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REPORT TITLE/ TITTEL

FINAL REPORT

HYDROCARBON CHARACTERISATION OF WELL 31/3-3 TROLL FIELD

CLIENT/ OPPDRAGSGIVER
Saga Petroleum a.s.

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SUMMARY/ SAMMENDRAG

Four sandstone cores were extracted and analysed for their hydrocarbon content. None of them was seen to contain high amount of hydrocarbons. The main compounds in three of the samples were high molecular weight wax components, probably of low maturity, while one sample (sample 1) contained lower molecular weight hydrocarbons of early oil window maturity.

KEY WORDS/ STIKKORD
Well 31/3-3
Hydrocarbon characterisation
Troll field
GC-MS

18 MAR 1985
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CONTENTS

		Page
1.	INTRODUCTION	3
2.	EXPERIMENTAL	5
2.1	Extractable organic matter	5
2.2	Chromatographic separation	5
2.3	Urea adduction	5
2.4	Gas chromatographic analysis	5
2.5	Gas chromatography - mass spectrometry (GC-MS)	6
2.6	$\delta^{13}C$ isotope analysis	6
3.	RESULTS AND DISCUSSION	7
3.1	Gross composition	7
3.2	Gas chromatographic analysis of saturated hydrocarbons	7
3.3	Gas chromatograms of branched/cyclic hydrocarbons	8
3.4	Gas chromatographic analysis of aromatic hydrocarbons	8
3.5	GC-MS analysis of saturated terpanes and steranes	8
3.6	GC-MS analysis of aromatic hydrocarbons	9
3.7	$\delta^{13}C$ isotope analysis	9
4.	CONCLUSIONS	10
5.	REFERENCES	11
	APPENDIX Molecular ratios from terpane and sterane mass chromatograms applied as maturity and source characteristic parameters	12
	TABLES	
Table 1:	Amounts of asphaltenes	14
Table 2a:	Concentration of EOM and chromatographic fractions	15
Table 2b:	Weight of EOM and chromatographic fractions	16
Table 2c:	Concentration of EOM and chromatographic fractions	17
Table 2d:	Composition in % of material extracted from the rock	18
Table 3:	Tabulation of data from the gas chromatograms	19
Table 4:	Molecular ratios from aromatic hydrocarbon gas chromatograms	20
Table 5:	Molecular ratios calculated from terpane and sterane mass chromatograms. Maturity ratios.	21
Table 6:	Molecular ratios calculated from terpane and sterane mass chromatograms. Source characteristic and maturity ratios.	22
Table 7:	$\delta^{13}C$ isotope results	23a
	FIGURES	
Figure 1:	Quantity of organic carbon and extractable C_{15}^{+} hydrocarbons in sediments (after Hunt, 1979).	23
Figure 2:	Gas chromatograms of saturated hydrocarbons.	24
Figure 3:	Gas chromatograms of branched/cyclic hydrocarbons.	29
Figure 4:	Gas chromatograms of aromatic hydrocarbons.	34
Figure 5a:	Mass chromatograms representing terpanes (m/z 191).	39
Figure 5b:	Mass chromatograms representing steranes (m/z 217 and 218).	42
Figure 6:	Mass chromatograms of aromatic hydrocarbons.	47

1. INTRODUCTION

Four sandstone cores from well 31/3-3 in the Troll field were analysed to characterise the hydrocarbons. The location of the well is shown on the location map, while sample information is given below:

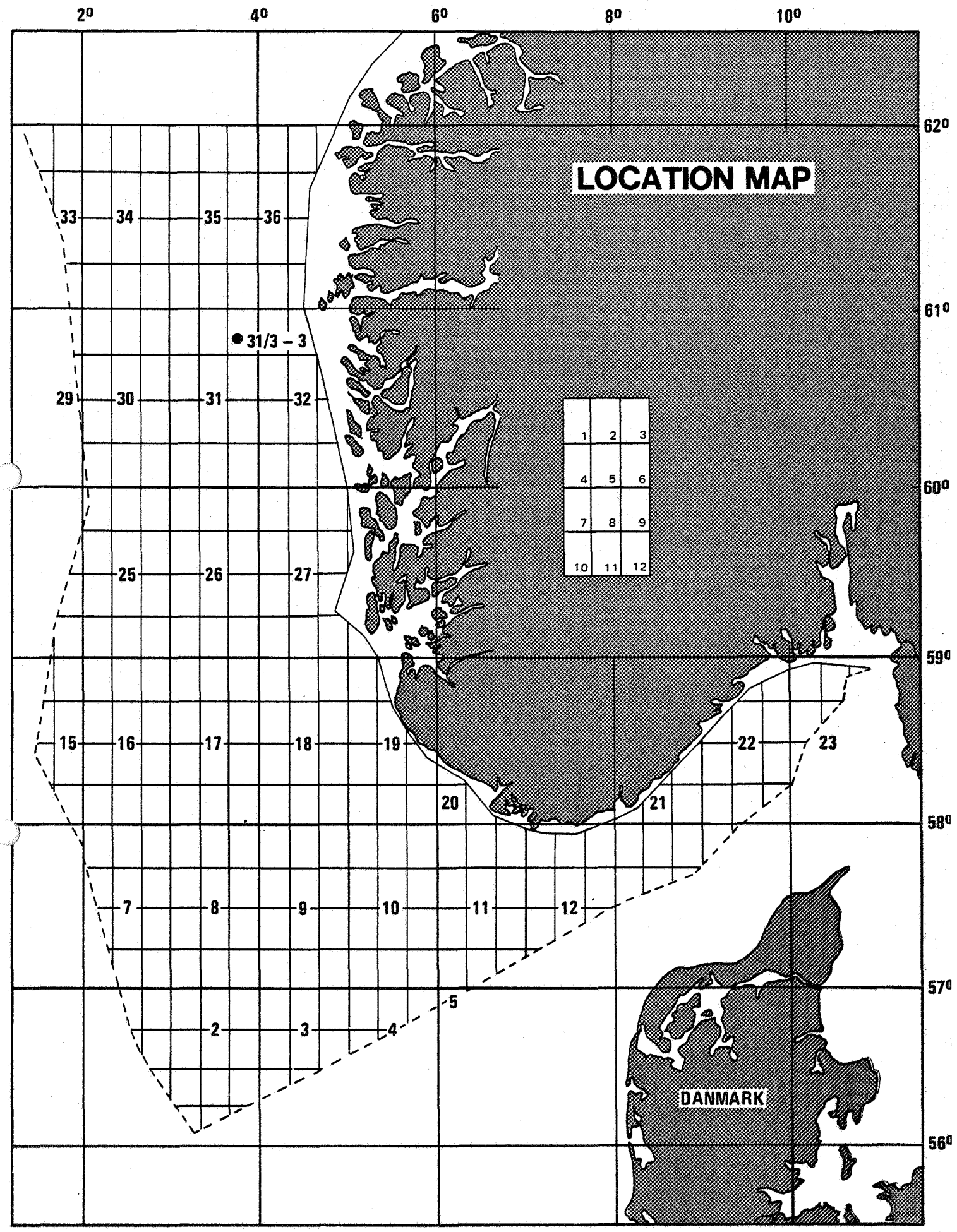
IKU code	Sample type	Sample code
B-9015	Sst. core	1
B-9016	Sst. core	2
B-9017	Sst. core	3
B-9018	Sst. core	4

No sample depths were given for any of the cores.

The following analyses were performed on the samples:

- Extraction of organic matter from the cores.
- Chromatographic separation into saturated and aromatic hydrocarbons and nonhydrocarbons (NSO's and asphaltenes).
- Urea-adduction of saturated hydrocarbons.
- Gas chromatography of saturated, branched/cyclic and aromatic hydrocarbons.
- GC-MS of saturated and aromatic biomarkers.
- 13C/12C isotope ratios of saturated and aromatic hydrocarbons.

One copy of this draft report has been approved by Saga Petroleum, before 10 copies of this final report were sent out.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LOCATION MAP
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2. EXPERIMENTAL

2.1 Extractable Organic Matter

Powdered rock was extracted by flowblending for 3 minutes using dichloromethane (DCM) and methanol (1%) as solvent. The DCM used was of organic geochemical grade and blank analyses showed the occurrence of negligible amounts of contaminating hydrocarbons. Activated copper fillings were used to remove any free sulphur from the samples. After extraction the solvent was removed on a Buchi Rotavapor and the amount of extractable organic matter (EOM) was determined.

2.2 Chromatographic separation

The extractable organic matter (EOM) was separated into saturated fraction, aromatic fraction and non hydrocarbon fraction using a MPLC system with hexane as eluant (Radke et al., Anal. Chem., 1980). The various fractions were evaporated on a Buchi Rotavapor and transferred to glass vials and dried in stream of nitrogen.

2.3 Urea adduction

Urea-adduction was performed on the saturated hydrocarbon fraction. The sample containing 5 mg of n-alkanes was dissolved in 2 ml of n-hexane and 1 ml of acetone was added. A saturated solution of urea in methanol (1 ml) was then added dropwise. The solvent was removed (N_2) and the adduction step repeated twice. The white crystals were rinsed (3x5ml hexane) and the combined extract filtered (cotton wool plug covered with Al_2O_3), to afford a non-adduct. GC analyses were performed on the samples after the urea adduction, using the same conditions as for the other GC analyses.

2.4 Gas chromatographic analysis

The saturated, the branched/cyclic and the aromatic hydrocarbon fractions were each diluted with n-hexane and analysed on a HP 5730A. The GC is equipped with a 15m DB-1 fused silica column and hydrogen (ca. 2.5 ml/min.) is used as carrier gas. Injections are performed in split mode (split ratio 1:10). The temperature program applied is 80°C (2 min.) to 280°C at 4°C/min.

The data processing for all the GC analyses was performed on a VG Multichrom lab data system.

2.5 Gas chromatography - mass spectrometry (GC-MS)

GC-MS analyses were performed on a VG Micromass 70-70H GC-MS-DS system. The Varian Series 3700 GC was fitted with a fused silica OV-1 capillary column (30m x 0.3mm i.d.). Helium (0.7kg/cm^2) was used as carrier gas and the injections were performed in split mode (1.5µl, split ratio 1:15). The GC oven was programmed from 70^{o}C to 280^{o}C at 4^{o}C/min. after an initial isothermal period of 2 minutes.

The saturated hydrocarbons were analysed in multiple ion mode (MID) at a scan cycle time of approximately 2 secs. Full data collection was applied for the aromatic hydrocarbons at a scan time of 1 sec/decade. The mass spectrometer operated at 70eV electron energy and an ion source temperature of 200^{o}C. Data acquisition was done by VG data systems.

Peak identification was performed applying knowledge of elution patterns in certain mass chromatograms. Calculation of peak ratios was done from peak height in the appropriate mass chromatograms.

2.6 δ^{13}C isotope analysis

The δ^{13}C isotope analysis was performed by mass spectrometry at Institute for Energy Technology (IFE) in Oslo according to their method. Their reference value for the standard NBS-22 is -29.8.

3. RESULTS AND DISCUSSION

3.1 Gross composition

The gravimetric data showing the gross composition of the samples are given in Tables 1 and 2a-d.

Generally the amount of extractable hydrocarbons in the four sandstone cores is low, only sample 3 (B-9017) can be classified as having a good content of organic matter and hydrocarbons. If the classification used by Hunt (1979) is applied (Figure 1) none of the cores contain enough hydrocarbons to be said to have potential as reservoir rocks.

Asphaltene compounds account for 6.6% or less of the core extracts. The variation between the individual core samples is most likely due to the generally low sample weights.

The SAT/ARO ratio varies from 0.3 to 1.6 and is especially low for sample 2. This same sample has also a very low weights of both saturated and aromatic hydrocarbons, a fact that will affect the SAT/ARO ratio.

3.2 Gas chromatographic analysis of saturated hydrocarbons

Gas chromatograms of the total saturated hydrocarbons are shown in Figure 2, while the tabulated data are given in Table 3.

All four core samples are dominated by high molecular weight wax components in the saturated gas chromatograms. Only sample 1 (B-9015) show abundant alkanes below nC_{20} without any sign of biodegradation. The other three samples contain less relative abundance of low molecular weight alkanes, and at least two of them seem to have experienced some degree of biodegradation, or they contain hydrocarbons of low maturity.

The pristane/nC_{17} ratio reflects the same effect of biodegradation or low maturity with the high values for two samples. The pristane/phytane ratio is high for the sample 3 (B-9017), indicating an input of terrestrial organic matter. The other three samples have lower pristane/-phytane ratios, but with the combined effect of possible biodegradation/-low maturity and high input of waxy components it is difficult to conclude about the source of these hydrocarbons.

3.3 Gas chromatograms of branched/cyclic hydrocarbons

Gas chromatograms of branched/cyclic components are shown in Figure 3.

All four cores show a complex distribution of compounds in the branched/-cyclic chromatograms. Only one sample B-9015 contain the commonly seen isoprenoids (pristane and phytane) as the main components, reflecting the same content of low molecular weight hydrocarbons as the saturated fraction chromatogram. Identification of other individual components is not possible based only on the gas chromatograms, and it is thus difficult to conclude very much from these chromatograms.

3.4 Gas chromatographic analysis of aromatic hydrocarbons

Gas chromatograms of aromatic hydrocarbon fractions are given in Figure 4.

All samples except for sample 2 (B-9016) show the normal distribution of alkylated naphthalenes and phenanthrenes, representative of mature hydrocarbons. The somewhat different distribution in sample 2 is most likely due to the low weight of this aromatic fraction and to loss of the low molecular weight naphthalenes during the work-up procedure.

The molecular ratios given in Table 4 suggest that the aromatic hydrocarbons are of a maturity early in the oil window, the MPI 1 values corresponding to a vitrinite reflectance of 0.6-0.7 for type III kerogens. Sample 1 seems to have somewhat higher maturity than the other three.

3.5 GC-MS analysis of saturated terpanes and steranes

Mass chromatograms representing terpanes (m/z 191) and steranes (m/z 217 and 218) are shown in Figure 5, and molecular ratios calculated from the chromatograms are given in Table 5 and 6.

The terpane mass chromatograms (m/z 191) are dominated by the ubiquitous 17α(H),21β(H),-hopanes, although a high input of tricyclic terpanes and also of 28,30-bisnorhopane is seen.

Relatively low maturity is encountered especially for three of the samples. The high relative amount of 22R C_{31} 17α(H),21β(H)-hopane (H)

in sample B-9015 is most likely due to coelution with another terpane, possibly gammacerane, since the other extended hopanes show a mature distribution of 22S and R isomers in this sample. Similar low maturity for the three samples is also seen from the sterane chromatograms.

3.6 GC-MS analysis of aromatic hydrocarbons

Mass chromatograms of aromatic hydrocarbons are presented in Figure 6.

The chromatograms representing monocyclic benzenes show that sample 1 (B-9015) contains highest abundance of these compounds with a wide molecular weight range. The other samples all show a less clear distribution of monocyclic benzenes. This is similar to what was seen from the saturated hydrocarbon gas chromatograms with sample 1 containing more low molecular weight components.

Of the other mass chromatograms the methyl-phenanthrenes (m/z 192) show the same as the total aromatic chromatograms. Sample 1 (B-9015) has a methyl-phenanthrene distribution representative of more mature hydrocarbons than what is seen for the other samples.

3.7 $\delta^{13}C$ isotope analysis

The carbon isotope data given in Table 7 show relatively big variations between the four samples. The low amount of extracts from the cores may affect the consistency in the data, but it may be suggested that input from two different source rocks has taken place. The low $\delta^{13}C$ ratios in sample 1 could indicate that the low molecular weight compounds in this sample were generated from a more marine source rock than the waxy compounds that are dominating the other three samples. Biodegradation may affect the results in the way seen for sample 3.

4. CONCLUSIONS

The four core samples were all found to contain low amount of extractable organic matter, with high molecular weight waxy components as the main components especially in three of the samples. Sample 1 has a relatively high content of low molecular weight alkanes in the range C_{12}-C_{20}.

The maturity of sample 1 is higher than that of the other three, possibly indicating that the waxy compounds represent a low maturity origin, and the low molecular weight alkanes in sample 1 could then represent a more mature source well into the oil window.

5. REFERENCES

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APPENDIX

Molecular ratios from terpane and sterane mass chromatograms applied as maturity and source characteristic parameters

Geochemical fossils or biological marker components are characteristic of the type of organic matter present at the time the sediments were deposited. The biological isomers of these components undergo changes due to increased maturity in particular, but also to a certain degree caused by migration and weathering processes.

Source characteristic parameters

In the m/z 191 mass chromatograms which represent the terpanes, the hopanes and moretanes are the major components in most extracts and oils. Of the hopanes the C_{27} and C_{29}-C_{35} homologs are ubiquitous, while the C_{28} bisnorhopane is believed to be typical of certain types of source rocks. This is also the case for the component, probably gamma-cerane, sometimes seen to coelute with the 22S isomer of the C_{31} 17α(H)-hopanes (H). In the sterane mass chromatograms, m/z 217 and m/z 218, the molecular weight distribution of the C_{27}-C_{29} regular steranes is believed to be representative of the original input of organic matter. The highest molecular weight compounds, the C_{29} steranes, represent organic matter of terrestrial origin, while the lower molecular weight analogs originate from more marine type environments.

Maturity dependant parameters

The biological isomers of the hopanes, the 17β(H), 21β(H)-hopanes, undergo structural changes during the maturation process. The isomerisation reactions are thought to be produced via the 17β(H), 21α(H)-hopanes (moretanes) to the most stable 17α(H), 21β(H)-hopanes. At equilibrium 100% of the 17α(H)-hopanes are seen. The ratio αβ/αβ+βα is used to describe this reaction. In the extended hopanes ($\geq C_{31}$), the thermally stable S configurations at C-22 become increasingly more abundant as compared to the biologically preferred R configurations at increased maturity level. The equilibrium ratio is approximately 60% of the 22S configuration. Another ratio that is known to change with maturity is the Tm/Ts (Seifert et al., 1978) of the C_{27} hopanes. The maturable 18α(H)-trisnorneohopane (Tm) is reduced in intensity relative to the more stable 17α(H)-trisnorneohopane (Ts), causing the Tm/Ts to decrease at increased

maturity. This ratio is also believed to be source dependant, and this should be born in mind when applying the ratio for maturity comparison. The amount of tricyclic terpanes is also to a certain extent seen to be maturity dependant.

Two isomerisation reactions taking place in the steranes are most commonly applied for maturity assignments from the m/z 217 mass chromatograms. The biologically preferred 14α(H), 17α(H)-isomers of the regular steranes is transformed to the thermally stable 14β(H), 17β(H)-steranes, the %ββ approaching 75% at equilibrium. An equilibrium concentration of 50% is seen of the stable S configuration at C-20 as opposed to the 100% of the biological 20R epimer (Mackenzie et al., 1980). The abundance of rearranged steranes increased with increasingly maturity.

One of the reactions taking place at an early stage of diagenesis is the aromatisation of steranes, leading to the formation of mono- and tri-aromatic analogs. This process is measured as the abundance of tri-aromatic relative to mono-aromatic compounds (% tri/tri + mono) in the m/z 231 and 253 mass chromatograms, respectively. In addition the degree of side chain cracking, as $\%C_{20}/C_{26,\ 27}$ and $\%C_{21}/C_{28,29}$ respectively, is applied. These cracking processes are also taking place during early diagenesis, and are used for maturity assignment together with the previously mentioned ratios.

Migration and weathering

The effect on the geochemical fossils of migration and weathering, is less apparent than the maturity induced changes. Migration is believed to cause an increase in the relative amounts of rearranged and 14β(H), 17β(H) regular steranes (Seifert and Moldowan, 1978, 1981). Severe biological alteration leads to the formation of desmethyl-hopanes (Seifert and Moldowan, 1979).

Table 1: Amounts of asphaltenes

Sample code	EOM (mg)	Asphaltenes	
		(mg)	(%)
B-9015, 1	40.3	0.7	1.7
B-9016, 2	74.7	-	-
B-9017, 3	65.8	4.3	6.6
B-9018, 4	40.6	1.3	3.2

T A B L E : 2a

CONCENTRATION OF EOM AND CHROMATOGRAPHIC FRACTIONS

IKU-No	SAMPLE	Rock Extr. (g)	EOM (mg)	Sat. (mg)	Aro. (mg)	HC (mg)	Non HC (mg)	TOC (%)
B 9015	1	314.0	40.3	8.2	5.8	14.0	26.3	0.09
B 9016	2	206.7	74.7	0.4*	1.4*	1.8	72.9	0.16
B 9017	3	97.8	65.8	5.9	9.1	15.0	50.8	1.67
B 9018	4	190.1	40.6	4.1	2.6	6.7	33.9	0.50

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* Fraction with sample weight less than 2mg should be considered with care

T A B L E : 2b

WEIGHT OF EOM AND CHROMATOGRAPHIC FRACTIONS

(Weight ppm OF rock)

IKU-No	SAMPLE	EOM	Sat.	Aro.	HC	Non HC
B 9015	1	128	26	18	45	84
B 9016	2	361	2	7	9	353
B 9017	3	673	60	93	153	519
B 9018	4	214	22	14	35	178

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T A B L E : 2c

CONCENTRATION OF EOM AND CHROMATOGRAPHIC FRACTIONS

(mg/g TOC)

IKU-No	SAMPLE	EOM	Sat.	Aro.	HC	Non HC
B 9015	1	142.6	29.0	20.5	49.5	93.1
B 9016	2	225.9	1.2	4.2	5.4	220.4
B 9017	3	40.3	3.6	5.6	9.2	31.1
B 9018	4	42.7	4.3	2.7	7.0	35.7

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T A B L E : 2d

COMPOSITION IN % OF MATERIAL EXTRACTED FROM THE ROCK

IKU-No	SAMPLE	Sat / EOM	Aro / EOM	HC / EOM	SAT / Aro	Non HC / EOM	HC / Non HC
B 9015	1	20.3	14.4	34.7	141.4	65.3	53.2
B 9016	2	0.5	1.9	2.4	28.6	97.6	2.5
B 9017	3	9.0	13.8	22.8	64.8	77.2	29.5
B 9018	4	10.1	6.4	16.5	157.7	83.5	19.8

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T A B L E 3

TABULATION OF DATA FROM THE GASCHROMATOGRAMS

IKU No.	SAMPLE	PRISTANE / n-C17	PRISTANE / PHYTANE	CPI-1	CPI-2
B 9015	1	0.5	1.4	1.0	1.0
B 9016	2	0.6	0.7	1.0	1.0
B 9017	3	1.3	3.7	1.0	1.1
B 9018	4	0.9	1.8	1.0	1.0

DATE : 13 - 2 - 85.

$$CPI\text{-}1 = \frac{2 \times nC_{27}}{nC_{26}+nC_{28}}$$

$$CPI\text{-}2 = \frac{1}{2}\left(\frac{C_{25}+C_{27}+C_{29}+C_{31}}{C_{24}+C_{26}+C_{28}+C_{30}} + \frac{C_{25}+C_{27}+C_{29}+C_{31}}{C_{26}+C_{28}+C_{30}+C_{32}}\right)$$

Table 4: Molecular ratios from aromatic hydrocarbon gas chromatograms

Sample code	MN	MPI 1
B-9015, 1	1.2	0.70
B-9016, 2	-	0.45
B-9017, 3	1.4	0.48
B-9018, 4	1.4	0.41

MN = 2-/1-methylnaphthalenes

$$\text{MPI 1} = \frac{1.5(\text{2- + 3-methylphenanthrene})}{\text{phenanthrene + 1- + 9-methylphenanthrene}}$$

Table 5

Molecular ratios calculated from terpane and sterane mass chromatograms. Maturity ratios.

IKU No.	DEPTH	1) αβ/αβ + βα	2) %22S	3) %ββ	4) %20S
B9015	1	0.84	56.5	56.2	39.2
B9016	2	0.84	42.8	46.9	28.3
B9017	3	0.82	27.7	57.1	21.7
B9018	4	0.78	38.5	55.4	25.5

1) E/E+F in m/z 191.
2) % distribution between first and second elution isomers of doublet J (m/z 191)
3) 2(r+s)/(q+t+2(r+s)) in m/z 217.
4) q/q+t in m/z 217.

Table 6

Molecular ratios calculated from terpane and sterane mass chromatograms. Source characteristic and maturity ratios.

IKU No.	DEPTH	1) Q/E	2) Tm/Ts	3) X/E	4) a/a+j	5) Z/E
B9015	1	0.08	1.40	0.04	0.49	0.07
B9016	2	0.35	2.00	0.00	0.29	0.03
B9017	3	0.10	7.33	0.00	0.35	0.41
B9018	4	0.25	2.14	0.00	0.40	0.15

1) Relative abundance of tricyclic terpanes(Q/E in m/z 191).
2) B/A in m/z 191.
3) Relative abundance of unknown(X/E in m/z 191).
4) Relative abundance of C27 rearranged steranes(a/a+j).
5) Relative abundance of bisnorhopane(Z/E in m/z 191).

Table 7. $\delta^{13}C$ isotope results

IKU code	Sample code	SAT	ARO
B-9015	1	-29.6	-28.3
B-9016	2	-28.5	-26.5
B-9017	3	-26.6	-23.9
B-9018	4	-28.2	-24.1

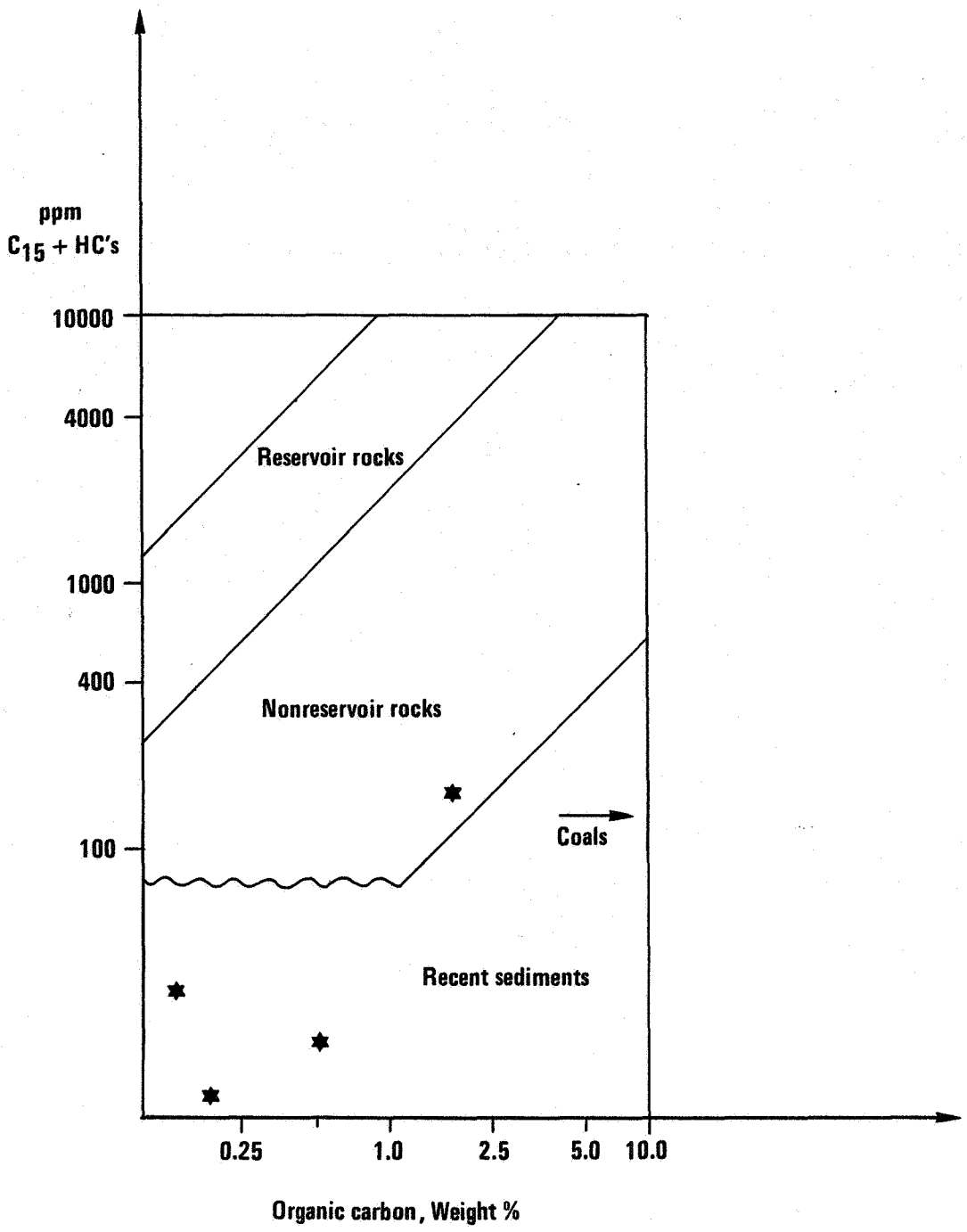
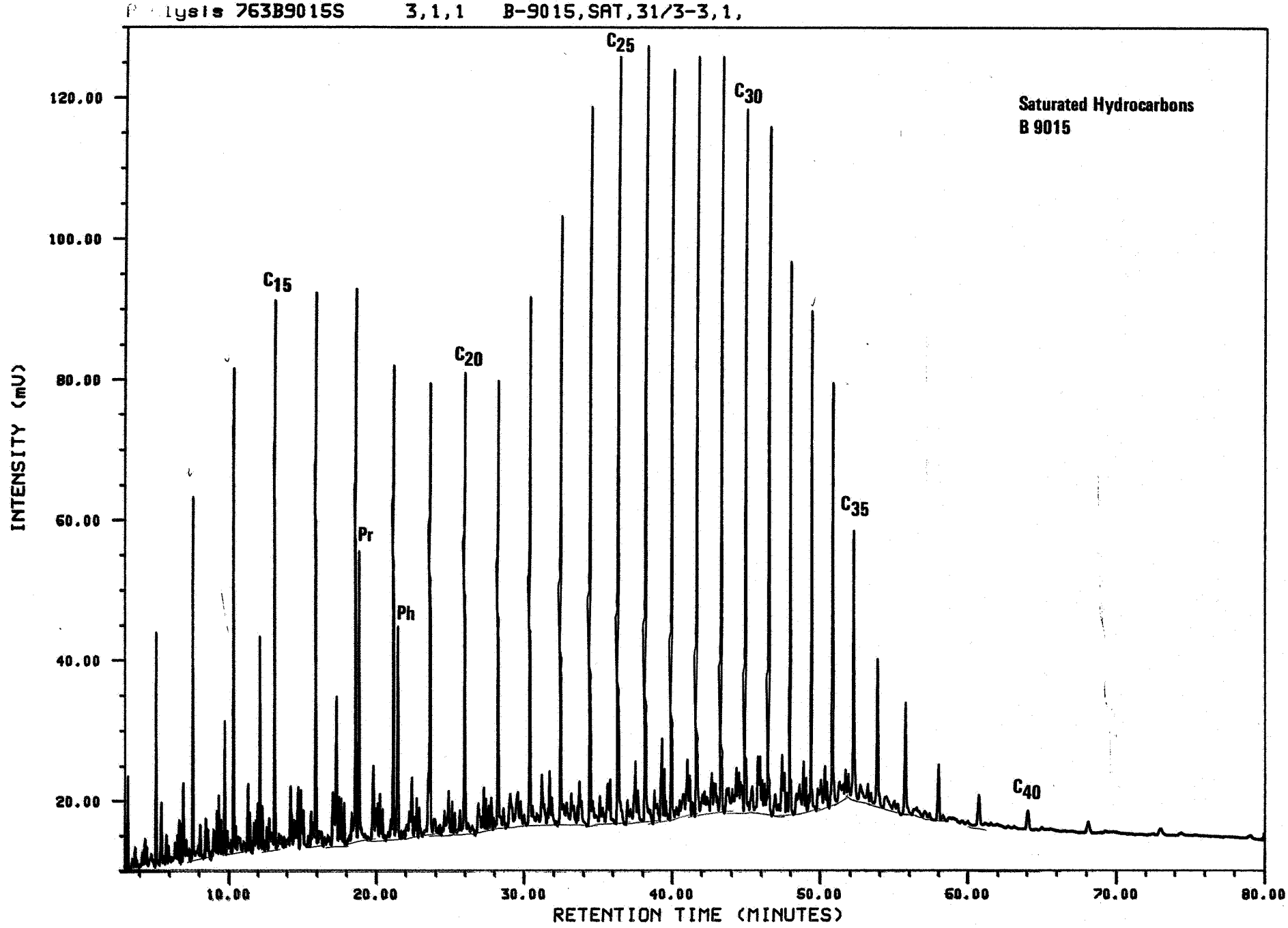


Figure 1. Quantity of organic carbon and extractable C_{15} + hydrocarbons in sediments (after Hunt, 1979)

Figure 2

Gas chromatograms of saturated hydrocarbons

Pr	-	pristane
Ph	-	phytane
nC_{15} etc	-	n-alkanes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C25
C30
C15
C20
C35
C40
Pr
Ph
INTENSITY (mV)
120.00
100.00
80.00
60.00
40.00
20.00
10.00
20.00
30.00
40.00
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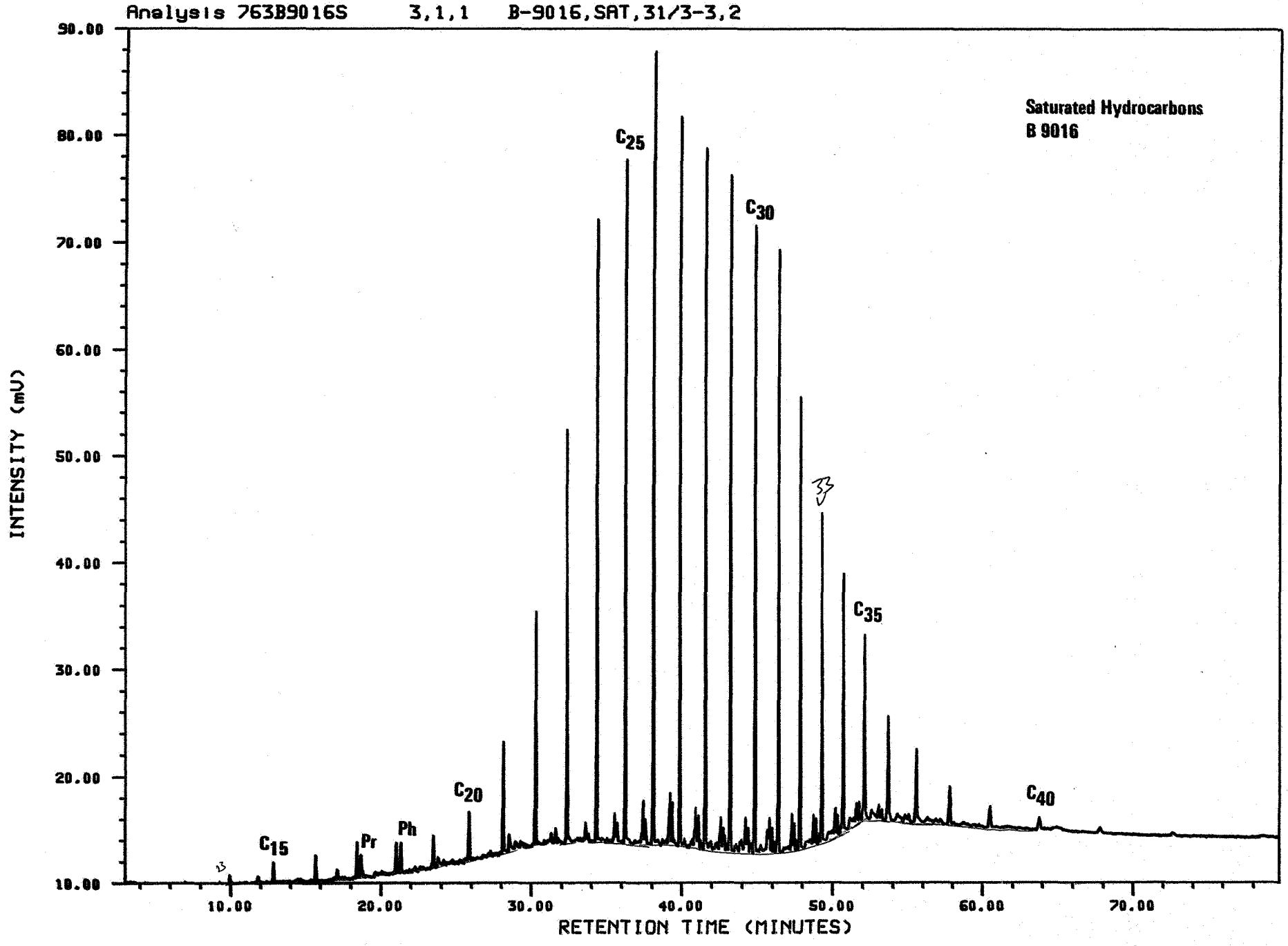
60.00
70.00
80.00
RETENTION TIME (MINUTES)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B 9016
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20.00
10.00
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C15
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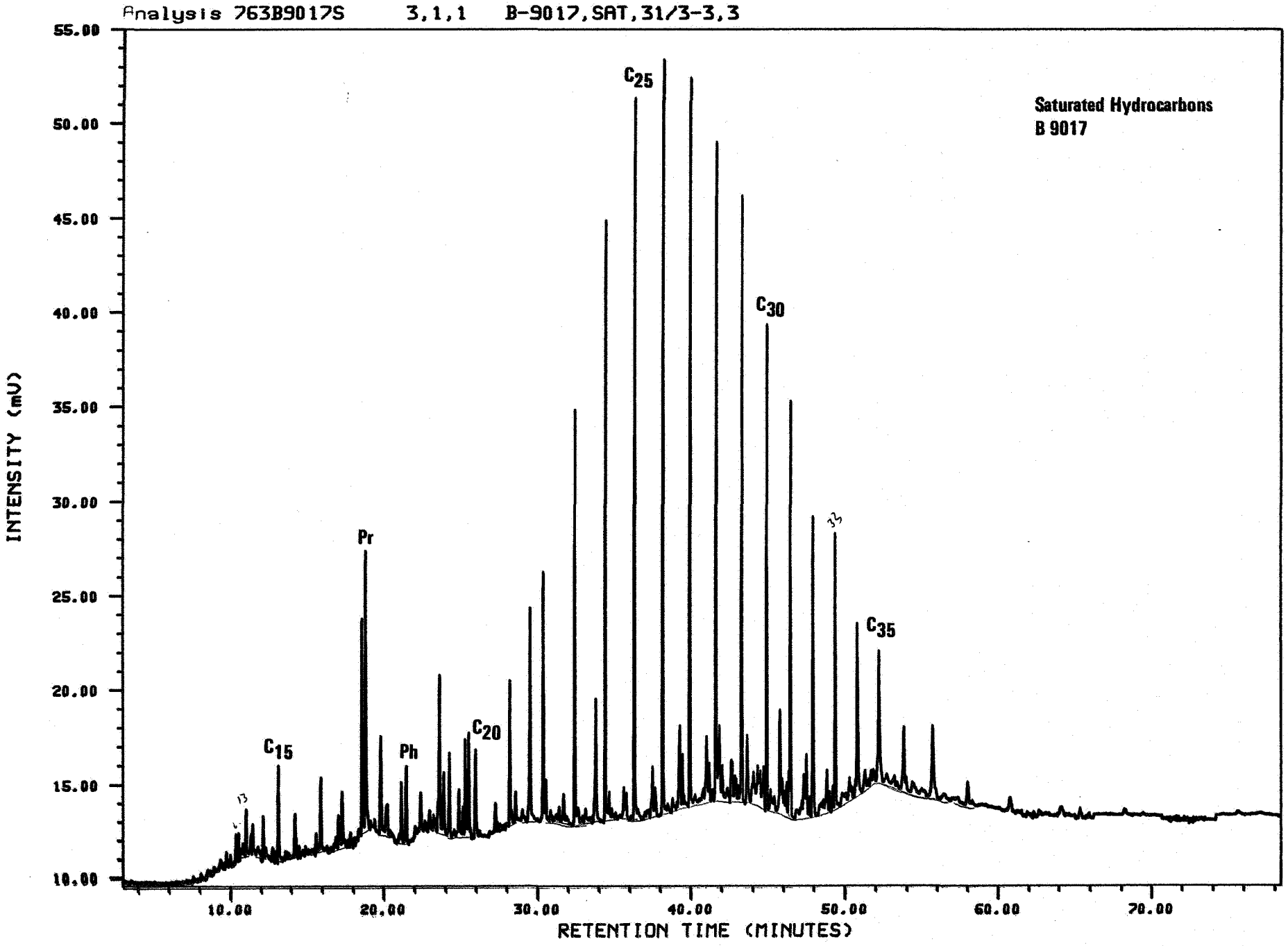
Ph
C20
C25
C30
C35
C40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Saturated Hydrocarbons
B 9017
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35.00
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70.00
C15
Pr
Ph
C20
C25
C30
C35

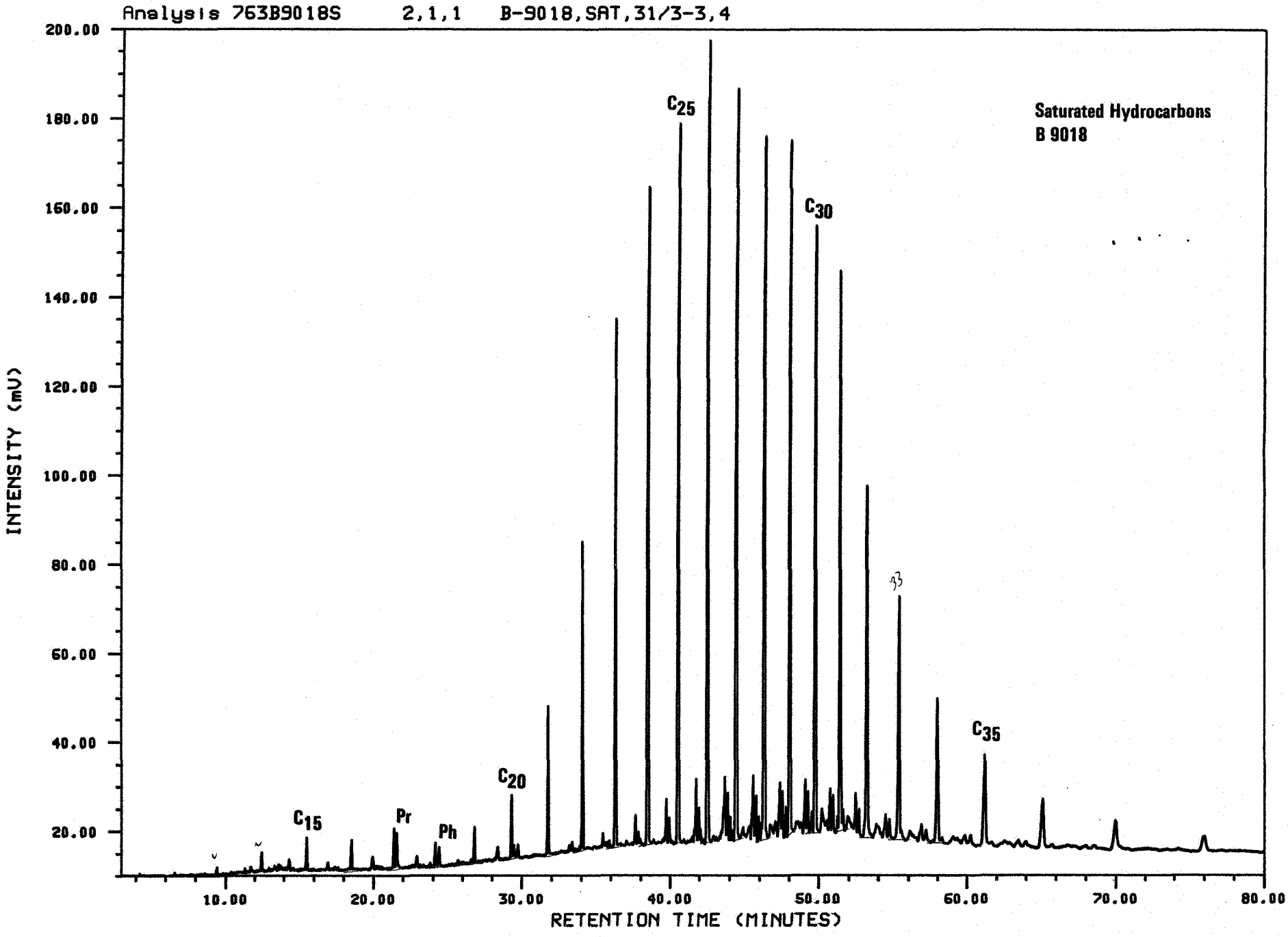
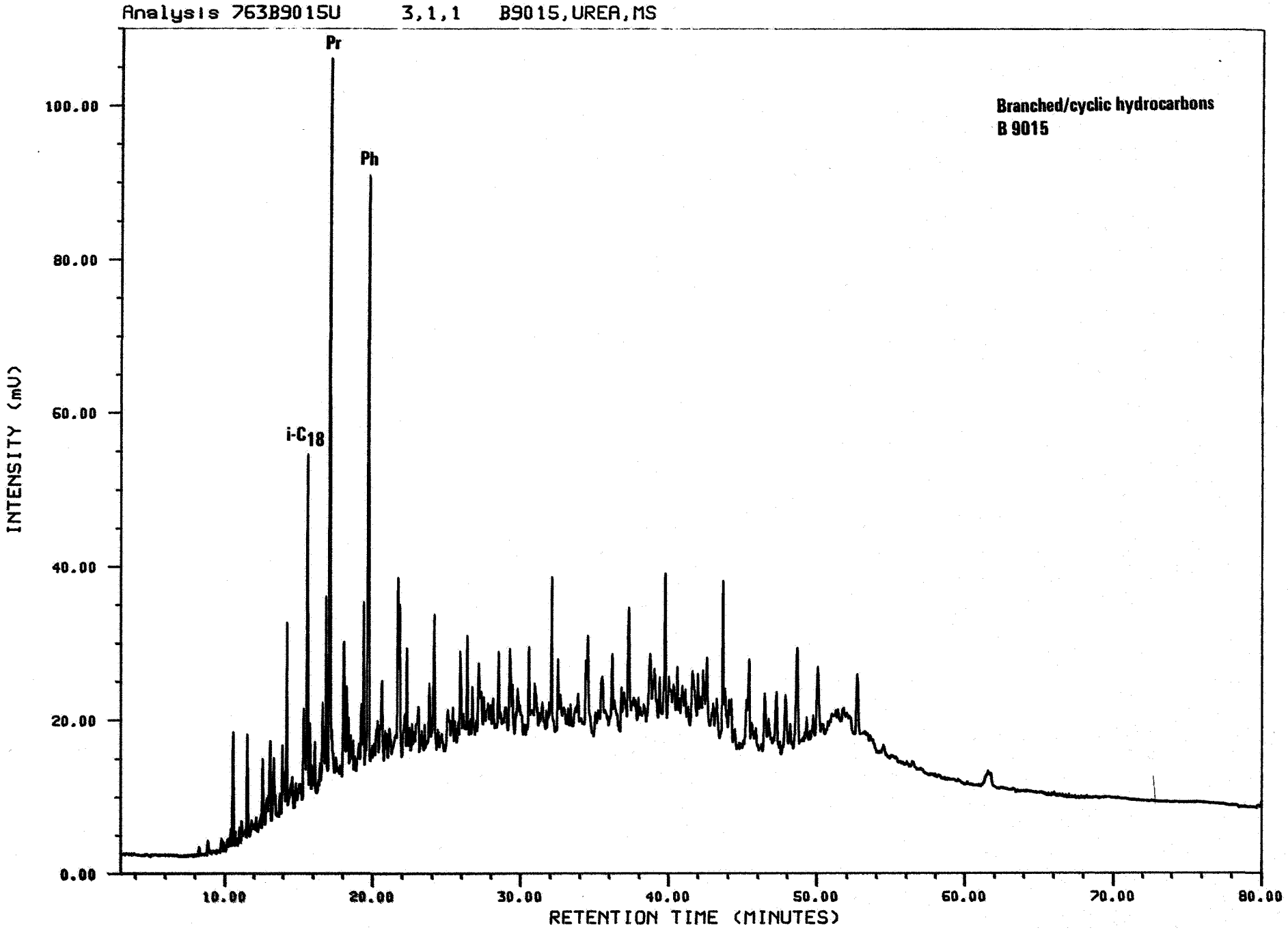
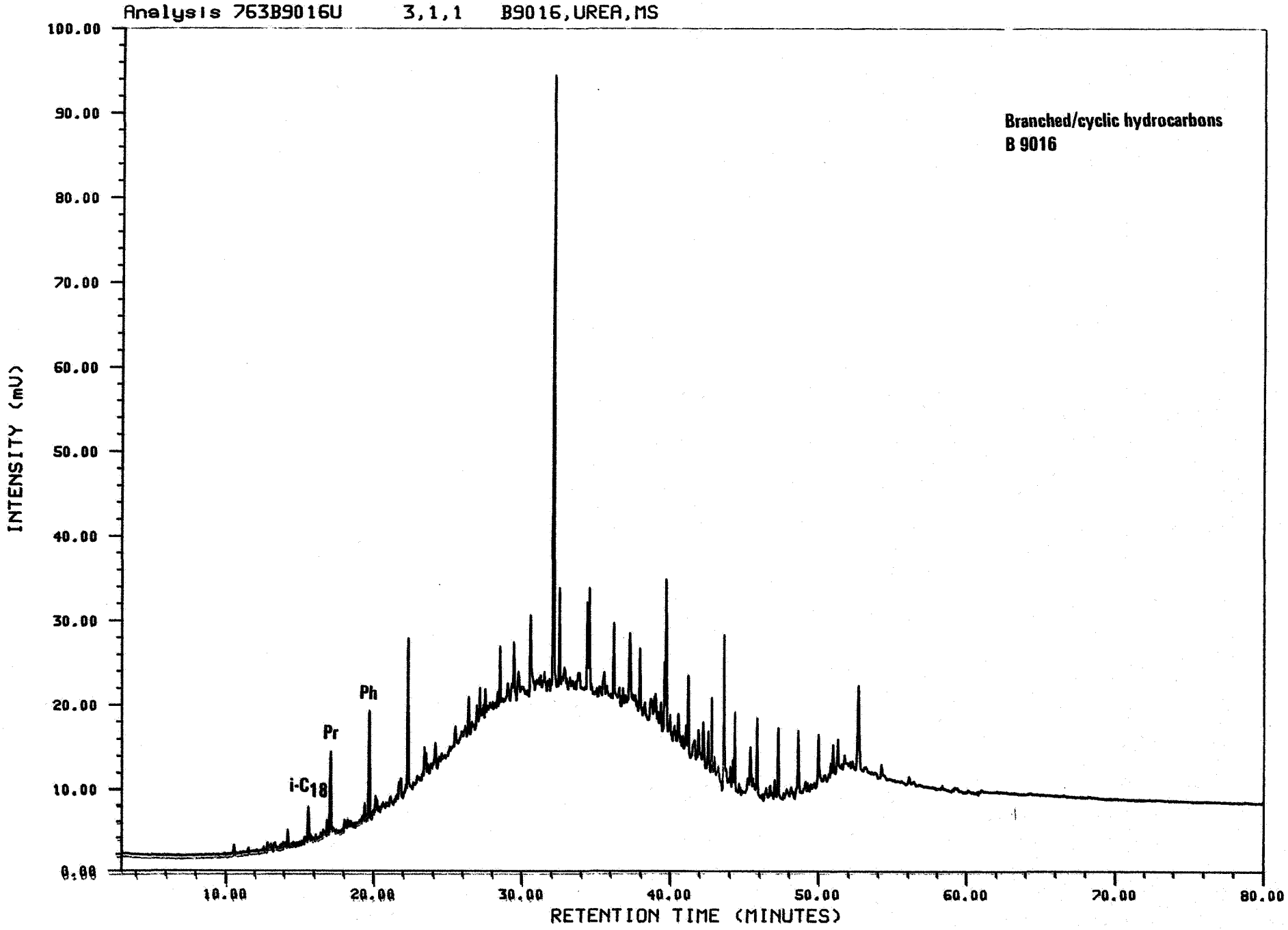

Analysis 763B9018S 2,1,1 B-9018,SAT,31/3-3,4
Saturated Hydrocarbons
B 9018
INTENSITY (mV)
RETENTION TIME (MINUTES)
200.00
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
C15
Pr
Ph
C20
C25
C30
C35

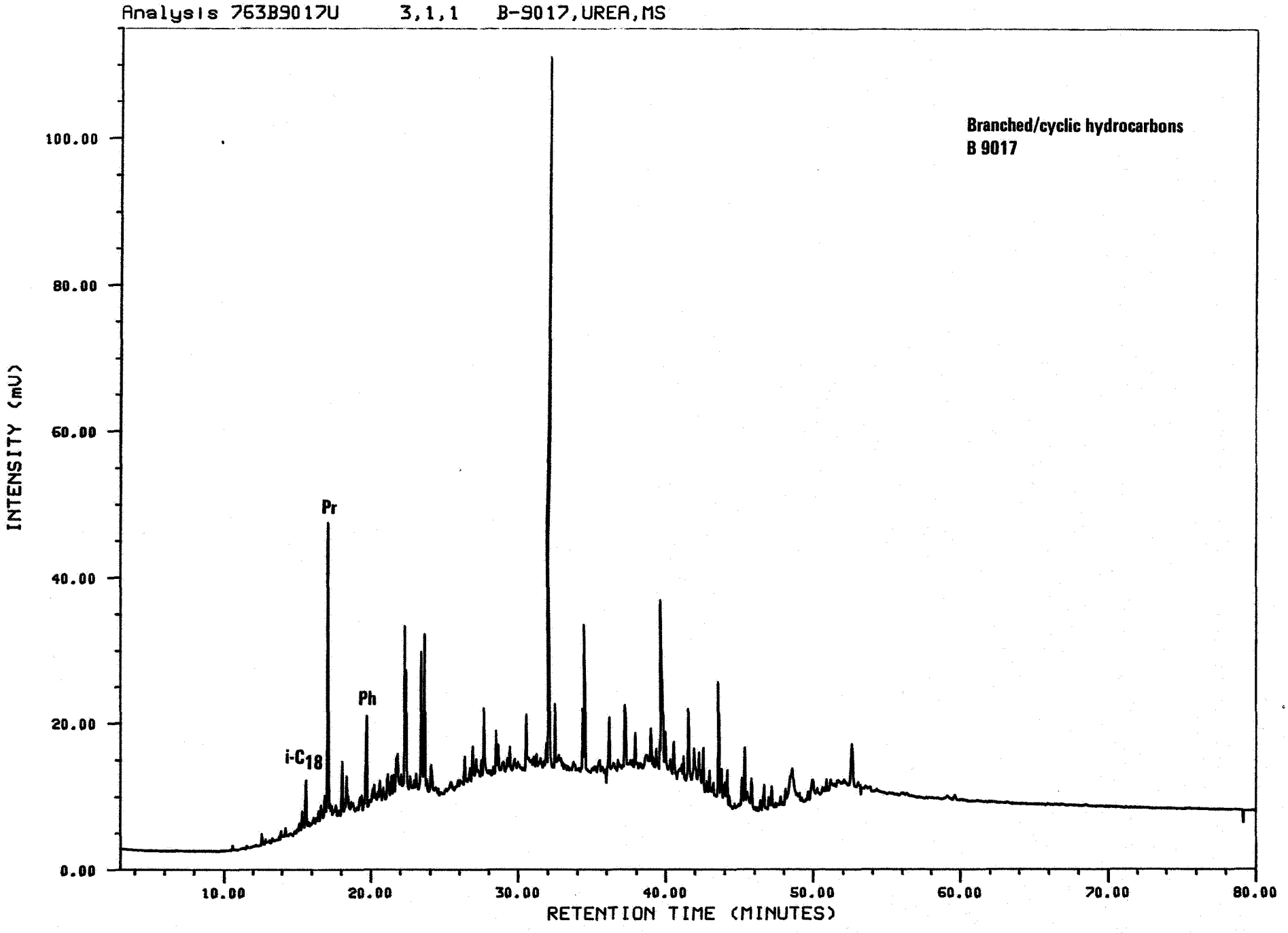
Figure 3

Gas chromatograms of branched/cyclic hydrocarbons

Pr	-	pristane
Ph	-	phytane
iC_{18} etc	-	isoprenoids


Analysis 763B9015U 3,1,1 B9015,UREA,MS
Branched/cyclic hydrocarbons
B 9015
Pr
Ph
i-C18
INTENSITY (mV)
100.00
80.00
60.00
40.00
20.00
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
RETENTION TIME (MINUTES)


Analysis 763B9016U 3,1,1 B9016,UREA,MS
Branched/cyclic hydrocarbons
B 9016
INTENSITY (mV)
RETENTION TIME (MINUTES)
i-C18
Pr
Ph
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00


Analysis 763B9017U 3,1,1 B-9017,UREA,MS
Branched/cyclic hydrocarbons
B 9017
INTENSITY (mV)
100.00
80.00
60.00
40.00
20.00
0.00
Pr
Ph
i-C18
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
RETENTION TIME (MINUTES)

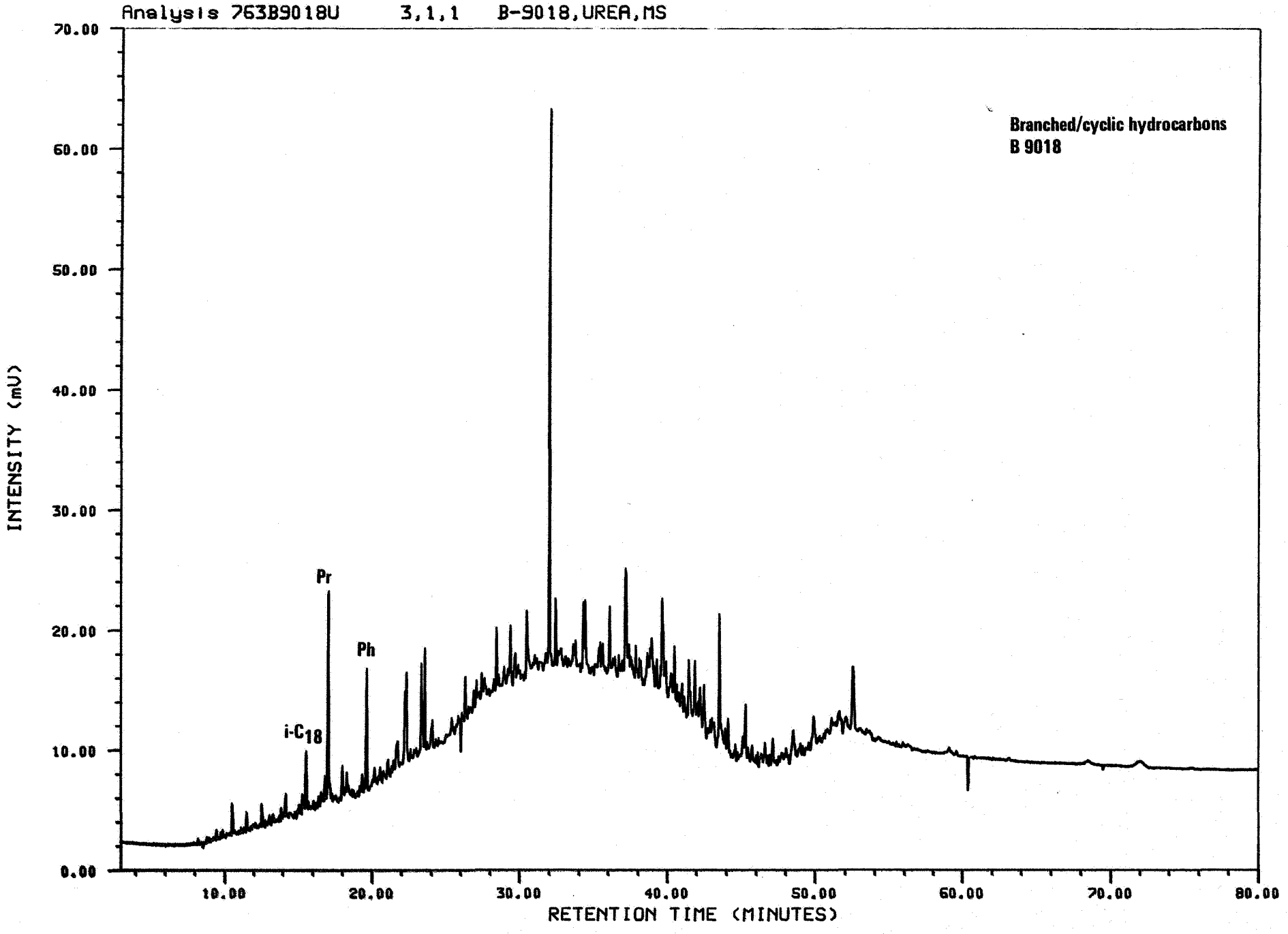
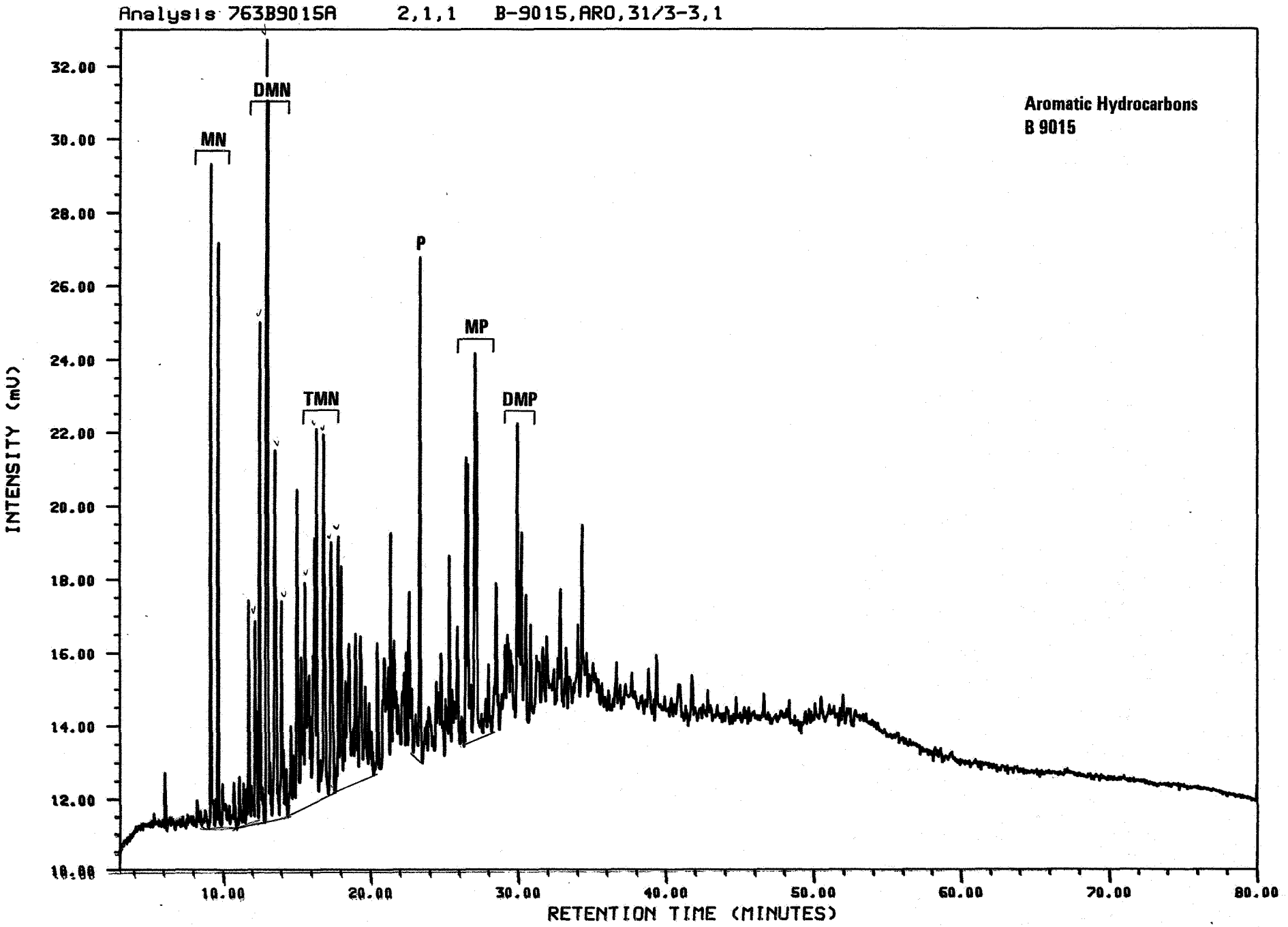
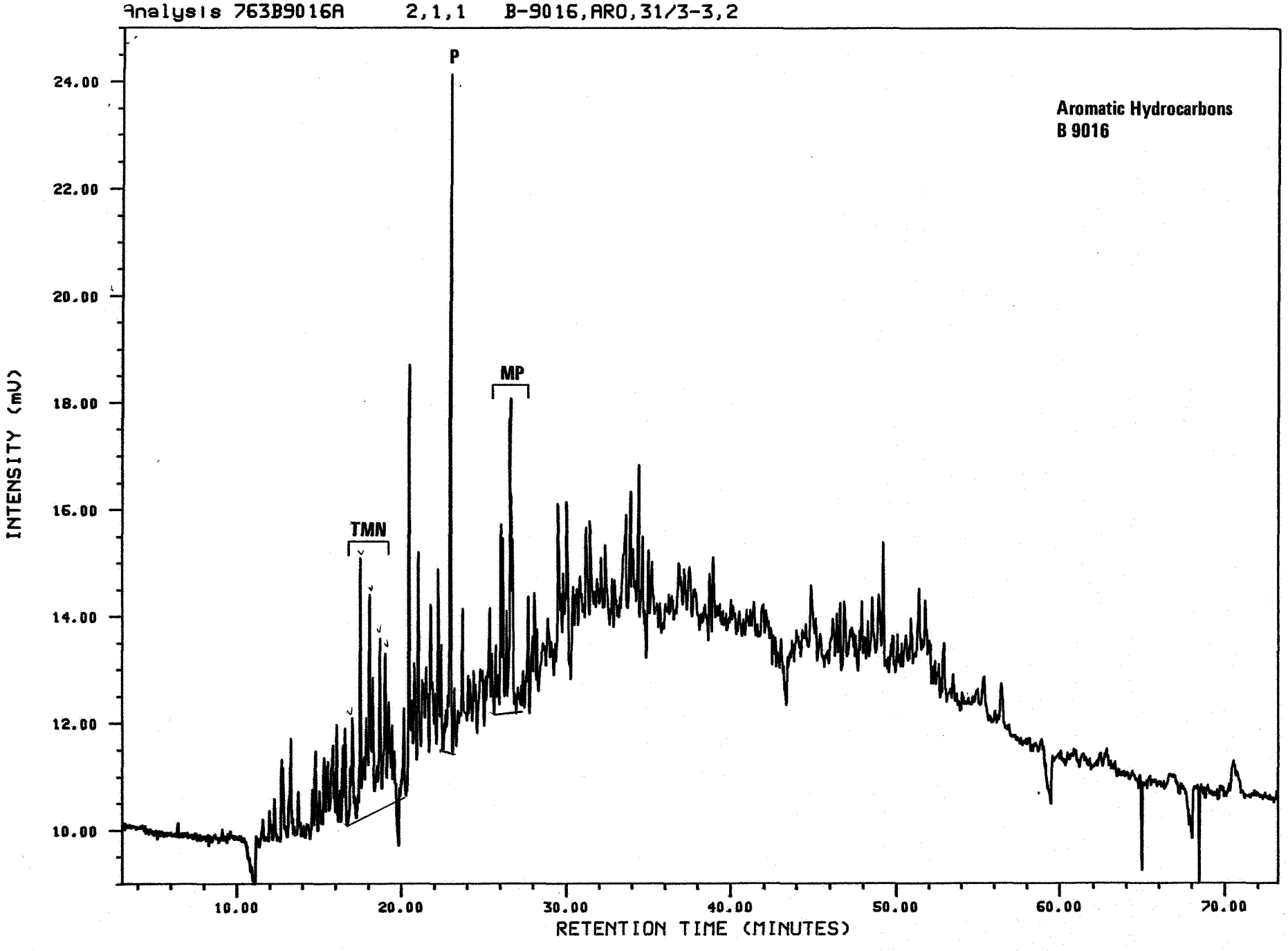

Analysis 763B9018U 3,1,1 B-9018,UREA,MS
Branched/cyclic hydrocarbons
B 9018
INTENSITY (mV)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Pr
Ph
i-C18
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
RETENTION TIME (MINUTES)

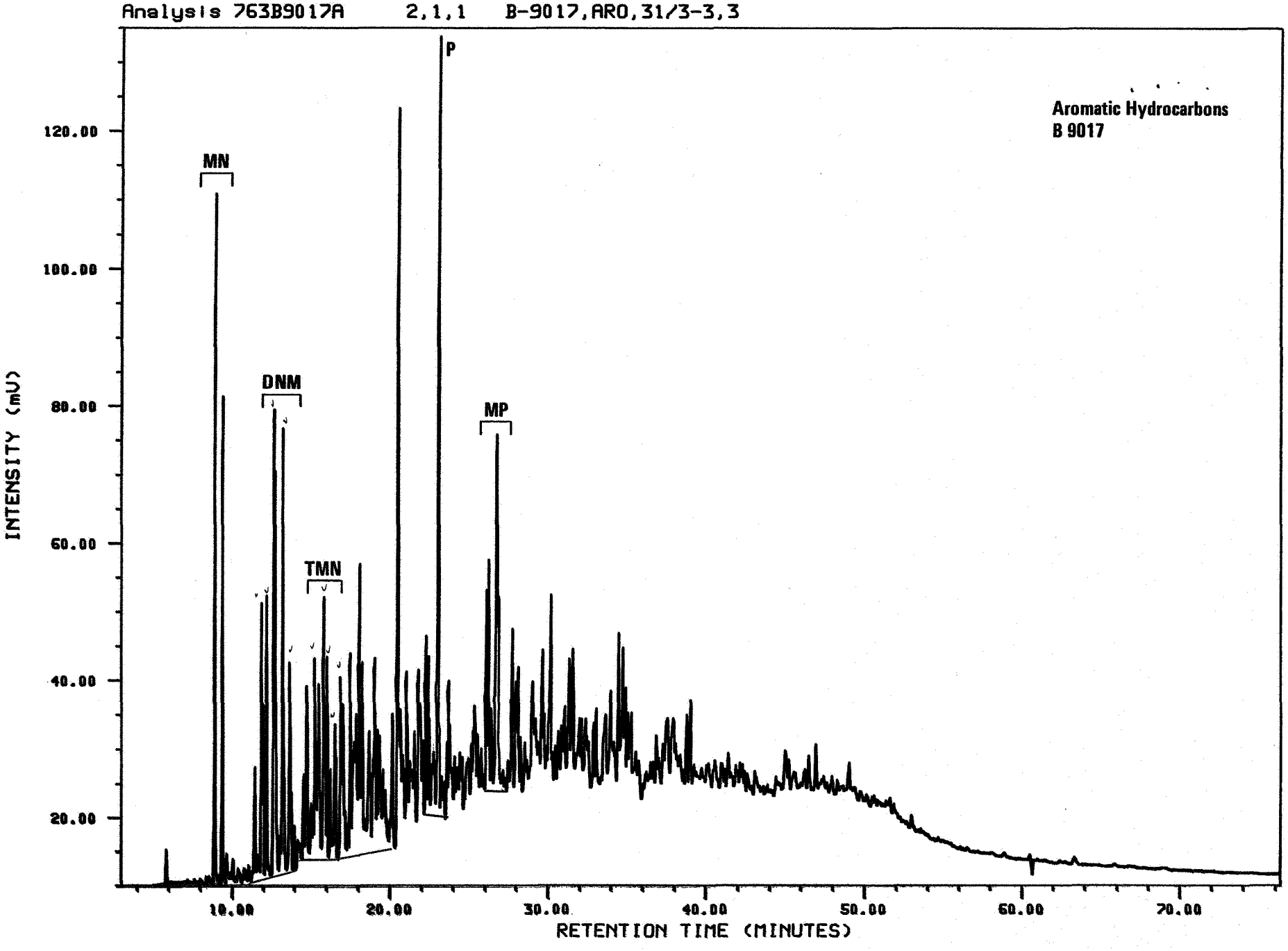
Figure 4

Gas chromatograms of aromatic hydrocarbons

N,MN,DMN,TMN	-	naphthalene and alkylated homologs
P,MP,DMP	-	phenanthrene and alkylated homologs


Analysis 763B9015A 2,1,1 B-9015,ARO,31/3-3,1
Aromatic Hydrocarbons
B 9015
MN
DMN
TMN
P
MP
DMP
INTENSITY (mV)
32.00
30.00
28.00
26.00
24.00
22.00
20.00
18.00
16.00
14.00
12.00
10.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
RETENTION TIME (MINUTES)


Analysis 763B9016A 2,1,1 B-9016,ARO,31/3-3,2
Aromatic Hydrocarbons
B 9016
P
MP
TMN
INTENSITY (mV)
24.00
22.00
20.00
18.00
16.00
14.00
12.00
10.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
RETENTION TIME (MINUTES)


Analysis 763B9017A 2,1,1 B-9017,ARO,31/3-3,3
Aromatic Hydrocarbons
B 9017
MN
DNM
TMN
P
MP
INTENSITY (mV)
120.00
100.00
80.00
60.00
40.00
20.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
RETENTION TIME (MINUTES)

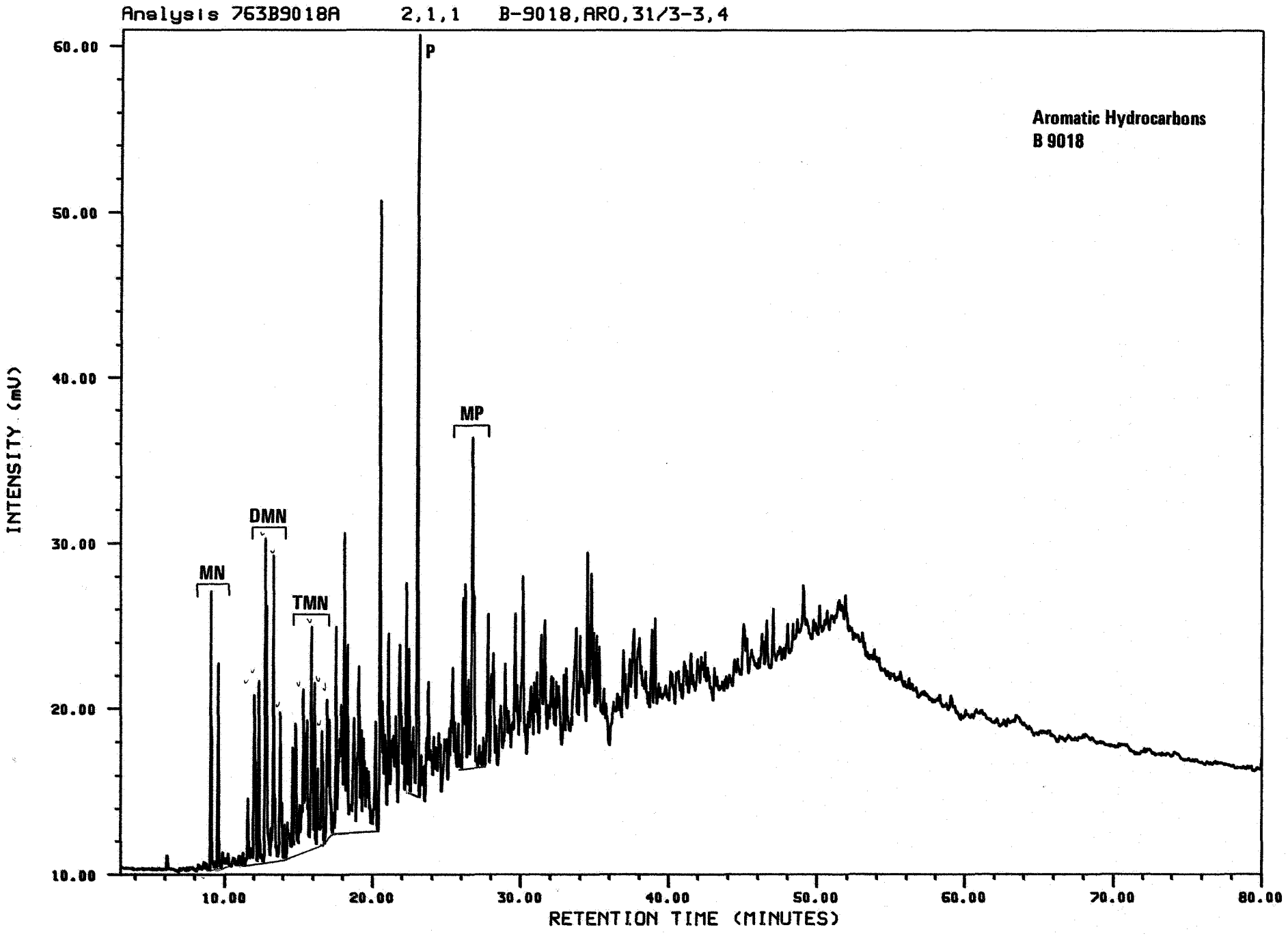
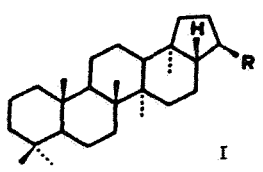

Analysis 763B9018A 2,1,1 B-9018,ARO,31/3-3,4
Aromatic Hydrocarbons
B 9018
P
MP
DMN
MN
TMN
INTENSITY (mV)
60.00
50.00
40.00
30.00
20.00
10.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
RETENTION TIME (MINUTES)

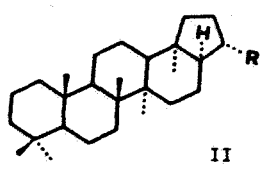
Figure 5a

Mass chromatograms representing terpanes (m/z 191)

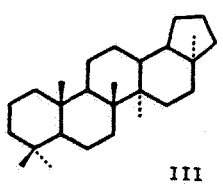
A	T_s, 18α(H)-trisnorneohopane	$C_{27}H_{46}$	(III)
B	T_m, 17α(H)-trisnorhopane	$C_{27}H_{46}$	(I,R=H)
C	17α(H)-norhopane	$C_{29}H_{50}$	(I,R=C_2H_5)
D	17β(H)-normoretane	$C_{29}H_{50}$	(II,R=C_2H_5)
E	17α(H)-hopane	$C_{30}H_{52}$	(I,R=C_3H_7)
F	17β(H)-moretane	$C_{30}H_{52}$	(II,R=C_3H_7)
G	17α(H)-homohopane (22S)	$C_{31}H_{54}$	(I,R=C_4H_9)
H	17α(H)-homohopane (22R) + unknown triterpane (gammacerane?)	$C_{31}H_{54}$	(I,R=C_4H_9)
I	17β(H)-homomoretane	$C_{31}H_{54}$	(II,R=C_4H_9)
J	17α(H)-bishomohopane (22S,22R)	$C_{32}H_{56}$	(I,R=C_5H_{11})
K	17α(H)-trishomohopane (22S,22R)	$C_{33}H_{58}$	(I,R=C_6H_{13})
L	17α(H)-tetrakishomohopane (22S,22R)	$C_{34}H_{60}$	(I,R,=C_7H_{15})
M	17α(H)-pentakishomohopane (22S,22R)	$C_{35}H_{62}$	(I,R=C_8H_{17})
Z	bisnorhopane	$C_{28}H_{48}$	
X	unknown triterpane	$C_{30}H_{52}$	
P	tricyclic terpane	$C_{23}H_{42}$	(IV,R=C_4H_9)
Q	tricyclic terpane	$C_{24}H_{44}$	(IV,R=C_5H_{11})
R	tricyclic terpane (17R,17S)	$C_{25}H_{46}$	(IV,R=C_6H_{13})
S	tetracyclic terpane	$C_{24}H_{42}$	(V)
T	tricyclic terpane (17R,17S)	$C_{26}H_{48}$	(IV,R=C_7H_{15})



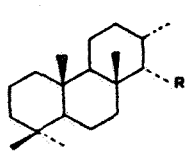
I

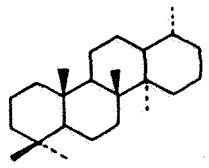


II

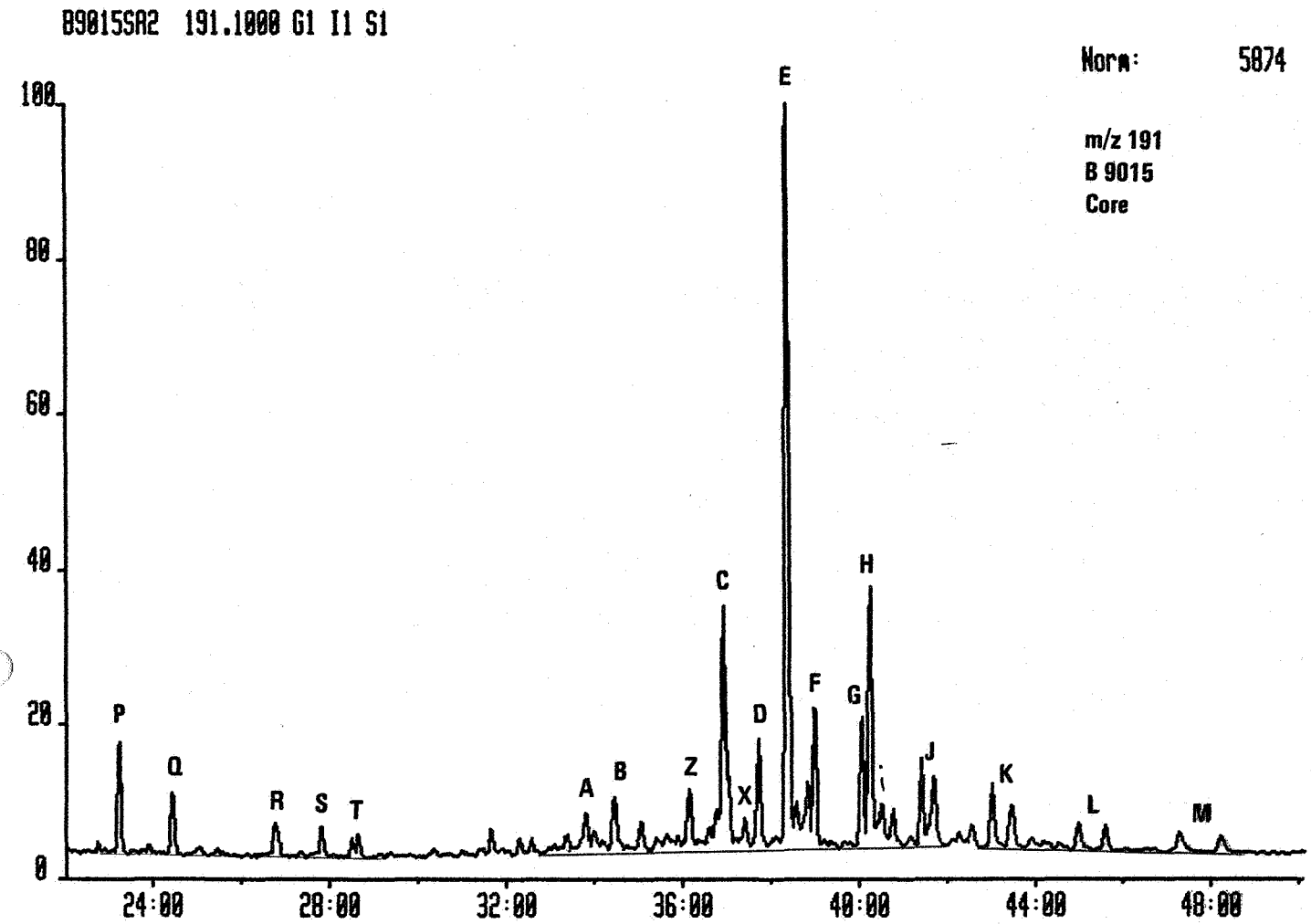


III





IKU


B9015SA2 191.1000 G1 I1 S1
Norm: 5874
m/z 191
B 9015
Core
100
80
60
40
20
0
P
Q
R
S
T
A
B
Z
C
X
D
E
F
G
H
J
K
L
M
24:00
28:00
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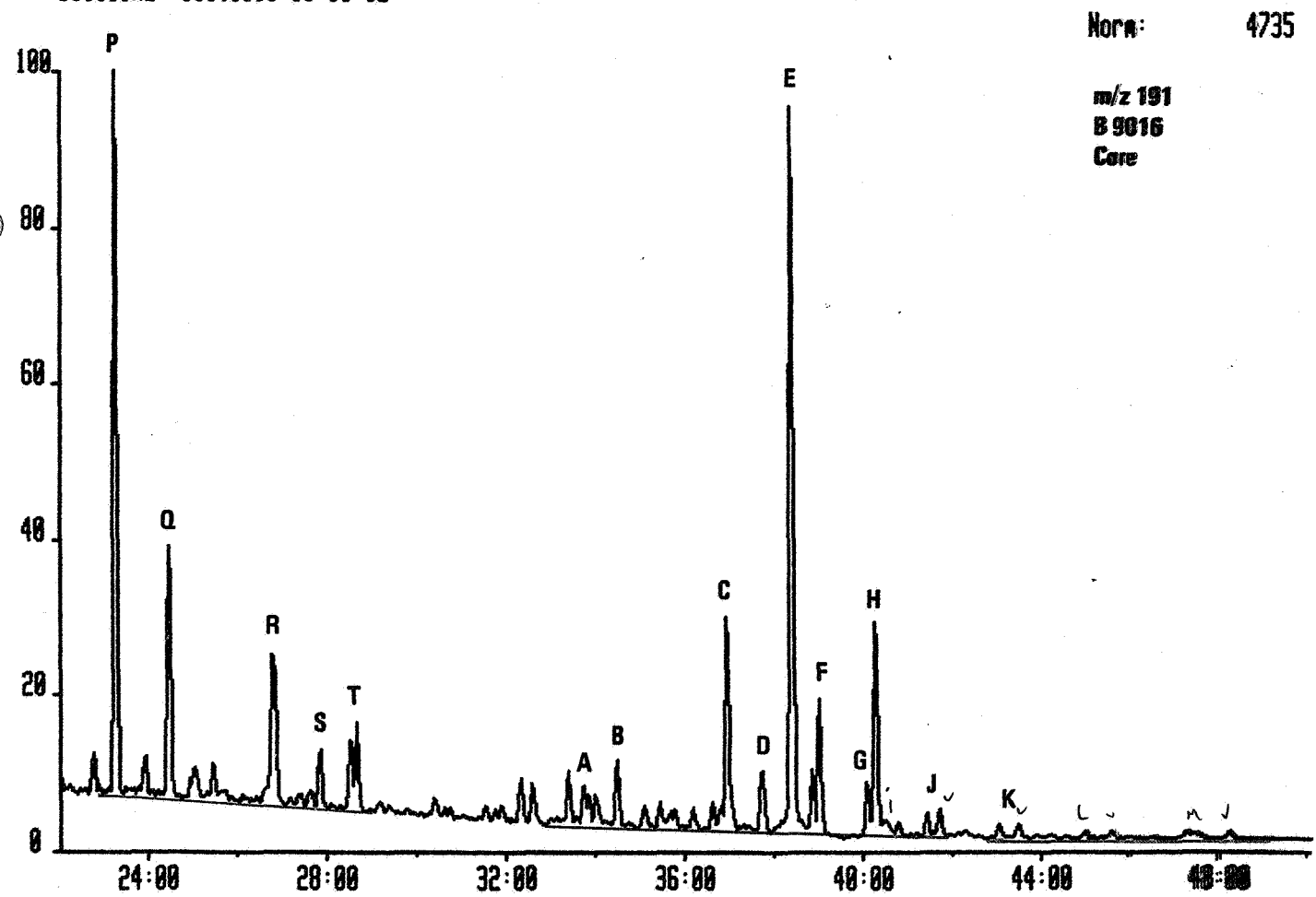
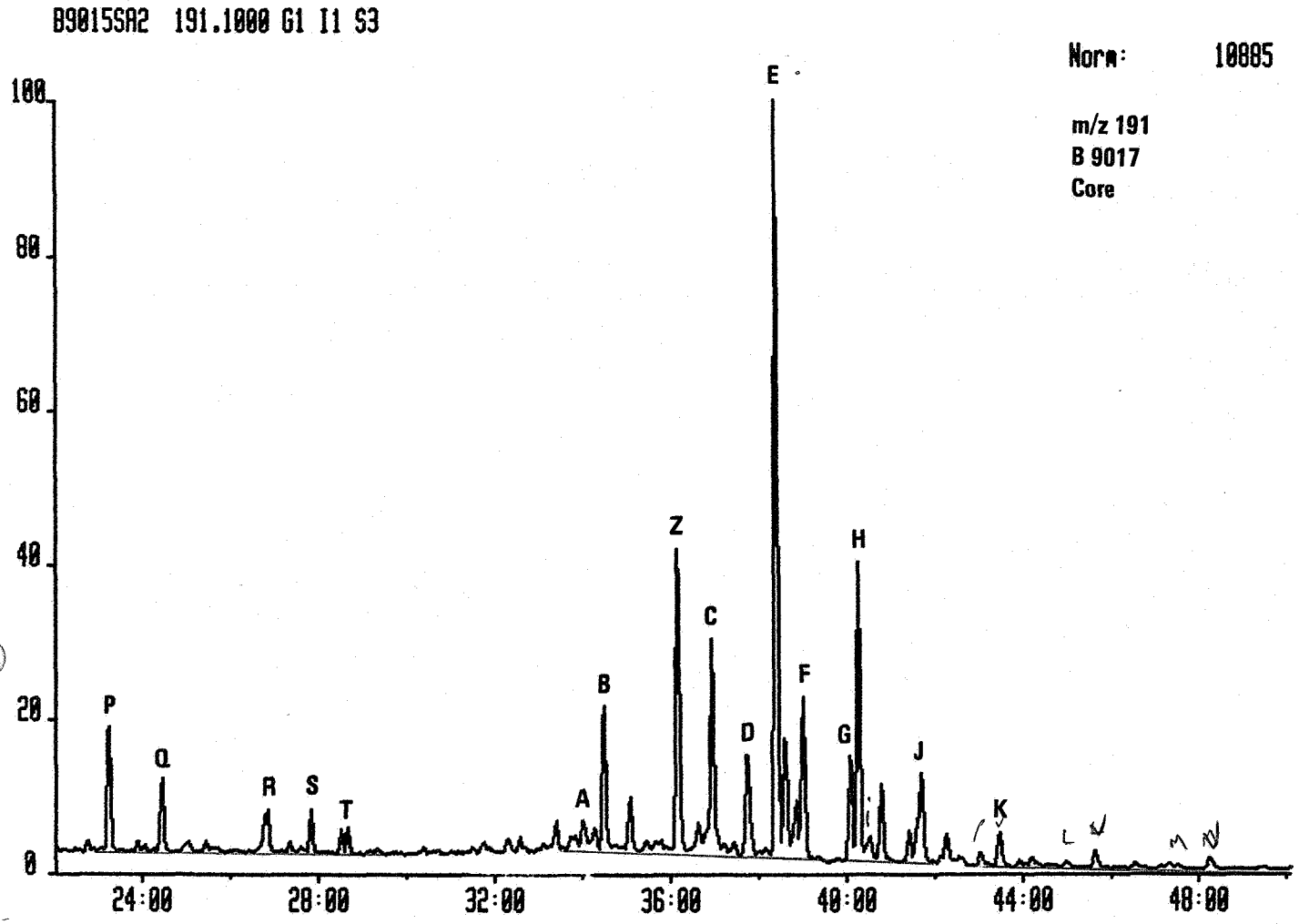
36:00
40:00
44:00
48:00


B9015SA2 191.1000 G1 I1 S2
Norm: 4735
m/z 191
B 9016
Core
100
80
60
40
20
0
P
Q
R
S
T
A
B
C
D
E
F
G
H
J
K
24:00
28:00
32:00
36:00
40:00
44:00

IKU


B9015SA2 191.1000 G1 I1 S3
Norm: 10885
m/z 191
B 9017
Core
100
80
60
40
20
0
24:00
28:00
32:00
36:00
40:00
44:00
48:00
P
Q
R
S
T
A
B
Z
C
D
E
F
G
H
J
K

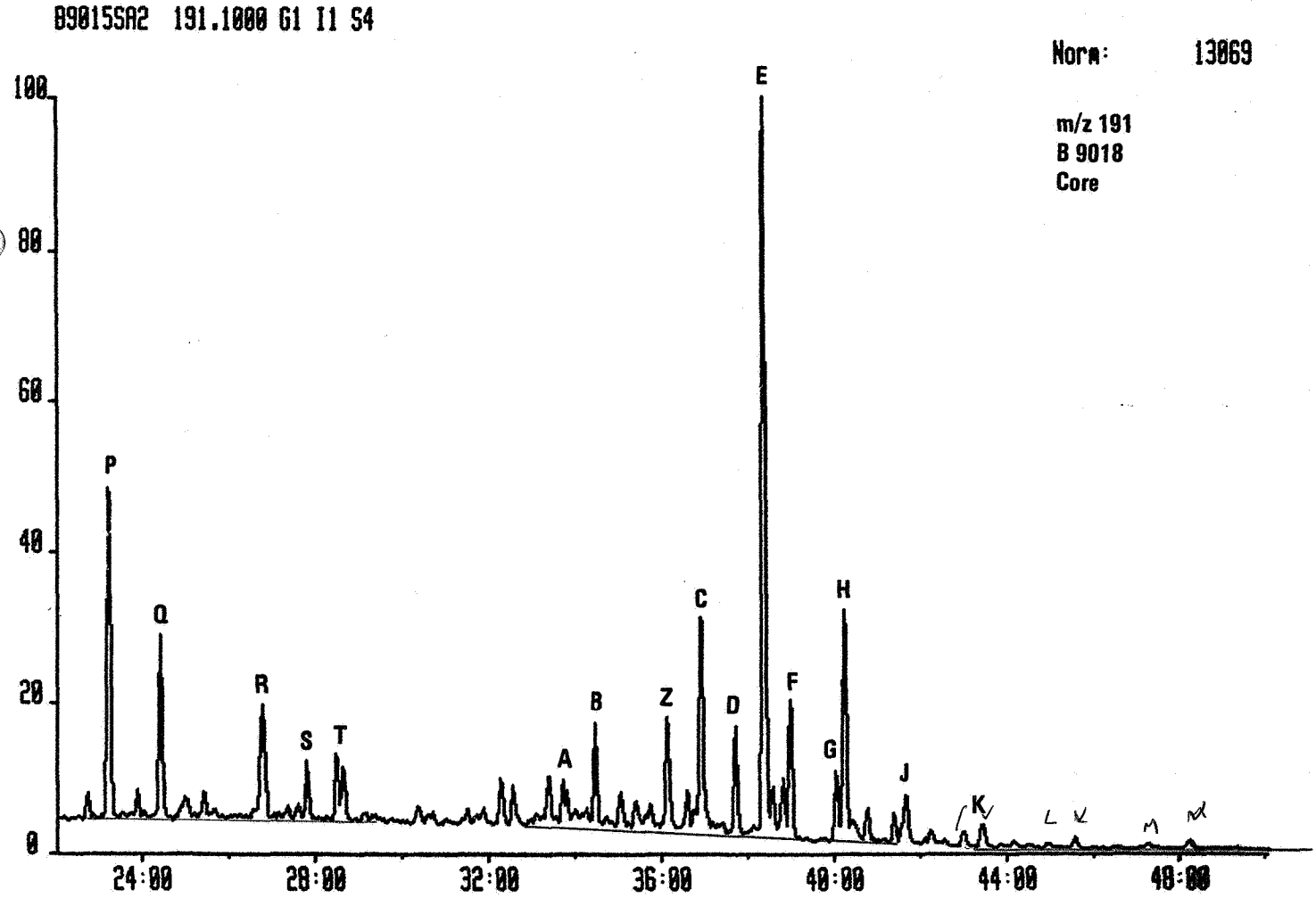
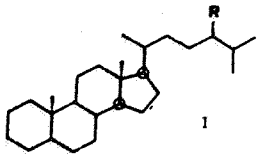

B9015SA2 191.1000 G1 I1 S4
Norm: 13069
m/z 191
B 9018
Core
100
80
60
40
20
0
24:00
28:00
32:00
36:00
40:00
44:00
48:00
P
Q
R
S
T
A
B
Z
C
D
E
F
G
H
J
K

Figure 5b

Mass chromatograms representing steranes (m/z 217 and 218)

a	13β(H),17α(H)-diasterane (20S)	$C_{27}H_{48}$	(III,R=H)
b	13β(H),17α(H)-diasterane (20R)	$C_{27}H_{48}$	(III,R=H)
c	13α(H),17β(H)-diasterane (20S)	$C_{27}H_{48}$	(IV,R=H)
d	13α(H),17β(H)-diasterane (20R)	$C_{27}H_{48}$	(IV,R=H)
e	13β(H),17α(H)-diasterane (20S)	$C_{28}H_{50}$	(III,R=CH_3)
f	13β(H),17α(H)-diasterane (20R)	$C_{28}H_{50}$	(III,R=CH_3)
g	13α(H),17β(H)-diasterane (20S)	$C_{28}H_{50}$	(IV,R=CH_3)
	+ 14α(H),17α(H)-sterane (20S)	$C_{27}H_{48}$	(I,R=H)
h	13β(H),17α(H)-diasterane (20S)	$C_{29}H_{52}$	(III,R=C_2H_5)
	+ 14β(H),17β(H)-sterane (20R)	$C_{27}H_{48}$	(II,R=H)
i	14β(H),17β(H)-sterane (20S)	$C_{27}H_{48}$	(II,R=H)
	+ 13α(H),17β(H)-diasterane (20R)	$C_{28}H_{50}$	(IV,R=CH_3)
j	14α(H),17α(H)-sterane (20R)	$C_{27}H_{48}$	(I,R=H)
k	13β(H),17α(H)-diasterane (20R)	$C_{29}H_{52}$	(III,R=C_2H_5)
l	13α(H),17β(H)-diasterane (20S)	$C_{29}H_{52}$	(III,R=C_2H_5)
m	14α(H),17α(H)-sterane (20S)	$C_{28}H_{50}$	(I,R=CH_3)
n	13α(H),17β(H)-diasterane (20R)	$C_{29}H_{52}$	(III,R=C_2H_5)
	+ 14β (H),17β (H)-sterane (20R)	$C_{28}H_{50}$	(II,R=CH_3)
o	14β(H),17β(H)-sterane (20S)	$C_{28}H_{50}$	(II,R=CH_3)
p	14α(H),17α(H)-sterane (20R)	$C_{28}H_{50}$	(I,R=CH_3)
q	14α(H),17α(H)-sterane (20S)	$C_{29}H_{52}$	(I,R=C_2H_5)
r	14β(H),17β(H)-sterane (20R)	$C_{29}H_{52}$	(II,R=C_2H_5)
	+ unknown sterane		
s	14β(H),17β(H)-sterane (20S)	$C_{29}H_{52}$	(II,R=C_2H_5)
t	14β(H),17β(H)-sterane (20R)	$C_{29}H_{52}$	(I,R=C_2H_5)
u	5α(H)-sterane	$C_{21}H_{36}$	(V,R=C_2H_5)
v	5α(H)-sterane	$C_{22}H_{38}$	(IV,R=C_3H_7)



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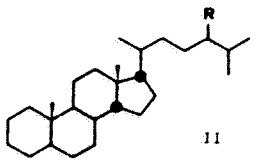
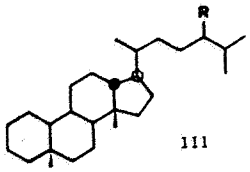
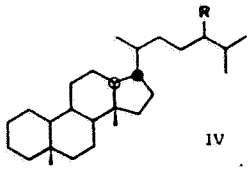


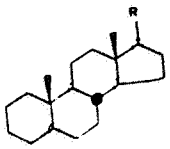
II



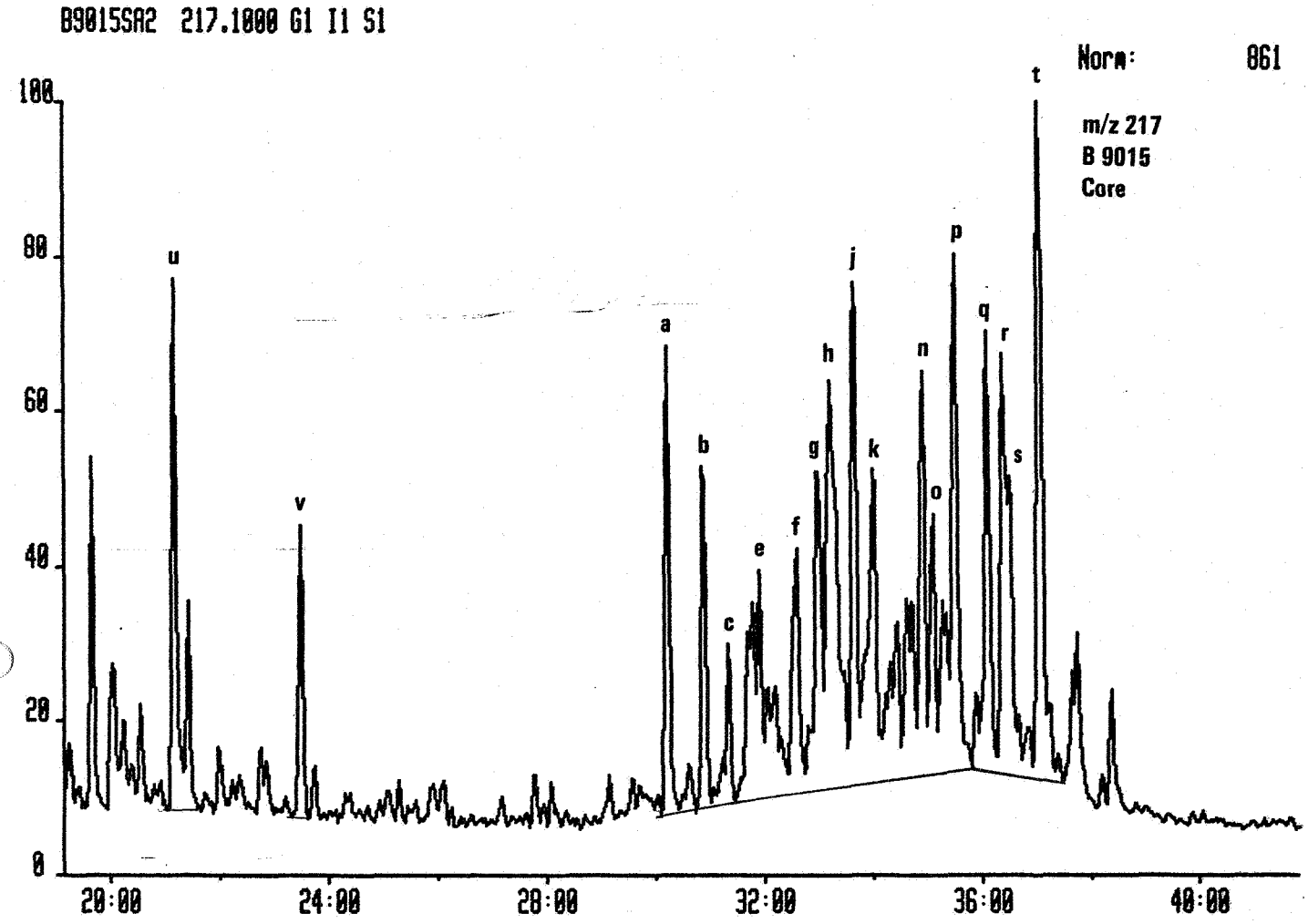
III



IV



IKU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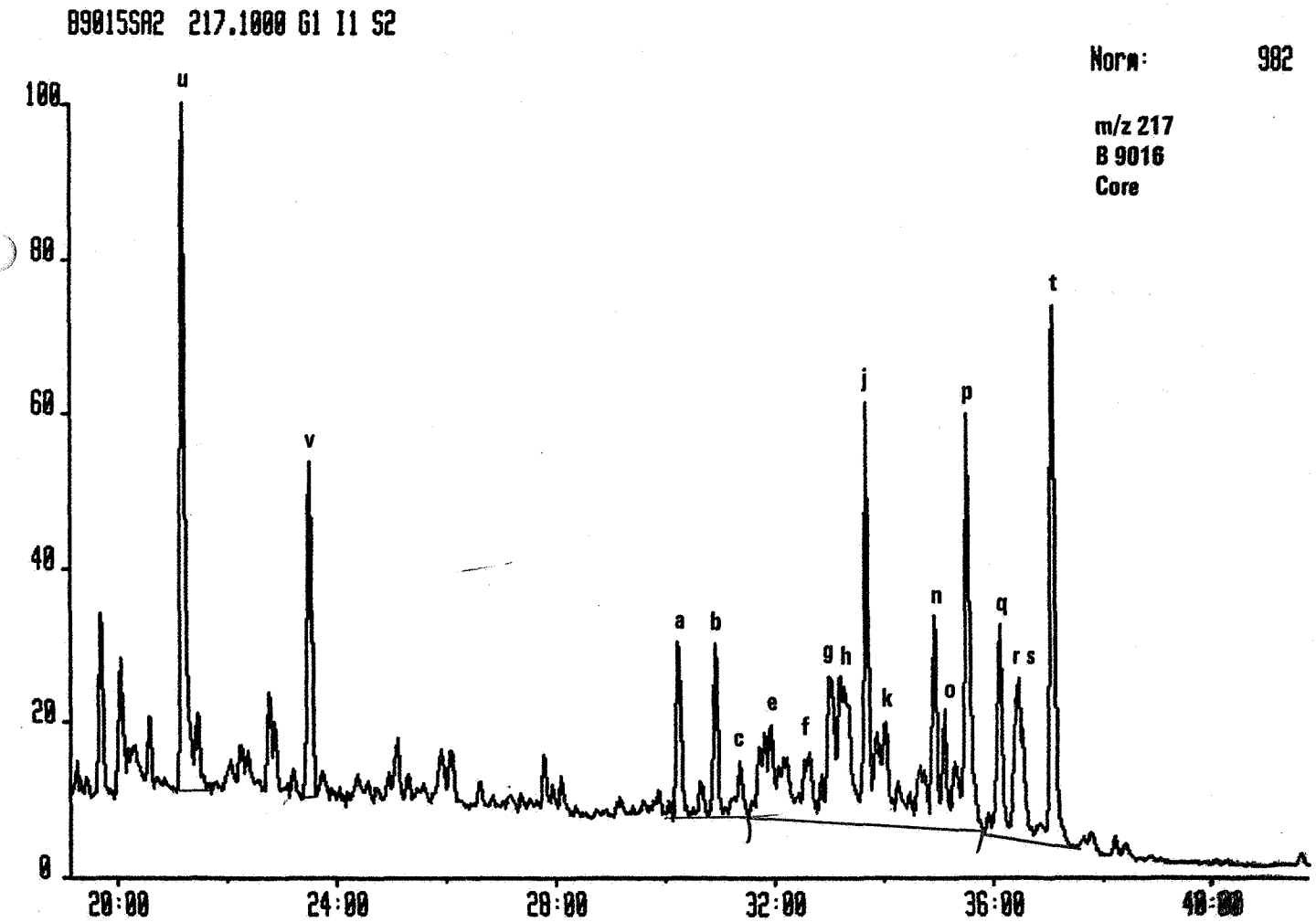
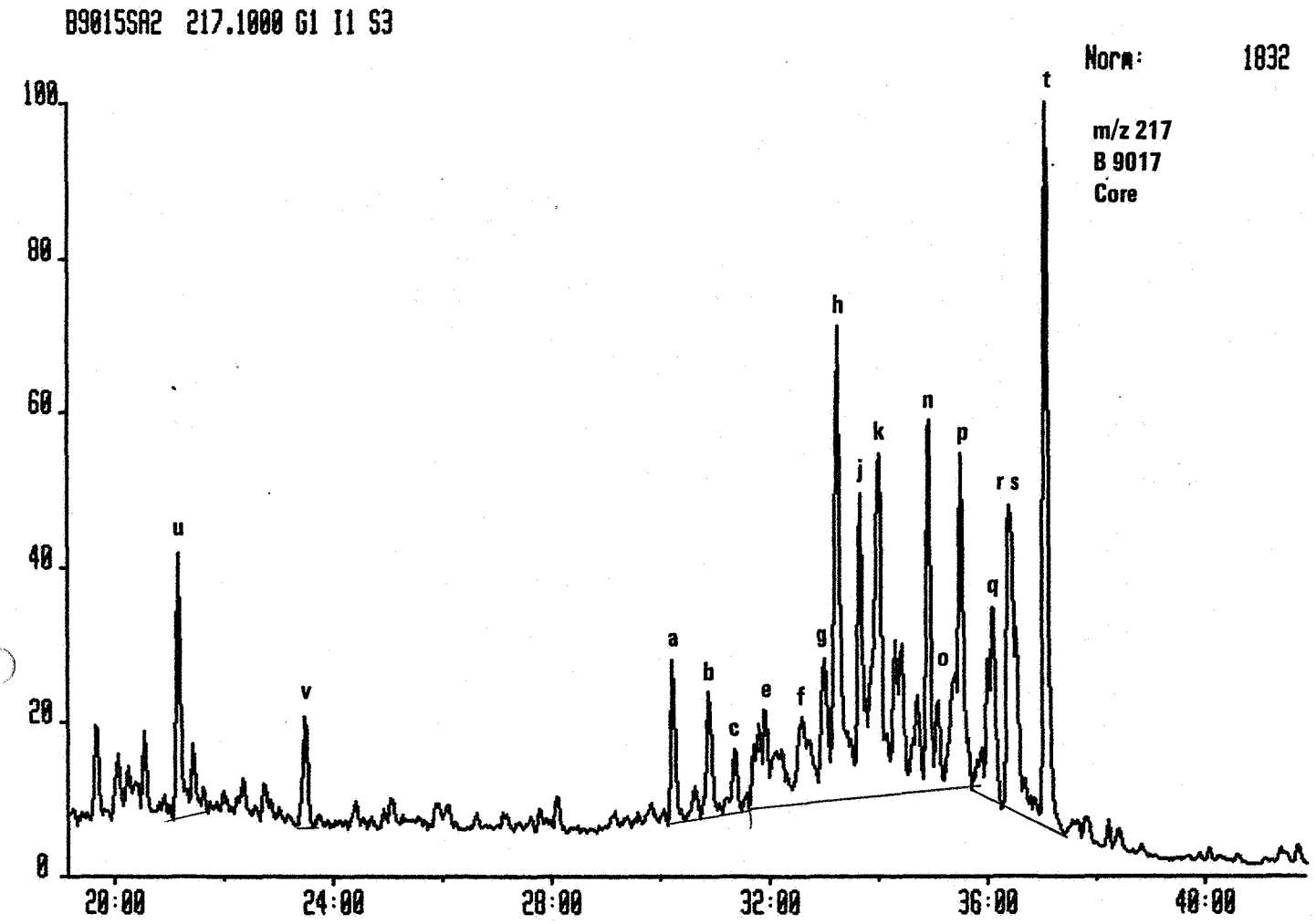
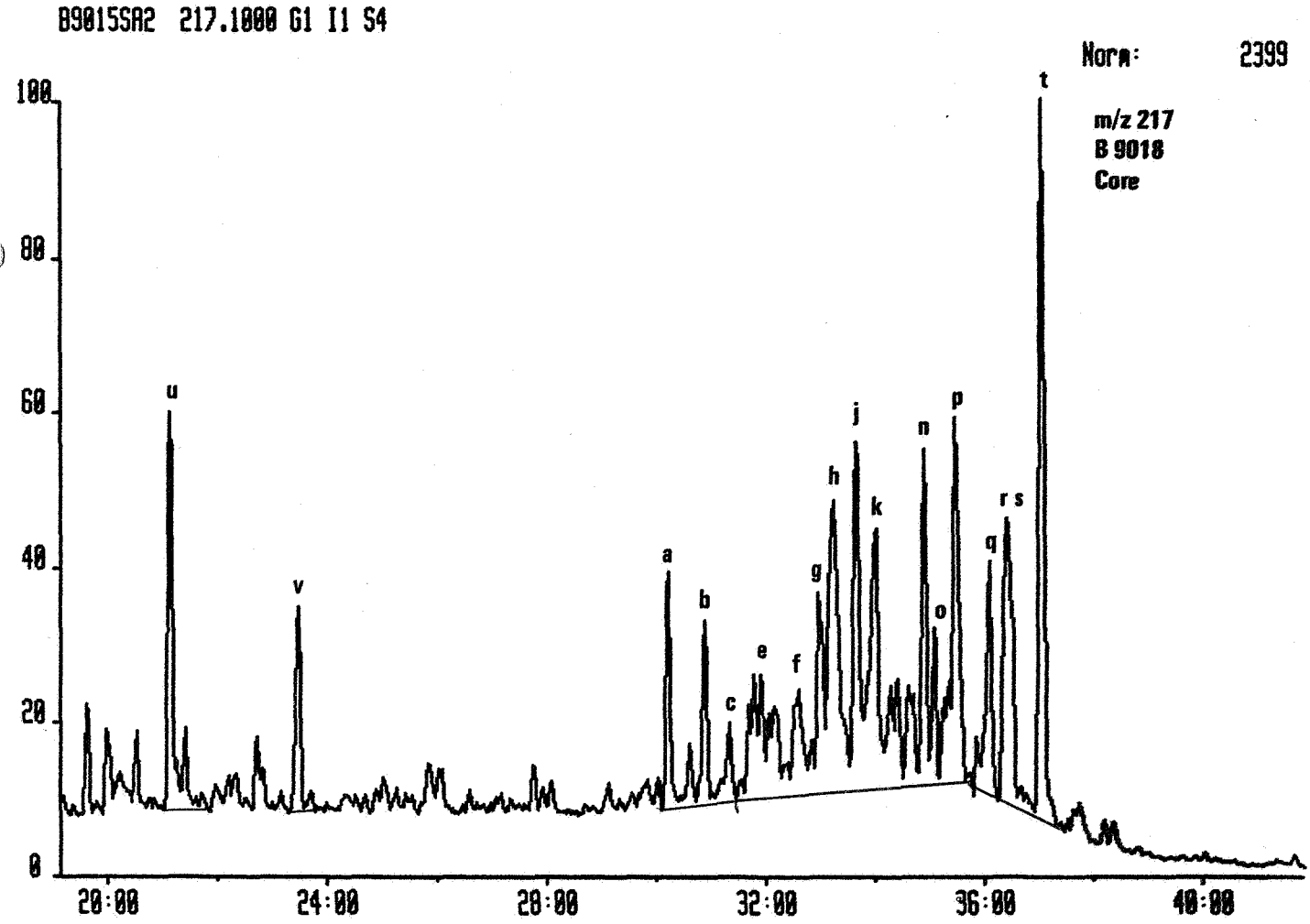
Norm: 861
m/z 217
B 9015
Core
100
80
60
40
20
0
20:00
24:00
28:00
32:00
36:00
40:00
u
v
a
b
c
e
f
g
h
j
k
n
o
p
q
r
s
t


B9015SA2 217.1000 G1 I1 S2
Norm: 982
m/z 217
B 9016
Core
100
80
60
40
20
0
20:00
24:00
28:00
32:00
36:00
40:00
u
v
a
b
c
e
f
g h
j
k
n
o
p
q
r s
t

IKU


B9015SA2 217.1000 G1 I1 S3
Norm: 1832
m/z 217
B 9017
Core
100
80
60
40
20
0
20:00
24:00
28:00
32:00
36:00
40:00
t
u
v
a
b
c
e
f
g
h
j
k
n
o
p
q
r s


B9015SA2 217.1000 G1 I1 S4
Norm: 2399
m/z 217
B 9018
Core
100
80
60
40
20
0
20:00
24:00
28:00
32:00
36:00
40:00
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u
v
a
b
c
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f
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h
j
k
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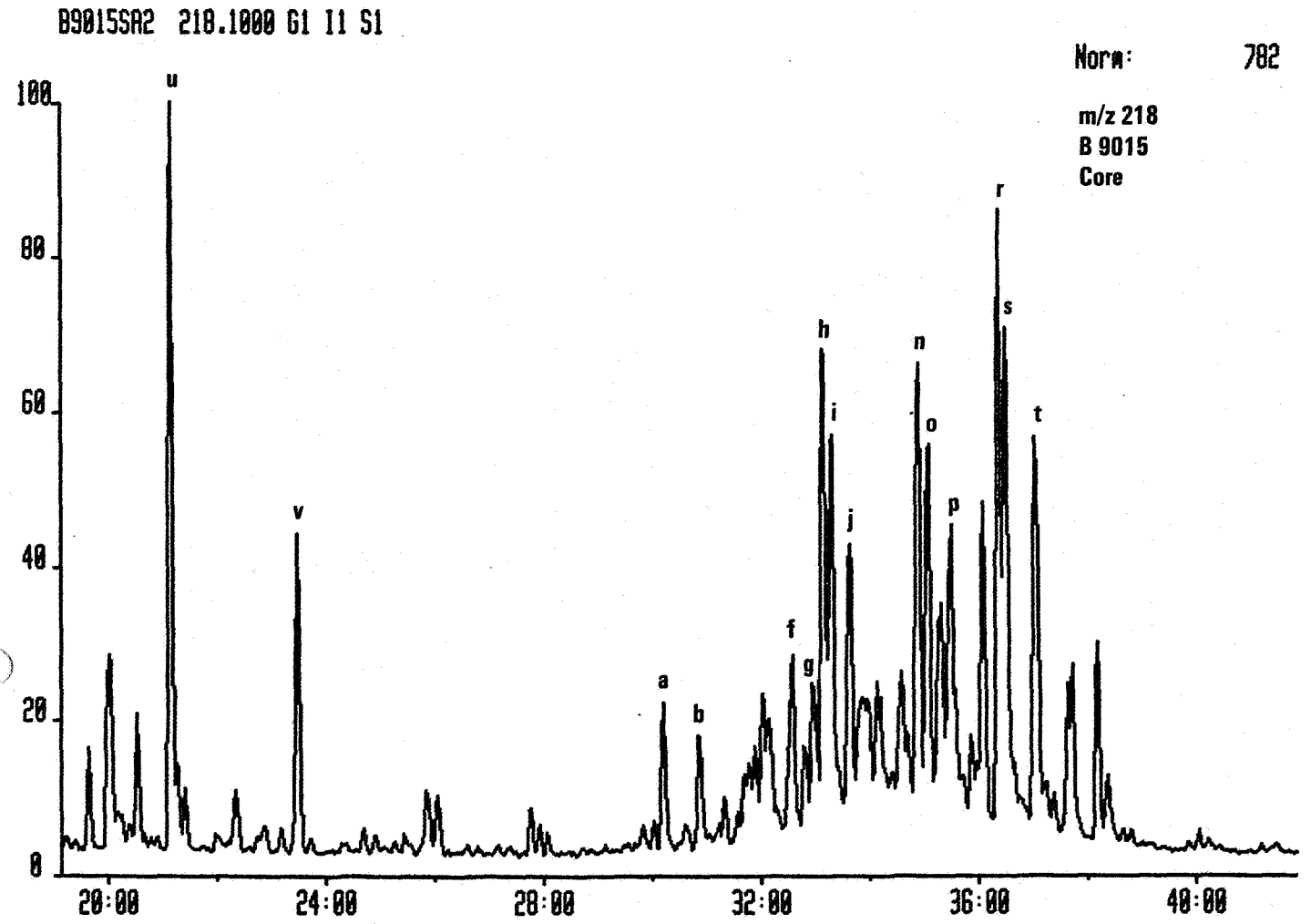
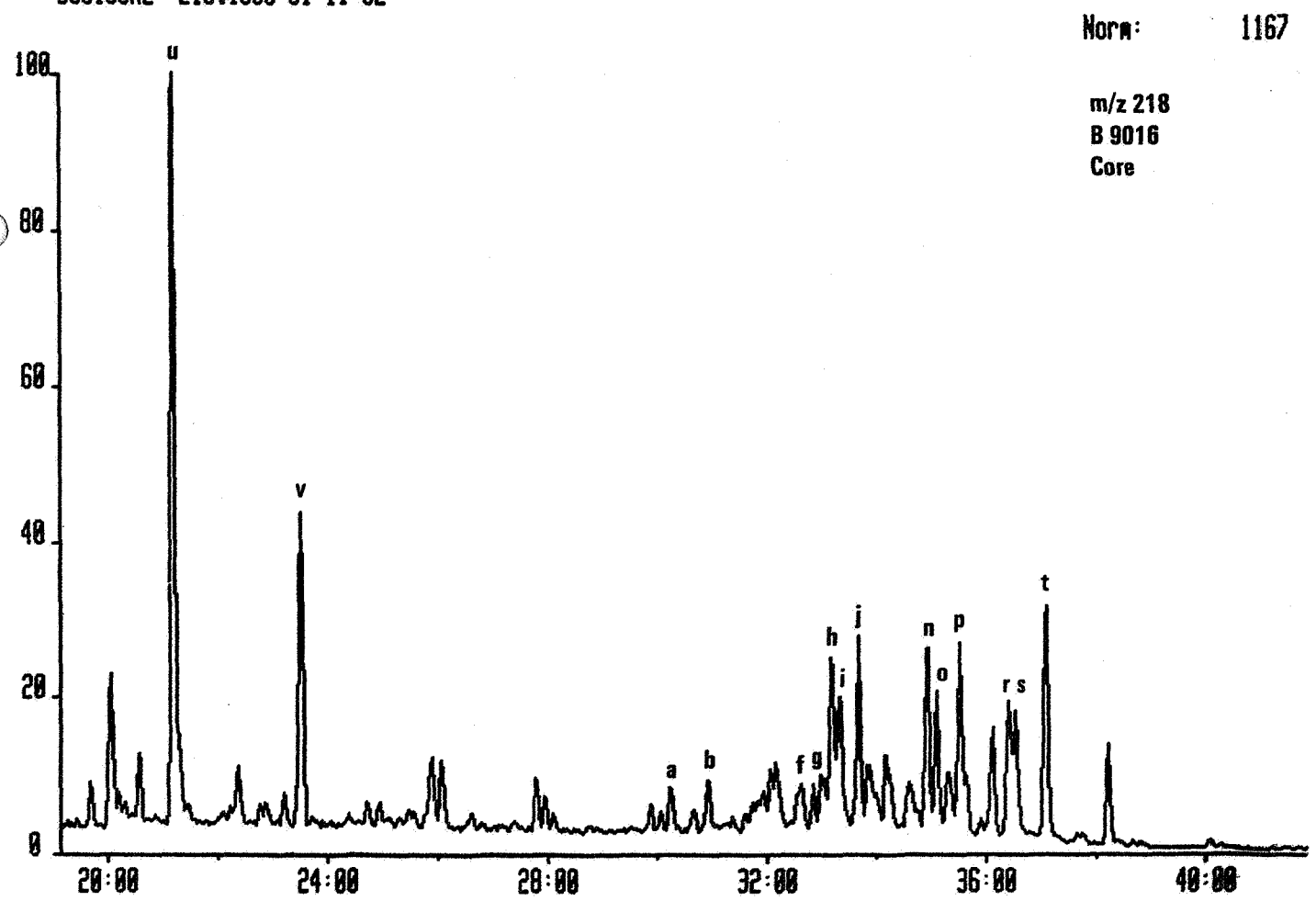
o
p
q
r s


B9015SA2 218.1000 G1 I1 S1
Norm: 782
m/z 218
B 9015
Core
100
80
60
40
20
0
20:00
24:00
28:00
32:00
36:00
40:00
u
v
a
b
f
g
h
i
j
n
o
p
r
s
t


B9015SA2 218.1000 G1 I1 S2
Norm: 1167
m/z 218
B 9016
Core
100
80
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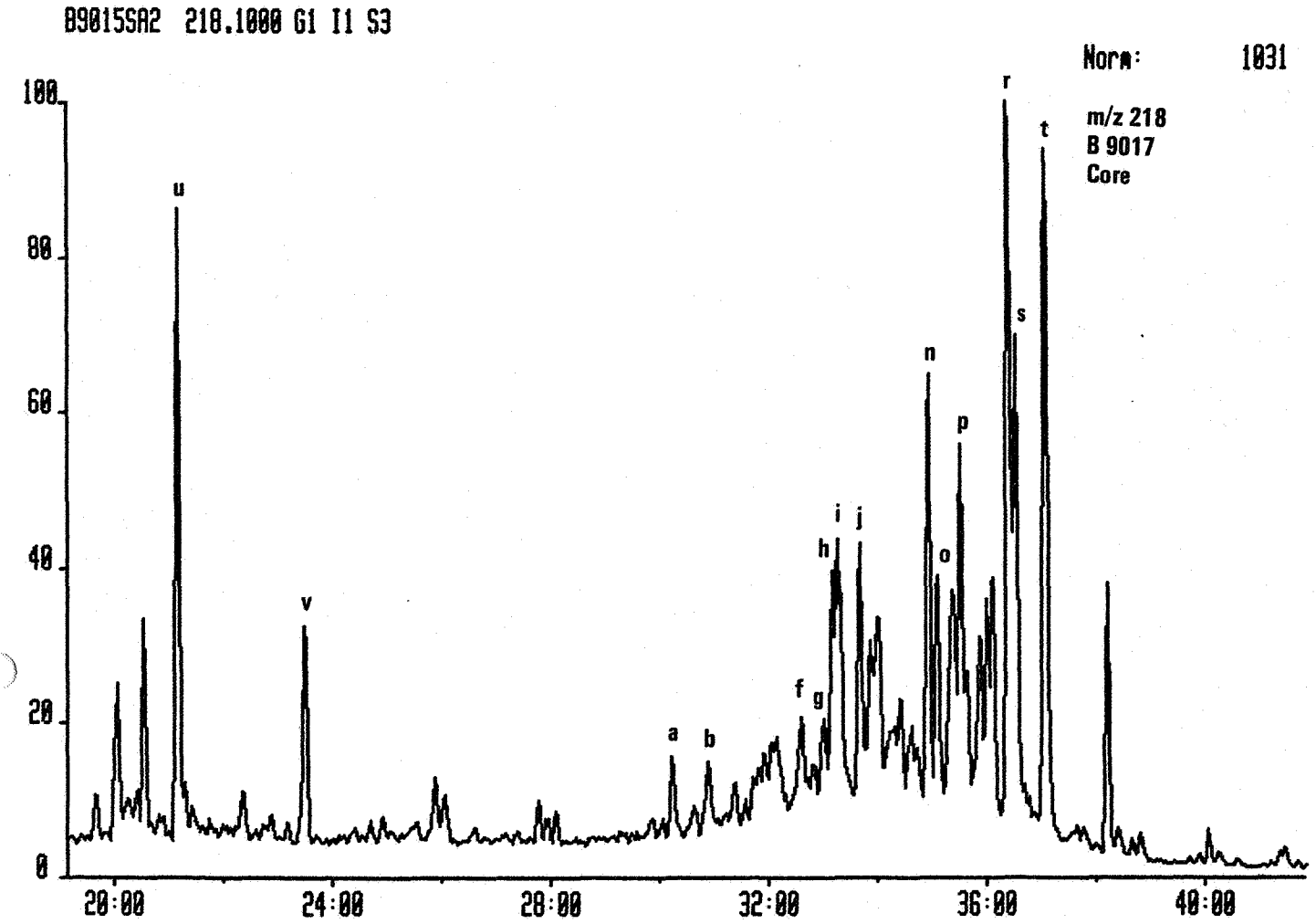
40
20
0
20:00
24:00
28:00
32:00
36:00
40:00
u
v
a
b
f
g
h
i
j
n
o
p
r
s
t

IKU


89015SA2 218.1000 G1 I1 S3
Norm: 1031
m/z 218
B 9017
Core
100
80
60
40
20
0
20:00
24:00
28:00
32:00
36:00
40:00
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v
a
b
f
g
h
i
j
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o
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s
t

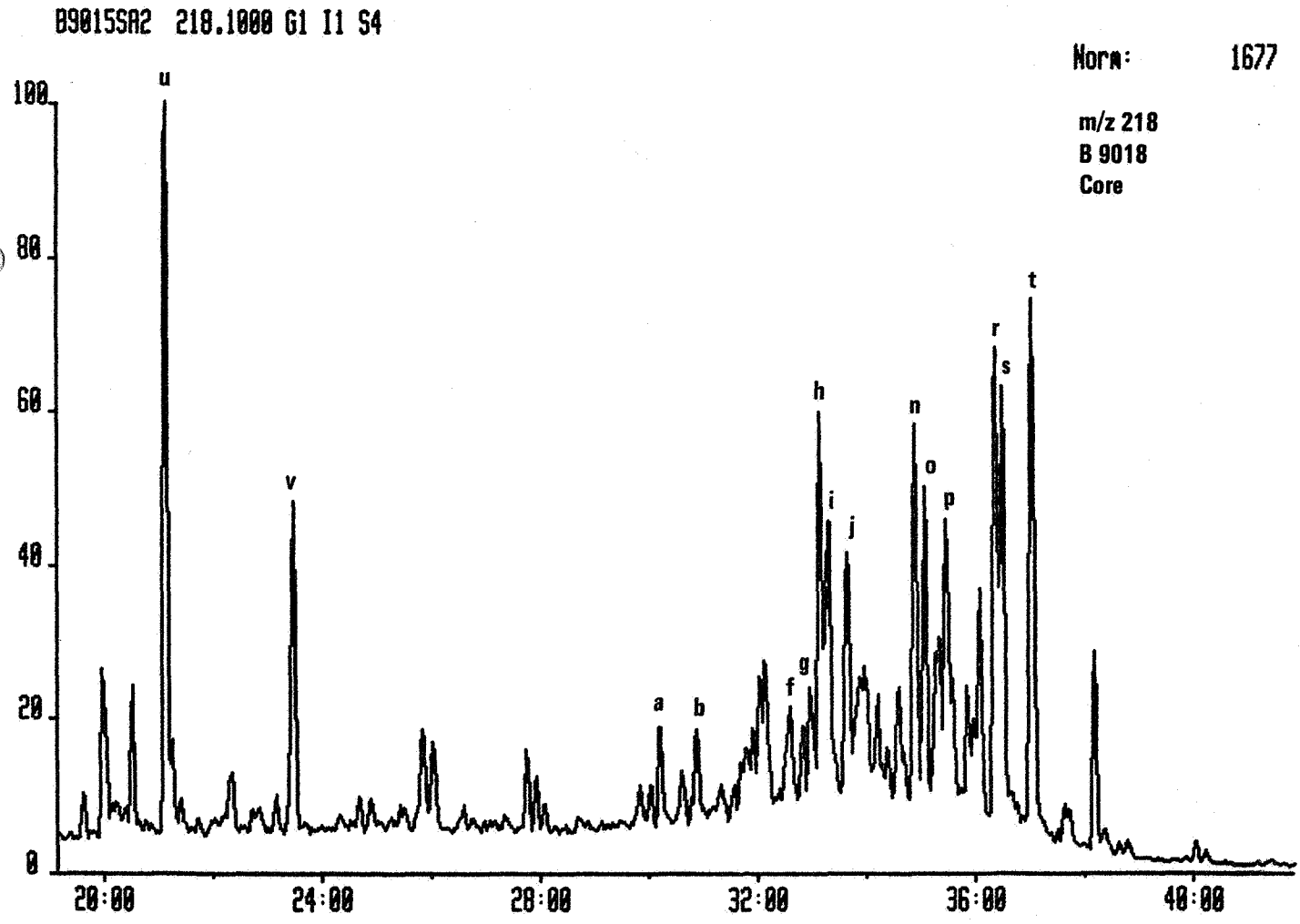
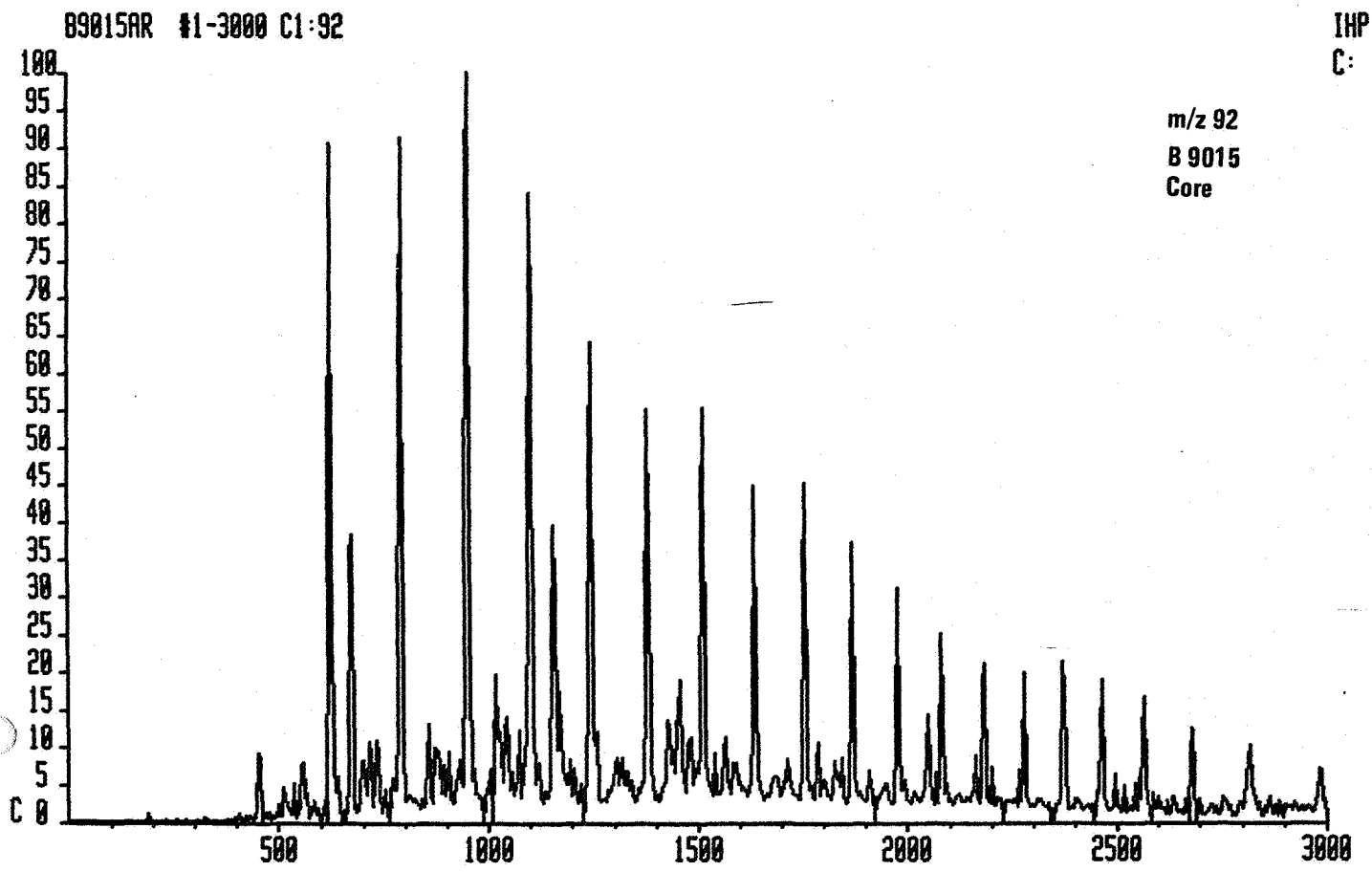
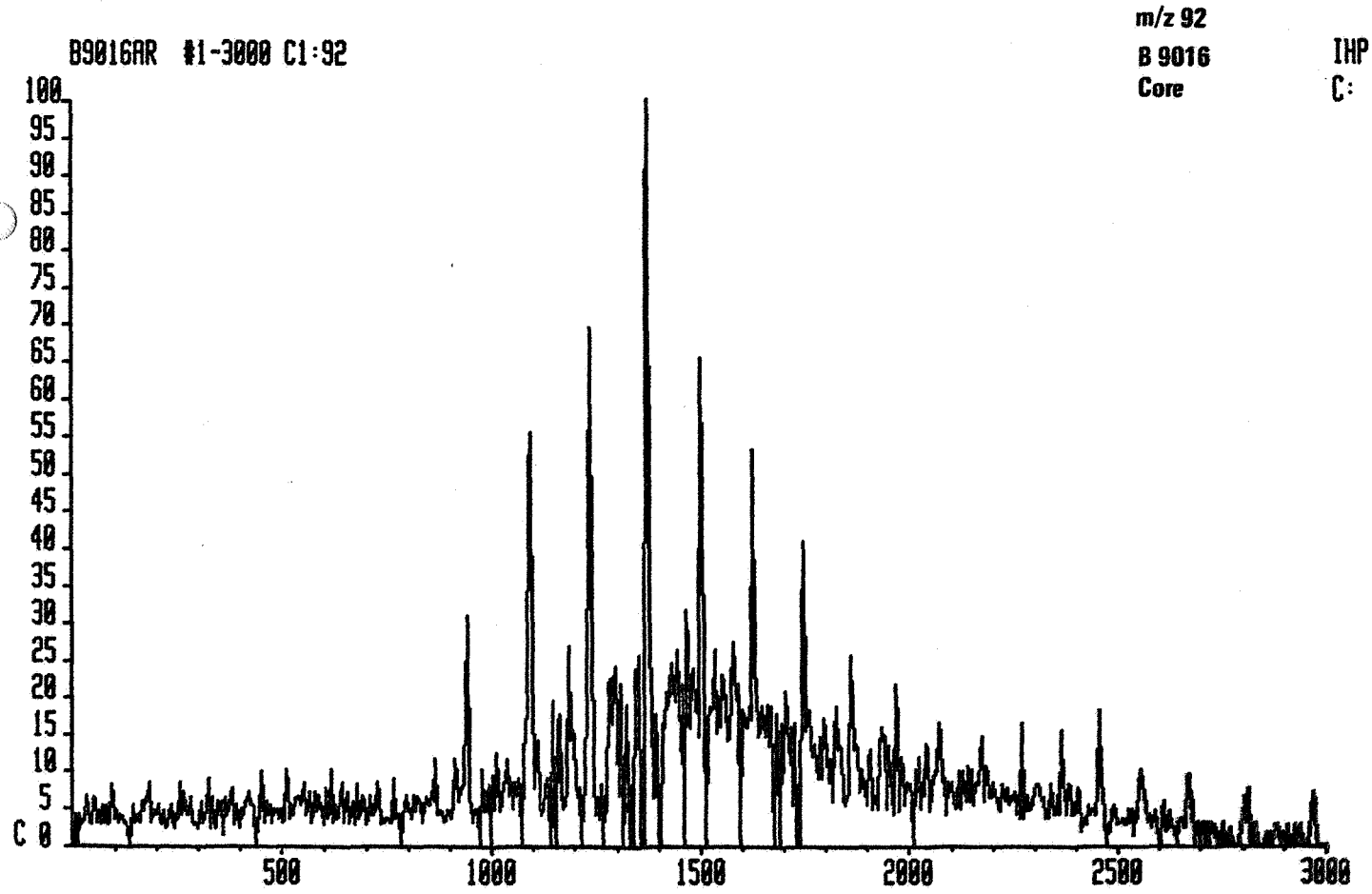

89015SA2 218.1000 G1 I1 S4
Norm: 1677
m/z 218
B 9018
Core
100
80
60
40
20
0
20:00
24:00
28:00
32:00
36:00
40:00
u
v
a
b
f
g
h
i
j
n
o
p
r
s
t

Figure 6

Mass chromatograms of aromatic hydrocarbons

m/z 92,106	-	alkylated benzenes
m/z 142,156,170	-	alkylated naphthalenes
m/z 178,192,206	-	alkylated phenanthrenes
m/z 184,198,212	-	alkylated dibenzothiophenes
m/z 231	-	triaromatic steranes
m/z 253	-	monoaromatic steranes


B9015AR #1-3000 C1:92
IHP
C:
m/z 92
B 9015
Core
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
C 0
500
1000
1500
2000
2500
3000


B9016AR #1-3000 C1:92
m/z 92
B 9016
Core
IHP
C:
100
95
90
85
80
75
70
65
60
55
50
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40
35
30
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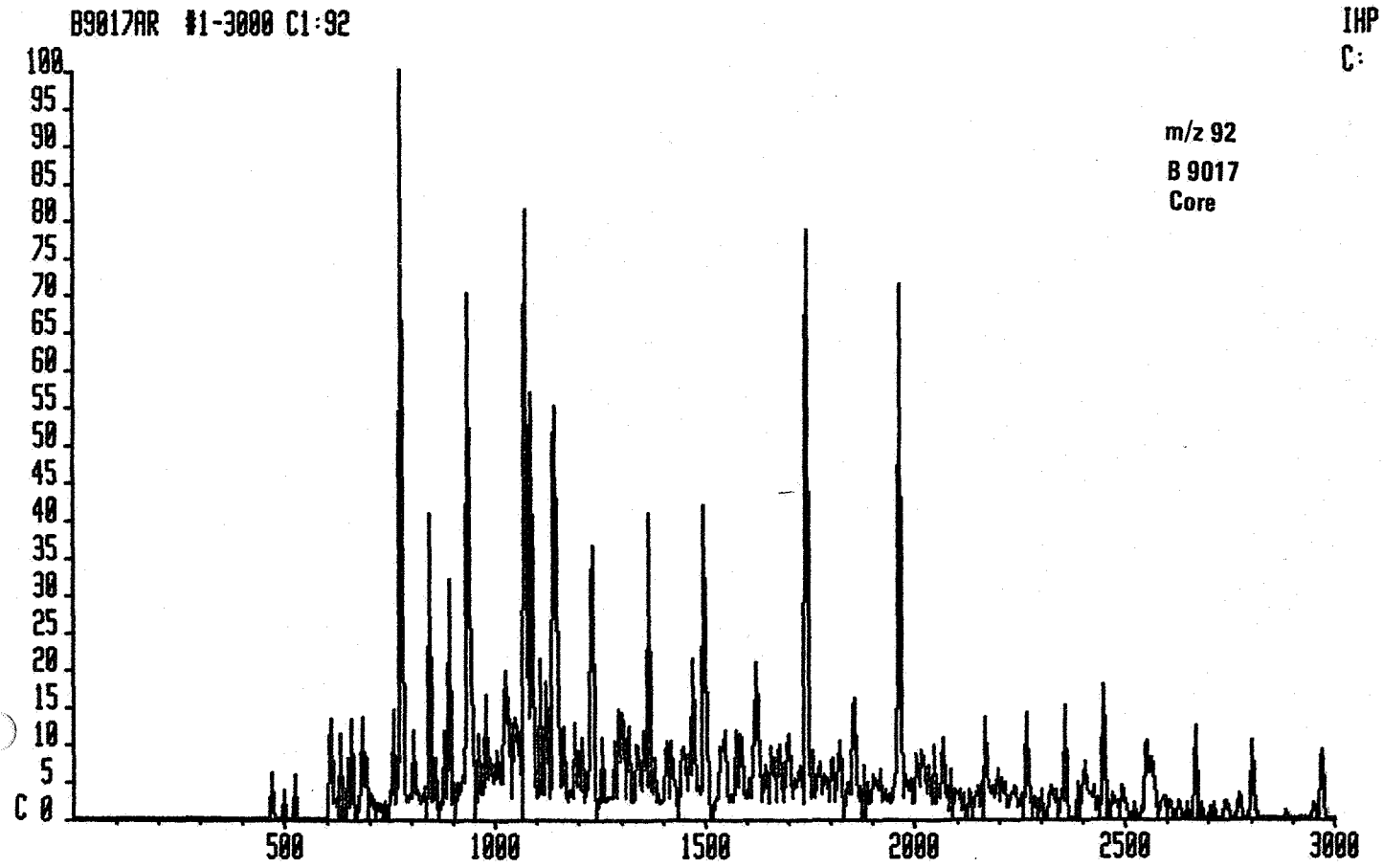
20
15
10
5
C 0
500
1000
1500
2000
2500
3000

IKU


B9017AR #1-3000 C1:92
IHP
C:
m/z 92
B 9017
Core
100
95
90
85
80
75
70
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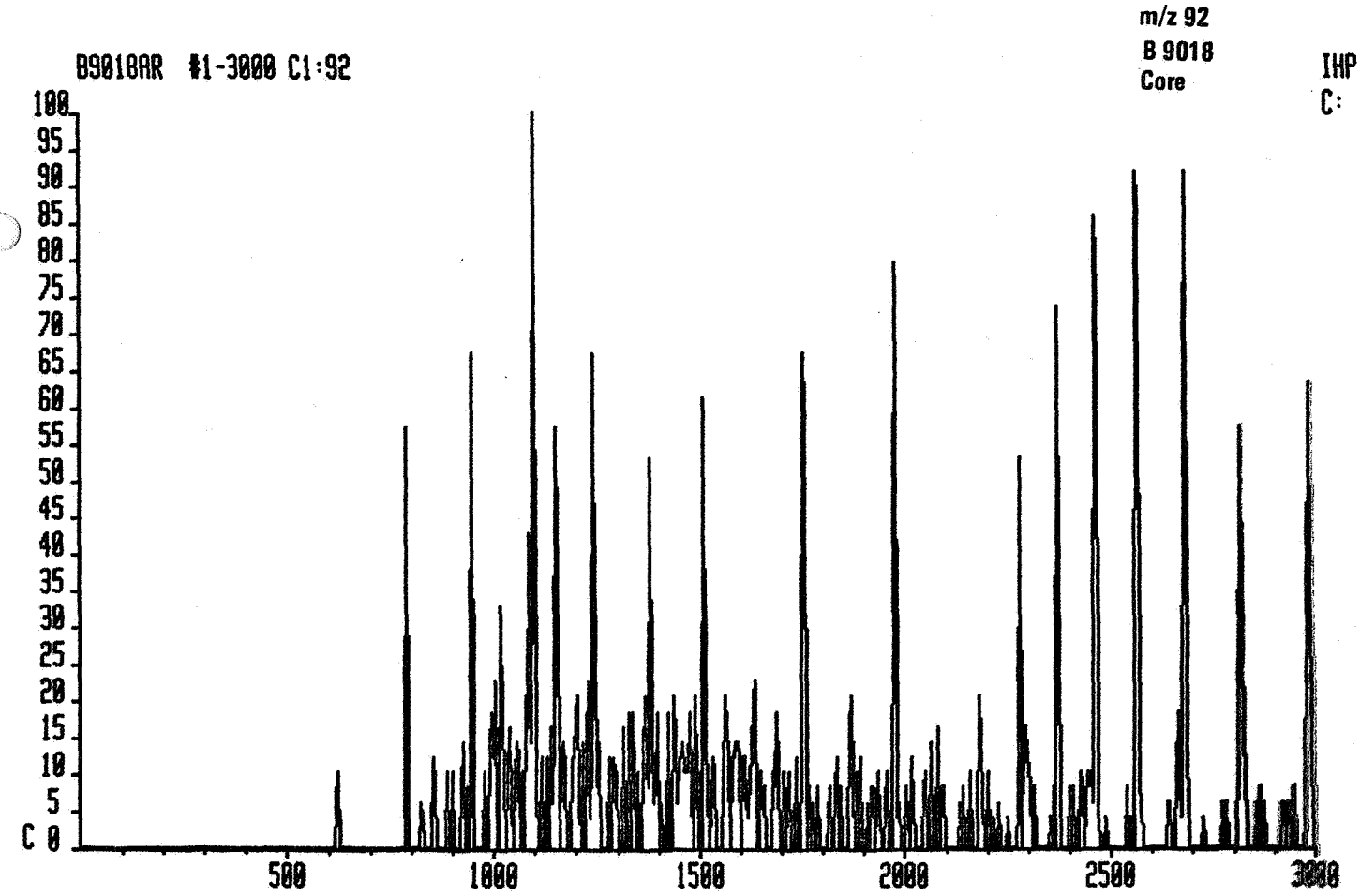
45
40
35
30
25
20
15
10
5
C 0
500
1000
1500
2000
2500
3000


m/z 92
B 9018
Core
B9018AR #1-3000 C1:92
IHP
C:
100
95
90
85
80
75
70
65
60
55
50
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30
25
20
15
10
5
C 0
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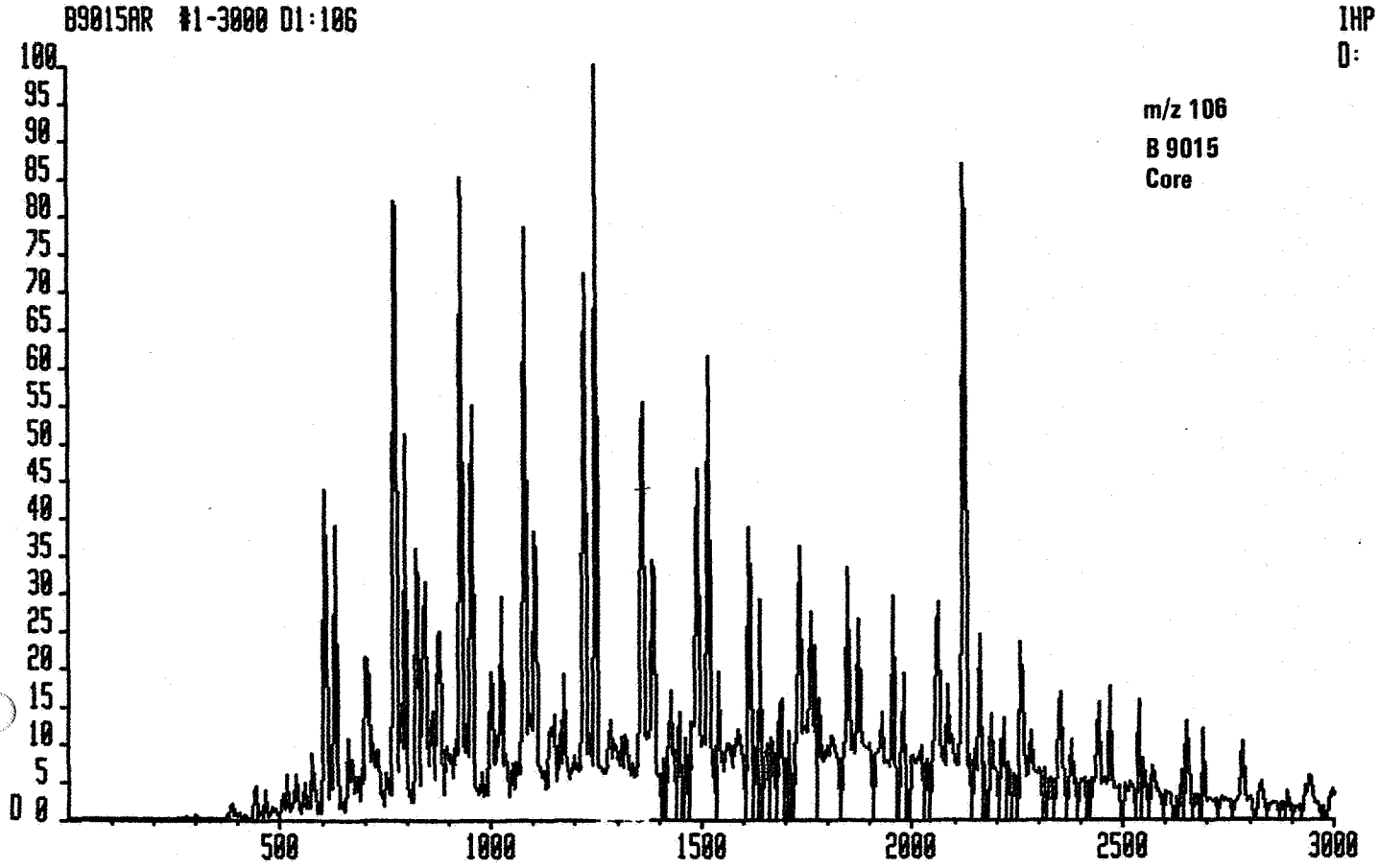
1000
1500
2000
2500
3000

IKU


B9015AR #1-3000 D1:106
IHP
D:
m/z 106
B 9015
Core
100
95
90
85
80
75
70
65
60
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45
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25
20
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5
D 0
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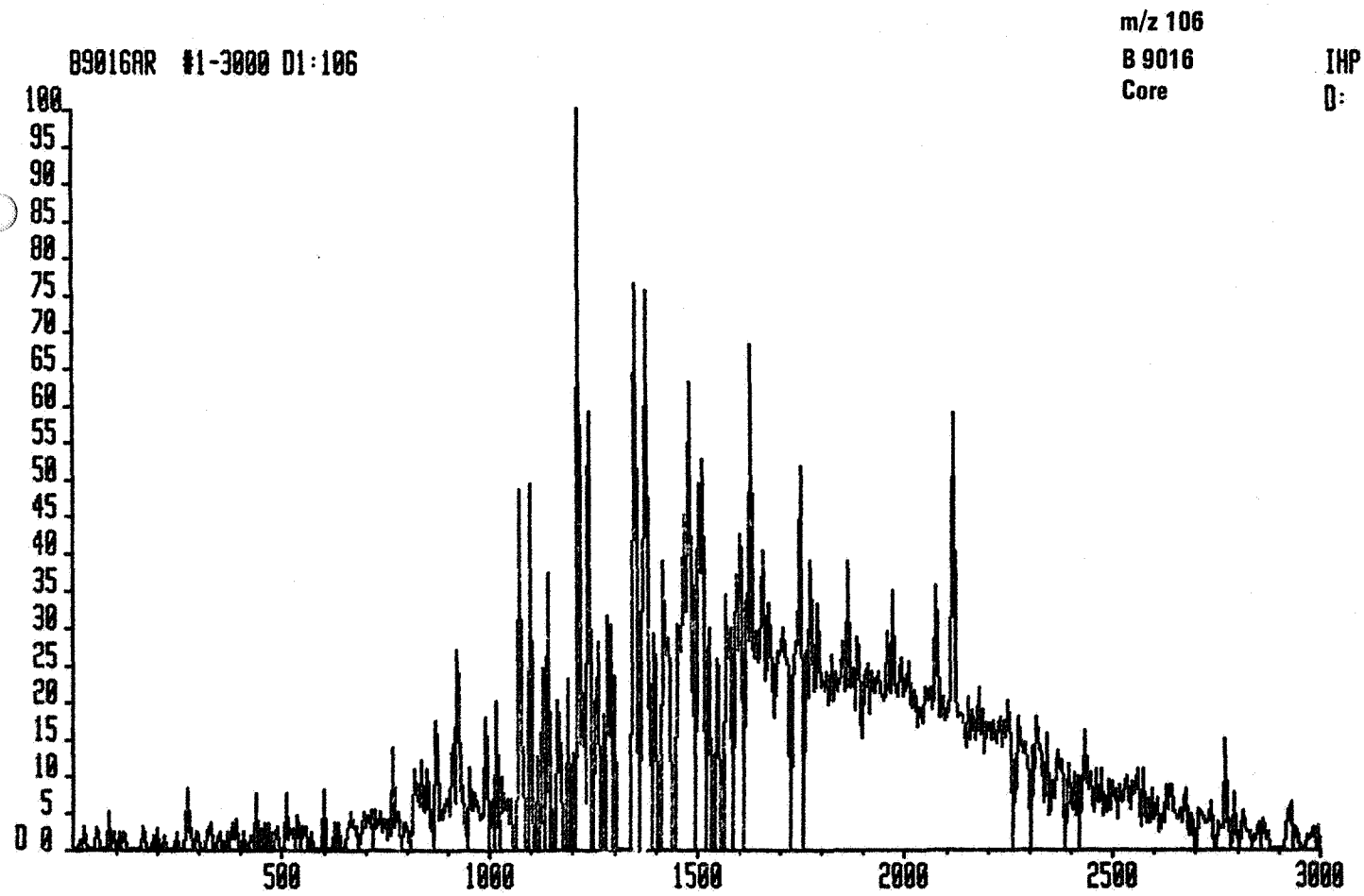
1500
2000
2500
3000


m/z 106
B 9016
Core
B9016AR #1-3000 D1:106
IHP
D:
100
95
90
85
80
75
70
65
60
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50
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35
30
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20
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10
5
D 0
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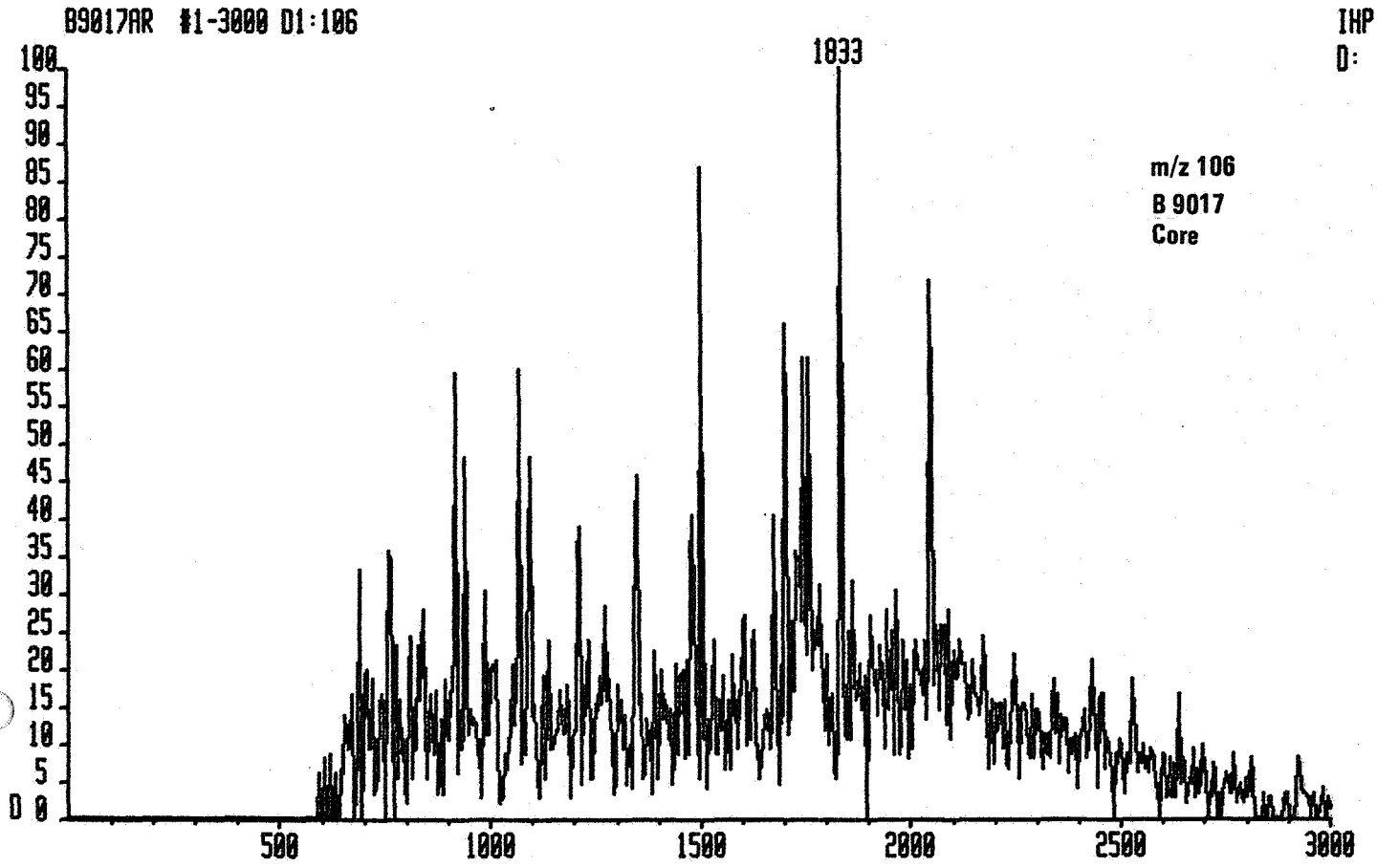
1000
1500
2000
2500
3000

IKU


B9017AR #1-3000 D1:106
IHP
D:
1833
m/z 106
B 9017
Core
100
95
90
85
80
75
70
65
60
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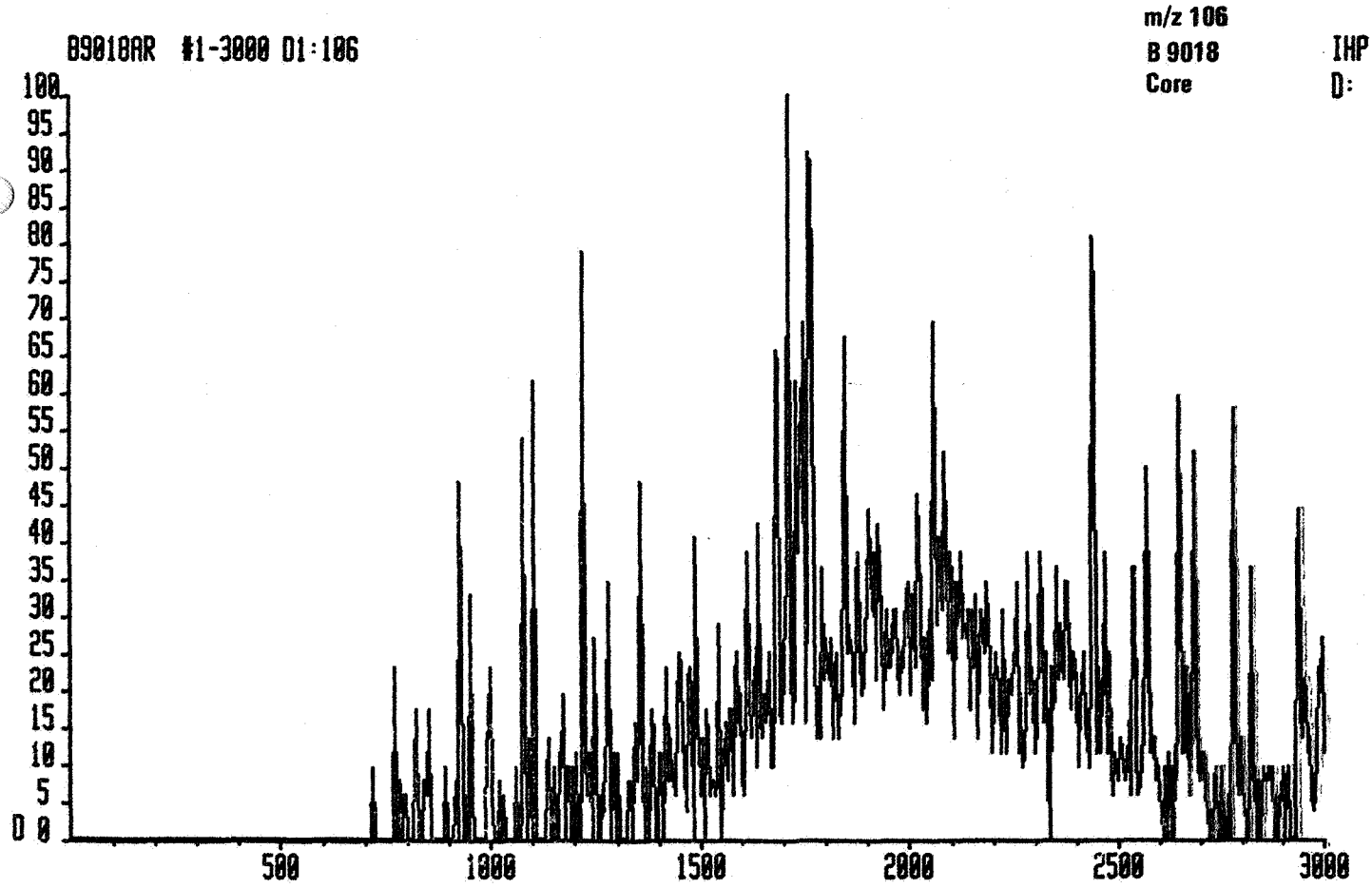
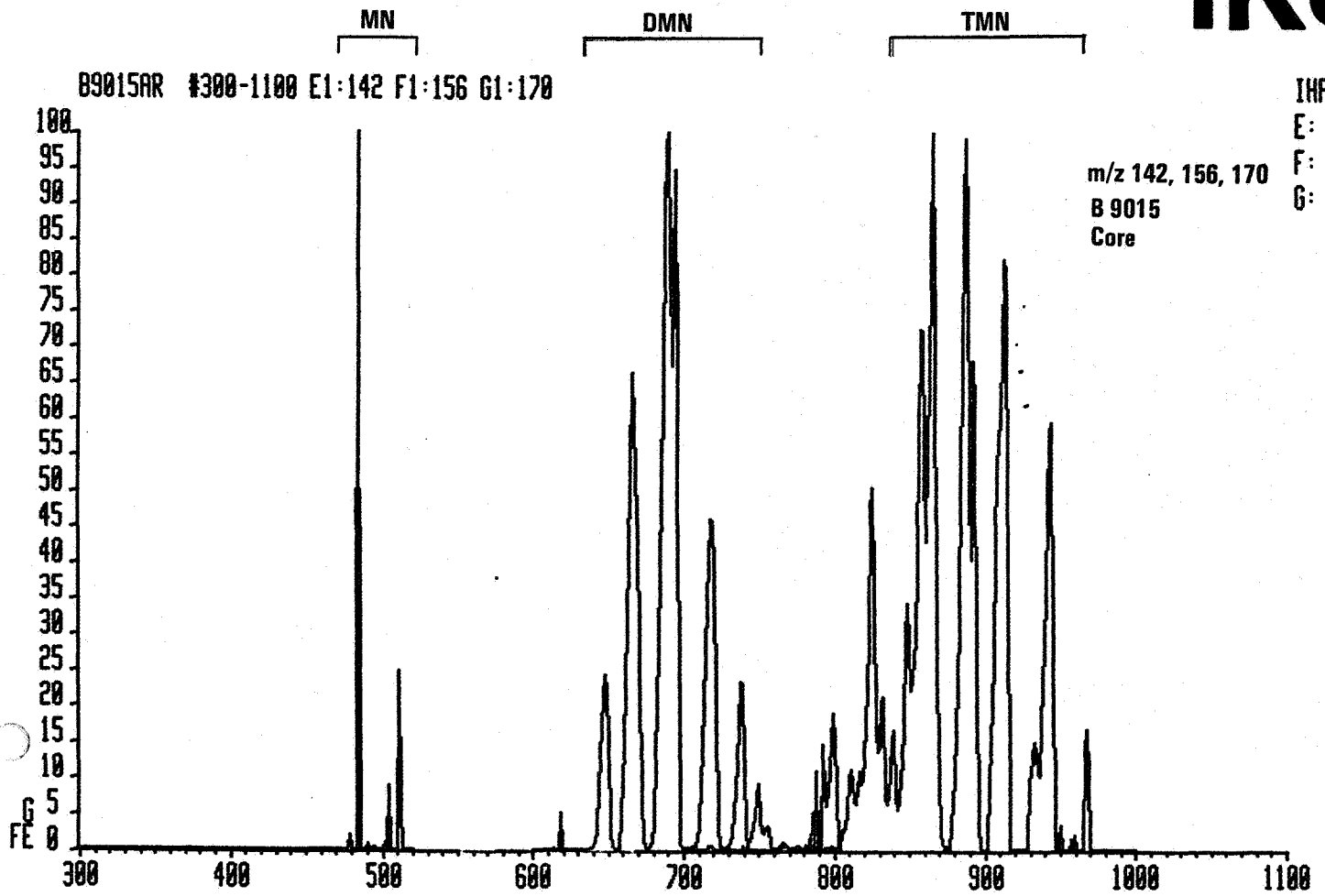
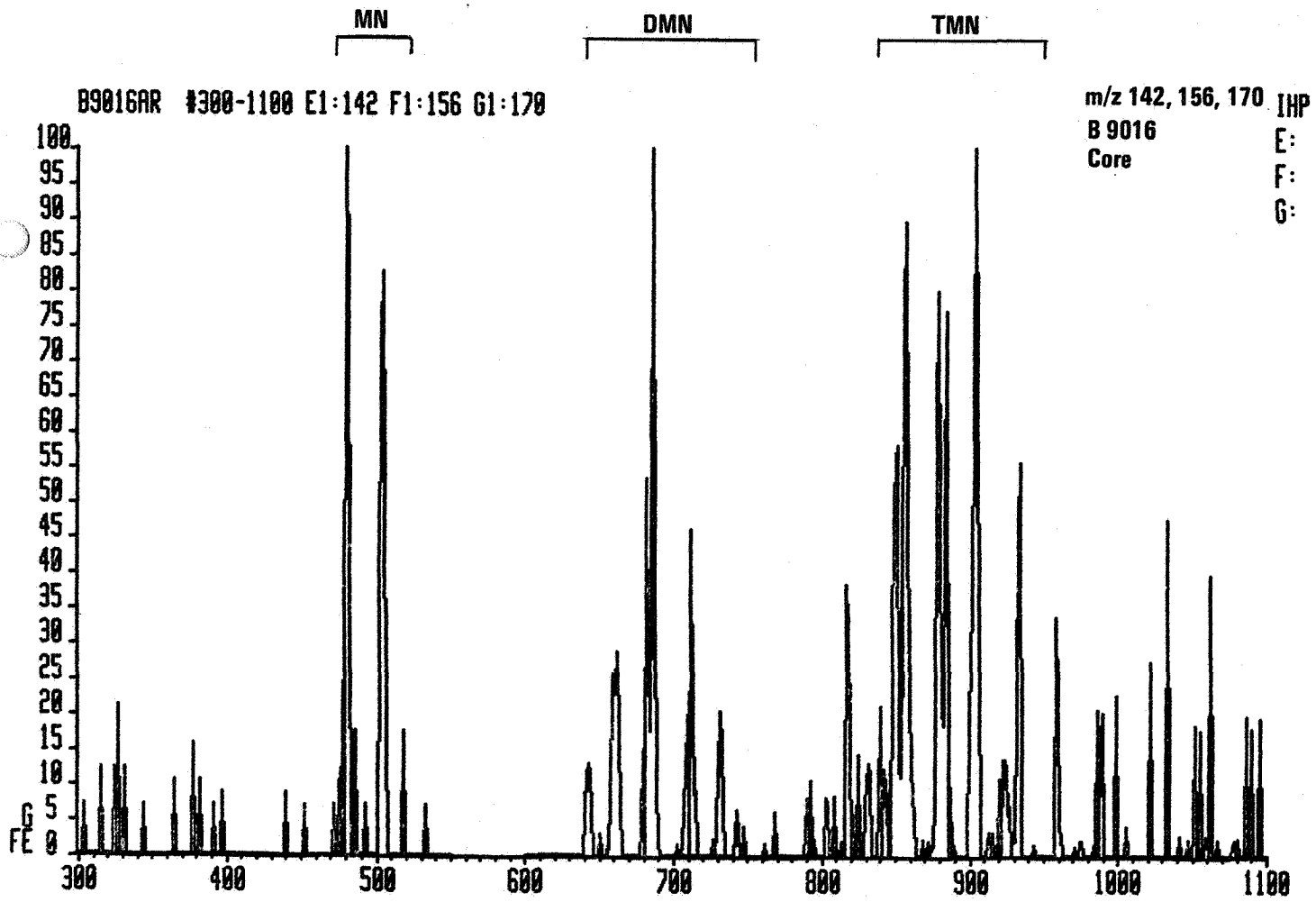
45
40
35
30
25
20
15
10
5
D 0
500
1000
1500
2000
2500
3000

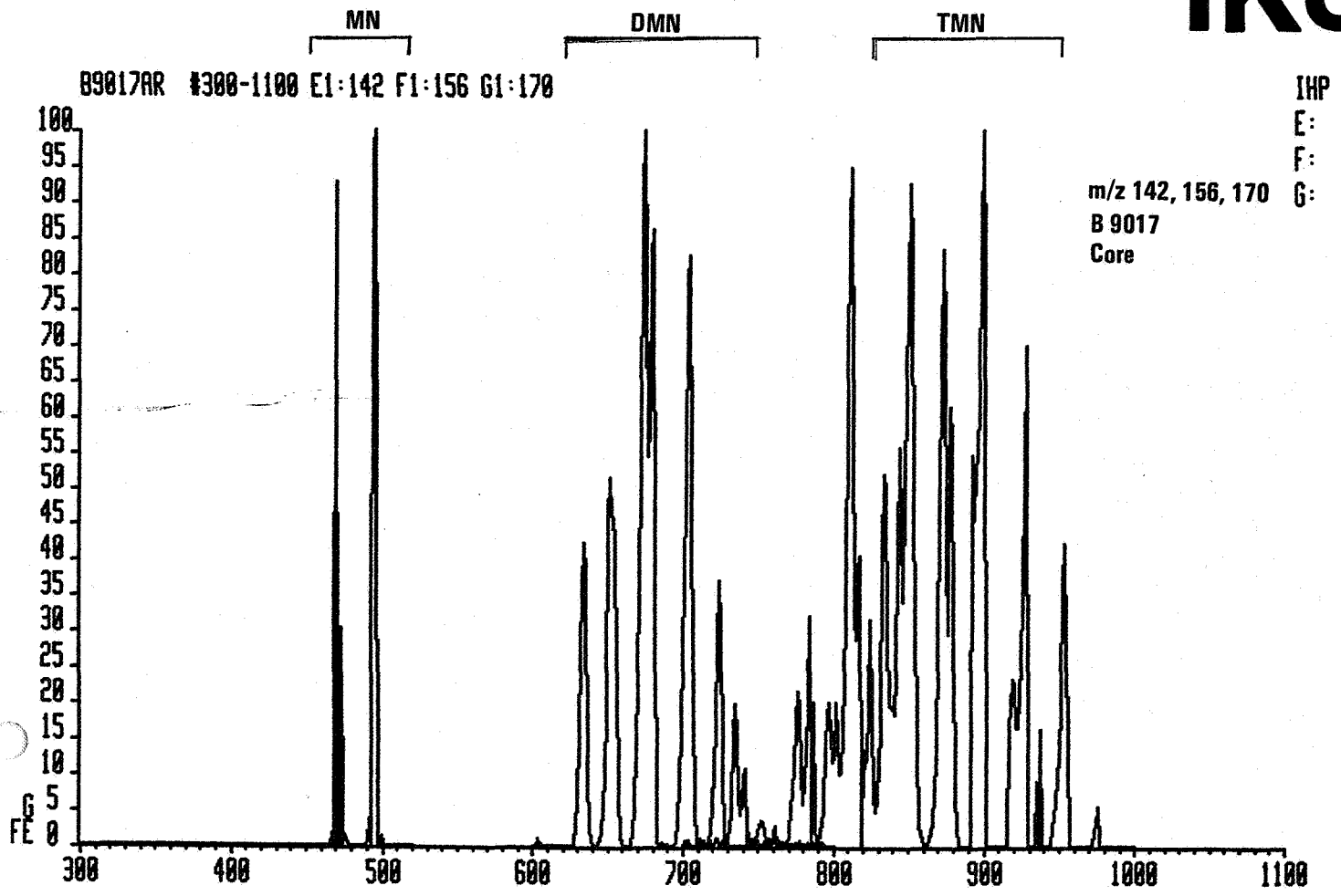

B9018AR #1-3000 D1:106
m/z 106
B 9018
Core
IHP
D:
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
D 0
500
1000
1500
2000
2500
3000

IKU


MN
DMN
TMN
B9015AR #300-1100 E1:142 F1:156 G1:170
IHP
E: 1
F: 1
G:
m/z 142, 156, 170
B 9015
Core
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
G
FE
300
400
500
600
700
800
900
1000
1100


MN
DMN
TMN
B9016AR #300-1100 E1:142 F1:156 G1:170
m/z 142, 156, 170
B 9016
Core
IHP
E:
F:
G:
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
G
FE
300
400
500
600
700
800
900
1000
1100

IKU


MN
DMN
TMN
B9017AR #300-1100 E1:142 F1:156 G1:170
IHP
E:
F:
G:
m/z 142, 156, 170
B 9017
Core
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
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FE
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1000
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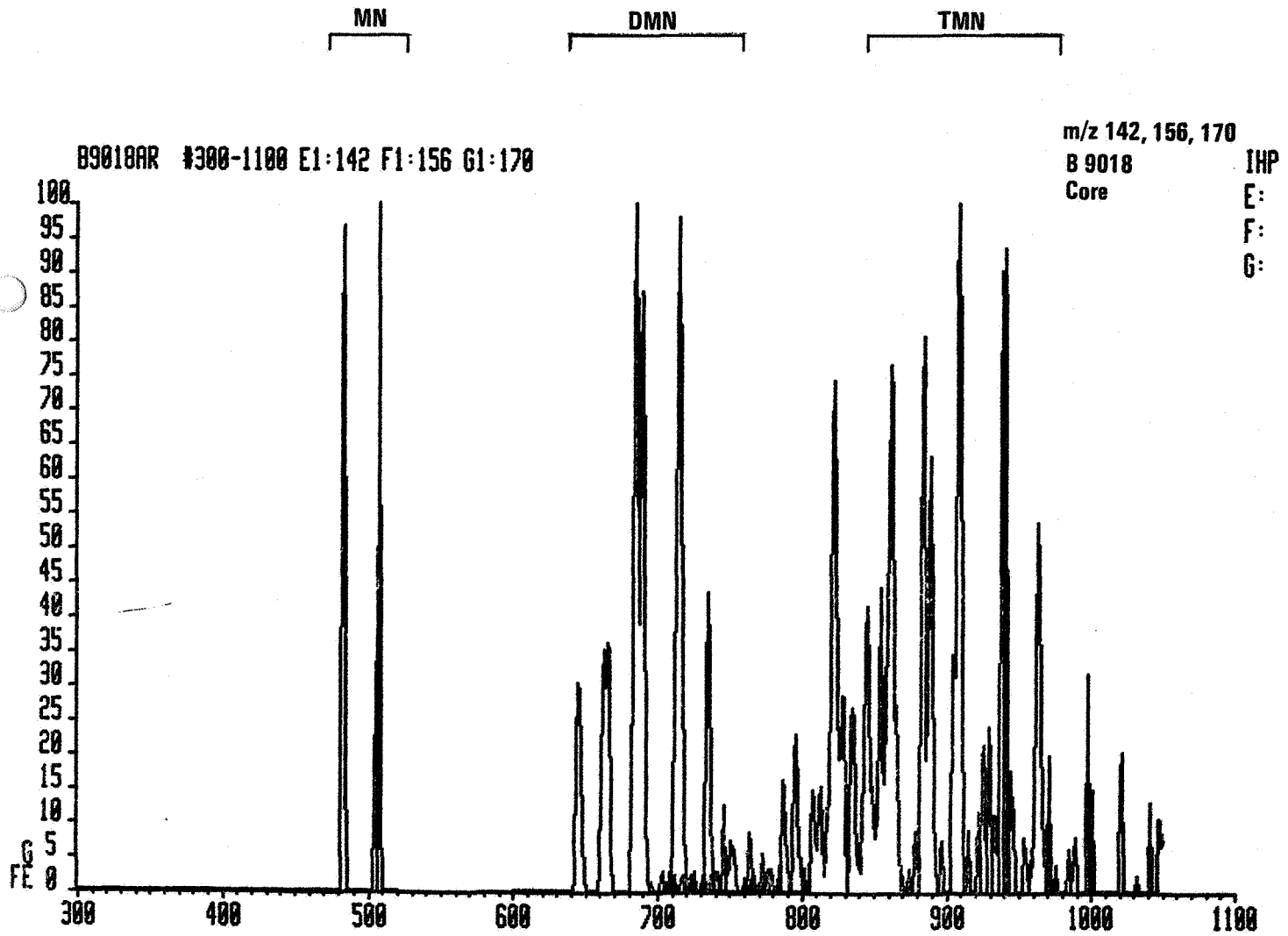
MN
DMN
TMN
m/z 142, 156, 170
B 9018
Core
IHP
E:
F:
G:
B9018AR #300-1100 E1:142 F1:156 G1:170
100
95
90
85
80
75
70
65
60
55
50
45
40
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15
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G
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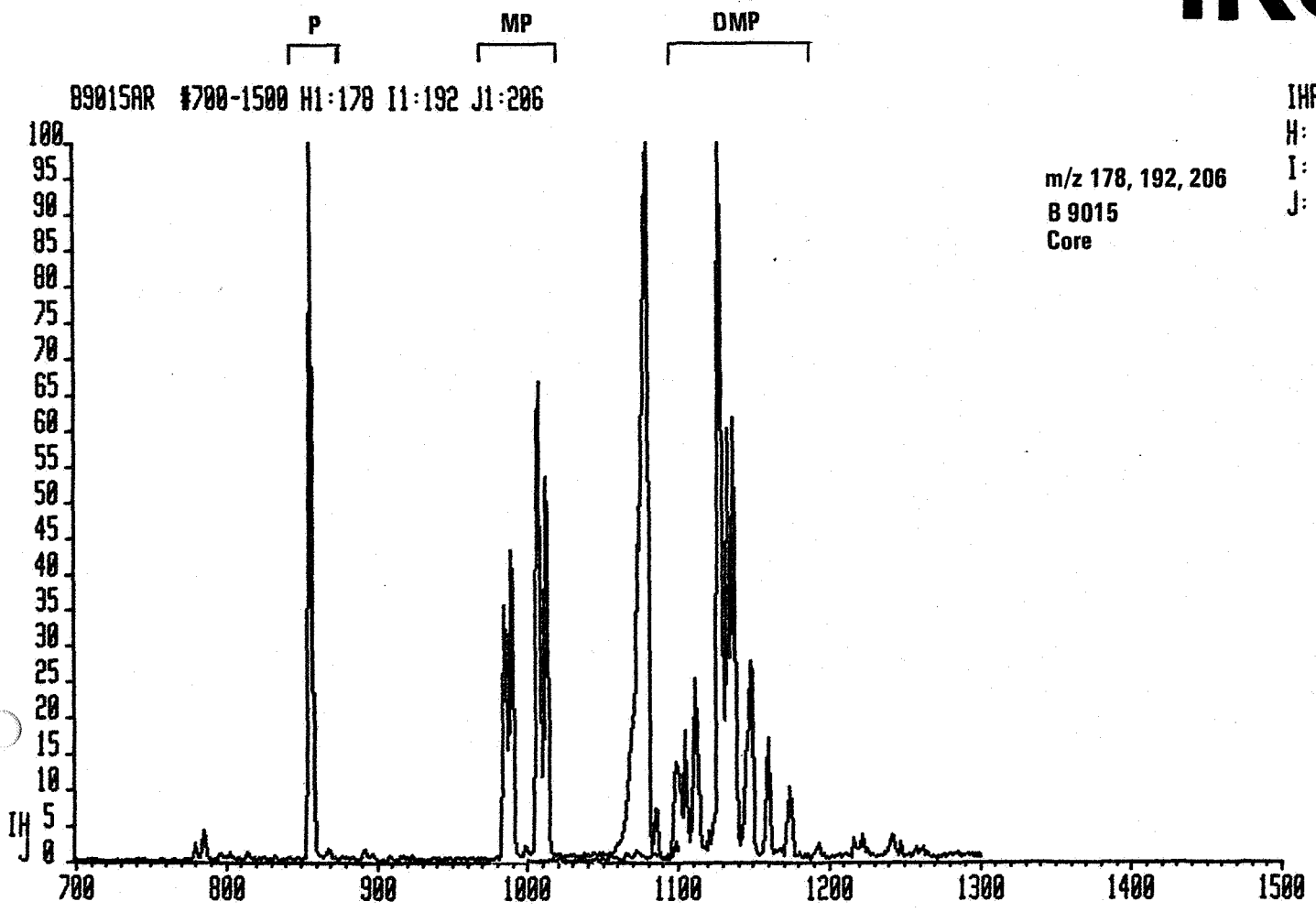
1100

IKU


P
MP
DMP
B9015AR #700-1500 H1:178 I1:192 J1:206
IHP
H: 4
I: 3
J: 1
m/z 178, 192, 206
B 9015
Core
IHJ
100
95
90
85
80
75
70
65
60
55
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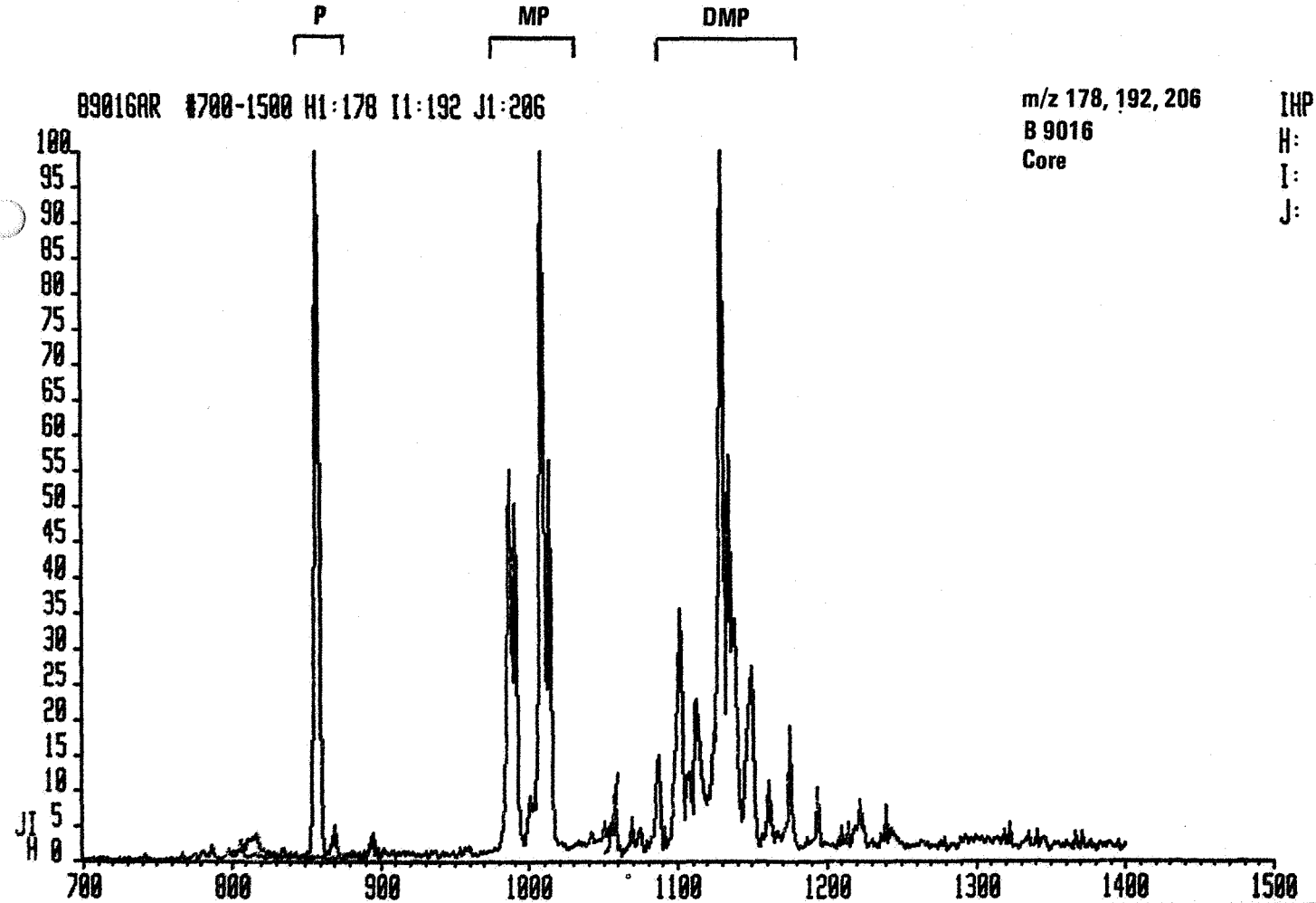
P
MP
DMP
B9016AR #700-1500 H1:178 I1:192 J1:206
m/z 178, 192, 206
B 9016
Core
IHP
H: 4
I: 1
J:
JIH
100
95
90
85
80
75
70
65
60
55
50
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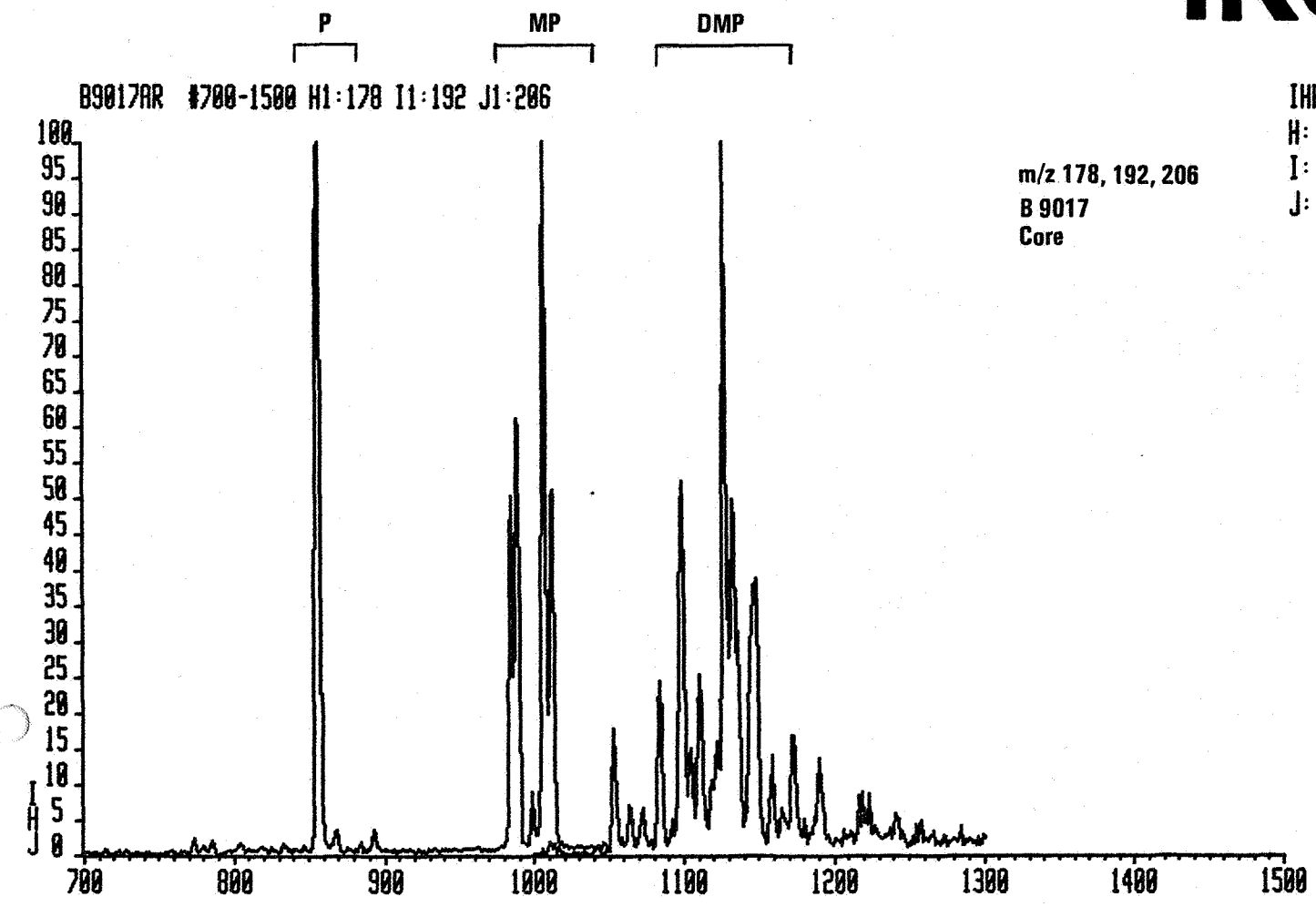
IKU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MP
DMP
B9017AR #700-1500 H1:178 I1:192 J1:206
IHP
H: 6
I: 3
J:
m/z 178, 192, 206
B 9017
Core
100
95
90
85
80
75
70
65
60
55
50
45
40
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5
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I
H
J
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1000
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1300
1400
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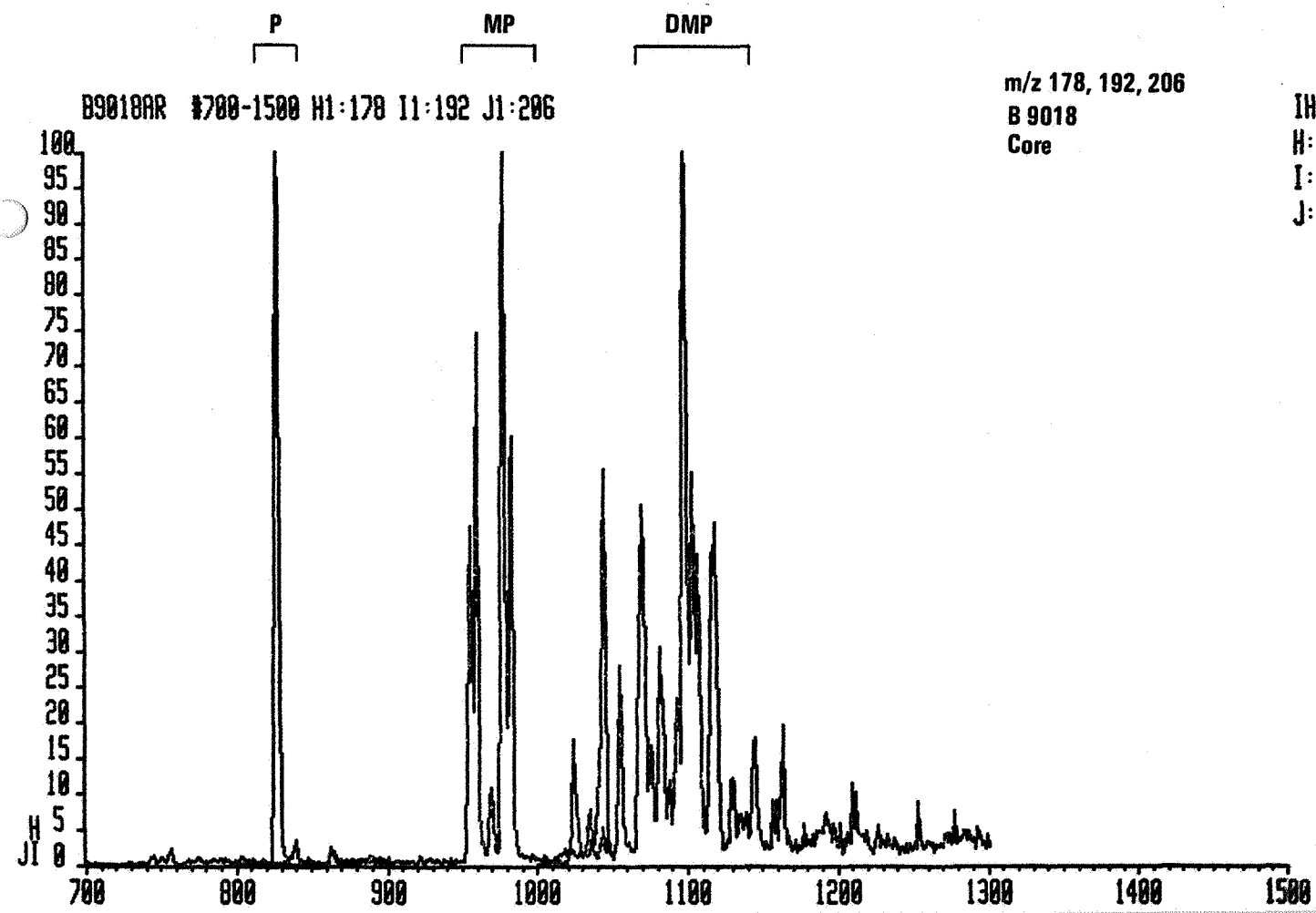
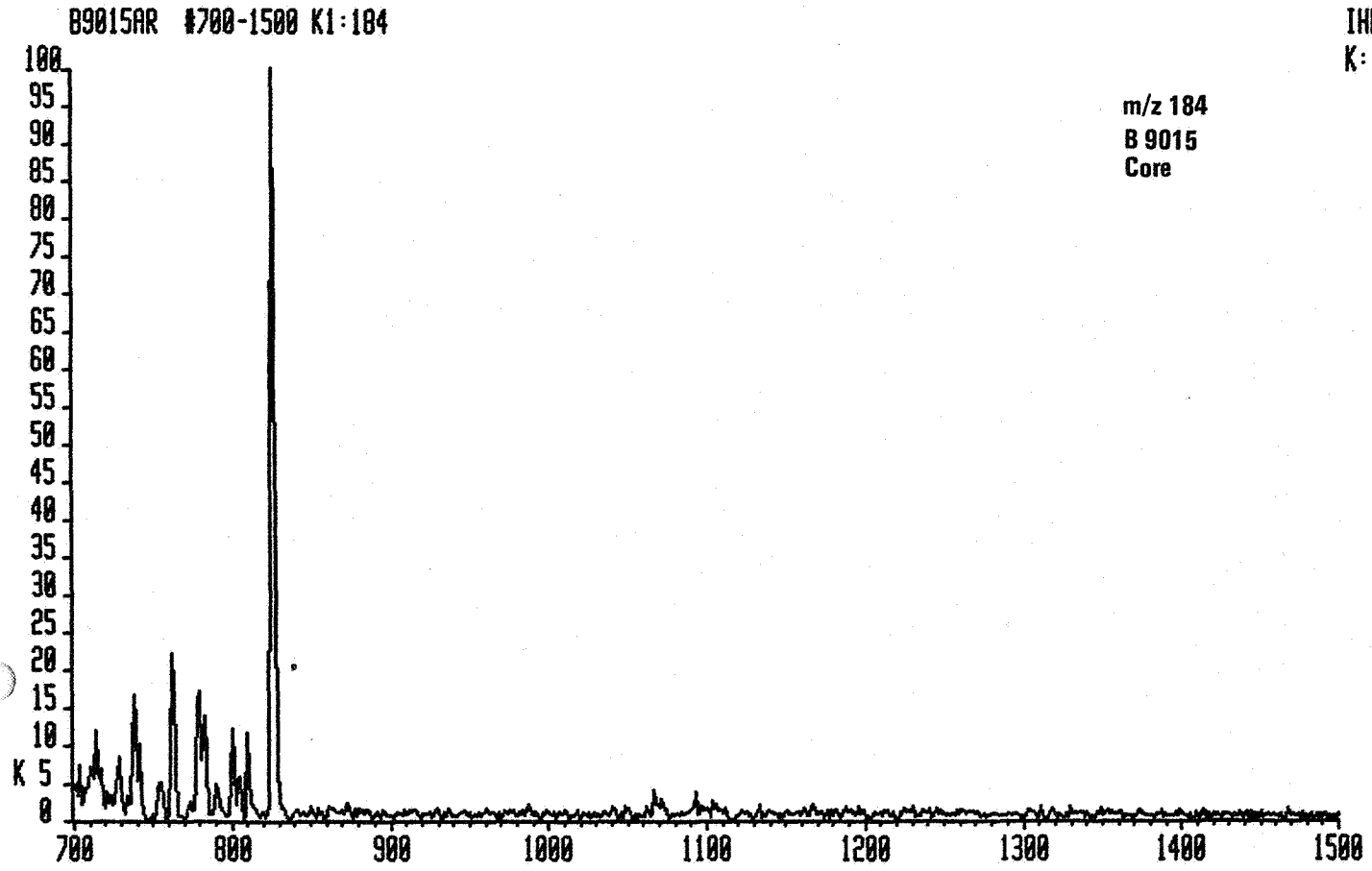

P
MP
DMP
B9018AR #700-1500 H1:178 I1:192 J1:206
m/z 178, 192, 206
B 9018
Core
IHP
H: 6
I: 2
J:
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
H
J I
700
800
900
1000
1100
1200
1300
1400
1500

IKU


B9015AR #700-1500 K1:184
IHP
K: 1
m/z 184
B 9015
Core
K
100
95
90
85
80
75
70
65
60
55
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1400
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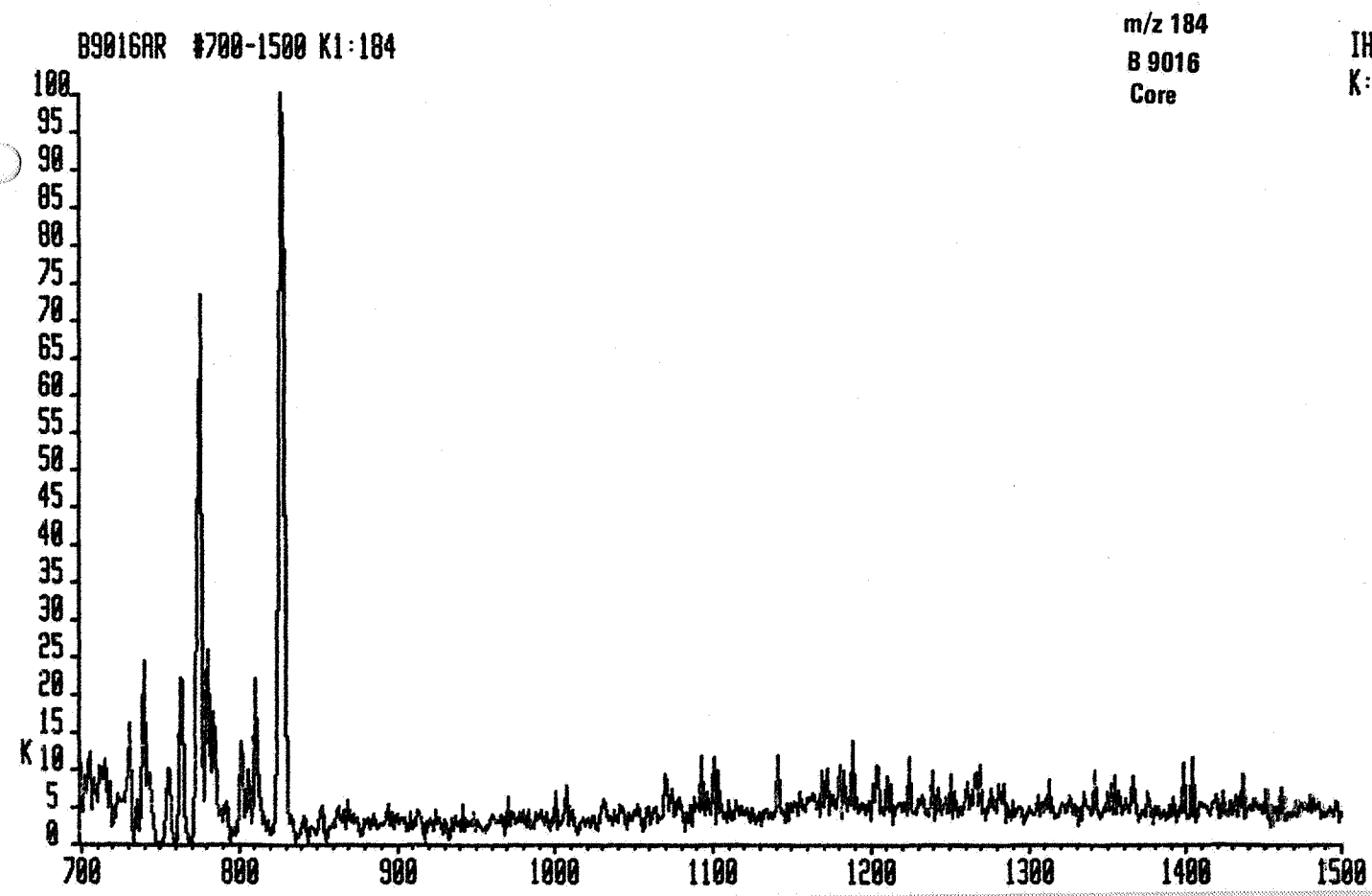
B9016AR #700-1500 K1:184
m/z 184
B 9016
Core
IHP
K:
K
100
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90
85
80
75
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60
55
50
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15
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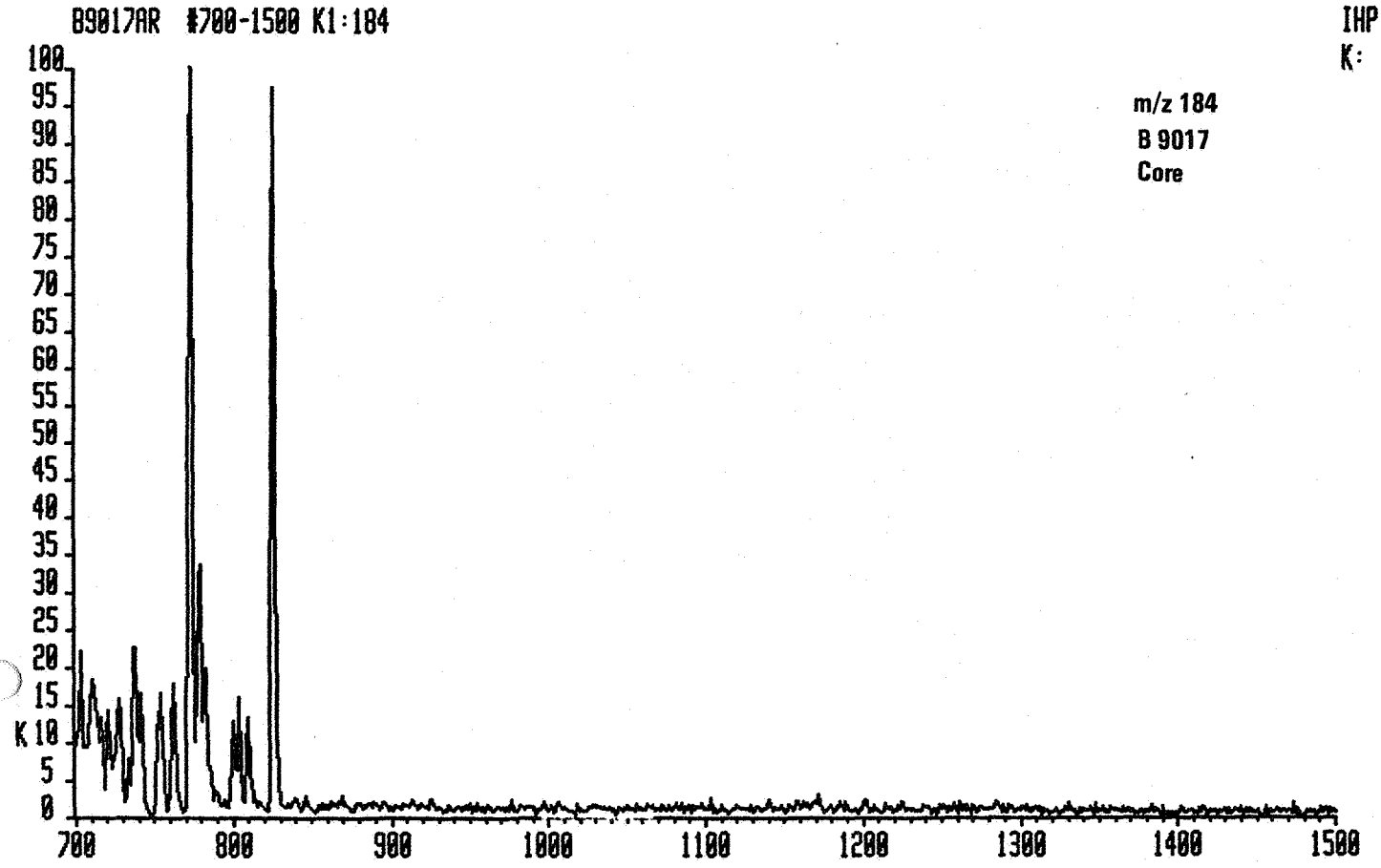
1400
1500

IKU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IHP
K: 1
m/z 184
B 9017
Core
100
95
90
85
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75
70
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60
55
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K 10
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900
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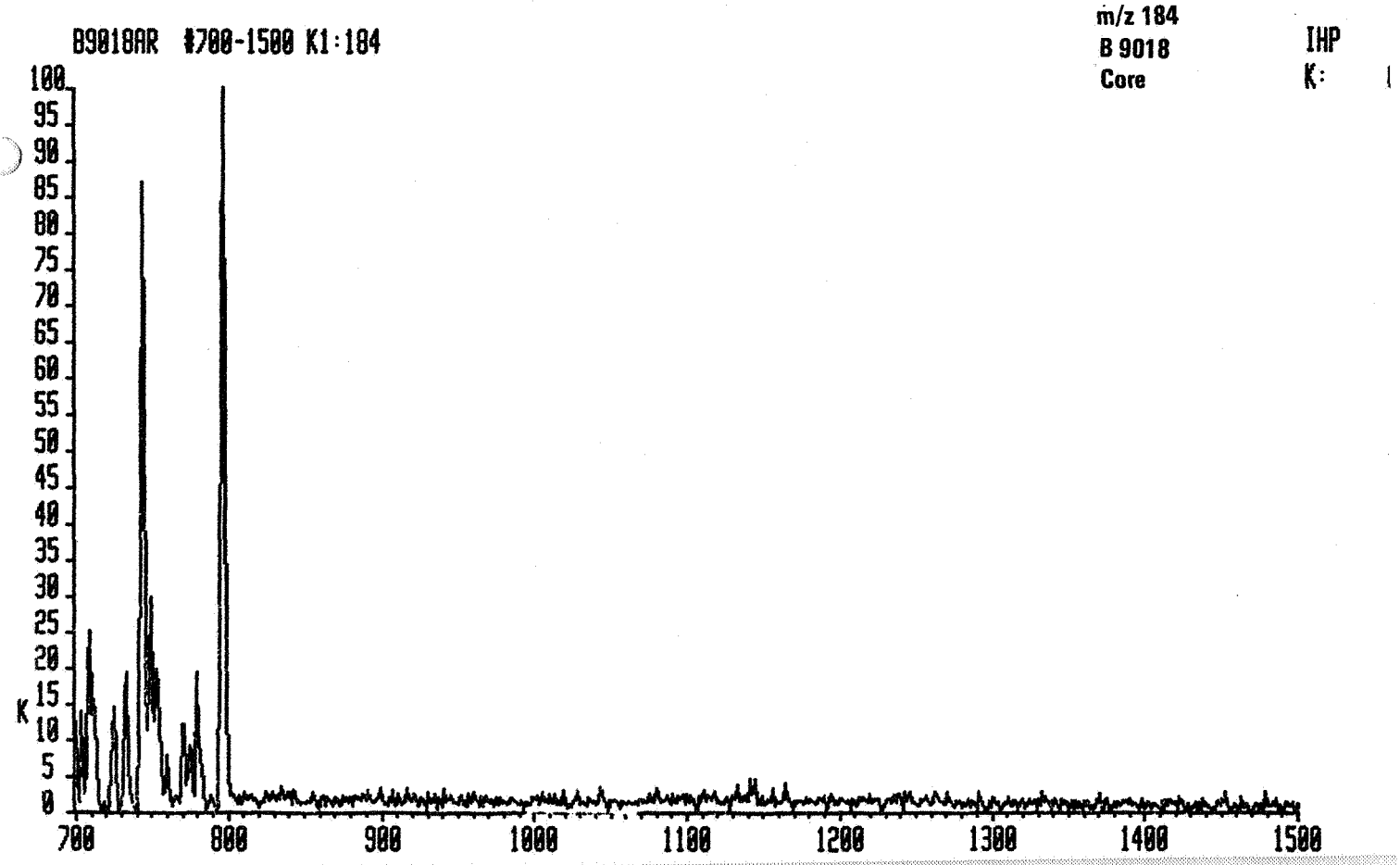
B9018AR #700-1500 K1:184
m/z 184
B 9018
Core
IHP
K:
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90
85
80
75
70
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60
55
50
45
40
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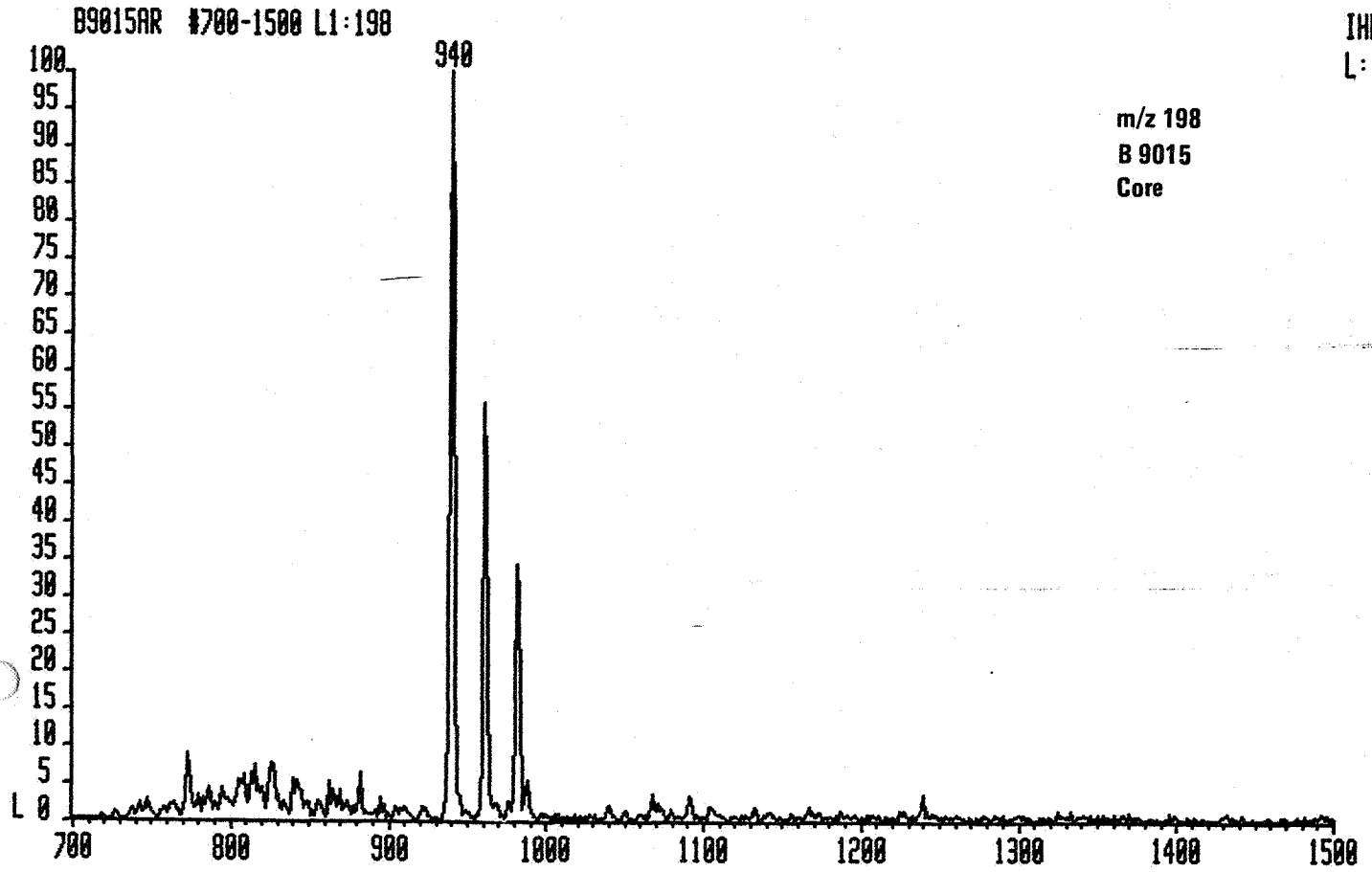
25
20
15
K 10
5
0
700
800
900
1000
1100
1200
1300
1400
1500

IKU


B9015AR #700-1500 L1:198
940
IHP
L: 1
m/z 198
B 9015
Core
100
95
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85
80
75
70
65
60
55
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45
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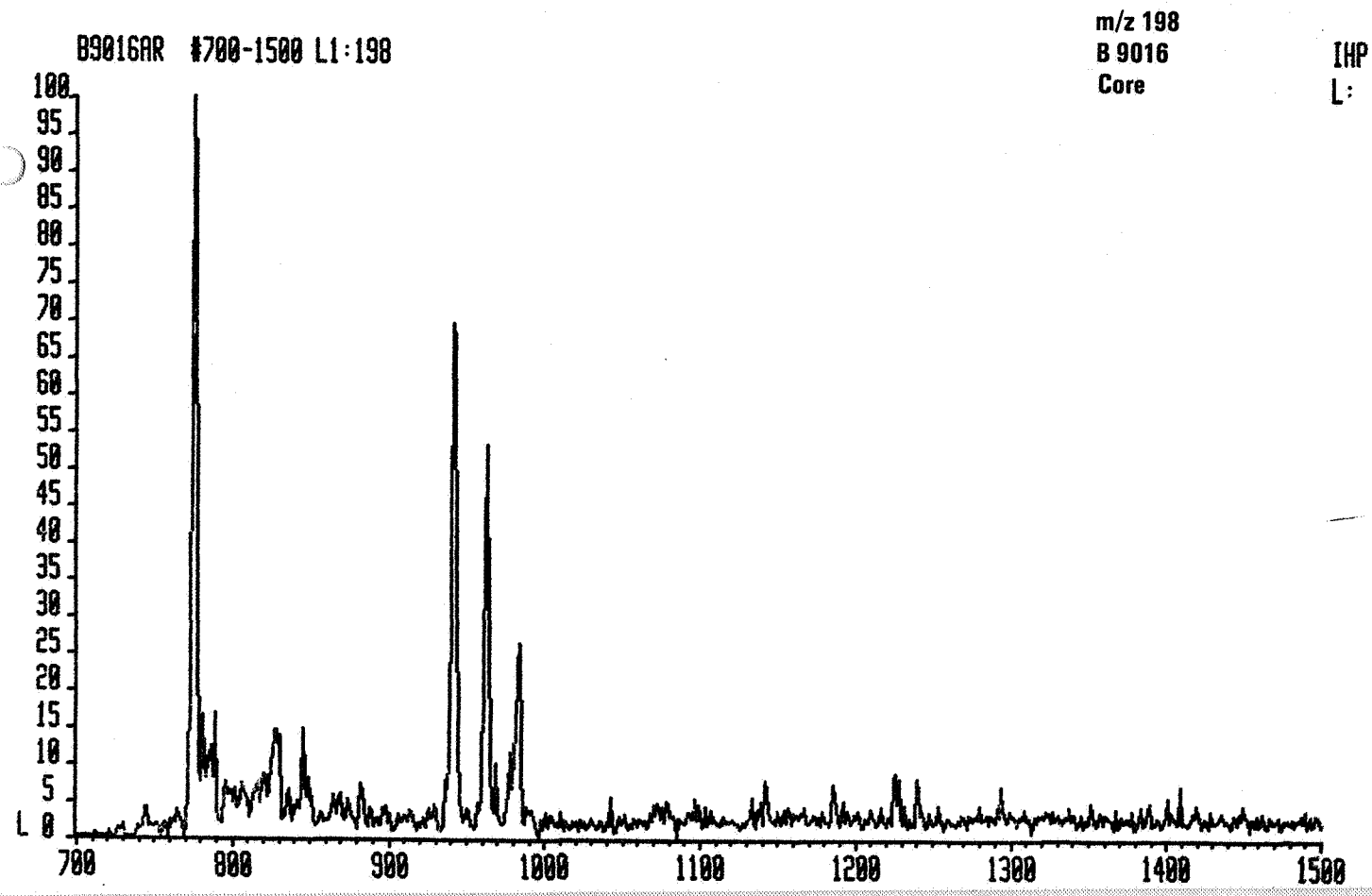
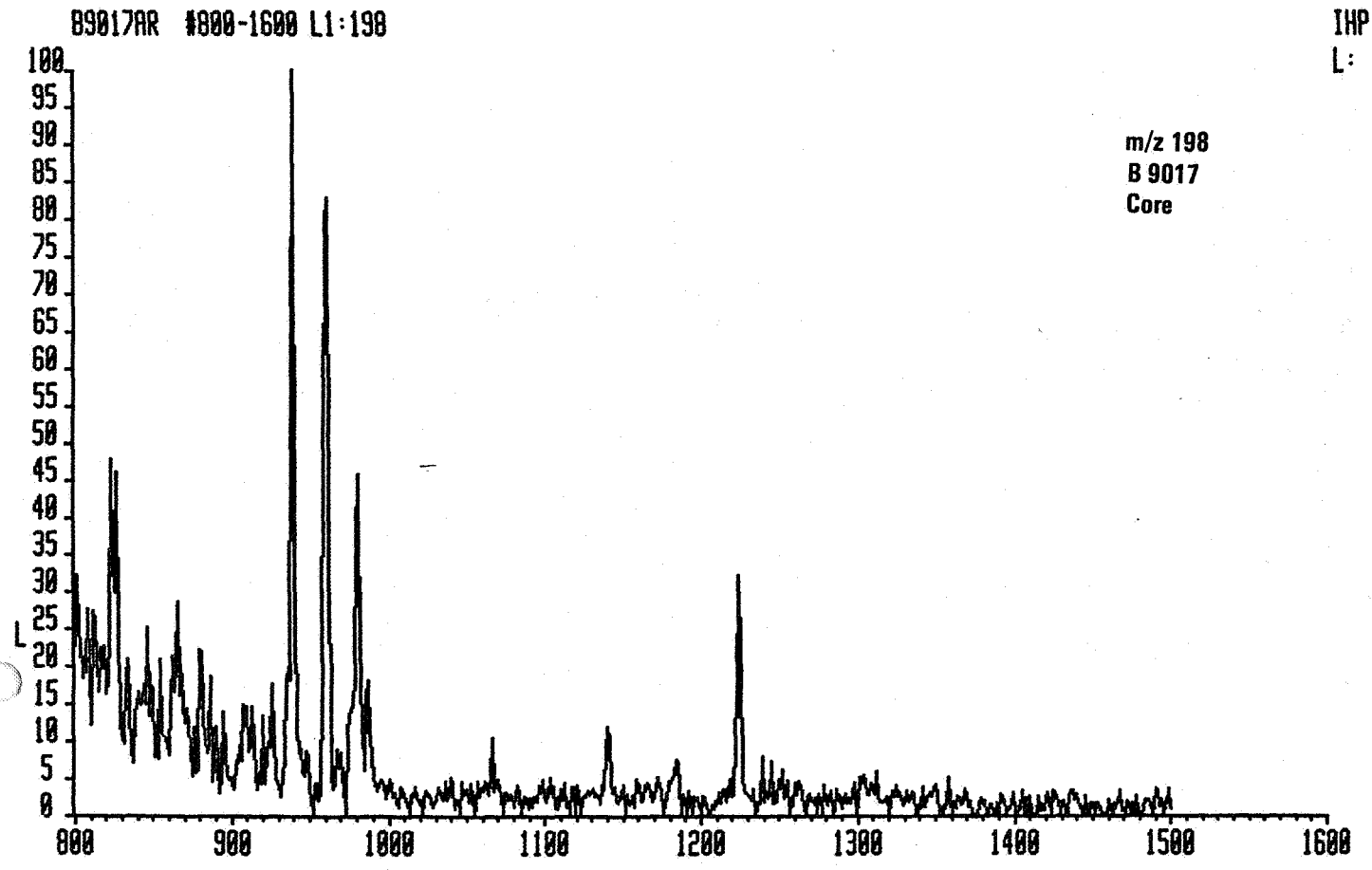
25
20
15
10
5
L 0
700
800
900
1000
1100
1200
1300
1400
1500


B9016AR #700-1500 L1:198
m/z 198
B 9016
Core
IHP
L:
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
L 0
700
800
900
1000
1100
1200
1300
1400
1500


B9017AR #800-1600 L1:198
IHP
L:
m/z 198
B 9017
Core
L
100
95
90
85
80
75
70
65
60
55
50
45
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1400
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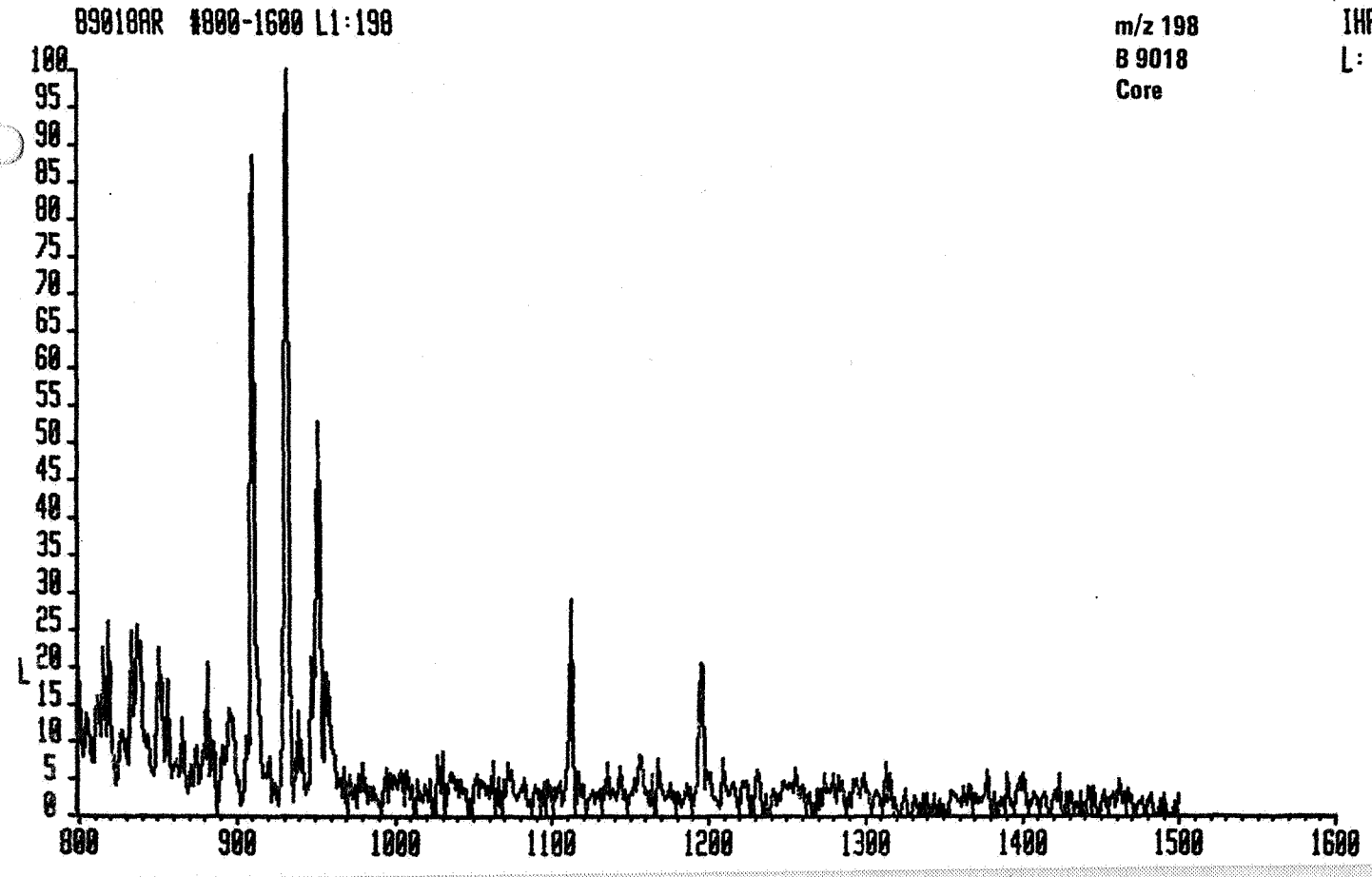
1600


B9018AR #800-1600 L1:198
m/z 198
B 9018
Core
IHP
L:
L
100
95
90
85
80
75
70
65
60
55
50
45
40
35
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20
15
10
5
0
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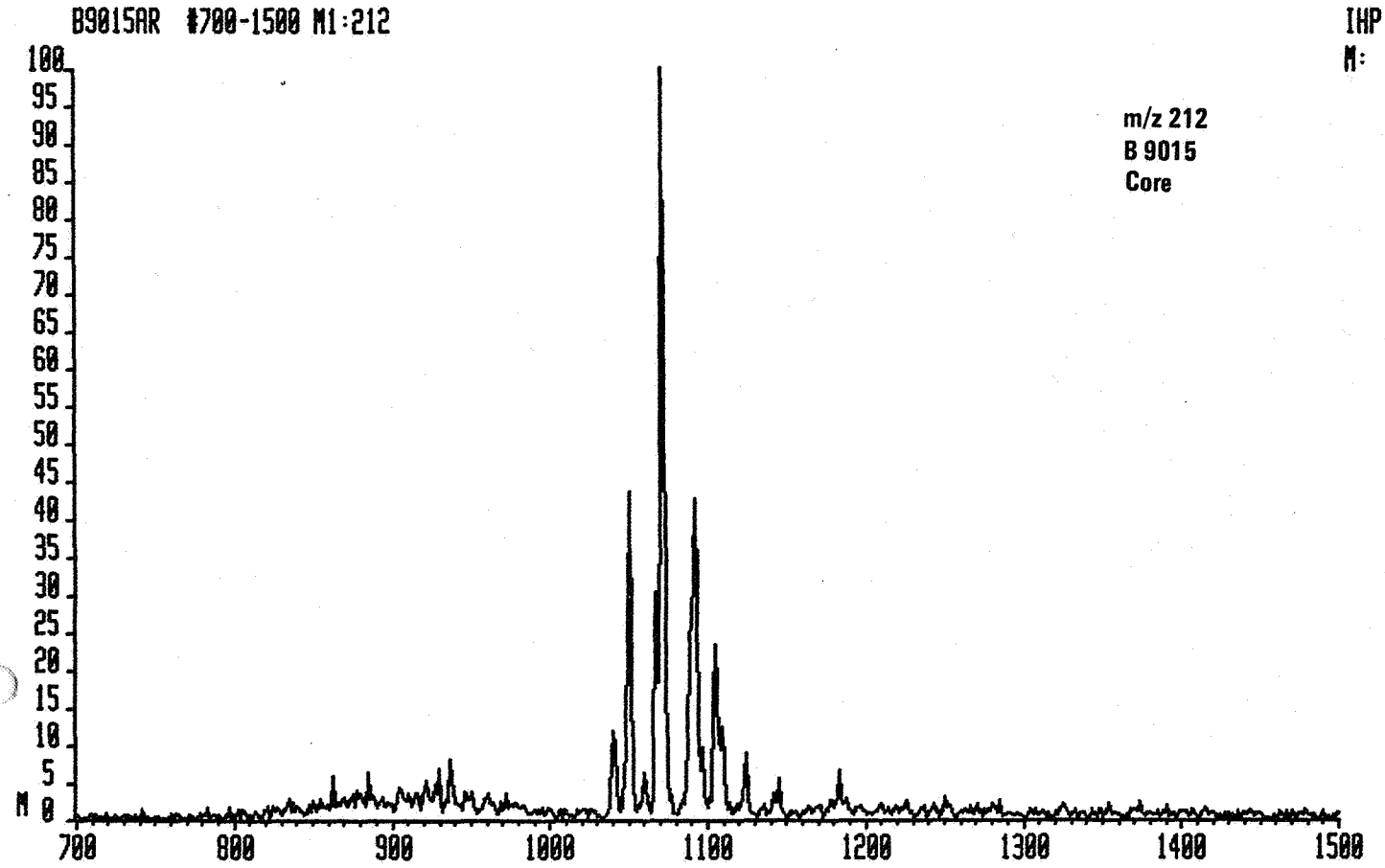
1100
1200
1300
1400
1500
1600

IKU


B9015AR #700-1500 M1:212
IHP
M:
m/z 212
B 9015
Core
100
95
90
85
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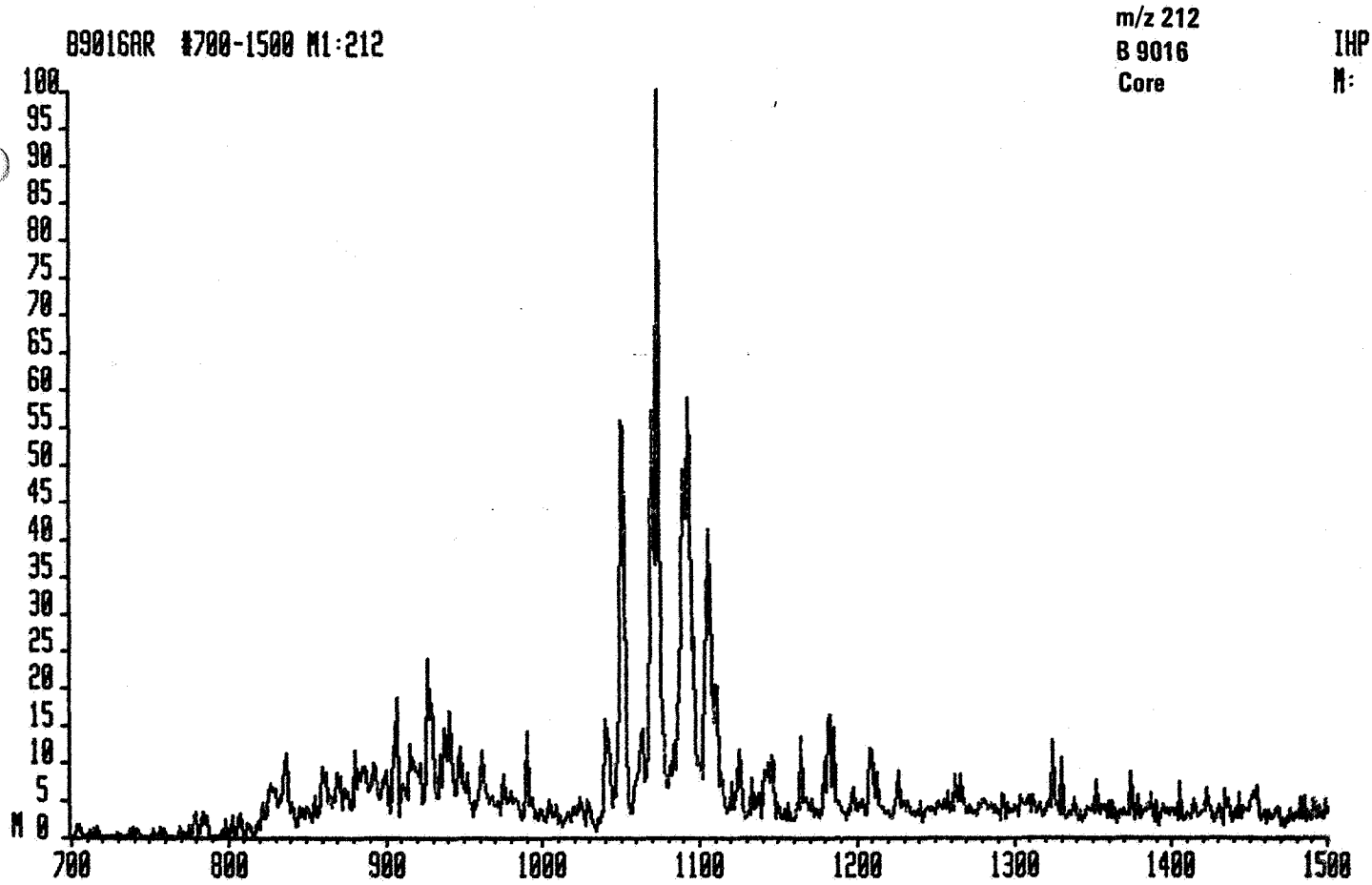
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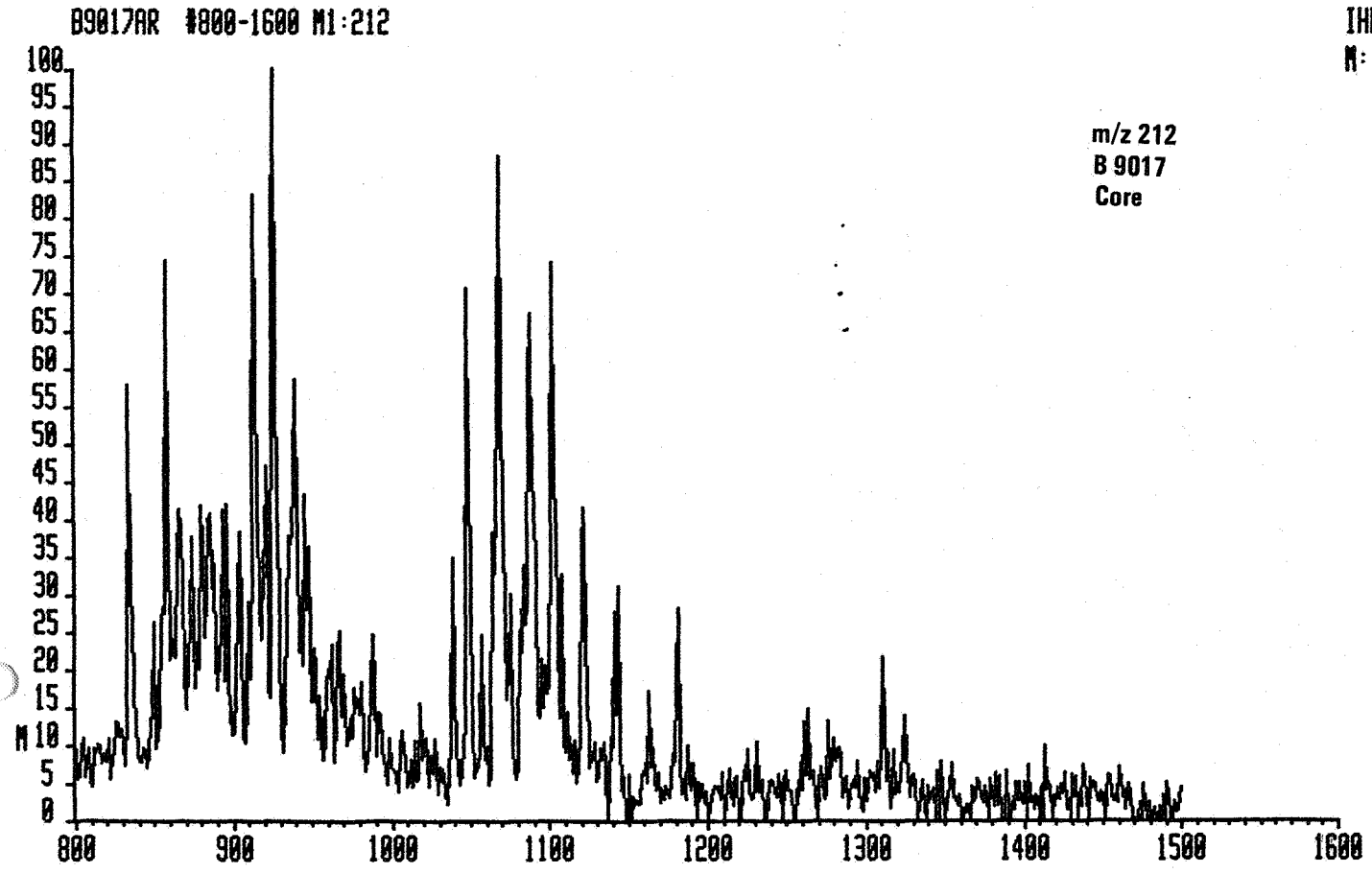
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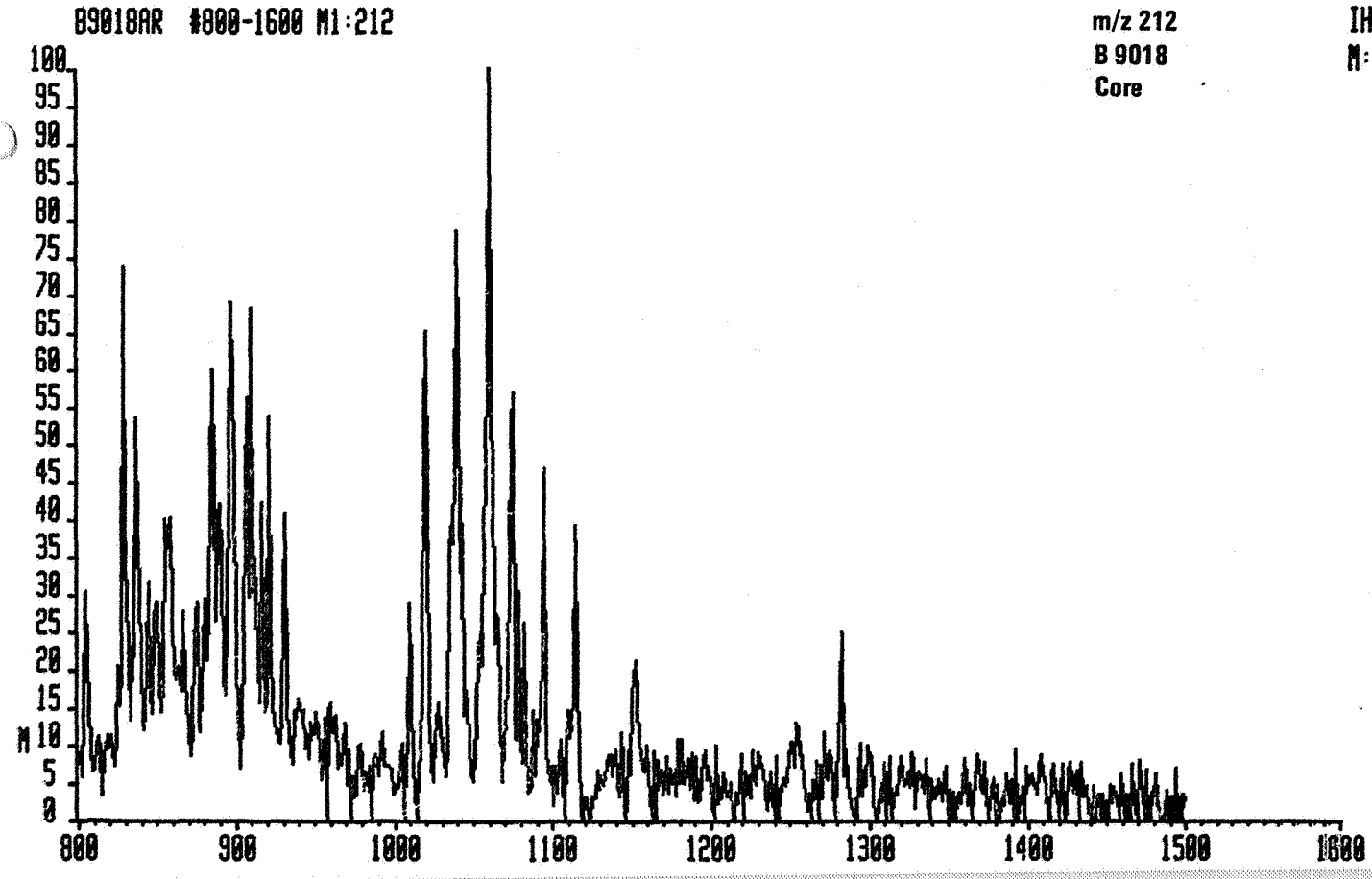
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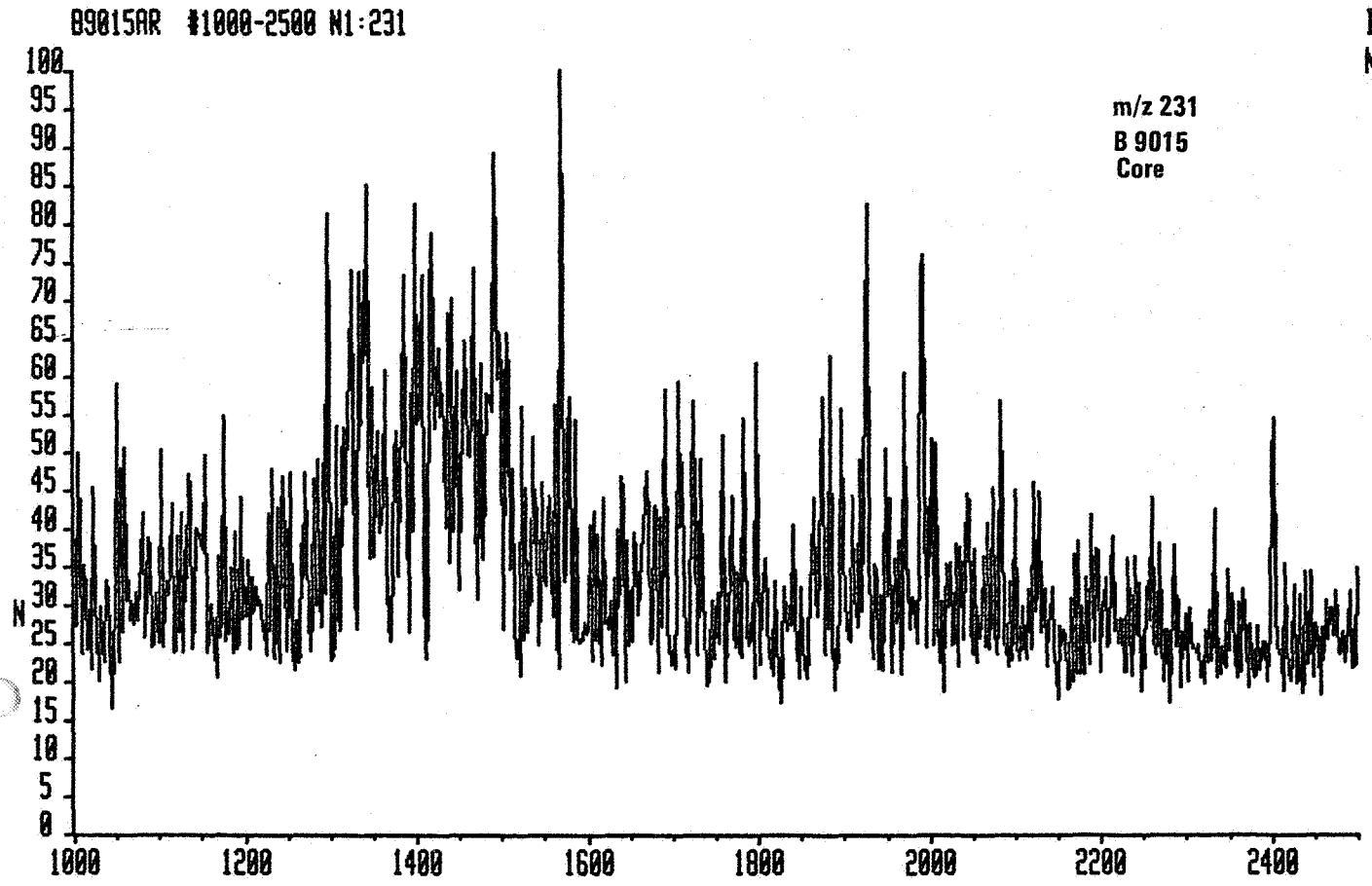
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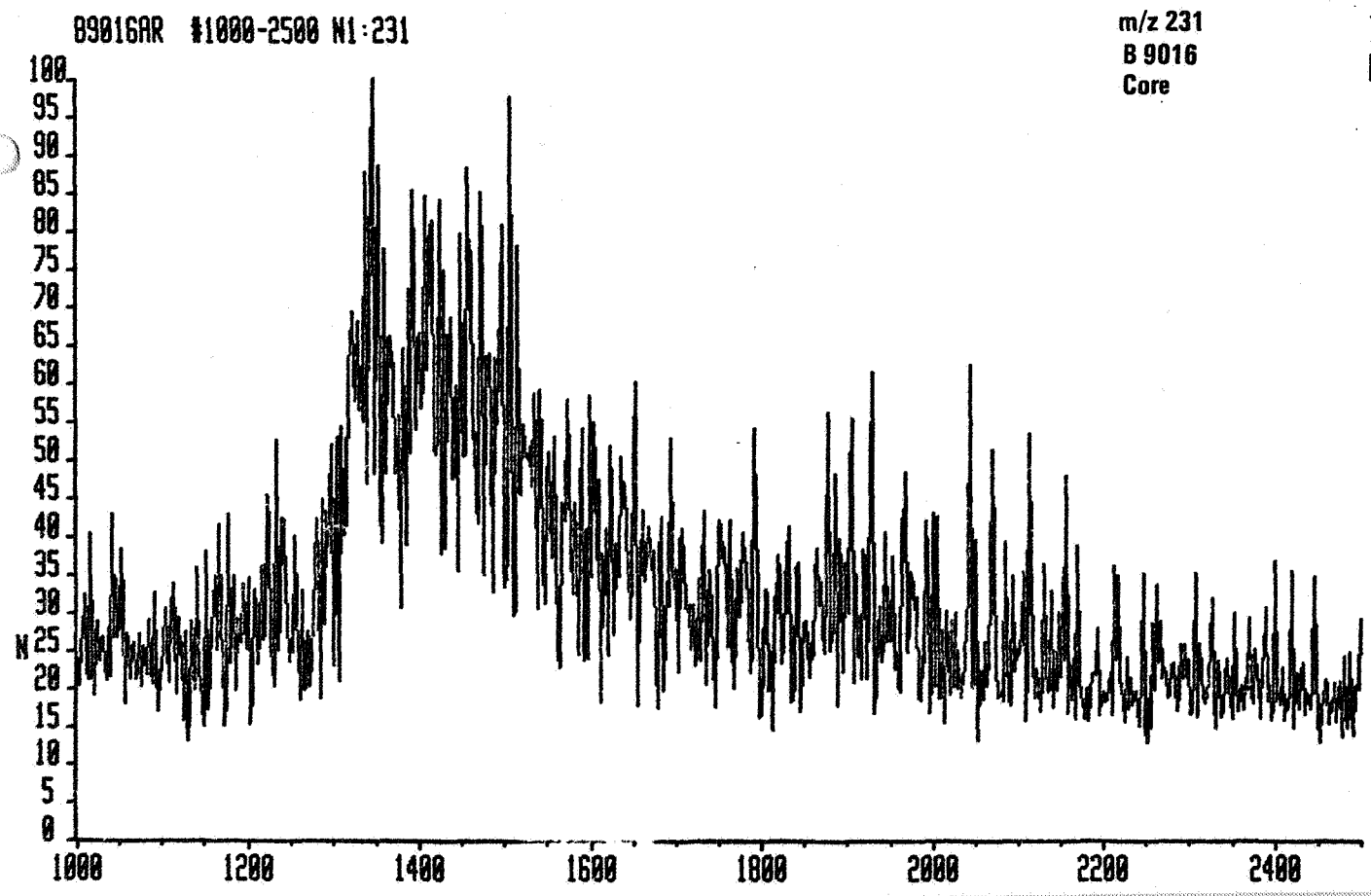
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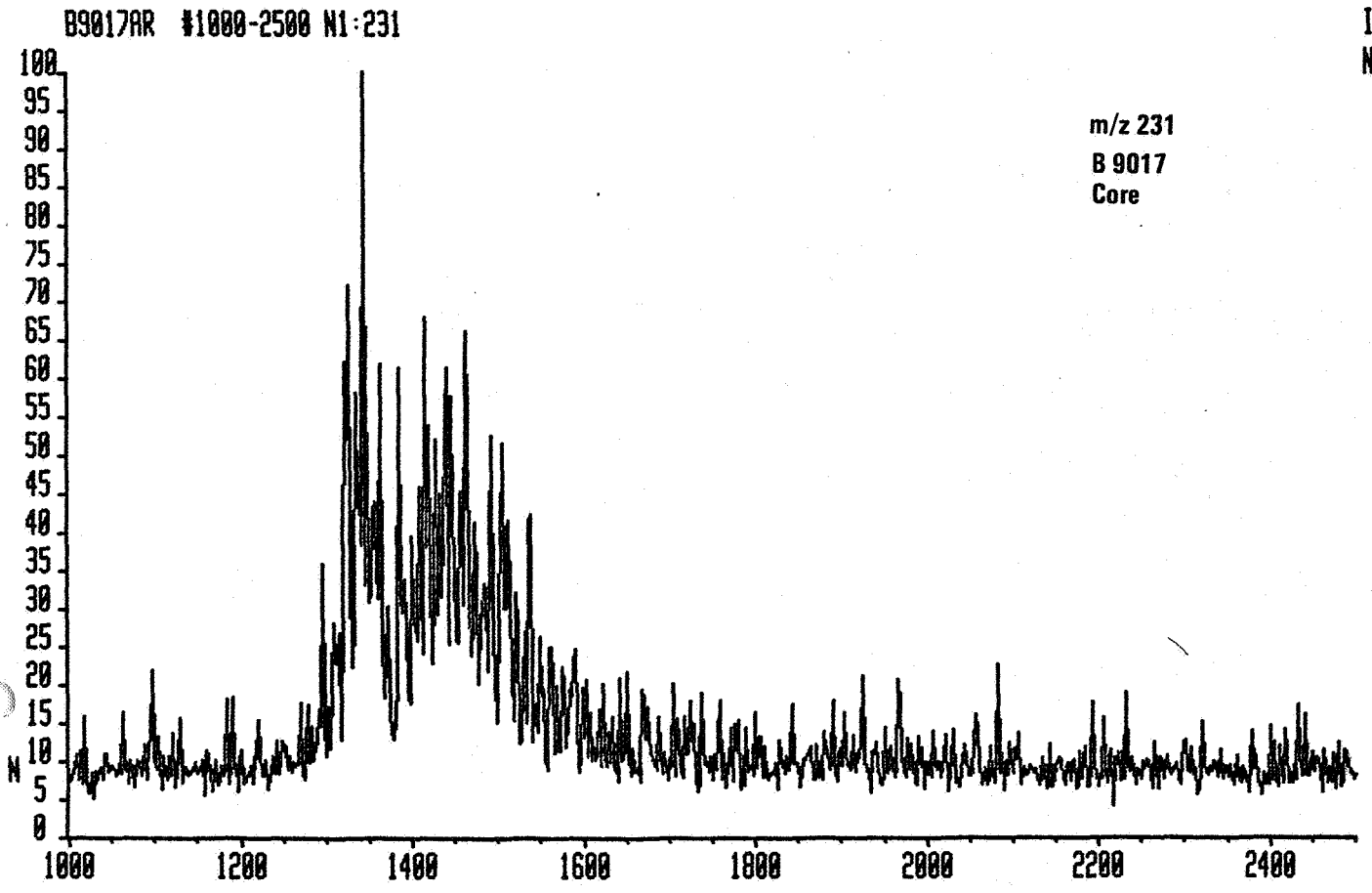
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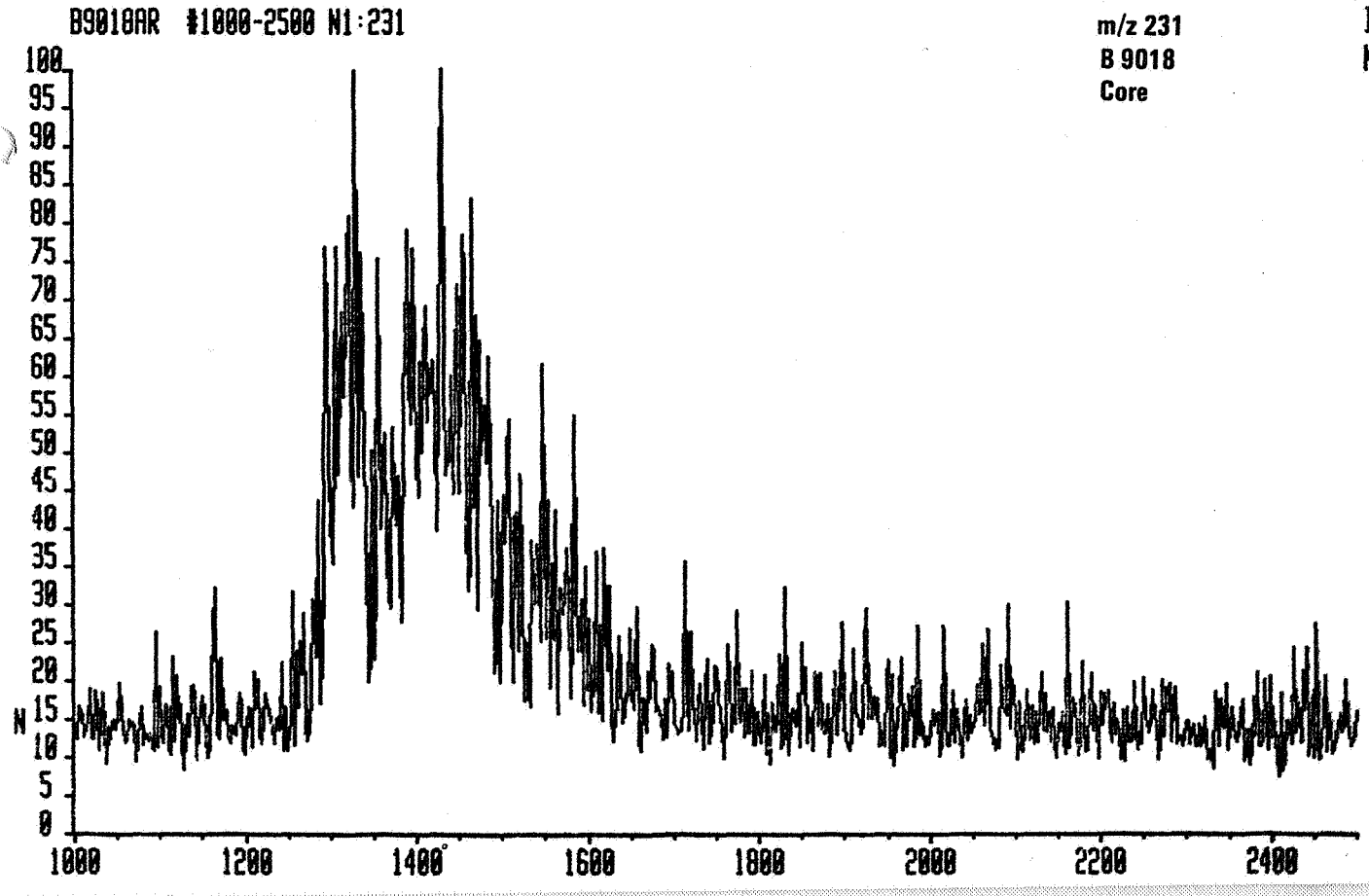
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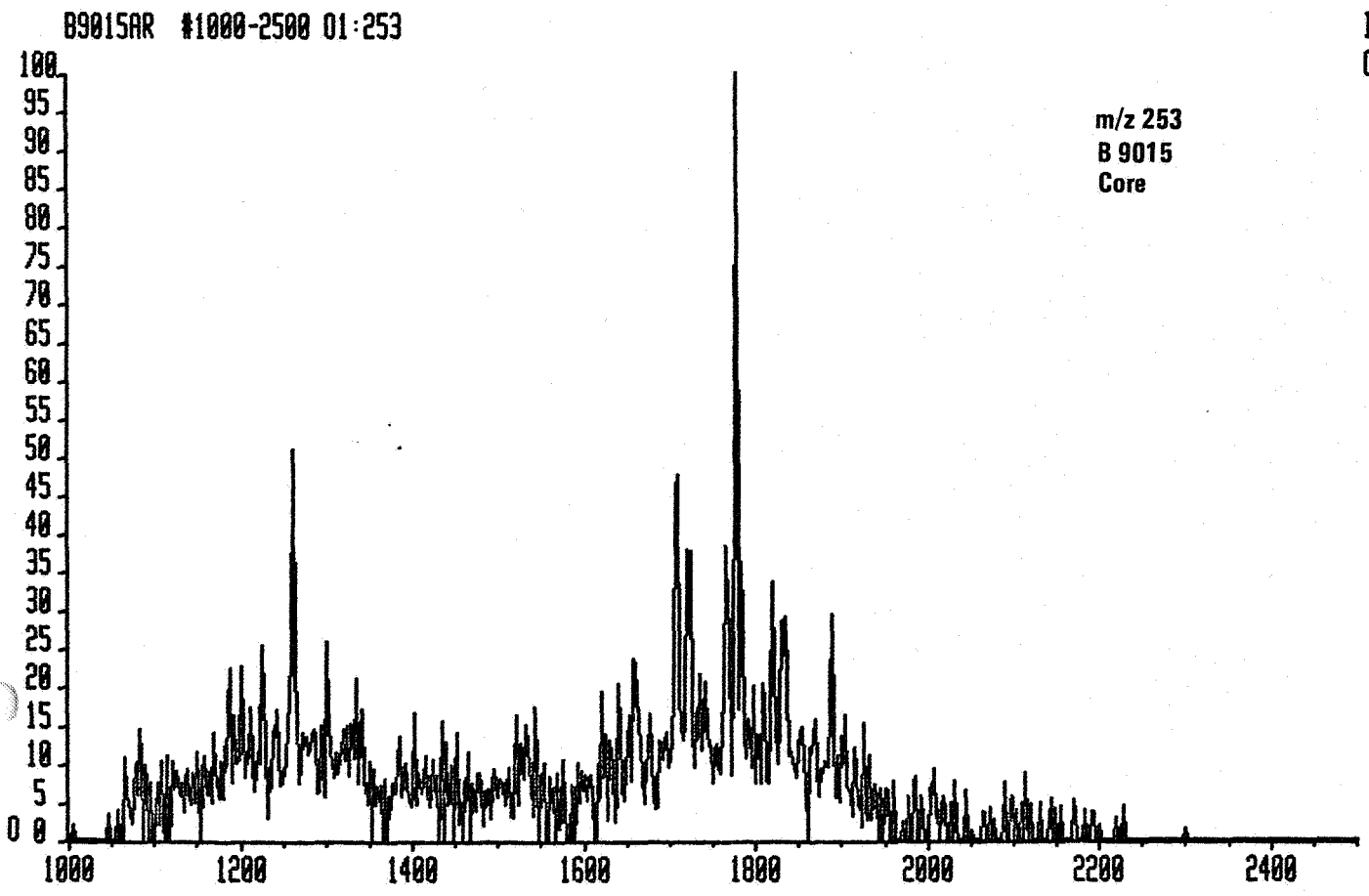
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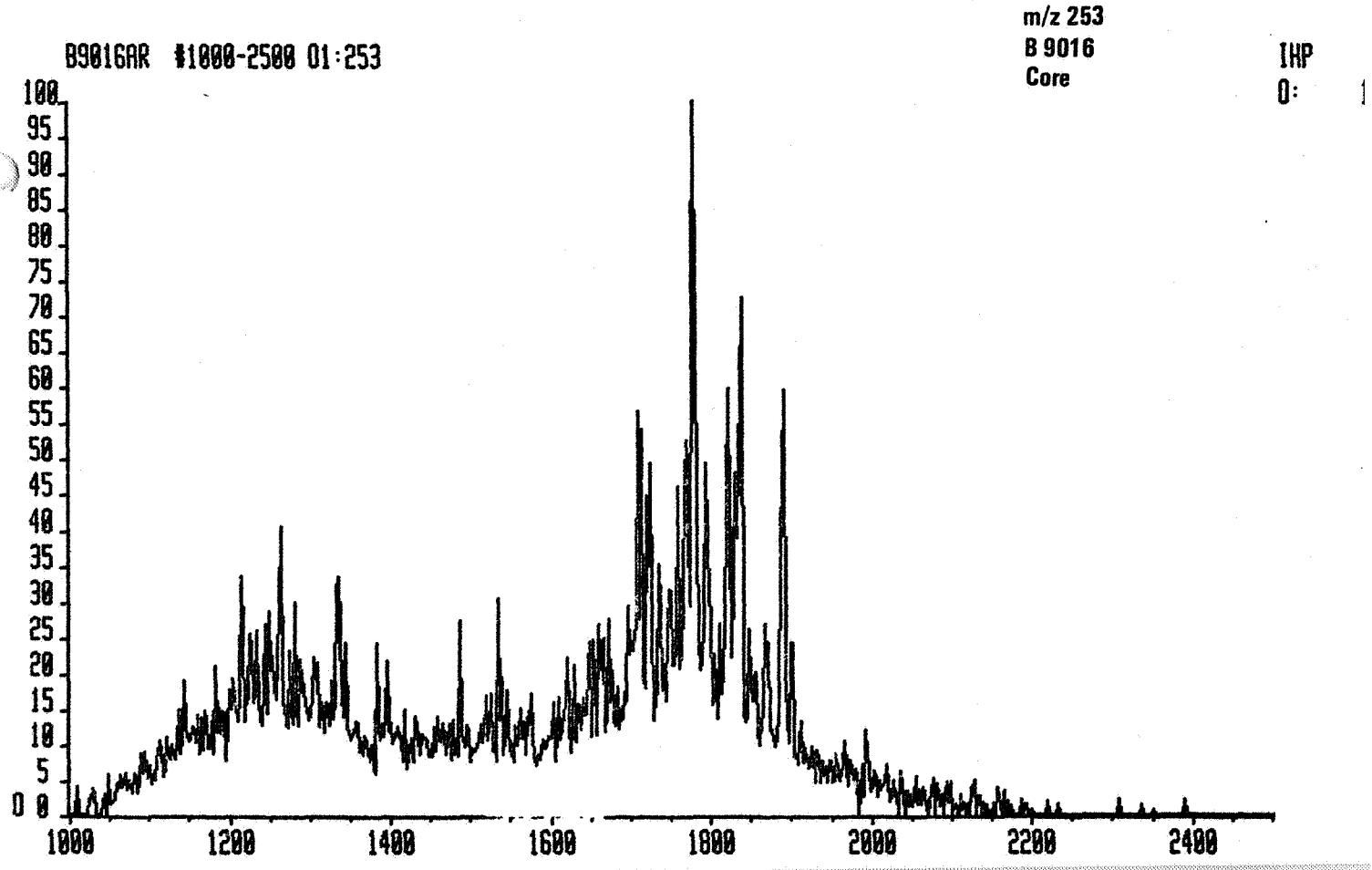
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B 9016
Core
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IHP
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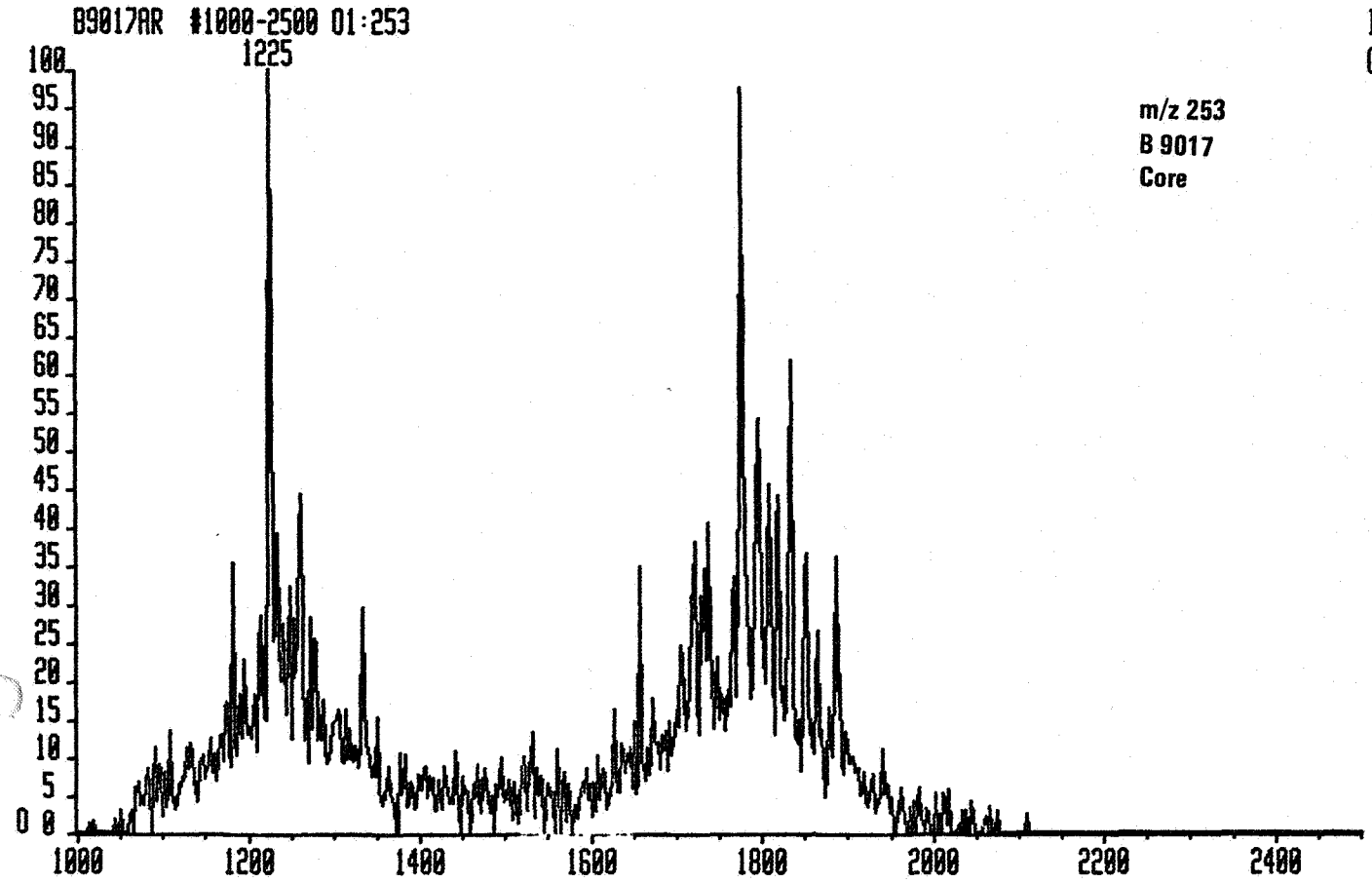
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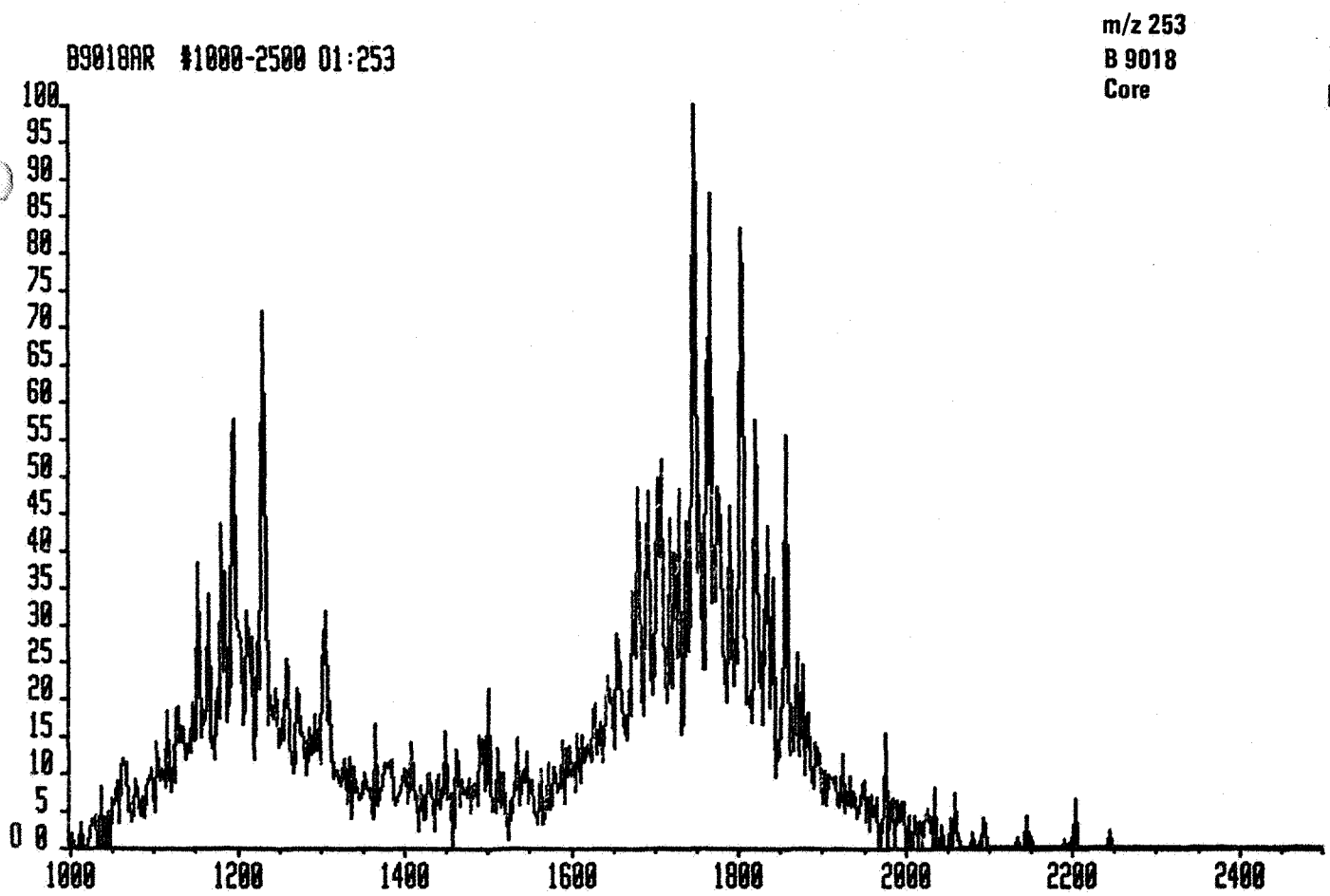
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Core
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IHP
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