

# OIL CORRELATION STUDY

## GUDGEON-1

Prepared for:

ESSO Australia Ltd

January, 1996

PETROLEUM DIVISION

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## **OIL CORRELATION STUDY**

### **GUDGEON-1**

#### **Introduction**

Two oil samples (CH19 and CH71) from the well Gudgeon-1, drilled by ESSO Australia Limited in Bass Strait, were submitted for geochemical analyses.

The aim of this study was to characterise the oils in terms of source and maturity and to establish a possible genetic relationship between them.

#### **Analytical Procedures**

Upon arrival at the laboratory, API gravity, viscosity and paraffin wax content were determined on the two oils. Both samples were then analysed by whole oil GC, liquid chromatography to separate saturate, aromatic and NSO fractions and GC of the saturate fractions. The saturates were subsequently separated into branched/cyclics and straight chain compounds and GC-MS analyses were carried out on the branched/cyclic saturates and the aromatics.

Analytical results are presented in the following figures and tables:

Types of Analysis	Figure	Table
GC whole oil	1	1
Physical Properties	-	2
Liquid chromatography	-	2
GC sat. fraction	2	3
GC-MS branched/cyclic	3	4
GC-MS aromatics	4	5

Analytical procedures applied are summarised in the Theory and Methods chapter in the back of this report.

**General Information**

Two copies of this report have been sent to Mr. Andy Mills at ESSO Australia Limited in Melbourne. Any queries related to it may be directed to Dr. Birgitta Hartung-Kagi at Geotechnical Services Pty Ltd.

All data and information are proprietary to ESSO Australia Limited and regarded as highly confidential by all Geotech personnel.

Geotechnical Services Pty Ltd shall not be responsible or liable for the results of any actions taken on the basis of the information contained in this study, nor for any errors or omissions in it.

## Results and Interpretation

Based on physical properties, compositional analyses and biomarker patterns, the oil samples labelled CH19 AND CH71 are believed to be genetically related.

The oils are rich in saturates (88.4 and 88.3%), with only relatively low levels of aromatics (9.1 and 8.4%) and very low proportions of NSOs (2.4 and 3.3%). They consist predominantly of C<sub>9</sub> to C<sub>25</sub> compounds but also show considerable levels of higher plant waxes (n-C<sub>23+</sub>).

Sample CH19 is overall slightly lighter than CH71, as reflected in higher levels of n-alkanes up to C<sub>10</sub> and lower levels of compounds in the n-C<sub>11+</sub> range, together with a lower paraffin wax content.

The reasons for these slight compositional differences are believed to be secondary, that is, they could be due to water washing or migrational effects. The differences are not regarded as due to different origins of the two oil samples but are in line with oil from the same source being reservoired in different reservoir sections.

Biomarker patterns for the two oils are very similar and characterise the same organic source facies and maturity.

The organic matter which generated the oils was highly terrestrial, i.e. almost entirely higher plant derived, as reflected in low C<sub>27</sub>/C<sub>29</sub> diasterane and sterane ratios between 0.11 and 0.24, the presence of cadalene and a full suite of bi-, tri- and tetracyclic diterpanes (kaurane, phyllocladane, isopimarane, beyerane, 17-nortetracyclane, 19-norlabdane and rimuane), markers for resinous matter in higher plants.

The environment under which this source material was deposited was oxic, as indicated by pristane/phytane ratios of around 6.5.

There is good agreement between sterane, triterpane and methylphenanthrene-based maturity parameters, all of which characterise a maturity level of approximately 0.8 to 0.9% V<sub>R</sub> equivalent.

TABLE 1-1  
SUMMARY OF WHOLE OIL ANALYSIS

WELL = GUDGEON 1  
COUNTRY = AUSTRALIA  
BASIN = BASS STRAIT

DEPTH 1 = N/A      DEPTH UNIT = N/A  
DEPTH 2 = N/A      DATE OF JOB = Dec-95

**GUDGEON 1, CH 19, Crude Oil**

**COMPOSITION BY CARBON NUMBER**

Carbon No.	Rel.Wt%
1 - 3	0.15
4	0.68
5	0.95
6	1.98
7	4.34
8	7.47
9	7.65
10	6.94
11	5.71
12	5.45
13	5.59
14	5.14
15	4.88
16	3.68
17	5.39
18	3.37
19	3.25
20	3.17
21	3.19
22	3.09
23	3.08
24	2.95
25	2.83
26	2.39
27	2.23
28	1.57
29	1.16
30	0.67
31	0.51
32	0.31
33	0.23

**COMPOSITION OF C4-C8 FRACTION**

Compound	Rel.Wt%
isobutane (A)	2.83
n-butane (B)	3.36
isopentane (C)	3.84
n-pentane (D)	4.47
2,2-dimethylbutane (E)	0.15
cyclopentane (F)	0.27
2,3-dimethylbutane (G)	0.50
2-methylpentane (H)	3.55
3-methylpentane (I)	1.86
n-hexane (J)	7.29
methylcyclopentane (K)	1.95
2,4-dimethylpentane (L)	0.51
benzene (M)	0.14
cyclohexane (N)	2.50
1,1-dimethylcyclopentane (O)	0.83
2-methylhexane (P)	3.68
3-methylhexane (Q)	3.98
1 cis-3-dimethylcyclopentane (R)	0.76
1 trans-3-dimethylcyclopentane (S)	1.21
1 trans-2-dimethylcyclopentane (T)	0.19
n-heptane (U)	14.53
methylcyclohexane (V)	12.03
1 cis-2-dimethylcyclopentane (W)	0.55
toluene (X)	1.06
n-octane (Y)	24.19
ethylbenzene (Z)	1.28
M + P-xylene (AA)	2.11
O-xylene (BB)	0.39

**CALCULATED DATA - C12+ FRACTION**

Pristane/Phytane	7.01
Pristane/n-C17	0.53
Phytane/n-C18	0.08
TMTD/Pristane	0.61
(C21 + C22)/(C28 + C29)	2.48

**CALCULATED DATA - C4-C8 FRACTION**

Paraffin Index I	3.54
Paraffin Index II	36.59
N/K (Maturity)	1.28
C/D (Maturity)	0.86
J/K (Maturity)	3.73
I/M (Water washing)	13.53
I/J (Biodegradation)	0.26

**NOTES :**

TMTD = Trimethyltridecane  
- = Below detection limit  
or not measured

Paraffin Index I =  $(P + Q)/(R + S + T)$

Paraffin Index II = %U in listed

compounds N to V

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TABLE 1-2  
SUMMARY OF WHOLE OIL ANALYSIS

WELL = GUDGEON 1  
COUNTRY = AUSTRALIA  
BASIN = BASS STRAIT

DEPTH 1 = N/A      DEPTH UNIT = N/A  
DEPTH 2 = N/A      DATE OF JOB = Dec-95

**GUDGEON 1, CH 71, Crude Oil**

**COMPOSITION BY CARBON NUMBER**

Carbon No.	Rel.Wt%
1 - 3	0.54
4	0.32
5	0.52
6	1.08
7	2.17
8	4.14
9	5.35
10	5.90
11	5.41
12	5.66
13	5.92
14	5.37
15	5.34
16	4.23
17	6.37
18	3.89
19	3.76
20	3.77
21	3.76
22	3.66
23	3.65
24	3.52
25	3.45
26	2.92
27	2.78
28	2.00
29	1.59
30	1.02
31	0.85
32	0.55
33	0.49

**CALCULATED DATA - C12+ FRACTION**

Pristane/Phytane	7.09
Pristane/n-C17	0.53
Phytane/n-C18	0.08
TMTD/Pristane	0.58
(C21 + C22)/(C28 + C29)	2.18

**NOTES :**

TMTD = Trimethyltridecane  
- = Below detection limit  
or not measured

**COMPOSITION OF C4-C8 FRACTION**

Compound	Rel.Wt%
isobutane (A)	2.02
n-butane (B)	3.47
isopentane (C)	4.08
n-pentane (D)	4.63
2,2-dimethylbutane (E)	0.16
cyclopentane (F)	0.28
2,3-dimethylbutane (G)	0.52
2-methylpentane (H)	3.48
3-methylpentane (I)	1.88
n-hexane (J)	7.35
methylcyclopentane (K)	2.18
2,4-dimethylpentane (L)	0.51
benzene (M)	0.17
cyclohexane (N)	2.84
1,1-dimethylcyclopentane (O)	0.82
2-methylhexane (P)	3.40
3-methylhexane (Q)	3.83
1 cis-3-dimethylcyclopentane (R)	0.77
1 trans-3-dimethylcyclopentane (S)	1.29
1 trans-2-dimethylcyclopentane (T)	0.19
n-heptane (U)	12.65
methylcyclohexane (V)	12.04
1 cis-2-dimethylcyclopentane (W)	0.52
toluene (X)	1.38
n-octane (Y)	24.95
ethylbenzene (Z)	1.46
M + P-xylene (AA)	2.72
O-xylene (BB)	0.42

**CALCULATED DATA - C4-C8 FRACTION**

Paraffin Index I	3.22
Paraffin Index II	33.44
N/K (Maturity)	1.30
C/D (Maturity)	0.88
J/K (Maturity)	3.38
I/M (Water washing)	10.80
I/J (Biodegradation)	0.26

Paraffin Index I =  $(P + Q)/(R + S + T)$

Paraffin Index II = %U in listed

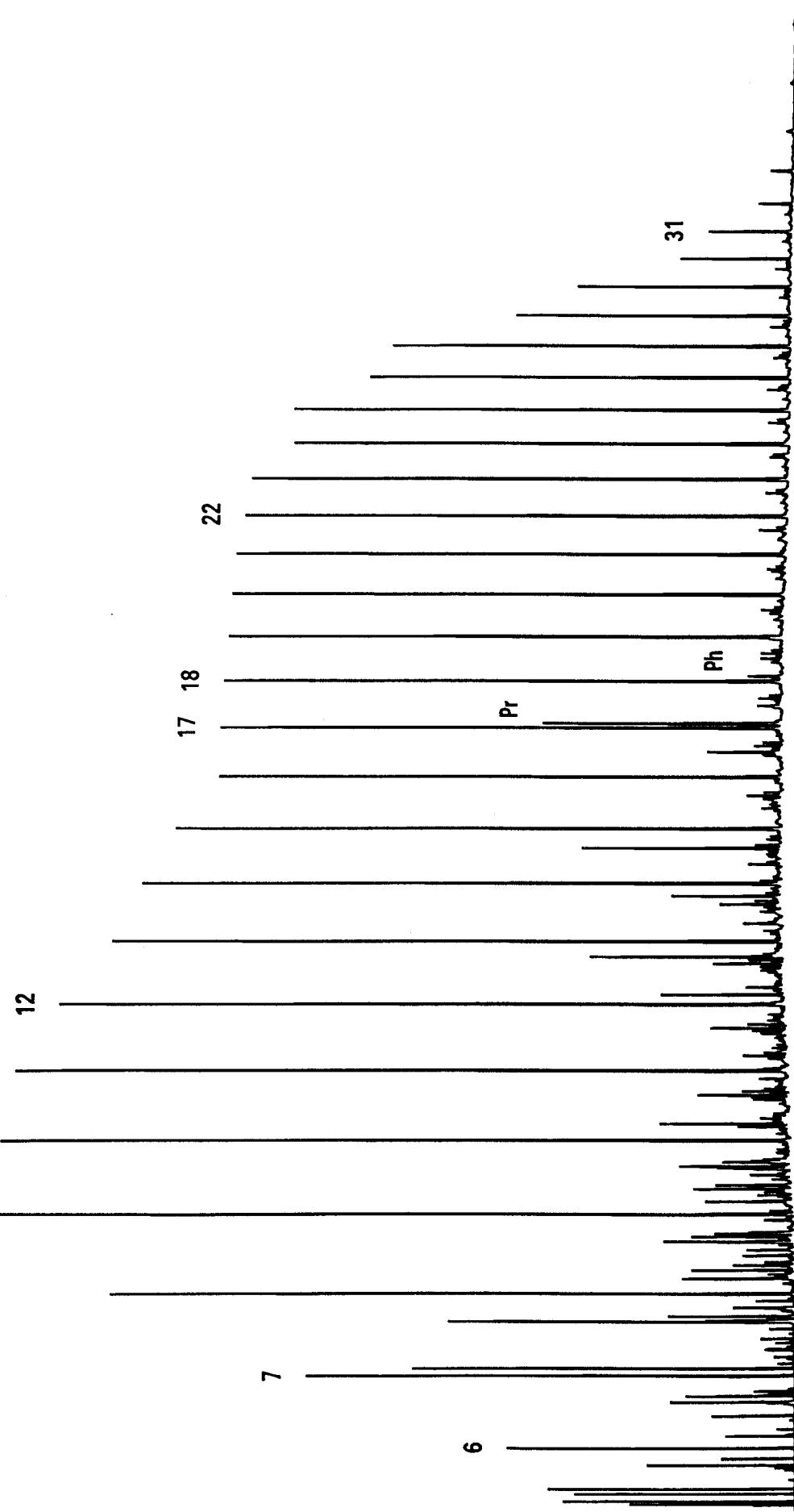
compounds N to V  
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**GUDGEON 1, CH 19**

Whole Oil

C1-C33 GLC

FIGURE 1-1-1

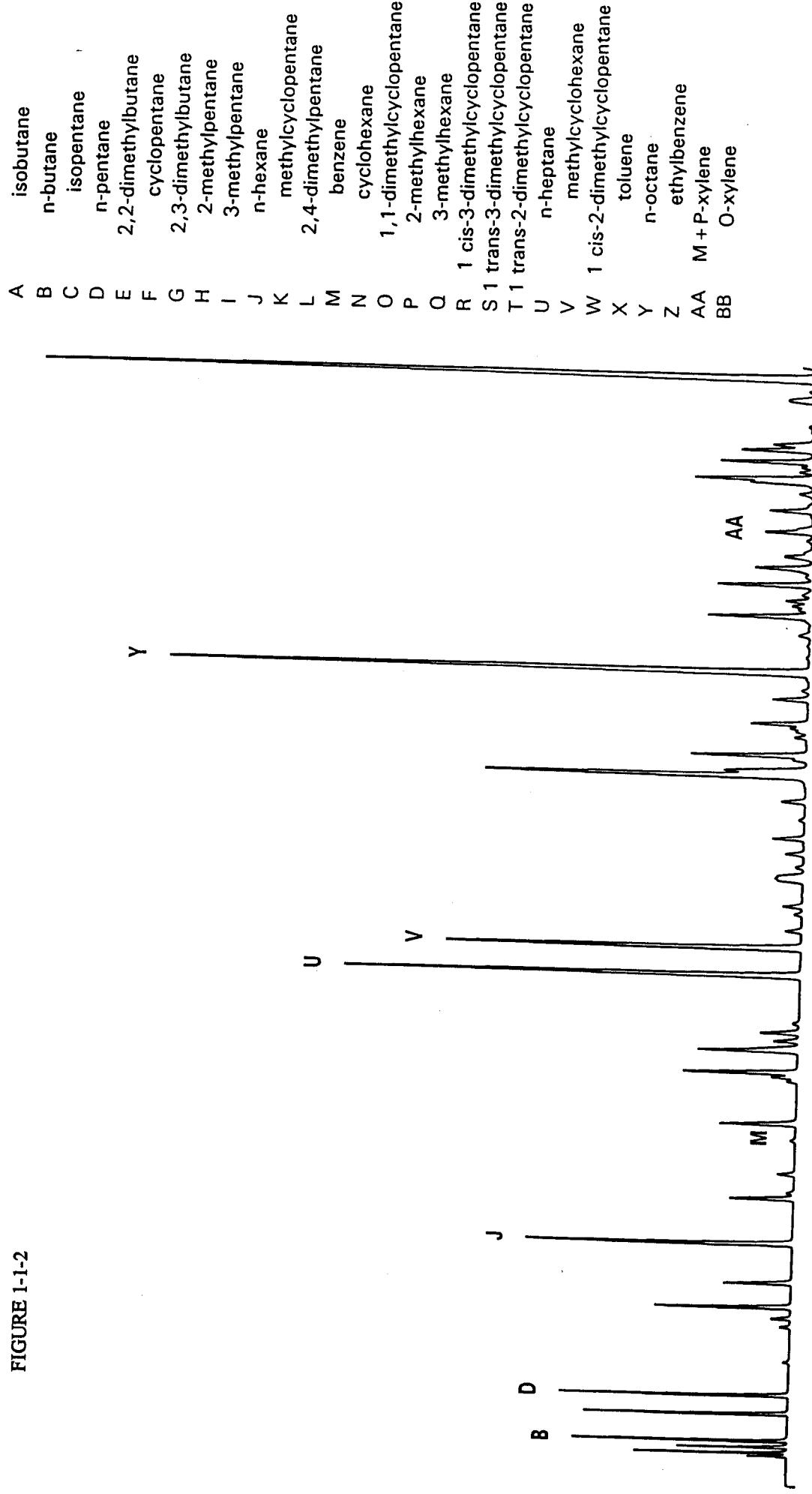


230W01

**GUDGEON 1, CH 19**  
**Gasoline Range Whole Oil**  
**C1-C8 GLC**

FIGURE 1-1-2

**C4-C8 Compounds**



**GUDGEON 1, CH71**

Whole Oil

C1-C33 GLC

FIGURE 1-2-1

12

9

17

22

18

17

7

6

Pr

Ph

31

230W02

**GUDGEON 1, CH 71**  
**Gasoline Range Whole Oil**  
**C1-C8 GLC**

**FIGURE 1-2-2**

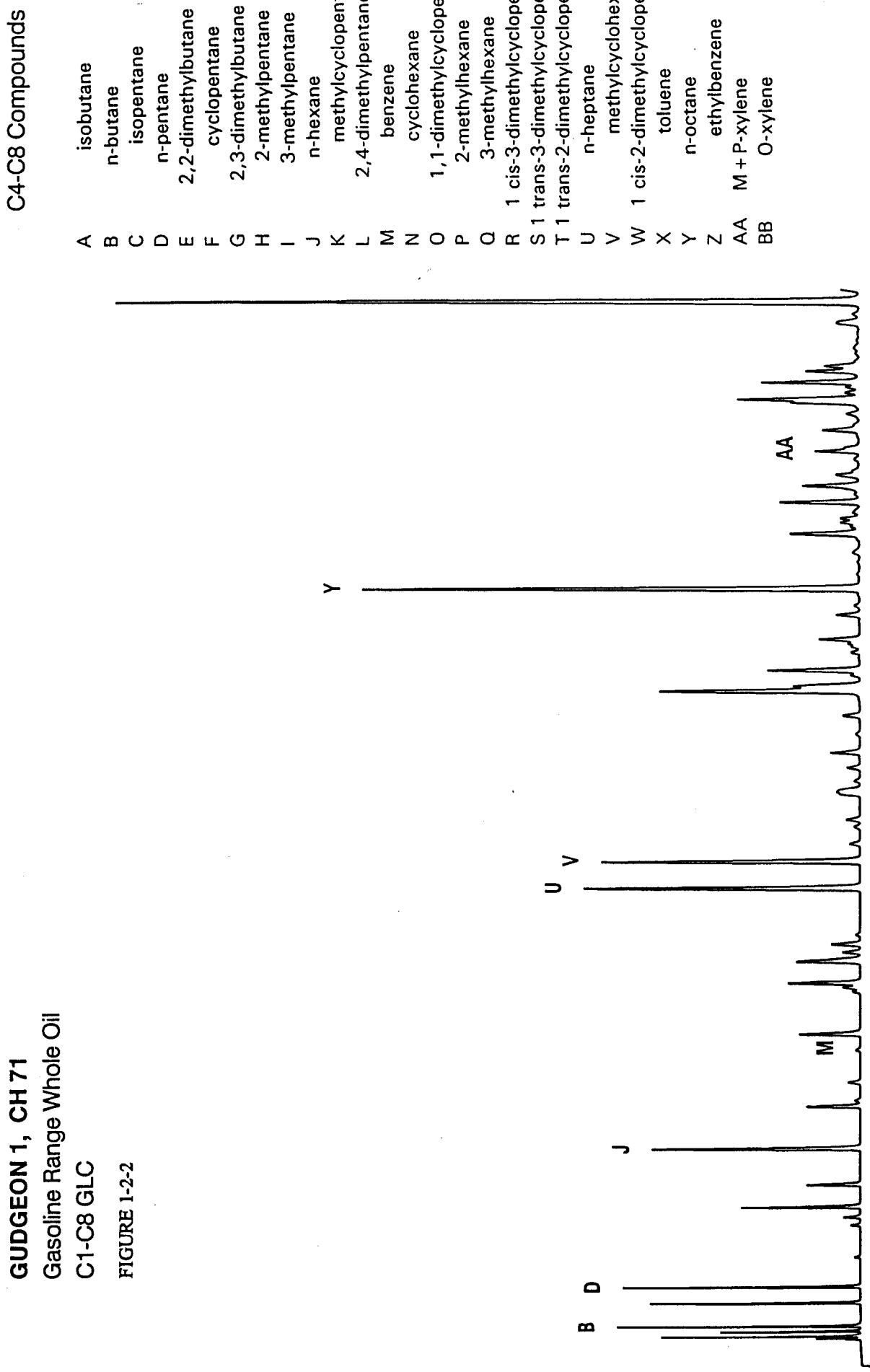


TABLE 2

## Summary of Physical Property and Sulphur Data

**GUDGEON 1**

Dec-95

SAMPLES	API	%SULPHUR	VISCOSITY	VISCOSITY
	GRAVITY	(W/W)	at 25°C (cSt)	at 60°C (cSt)
CH 19	45.0	nd	3.82	1.98
CH 71	43.3	nd	nd	2.43

TABLE 2

## Summary of Liquid Chromatography (Compositional data)

**GUDGEON 1**

Dec-95

SAMPLES	---Hydrocarbons---			---Nonhydrocarbons-----			SAT	ASPH	HC
	%SAT	%AROM	%HC's	%NSO's	%ASPH	%Non HC's	AROM	NSO	Non HC
CH 19	88.4	9.1	97.6	2.4	nd	2.4	9.7	nd	40.2
CH 71	88.3	8.4	96.7	3.3	nd	3.3	10.5	nd	29.2

nd = no data

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TABLE 2-1

**PARAFFIN WAX CONTENT**

<b>Sample</b>	<b>%</b>
<b>GUDGEON 1</b>	
CH 19	31.2
CH 71	38.2

\* Calculated as the percent of n-alkane waxes in the boiling range 150-280 degrees C in the whole oil.

TABLE 3

## Summary of Gas Chromatography Data

**GUDGEON 1**

## A. Alkane Compositional Data

SAMPLES	Prist./Phyt.	Prist./n-C17	Phyt./n-C18	CPI(1)	CPI(2)	(C21+C22)/(C28+C29)
CH 19	6.61	0.53	0.08	1.10	1.08	2.53
CH 71	6.54	0.53	0.08	1.10	1.07	2.22

TABLE 3

## Summary of Gas Chromatography Data

**GUDGEON 1**

## B. n-Alkane Distributions

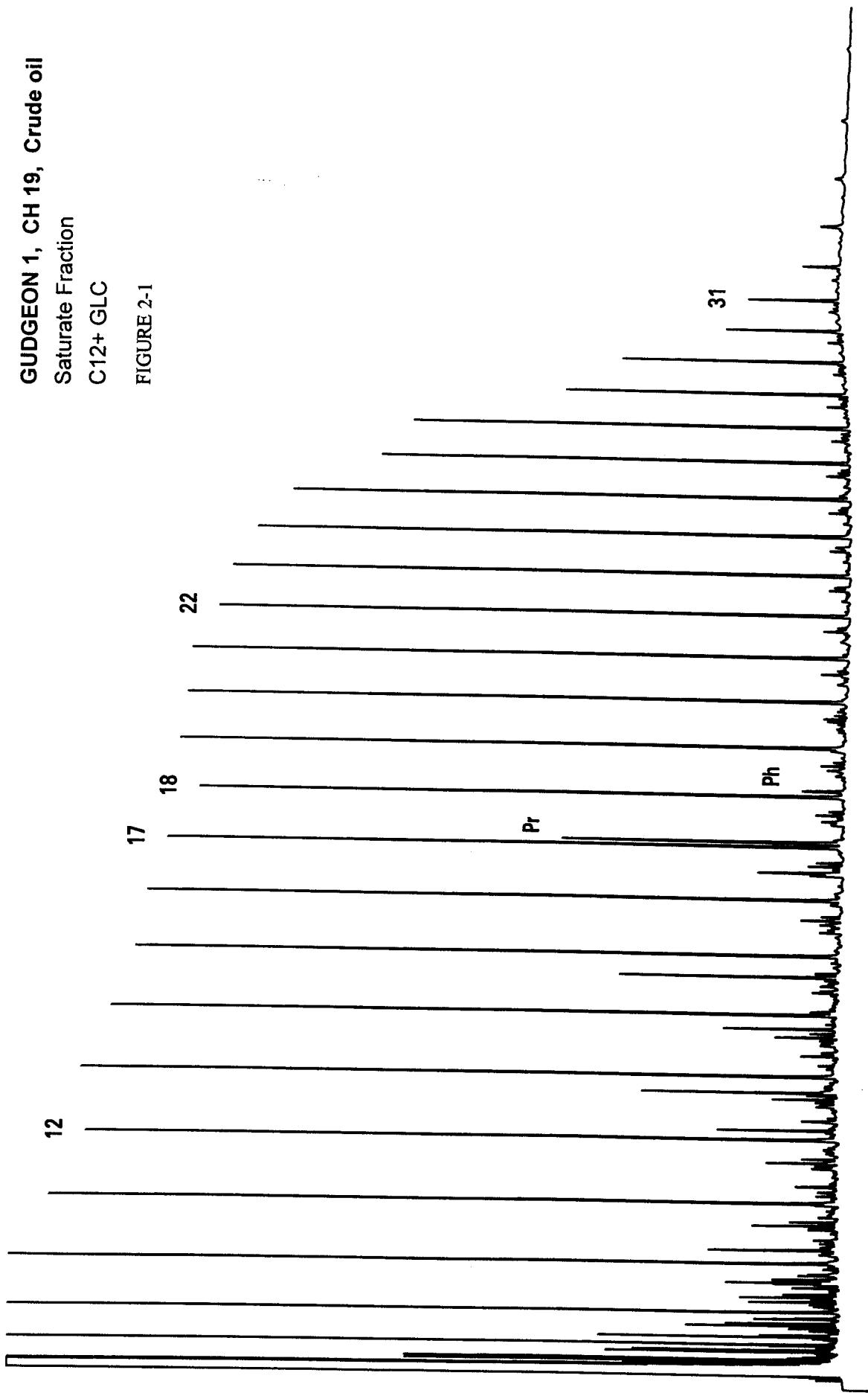
SAMPLES	nC1	nC1	nC1	nC1	nC16	nC1	iC19	nC18	iC20	nC1	nC2	nC21	nC2	nC2	nC2	nC2	nC2	nC2	nC3	nC31		
CH 19	6.0	6.0	6.0	6.1	6.0	6.1	3.2	5.9	0.5	5.9	5.9	5.8	5.7	5.7	5.4	5.2	4.1	3.9	2.5	2.0	1.1	1.0
CH 71	5.5	5.5	5.6	5.9	5.7	5.8	3.1	5.7	0.5	5.8	5.8	5.9	5.9	5.9	5.6	5.5	4.5	4.4	2.9	2.3	1.3	1.1

nd = no data

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GUDGEON 1, CH 19, Crude oil  
Saturate Fraction  
C12+ GLC

FIGURE 2-1

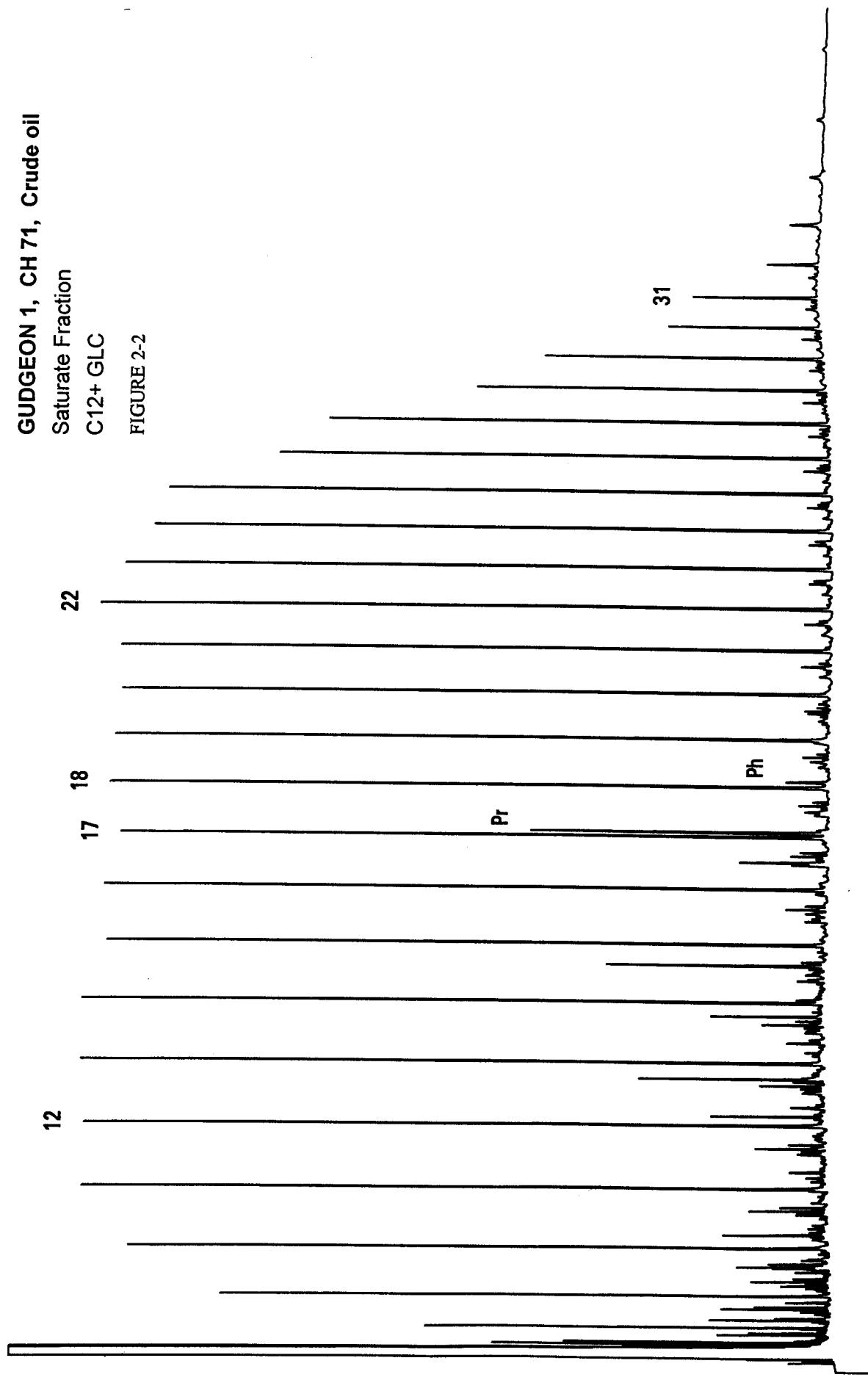


2230E01

**GUDGEON 1, CH 71, Crude oil**

Saturate Fraction  
C12+ GLC

FIGURE 2-2



2230ED2

TABLE 4-1

## SELECTED PARAMETERS FROM GC/MS ANALYSIS

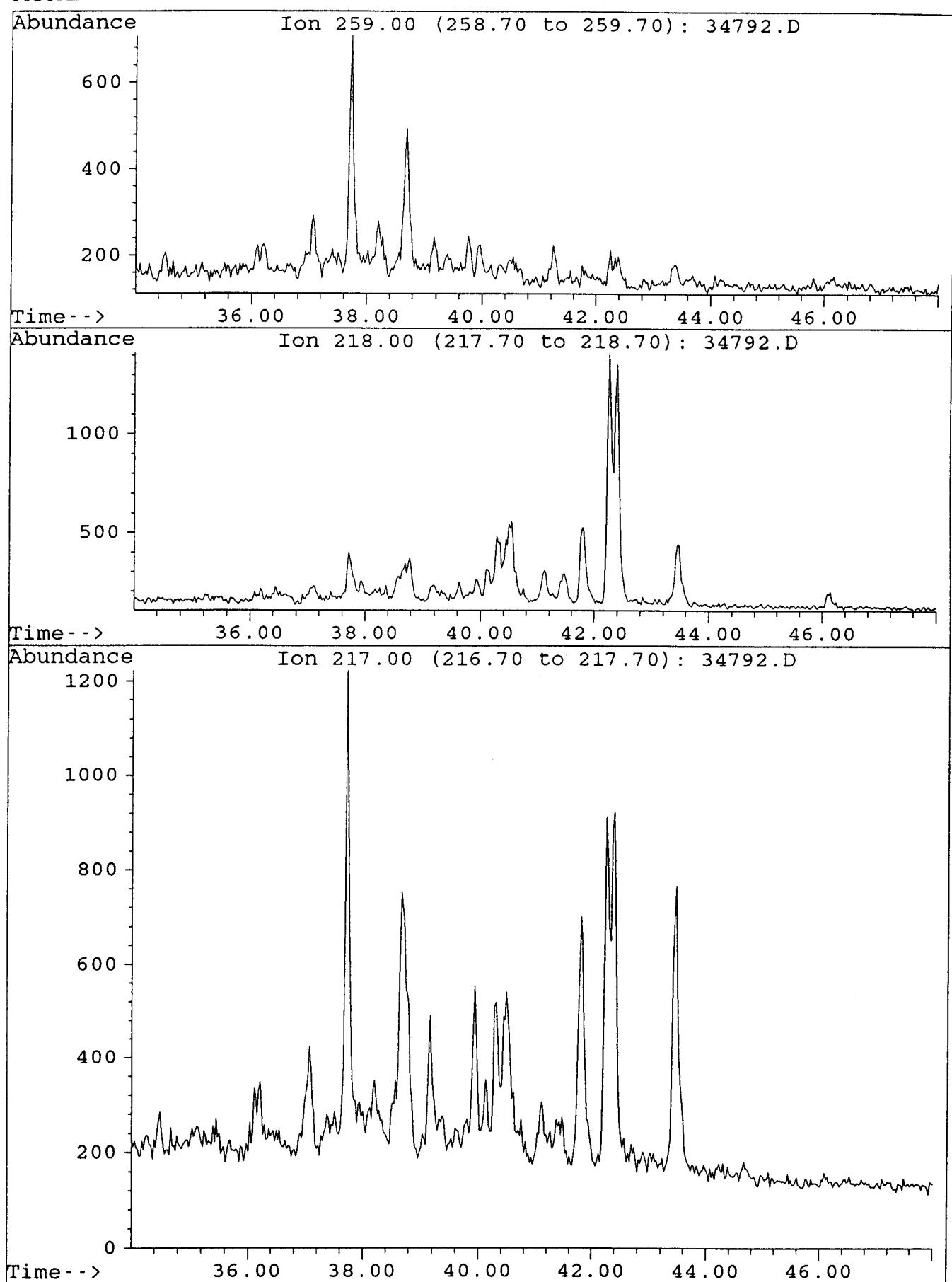
## GUDGEON 1, CH-19, Crude Oil

	<u>Parameter</u>	<u>Ion(s)</u>	<u>Value</u>
1.	$18\alpha$ (H)-hopane/ $17\alpha$ (H)-hopane (Ts/Tm)	191	nd
2.	C30 hopane/C30 moretane	191	nd
3.	C31 22S hopane/C31 22R hopane	191	nd
4.	C32 22S hopane/C32 22R hopane	191	nd
5.	C29 20S $\alpha\alpha\alpha$ sterane/C29 20R $\alpha\alpha\alpha$ sterane	217	nd
6.	C29 $\alpha\alpha\alpha$ steranes (20S / 20S+20R)	217	nd
7.	C29 $\alpha\beta\beta$ steranes	217	nd
8.	C27/C29 diasteranes	259	nd
9.	C27/C29 steranes	217	nd
10.	$18\alpha$ (H)-oleanane/C30 hopane	191	nd
11.	C29 diasteranes	217	nd
12.	C29 $\alpha\alpha\alpha$ steranes + C29 $\alpha\beta\beta$ steranes	191/217	nd
13.	C15 drimane/C16 homodrimane	123	0.61
14.	Rearranged drimanes/normal drimanes	123	0.98

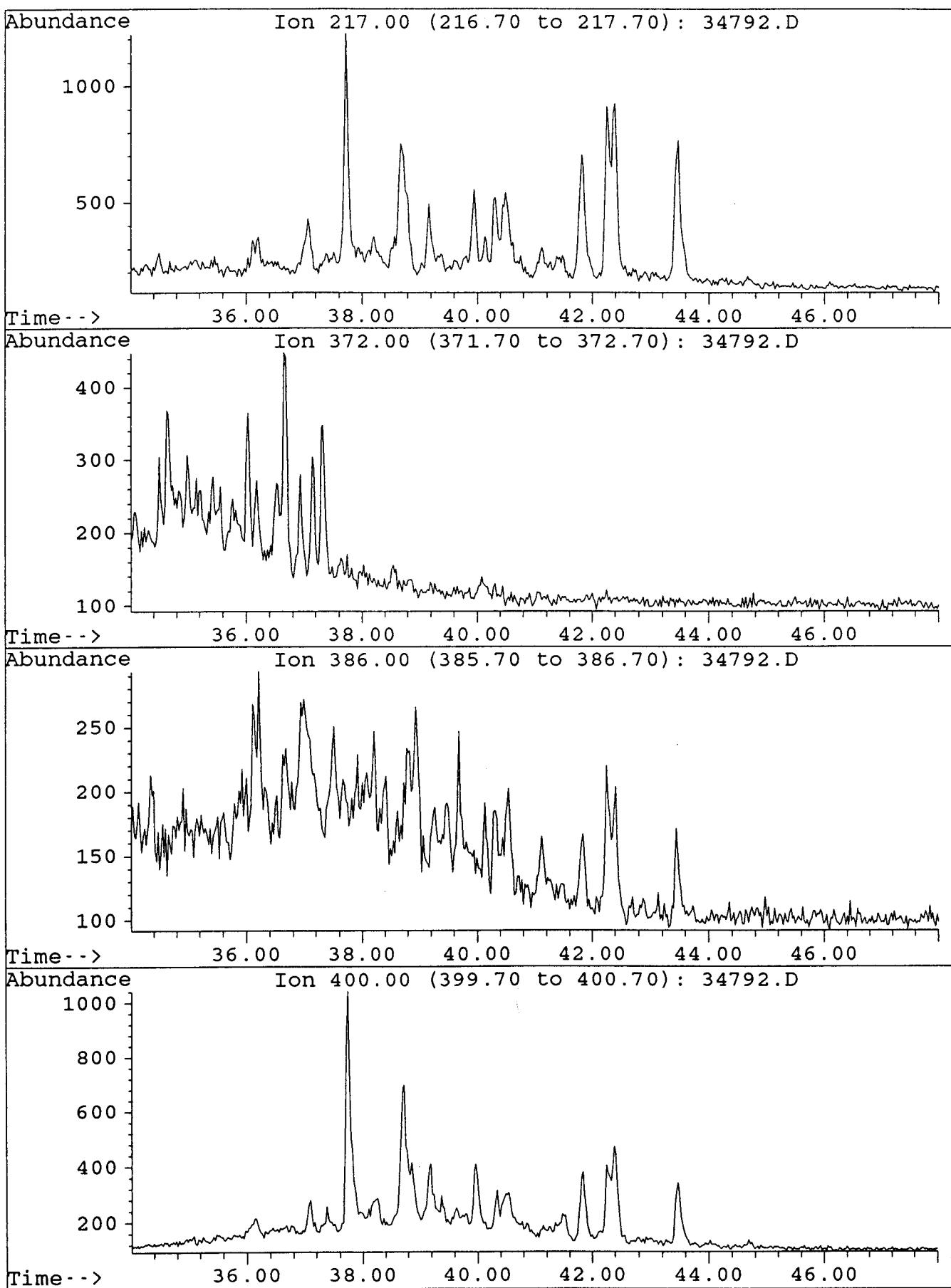
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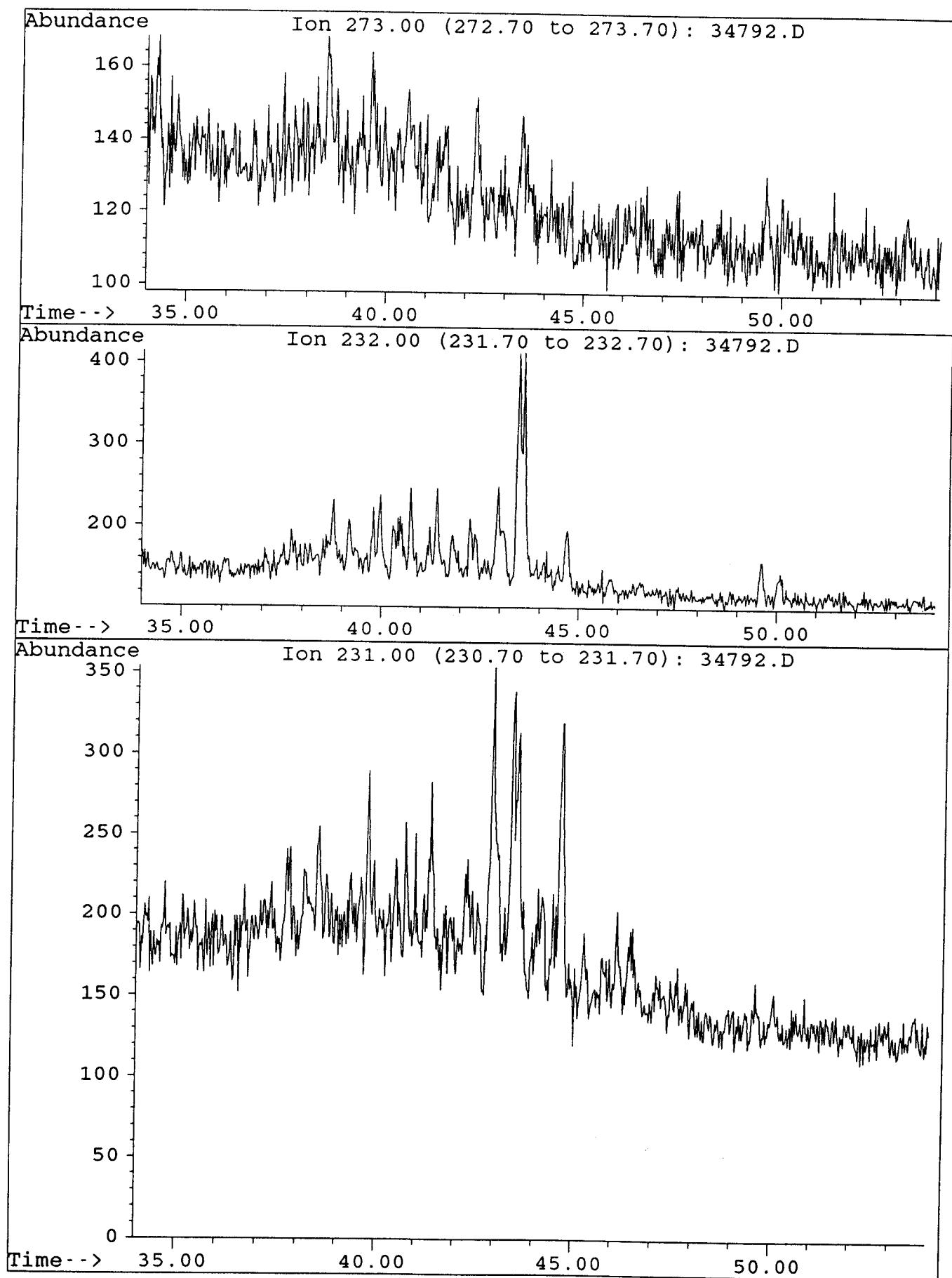
FIGURE 3-1-2



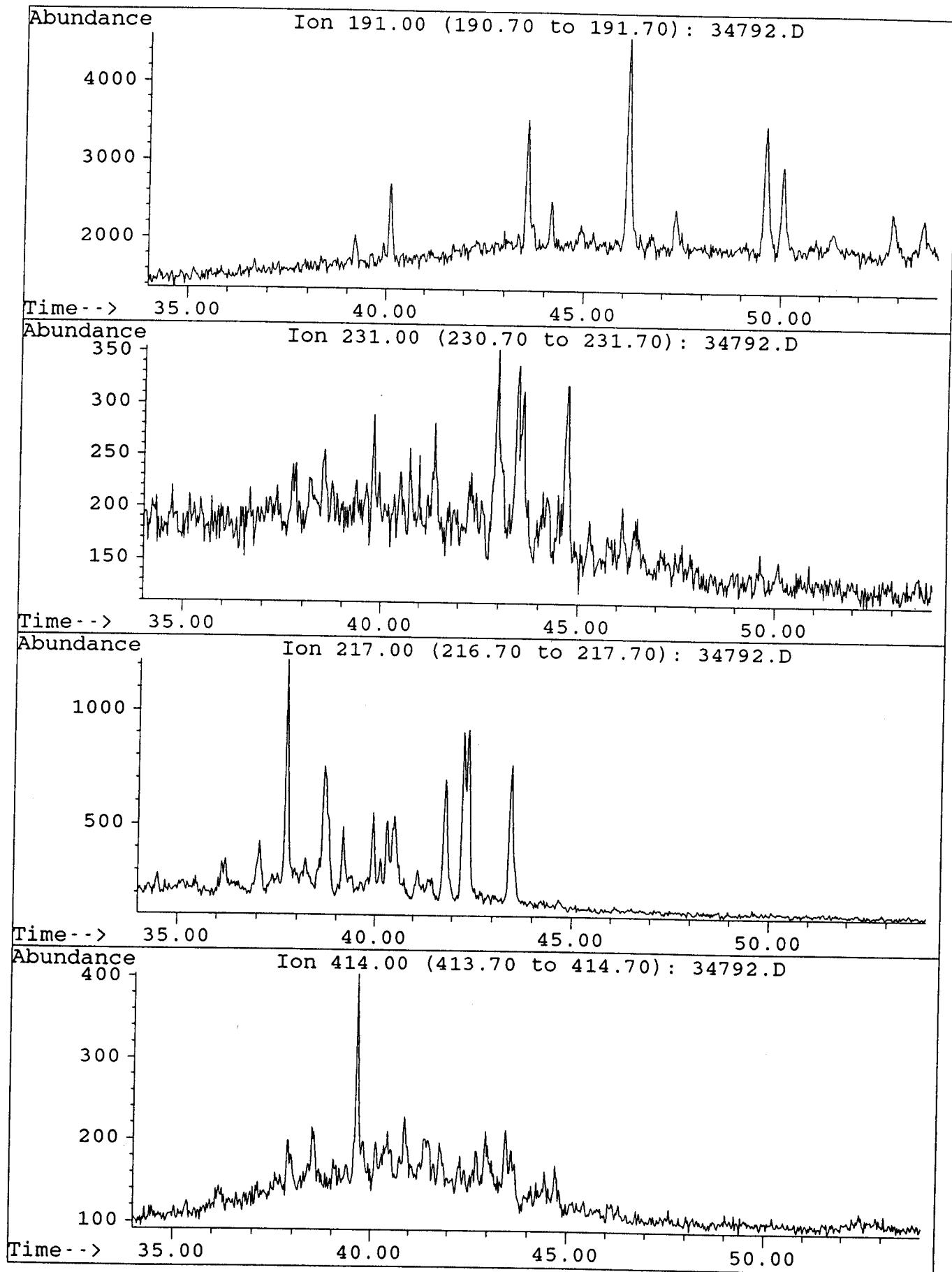
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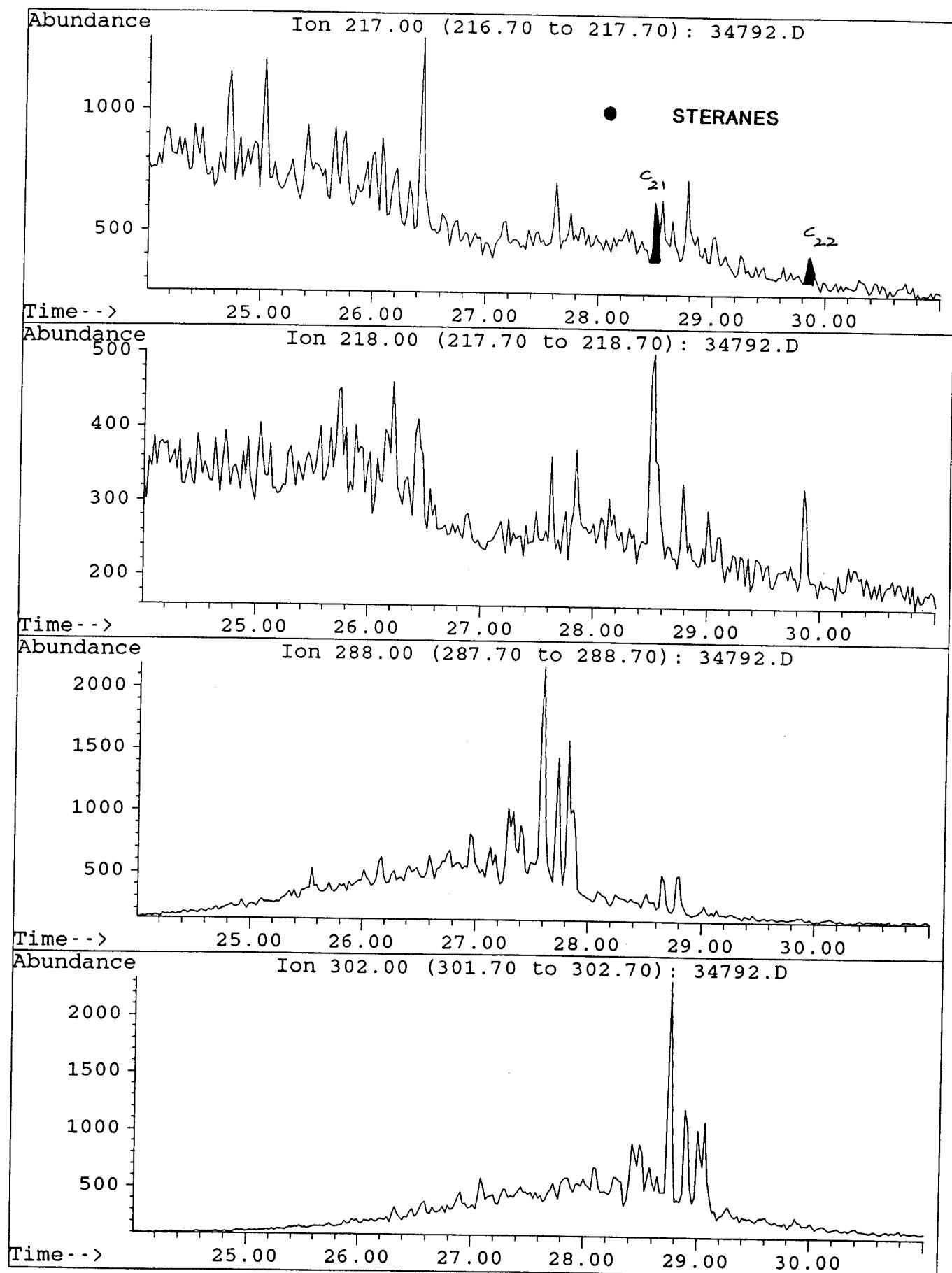
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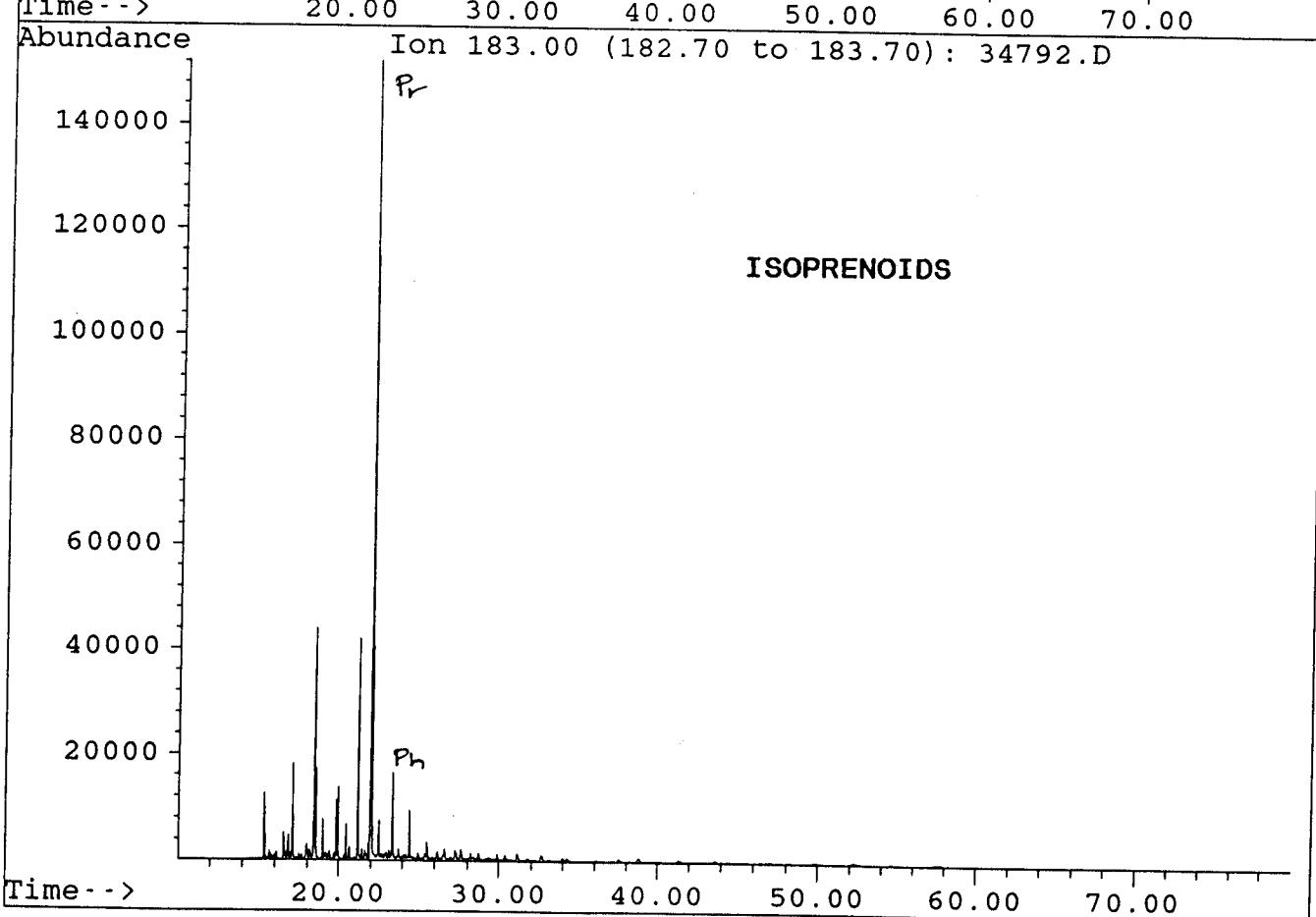
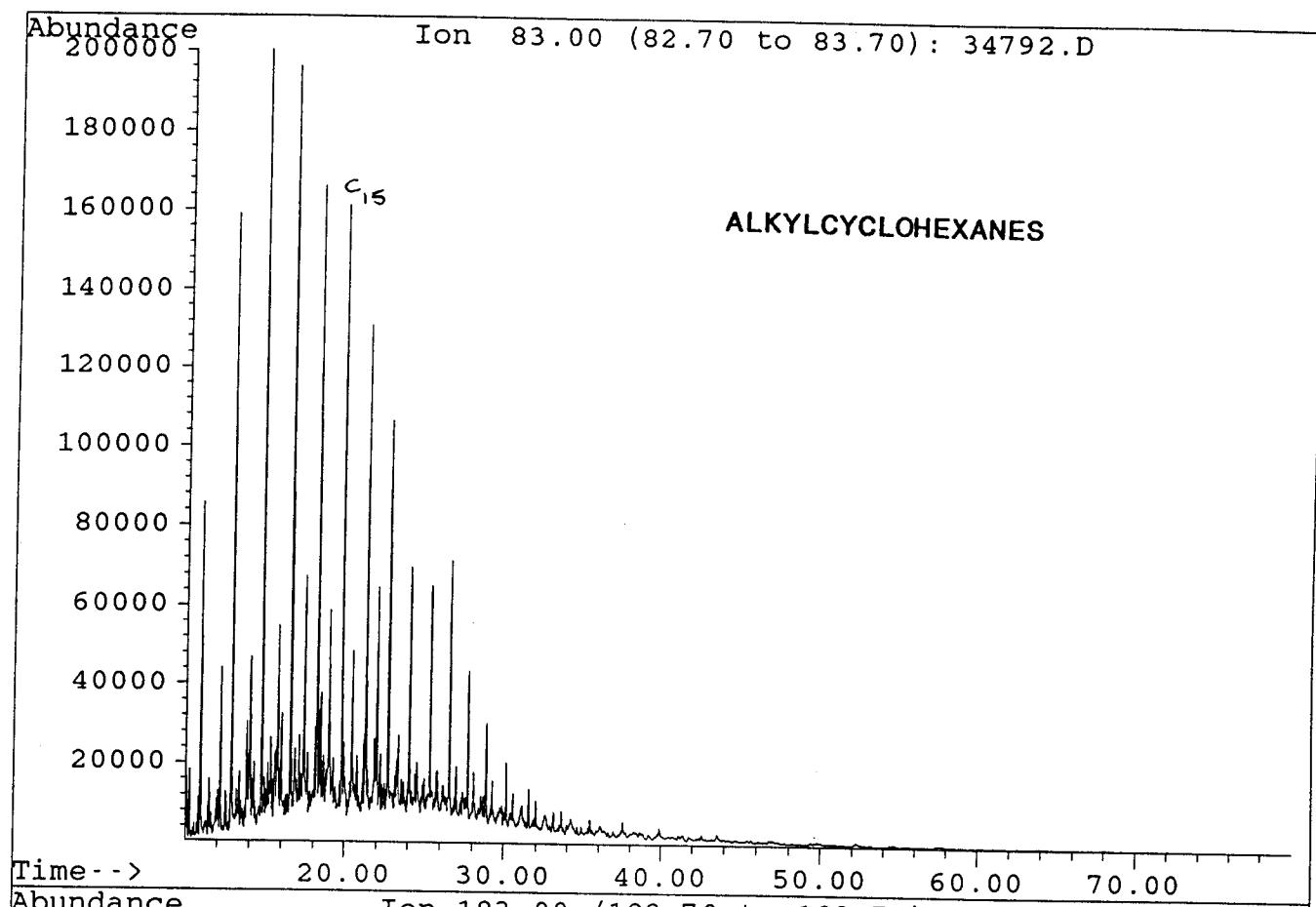
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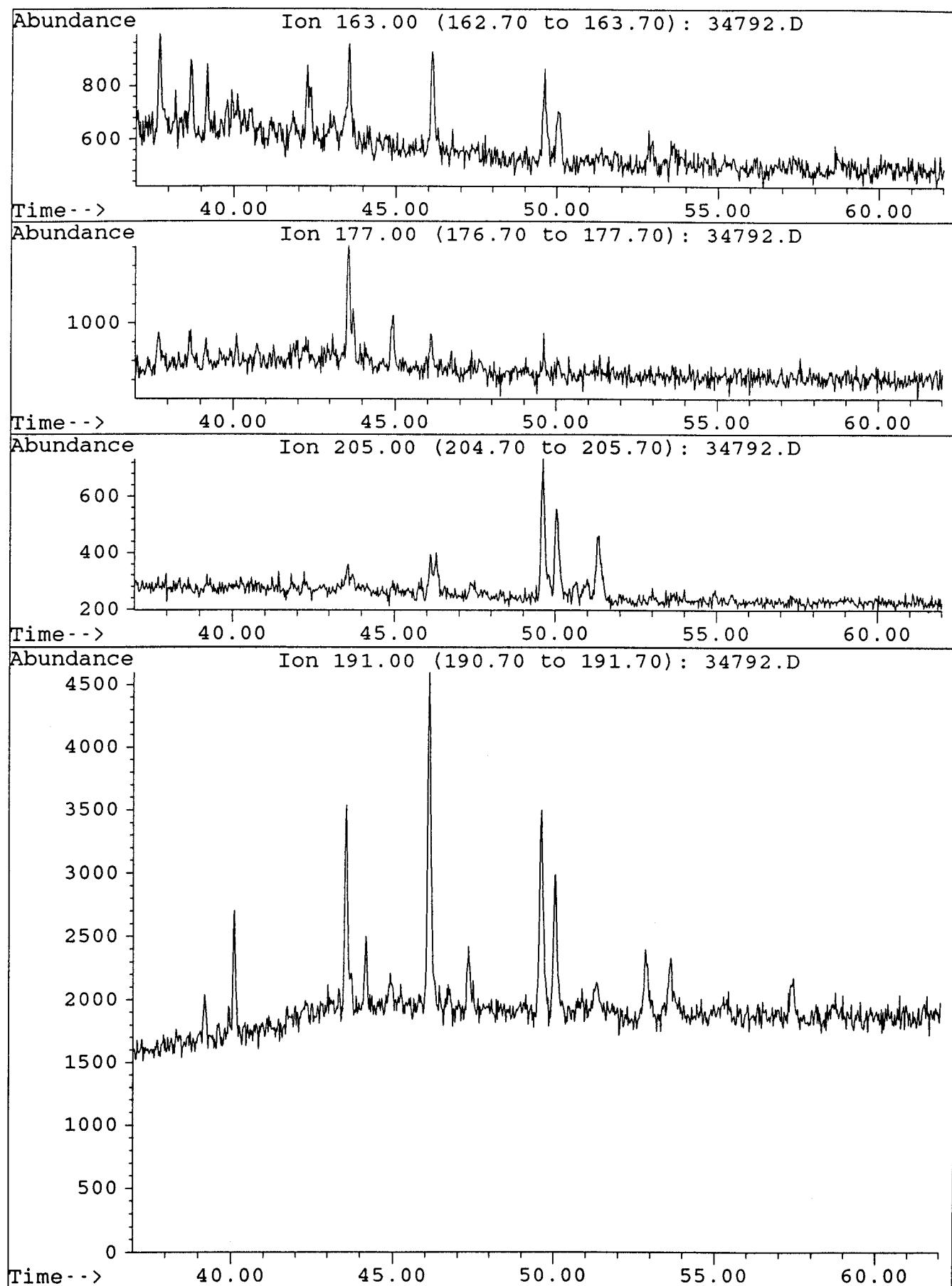
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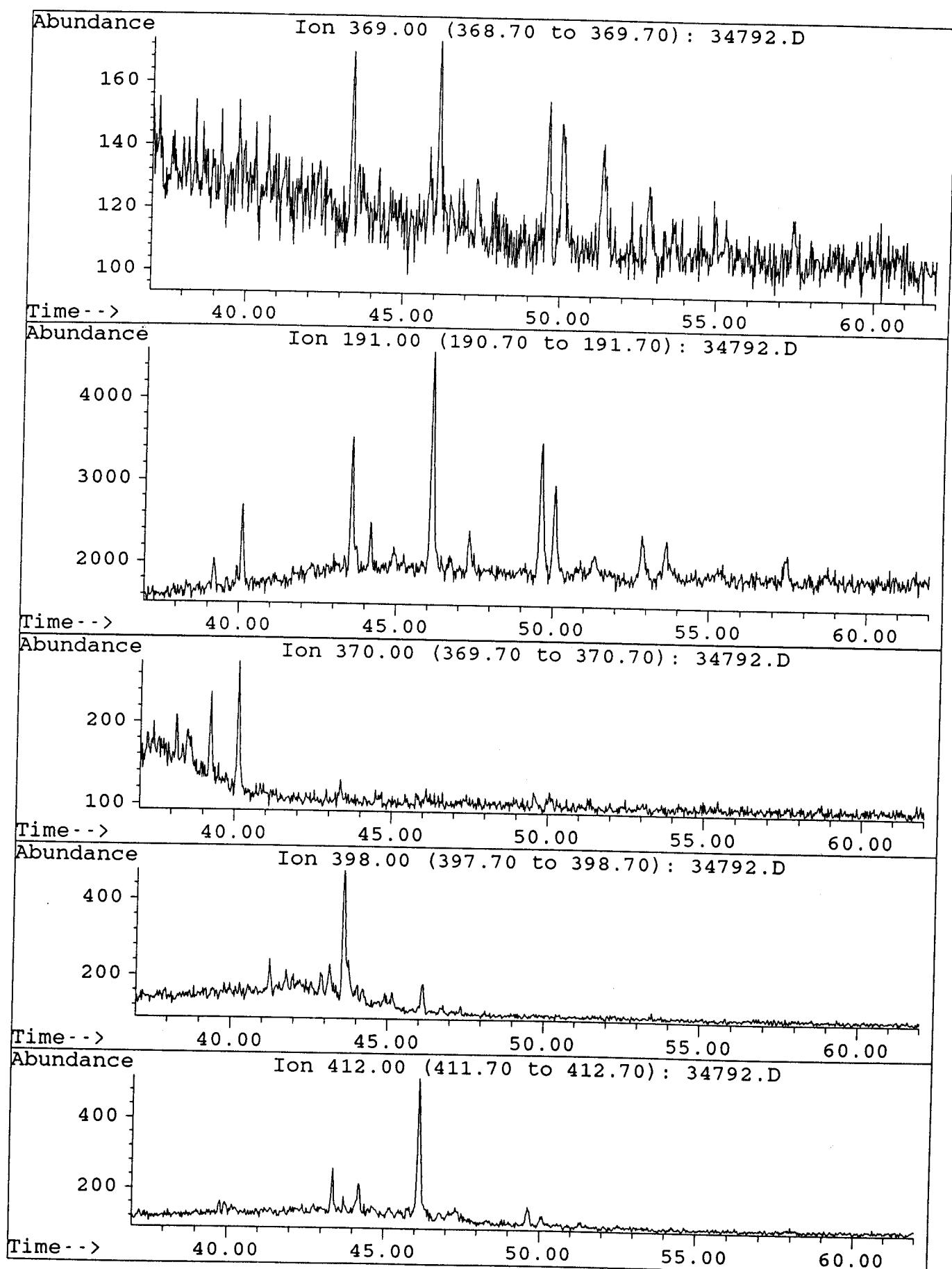
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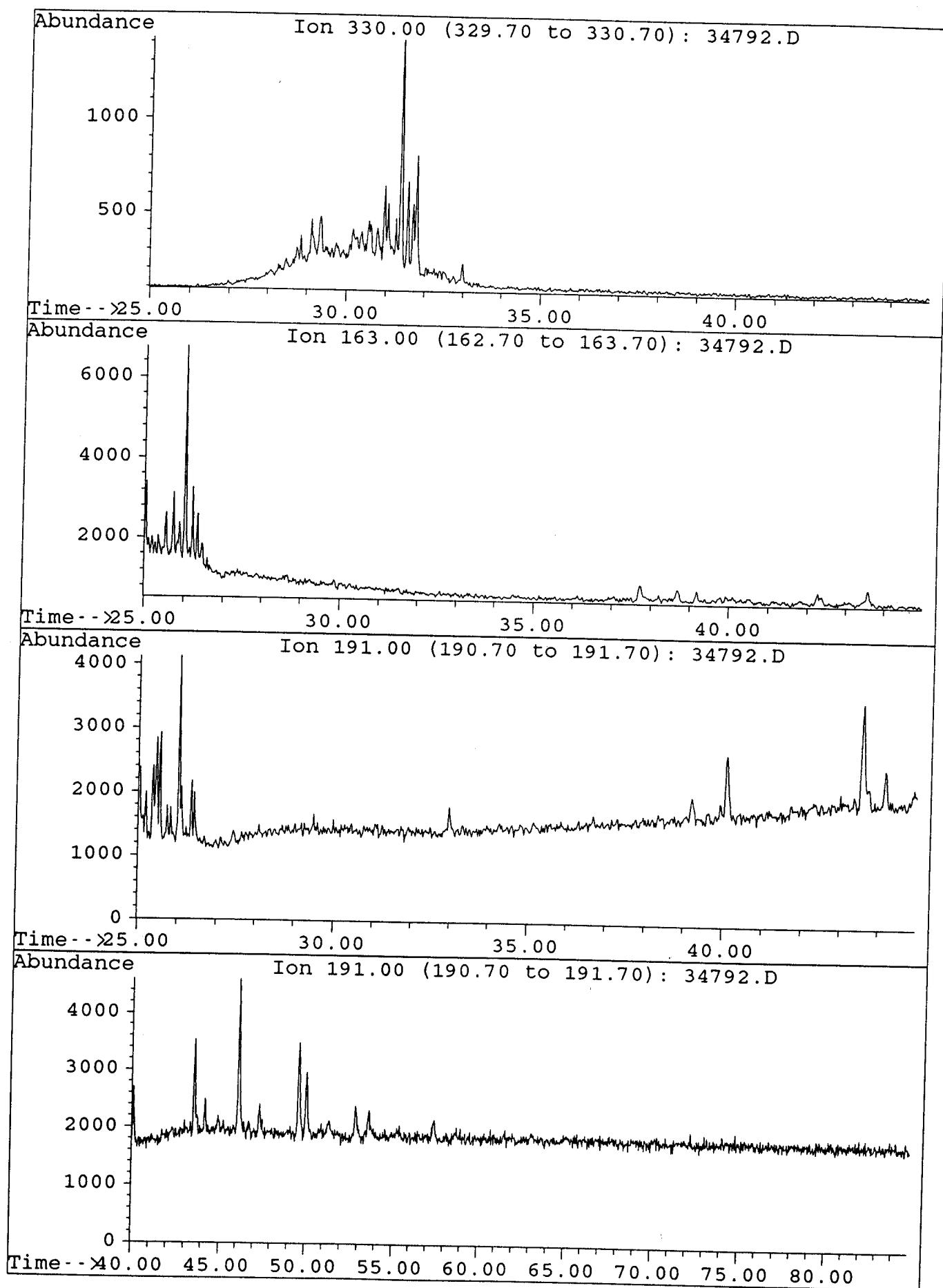
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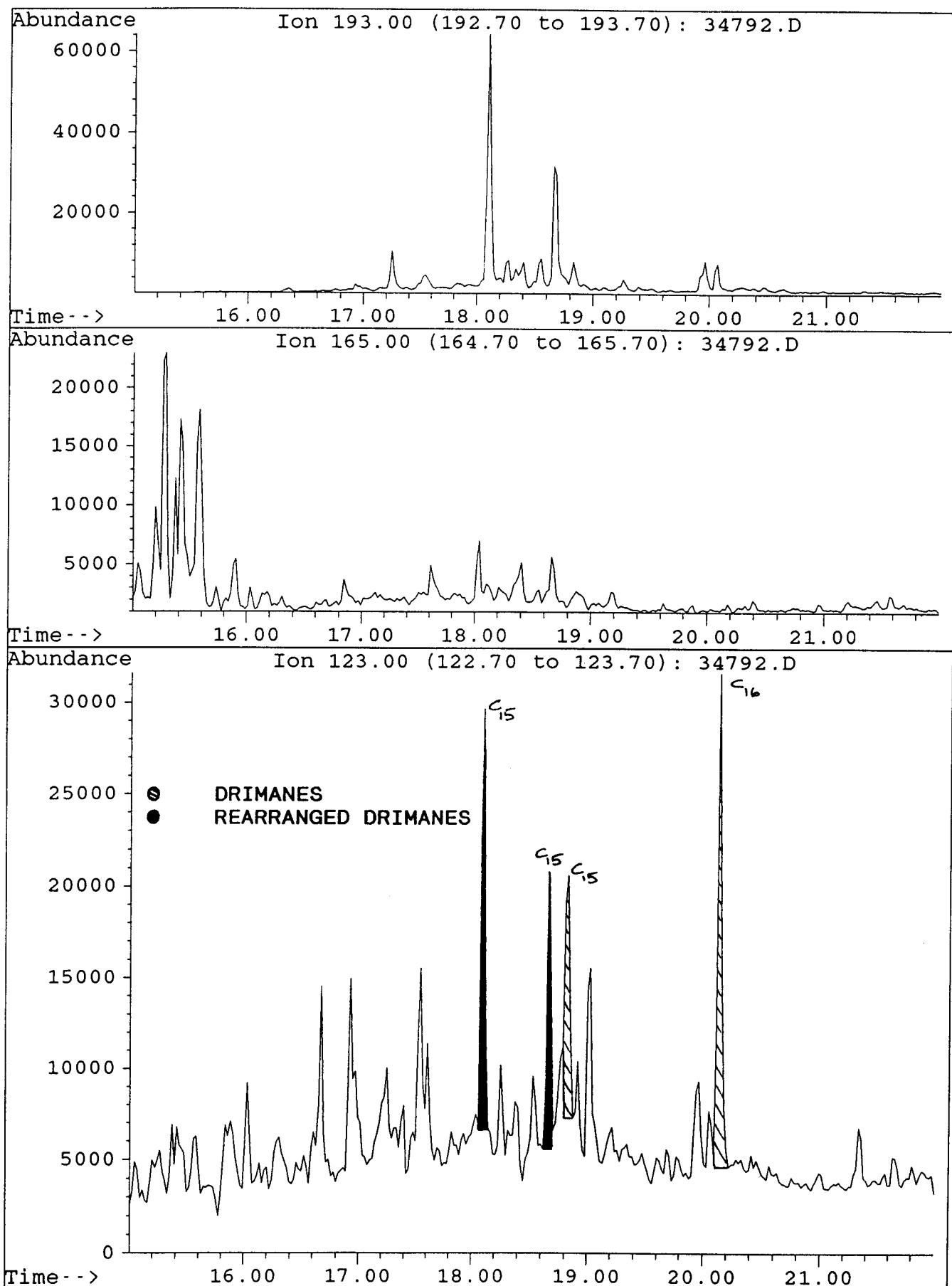
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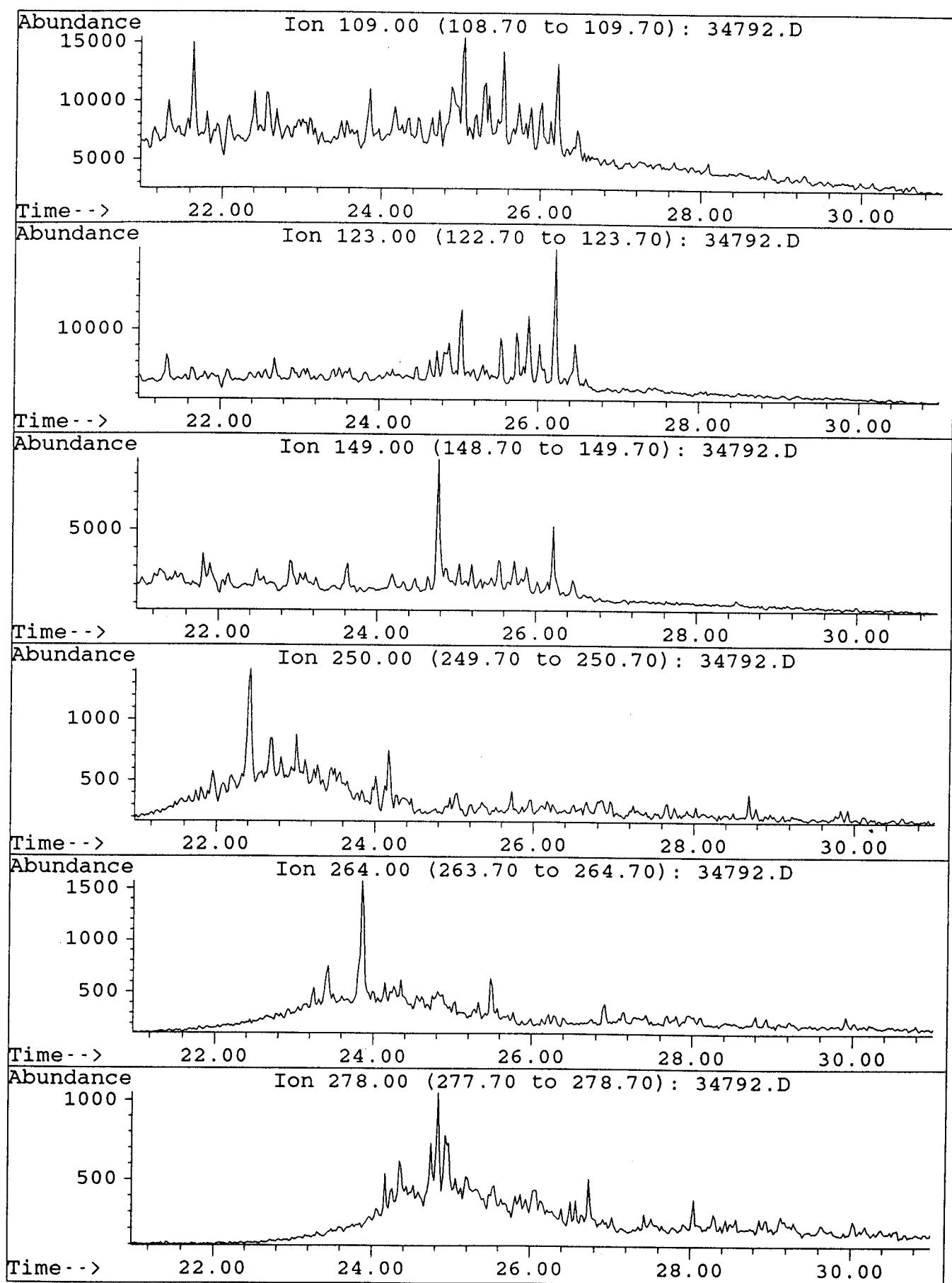
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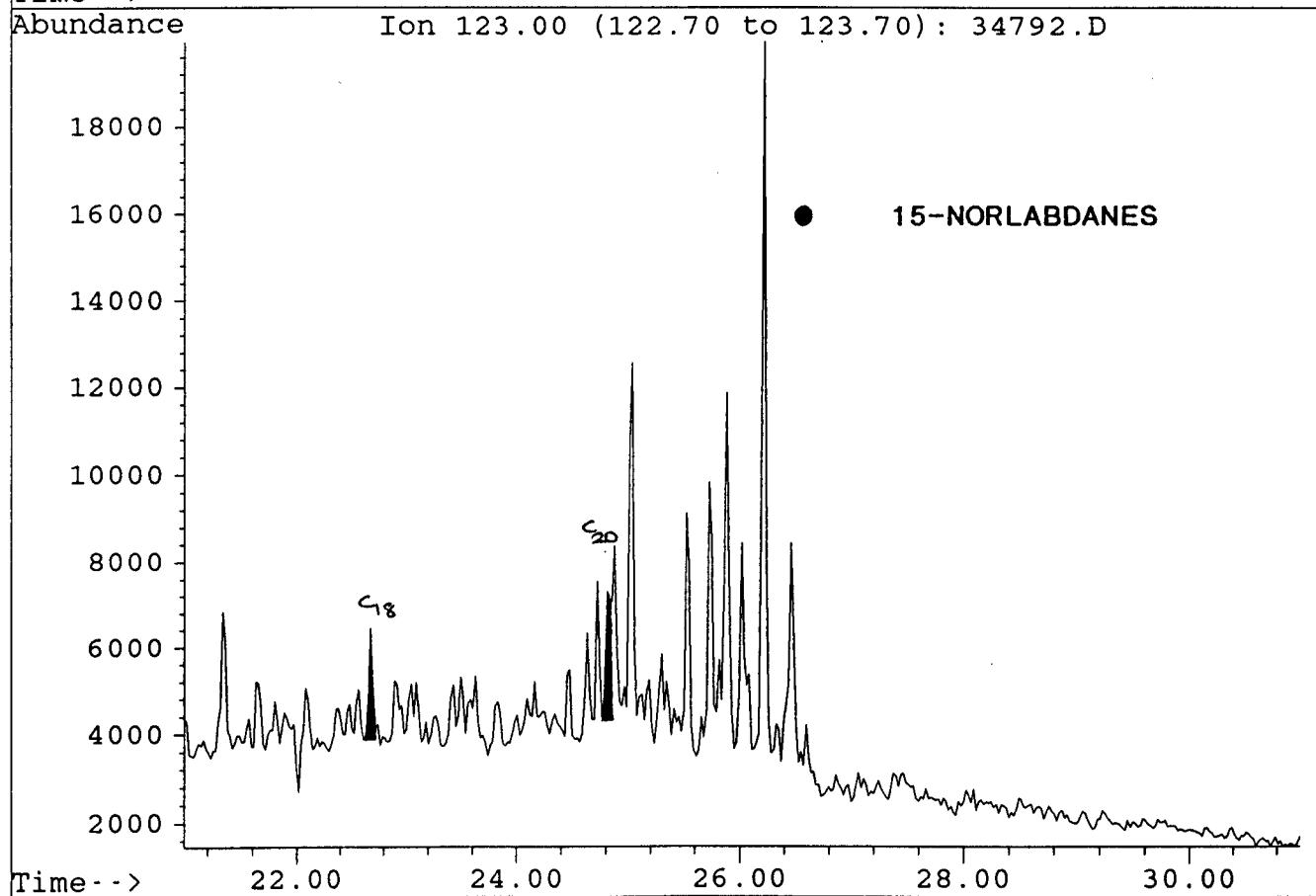
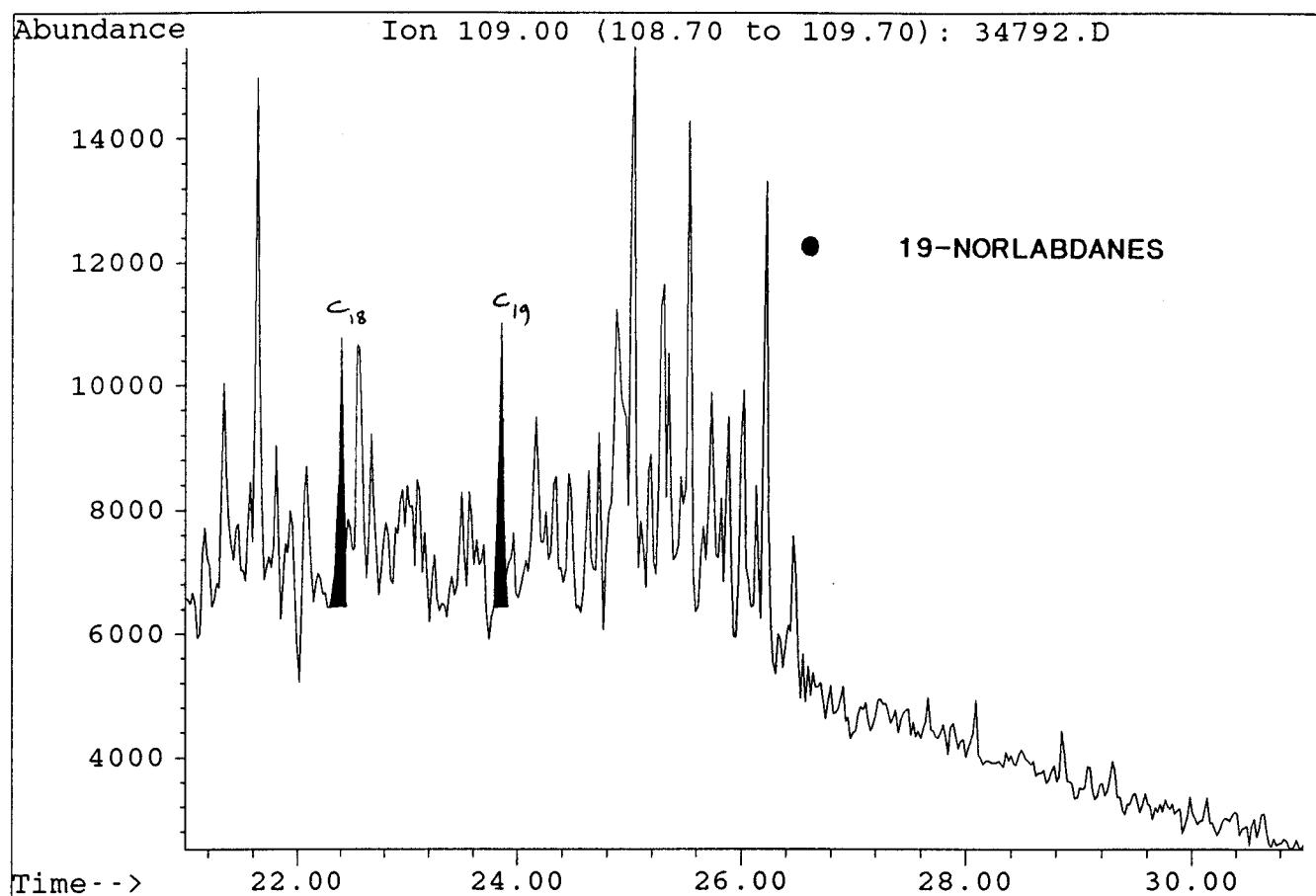
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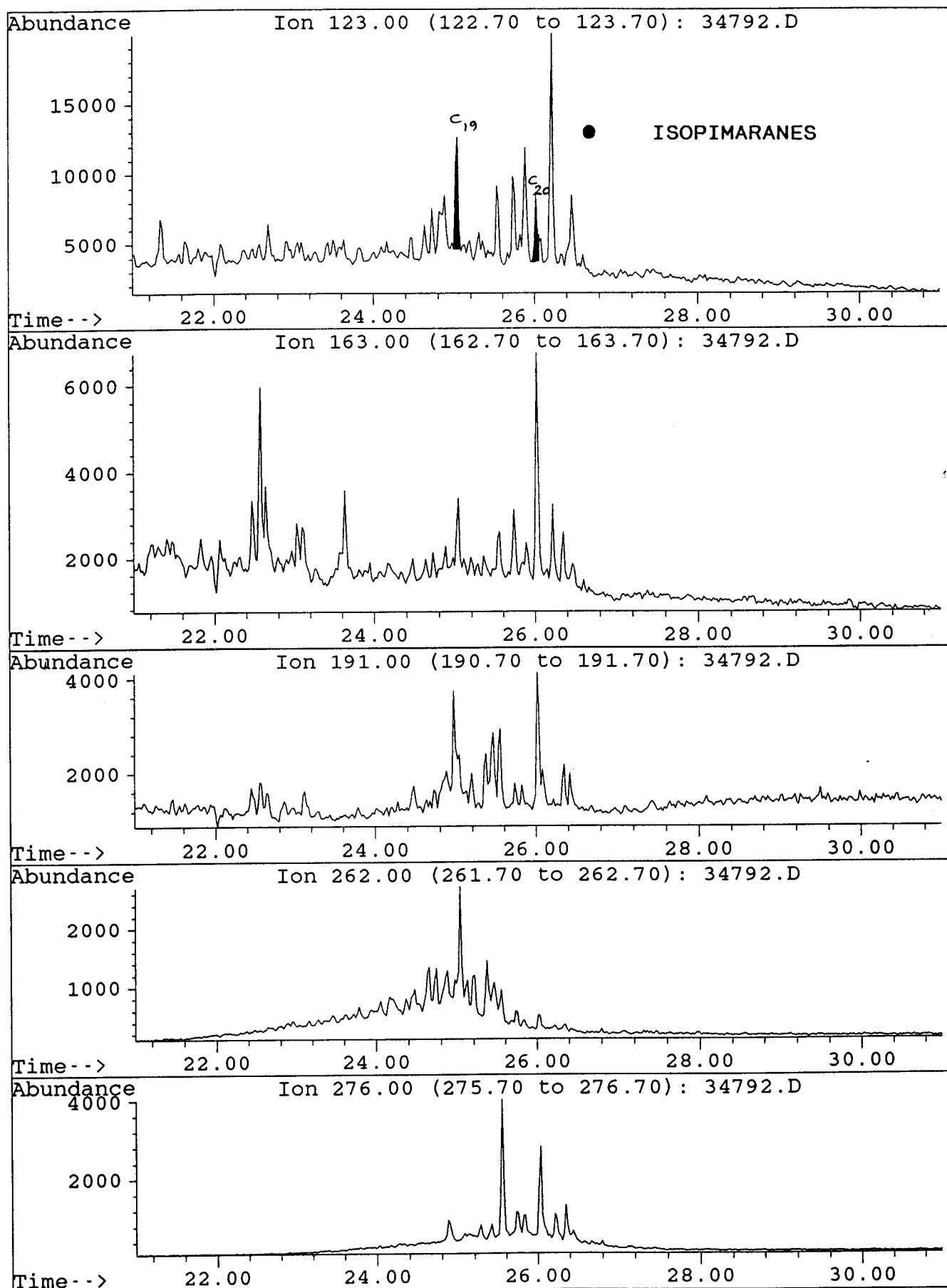
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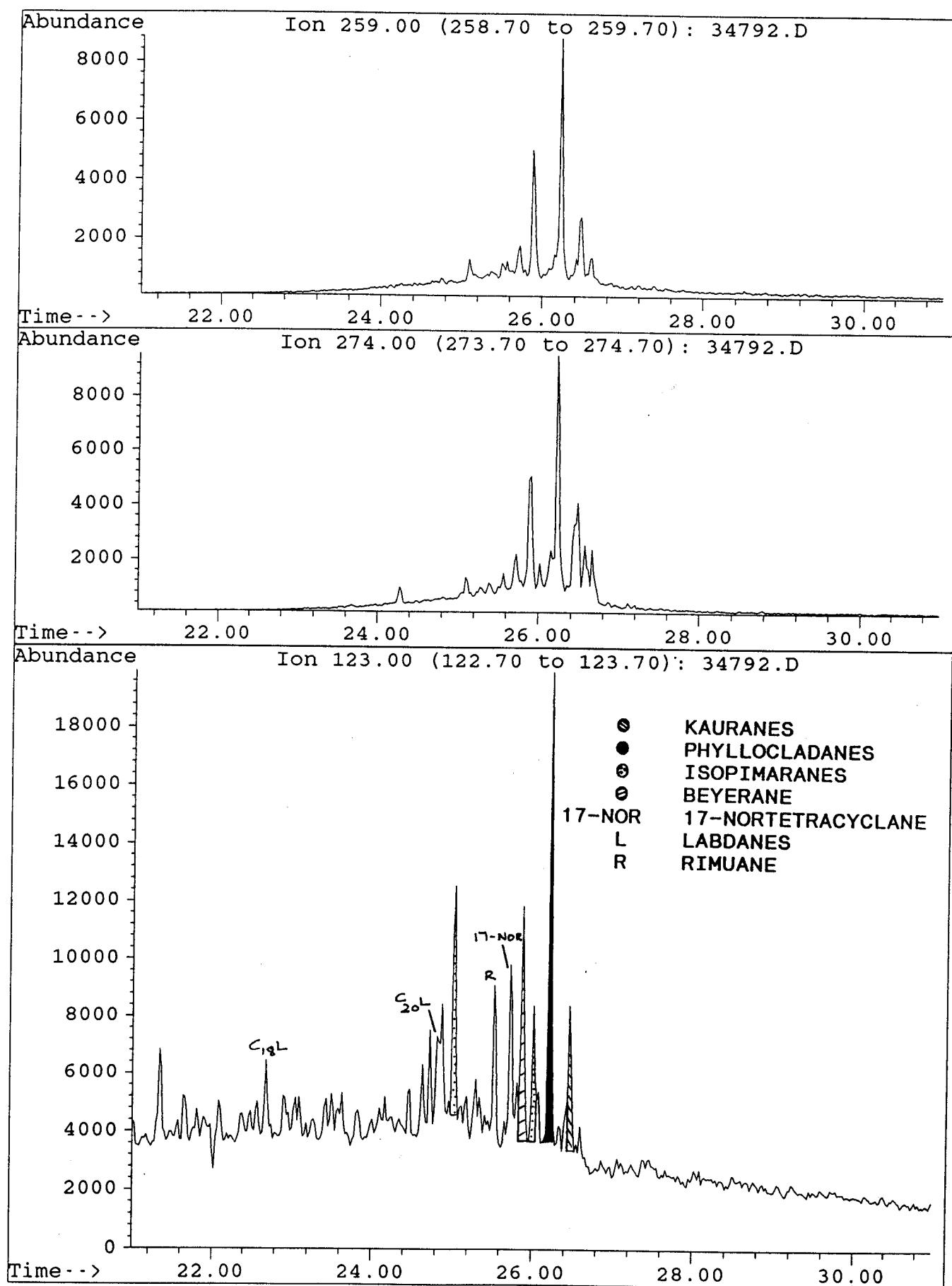


TABLE 4-1S

## SELECTED PARAMETERS FROM GC/MS ANALYSIS

GUDGEON 1, CH-19, Crude Oil

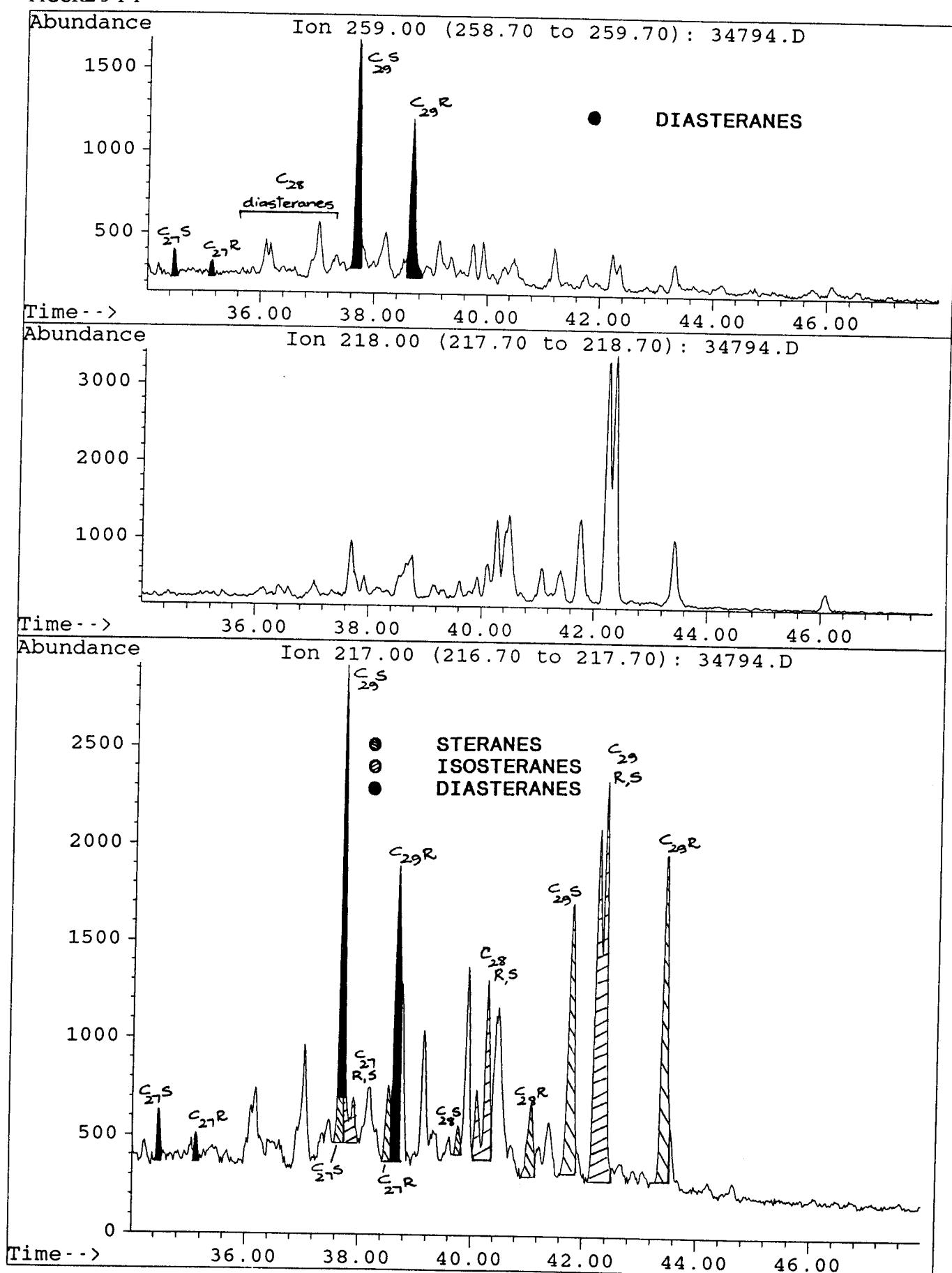
Special SIM

	<u>Parameter</u>	<u>Ion(s)</u>	<u>Value</u>
1.	18 $\alpha$ (H)-hopane/17 $\alpha$ (H)-hopane (Ts/Tm)	191	0.36
2.	C30 hopane/C30 moretane	191	4.90
3.	C31 22S hopane/C31 22R hopane	191	1.36
4.	C32 22S hopane/C32 22R hopane	191	1.40
5.	C29 20S $\alpha\alpha\alpha$ sterane/C29 20R $\alpha\alpha\alpha$ sterane	217	0.84
6.	C29 $\alpha\alpha\alpha$ steranes (20S / 20S+20R)	217	0.46
7.	C29 $\alpha\beta\beta$ steranes	217	0.55
	C29 $\alpha\alpha\alpha$ steranes + C29 $\alpha\beta\beta$ steranes		
8.	C27/C29 diasteranes	259	0.12
9.	C27/C29 steranes	217	0.24
10.	18 $\alpha$ (H)-oleanane/C30 hopane	191	nd
11.	C29 diasteranes	217	0.54
	C29 $\alpha\alpha\alpha$ steranes + C29 $\alpha\beta\beta$ steranes		
12.	C30 (hopane + moretane)	191/217	0.76
	C29 (steranes + diasteranes)		
13.	C15 drimane/C16 homodrimane	123	nd
14.	Rearranged drimanes/normal drimanes	123	nd

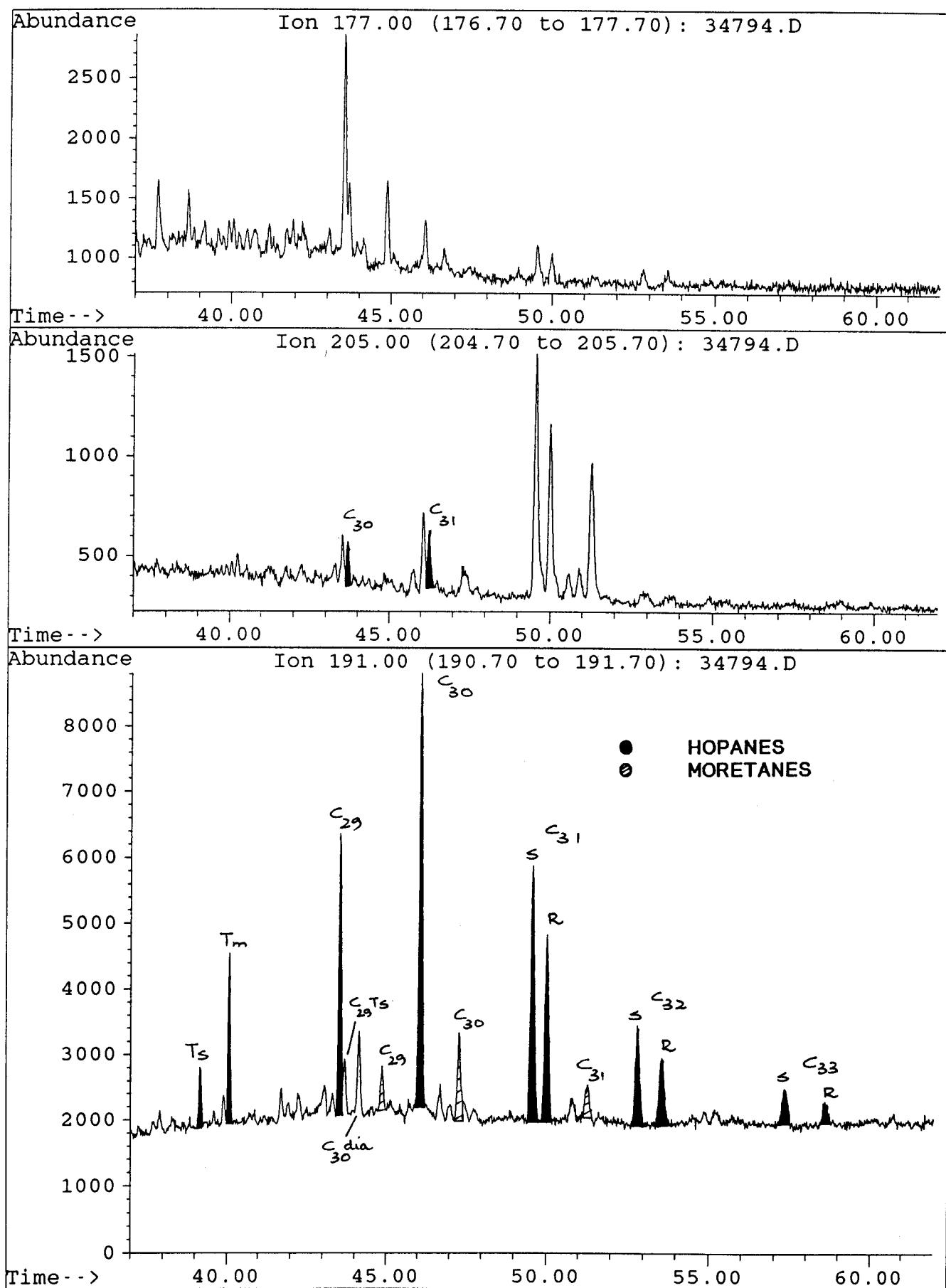
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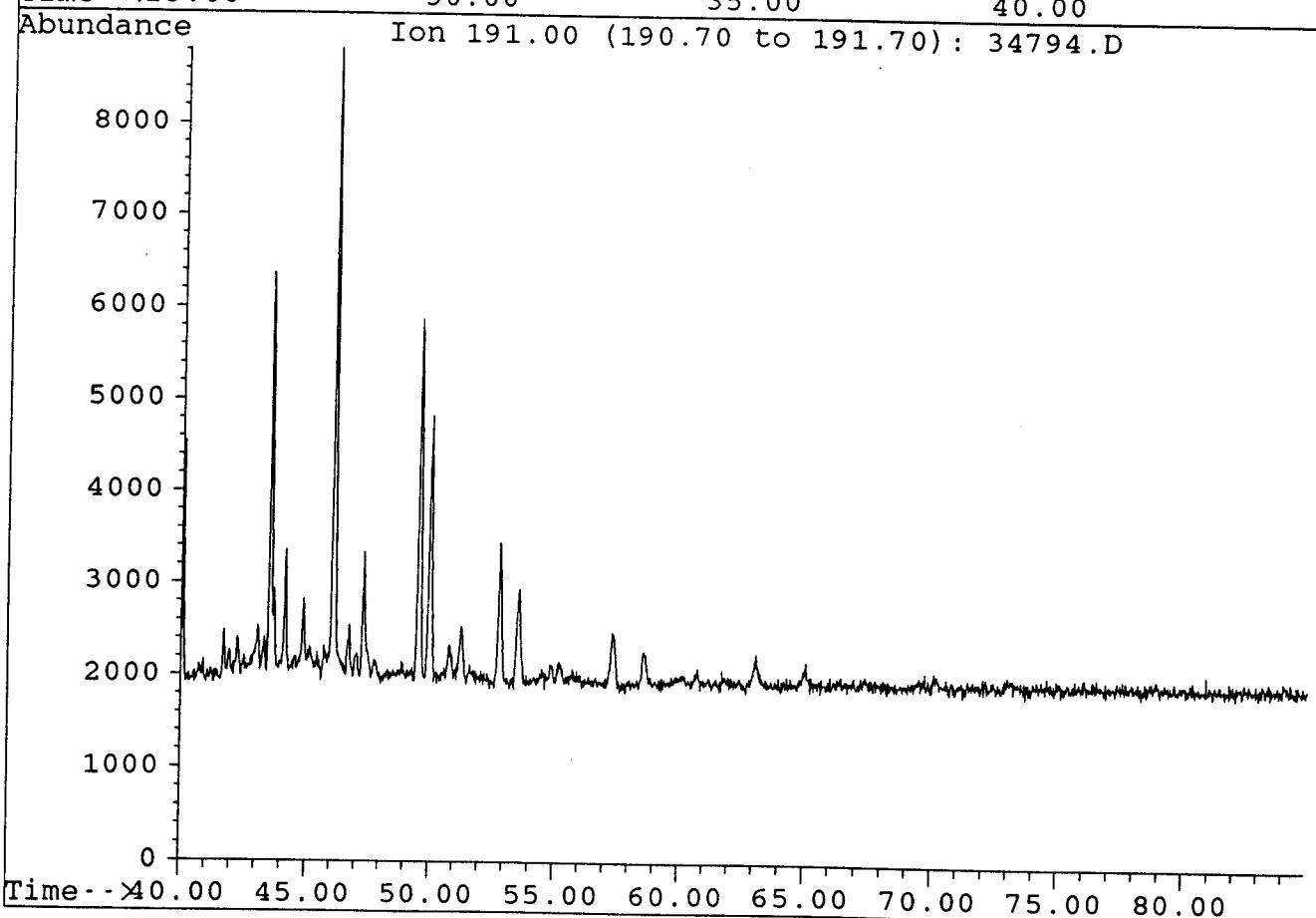
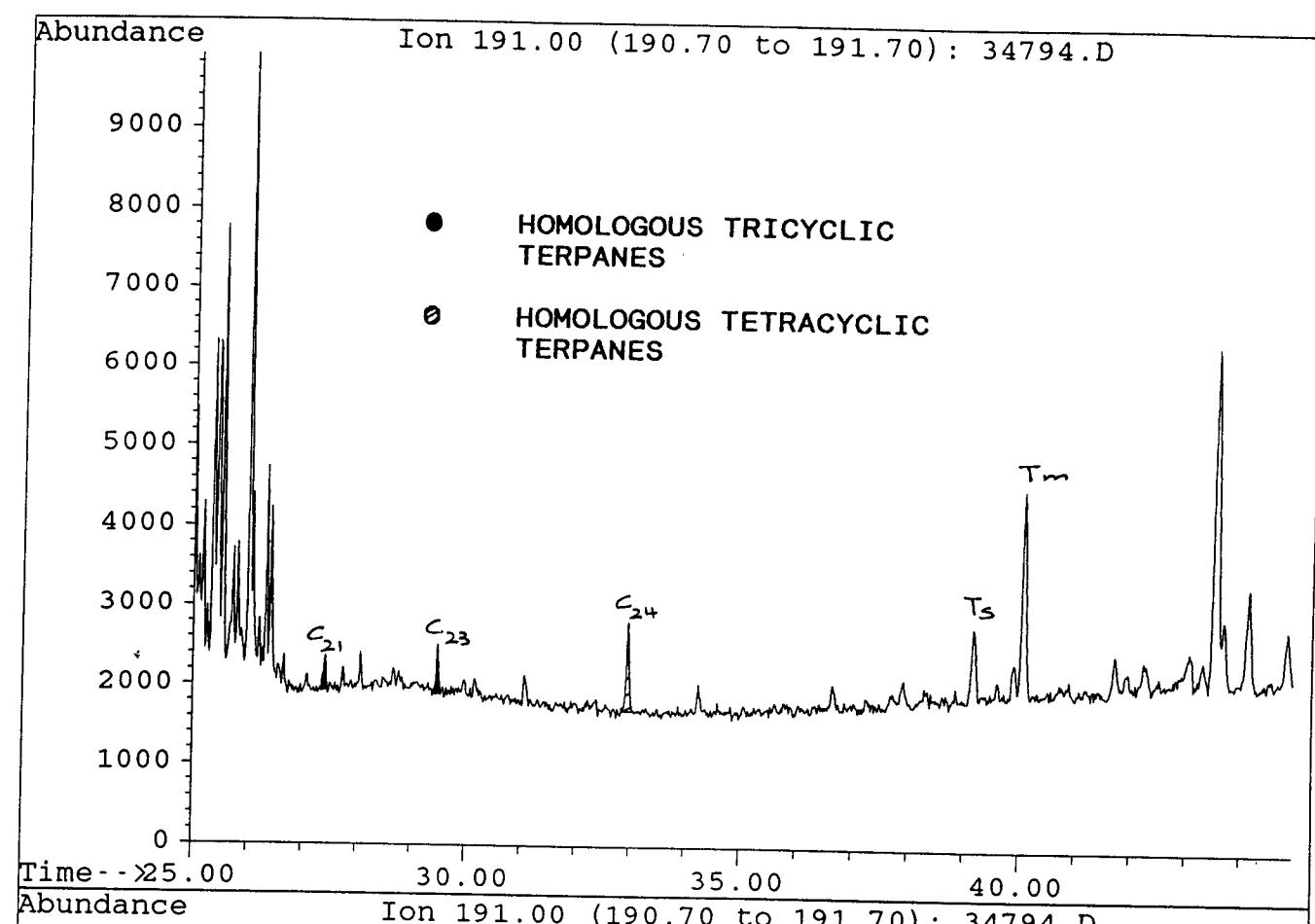
FIGURE 3-1-1



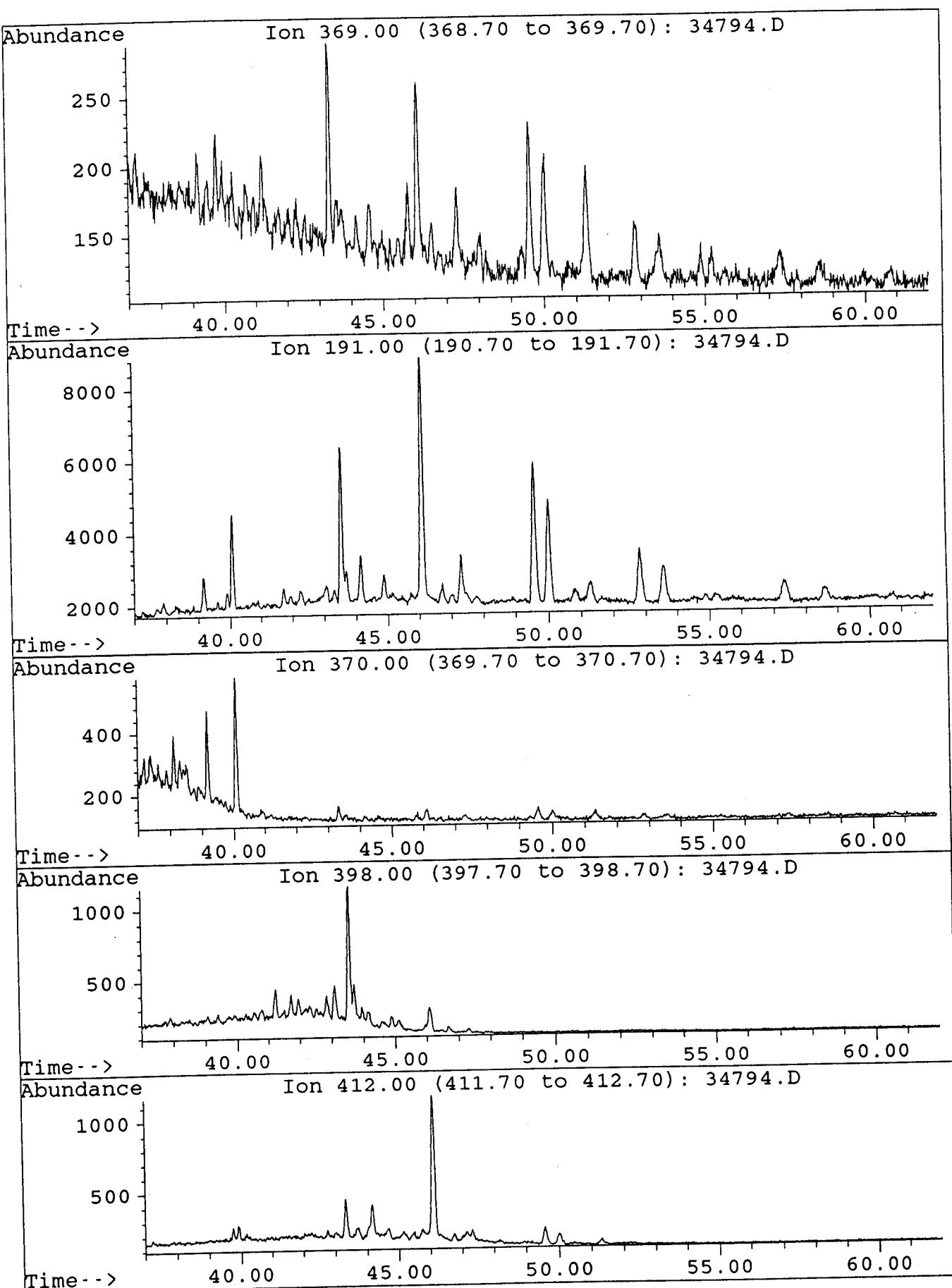
File : 34794.D  
Sample : GUDGEON #1 CH-19 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



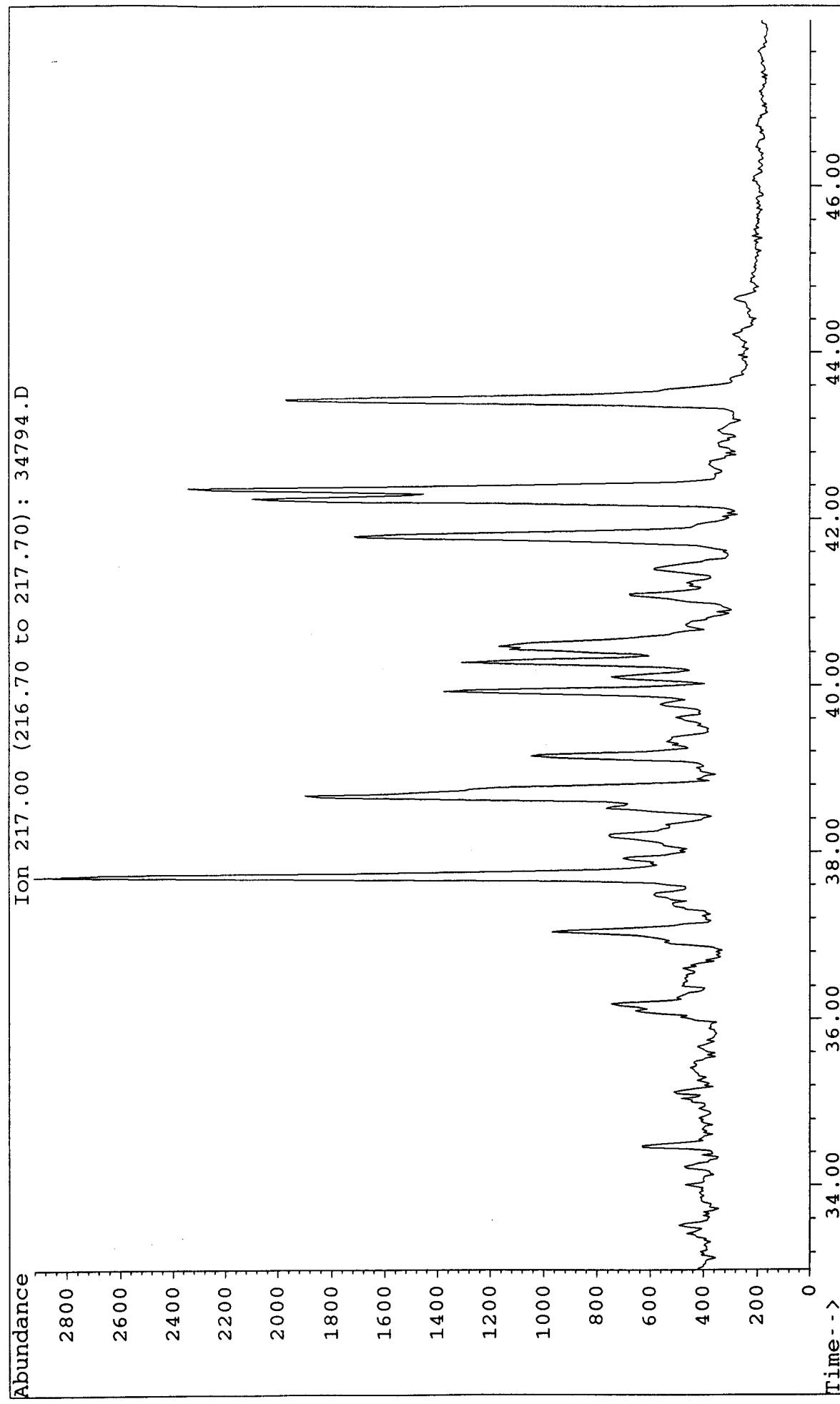
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Sample : GUDGEON #1 CH-19 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



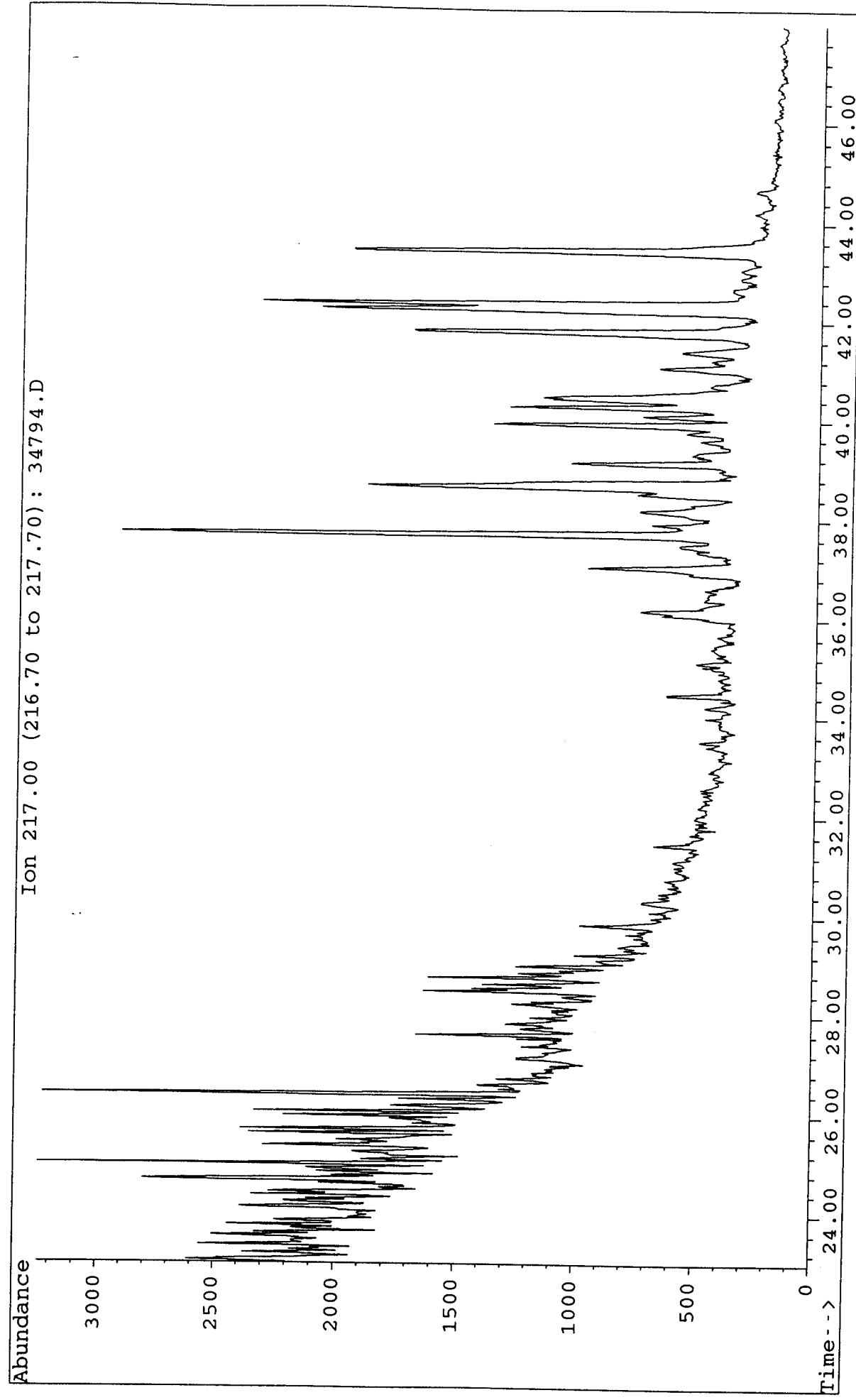
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Sample : GUDGEON #1 CH-19 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



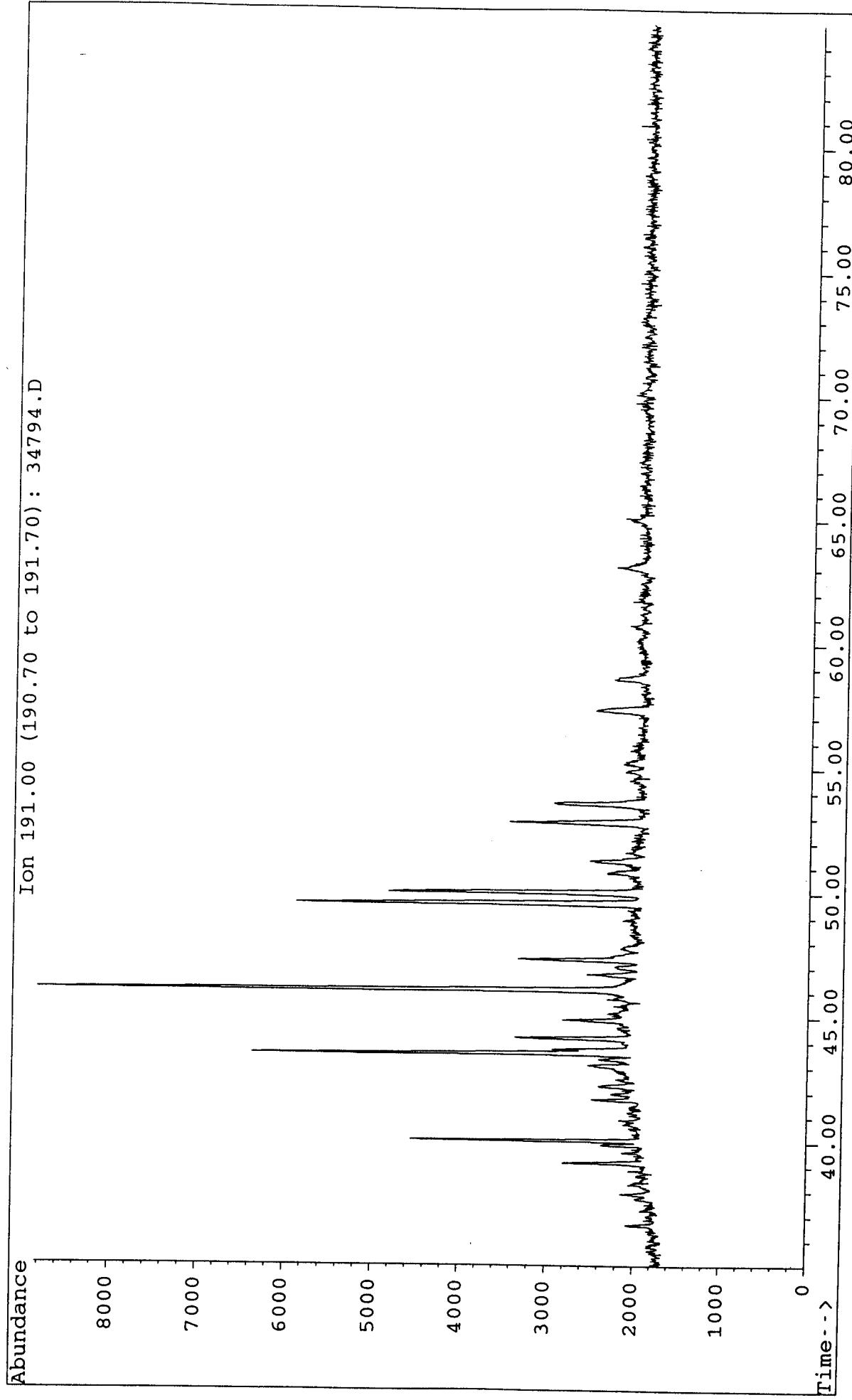
File : 34794.D  
Sample : GUDGEON #1 CH-19 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



File : 34794.D  
Sample : GUDGEON #1 CH-19 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



File : 34794.D  
Sample : GUDGEBON #1 CH-19 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



File : 34794.D  
Sample : GUDGEON #1 CH-19 B/C  
Misc. Info : COL#164. 18-12-95. SJF.

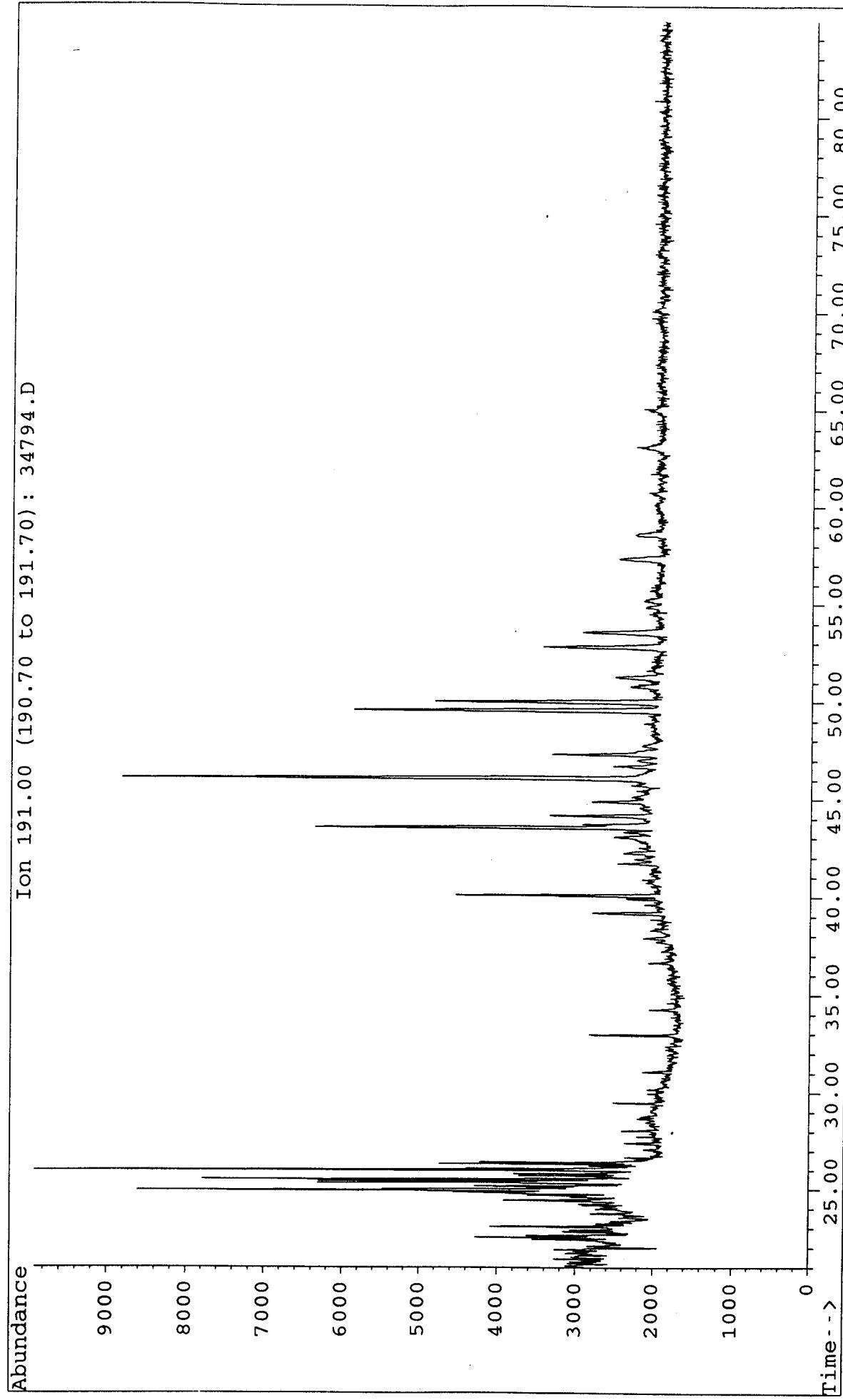


TABLE 4-2S

## SELECTED PARAMETERS FROM GC/MS ANALYSIS

**GUDGEON 1, CH-71, Crude Oil**

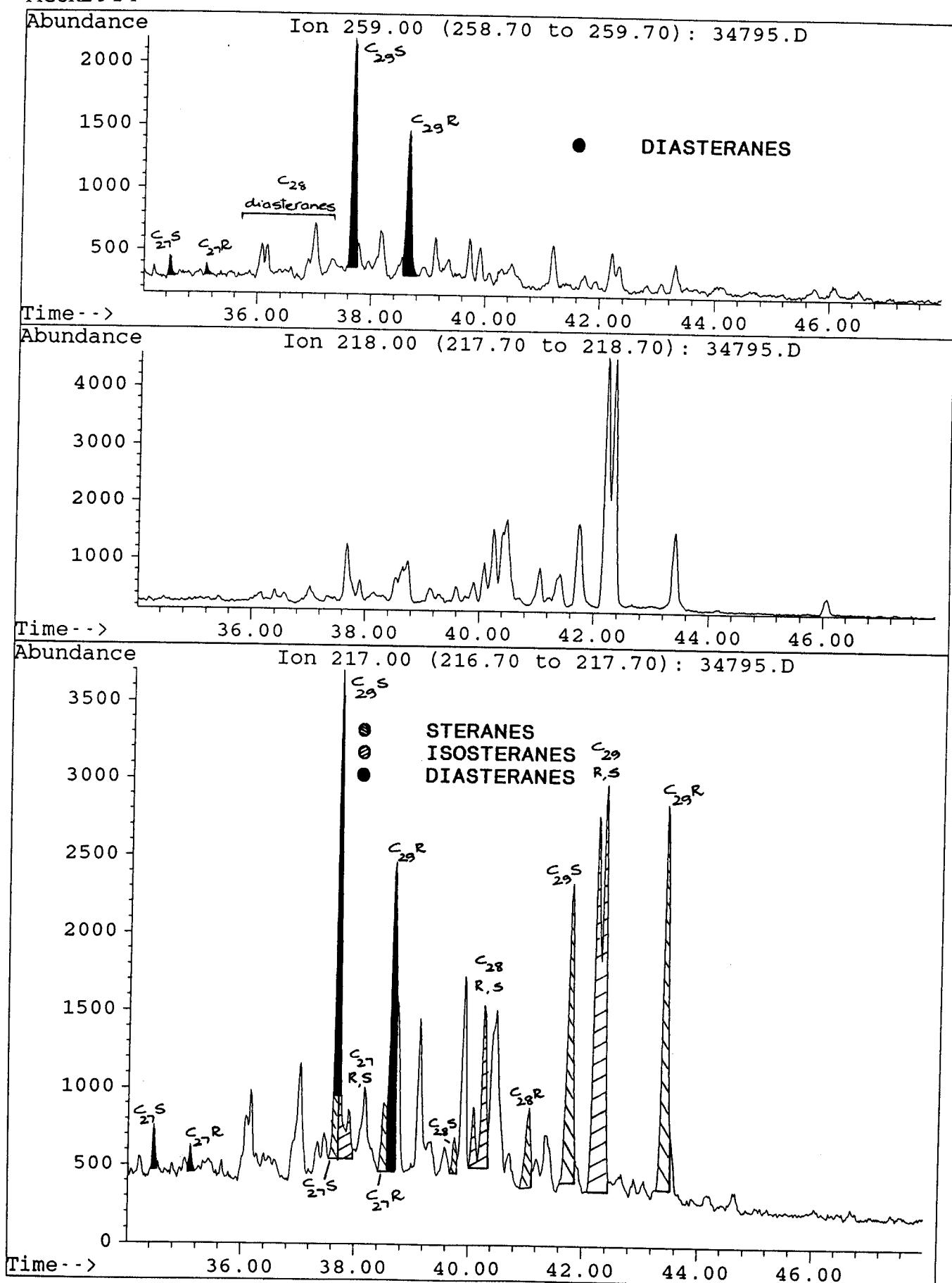
Special SIM

	<u>Parameter</u>	<u>Ion(s)</u>	<u>Value</u>
1.	$18\alpha$ (H)-hopane/ $17\alpha$ (H)-hopane (Ts/Tm)	191	0.41
2.	C30 hopane/C30 moretane	191	5.38
3.	C31 22S hopane/C31 22R hopane	191	1.30
4.	C32 22S hopane/C32 22R hopane	191	1.34
5.	C29 20S $\alpha\alpha\alpha$ sterane/C29 20R $\alpha\alpha\alpha$ sterane	217	0.79
6.	C29 $\alpha\alpha\alpha$ steranes (20S / 20S+20R)	217	0.44
7.	C29 $\alpha\beta\beta$ steranes	217	0.53
	C29 $\alpha\alpha\alpha$ steranes + C29 $\alpha\beta\beta$ steranes		
8.	C27/C29 diasteranes	259	0.11
9.	C27/C29 steranes	217	0.18
10.	$18\alpha$ (H)-oleanane/C30 hopane	191	nd
11.	C29 diasteranes	217	0.55
	C29 $\alpha\alpha\alpha$ steranes + C29 $\alpha\beta\beta$ steranes		
12.	C30 (hopane + moretane)	191/217	0.70
	C29 (steranes + diasteranes)		
13.	C15 drimane/C16 homodrimane	123	nd
14.	Rearranged drimanes/normal drimanes	123	nd

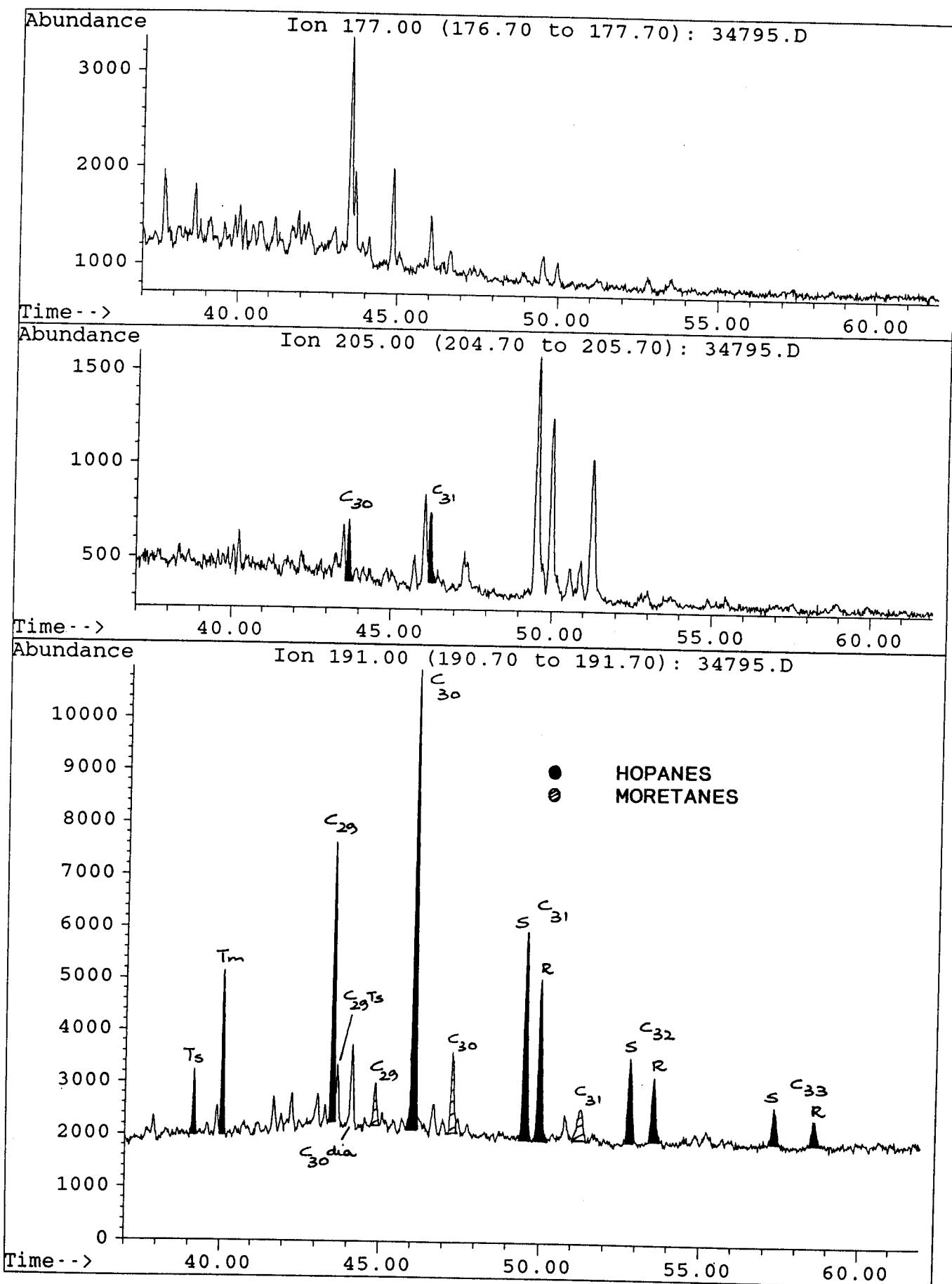
nd = not detectable

File : 34795.D  
Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.

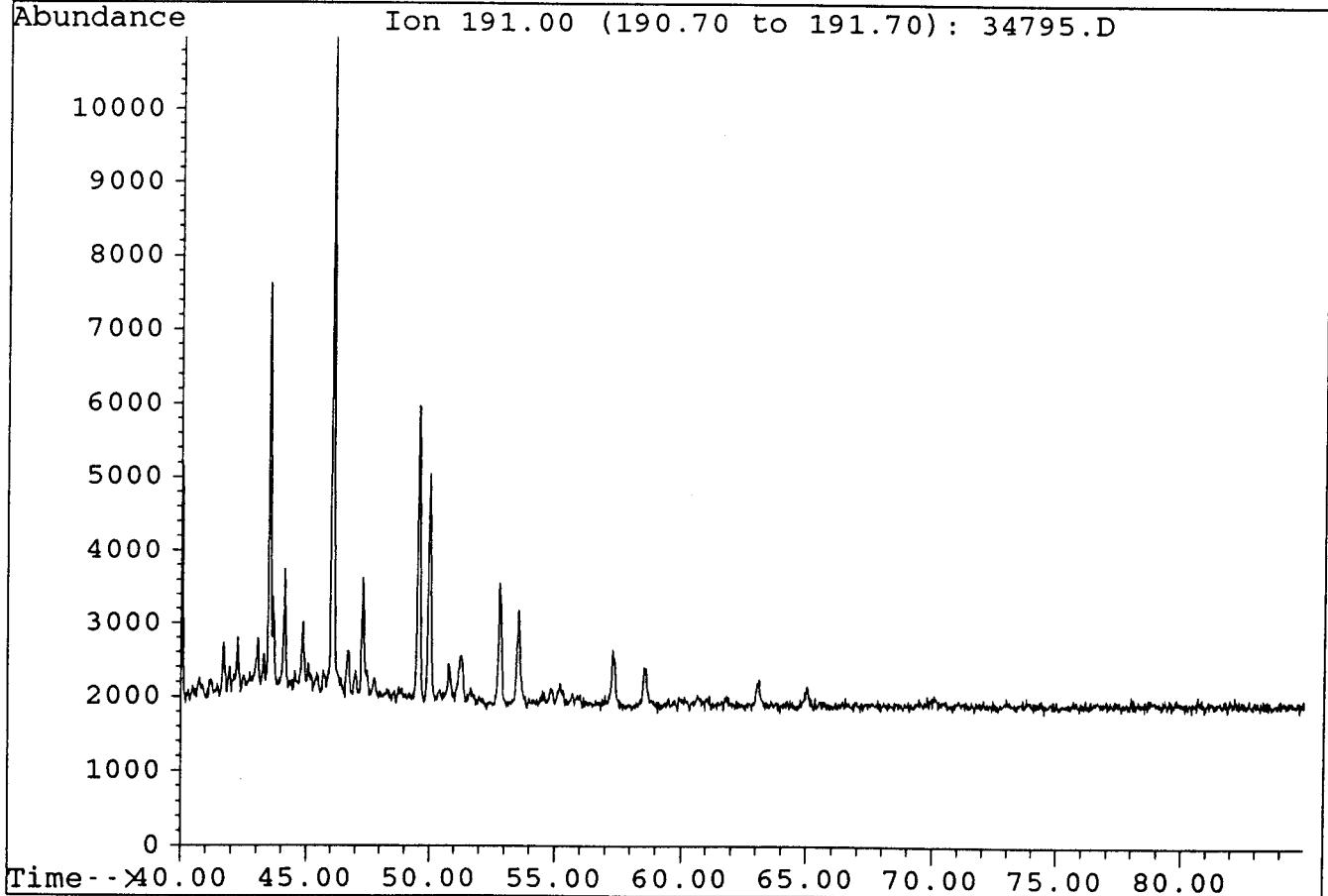
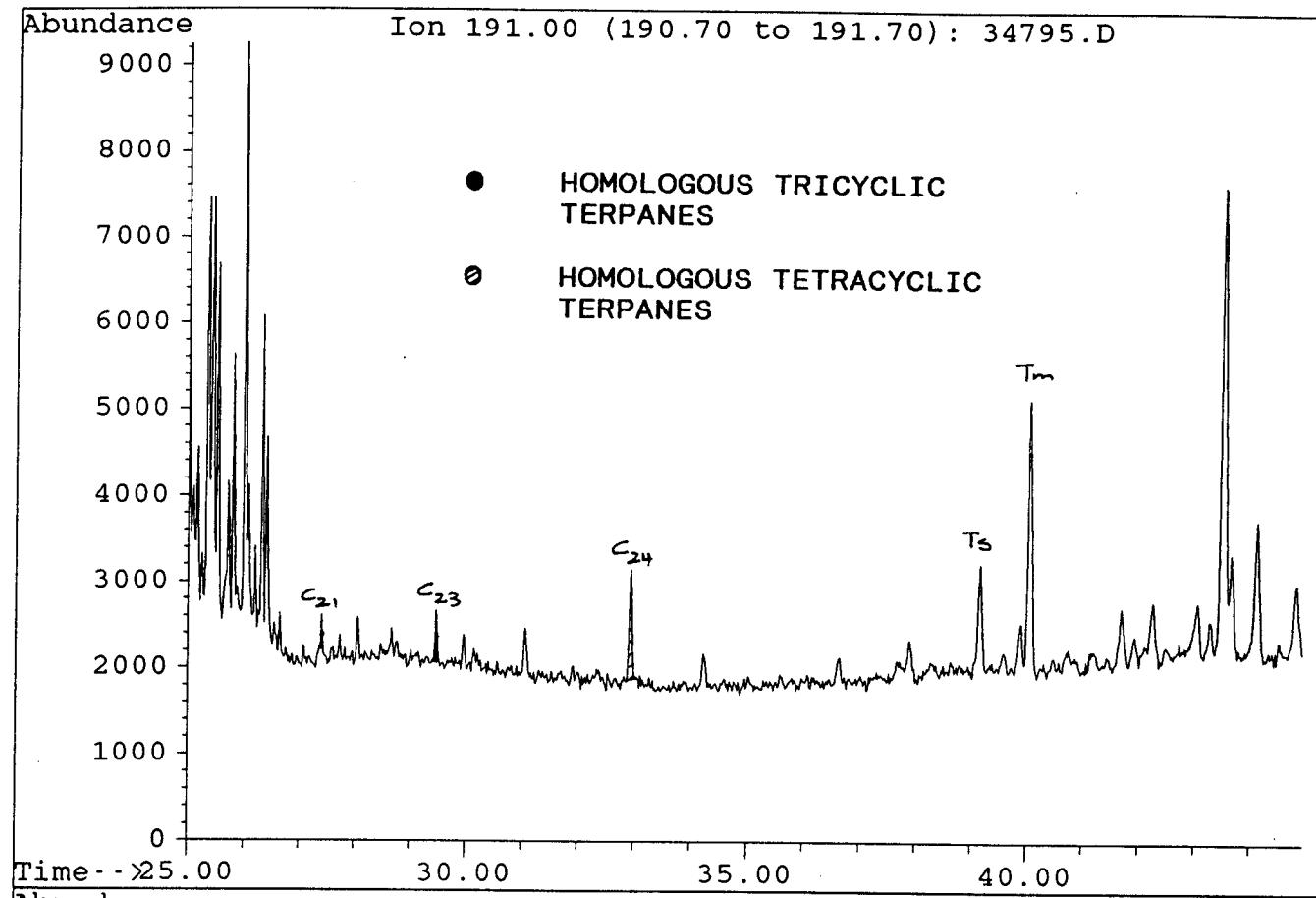
**FIGURE 3-2-1**



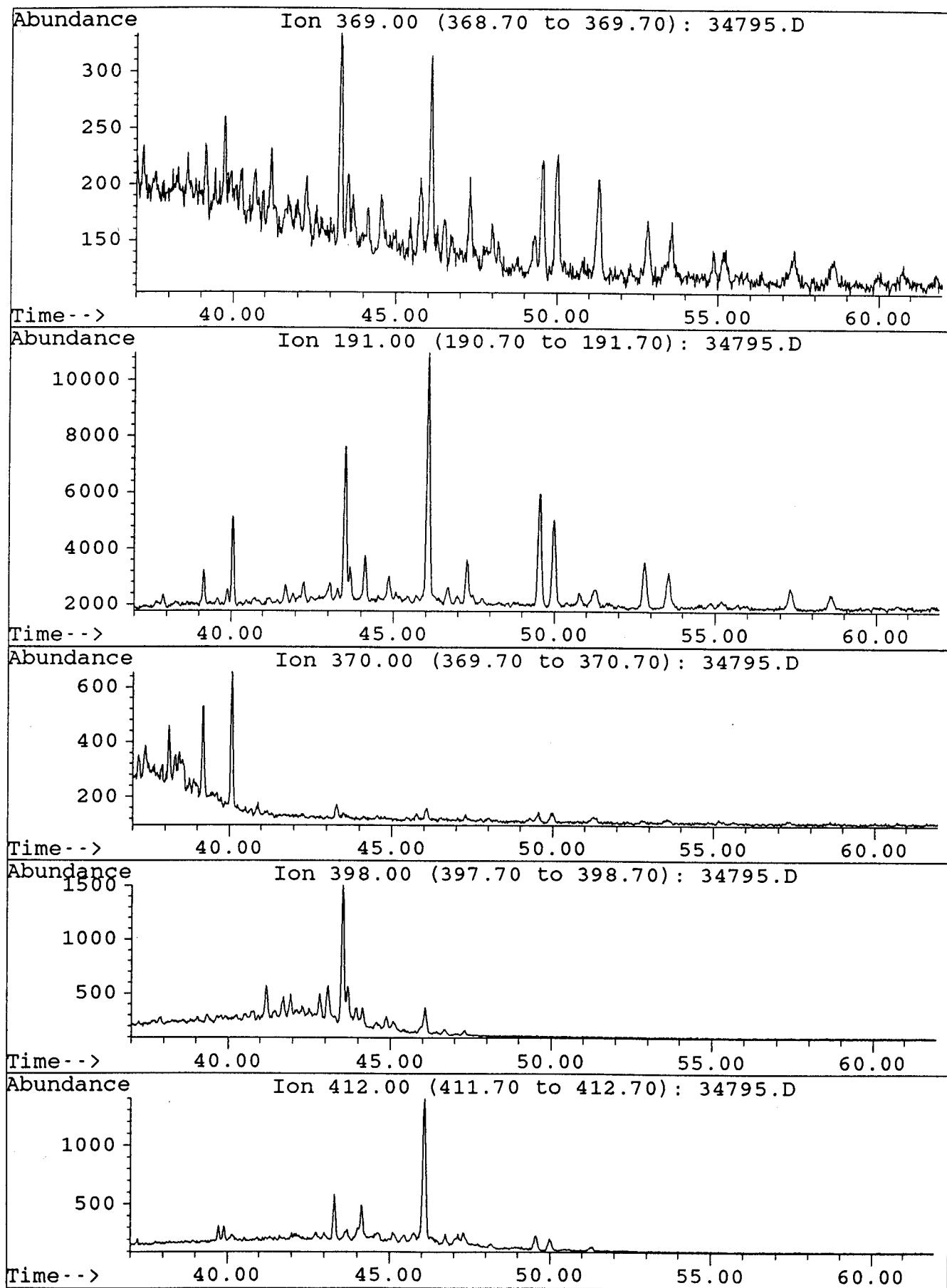
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Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



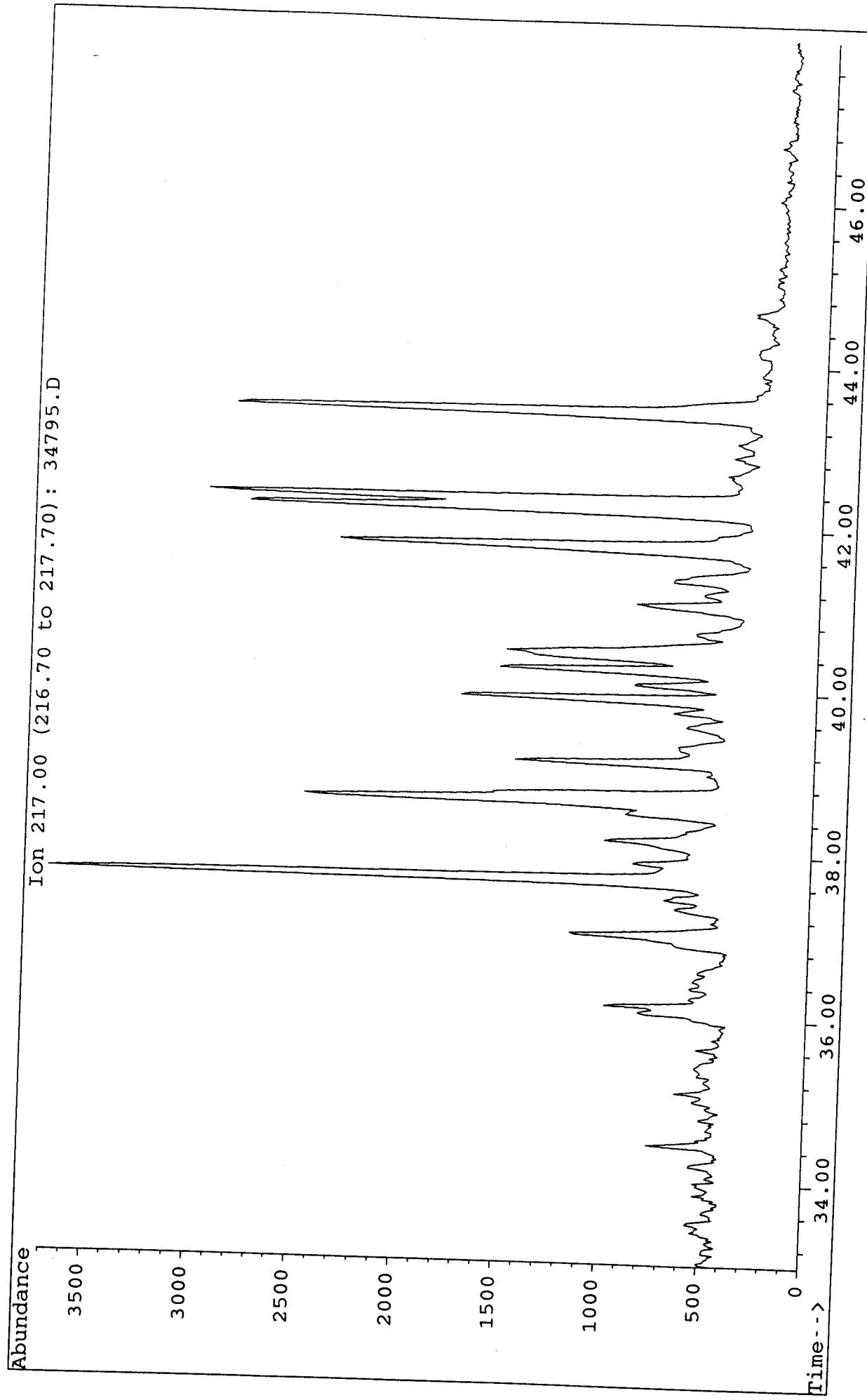
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Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



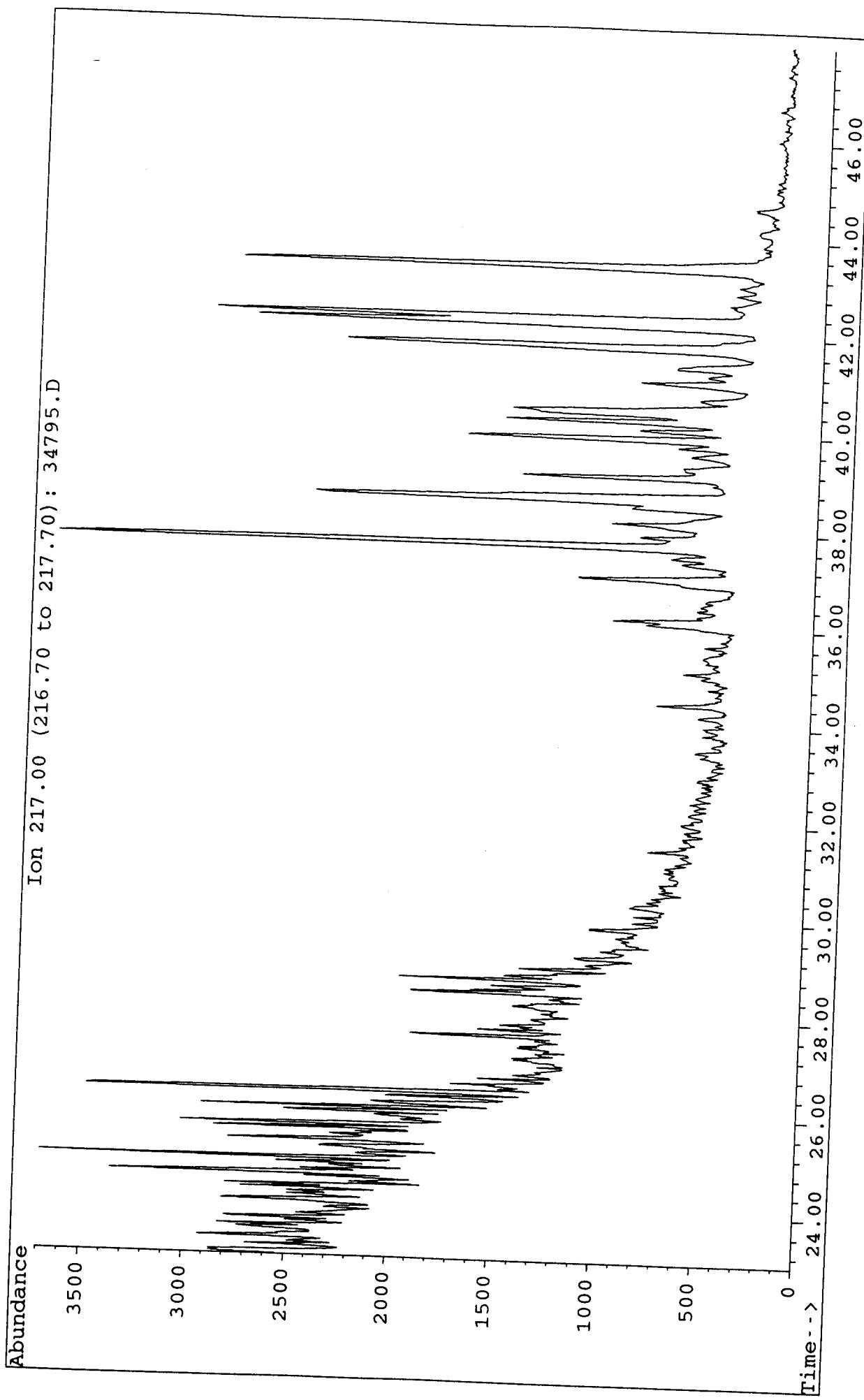
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Misc. Info : COL#164. 18-12-95. SJF.



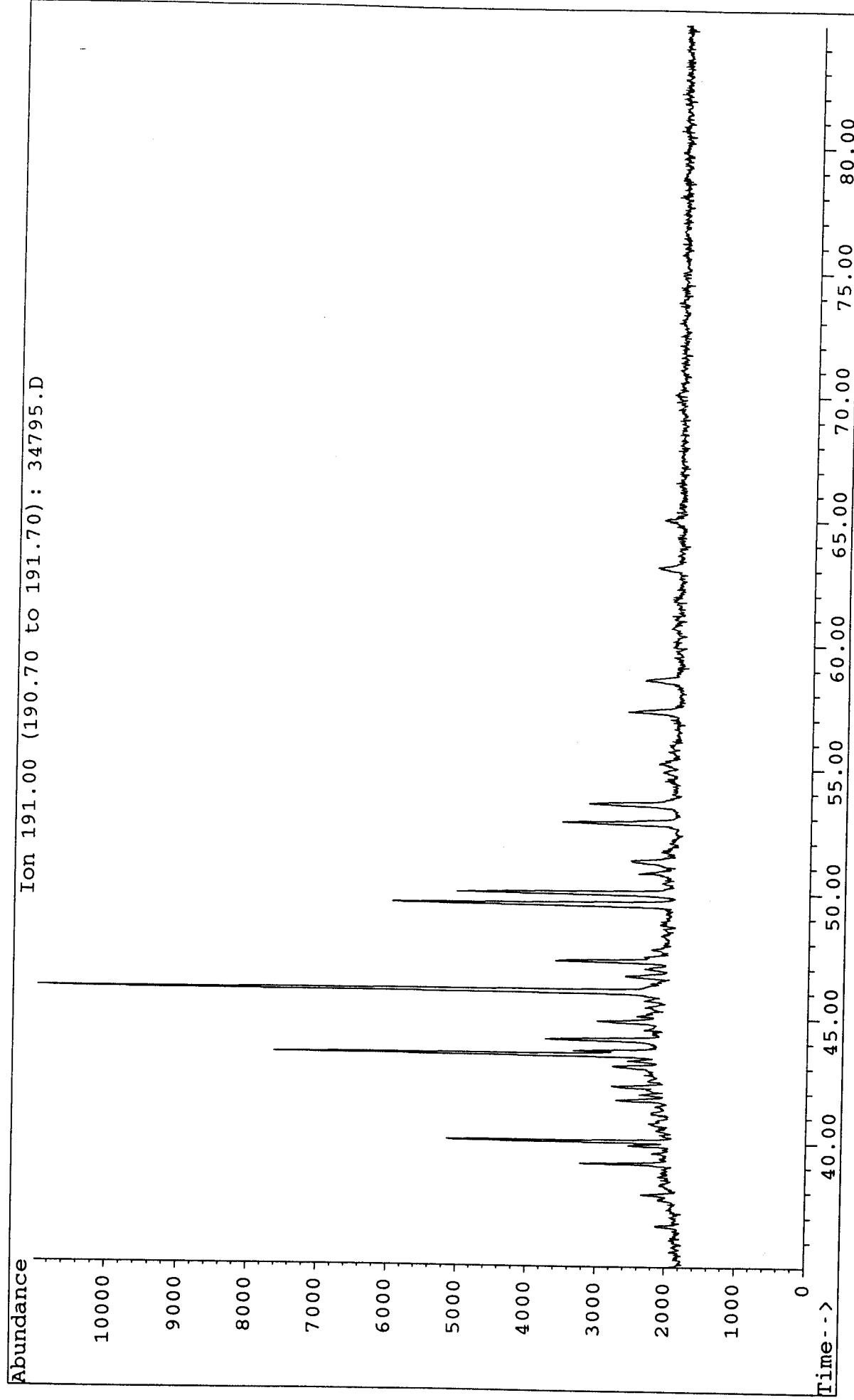
File : 34795.D  
Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



Spec. Info : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



34795.D  
Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.

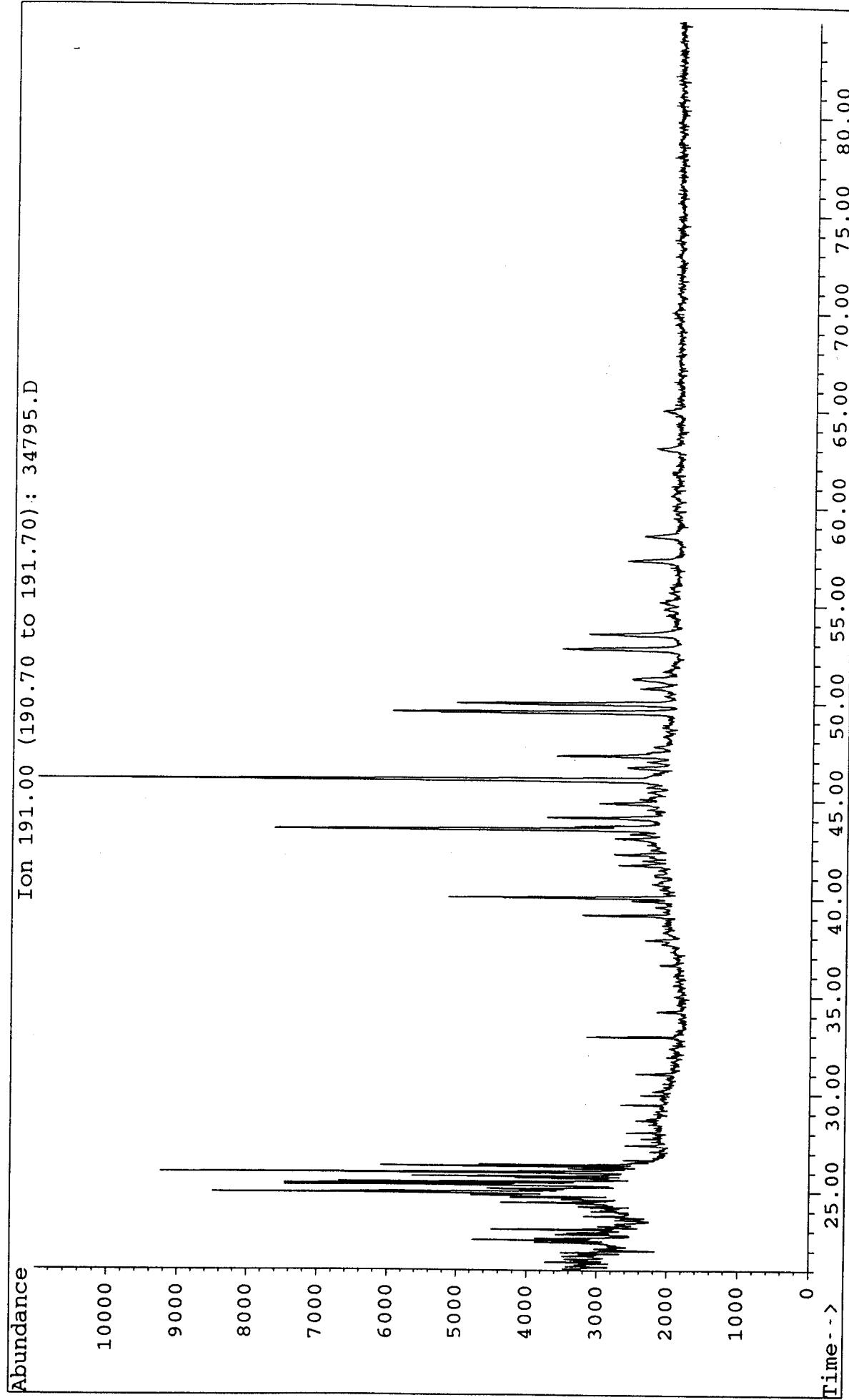


TABLE 4-2

## SELECTED PARAMETERS FROM GC/MS ANALYSIS

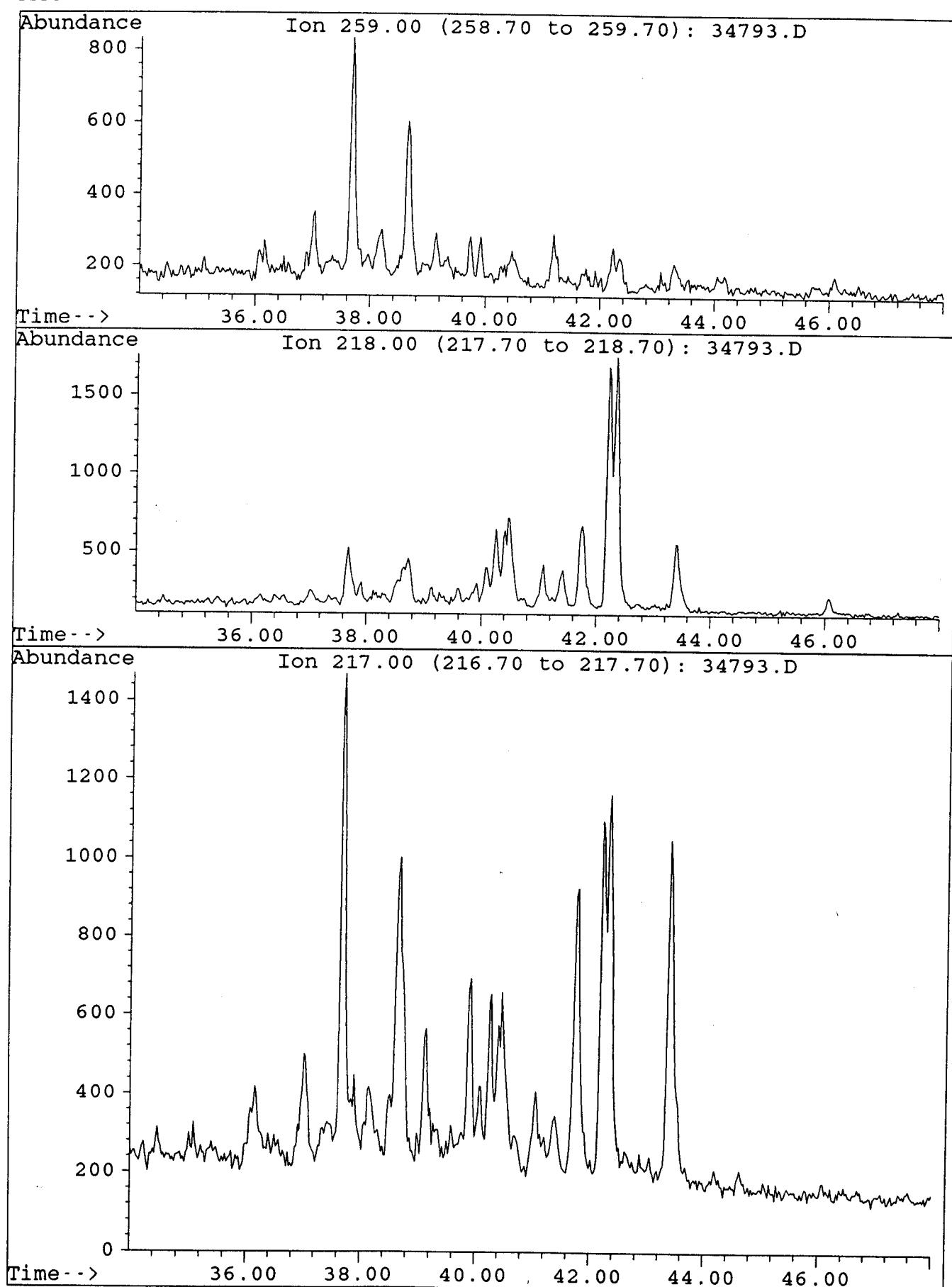
## GUDGEON 1, CH-71, Crude Oil

	<u>Parameter</u>	<u>Ion(s)</u>	<u>Value</u>
1.	18 $\alpha$ (H)- hopane/17 $\alpha$ (H)-hopane (Ts/Tm)	191	nd
2.	C30 hopane/C30 moretane	191	nd
3.	C31 22S hopane/C31 22R hopane	191	nd
4.	C32 22S hopane/C32 22R hopane	191	nd
5.	C29 20S $\alpha\alpha\alpha$ sterane/C29 20R $\alpha\alpha\alpha$ sterane	217	nd
6.	C29 $\alpha\alpha\alpha$ steranes (20S / 20S+20R)	217	nd
	C29 $\alpha\beta\beta$ steranes		
7.	C29 $\alpha\alpha\alpha$ steranes + C29 $\alpha\beta\beta$ steranes	217	nd
8.	C27/C29 diasteranes	259	nd
9.	C27/C29 steranes	217	nd
10.	18 $\alpha$ (H)-oleanane/C30 hopane	191	nd
	C29 diasteranes		
11.	C29 $\alpha\alpha\alpha$ steranes + C29 $\alpha\beta\beta$ steranes	217	nd
	C30 (hopane + moretane)		
12.	C29 (steranes + diasteranes)	191/217	nd
13.	C15 drimane/C16 homodrimane	123	0.67
14.	Rearranged drimanes/normal drimanes	123	0.93

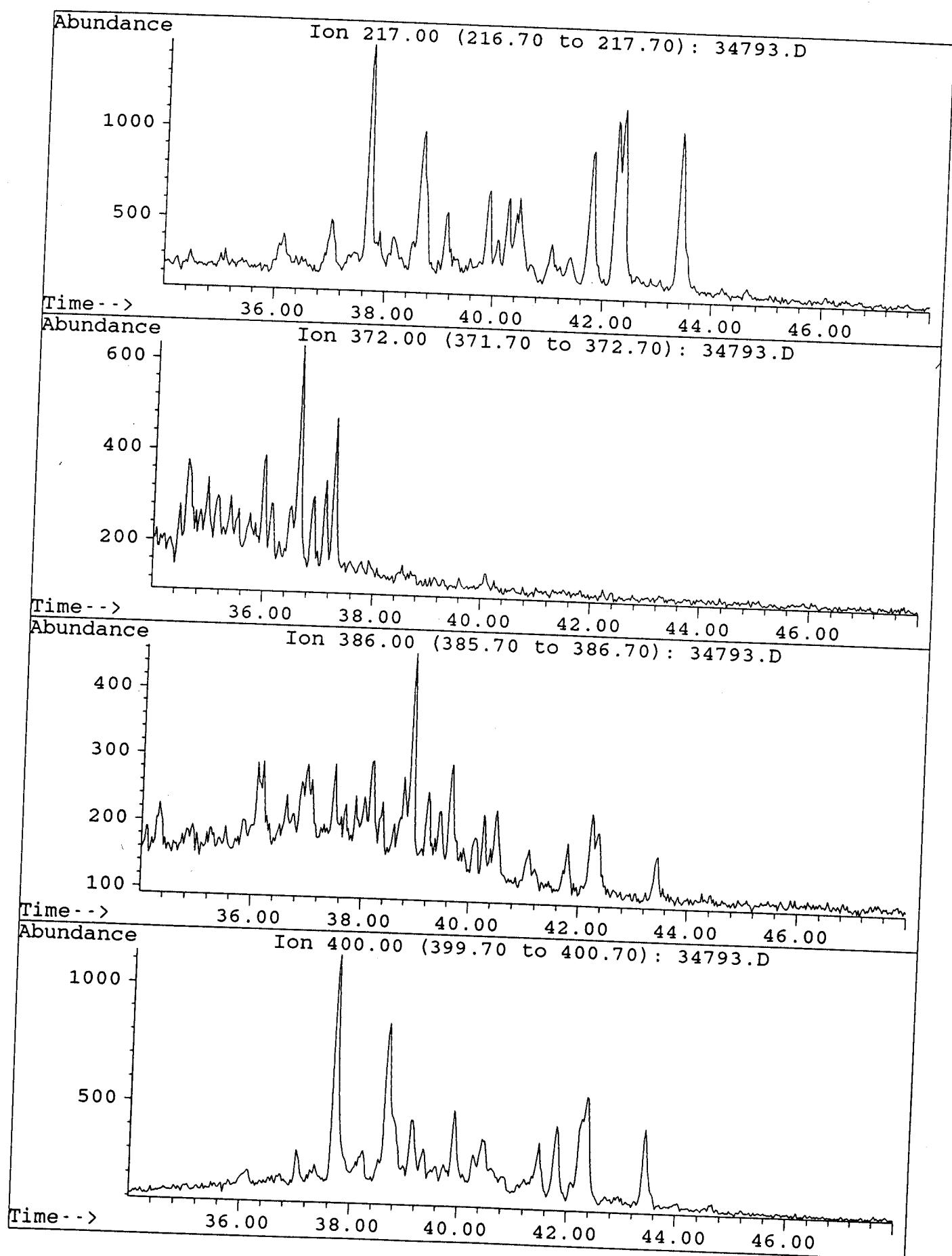
nd = not detectable

File : 34793.D  
Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.

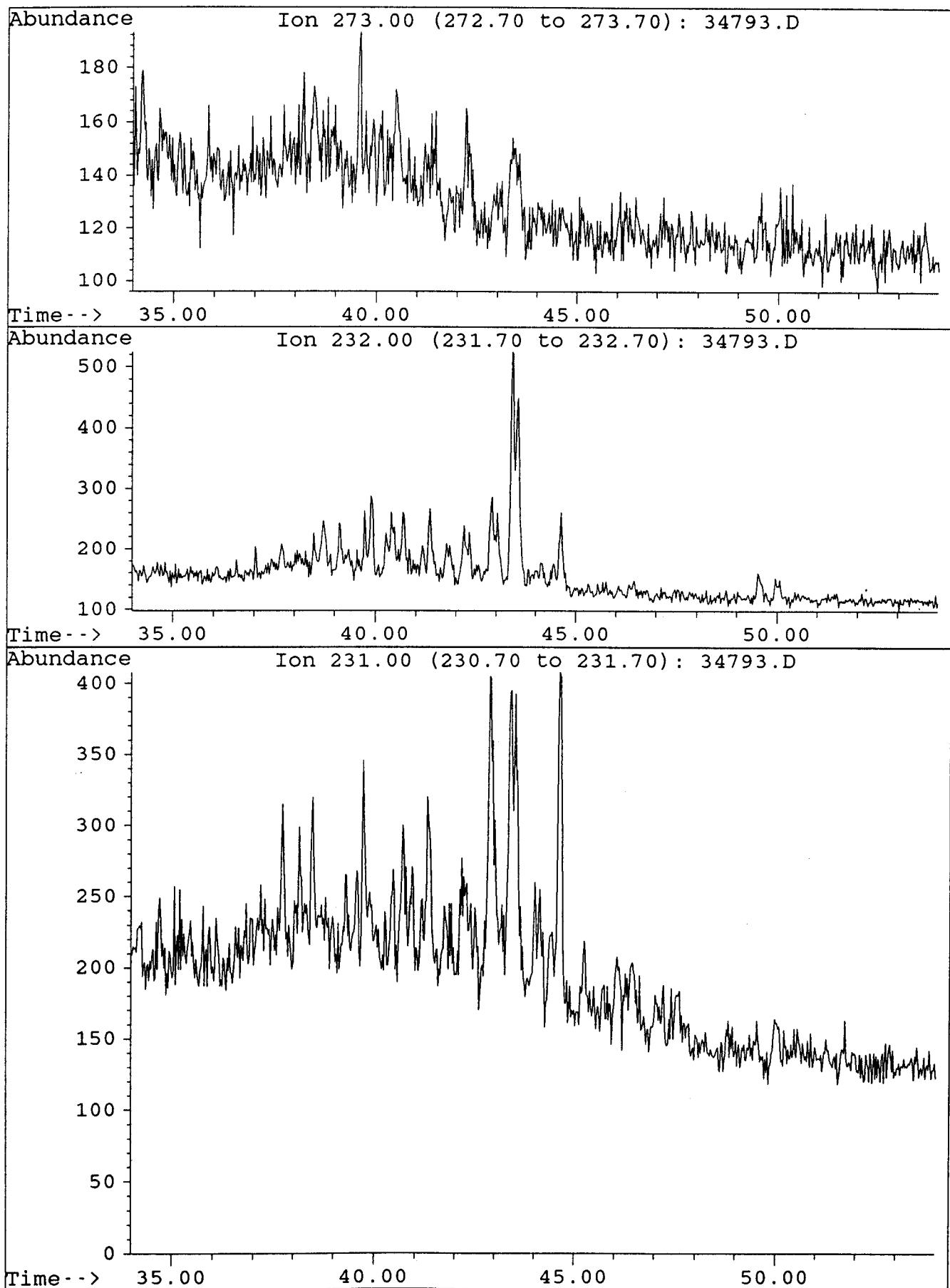
FIGURE 3-2-2



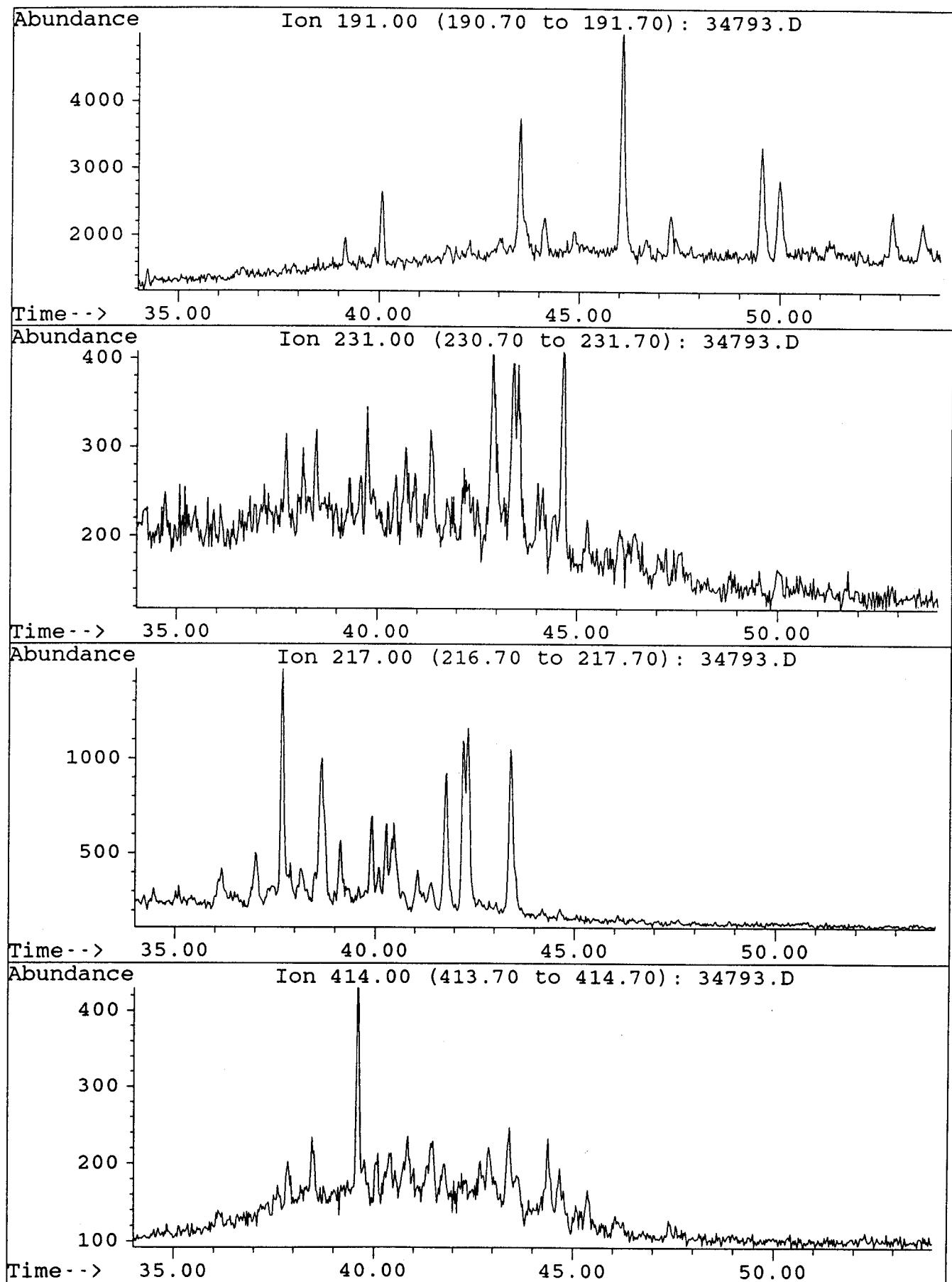
File : 34793.D  
Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



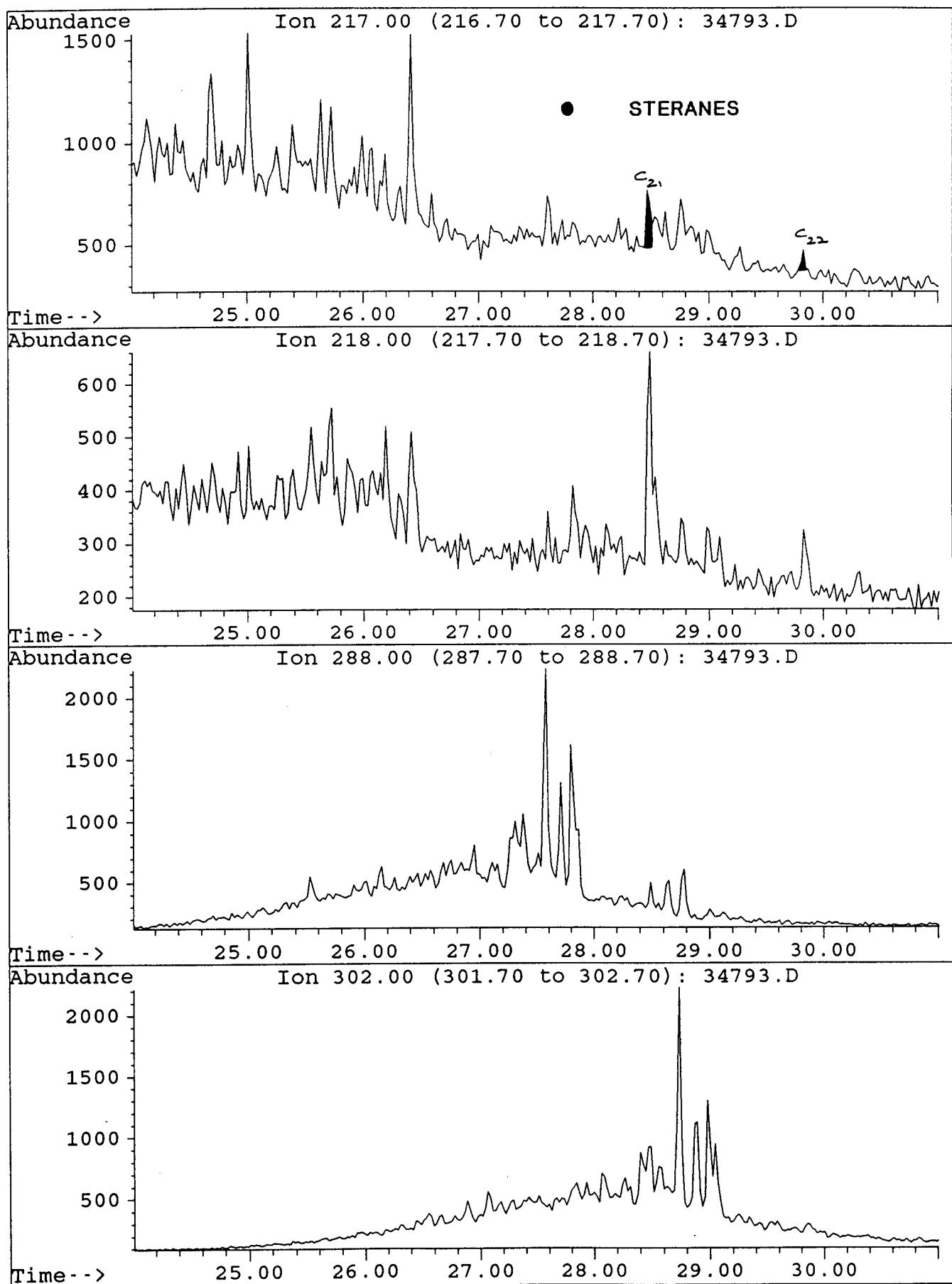
File : 34793.D  
Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



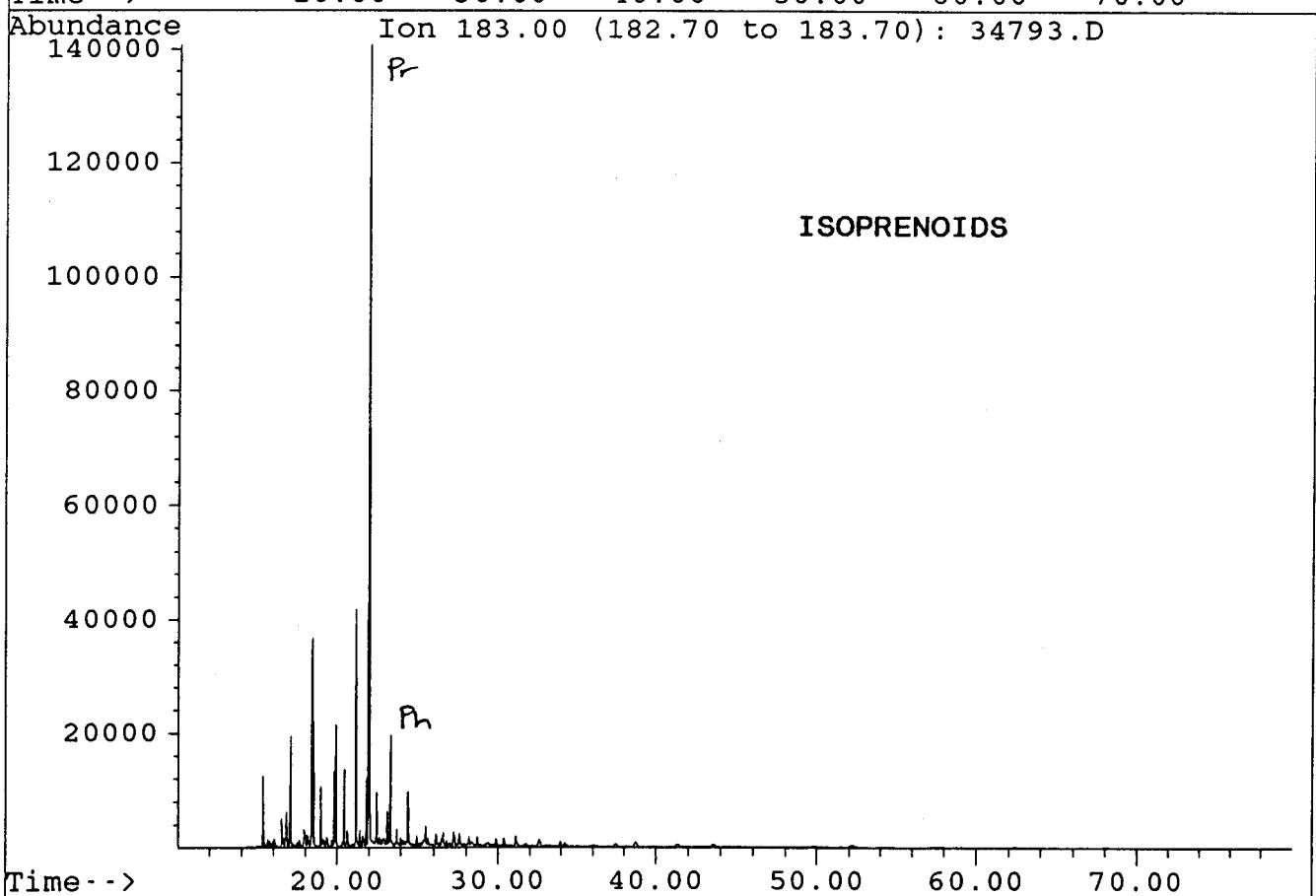
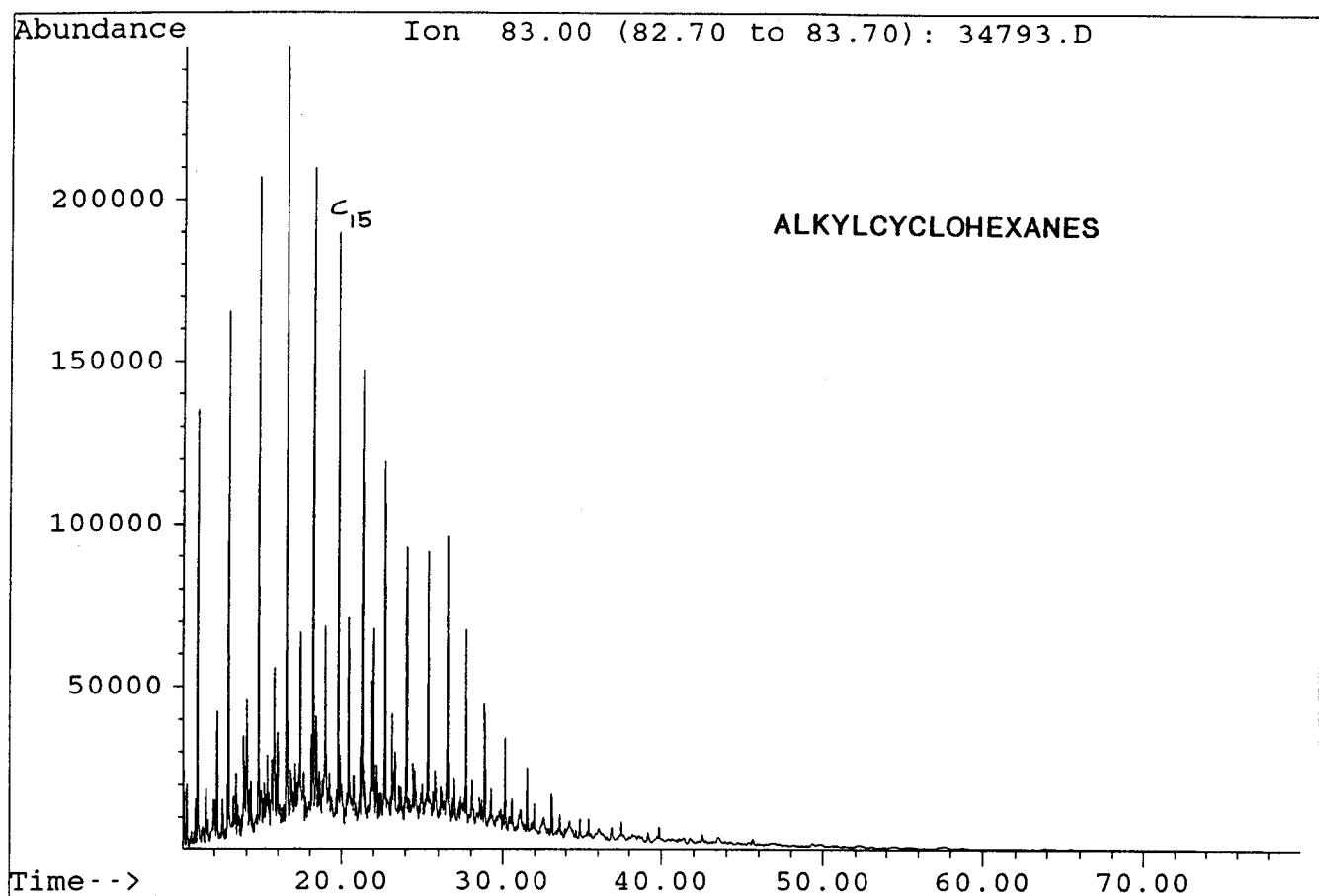
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Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



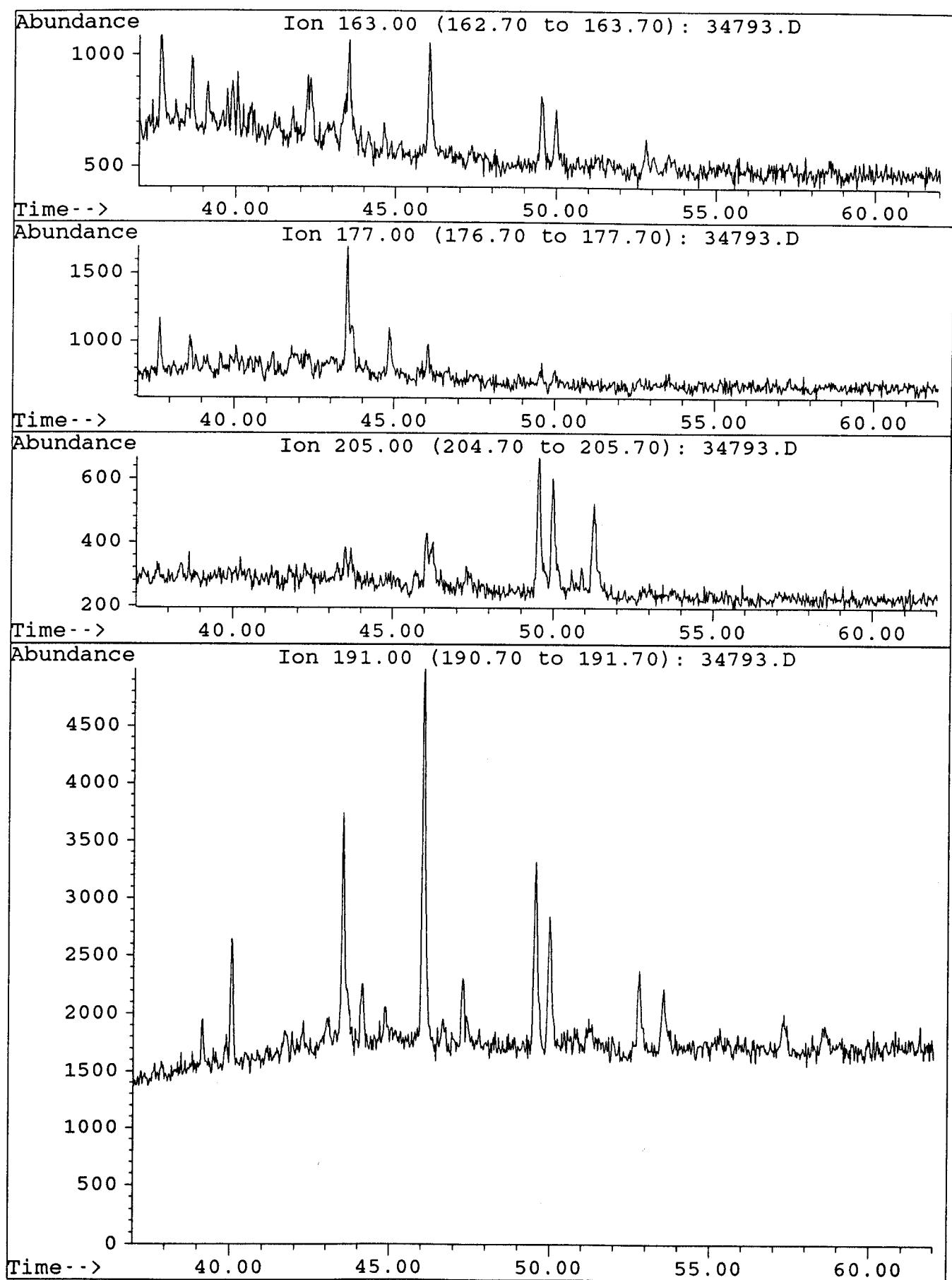
File : 34793.D  
Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



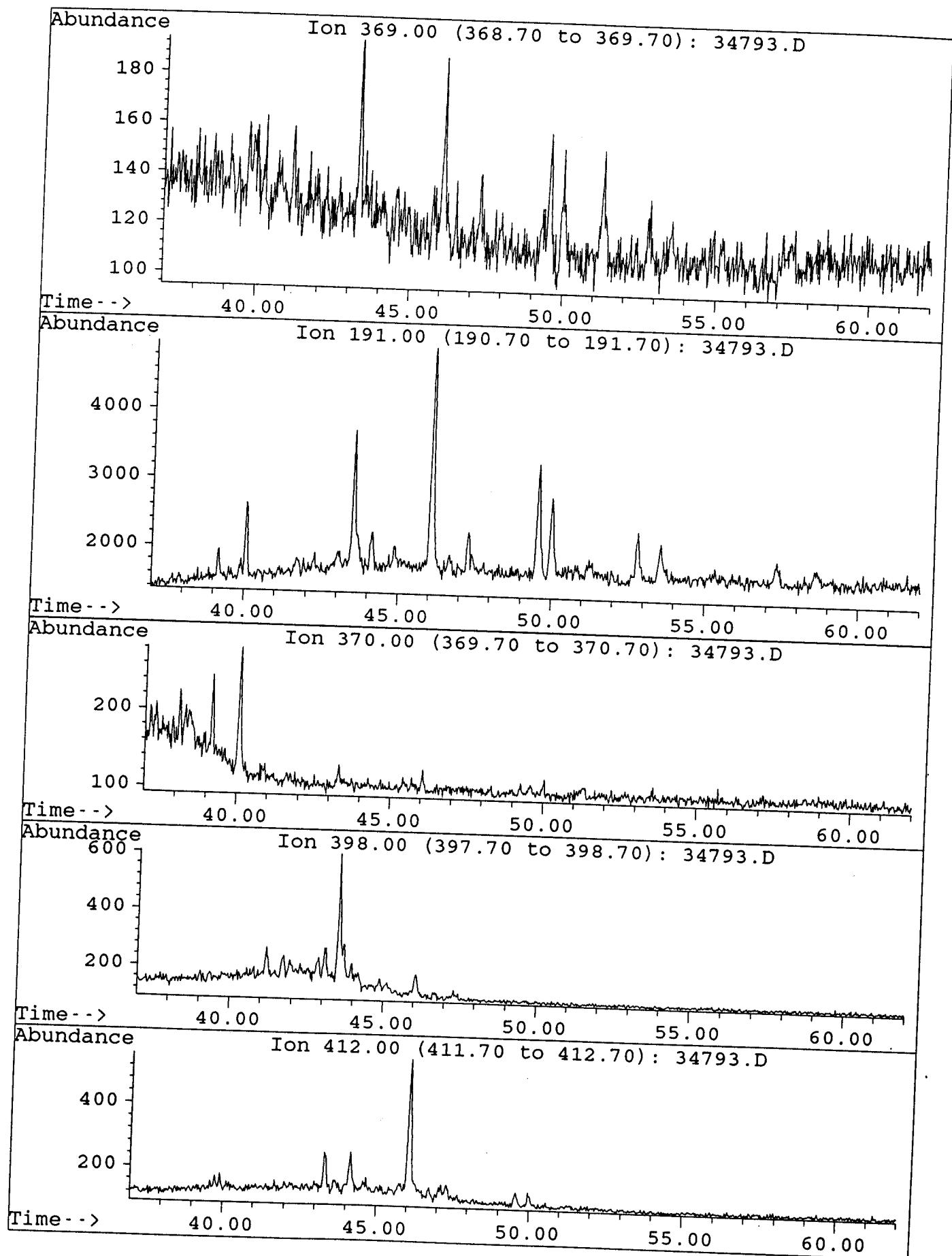
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Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



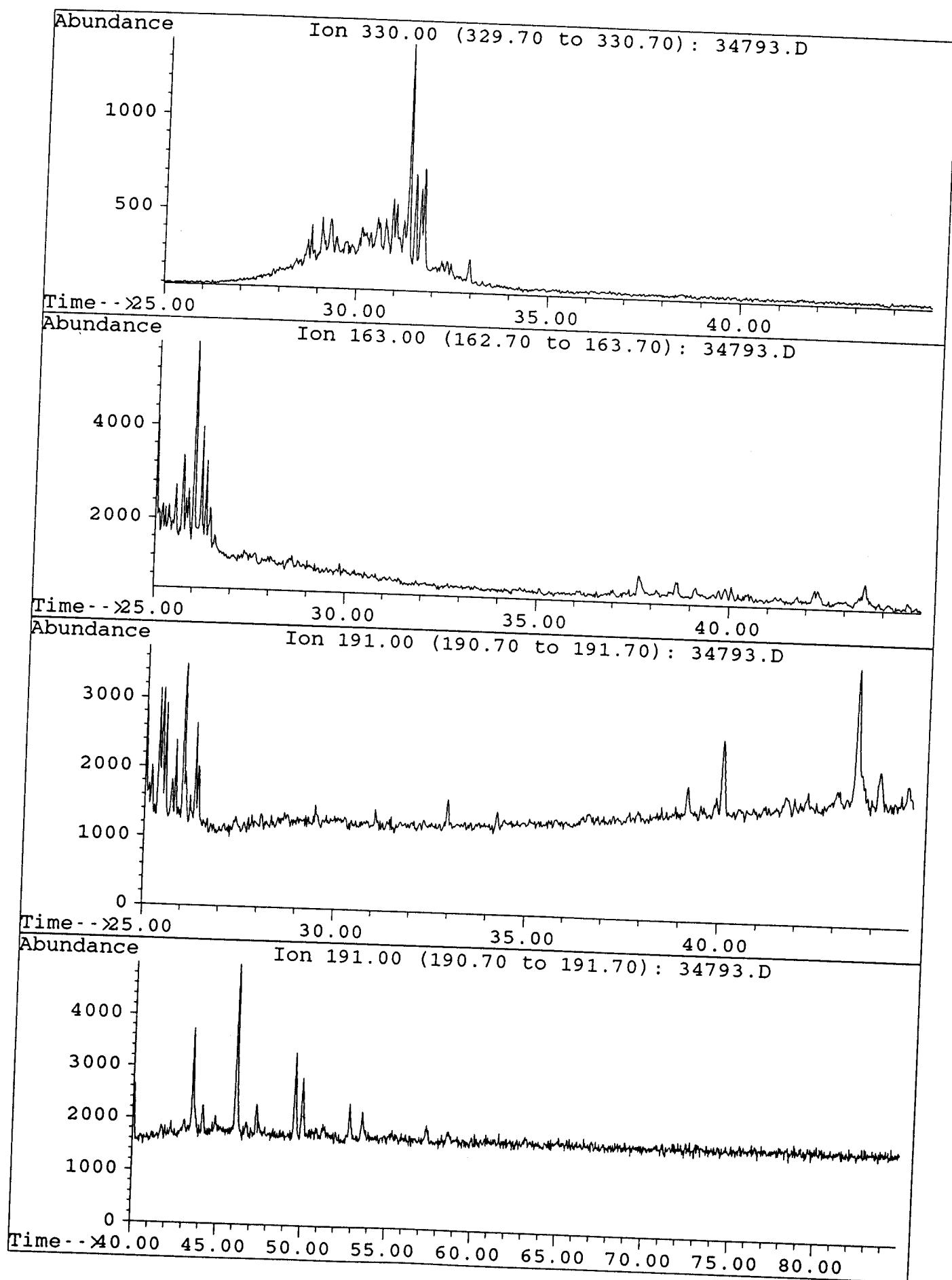
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Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



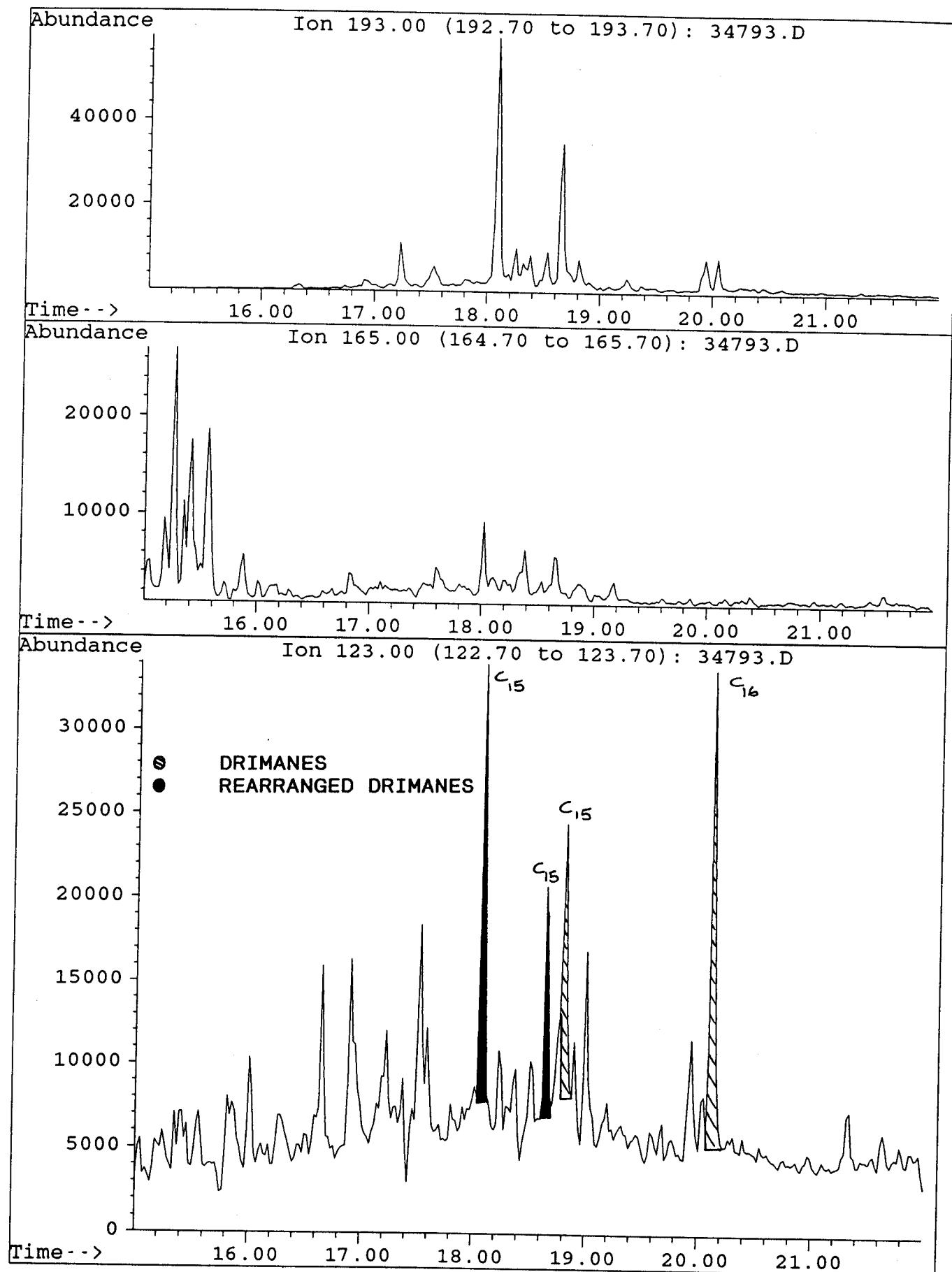
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Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



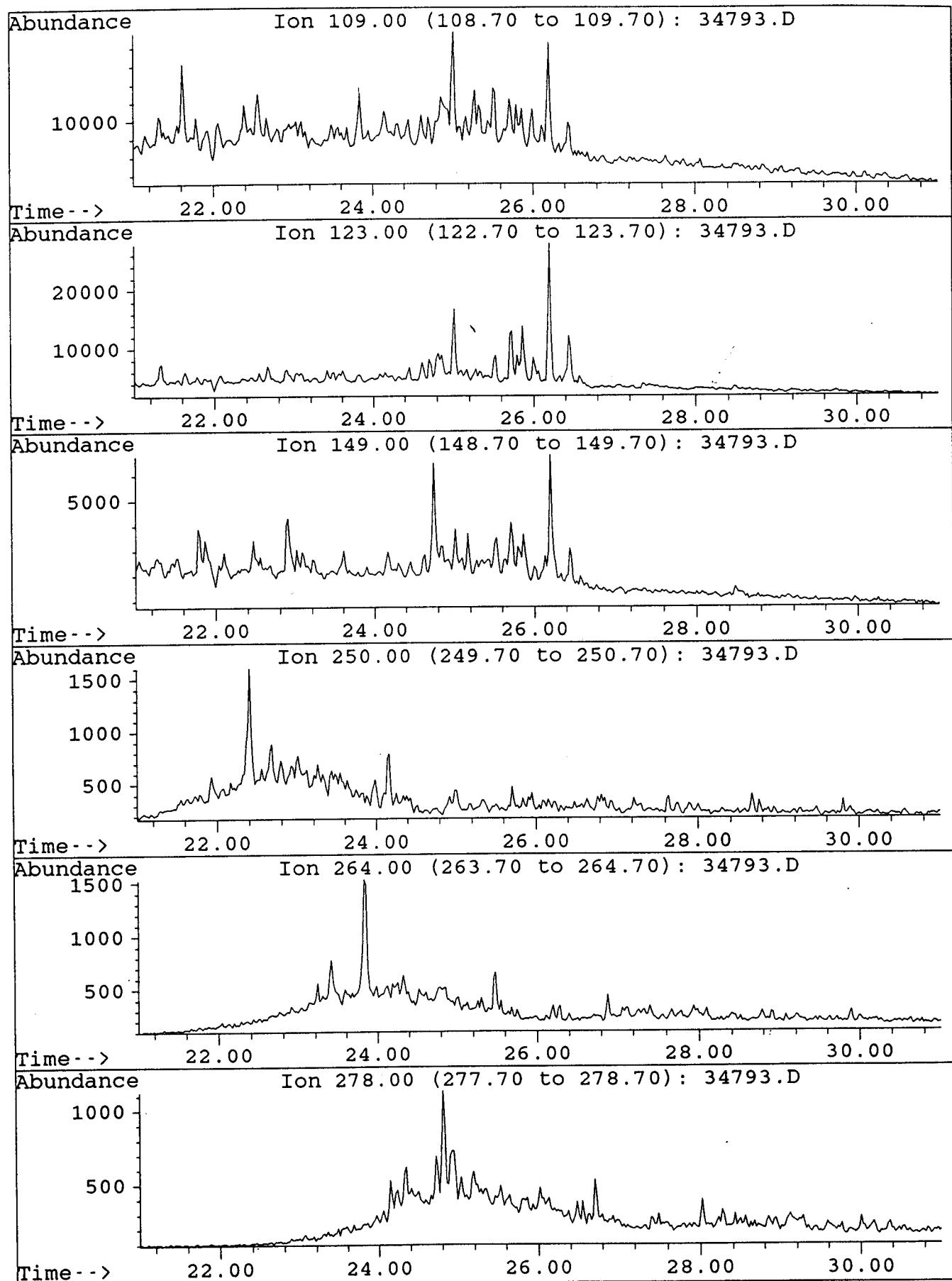
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Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



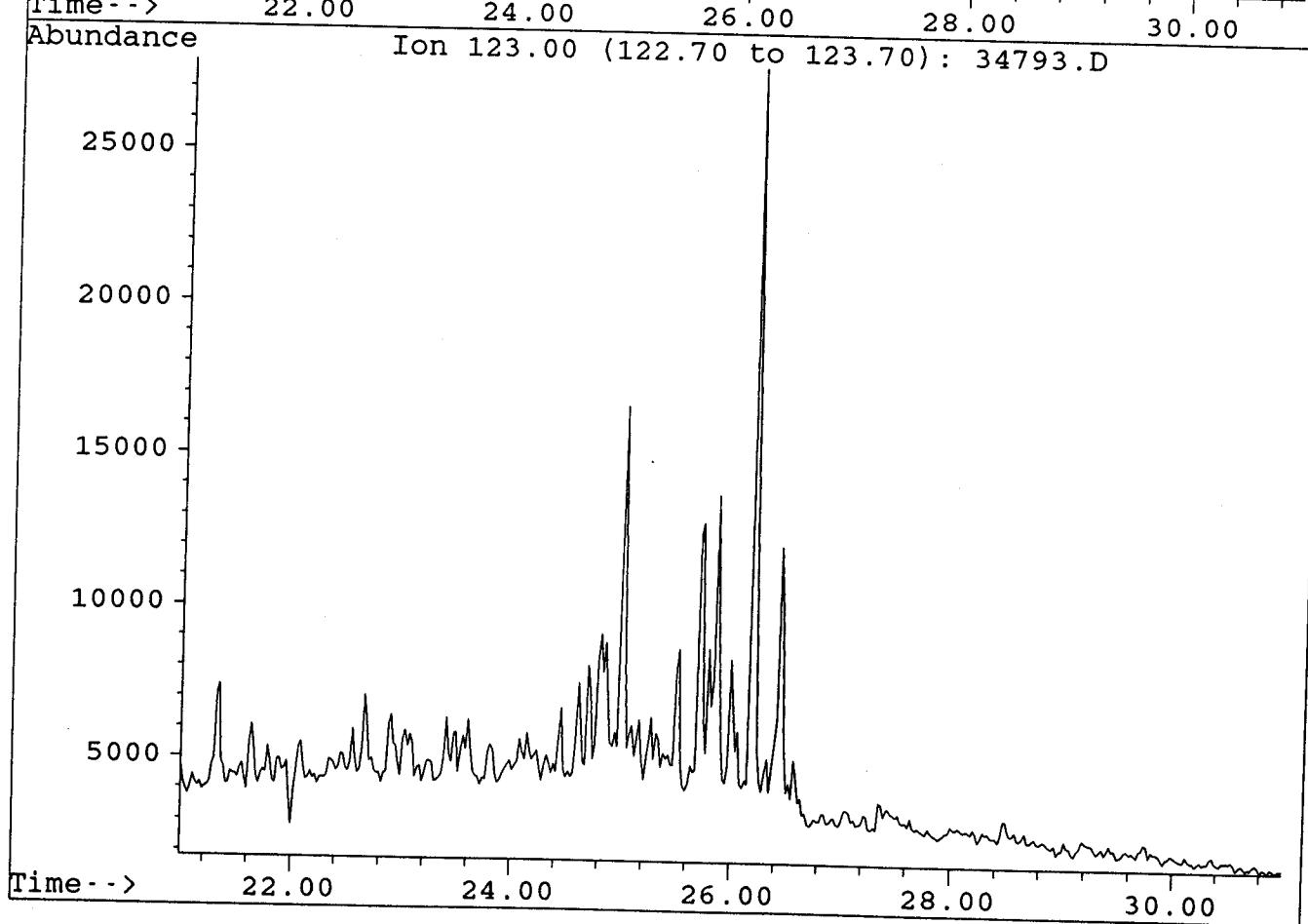
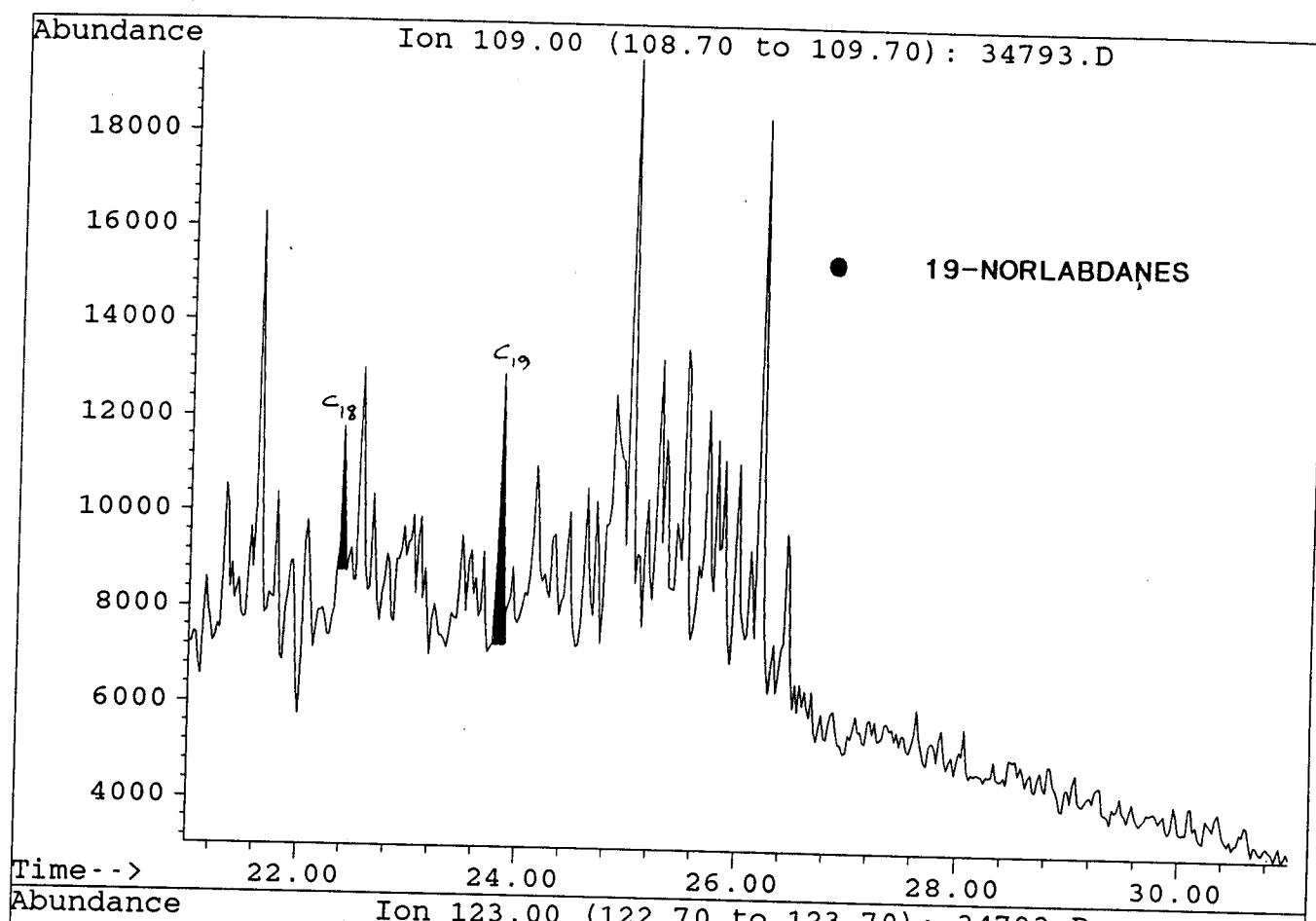
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Misc. Info : COL#164. 18-12-95. SJF.



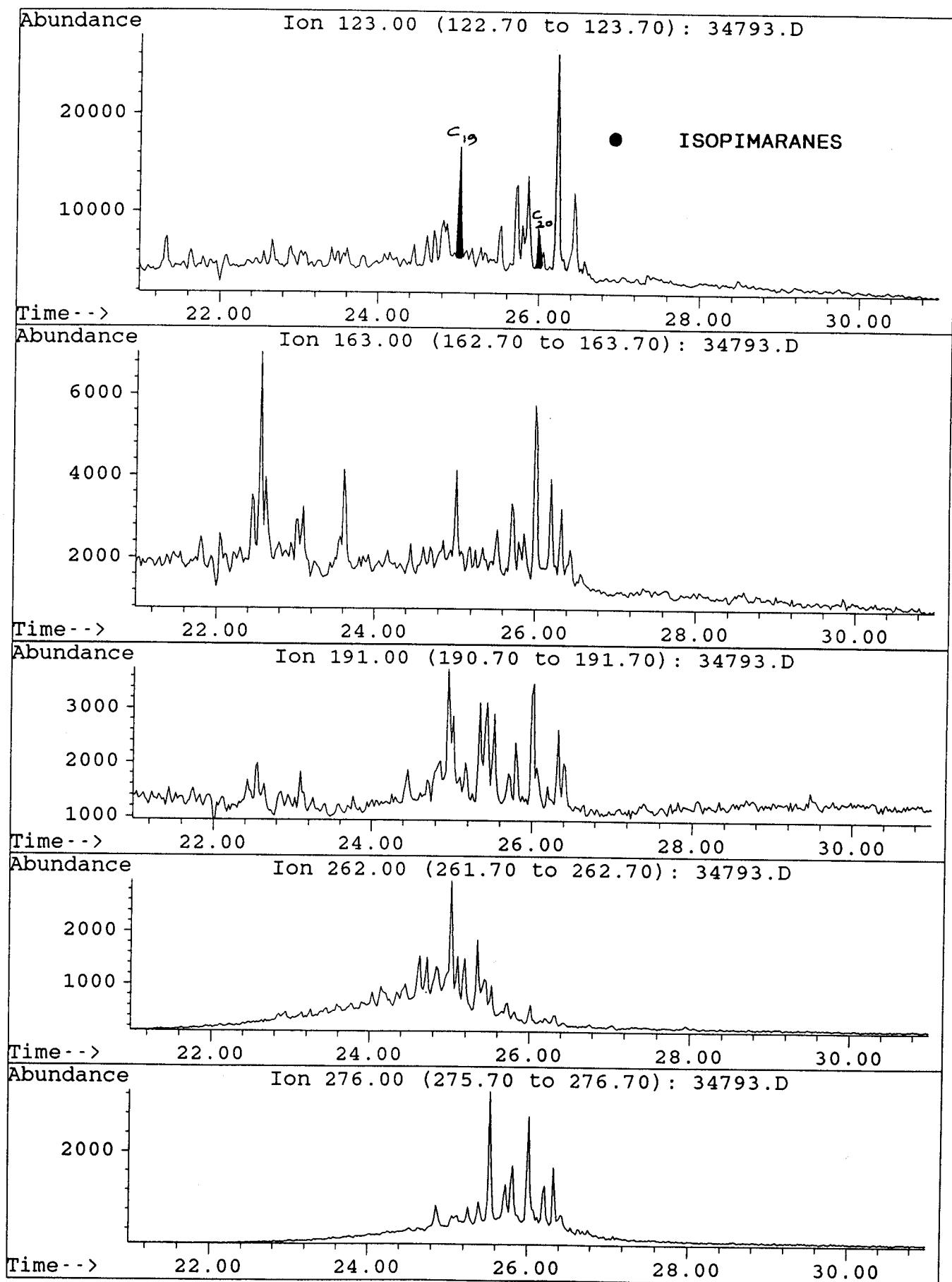
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Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



File : 34793.D  
Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



File : 34793.D  
Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.



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Sample : GUDGEON #1 CH-71 B/C  
Misc. Info : COL#164. 18-12-95. SJF.

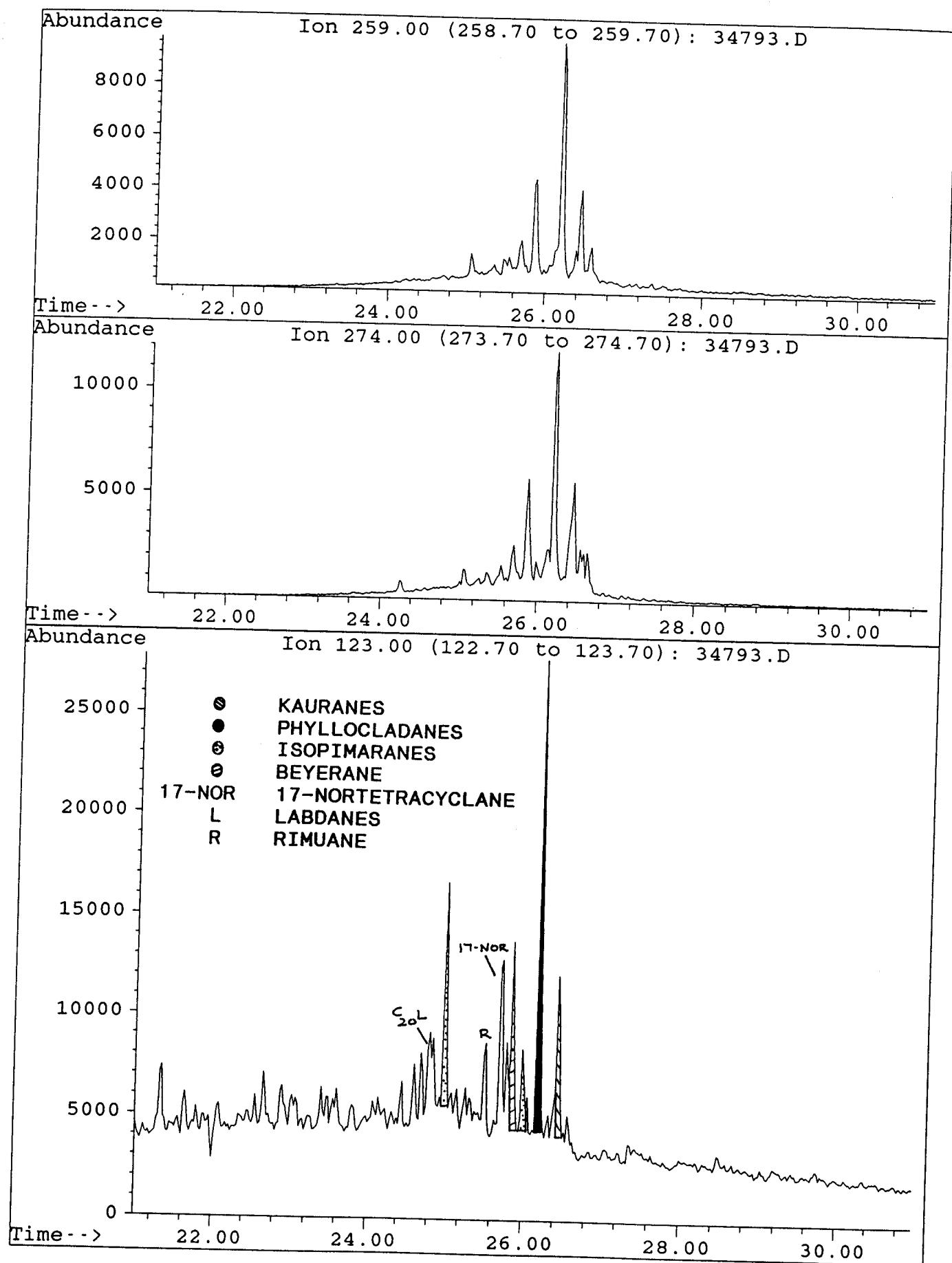


TABLE 5

## SELECTED AROMATIC PARAMETERS

GUDGEON 1	Dec-95
-----------	--------

DEPTH	TYPE	DNR-1	DNR-5	DNR-6	TNR-1	TNR-5	TNR-6	MPR-1	MPI-1	MPI-2	Rc(a)	Rc(b)
CH-19	Crude Oil	7.51	nd	2.84	0.71	0.53	0.48	2.00	0.79	0.82	0.87	1.83
CH-71	Crude Oil	6.83	nd	2.44	0.66	0.57	0.63	1.92	0.67	0.68	0.80	1.90

response factors have been applied to DNR 6, TNR 1, TNR 5, MPI 1 and MPI 2

TABLE 5

## SELECTED AROMATIC PARAMETERS CONT.

GUDGEON 1	Dec-95
-----------	--------

DEPTH	TYPE	1,7-DMP/X (m/z 206)	RETENE/9-MP (m/z 219,192)	1MP/9MP	HPI
CH-19	Crude Oil	0.61	1.72	0.77	nd
CH-71	Crude Oil	0.65	3.14	0.77	nd

HPI = Higher Plant Index (i.e (retene + cadalene + iHMN-IV)/1,3,6,7-TeMN) )

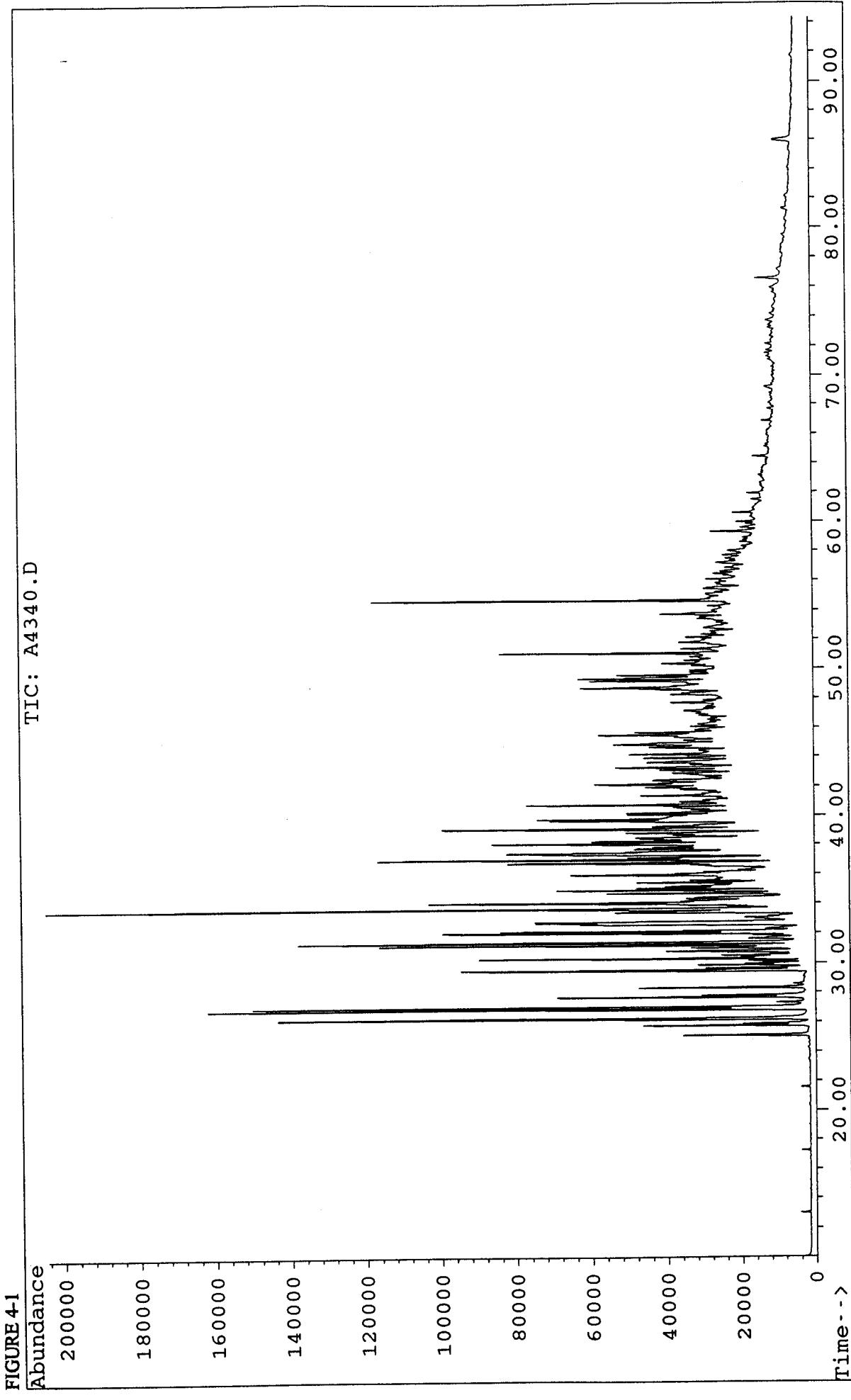
nd = no data

iHMN-IV = RODB

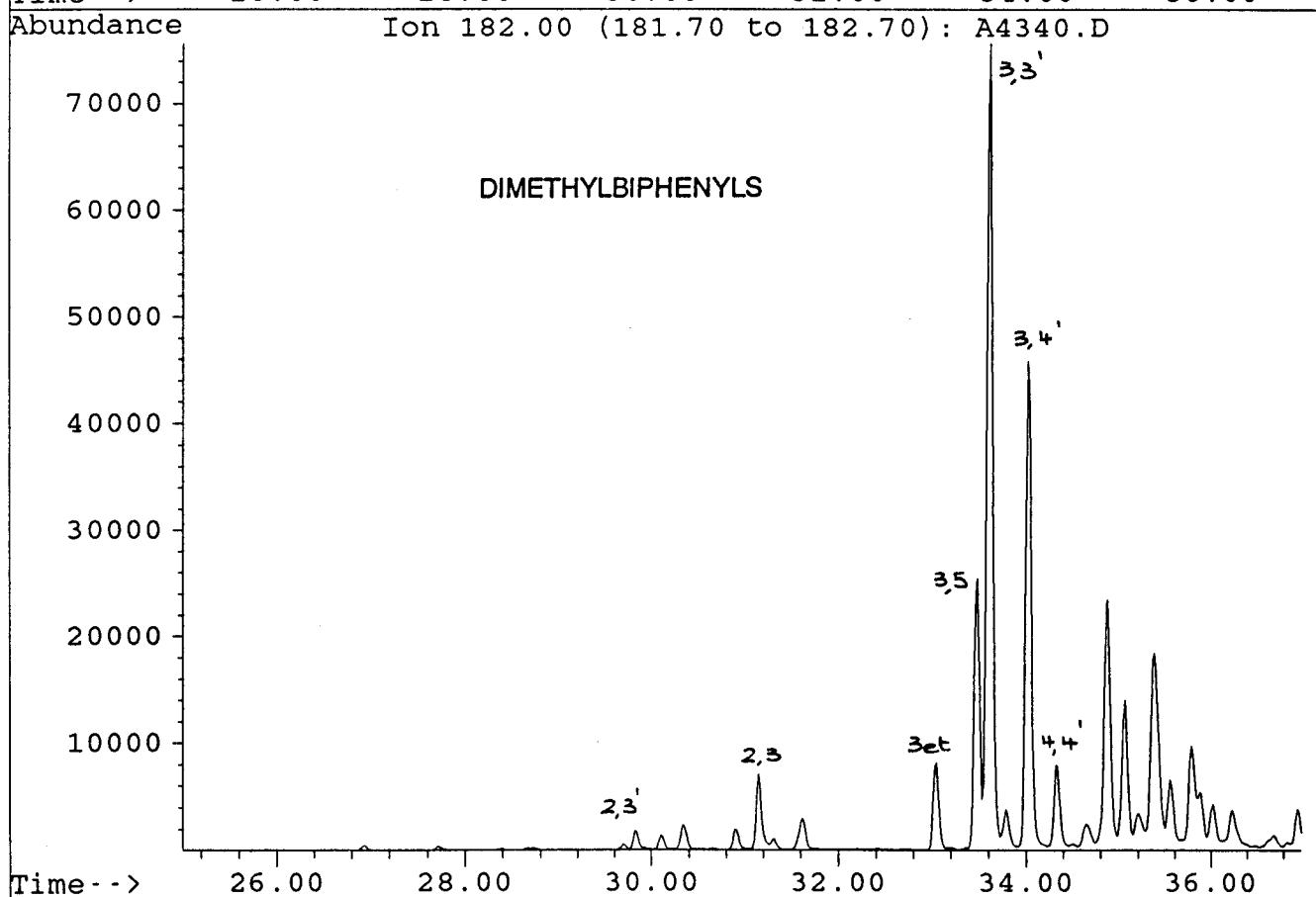
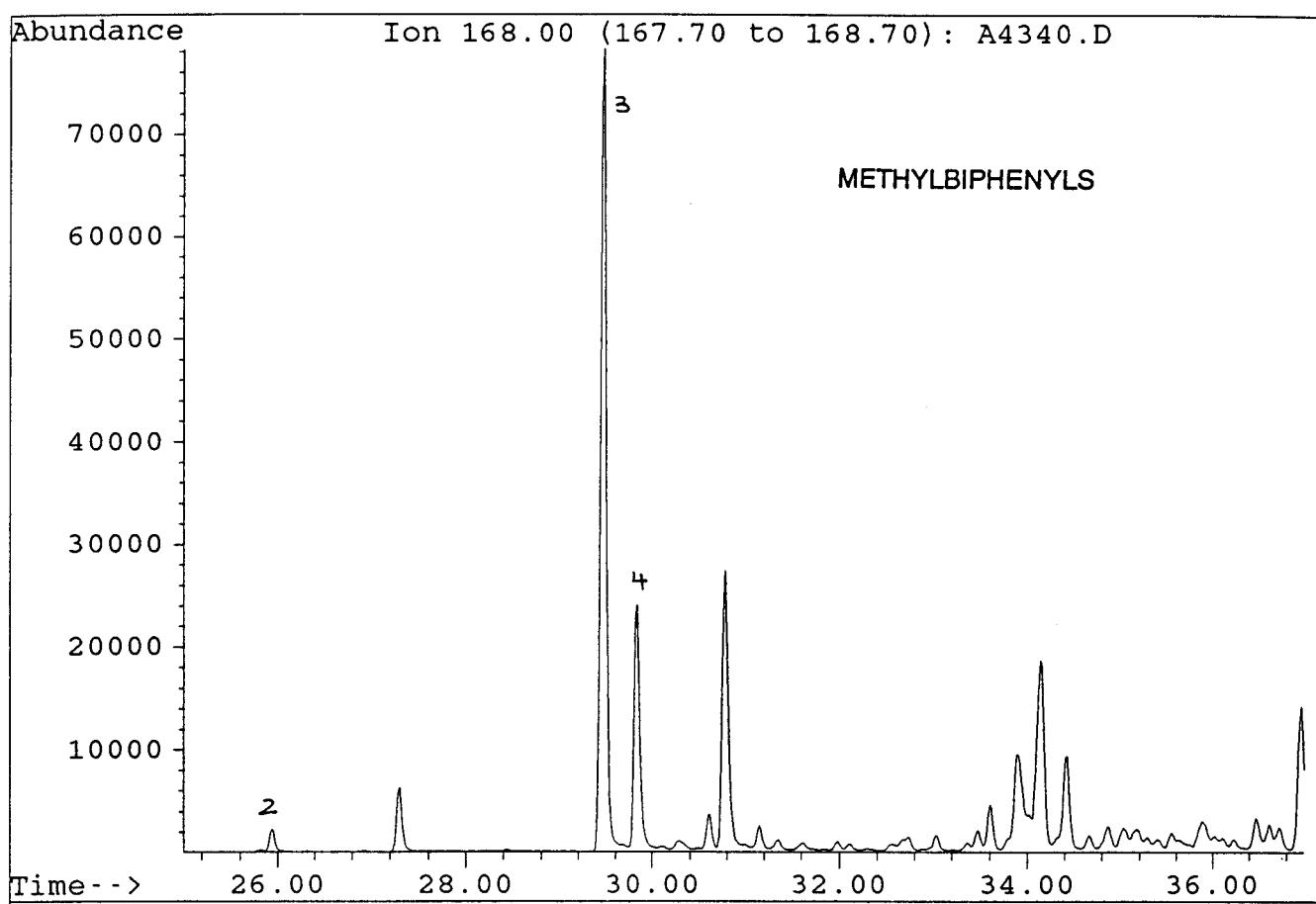
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File : A4340.D  
Sample : GUDGEON#1, CH-19. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.

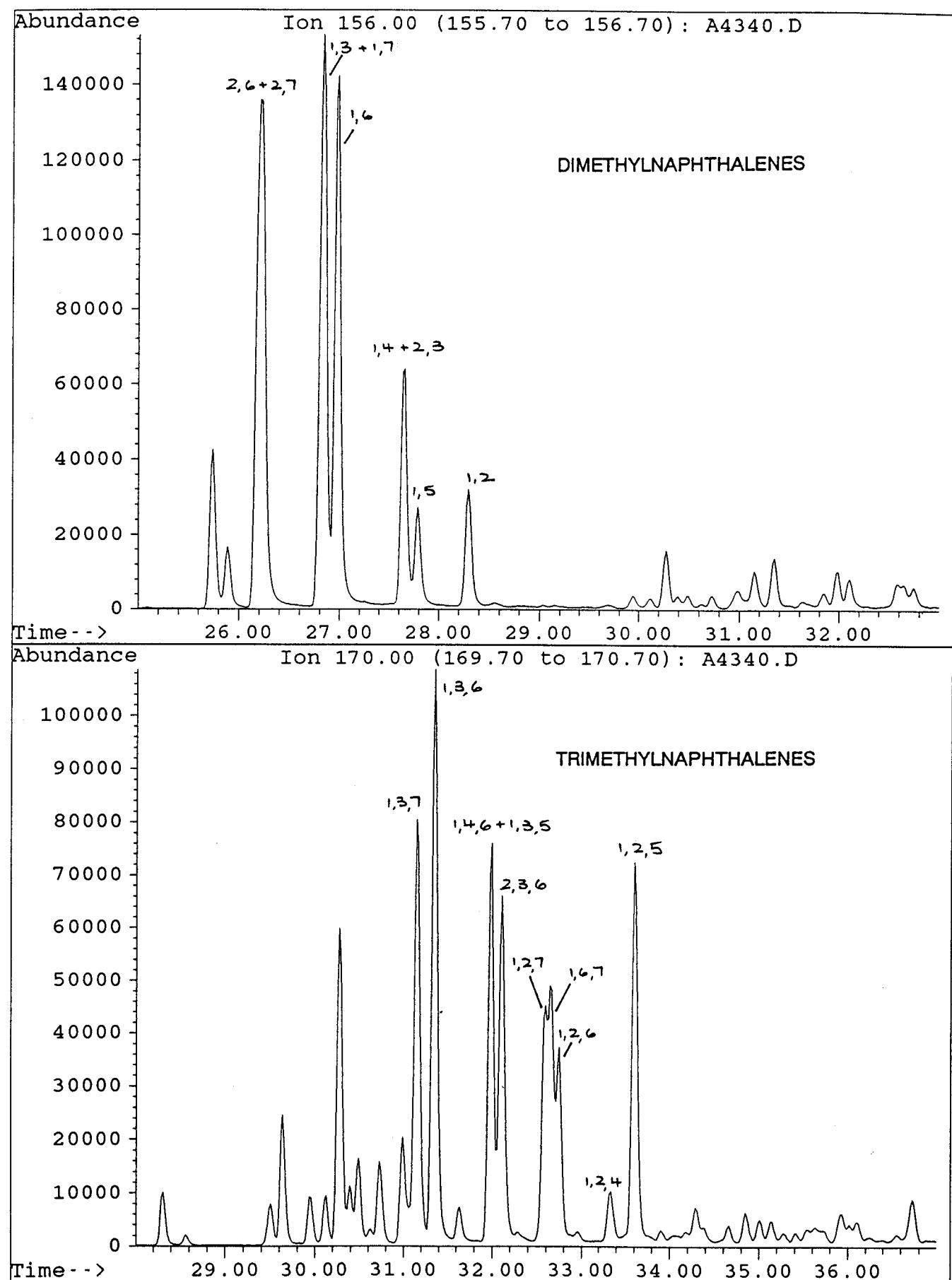
FIGURE 4-1



File : A4340.D  
Sample : GUDGEON#1, CH-19. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.

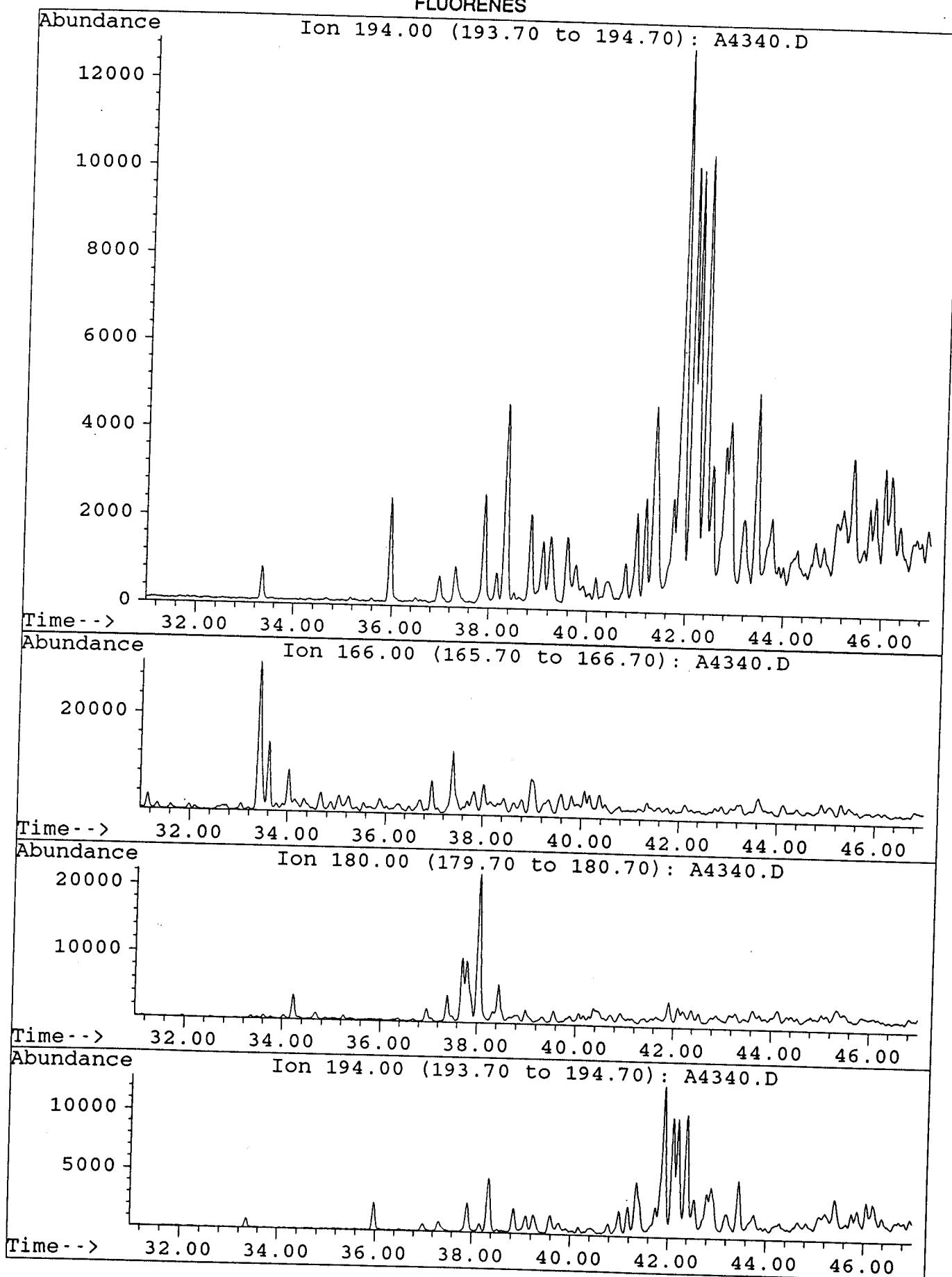


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Sample : GUDGEON#1, CH-19. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.

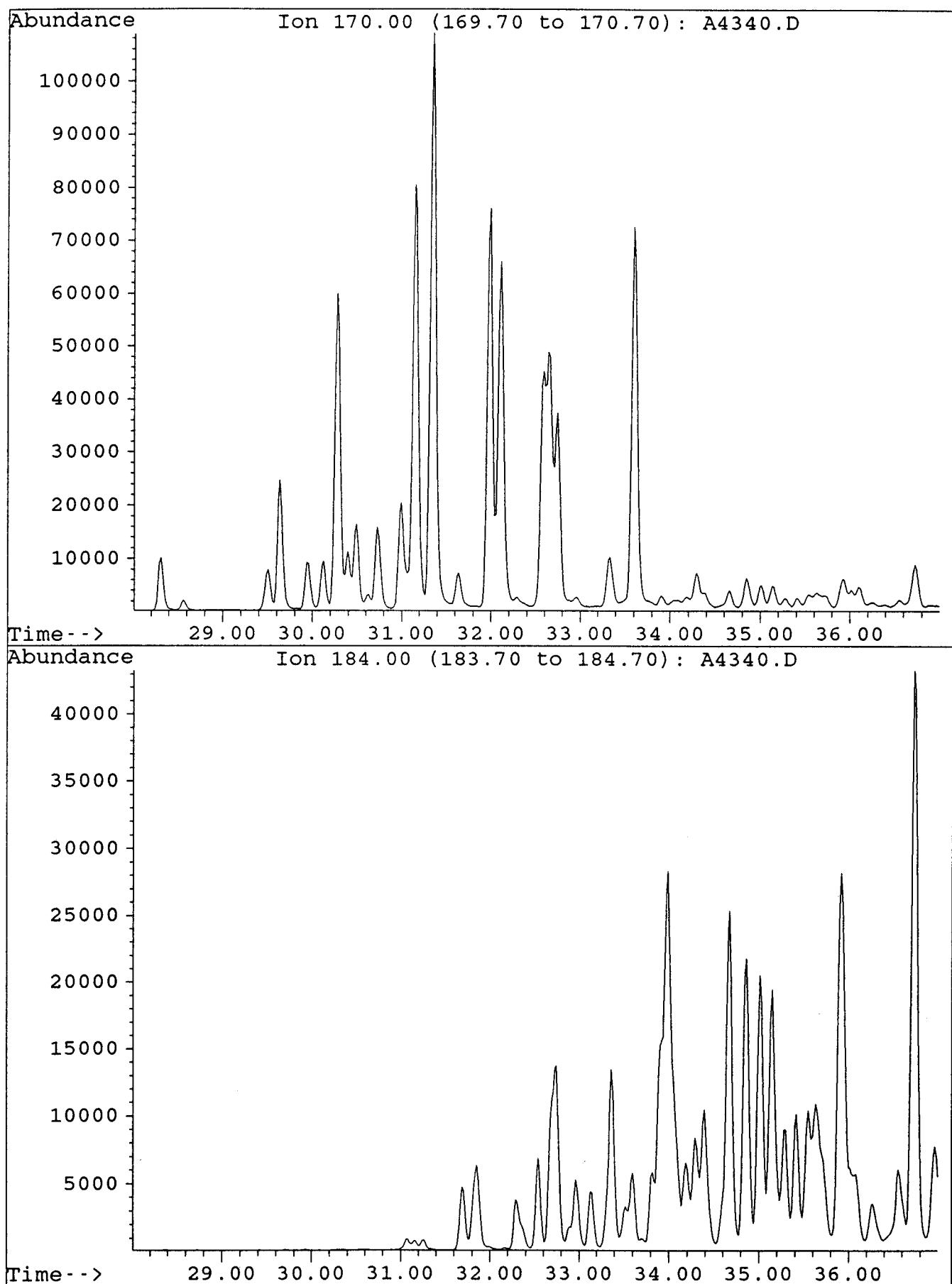


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Sample : GUDGEON#1, CH-19. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.

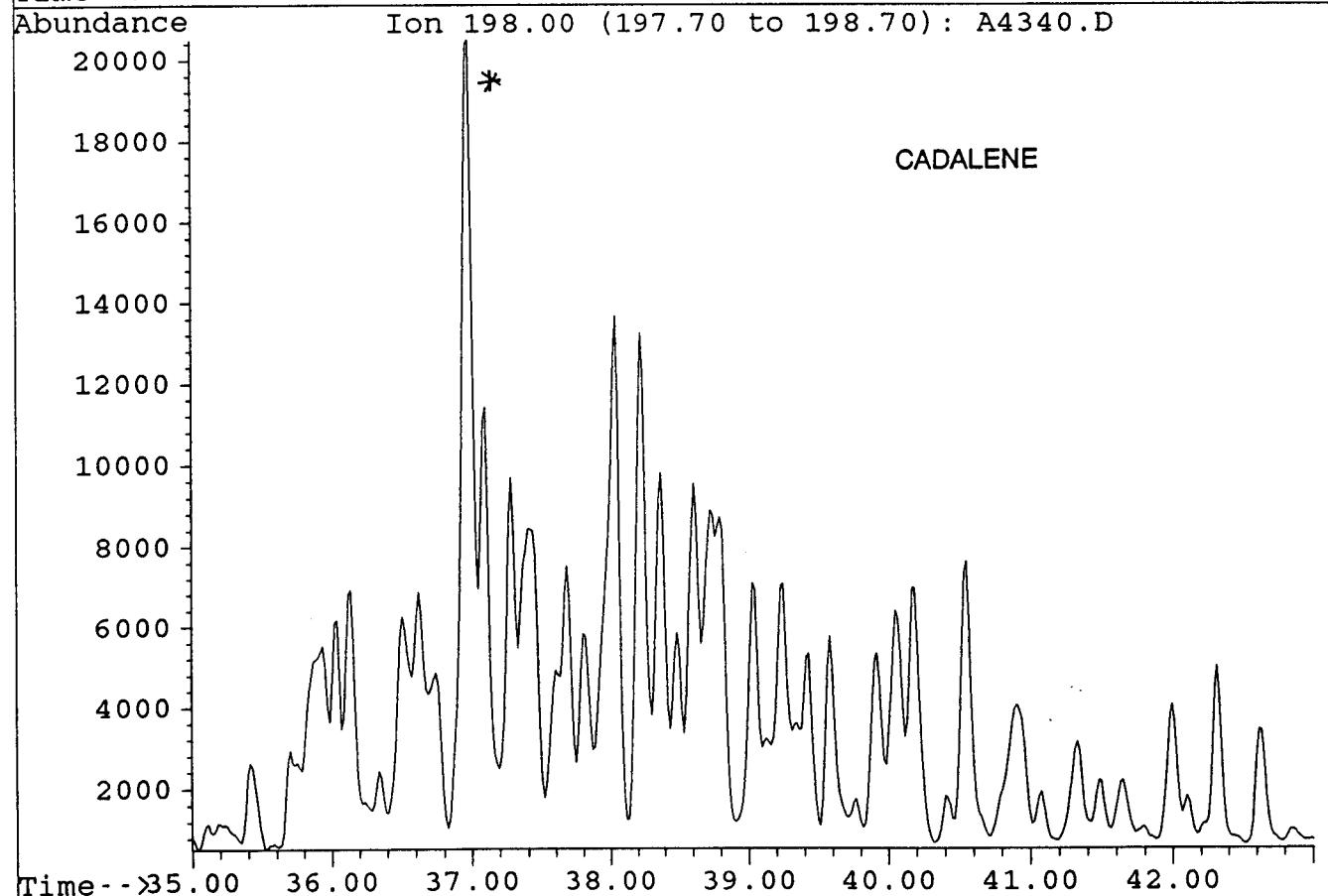
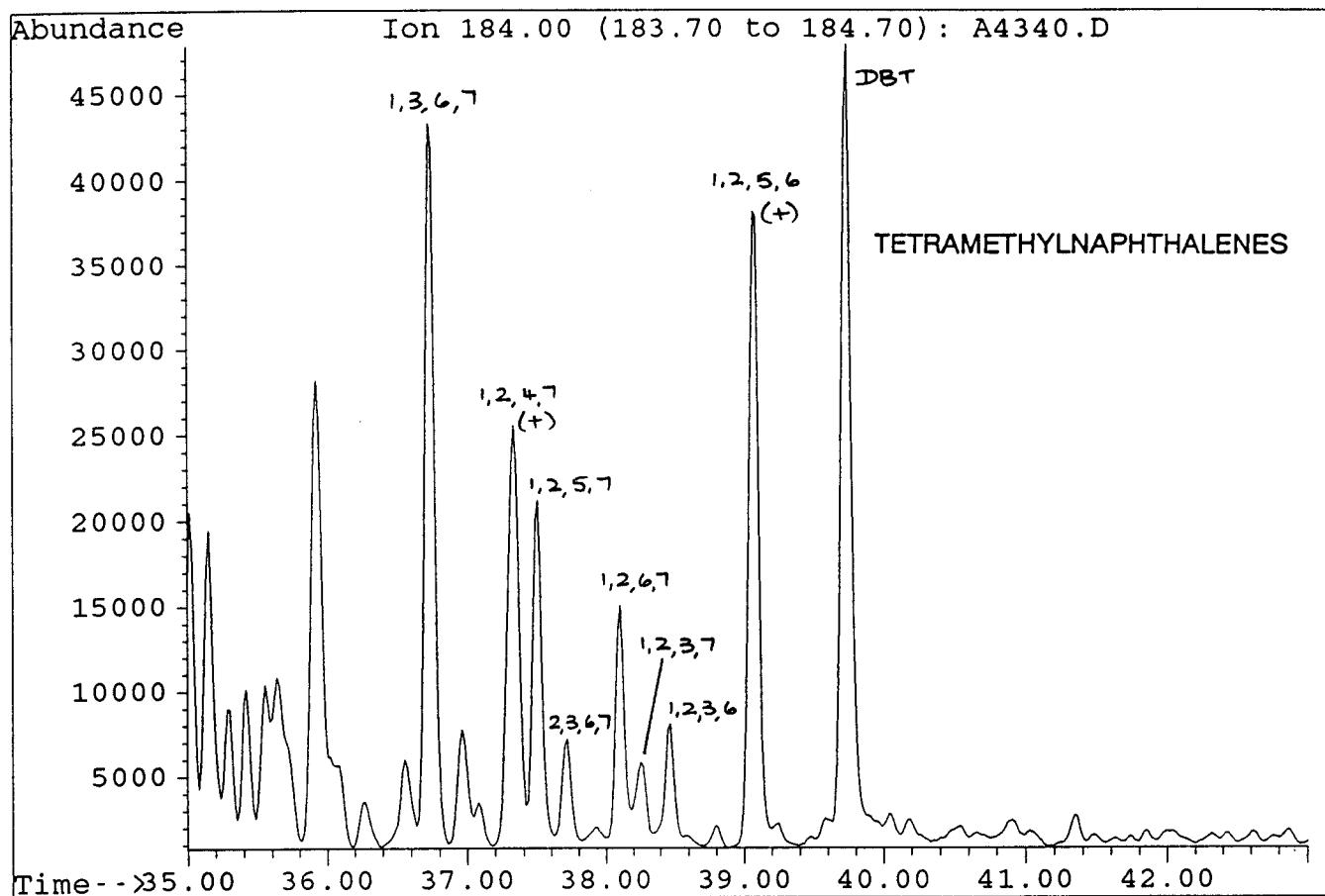
FLUORENES



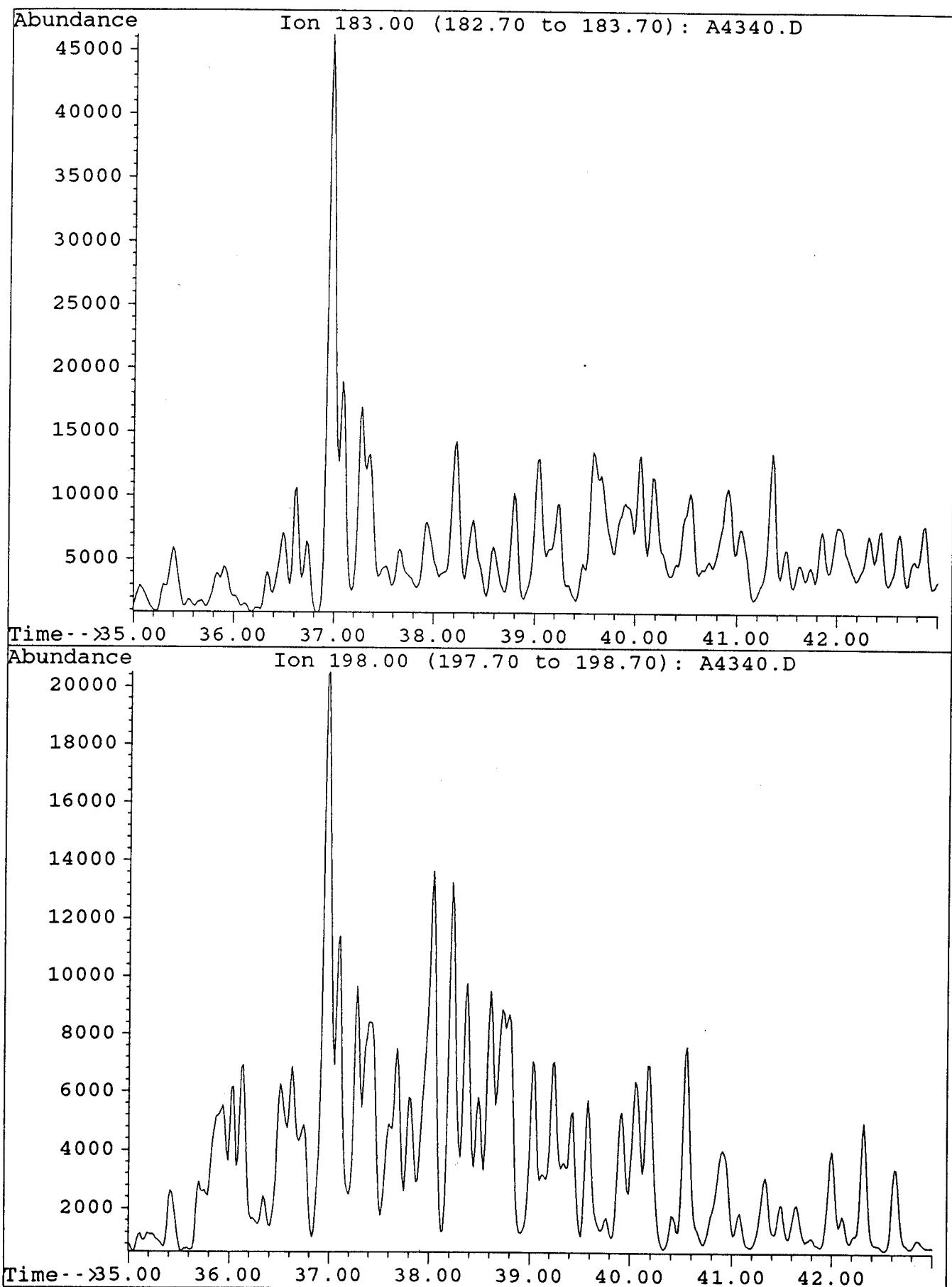
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Sample : GUDGEON#1, CH-19. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.



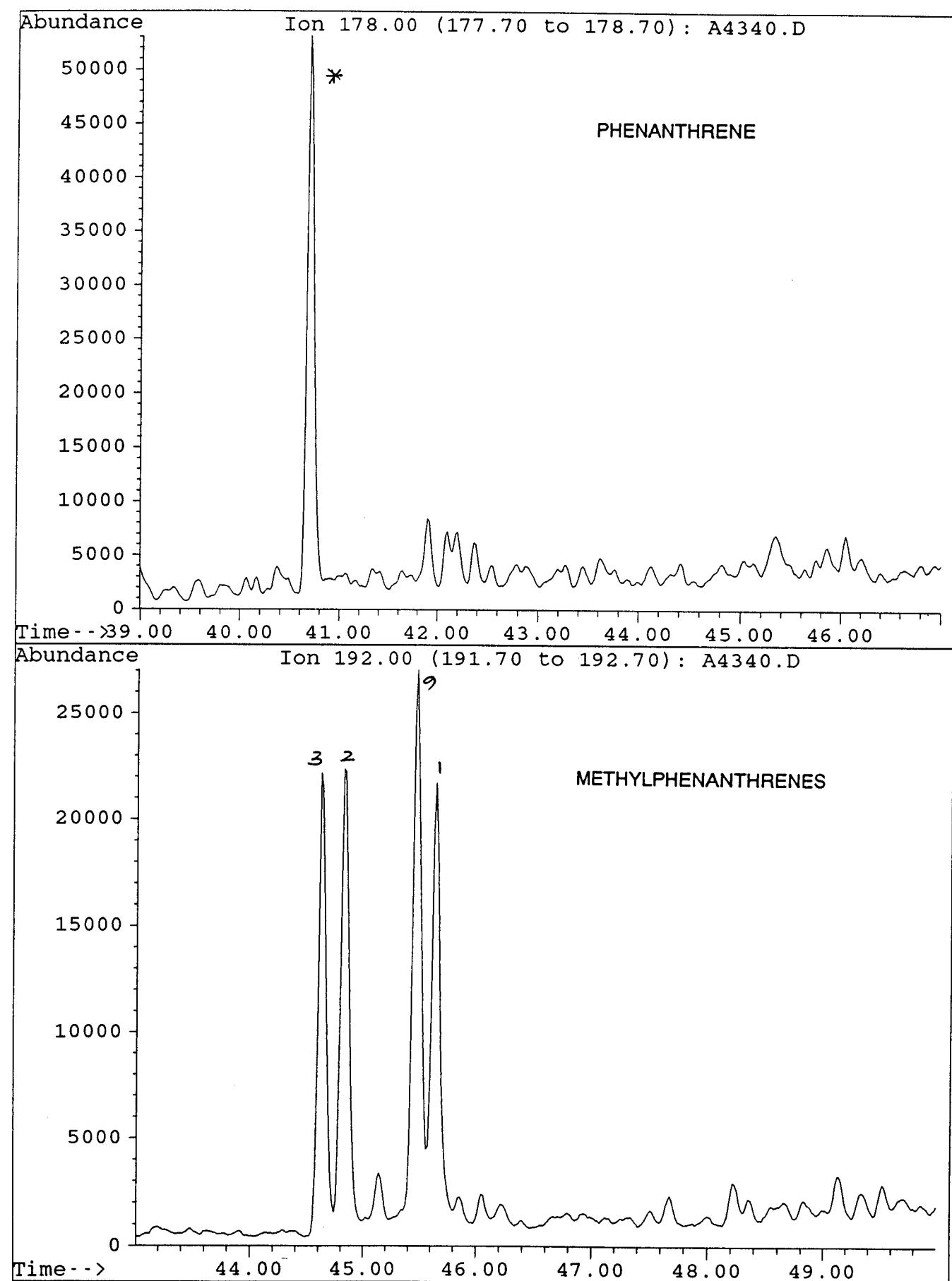
File : A4340.D  
Sample : GUDGEON#1, CH-19. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.



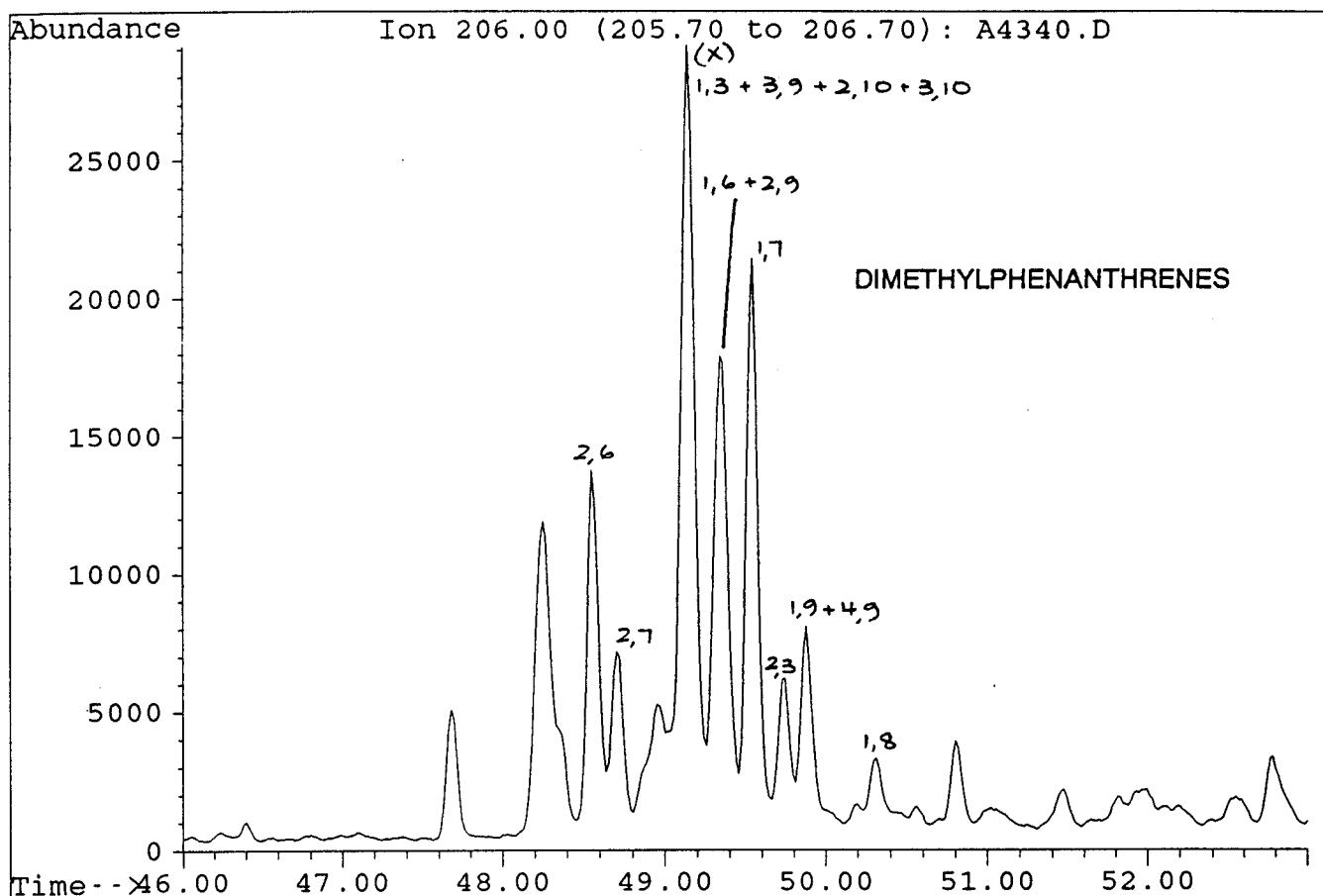
File : A4340.D  
Sample : GUDGEON#1, CH-19. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.



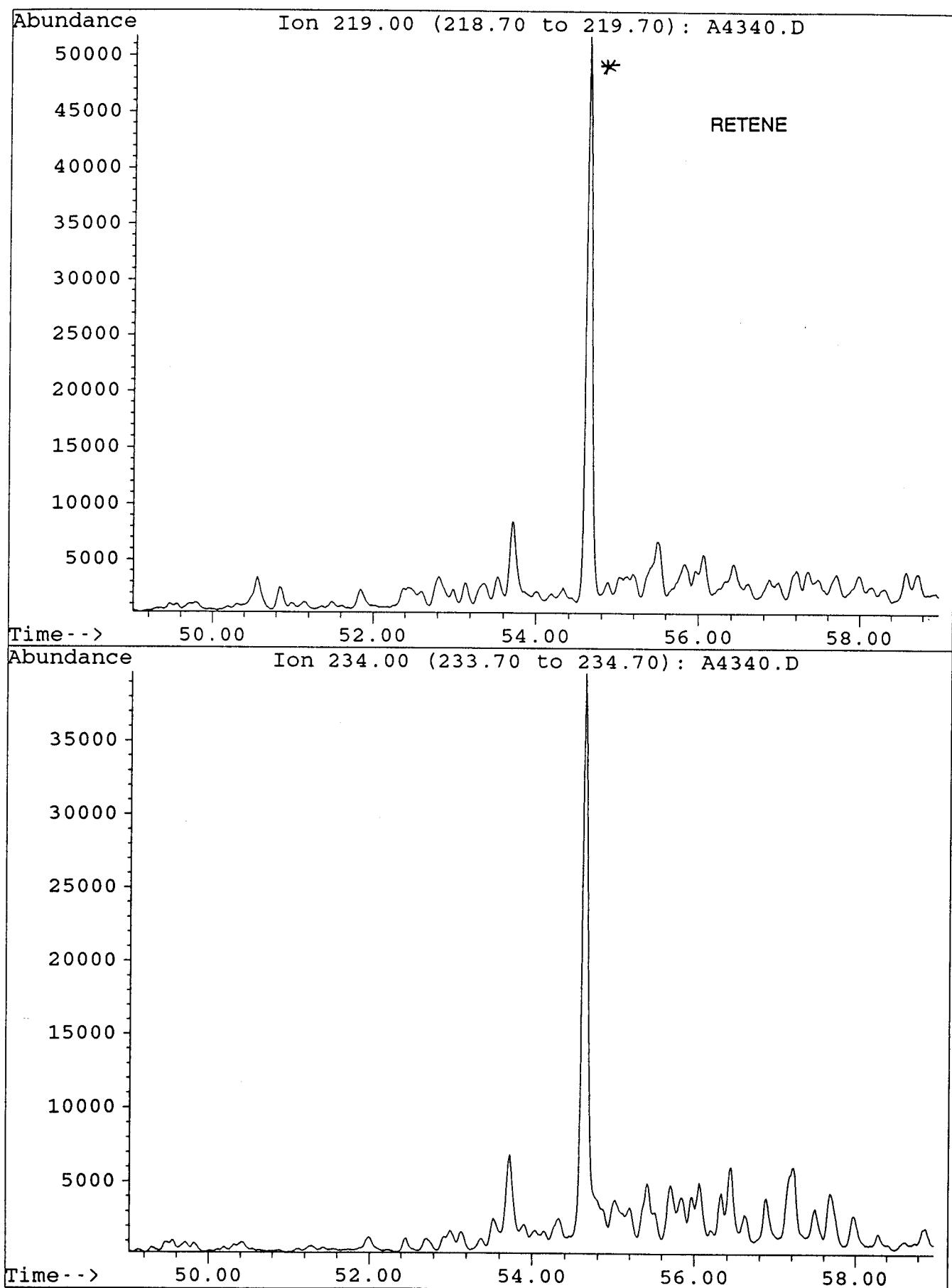
File : A4340.D  
Sample : GUDGEON#1, CH-19. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.



File : A4340.D  
Sample : GUDGEON#1, CH-19. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.

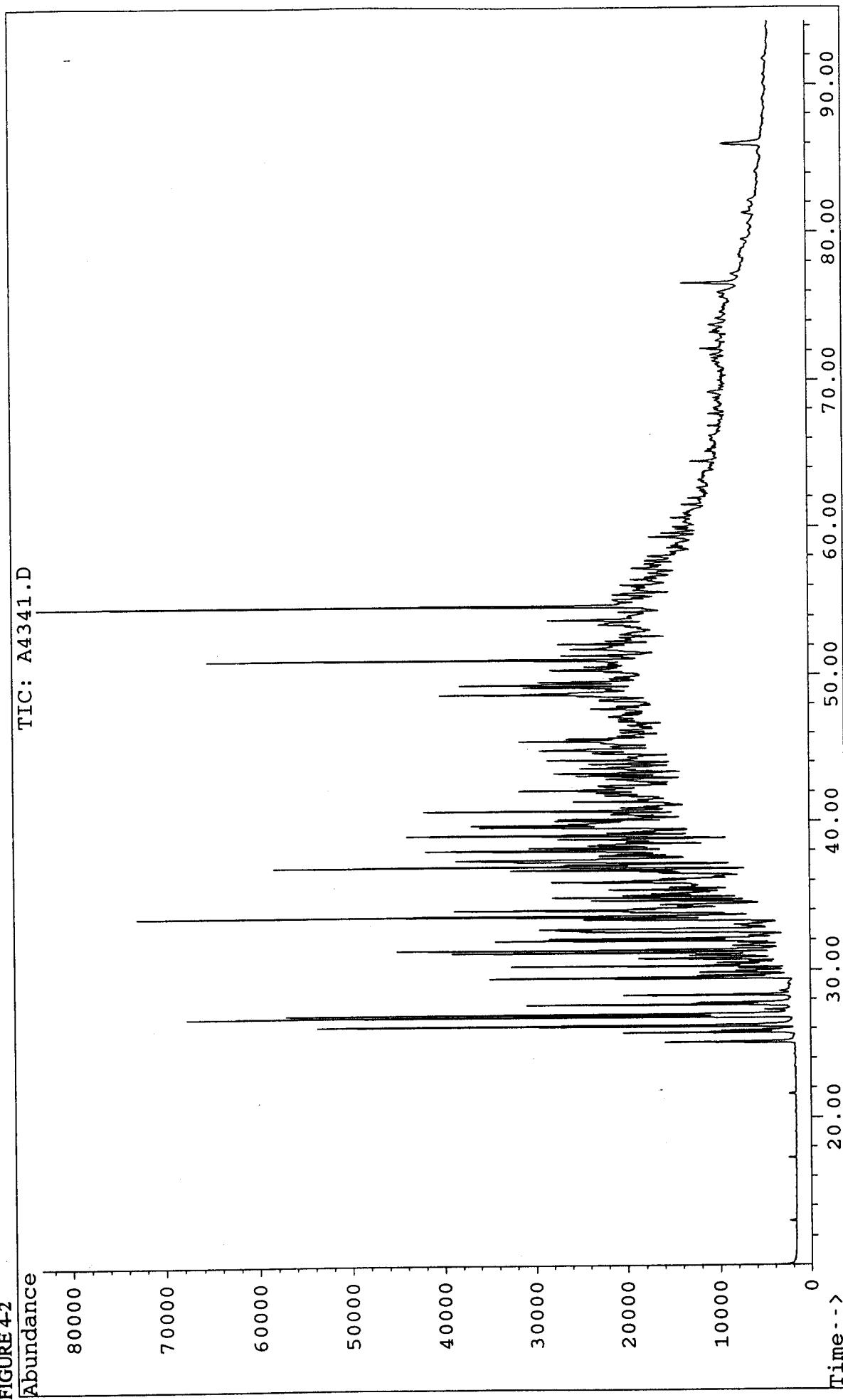


File : A4340.D  
Sample : GUDGEON#1, CH-19. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.

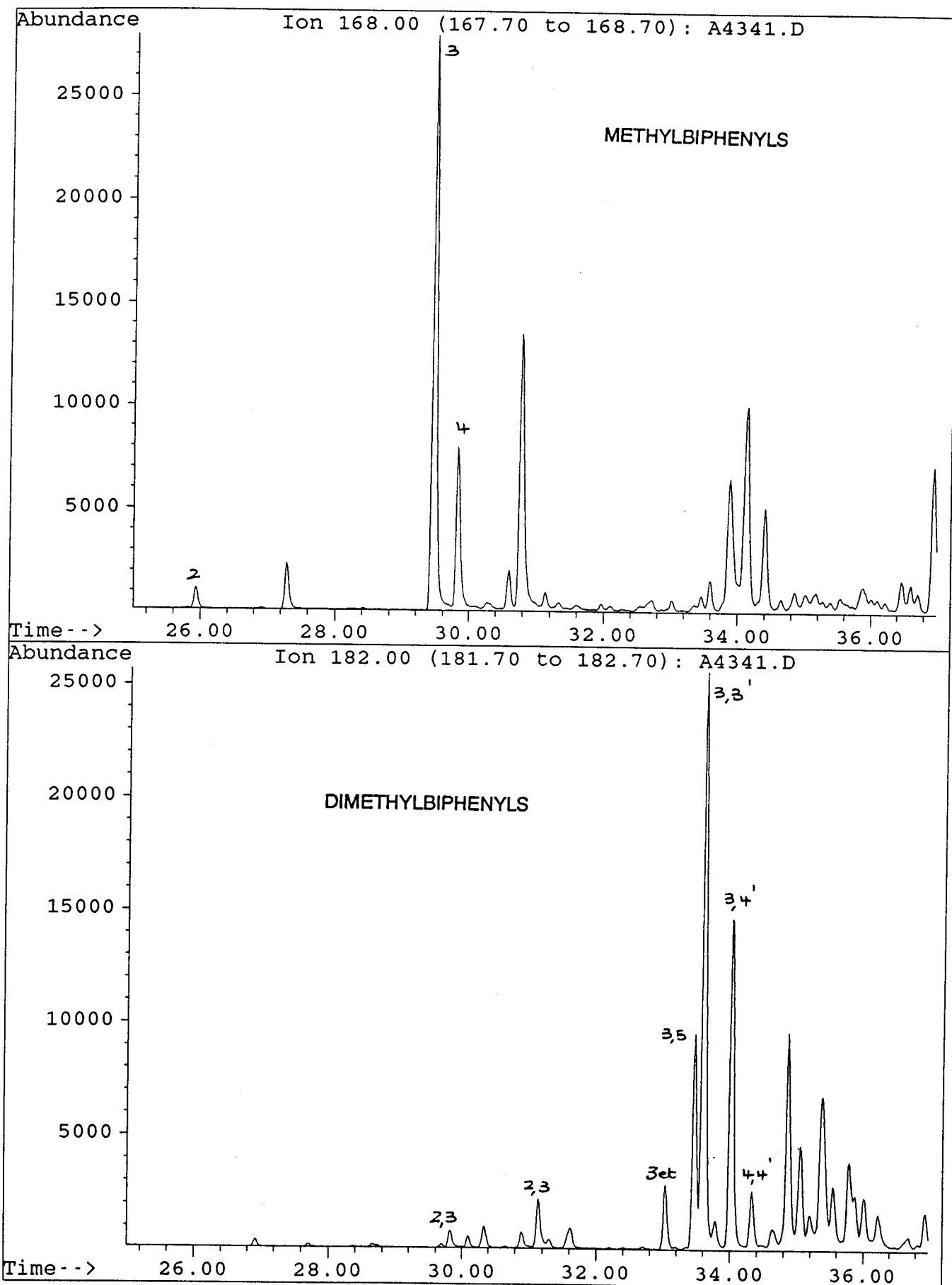


Sample : GUDGEON#1, CH-71: AROS.  
Misc. Info : COL#155. 19-12-95. GEC.

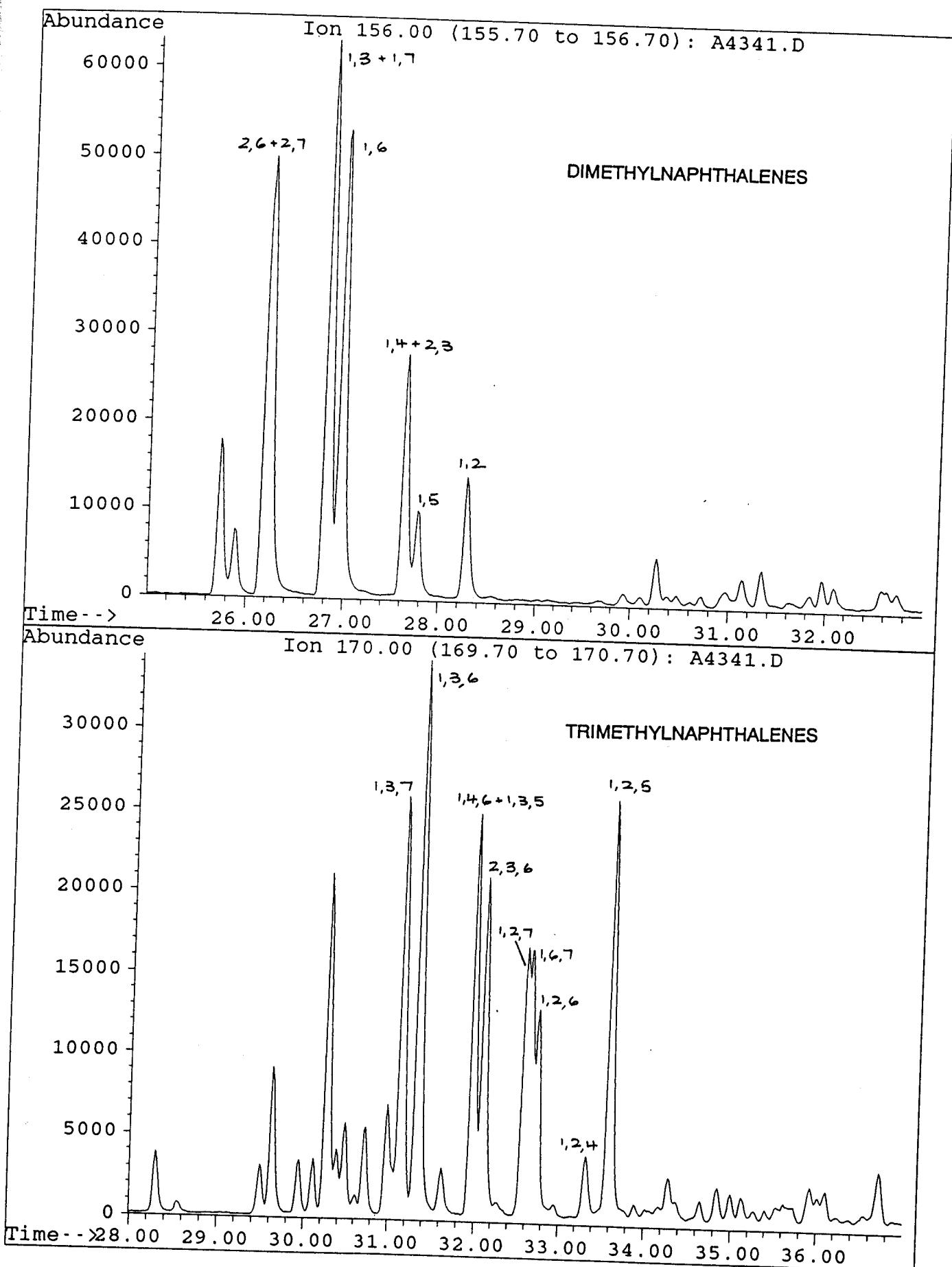
FIGURE 4-2



File : A4341.D  
Sample : GUDGEON#1, CH-71. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.

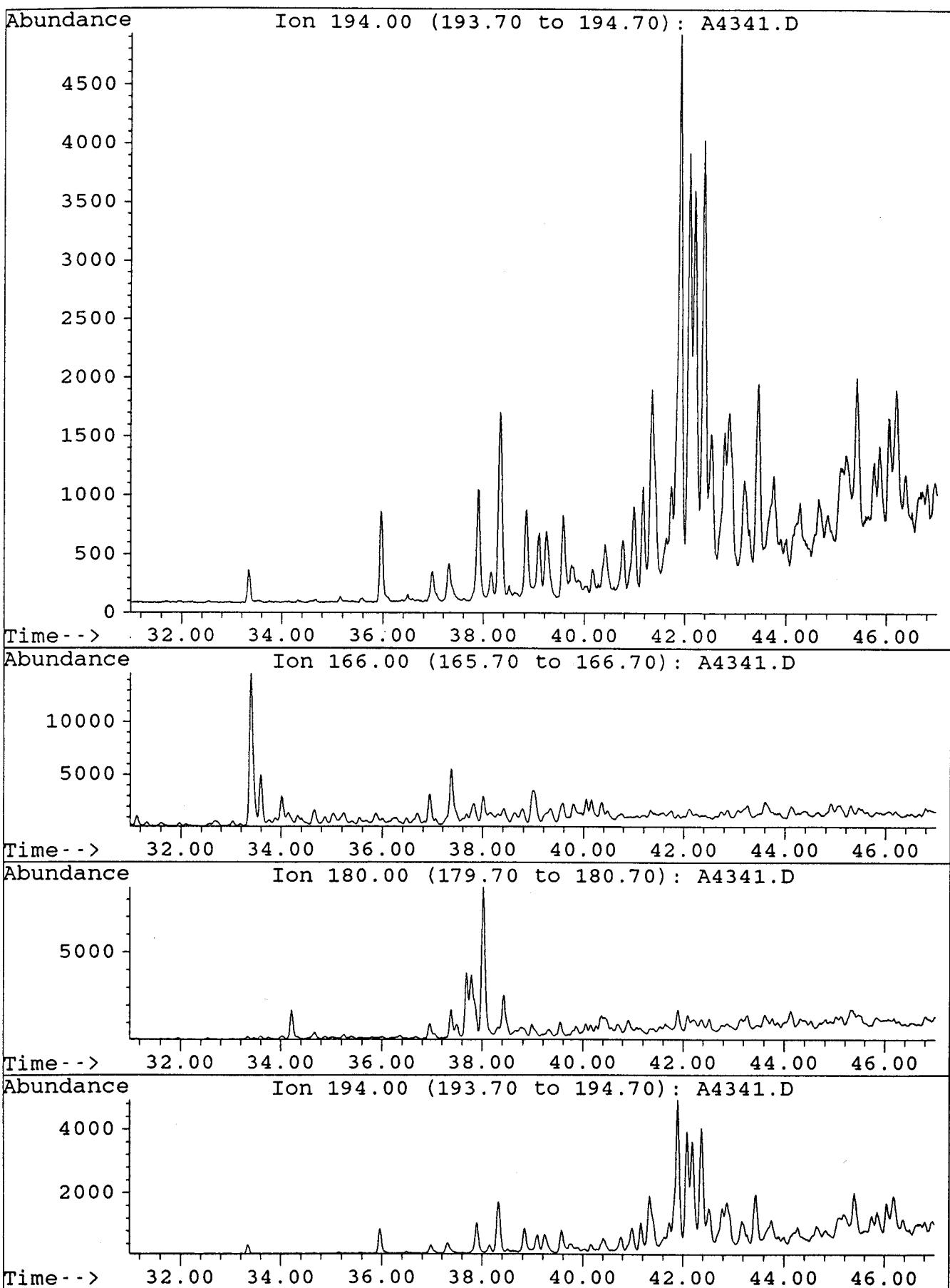


File : A4341.D  
Sample : GUDGEON#1, CH-71. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.

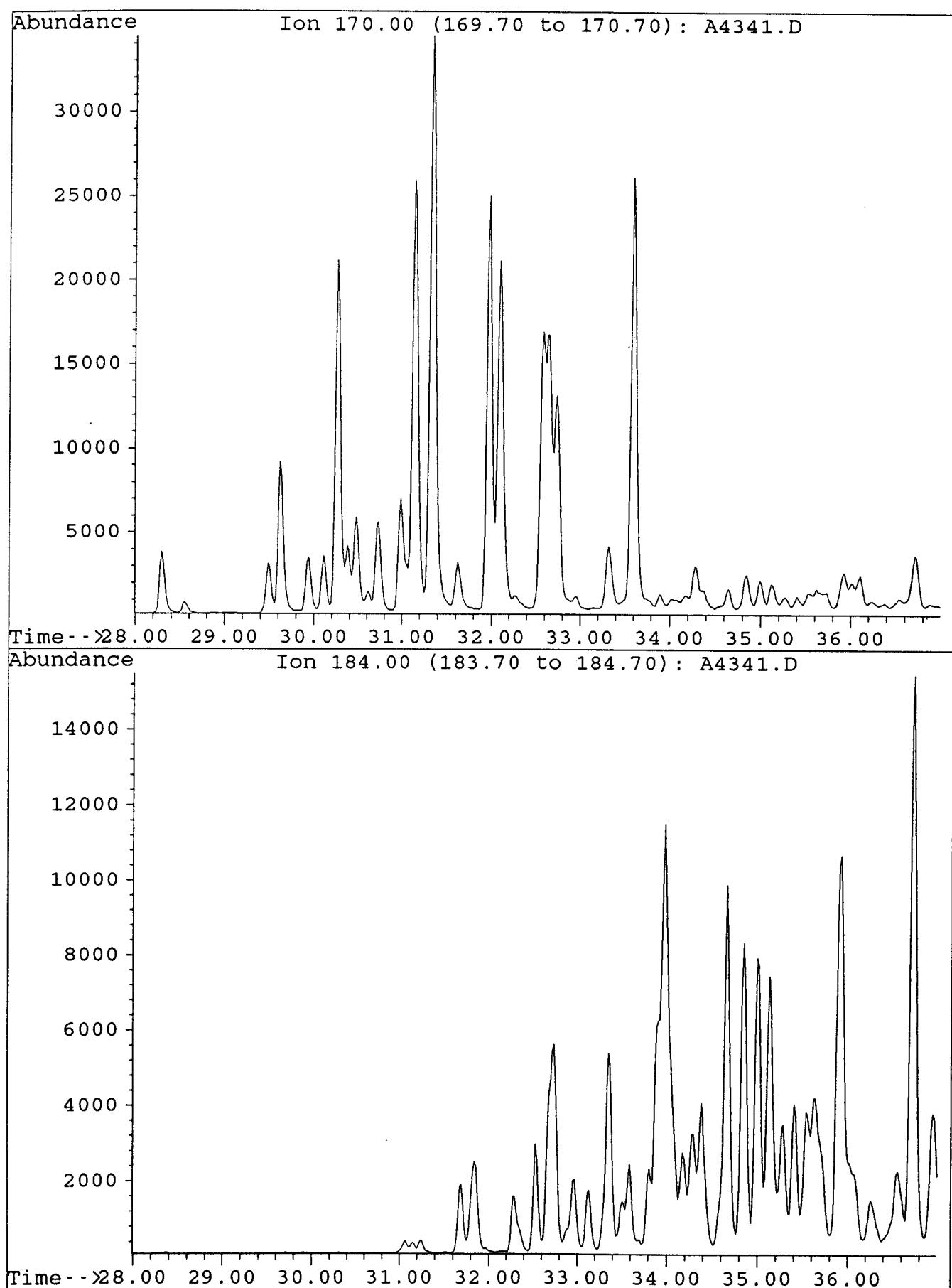


File : A4341.D  
Sample : GUDGEON#1, CH-71. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.

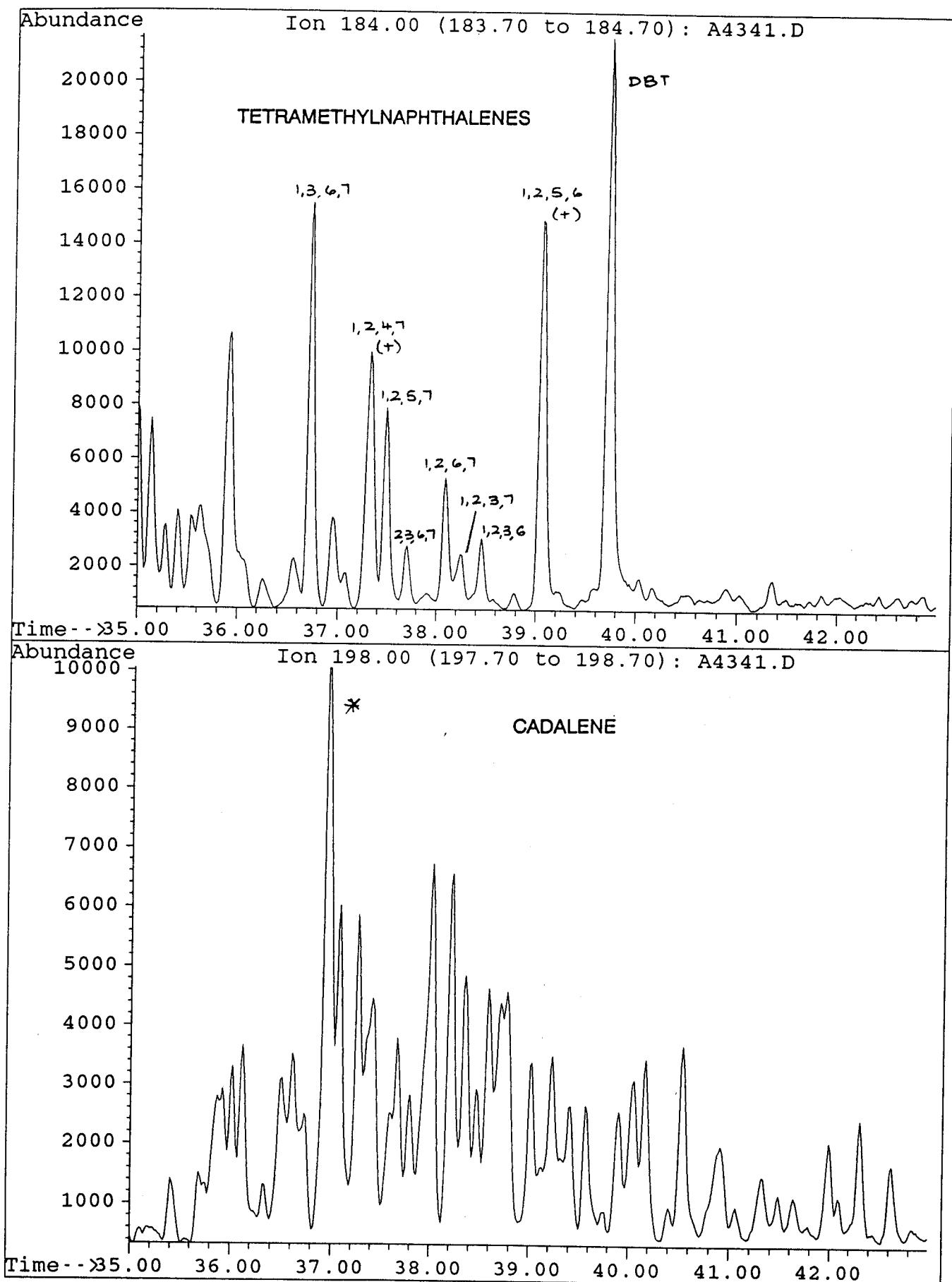
FLUORENES



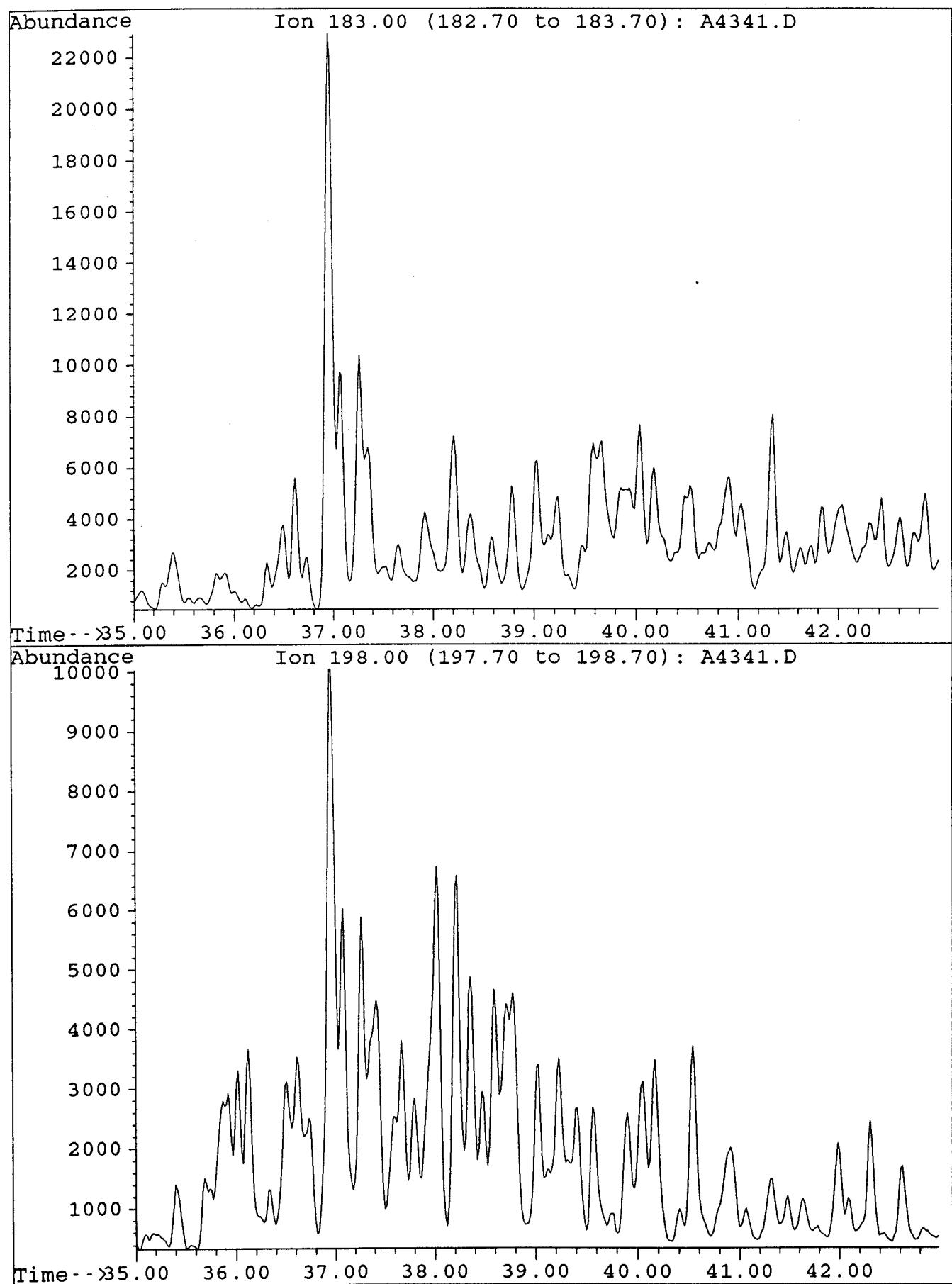
File : A4341.D  
Sample : GUDGEON#1, CH-71. AROS.  
Misc. Info : COL#155. 19-12-95. GEC.



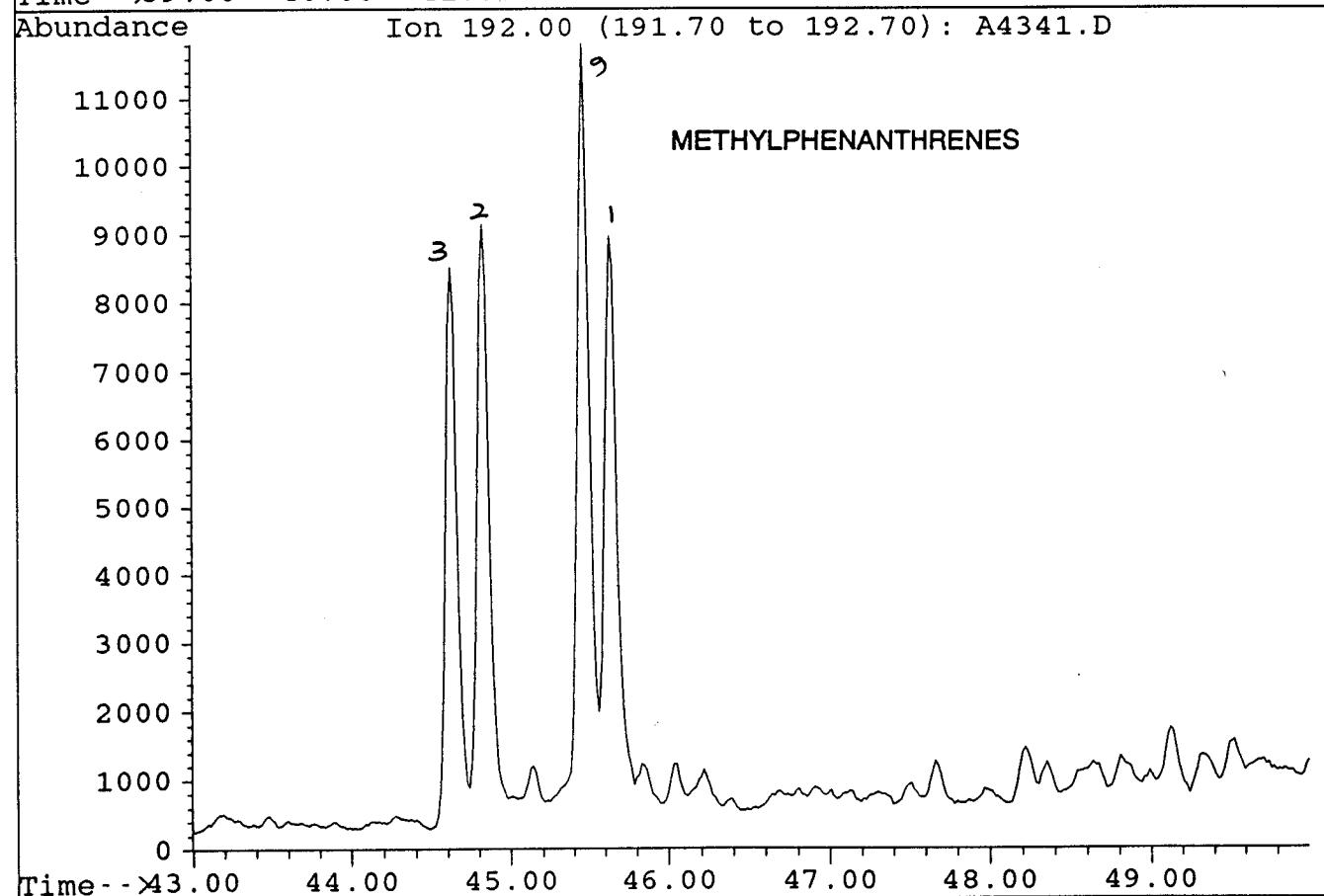
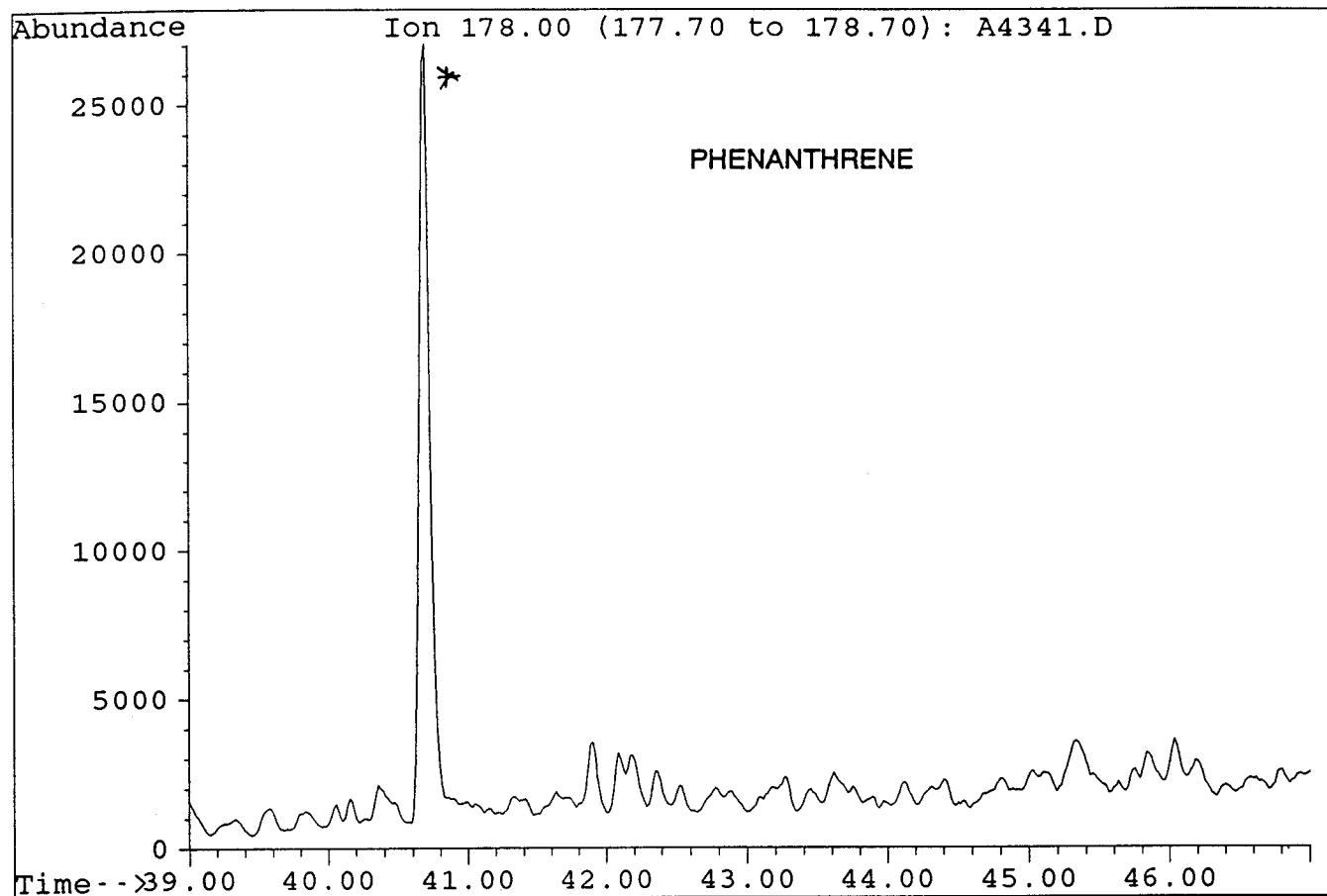
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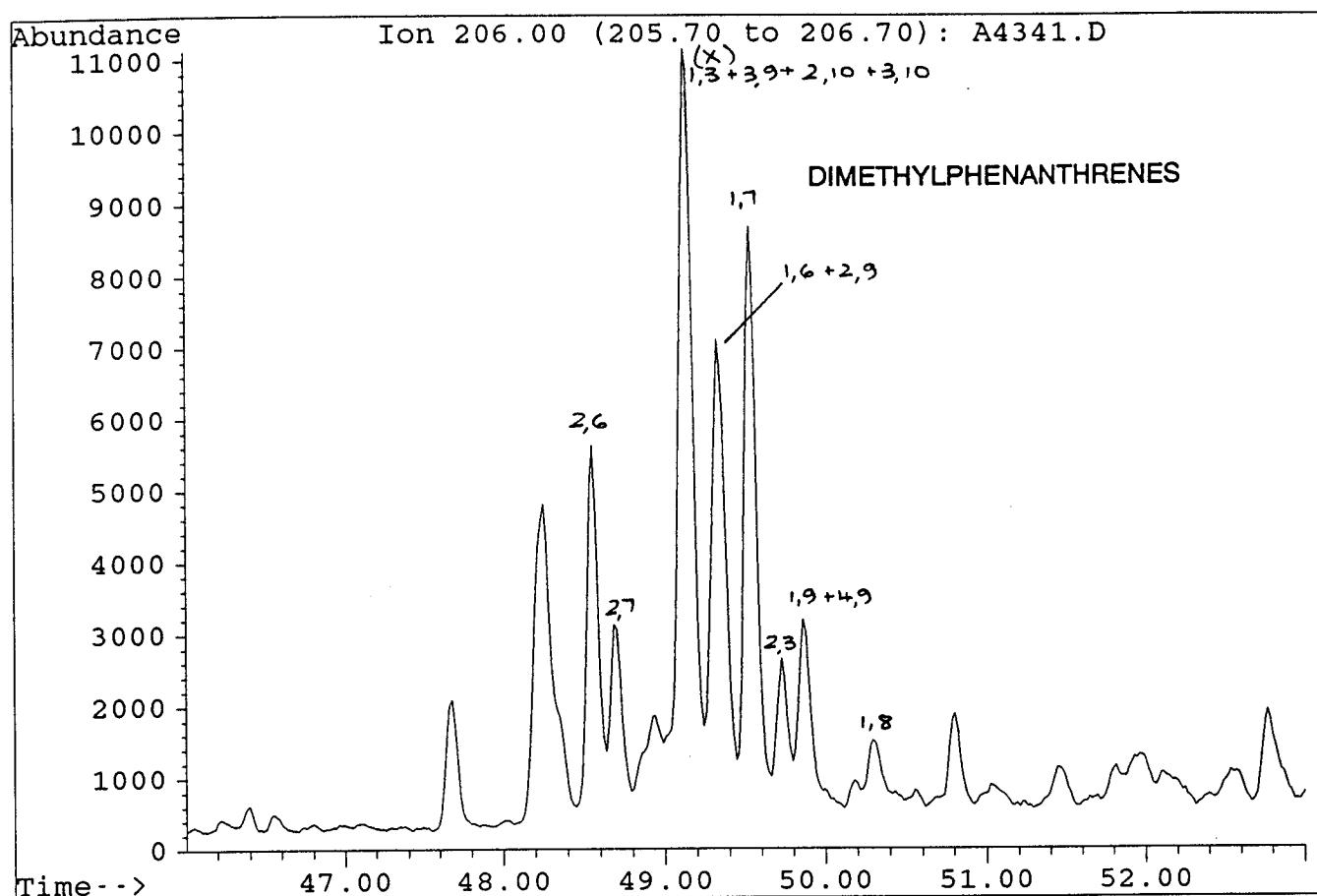
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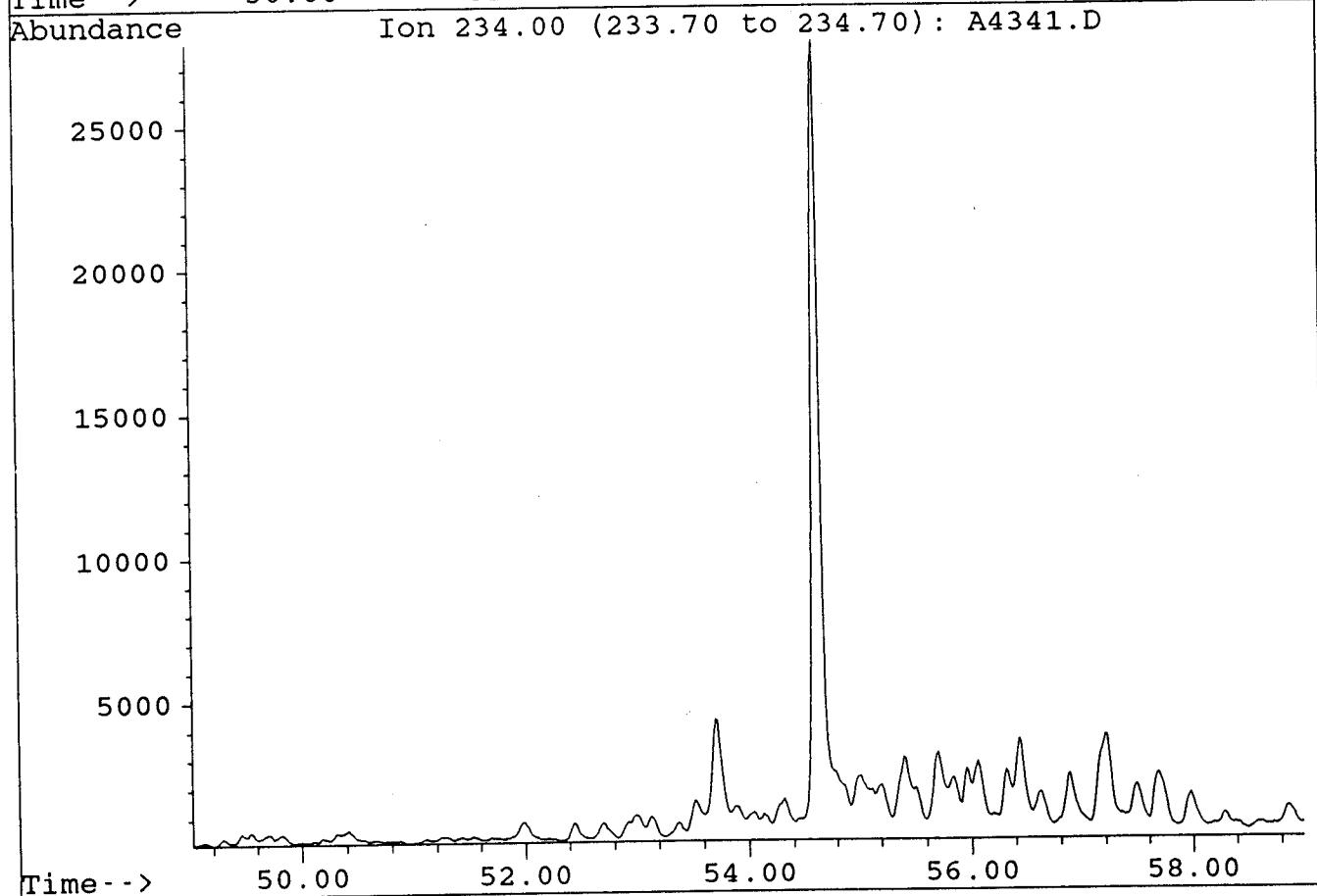
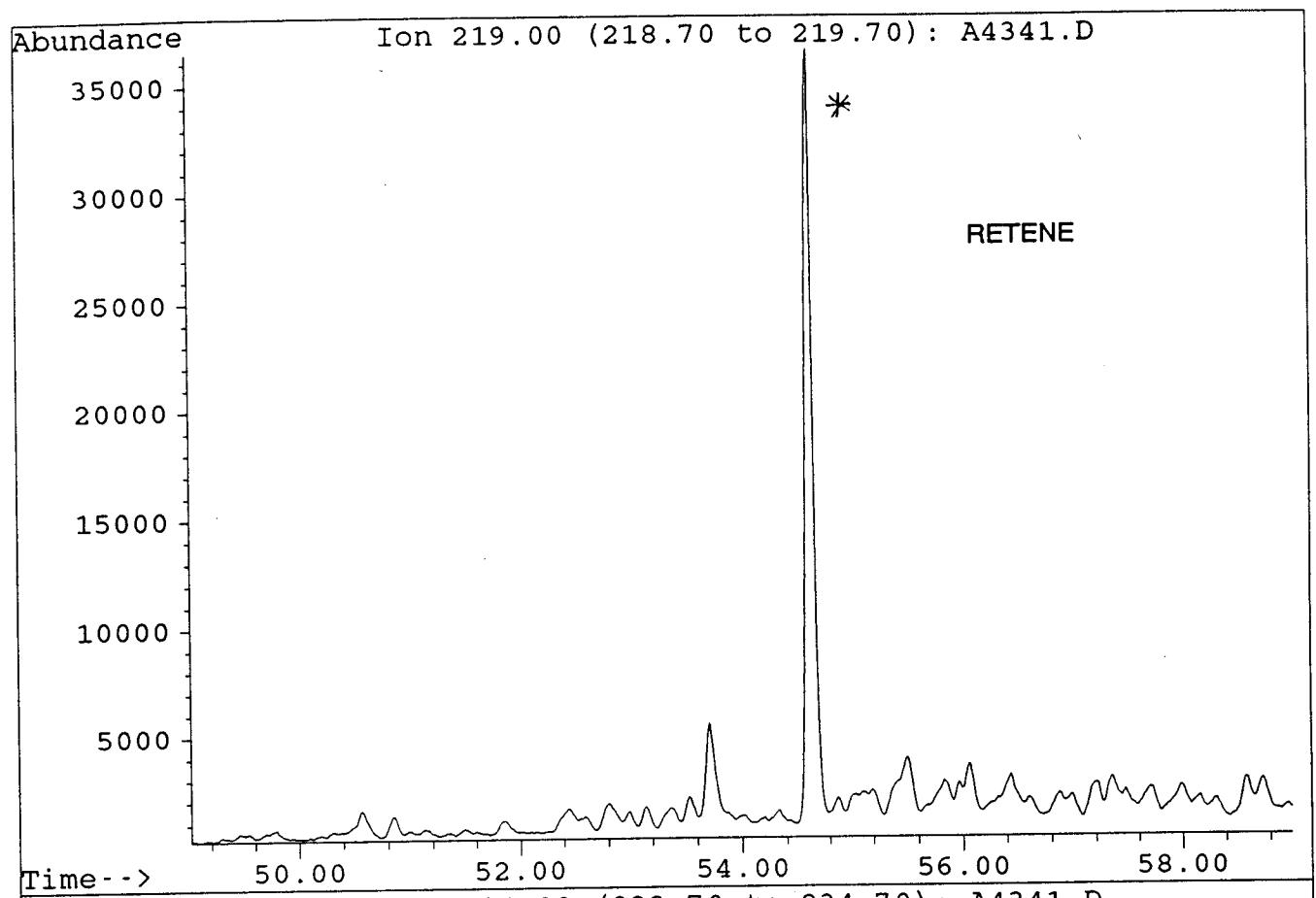
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Misc. Info : COL#155. 19-12-95. GEC.



File : A4341.D  
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## PETROLEUM GEOCHEMISTRY

### **1.0 INTRODUCTION**

Petroleum geochemistry is primarily concerned with the application of organic chemistry to samples of geological interest in hydrocarbon exploration.

Analyses can be carried out on cuttings, sidewall cores, conventional cores, relatively unweathered outcrop samples and fluid hydrocarbons (oil, condensate, gas).

Source rock evaluation is best performed on sidewall cores, since cuttings are more susceptible to contamination from both cavings and organic additives in the mud system. In petroleum geochemical studies it is vitally important for the geochemist/geologist to be aware of the type of mud additives used and the stage at which they are used during the drilling program. Any anomalous results must be carefully considered in conjunction with mud system records.

Petroleum geochemistry in exploration is applied for three major purposes:

1. Identification of richness, maturity and type of kerogen in (a large number of) whole rock samples by screening analyses.
2. Semi-detailed characterisation of kerogen in sediments from selected source intervals, to determine maturity, source type and genetic potential.
3. Detailed characterisation of petroleum fluids (extracts, oils and condensates) by assessment of thermal maturity, source type and depositional environment to enable oil-to-oil and oil-to-source rock correlation studies.

## 2.0 THEORY & METHODS

Samples are analysed according to the scheme illustrated in Figure 1 which shows the order and type of analysis for both screening and detailed tests.

### 2.1 Screening Analyses of Whole Rock Samples

#### 2.1.1 Headspace/Cuttings Gas Analysis

The headspace sample is usually provided in a sealed tin can which holds both cuttings and water to approximately three quarters capacity. This allows the volatile hydrocarbons to diffuse easily into an appreciable headspace.

The gas is taken into a syringe through a silicone seal on the lid of the container and analysed by packed column gas chromatography using the following conditions:

Instrument:	Shimadzu GC-8APF
Column:	6'x 1/8" Chromosorb 102
Injector/Detector Temperature:	120°C
Column Temperature:	110°C
Carrier Gas:	Nitrogen

Cuttings gas analysis is performed in the same manner but on samples which do not liberate volatile gases readily. These sediments are subjected to very vigorous agitation prior to sampling.

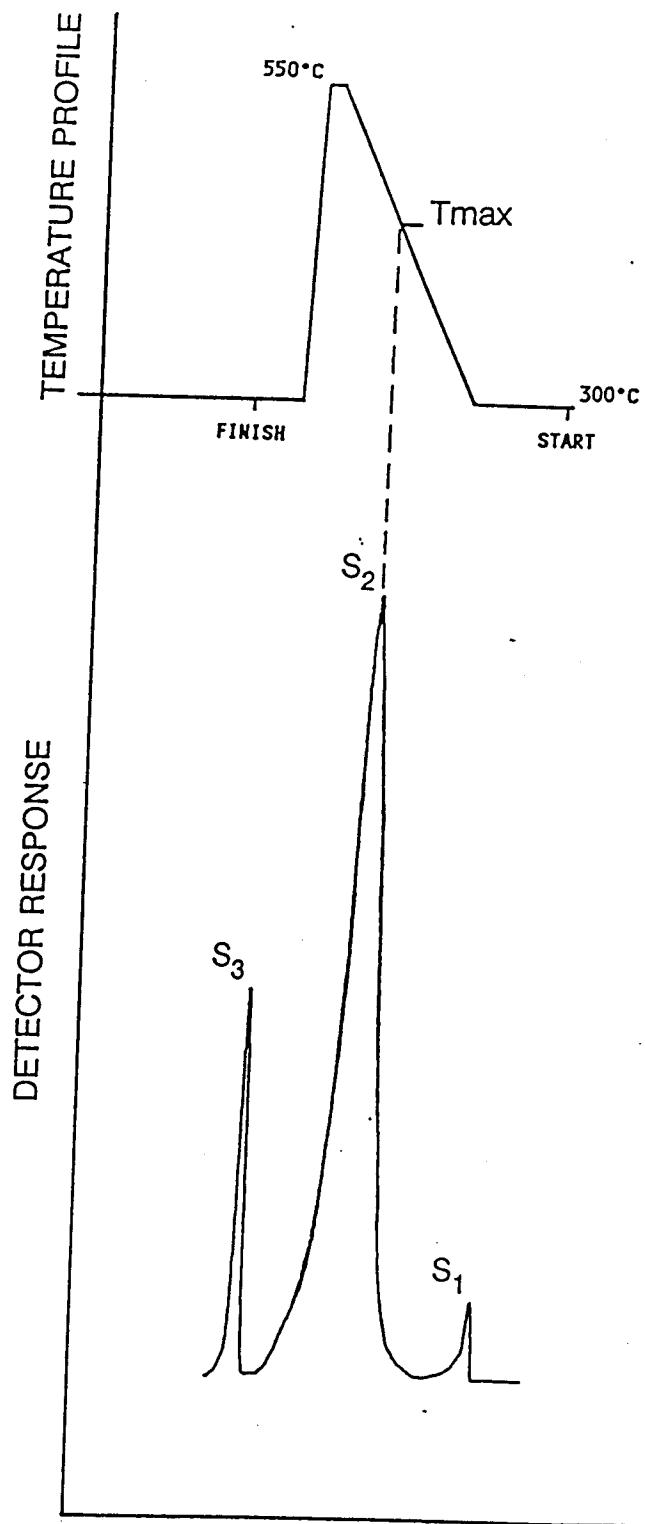
Values are given as volume of gas per million volumes of sediment (ppm) for each hydrocarbon (methane, ethane, propane, iso- and n-butane), as composite values including C5-C7, and as ratios.

Headspace/cuttings gas analyses are used as a screening technique to identify zones of significant gas generation and out-of-place gas (Letran et al, 1974). The classification for gas content is listed below:

Total gas content (C1;C2-C4; or C5-C7)	Description
10 - 100ppm	very lean - lean
100 - 1,000	lean - moderate
1,000 - 10,000	moderate - rich
10,000 - 100,000	rich - very rich

FIGURE 2

SCHEMATIC PYROGRAM OF ROCK-EVAL PYROLYSIS



The abundance of C<sub>2</sub>-C<sub>4</sub> components (wet gas) is used to locate the zone of oil generation, since wet gas is commonly associated with petroleum (Fuex, 1977).

It is important to ensure that the gases analysed are not of a biogenic origin, so an anti-bacterial agent must be added to the cuttings when they are stored in water.

### 2.1.2 Sample Preparation

Depending on drilling mud content, cuttings samples may be water washed before they are air dried, picked free of contaminants and cavings, and then crushed to 0.1mm using a ring pulveriser.

Sidewall cores are freed of mud cake and other visible contaminants, sampled according to homogeneity, air dried and hand crushed to 0.1mm grain size.

Conventional core and outcrop samples are inspected for visible contaminants and crushed to 1/8" chips using a jaw crusher. After air drying, the chips are crushed with a ring pulveriser to small particle size (0.1mm).

Petroleum aqueous mixtures are separated into oil and water/mud fractions by decanting off the oil layer and producing a clean separation by gently centrifuging the oil. If separation by this method is not effective, the petroleum is solvent extracted.

### 2.1.3 Total Organic Carbon(TOC)

The TOC value is determined on crushed sediment. The minimum sample requirement is one gram, however, results may be obtained from as little as 0.2mg in very rich samples. Carbonate minerals are first removed by acid digest (HC1) and the remaining sample heated to 1700°C (Leco Induction Furnace) in an atmosphere of pure oxygen. The CO<sub>2</sub> produced is measured with an infra-red detector, and values calculated according to standard calibration.

TOC is expressed as % of rock and is used as a screening procedure to classify source rock richness:

Classification	Clastics	Carbonates
Poor	0.00 – 0.50	0.00 – 0.25
Fair	0.50 – 1.00	0.25 – 0.50
Good	1.00 – 2.00	0.50 – 1.00
Very Good	2.00 – 4.00	1.00 – 2.00
Excellent	> 4.00	> 2.00

#### 2.1.4 Rock-Eval Pyrolysis

Although a preliminary source rock classification is made using TOC data, a more accurate assessment of organic source type and maturity is possible by Rock-Eval pyrolysis. Two types of Rock-Eval analyses are offered: "one run" which involves pyrolysis of the crushed but otherwise untreated sediment and "two run" which involves pyrolysis of both the crushed, untreated sediment and the decarbonated sediment. The "two run" method provides more accurate S<sub>3</sub> values than the "one run" method. S<sub>1</sub> and S<sub>2</sub> values are of the same accuracy in both methods.

The method requires 0.4g of sample material, although reliable results can often be obtained from smaller amounts.

The crushed sediment is heated in an inert atmosphere of helium over a programmed temperature range. The resulting pyrogram is shown in Figure 2.

Hydrocarbons present in the free or adsorbed state (S<sub>1</sub>) are thermally distilled at 300°C and measured by a flame ionisation detector (FID). Hydrocarbons are then cracked from the kerogen (S<sub>2</sub>) during a temperature ramp from 300° to 550°C and also measured by FID. CO<sub>2</sub> released during the kerogen cracking process (S<sub>3</sub>) is trapped and subsequently measured by a thermal conductivity detector.

The amount of free hydrocarbons in the sediment (S<sub>1</sub>) represents milligrams of hydrocarbons distilled from one gram of rock and is a measure of both in situ and out-of-place petroleum.

Free hydrocarbon richness is described by the following:

S<sub>1</sub> (mg/g or kg/tonne)

0.20 – 0.40	fair
0.40 – 0.80	good
0.80 – 1.60	very good
> 1.60	excellent

The total amount of hydrocarbons present in the free state and as kerogen is a measure of the potential yield (genetic potential) of the sample ( $S_1 + S_2$ ) and is expressed as mg/g or rock.

Source rocks are classified accordingly:

$S_1 + S_2$ (mg/g)	Source Rock Quality
0.00 – 1.00	poor
1.00 – 2.00	marginal
2.00 – 6.00	moderate
6.00 – 10.00	good
10.00 – 20.00	very good
> 20.00	excellent

The Production Index (PI) represents the amount of petroleum generated relative to the total amount of hydrocarbons present ( $S_2 / (S_1 + S_2)$ ). It is a measure of the level of maturity of the sample. For oil prone sediments PI ranges from 0.1 at the onset of oil generation to 0.4 at peak oil generation. For gas prone sediments, PI shows only a small change with increasing maturity.

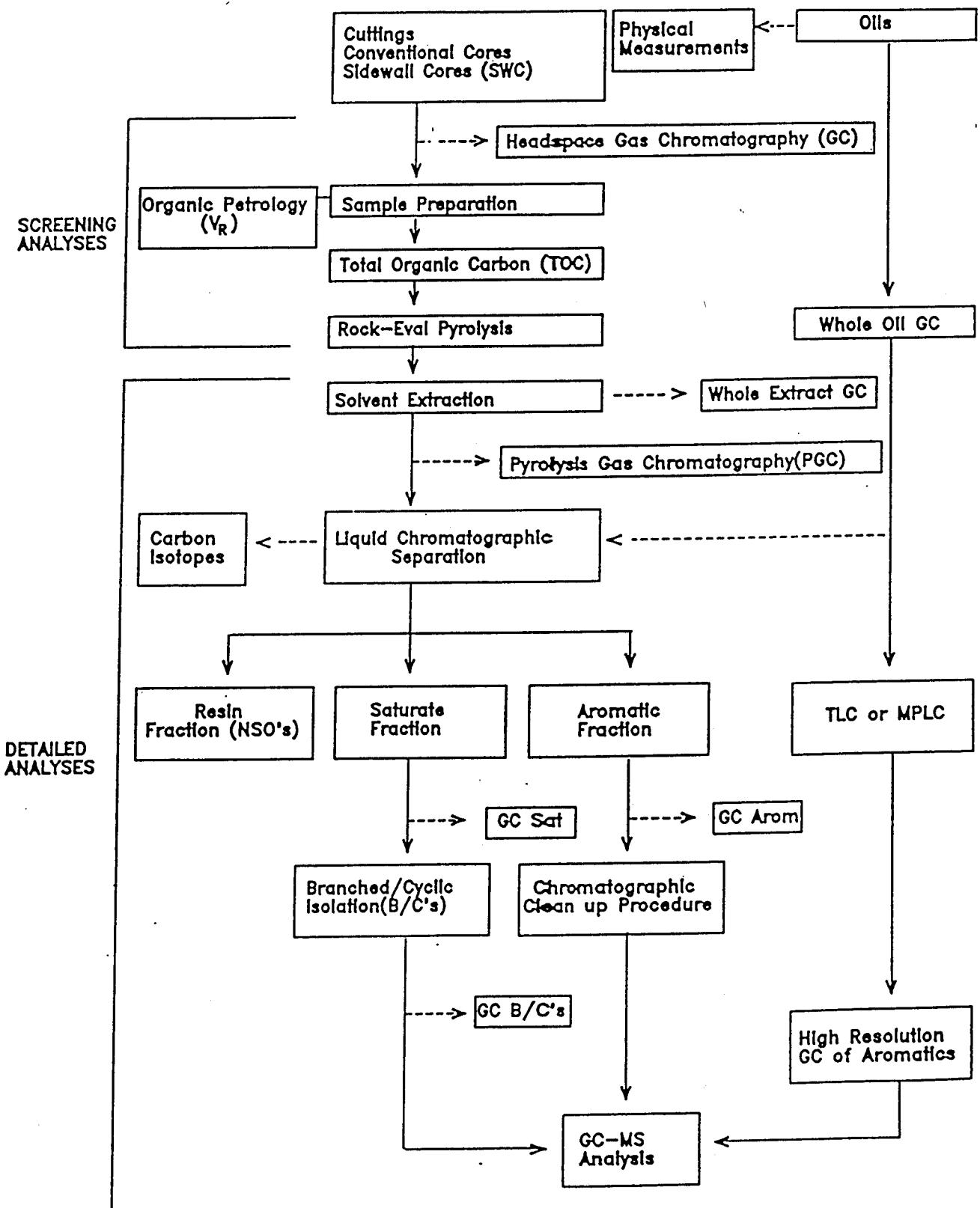
The temperature at which the maximum amount of  $S_2$  hydrocarbons is generated is called  $T_{max}$  (Figure 2). This temperature increases with the increasing maturity of sediments.

The variation of  $T_{max}$  is summarised as

< 430°C	immature
430/435°C – 460°C	mature (oil window)
> 460°C	overmature

Hydrogen Index ( $HI = S_2 \times 100/TOC$ ) and Oxygen Index ( $OI = S_3 \times 100/TOC$ ), when plotted against one another, provide information about the type of kerogen and the maturity of the sample. Both parameters decrease in value with increasing maturity. Samples with high HI and low OI are dominantly oil prone and samples with low HI and high OI are gas prone.

FIGURE 1  
FLOW DIAGRAM FOR PETROLEUM GEOCHEMICAL ANALYSES



## 2.2 Analysis of Kerogen

### 2.2.1 Organic Petrology – Vitrinite Reflectance

Vitrinite is a coal maceral which responds to increasing levels of thermal maturity. This response is measured microscopically by the percent of light reflected off the polished surface of a vitrinite particle immersed in oil.

Measurement of vitrinite reflectance can be carried out on uncrushed, washed and dried cuttings (10–50gms of sample material required), sidewall cores (2–10gms), conventional cores (2–10 gms) or outcrop samples (2–10gms).

The values given are for standard lower size limits. In special cases, however, useful data may be obtained from as little as 0.1gm.

For each sample a minimum of 25 fields is measured in order to establish a range and mean for reflectance values.

Maturity classifications according to vitrinite reflectance values are:

% VR (approx)	Maturity
0.2 – 0.55	immature
0.55 – 1.2	mature
1.2 – 1.8	overmature
> 1.8	severely altered

Following vitrinite reflectance measurements, microscopic examination in fluorescence mode allows the description of liptinite macerals and an estimate of their abundances. The amount of dispersed organic matter is reported and its composition described.

Vitrinite reflectance results and maceral descriptions are best obtained from coals or rocks deposited in environments which received large influxes of terrestrially derived organic matter. Vitrinite reflectance cannot be measured in rocks older than Devonian age, since land plants had not evolved prior to this time.

## 2.2.2 Pyrolysis Gas Chromatography

Pyrolysis gas chromatography (PGC) is performed on solvent extracted source rocks or isolated kerogens. The sample is pyrolysed by an SGE projector which is coupled directly to a Hewlett Packard 5890 gas chromatograph. The operating conditions are:

Pyrolysis temperature:	600°C
Column:	25m x 0.22mm ID BP-1 (SGE)
Carrier gas:	helium
Oven conditions:	-20° to 280°C @ 4°/min

Data are collected and recovered using DAPA scientific software.

Pyrolysis GC allows the examination of kerogen on the molecular level and thereby a better classification of source rocks with regard to source type and generative capacity than conventional bulk pyrolysis (ie. Rock-Eval). The analytical procedure is semi quantitative (with yield related to S<sub>2</sub> of Rock-Eval).

Samples are characterised according to the amounts of aliphatic, aromatic and phenolic components in the kerogen. The aliphatic carbon content of a kerogen is the critical factor in determining catagenic hydrocarbon yields in the earth's crust, while the gas/oil ratio is dictated by the distribution of the various structural elements in the kerogen (Larter, 1985). Using pyrogram fingerprint data, it is possible to distinguish substantial variations between kerogens, even those of the same bulk chemical type.

A major strength of pyrolysis methods is that, while quantitative yields of kerogens are maturity related, the qualitative pyrogram fingerprints obtained are relatively rank independent over much of the oil window (Espitalie et al, 1977; Van Graas et al, 1980; Larter, 1985). At high maturities (>1.2% VR) characteristics for all kerogen types tend to converge (Horstfield, 1984).

Data are presented by percentage and mg/g of individual substances as well as groups of compounds.

Significant parameters are:

$(C_1 - C_5)/C_6 + \text{abundance}$	gas/oil ratio
$C_9 - C_{31}$ (alkenes + alkanes)	oil yield
Type Index R:	aromaticity

(Larter & Douglas 1979, Larter and Senftle, 1985).

## 2.3 Detailed Analyses of Petroleum Fluids

### 2.3.1 Solvent Extraction of Sediment

The finely crushed sample (up to 100g) is extracted with dichloromethane (300mL) using sonic vibration. After Buchner flask filtration, the filtrate is re-vibrated with activated copper powder (1g) to remove elemental sulphur. The extractable organic matter (EOM) is afforded by further filtration and fractional distillation of the solvent.

Source rock richness based upon EOM is classified accordingly:

Yield	ppm
Poor	< 500
Fair/Good	500 - 2000
Very Good	2000 - 4000
Excellent	>4000

### 2.3.2 Liquid Chromatography Separation

Sediment extracts, crude oil and condensate samples are separated into fractions corresponding to three structural types:

saturated hydrocarbons	(SAT)
aromatic hydrocarbons	(AROM)
resins plus asphaltenes	(NSO)

This separation is achieved by liquid column chromatography using activated silicic acid adsorbent and eluting solvents of varying polarity. Saturated, aromatic

and NSO concentrates are recovered by fractional distillation/evaporation of the solvent and quantitative transfer to a small vial.

The amount of hydrocarbons (SAT plus AROM) can be used to classify source rock richness and the amount of saturates to classify oil source potential, according to the following criteria:

Classification	ppm HC	ppm SAT
Poor	0 - 300	0 - 200
Fair	300 - 600	200 - 400
Good	600 - 1200	400 - 800
Very Good	1200 - 2400	800 - 1600
Excellent	>2400	>1600

The composition of the extracts can also provide information about their levels of maturity and/or source type (LeTran et. al., 1974; Philippi, 1974). Generally, marine extracts have relatively low concentrations of saturated and NSO compounds at low levels of maturity, but these concentrations increase with increasing maturation. Terrestrially derived organic matter often has a low level of saturates and large amount of aromatic and NSO compounds, irrespective of the level of maturity.

Specific ratios are measured from solvent extraction and liquid chromatography data which give an indication of source type and maturity. EOM (mg)/TOC(g) can be used as a maturation indicator when plotted against depth for a given sedimentary sequence. Generally an EOM/TOC value of >100 indicates high maturity. If such a sample has a SAT (mg)/TOC(g) ratio <20, it is likely that the organic matter is gas prone. A value for SAT (mg)/TOC (g) >40 suggests an oil prone source type.

### 2.2.2 Capillary Gas Chromatography (GC)

C12+ gas chromatography is most commonly carried out on saturate fractions, but in certain instances it is used to examine whole extracts/oils, aromatic or branched/cyclic fractions. It is also used as a tool to identify contamination. The analyses are performed under the following conditions:

Instruments:	Hewlett Packard 5890 Gas Chromatography
Injector:	SGE OCI-3 on column
Column:	25m x 0.2mm ID BP-1
Injector Temp:	280°C
Detector Temp:	320°C
Column Temp:	45°C to 280°C at 40/min
Carrier Gas:	hydrogen

Data are collected using an IBM compatible PC and DAPA scientific software.

### 2.3.3.1 C<sub>12</sub>+ Saturate Gas Chromatography

Saturate GC results provide information pertaining to source type, maturity and depositional environment.

The n-alkane distribution from n-C<sub>12</sub> to n-C<sub>31</sub> is determined from the area under the peaks representing each of these n-alkanes. The profile can yield information about maturity and source type and is quantified in the C<sub>21</sub> + C<sub>22</sub>/C<sub>28</sub> + C<sub>29</sub> ratio and Carbon Preference Indices (CPI 1 and 2).

$$CPI(1) = \frac{(C_{23}+C_{25}+C_{27}+C_{29}) \text{ wt\%} + (C_{25}+C_{27}+C_{29}+C_{31}) \text{ wt\%}}{2 \times (C_{24}+C_{26}+C_{28}+C_{30}) \text{ wt\%}}$$

$$CPI(2) = \frac{(C_{23}+C_{25}+C_{27}) \text{ wt\%} + (C_{25}+C_{27}+C_{29}) \text{ wt\%}}{2 \times (C_{24}+C_{26}+C_{28}) \text{ wt\%}}$$

- carbon preference indices are approximately 1 for marine samples, regardless of maturity
- decrease from 20--> 1 for terrestrial samples as maturity increases

The C<sub>21</sub> + C<sub>22</sub>/C<sub>28</sub> + C<sub>29</sub> ratio is generally >1.5 for aquatic source material and <1.2 for terrestrial organic matter, however, the values increase with maturity.

Pristane/phytane (Pr/Ph) ratios can indicate depositional environments:

- . <3.0 - relatively reducing depositional environments;
- . 3.0-4.5 - mixed (reducing/oxidising) environments;
- . >4.5 - relatively oxidising depositional environments.

### 2.3.3.2 C<sub>1</sub> – C<sub>31</sub> Whole Oil Gas Chromatography

This analytical method is applied to oil and condensate samples. It provides a picture of the whole oil up to n-C<sub>31</sub> and allows quantitation of components with more than 4 carbon atoms. Several parameters are measured which illustrate

changes in the degree of biodegradation and water washing in the reservoir. Because these measurements are performed on very volatile components in the oil, care should be taken during sampling, transportation and storage of the fluid to minimise evaporation.

Whole oil analytical conditions are listed below:

Instrument:	Shimadzu GC-9A
Column:	25m x 0.2mm ID BP-1
Injector/Detector Temperature:	290°C
Column Temperature:	-20°C to 280°C at 40/min
Carrier Gas:	hydrogen

### 2.3.4 Carbon Isotope Analysis

This measurement is normally carried out on one or more of the following mixtures: topped oil, saturate fraction, aromatic fraction, NSO fraction. The organic matter is combusted in oxygen to produce carbon dioxide which is purified and transferred to an isotope mass spectrometer. The carbon isotope ratio ( $\delta\text{C}_{13}/\delta\text{C}_{12}$ ) is measured and compared to an international standard (the PeeDee Belemnite Limestone - PDB).

Carbon isotope analysis is most commonly used to identify the source of methane according to the following criteria (Furex 1977):

$\delta\text{C}_{13}\text{‰ PDB}$

- 75 to -55 Biogenic methane
- 58 to -40 Methane associated with oil
- 40 to -25 Thermal methane

Source rock-crude oil correlations have been attempted by observing the change in  $\delta\text{C}_{13}$  values of components of oils and rocks (Stahl 1977). Source rock extracts are usually isotopically heavier than the corresponding crude oil but are lighter than the asphaltenes of the oil and the kerogen of the rock (Hunt 1979). It has also been observed that marine organic carbon is generally isotopically heavier than contemporaneous terrestrial organic carbon (Tissot & Welte 1978). However, it should be noted that increasing maturity and biodegradation produce a shift toward heavier isotope values.

### 2.3.5 Gas Chromatography – Mass Spectrometry (GC/MS)

GC/MS analysis is normally performed on the branched and cyclic alkane fraction and/or the aromatic fraction of oils, condensates and sediment extracts. The specific fraction is first isolated and then injected into a gas chromatograph which is linked in series with a mass spectrometer. As compounds are eluted from the chromatography column they are bombarded with high energy electrons. This causes them to fragment into a number of ions each with a molecular weight less than that of the parent molecule. Individual compounds give a characteristic fragmentation pattern (mass spectrum), the major ions of which are presented in a series of mass fragmentograms [ie. plots of ion concentration against GC retention time].

GC/MS analysis can be carried out using one of the following modes of operation:

- (i) Acquire mode – in which all ions (within a broad range) in each mass spectrum are memorised by the data system.
- (ii) Selective Ion Monitoring (SIM) mode – in which only selected ions of interest are memorised by the data system.

#### 2.3.5.1 GC/MS Analysis of Branched/Cyclic Alkanes

The group of compounds to be analysed is first isolated from the saturate fraction by refluxing the sample with activated 5Å molecular sieves in cyclohexane for 24 hours. Branched/ cyclic alkanes, including alkylcyclohexanes, are recovered from the solvent by fractional distillation.

For condensates, and samples where information about alkylcyclohexanes is not required, the saturate fraction is passed through a small column packed with \_\_\_\_\_? adsorbent. The branched/cyclic alkanes are recovered from the eluting solvent by fractional distillation.

Analysis is carried out in the SIM mode with a total of 33 ions being recorded over different time spans.

Operating conditions are:

Instrument:	5987HP GC mass spec data system
Column:	60m x 0.25mm ID cross linked methyl-silicone DB-1 (J&W) column of 0.25 micron film thickness connected directly to the ion source
Injector:	OCI-3(SGE)
Carrier gas:	hydrogen
Oven Conditions:	50° to 274°C at 8° /min 274° to 280°C at 1° /min
EM Voltage:	2,000 - 2,300V
Electron Energy:	70eV
Source temperature:	250°C

GC/MS mass fragmentograms are examined for particular 'biomarker' compounds which can be related to biological precursors. These allow the characterisation of petroleum with regard to thermal maturity, source, depositional environment and biodegradation.

The significance of selected parameters from branched/cyclic GC/MS analysis is outlined below:

### 1. $18\alpha$ (H)-hopane/ $17\alpha$ (H)-hopane (Ts/Tm)

Maturity indicator. The ratio of  $18\alpha$  (H) trisnorhopane to  $17\alpha$  (H) trisnorhopane increases exponentially with increasing maturity from approximately 0.2 at the onset to approximately 1.0 at the peak of oil generation, ie. Tm decreases with maturity. This parameter is not reliable in very immature samples.

### 2. C<sub>30</sub> hopane/C<sub>30</sub> moretane

Maturity indicator. The conversion of C<sub>30</sub>  $17\beta$ ,  $21\beta$  hopane to  $17\beta$ ,  $21\alpha$  moretane is maturity dependent. Values increase from approximately 2.5 at the onset of oil generation to approximately 10. Once the hopane/moretane ratio has reached 10, no further changes occur. A value of 10 is believed to represent a maturity stage just after the onset of oil generation and hopane/moretane ratios are therefore useful mainly as indicators of immaturity in a qualitative sense.

### 3&4. C<sub>31</sub> and C<sub>32</sub> 22S/22R hopanes

Maturity indicator. An equilibrium between the biological R- and the geological S- configuration occurs on mild thermal maturation. A ratio of S:R = 60:40, ie, a value of 1.5, characterises this equilibrium which occurs before the onset of oil generation. The C<sub>32</sub> hopane pair is often more reliable for this purpose since co-elution sometimes affects the C<sub>31</sub> ratio.

### 5. C<sub>29</sub>20S $\alpha\alpha\alpha$ /C<sub>29</sub>20R $\alpha\alpha\alpha$ steranes

Maturity indicator. Upon maturation, the biologically produced 20R sterioisomer is diminished relative to the 20S form and a stabilisation is reached at approximately 55% 20R and 45% 20S compounds. VR equivalents are approximately 0.45% for a 20S/20R value of 0.2 and 0.8% for a 20S/20R value of 0.75. This parameter is most useful between maturity ranges equivalent to 0.4% to 1.0 VR.

### 6. C<sub>29</sub>20S $\alpha\alpha\alpha$ /C<sub>29</sub>20R $\alpha\alpha\alpha$ + C<sub>29</sub>20S $\alpha\alpha\alpha$ steranes

Maturity indicator. This ratio is a different way of expressing the relative abundance of the biological 20R to the geological 20S normal sterane (see parameter 5). Expressed as a percentage, a value of about 25% indicates the onset of oil generation, and of about 50% the peak of oil generation.

### 7. C<sub>29</sub> $\alpha\beta\beta$ /C<sub>29</sub> $\alpha\alpha\alpha$ + C<sub>29</sub> $\alpha\beta\beta$ steranes

Maturity indicator. The  $\alpha\alpha$  form is produced biologically. Its abundance diminishes upon maturation until a mixture of 65%  $\beta\beta$  (iso) steranes and 35%  $\alpha\alpha$  (normal) steranes is reached, which is equivalent to approximately 0.9% VR.

### 8&9. C<sub>27</sub>/C<sub>29</sub> diasteranes and steranes

Source indicator. It has been suggested that marine phytoplankton is characterised by a dominance of C<sub>27</sub> steranes and diasteranes whereas a preponderance of C<sub>29</sub> compounds indicates strong terrestrial contributions. Values smaller than 0.85 for C<sub>27</sub>/C<sub>29</sub> diasterane and sterane ratios are believed to be indicative for terrestrial organic matter, values between 0.85 and 1.43 for mixed organic material, and values greater than 1.43 for an input of predominantly marine organic matter.

It has been suggested, however, that marine sediments can also contain a predominance of C<sub>29</sub> steranes, so the above rules have to be applied with caution. Any simplistic interpretation of C<sub>27</sub>/C<sub>29</sub> steranes and diasteranes can be dangerous

and the interpretation of these data should be consistent with other geological evidence.

#### 10. $18\alpha$ (H) - oleanane/C<sub>30</sub> hopane

Source indicator. Oleanane is a triterpenoid compound which has often been reported from deltaic sediments of Late Cretaceous to Tertiary age. It is thought to be derived from certain angiosperms which developed in the late Cretaceous. If the  $18\alpha$  (H) - oleanane/C<sub>30</sub> hopane ratio is below 10, no significant proportions of oleanane are present. At higher values, it can be used as indicator for a reducing environment during deposition of land plant-derived organic matter.

#### 11. C<sub>29</sub> diasteranes/C<sub>29</sub> $\alpha\alpha\alpha$ steranes + C<sub>29</sub> $\alpha\beta\beta$ steranes

Source indicator. This parameter is used to characterise the oxidised of depositional environments. High values (up to 10) indicate oxic conditions, low values (down to 0.1) indicate reducing environments.

#### 12. C<sub>30</sub> (hopanes + moretanes)/C<sub>29</sub> (steranes + diasteranes)

Source indicator. Triterpanes are believed to be of prokaryotic (bacterial) origin, whereas steranes are derived from eukaryotic organisms. This ratio reflects the preservation of primary organic matter derived from eukaryotes, relative to growth and preservation of bacteria in the sediment after deposition.

#### 13. C<sub>15</sub> drimane/C<sub>16</sub> homodrimane

Drimanes and homodrimanes are ubiquitous compounds most likely derived from microbial activity in sediments. The C<sub>15</sub> drimane/C<sub>16</sub> homodrimane ratio is a useful parameter for correlation purposes in the low molecular weight region, especially for condensates which lack most conventional biomarkers. Drimanes are also useful to assess the degree of biodegradation as the removal of C<sub>15</sub> to C<sub>16</sub> bicyclics characterises an extensive level of biodegradation.

#### 14. Rearranged/normal drimanes

Like parameter 13, this ratio can be used for correlation purposes in samples without conventional biomarkers, and to assess levels of biodegradation.

### 2.3.5.2 GC/MS Analysis of Aromatics

The aromatic fraction or the oil to be analysed is first subjected to thin layer chromatography (TLC) or medium pressure liquid chromatography (MPLC) depending upon the analytical requirements.

1. Di- and tri- nuclear aromatic compounds are isolated by TLC. To effect this separation, the sample is applied to an alumina coated glass plate (0.6mm thickness). The plate is developed with hexane and the required band located using short wavelength UV light. The fraction is recovered by extraction and fractional distillation.

This aromatic fraction may be analysed by GC-FID, but GC/MS is recommended because of possible co-elution problems during GC.

Samples are analysed by GC/MS in the acquire mode scanning from 50 to 450 atomic mass units (amu).

Analytical conditions are:

Instrument:	HP5970 MSD
Column:	60m x 0.25mm ID, 0.25 micron film thickness, 5% phenylmethyl silicone column DB-5 (J&W) connected directly to the ion source
Injector:	automatic on-column
Carrier Gas:	helium
Oven Conditions:	70°C for 1 min 70°C --> 300°C at 3°/min
Data collection commences at	10 mins
Mass spectrometry	
Em Voltage	1500 - 1800V
Electron Energy	70eV

Mass fragmentograms are presented for alkylbiphenyls, alkynaphthalenes, alkylfluorenes and alkylphenanthrenes from a comprehensive data base. Aromatic compounds provide valuable information concerning thermal maturity since they can be applied outside the dynamic range of saturate biomarker indicators and are particularly useful when conventional biomarkers are present in low amounts (Radke & Welte, 1983; Alexander et al, 1985). Maturity ratios are tabled below:

### Aromatic Maturity Indicators

Abbrev.	Definition	Range oil onset	Wet gas
DNR 1	(2,6DMN, + 2,7DMN)/1,5DMN	1.5	10
DNR 2	2,7DMN/1,8DMN	50	2500
DNR 5	1,5DMN/1,8DMN	50	>3000
DNR 6	(2,6DMN + 2,7DMN)/(1,4DMN + 2,3 DMN)	0.8	2
TNR 1	(1,4,6TMN + 1,3,5TMN)/2,3,6TMN	0.5	4
MPR 1	(2MP + 3MP)/1MP	1.5	3
MPI 1	1.5 x (2MP + 3MP)/(PH + 1MP + 9MP)	0.3	1
MPI 2	(3 x 2MP)/(PH + 1MP + 9MP)	0.3	2
Rc(a)	0.6(MPI-1) + 0.4 (for % Rm <1.35)		
Rc(b)	-0.6(MPI-1) + 2.3 (for % Rm ≥1.35)		

(from Radke et al, 1982; Radke & Welte, 1983; Alexander et al, 1985)

Some aromatic marker compounds have specific natural product precursors and can be used as signatures for sediments of a particular source, depositional environment or geological age:

TNR 5	1,2,5TMN/1,3,6TMN	
TNR 6	1,2,7TMN/1,3,7TMN	(Strachen et al, 1988)
1,7/X	1,7DMP/(1,3 + 3,9 + 2,10 + 3,10 DMP)	
Retene/9MP		
1MP/9MP		(Alexander et al, 1988)

2. Mono- and triaromatic steranes are analysed by GC/MS under the same analytical conditions as used for di- and tri-nuclear aromatics. However isolation of this fraction is performed by MPLC. To achieve this, the saturate plus aromatic mixture is injected onto a Merck Si60 column. The separation is monitored with a refractive index detector for saturates and a UV absorbance detector for aromatics.

As aromatic steranes are generally present in low abundances, especially in oils, samples are analysed in the SIM mode and 16 ions are recorded.

The conversion of monoaromatic steranes to triaromatic steranes and the dimethylation of triaromatic steranes in sediments are considered to be maturity dependent (Mackenzie et al, 1981; Mackenzie, 1984). The triaromatic sterane maturity indicator should, however, not be applied to crude oils because migration effects appear to selectively deplete the triaromatic steranes.

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