	PPB 140°	32.66 Peak Area 220°	PPB 220°
Method Blank	76.22	74.15	4,137,086	762	3,780,227	741	0	0	0	0	0	0	0	0
Matrix Spike	81.95	87.23	4,447,751	819	4,447,060	872	0	0	290,229	8.51	2,509,675	850	2,334,860	9.16
Matrix Spike Dup	80.56	81.16	4,137,476	806	4,137,747	812	0	0	287,473	8.43	2,679,758	907	2,530,033	9.92
Trip Blank	85.04	89.87	4,615,665	850	4, 582,008	899	0	0	0	0	0	0	0	0
Equipment Blank	82.27	86.04	4,465,425	823	4,386,597	860	0	0	0	0	0	0	0	0
BT55743	68.71	71.38	3,728,960	687	3,639,118	714	25,924,837	1122	25,612,299	751	0	0	0	0
BT55743Spike	75.91	77.62	4,119,948	759	3,957,297	776	29,834,150	1292	29,148,836	855	2,569,818	870	2,322,462	9.11

TABLE 3

A Comparison of Dioxathion Standard Curve Peak Areas at Injecton port Temperatures of 140°C and 220°C

CONCENTRATION OF DIOXATHION (PPB)	AREA Peak #1 8:17 @ 220°	AREA Peak #2 32:67 @ 220°	AREA Peak #1 8:17 @ 140°	AREA Peak #2 32:67 @ 140°
10	0	0	0	0
100	48,744	211,555	0	317,593
500	172,273	1,342,216	0	1,525,991
1000	325,255	2,818,252	0	3,022,982
10000	3,354,621	30,357,694	271,286	35,727,623
100000	28,060,253	260,319,076	1,823,342	287,369,745
LINEARITY	0.999816732	0.999859964	0.99854932	0.999699157

APPENDIX 1

1A – Chromatogram Supplied by MS State
Run #1171 – 3.22 ng of Dioxathion
RT = 11.36 min

1B – Chromatogram Supplied by MS State
Run #1169 – 0.432 ng Chlorpyrifos
RT = 15.66 min
RRT = 0.723

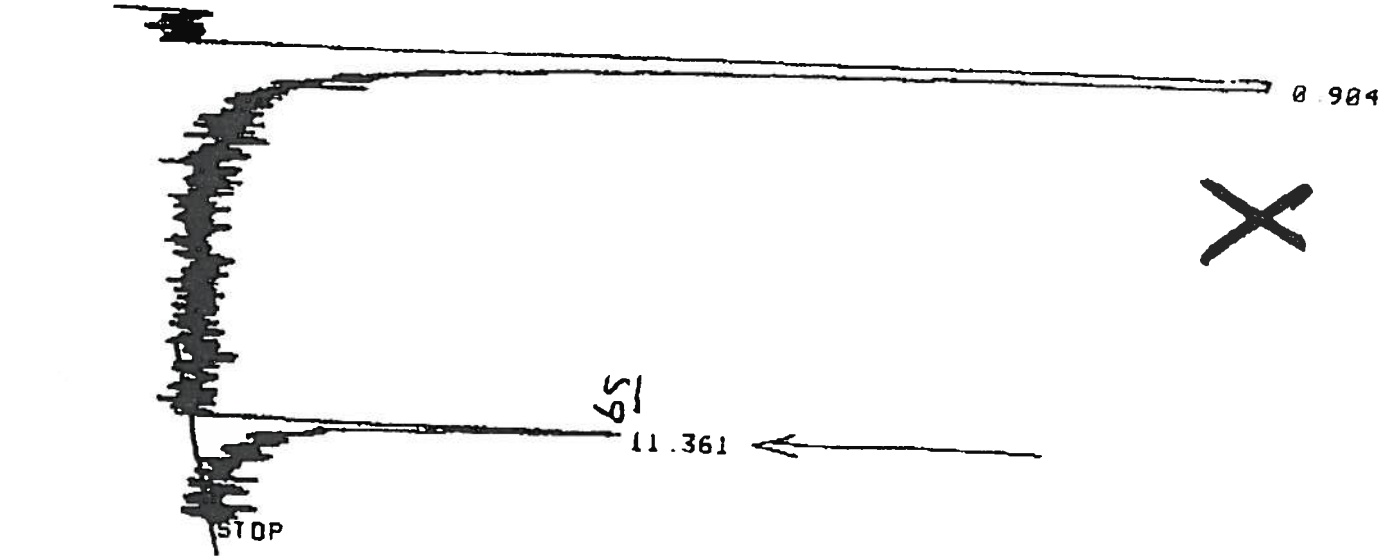
1C – Chromatogram Supplied by MS State
Run #1180
Hercules MW4
Dioxathion = 805ppb

MUL FACTOR=1.0000E+00

Miss State Chromatogram # 1
Dioxathion 4D.

*NOTEPAD

(USE BREAK OR CONTROL-Y TO END)
3.22 NG DIOXATHION
* RUN # 1171 SEP 30, 1998 04:10:37
START



RUN# 1171 SEP 30, 1998 04:10:37

AREAX

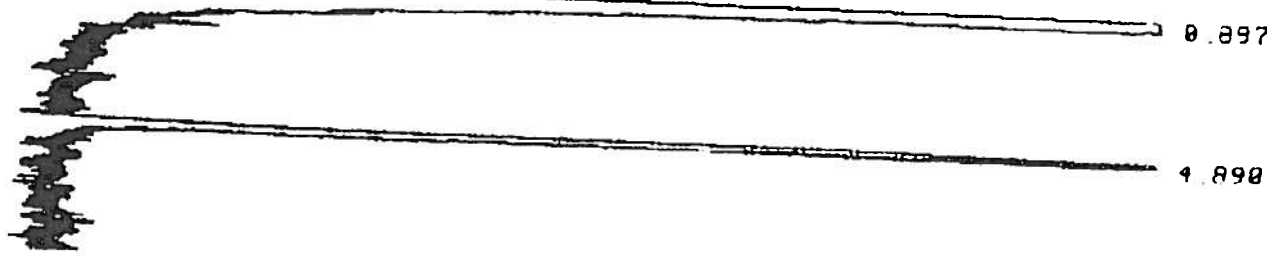
RT	AREA	TYPE	WIDTH	AREA%
.904	1496460	PB	.119	96.03987
11.361	61705	BV	.164	3.96011

TOTAL AREA=1558165
MUL FACTOR=1.0000E+00

Varian 3600 - FPD/P
DB-5 Megabore

*NOTEPAD

(USE BREAK OR CONTROL-Y TO END)
100 NG SP WATER
* RUN # 1172 SEP 30, 1998 04:31:19
START



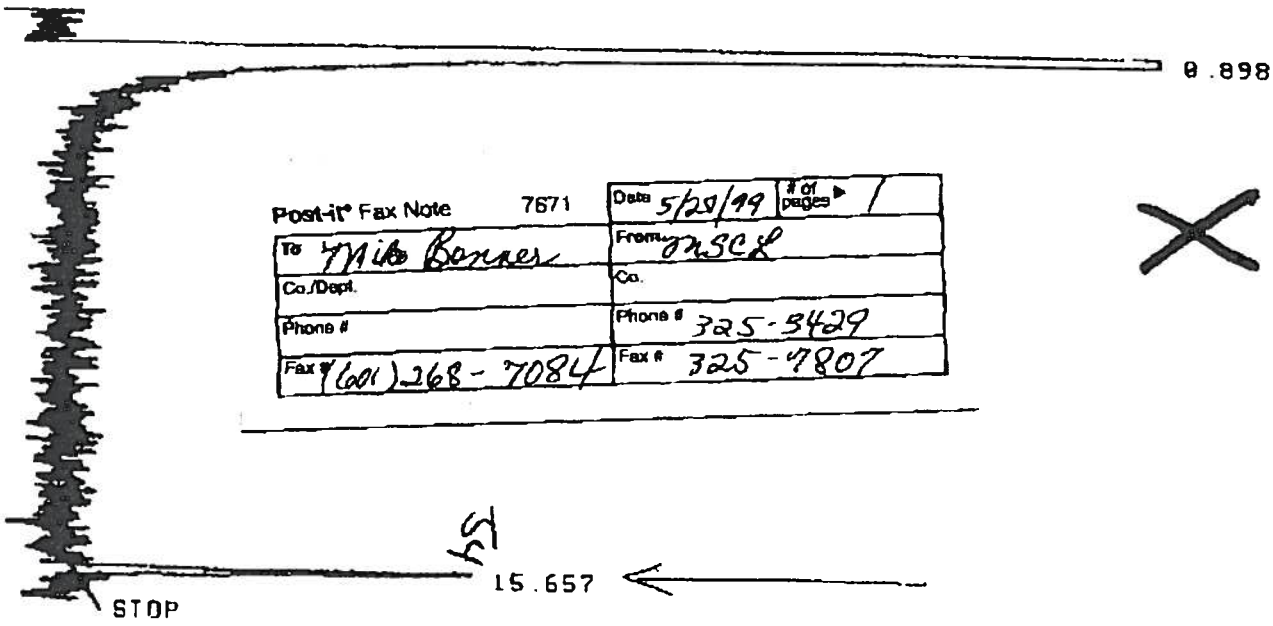
Appendix I-A

THRSH = 1
PK WD = 0 04

Miss State Chromatogram
Chlorpyrophos #2

*NOTEPAD

(USE BREAK OR CONTROL-Y TO END)
0.432 NG CHLORPYRIFOS
* RUN # 1169 SEP 30, 1998 03:33:40
START



Post-it® Fax Note 7671	Date 5/20/99	# of pages ▶ 1
To Mike Bonner	From JASCO	
Co./Dept.	Co.	
Phone #	Phone # 325-3429	
Fax # (601) 368-7084	Fax # 325-7807	

RUN# 1169 SEP 30, 1998 03:33:40

AREA%

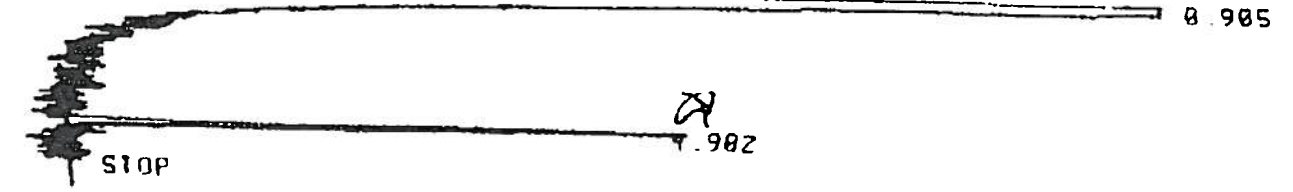
RT	AREA	TYPE	WIDTH	AREA%
.898	1589077	PB	.125	96.52694
15.657	57175	PU	.149	3.47306

TOTAL AREA=1646252
MUL FACTOR=1.0000E+00

Varian 3600-FPD/P
DW-V Measure

*NOTEPAD

(USE BREAK OR CONTROL-Y TO END)
0.393 NG CHLORMEPHOS
* RUN # 1170 SEP 30, 1998 04:00:03
START



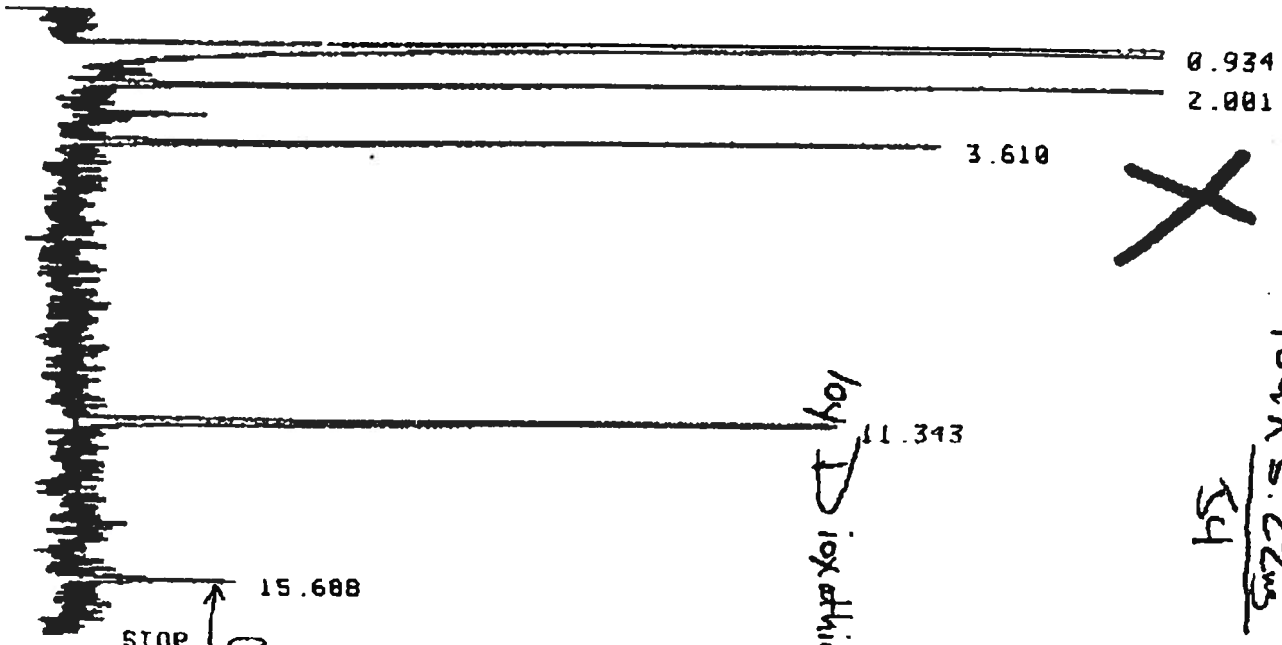
Appendix 1-B

TOTAL AREA=2585925
MUL FACTOR=1.0000E+00

Miss State Chromatogram #3

*NOTEPRO

(USE BREAK OR CONTROL-Y TO END) Groundwater from Hercules MW-c
7.7 MG 10896
* RUN # 1180 OCT 1, 1998 01:18:12
START



Chloroform
Dichlorobromomethane
Trichloroethene

RUN# 1180 OCT 1, 1998 01:18:12

AREA%

RT	AREA	TYPE	WIDTH	AREA%
.934	710178	PB	.073	77.16717
2.001	56676	PV	.055	6.15835
3.610	69877	VP	.077	6.50617
11.343	73219	PV	.108	7.95590
15.688	20361	VP	.130	2.21240

TOTAL AREA= 920311
MUL FACTOR=1.0000E+00

$\frac{10\mu X \ 2.22 ng}{5\mu} = \frac{4.20 ng}{7.7 ng} = 80.5 ppb$ Dichlorobromomethane

Varian 3600 - FPD/PFPD-S Megabore

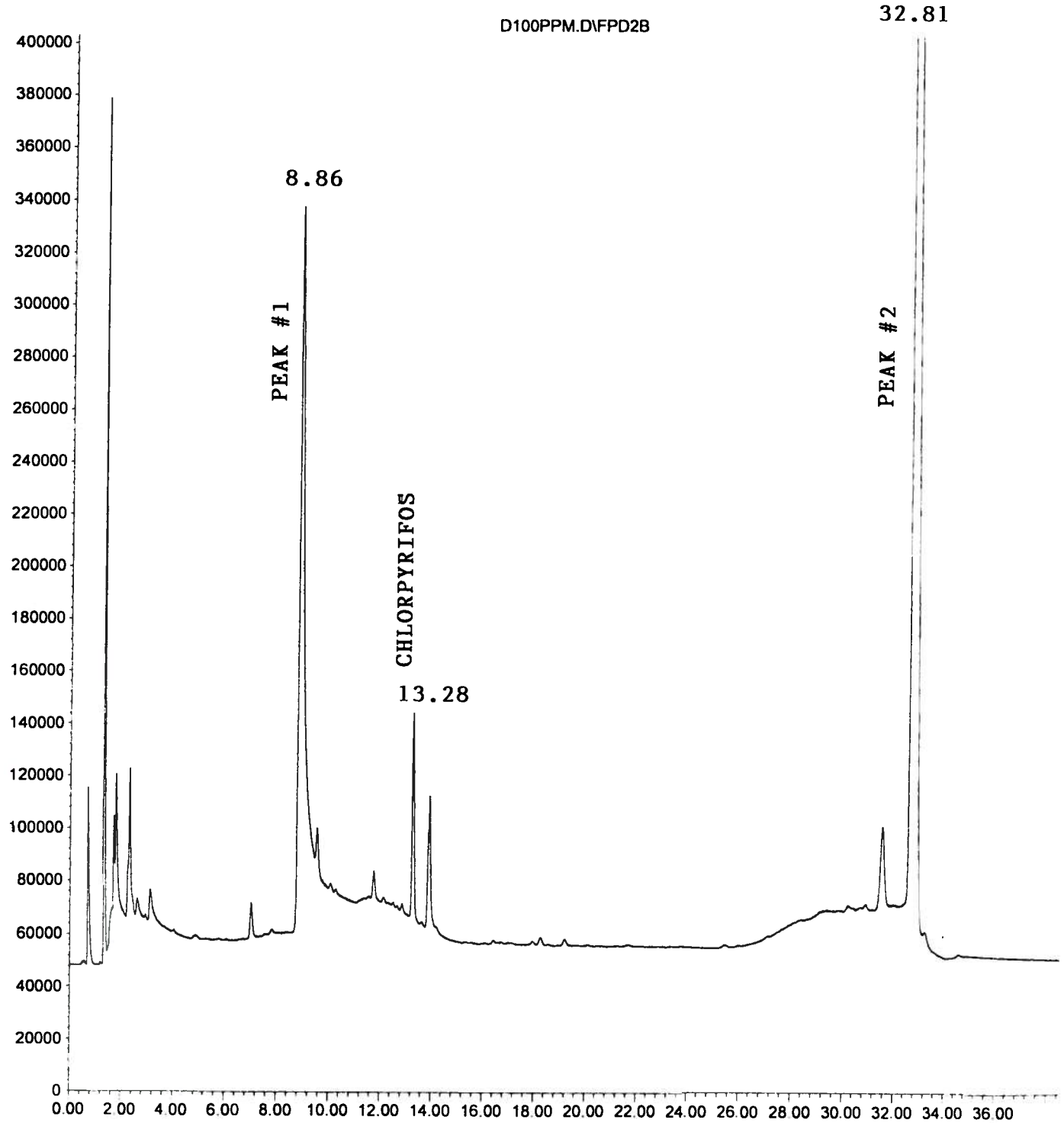
Appendix 1c

APPENDIX 2

2A – Chromatogram of Dioxathion Standard
Supplied by MS State
Peak #1 – RRT = 0.667
Peak #2 – RRT = 2.471

BONNER CHROMATOGRAM
MS STATE STANDARD
DIOXATHION @ 100ppm
GC/FPD

File : C:\HPCHEM\1\DATA\0699\062899\D100PPM.D
Operator : jps
Acquired : 30 Jun 99 12:16 using AcqMethod STATE.M
Instrument : FPD/FID I
Sample Name: Dioxathion @ 100ppm
Misc Info : injection 220
Vial Number: 17



APPENDIX 2A

APPENDIX 3

3A – GC/MS Chromatogram of Dioxathion Standard

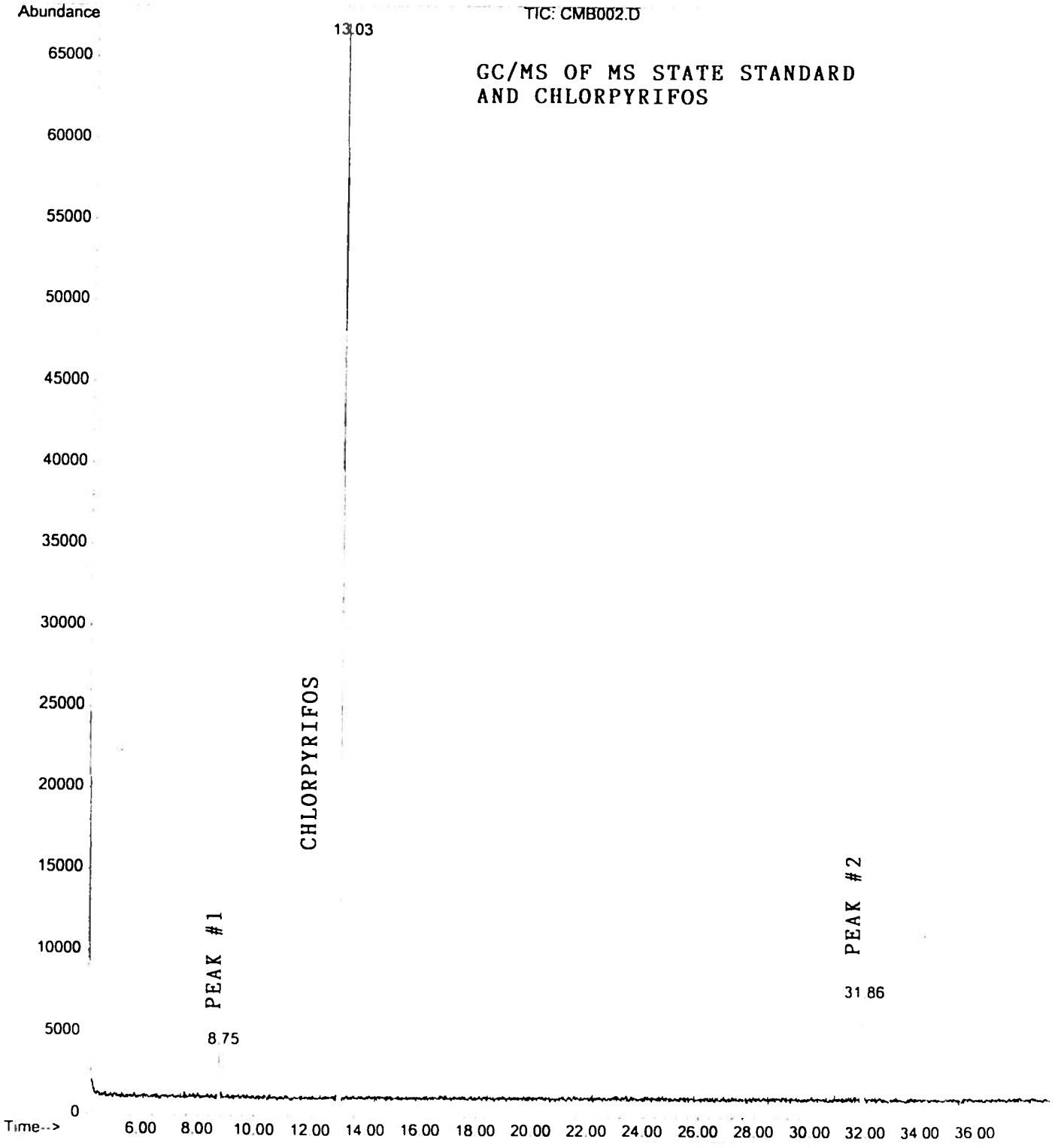
3B – Mass Spectrum Profile of Dioxathion from NBS Library

3C – Mass Spectrum Profile of Peak #2
RRT = 2.445 & RT = 31.9 min
NBS Library Match

3D – Mass Spectrum Profile of Peak #1
RRT = 0.671 & RT = 8.75 min
Does Not Match NBS Library

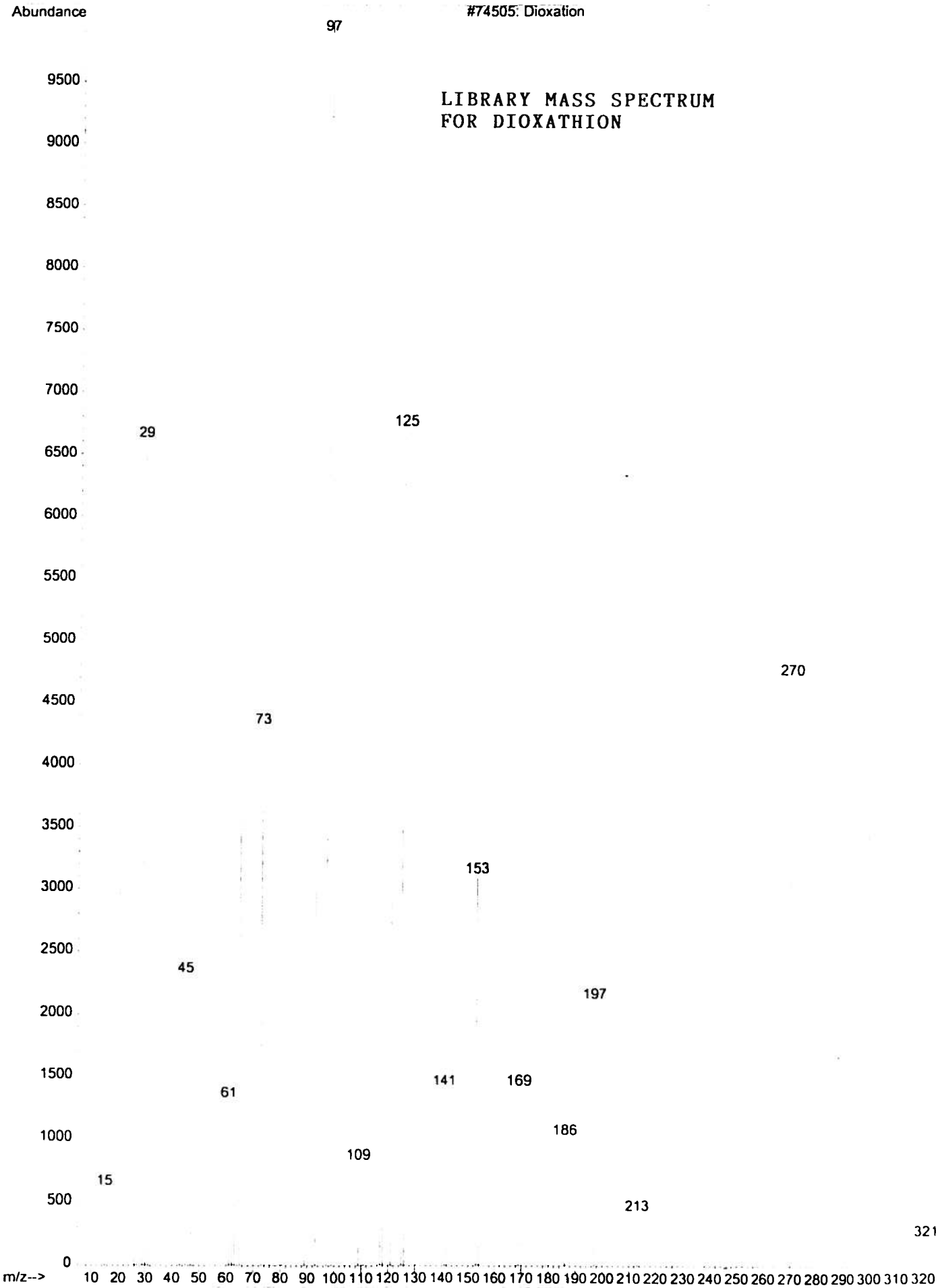
File : C:\HPCHEM\1\DATA\MISC\CMB002.D
Operator : JMR
Acquired : 30 Jun 99 11:09 am using AcqMethod CHRIS
Instrument : GC/MS Ins
Sample Name: Dioxathion/Chlorpyrifos
Misc Info : Det. 200/ Inj 220
Vial Number: 1

NOTE THIS CHROMATOGRAM IS FROM THE GC/MS

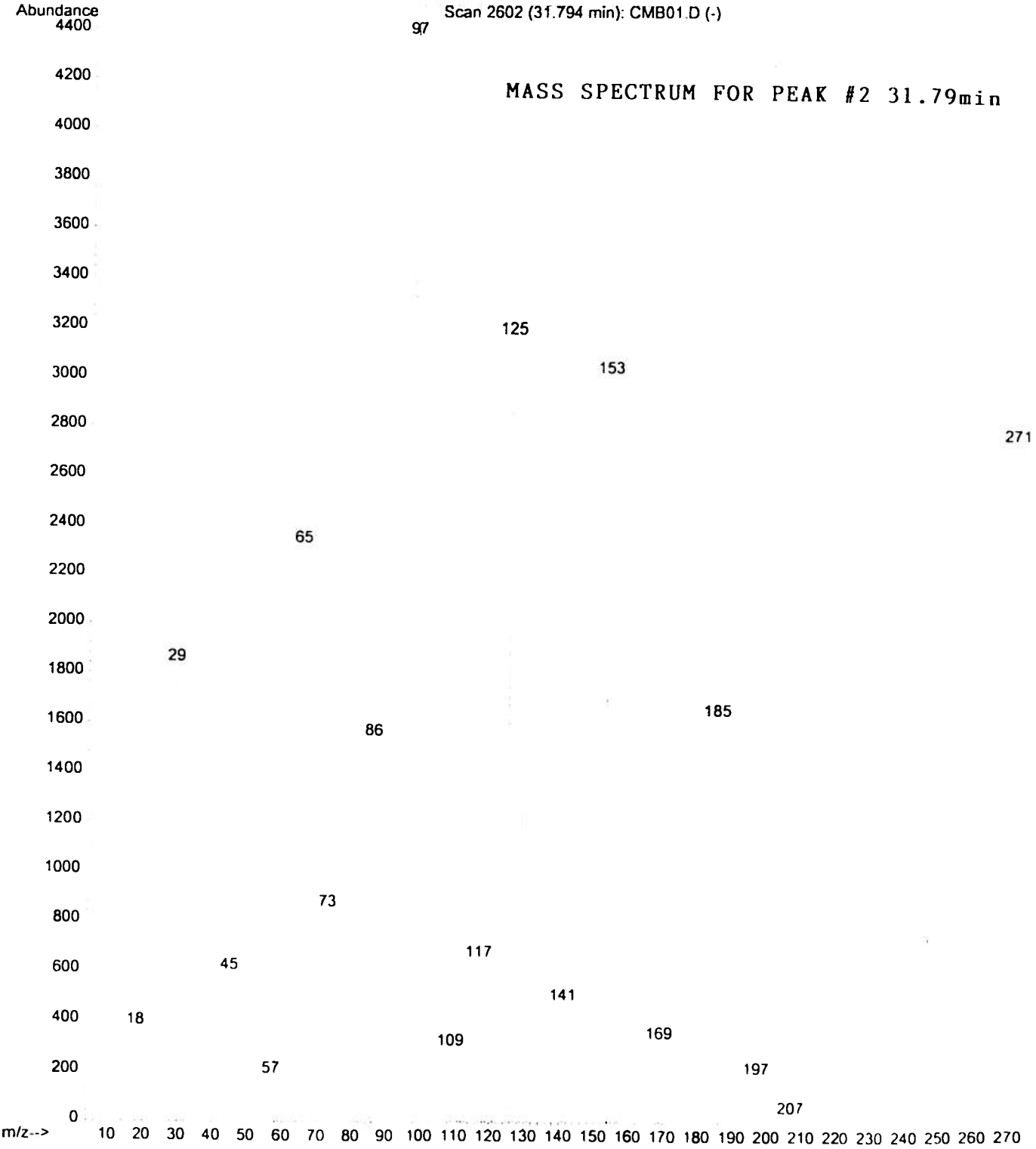


APPENDIX 3A

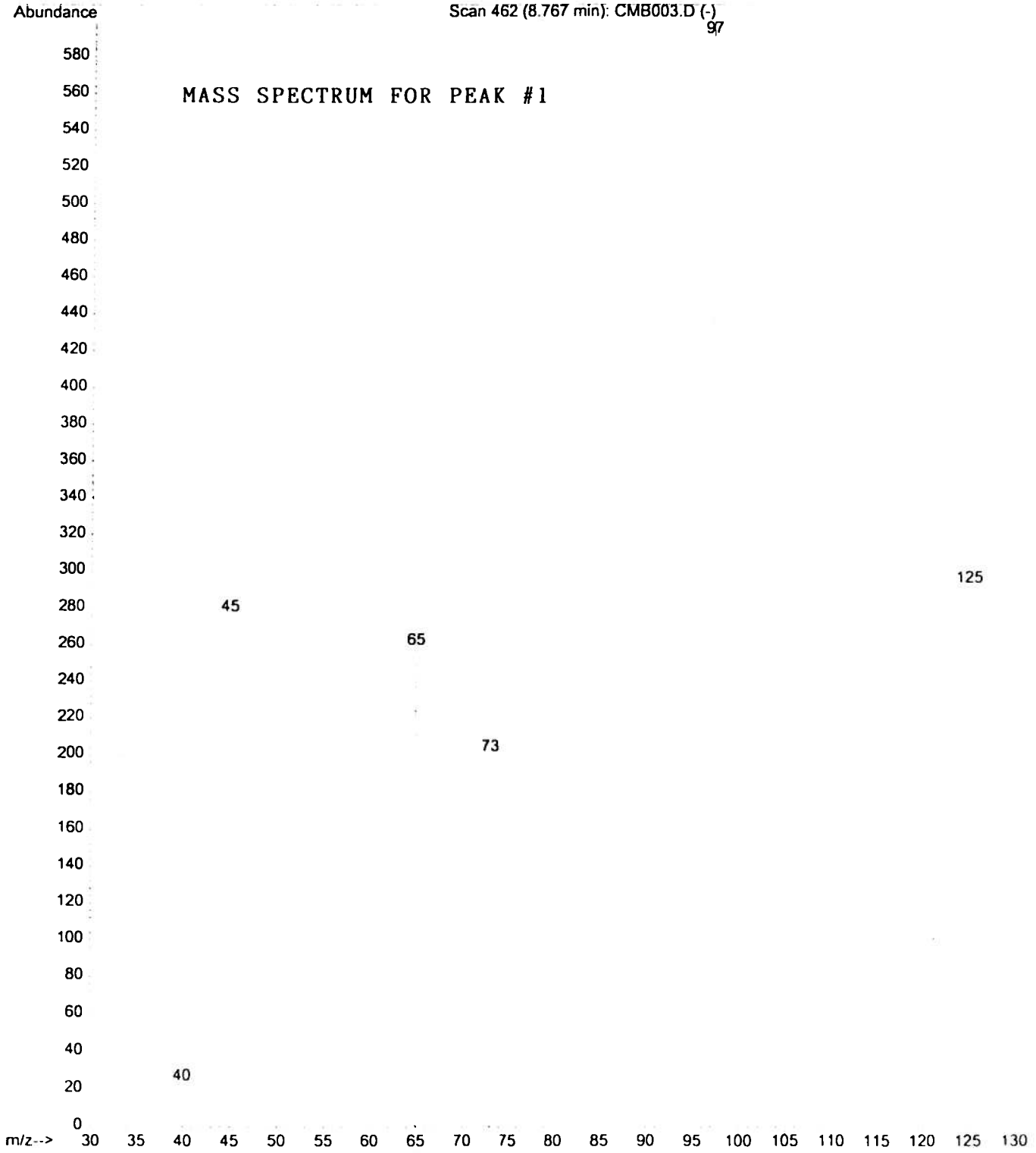
Library : C:\DATABASE\NBS75K.L



File : C:\HPCHEM\1\DATA\MISC\CMB01.D
Operator : cmb
Acquired : 22 Jun 99 11:50 am using AcqMethod CHRIS
Instrument : GC/MS Ins
Sample Name: dioxathion 100ppm
Misc Info : Injector 220 Detector 280
Vial Number: 1



File : C:\HPCHEM\1\DATA\MISC\CMB003.D
Operator : cmb
Acquired : 30 Jun 99 11:57 am using AcqMethod CHRIS
Instrument : GC/MS Ins
Sample Name: Dioxathion(100) no Chloropyrfos
Misc Info : Det. 200/ Inj 220
Vial Number: 1



APPENDIX 4

Raw Data

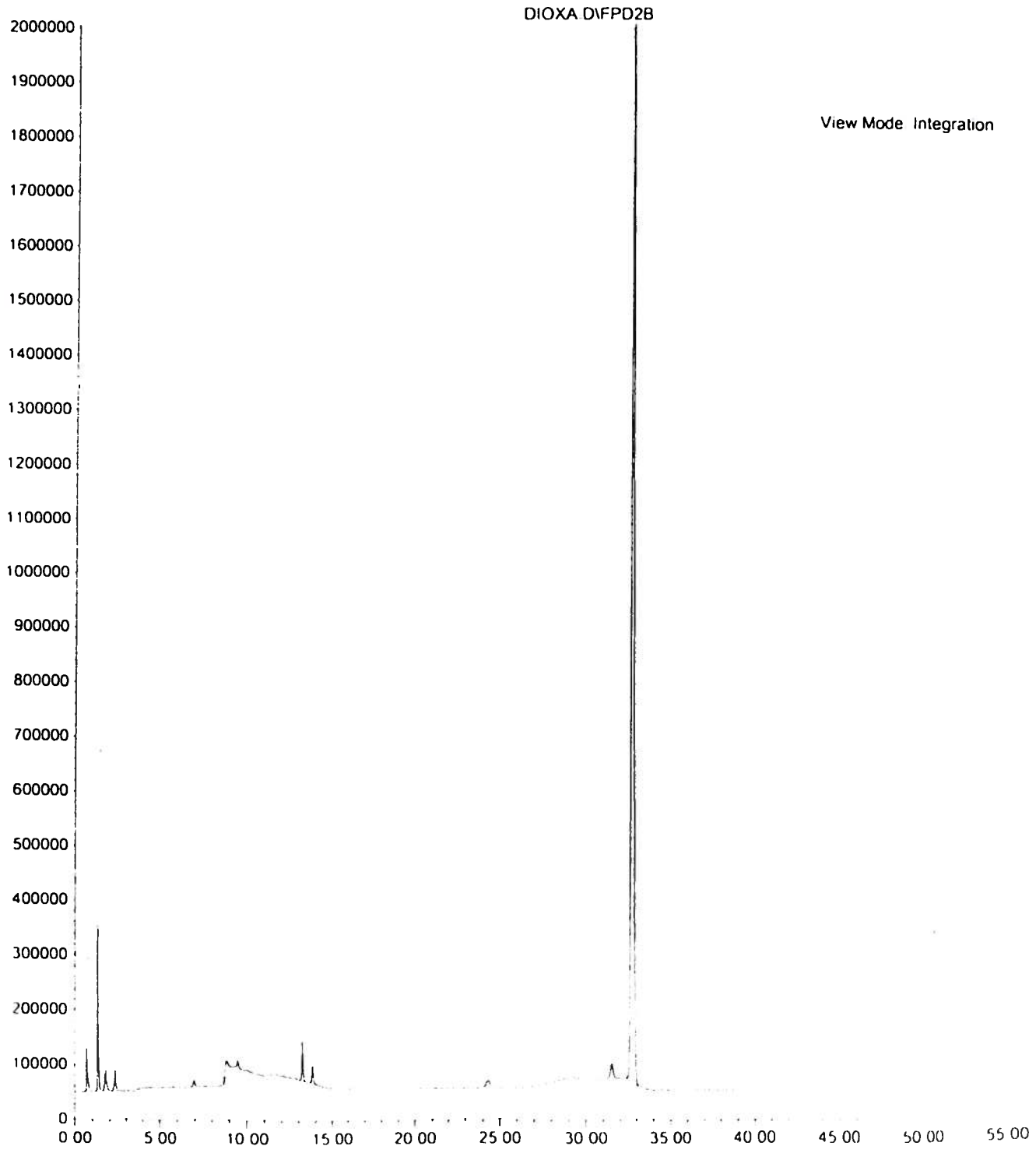
4A – Dioxathion Standard Analyzed at Injection Port of 140°C

4B – Dioxathion Standard Analyzed at Injection Port of 190°C

4C – Dioxathion Standard Analyzed at Injection Port of 220°C

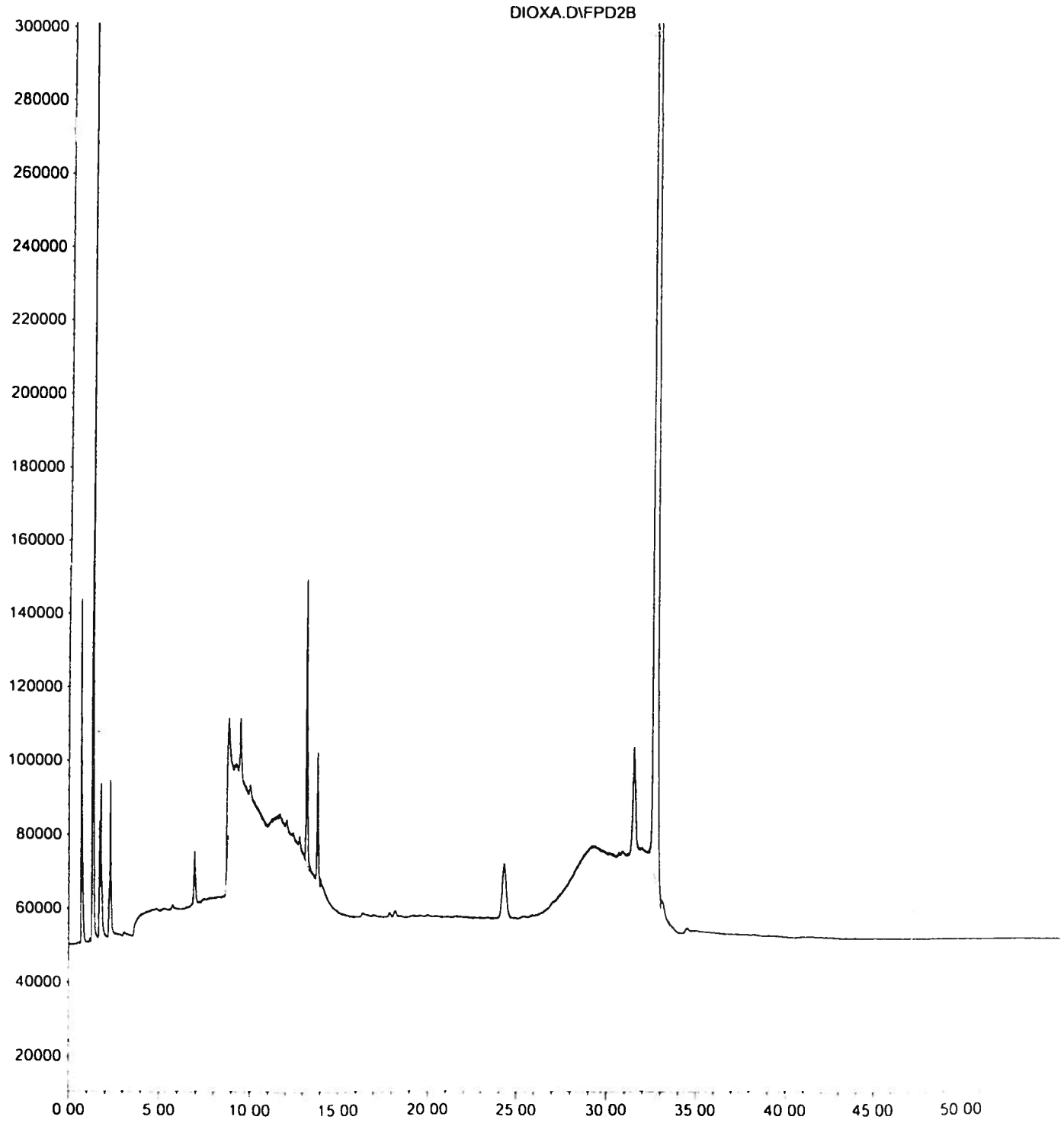
4A – Dioxathion Standard Analyzed at Injection Port of 140°C

File : C:\HPCHEM\1\DATA\072199\DIOXA.D
Operator :
Acquired : 21 Jul 99 15:12 using AcqMethod INJTEMP.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 140 degrees
Vial Number: 3

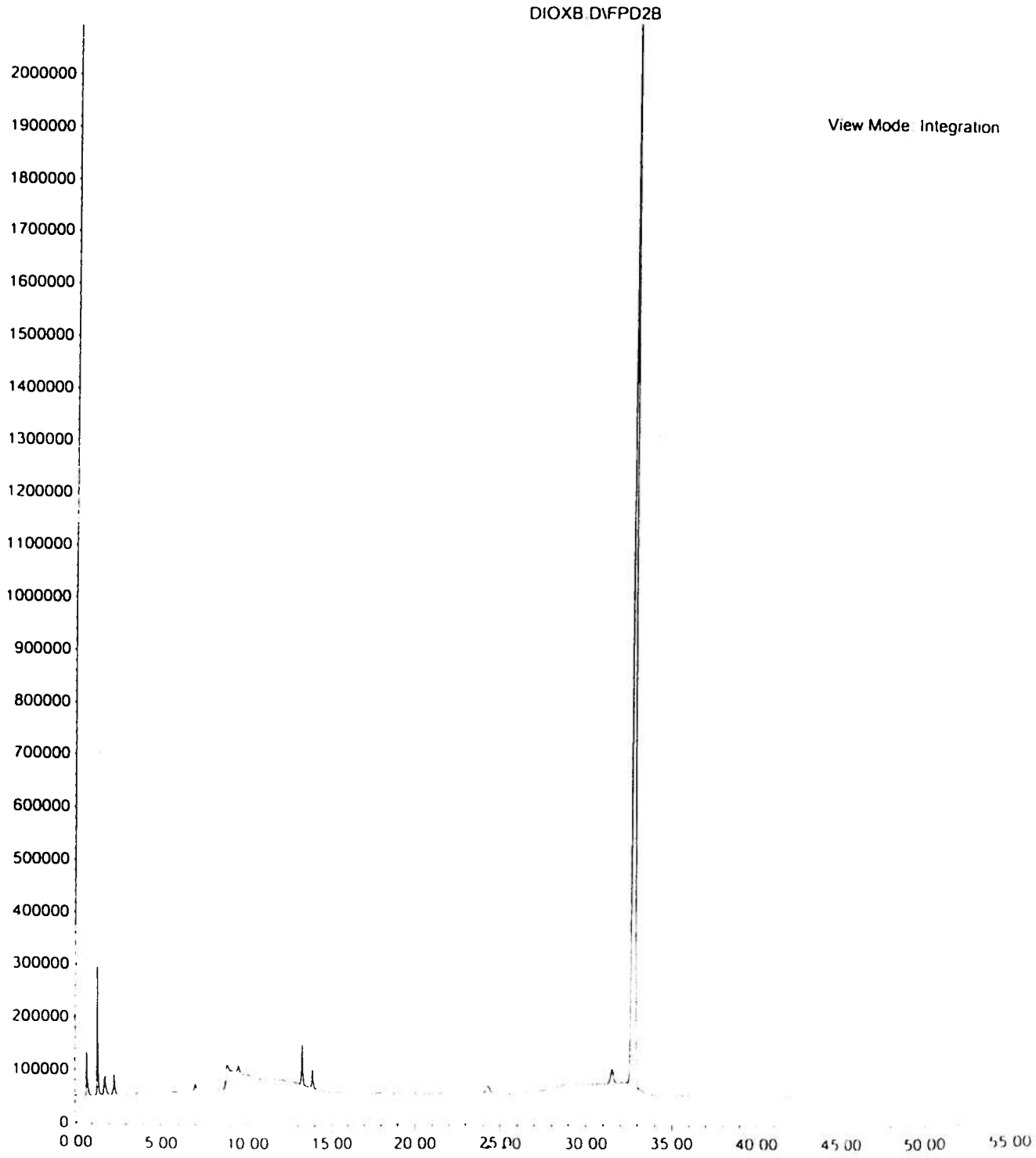


Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.860	M	0.201	3661503	8.655	9.059
2	13.227	M	0.093	4321251	13.098	13.384
3	32.747	M	0.182	211997570	32.434	33.082

File : C:\HPCHEM\1\DATA\072199\DIOXA.D
Operator :
Acquired : 21 Jul 99 15:12 using AcqMethod INJTEMP.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 140 degrees
Vial Number: 3

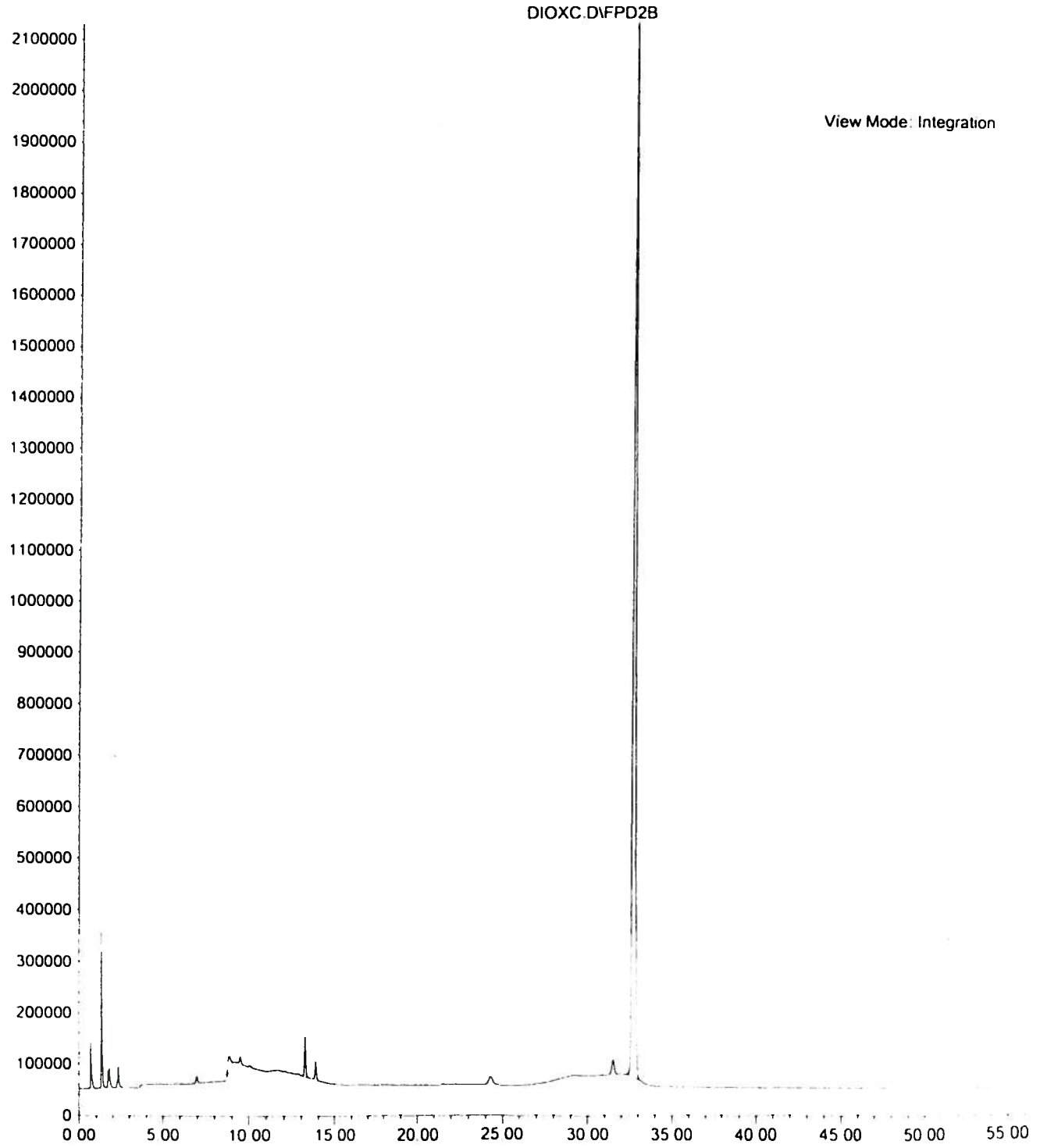


File : C:\HPCHEM\1\DATA\072199\DIOXB.D
Operator :
Acquired : 21 Jul 99 16:34 using AcqMethod INJTEMP.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 140 degrees
Vial Number: 3



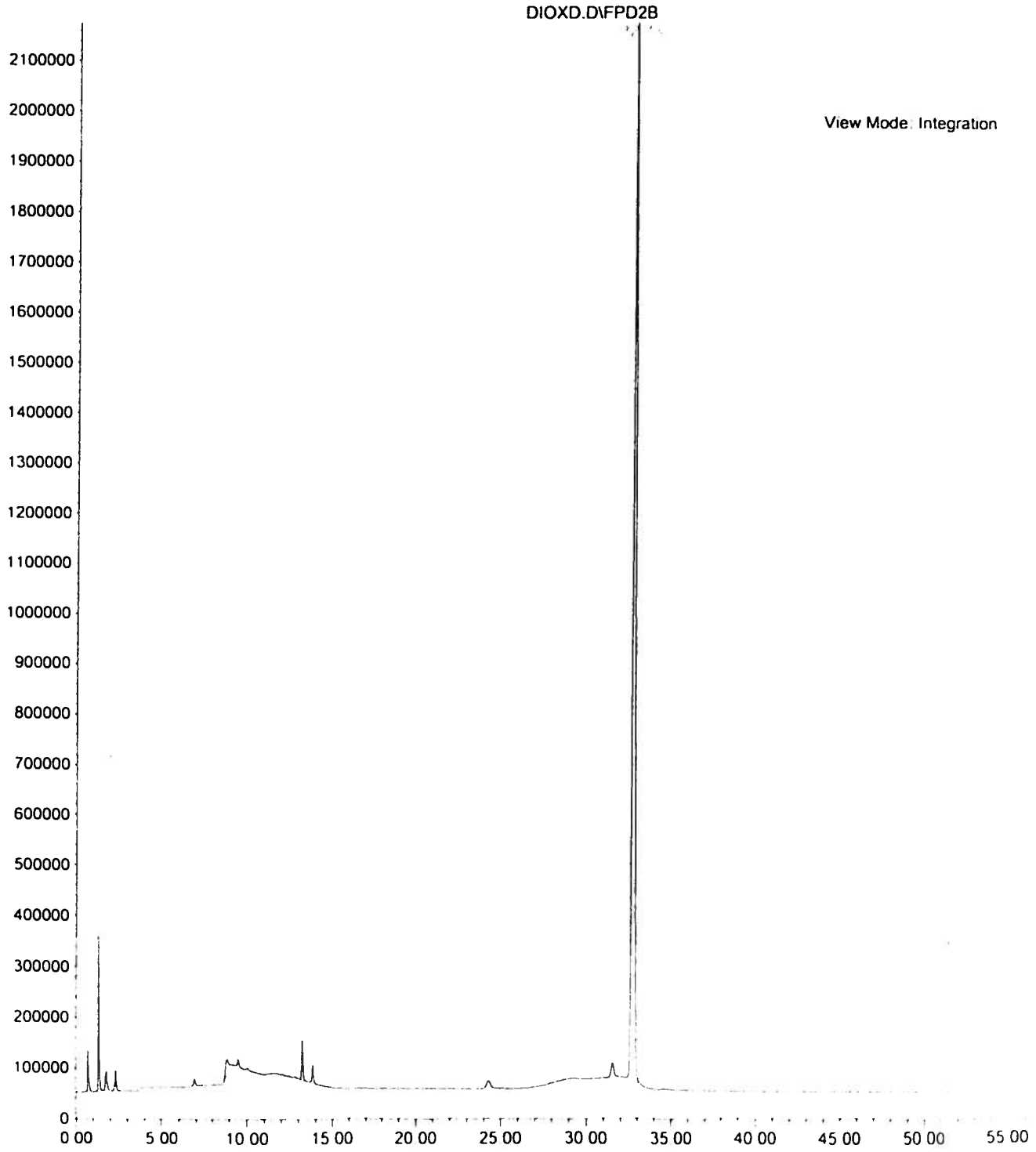
Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.856	M	0.193	3309698	8.662	9.006
2	13.225	M	0.094	4455198	13.074	13.383
3	32.735	M	0.181	220528545	32.417	33.056

File : C:\HPCHEM\1\DATA\072199\DIOXC.D
Operator :
Acquired : 21 Jul 99 17:57 using AcqMethod INJTEMP.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 140 degrees
Vial Number: 3



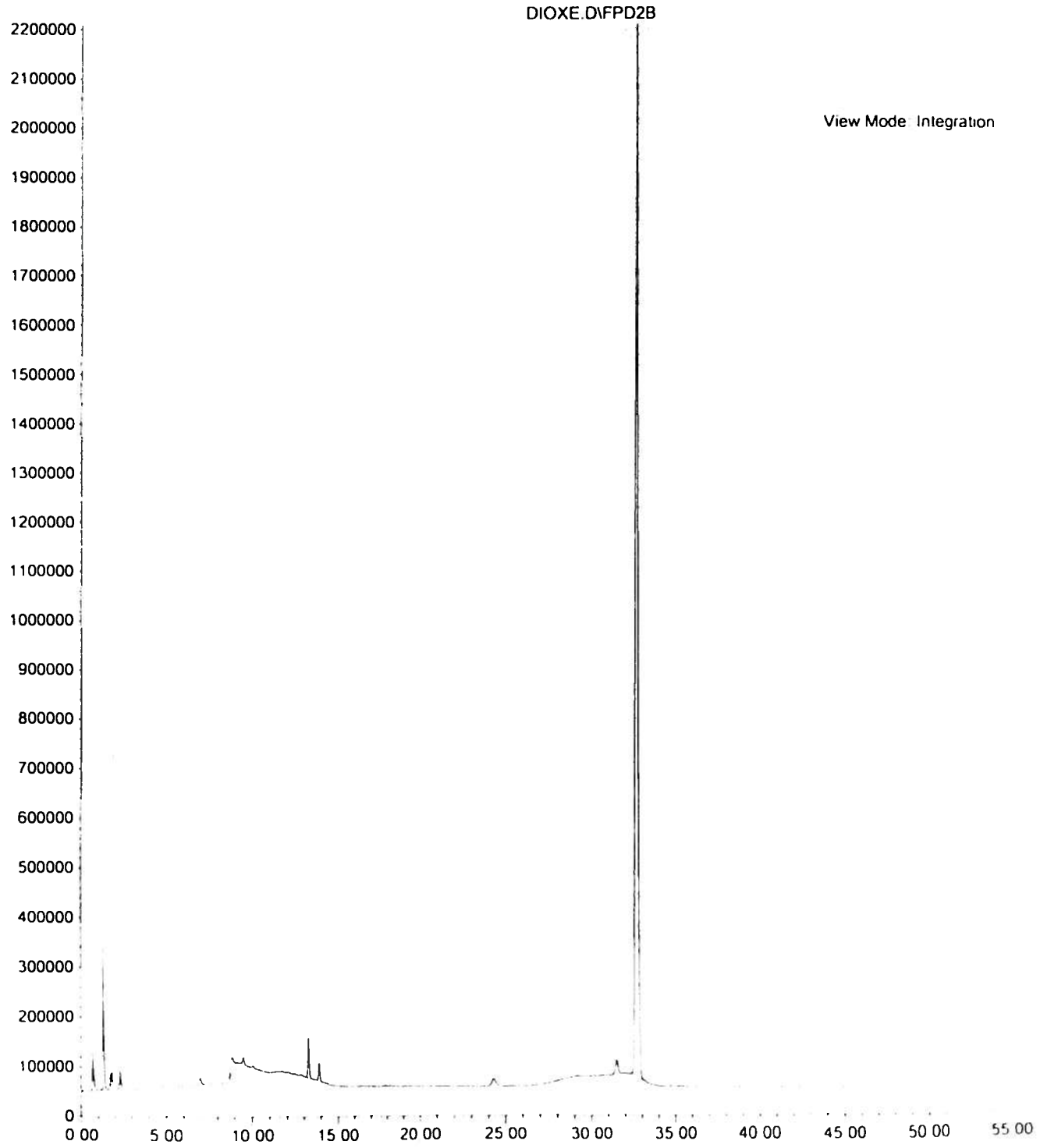
Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.866	M	0.204	3596355	8.639	9.043
2	13.221	M	0.094	4524343	13.093	13.385
3	32.730	M	0.182	224749442	32.369	33.065

File : C:\HPCHEM\1\DATA\072199\DIOXD.D
Operator :
Acquired : 21 Jul 99 19:20 using AcqMethod INJTEMP.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 140 degrees
Vial Number: 3



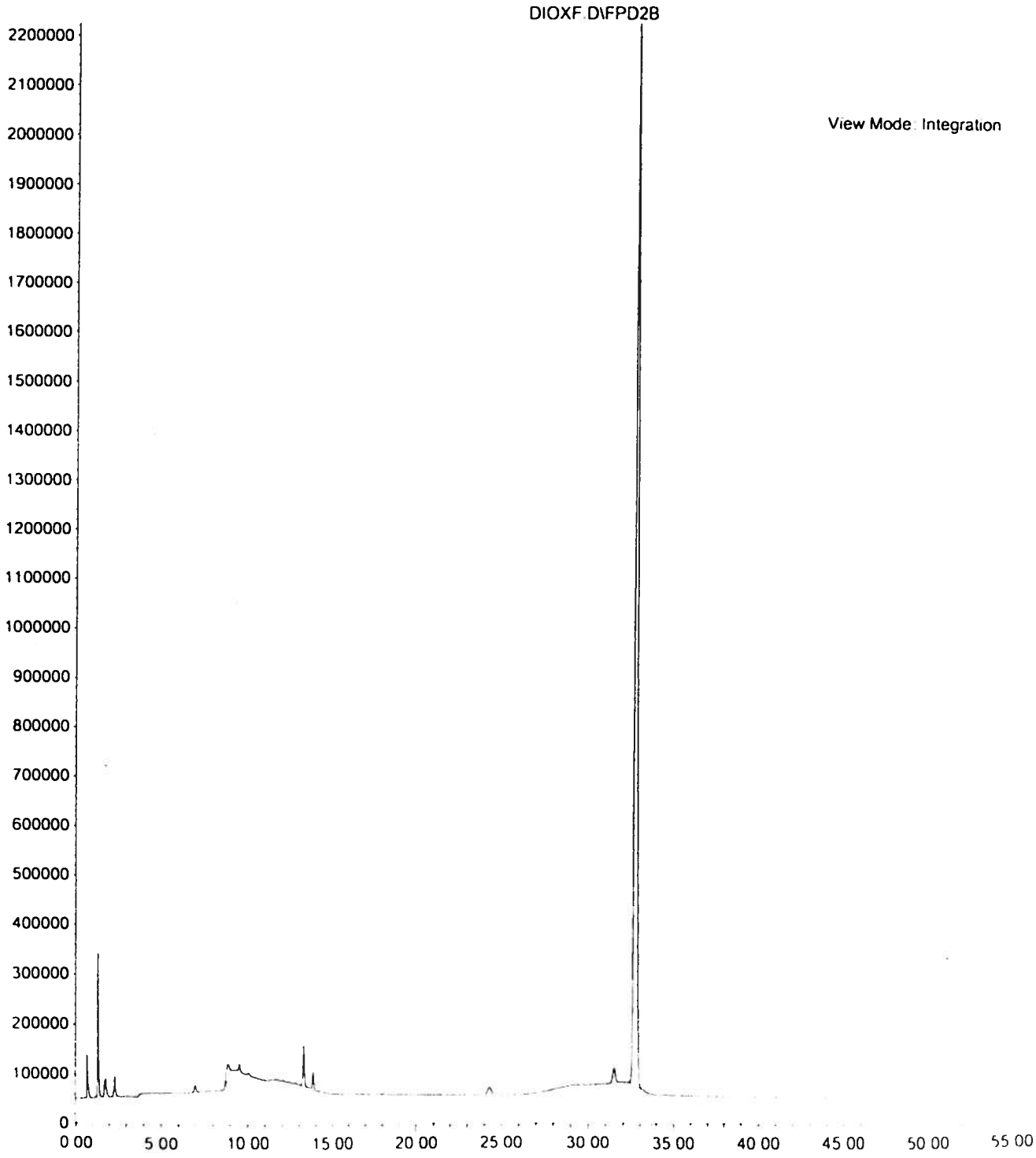
Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.876	M	0.207	3400280	8.644	9.029
2	13.226	M	0.092	4457611	13.072	13.361
3	32.729	M	0.182	229224594	32.383	33.083

File : C:\HPCHEM\1\DATA\072199\DIOXE.D
Operator :
Acquired : 21 Jul 99 20:43 using AcqMethod INJTEMP.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 140 degrees
Vial Number: 3



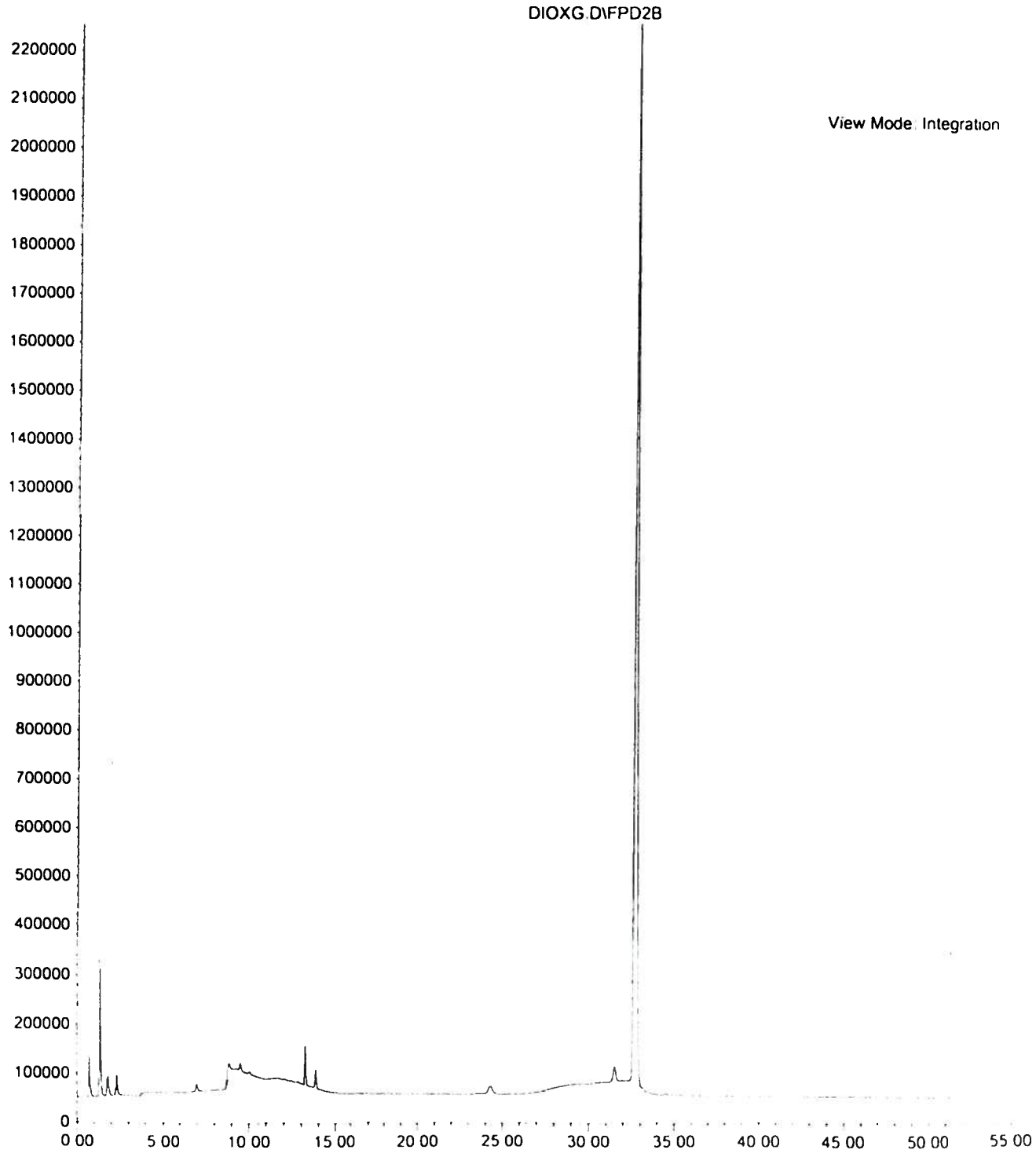
Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.853	M	0.184	3179532	8.641	9.010
2	13.228	M	0.091	4517534	13.111	13.365
3	32.722	M	0.181	231234855	32.382	33.065

File : C:\HPCHEM\1\DATA\072199\DIOXF.D
Operator :
Acquired : 21 Jul 99 22:06 using AcqMethod INJTEMP.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 140 degrees
Vial Number: 3



Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.859	M	0.187	3472164	8.654	9.006
2	13.230	M	0.093	4633435	13.097	13.386
3	32.719	M	0.181	233495837	32.360	33.071

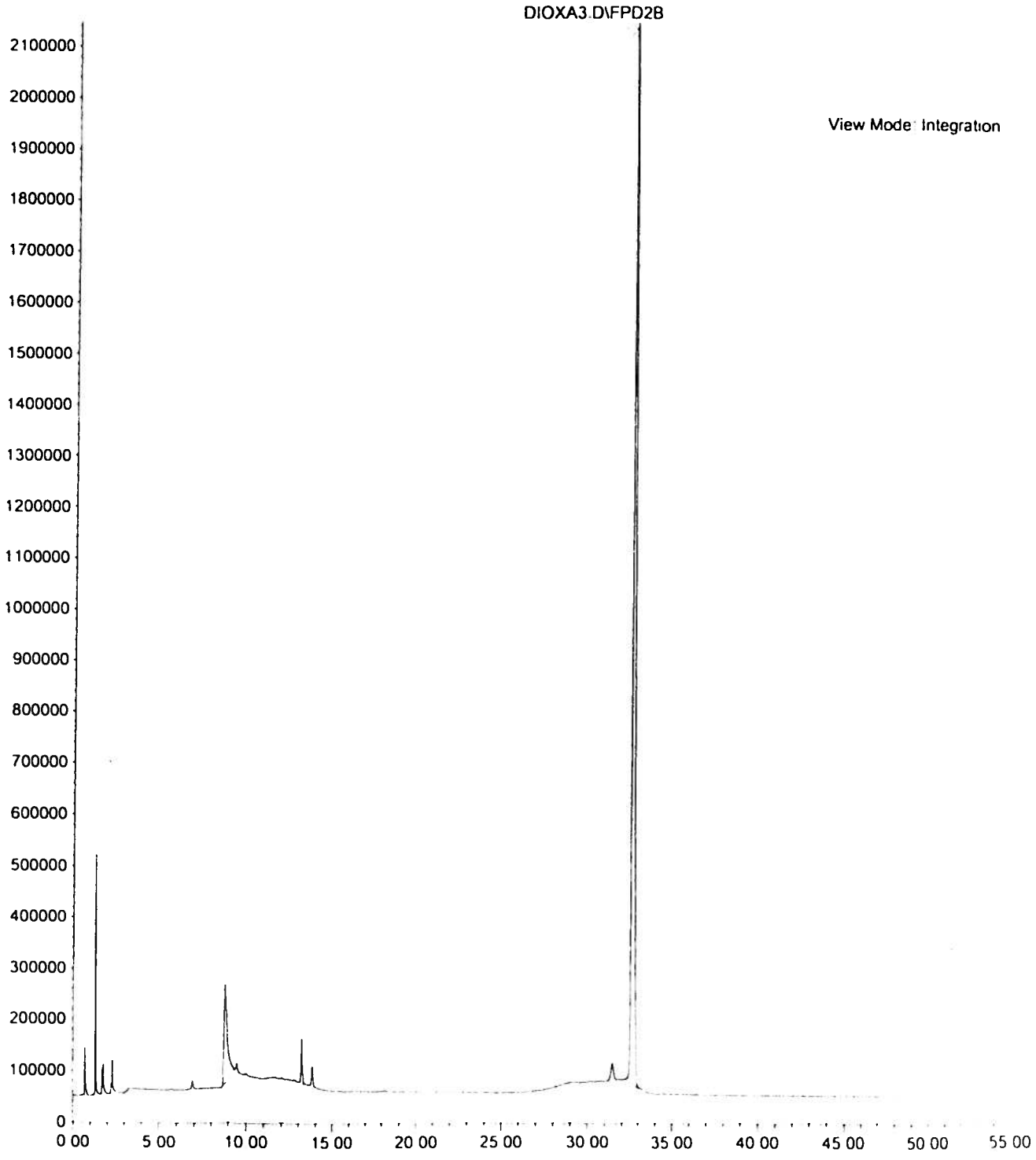
File : C:\HPCHEM\1\DATA\072199\DIOXG.D
Operator :
Acquired : 21 Jul 99 23:29 using AcqMethod INJTEMP.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 140 degrees
Vial Number: 3



Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.856	M	0.187	3519928	8.686	9.006
2	13.231	M	0.087	4258214	13.120	13.384
3	32.719	M	0.180	235144114	32.403	33.038

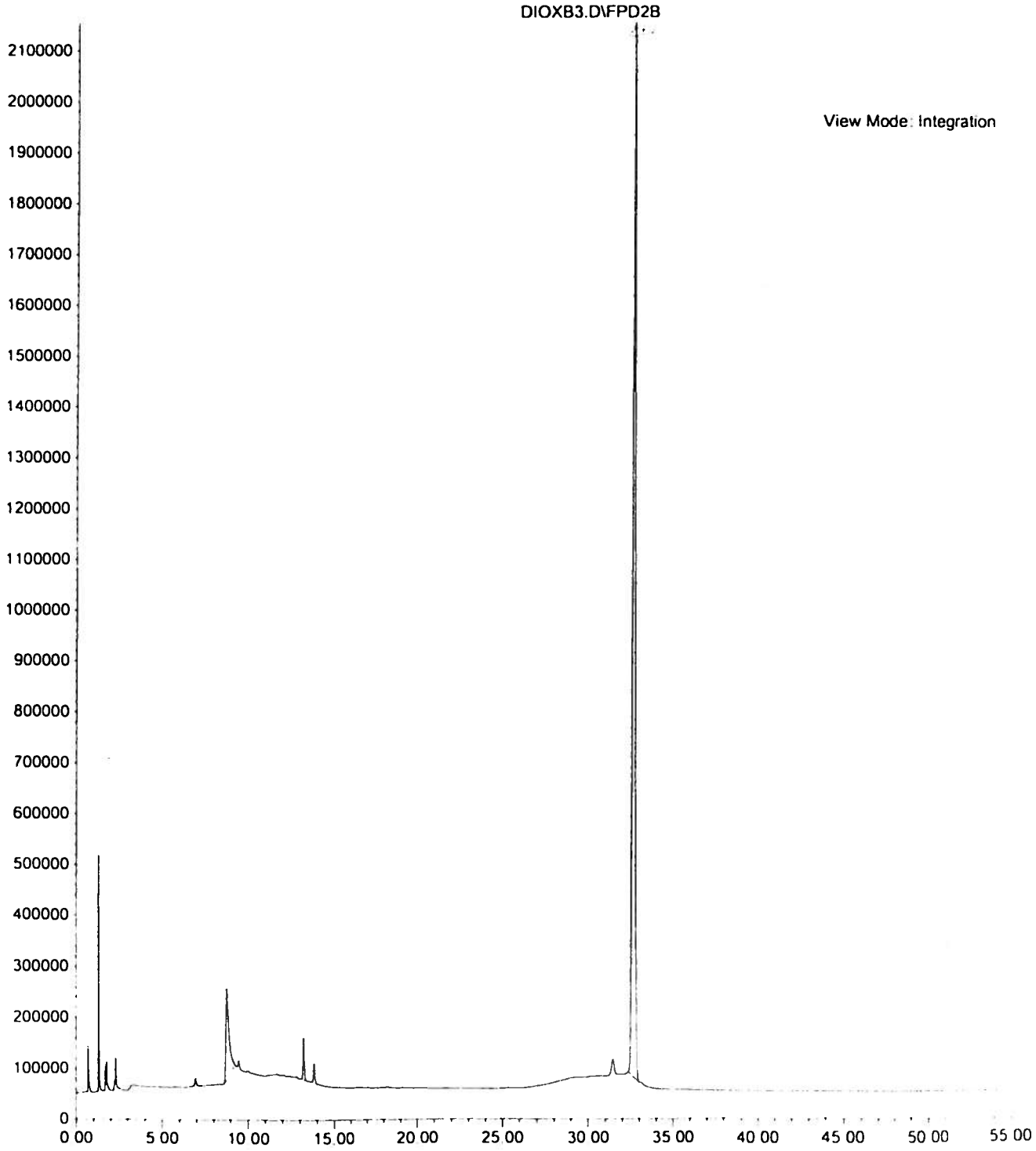
4B – Dioxathion Standard Analyzed at Injection Port of 190°C

File : C:\HPCHEM\1\DATA\072199\DIOXA3.D
Operator :
Acquired : 22 Jul 99 12:26 using AcqMethod STATE.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 190 degrees
Vial Number: 4



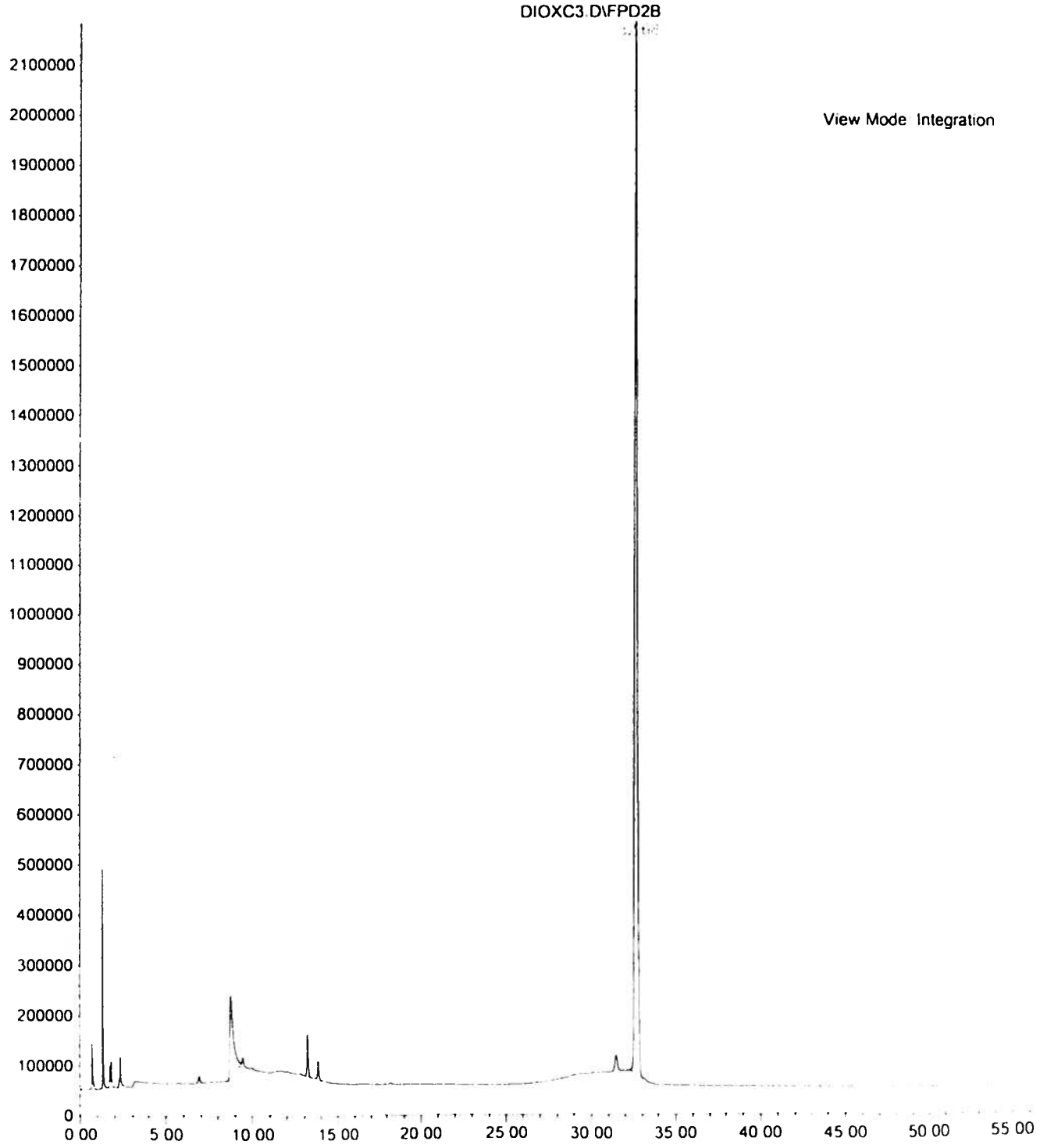
Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.790	M	0.232	26835902	8.597	9.323
2	13.208	M	0.089	4748962	13.050	13.345
3	32.673	M	0.179	223039399	32.294	33.008

File : C:\HPCHEM\1\DATA\072199\DIOXB3.D
Operator :
Acquired : 22 Jul 99 13:30 using AcqMethod STATE.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 190 degrees
Vial Number: 4



Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.780	M	0.245	26943578	8.632	9.386
2	13.205	M	0.090	4662562	13.064	13.349
3	32.676	M	0.180	223581528	32.394	32.979

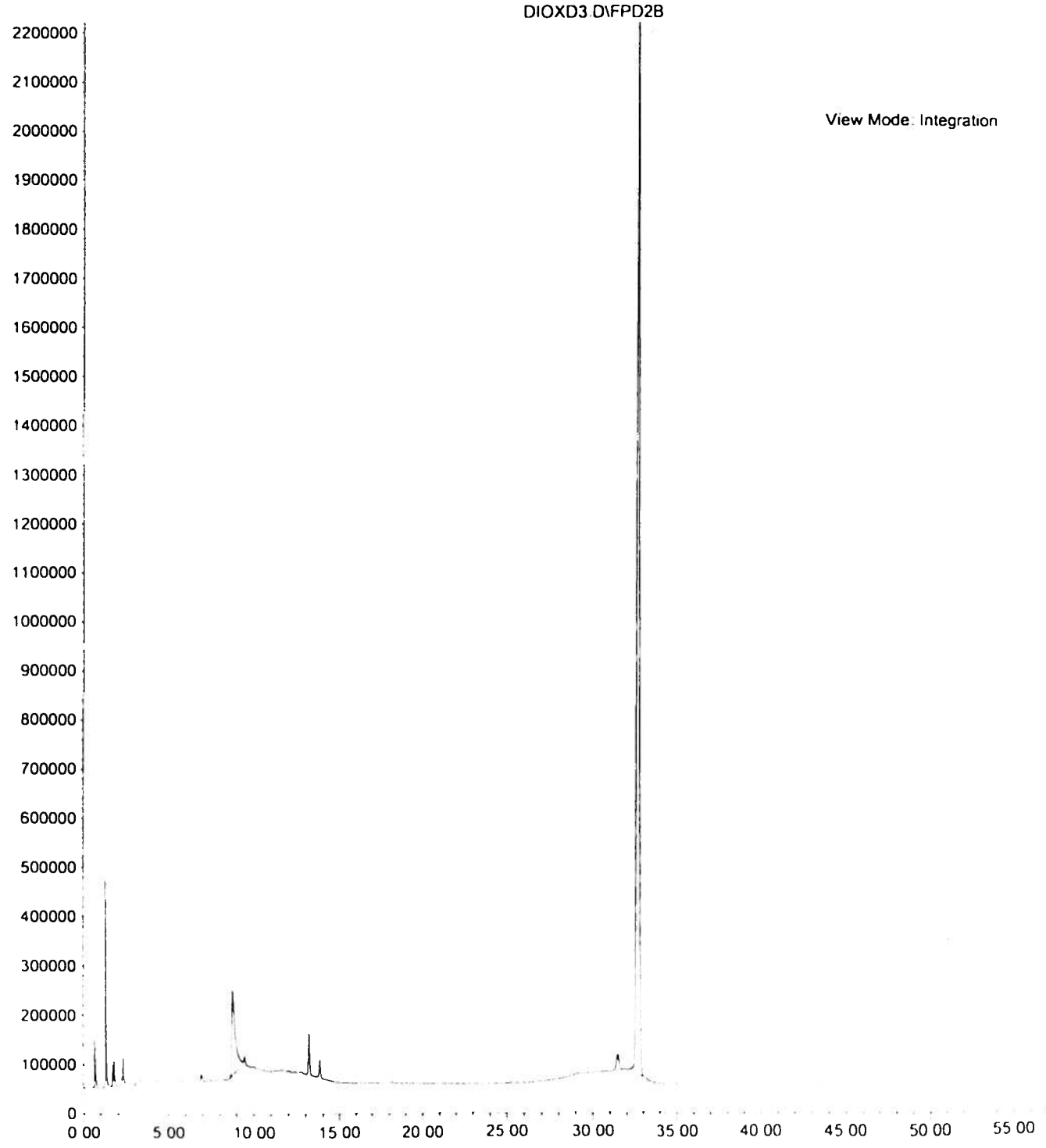
File : C:\HPCHEM\1\DATA\072199\DIOXC3.D
Operator :
Acquired : 22 Jul 99 15:39 using AcqMethod STATE.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 190 degrees
Vial Number: 4



D10XC3.D\FPD2B

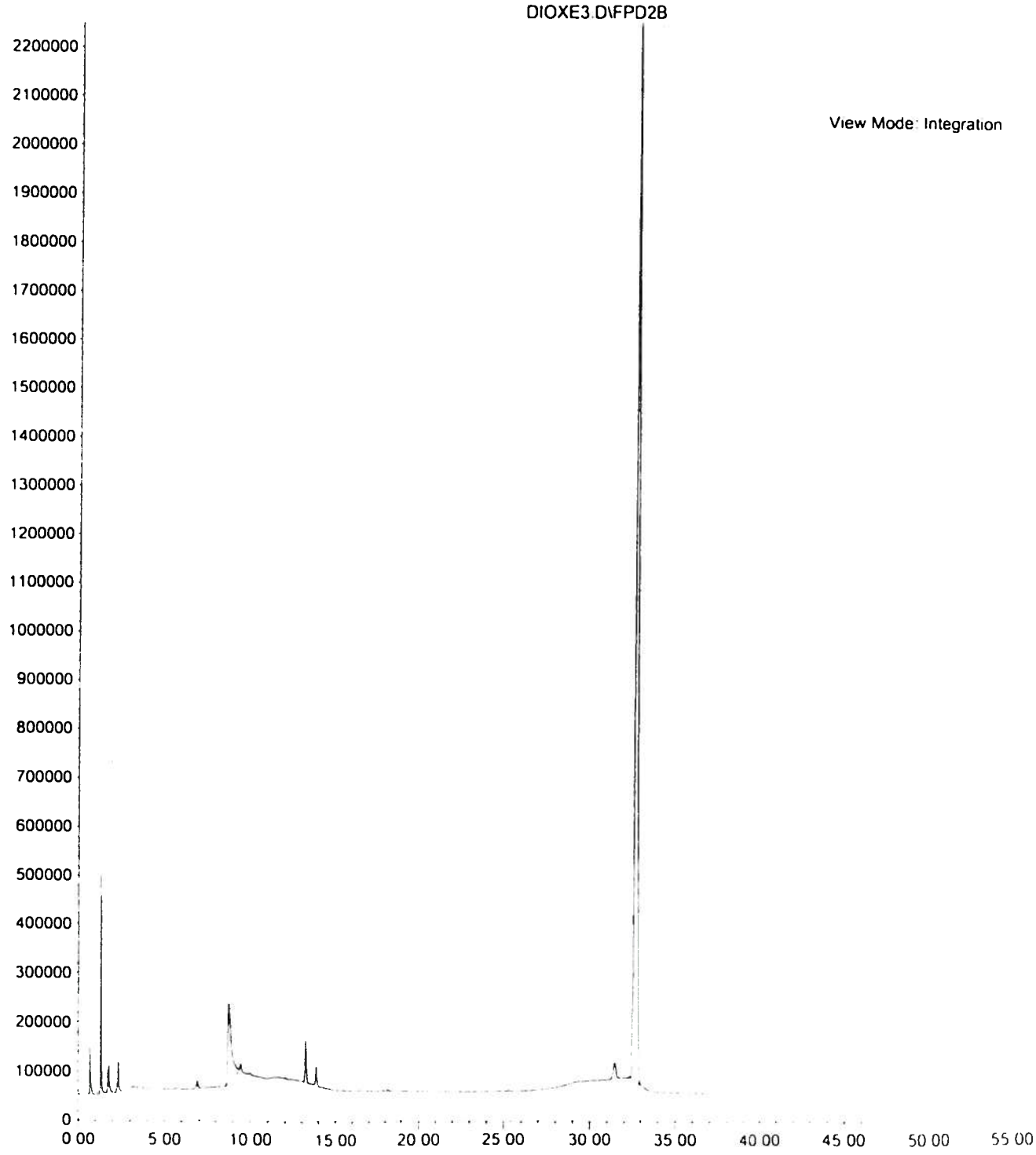
Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.783	M	0.250	24704408	8.607	9.371
2	13.207	M	0.089	4667440	13.066	13.344
3	32.677	M	0.180	227063957	32.306	33.015

File : C:\HPCHEM\1\DATA\072199\DIOXD3.D
Operator :
Acquired : 22 Jul 99 16:43 using AcqMethod STATE.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 190 degrees
Vial Number: 4



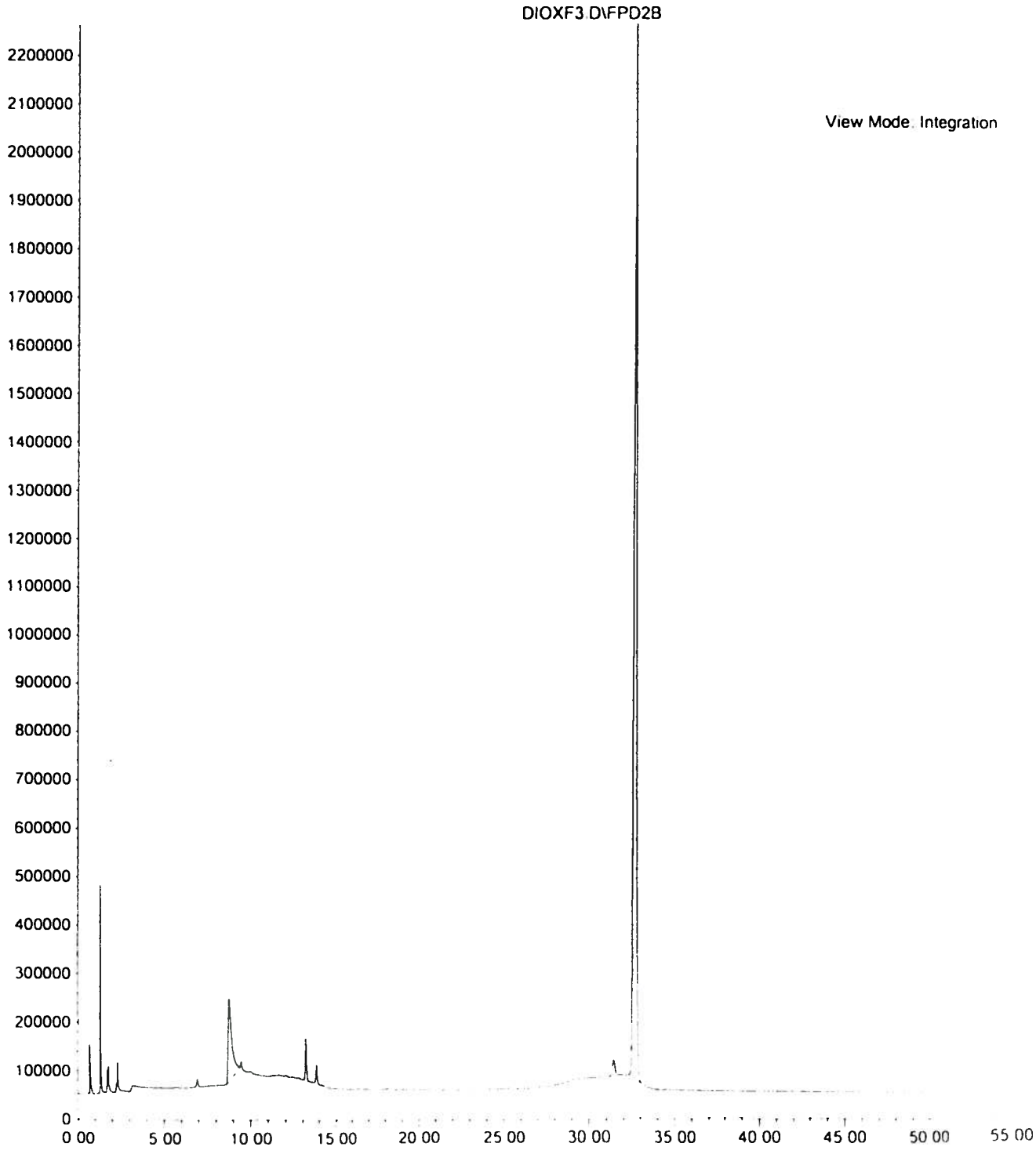
Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.780	M	0.247	25851068	8.530	9.385
2	13.201	M	0.093	4921065	13.053	13.350
3	32.675	M	0.178	228092392	32.269	33.034

File : C:\HPCHEM\1\DATA\072199\DIOXE3.D
Operator :
Acquired : 22 Jul 99 17:47 using AcqMethod STATE.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 190 degrees
Vial Number: 4



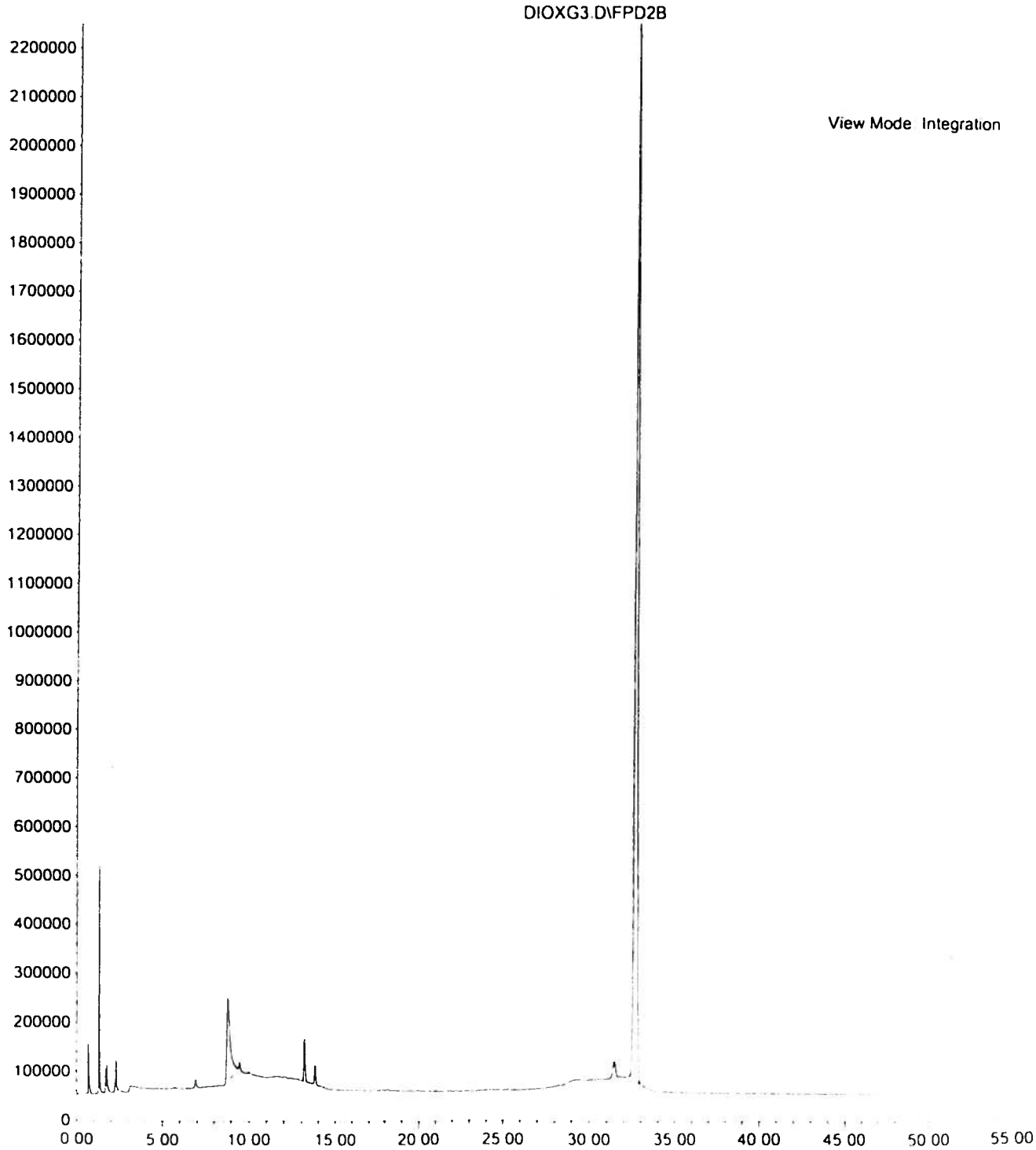
Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.775	M	0.248	24262766	8.561	9.355
2	13.198	M	0.093	4927239	13.060	13.343
3	32.673	M	0.178	231778415	32.337	33.027

File : C:\HPCHEM\1\DATA\072199\DIOXF3.D
Operator :
Acquired : 22 Jul 99 18:51 using AcqMethod STATE.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 190 degrees
Vial Number: 4



Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.779	M	0.248	25228732	8.615	9.368
2	13.201	M	0.090	4740706	13.078	13.320
3	32.674	M	0.178	232701733	32.332	32.981

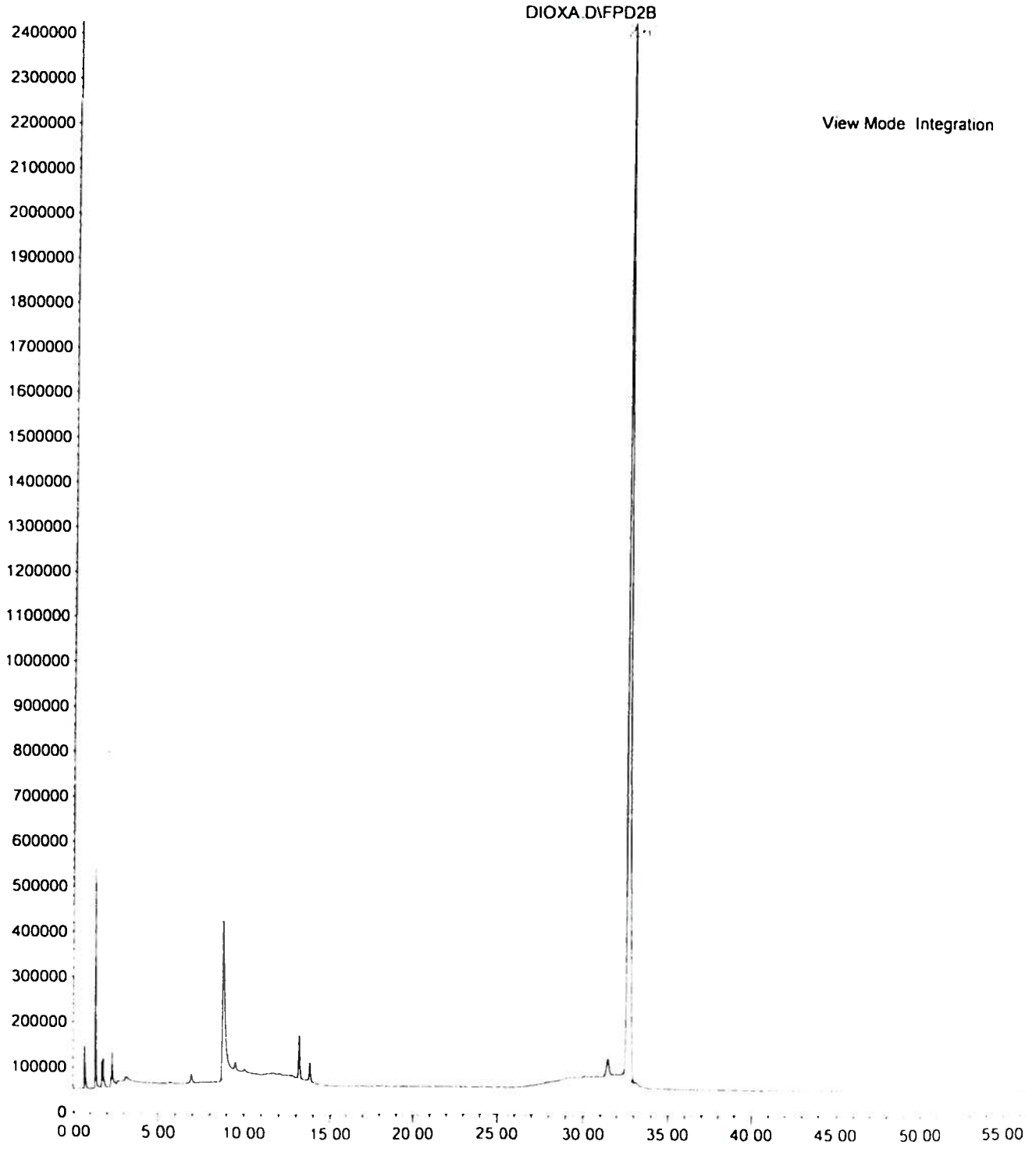
File : C:\HPCHEM\1\DATA\072199\DIOXG3.D
Operator :
Acquired : 22 Jul 99 19:55 using AcqMethod STATE.M
Instrument : FPD/FID I
Sample Name: Dioxathion Std. @ 100ppm
Misc Info : Spiked w chlor; Injection port @ 190 degrees
Vial Number: 4



Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.777	M	0.244	24982250	8.585	9.372
2	13.201	M	0.090	4773053	13.085	13.333
3	32.672	M	0.180	234932804	32.358	33.002

4C – Dioxathion Standard Analyzed at Injection Port of 220°C

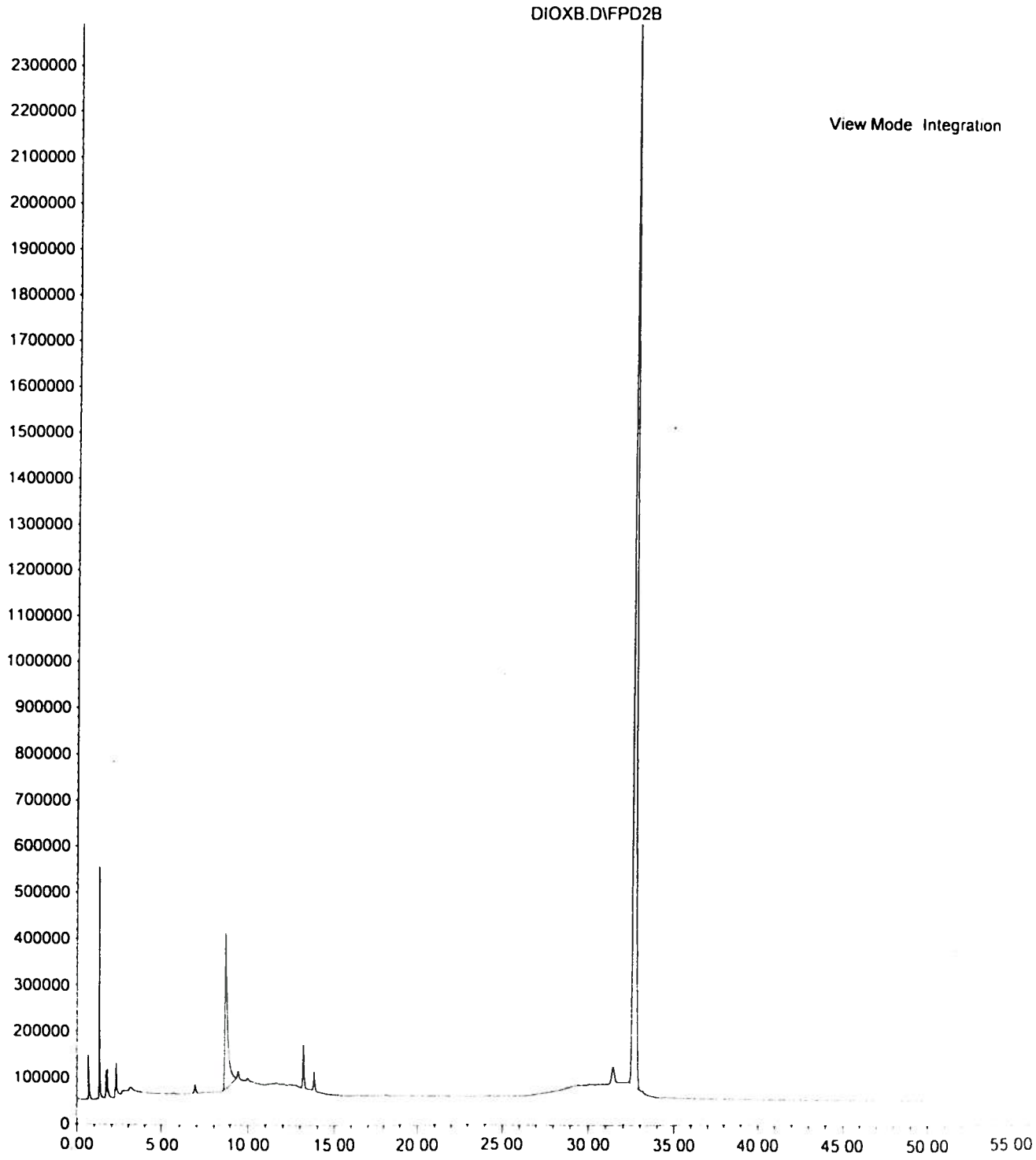
File : C:\HPCHEM\1\DATA\072699\DIOXA.D
Operator :
Acquired : 26 Jul 99 18:22 using AcqMethod STATE.M
Instrument : FPD/FID I
Sample Name: dioxathion std @ 100ppm
Misc Info : chlor @ 1ppm; injection port @ 220 degrees
Vial Number: 3



DIOXA.D\FPD2B

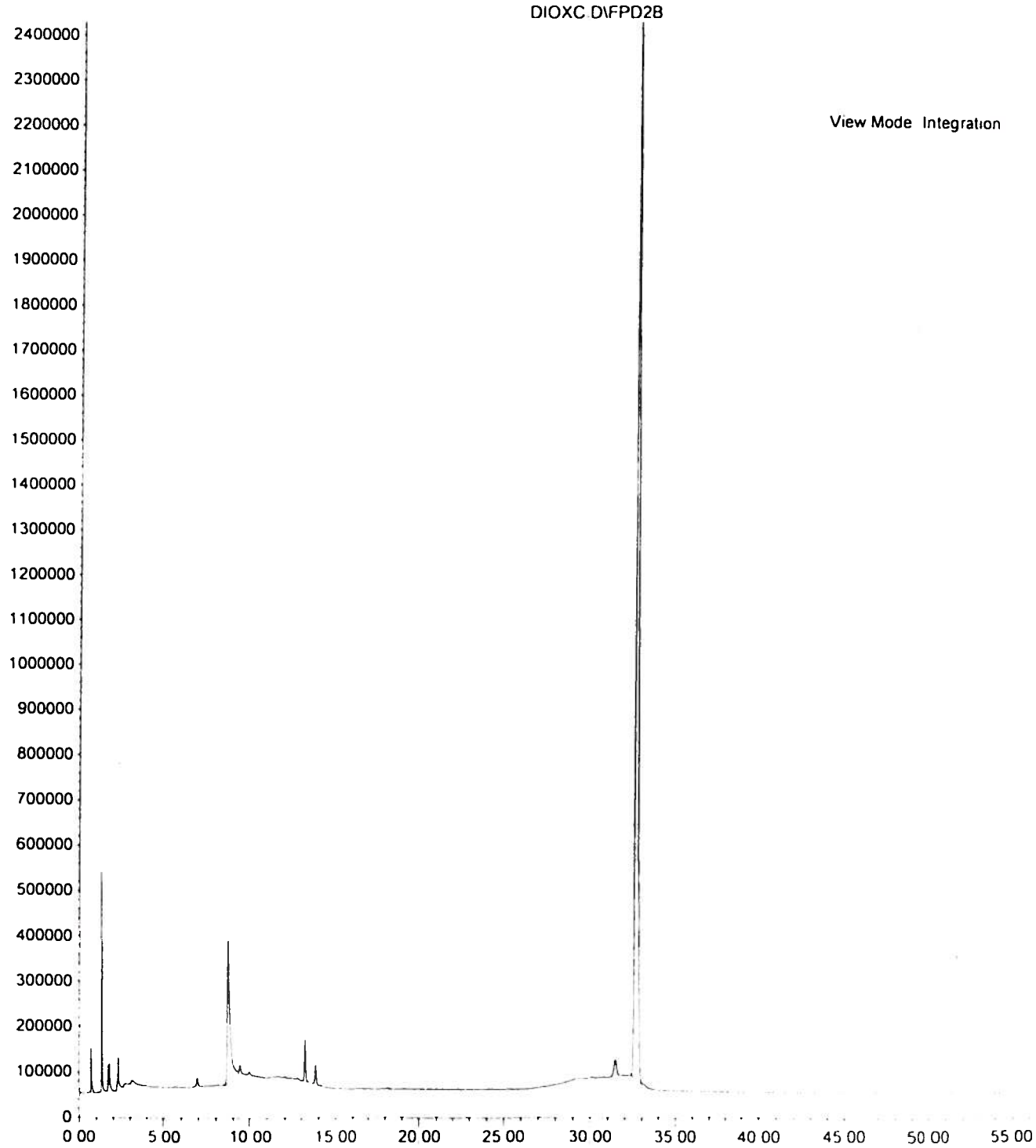
Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.749	M	0.181	38271410	8.578	9.334
2	13.188	M	0.088	5005377	13.077	13.315
3	32.691	M	0.179	251926013	32.382	33.009

File : C:\HPCHEM\1\DATA\072699\DIOXB.D
Operator :
Acquired : 26 Jul 99 19:26 using AcqMethod STATE.M
Instrument : FPD/FID I
Sample Name: dioxathion std @ 100ppm
Misc Info : chlor @ 1ppm; injection port @ 220 degrees
Vial Number: 3



Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	1.295	BB	0.034	11864006	1.250	1.420
2	8.751	BB	0.120	30928278	8.603	9.049
3	32.683	BB	0.144	247369039	32.409	33.027

File : C:\HPCHEM\1\DATA\072699\DIOXC.D
Operator :
Acquired : 26 Jul 99 20:30 using AcqMethod STATE.M
Instrument : FPD/FID I
Sample Name: dioxathion std @ 100ppm
Misc Info : chlor @ 1ppm; injection port @ 220 degrees
Vial Number: 3



Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	8.750	M	0.189	35980523	8.543	9.379
2	13.190	M	0.090	5181867	13.071	13.303
3	32.677	M	0.179	252268801	32.384	32.988