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REPORT TITLE

Source rock-crude oil correlation, wells 34/10-1 and 34/10-2.

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SUMMARY

Oil from well 34/10-1 was correlated with extracts from sediments in well 34/10-1 and 2 by means of using GC-MS analyses of steranes and triterpans. No correlation were found. The oil in 34/10-1 is most probably biodegraded.

KEY WORDS

Source rock-srude oil correlation.

INTRODUCTION

The problems connected to correlation between a crude oil and its possible source rock have for several years been a subject of attention in different laboratories around the world. (Barbat 1967, Barker 1975, Dow 1974, Erdman and Morris 1974, Jackson, Judges and Powel 1975, Leythaenser et al. 1975, Marzec et al. 1971, Mathews et al. 1971, Seifert 1975, Stahl and Carey Jr. 1975, Welte 1965, 1966, 1975, Williams 1974).

Various methods such as percentage of saturates (Baker 1962) percentage of aromatic (Baker 1962, Hunt and Jamieson 1956), isoprenoid composition (Maximow et al. 1973), porphysins (Gransch and Eisma1966), optical rotation (Brennuneman and Smith 1958), Spectroscopic methods, (Hunt et al. 1954, Riecker 1962, Wiesneder 1968), light hydrocarbons, Erdman and Morris 1974, Clayton and Swetland 1977, Schaefer, Leythaeuser and Weiner 1978 and isotopic ratios, Stahl 1978. Lately, steranes and triterpanes have been used more and more, and they have shown to be very effective, almost the only method useable if the oil have been biodegraded. (Leythaeuser et al. 1975, Seifert 1975, 1978, Hills & Whitehead 1966, Whitehead 1973, Pym et al. 1975, Huang and Meinschein 1976, Dorsselaer & Albrecht 1976, Seifert and Moldowan 1978, 1979).

The preliminary examination of the oil from well 34/10l showed this to contain almost no n-alkanes. This could have been caused by a slight biodegradation of the oil or that the oil was an early condensate from an algal source. The ratio of the iso/n-alkanes in the light fraction indicated the latter, i.e. immature oil. The large unresolved envelope in the gas chromatograms, found for most biodegraded oils was not seen. This made us believe the oil to be immature, but we would not rule out the possibility of the oil being slightly biodegraded before a GC-MS analyses of the sterane/ triterpane fraction together with a carbon isotope study were undertaken. The carbon isotope study will be done by another laboratory and will not be included in this report.

Together with the oilsample from well 34/10-1, five rock extracts from well 34/10-1 and six from well 34/10-2 were analysed to try to find a possible source for the oil.

Before we discuss the various results in details, we would, since this is a new tool for some companies, discuss the various parametres examined in detail.

Normally, the most mature oil posess the largest quantity of saturates. This sequence of increasing saturate yield with increasing maturity is paralleled by a step-wise decrease of the absolute concentration of tri- and pentacyclic triterpanes. By using this rule, Seifert and Moldowan (1978), found additional parametres which can be used in maturation study. Amongst these are the ratio between 18α (H)-22, 29, 30 -Trisnorhopane II (T_s) and 17α (H)-22, 29, 30 - Trisnorhopane (T_m) where T_ss is stable and T_mm is maturable. Another parameter is the ratio between $\Sigma C_{29} + C_{30}$ and $\Sigma C_{27} + C_{28}$. (See Table 1 and Fig. 1 for names of the compounds.)

Table 1 Structural assignments from triterpane mass fragmentograms[a]

Compound No. from Figure 2	Formula	Assignment	Carbon Skeleton II	Assignment Based on
1 (Ts)	$C_{27}H_{46}$	18α(H)-22,29,30-Trisnorhopane II	Structure I	Coinjection[b]
2 (Tm)	$C_{27}H_{46}$	17α(H)-22,29,30-Trisnorhopane	R_1 = H, R_2 = H	Authentic Standard
3	$C_{28}H_{46}$	Pentacyclic Triterpane		MAP
4	$C_{29}H_{50}$	17α(H),21β(H)-30-Norhopane	R_1 = H, R_2 = C_2H_5	Authentic Standard
5	$C_{30}H_{52}$	17α(H),21β(H)-Hopane	R_1 = H, R_2 = iC_3H_7	Authentic Standard
6	$C_{31}H_{54}$	22S- and 22R-17α(H),21β(H)-30-Homohopane	R_1 = H, R_2 = iC_4H_9 (S and R)	Authentic Standard
7	$C_{32}H_{56}$	22S- and 22R-17α(H),21β(H)-30,31-Bishomohopane	R_1 = H, R_2 = iC_5H_{11} (S and R)	MAP[c]
8	$C_{33}H_{58}$	22S- and 22R-17α(H),21β(H)-30,31,32-Trishomohopane	R_1 = H, R_2 = iC_6H_{13} (S and R)	MAP[c]
9	$C_{34}H_{60}$	22S- and 22R-17α(H),21β(H)-30,31,32,33-Tetrakishomohopane	R_1 = H, R_2 = iC_7H_{15} (S and R)	MAP[c]

[a] Cf. Fig. 2.
[b] With Nigerian triterpane concentrate (Hills and Whitehead, 1966).
[c] Recognition of the 22R and 22S stereochemistry is based on Ensminger *et al.* (1973) and Rohmer and Ourisson (1976b,c).

(From Seifert & Moldowan, 1978)

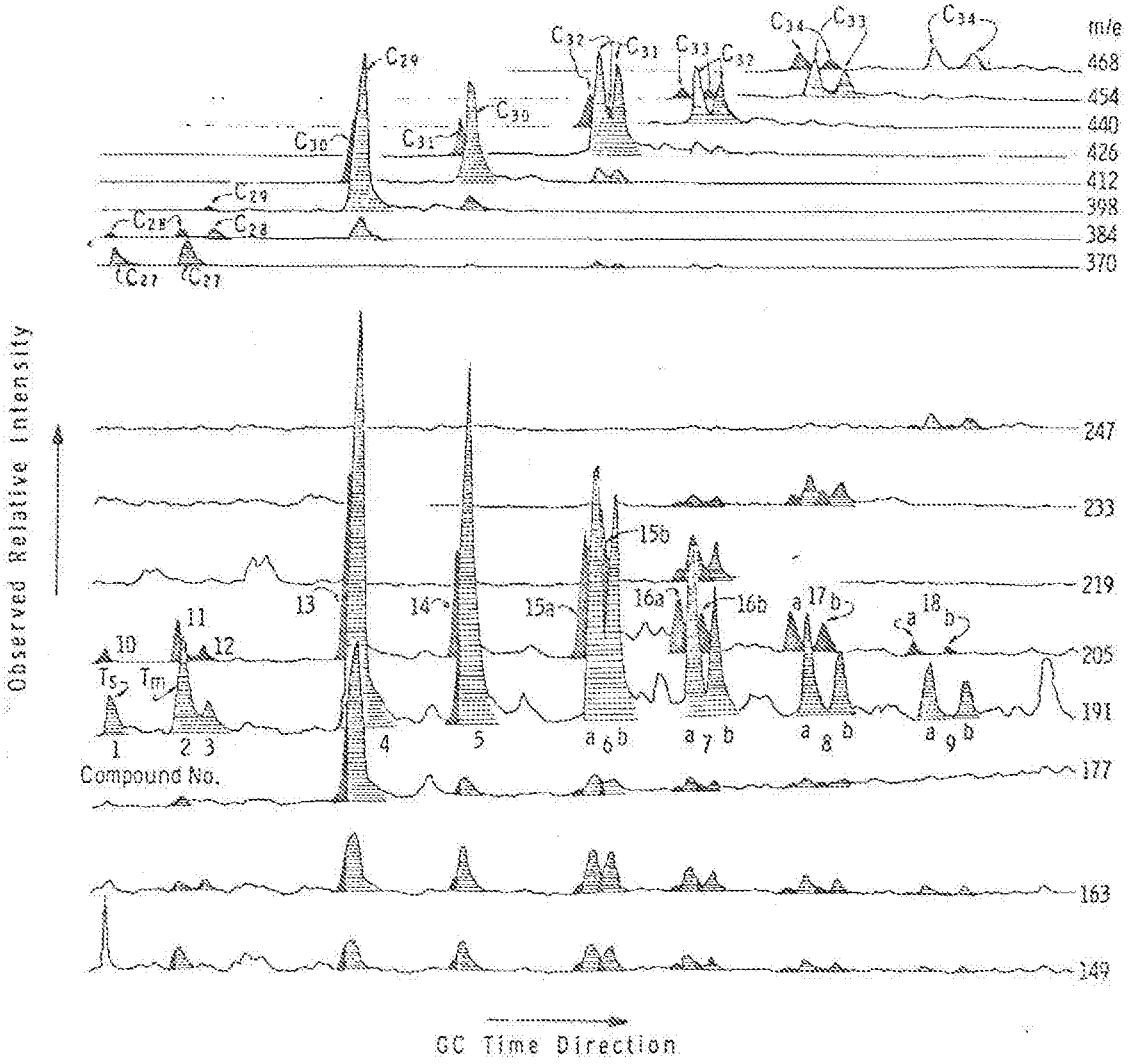


Fig. 1 [a]Parent[c] and fragment ion[b] map[c] of hopanes[d] and methylhopanes[e] in saturates of immature[f] Jurassic oil.

[a] m/e 370–m/e 468.
[b] m/e 149–m/e 247.
[c] INCOS Computer Software Chromatogram Display.
[d] Compounds 1–9, see Table 3.
[e] Compounds 10–18, see text.
[f] Oil 11D, Table 2.

(From Seifert & Moldowan, 1978)

A possible mechanism for the formation of 18α (H)-22, 29, 30 - Trisnorhopane II was wagely stated by Whitehead (1973) as rising by acid catalysis from a variety of possible triterpane precursors. Seifert and Moldowan (1978) prefere a simple side chain cleavage followed by an acid-catalysed methylshift. Whatever the actual mechanism, the formation of 18α (H)-22, 29, 30 - Trisnorphopane depends upon the presence of functionality in its precursors and thus, requires its formation during the earlier stages than reservoir maturation. On the other hand, T_s is more resistant to subsequent degradation than T_m, whereas, T_m degrades at about the same rate as all other 17α (H) Hopanes.

Allan, Bjorøy and Douglas (1975) reported also by use of GC-MS, the variation in the 17α (H) - Trisnorhopane 17β (H) - Trisnorhopane and the 17α (H) - Norhopane / 17β (H) - Norhopane ratios, i.e. these ratios decrases with increasing maturity.

In addition to the terpanebased parameters, the stranes are a most valuable supplement. In fact, regarding precursor product relationships, the steranes are better understood than any other type of biological marker hydrocarbons, bacause they are believed to arise predominatly from sterols.

Seifert (1977) observed the predominans of trans (5α) over cis (5β) - steranes in the shale of a good source rock/oil pair.

In a similar way as with the terpanes, Seifert and Moldowan (1978), found various ratios for steranes which are affected by maturation and migration, Table 2, Fig. 2.

The internal distribution of the three 5α -steranes (C_{27}-C_{29}) had previously been recognized as a valuable source rock/oil correlation parameter (Seifert 1977).

The steranes 1-5 and 7a of Fig.2 are most likely closely related to the rearranged strenes of skeletal type I rather than to the epimerized steranes of type II. Hydrogeneration of I in the geosphere would form III. Rearranged strenens I have been isolated from a shale by Rubinstein et al. (1975), while Mulheirn and Ryback (1974) have studied backbone epimers (II).

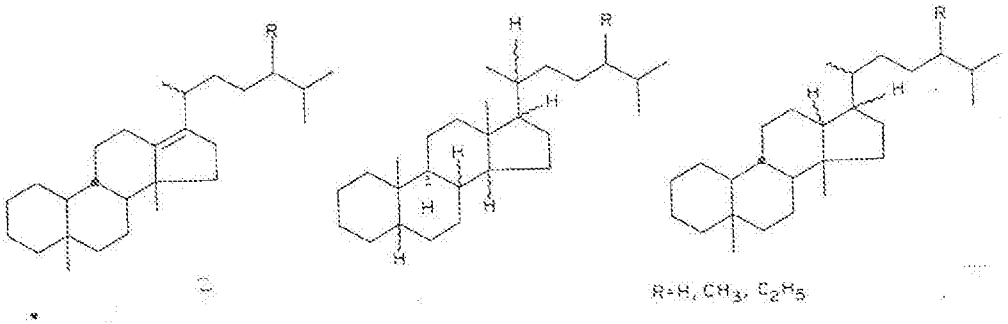


Table 2 Sterane internal distribution*

Formation	Depth, Ft	$\frac{20-22}{20-27}$	$\frac{21-22}{21-27}$	$\frac{27-28}{27-29}$	$\frac{28-29}{28-29}$	Rearranged $\frac{20-27}{20-27+21-27}$	27-Steranes $\frac{27S}{27S+27R}$
Carneros (1)	5655 Base	1.05	0.70	0.88	0.65	0.40	0.45
Carneros (2)	5872-5915	1.08	0.60	0.96	0.68	0.35	0.47
Carneros (3)	5950-5990	1.05	0.65	0.96	0.65	0.34	0.46
Carneros (4)	7194-7225	1.05	0.66	0.94	0.71	0.34	0.43
Carneros (5)	6425-6463	1.07	0.73	1.22	0.84	0.48	0.70
Carneros (6)	6480-6513	1.04	0.68	1.20	0.80	0.45	0.56
Phacoides (7)	7808-8630	0.88	0.81	1.37	0.85	0.64	0.33
Phacoides (8)	8210-8241	0.89	0.81	1.36	0.89	0.64	0.35
Phacoides (9)	9058-9074	0.87	0.80	1.40	0.90	0.66	0.33
Oceanic (10)	8858	0.90	0.67	1.19	0.74	0.73	0.31
Oceanic (11)	8834-8919	0.87	0.76	1.51	0.92	1.02	0.29
Parameter		1	2	3	4	5	6

* Data calculated by integration of peaks on m/e 217 MID profiles, Fig. 6. 5α-C_{27}, C_{28}, C_{29}, and 5β-C_{27}, C_{28}, C_{29}, refer to Compounds 8, 10, 13, and 6, 9b, 12, respectively, in Fig. 9 and Table 8.
[b] Compounds 1 + 3 + 5, Fig. 9 and Table 8.
[c] From Table 7.

(From Seifert & Moldowan, 1978)

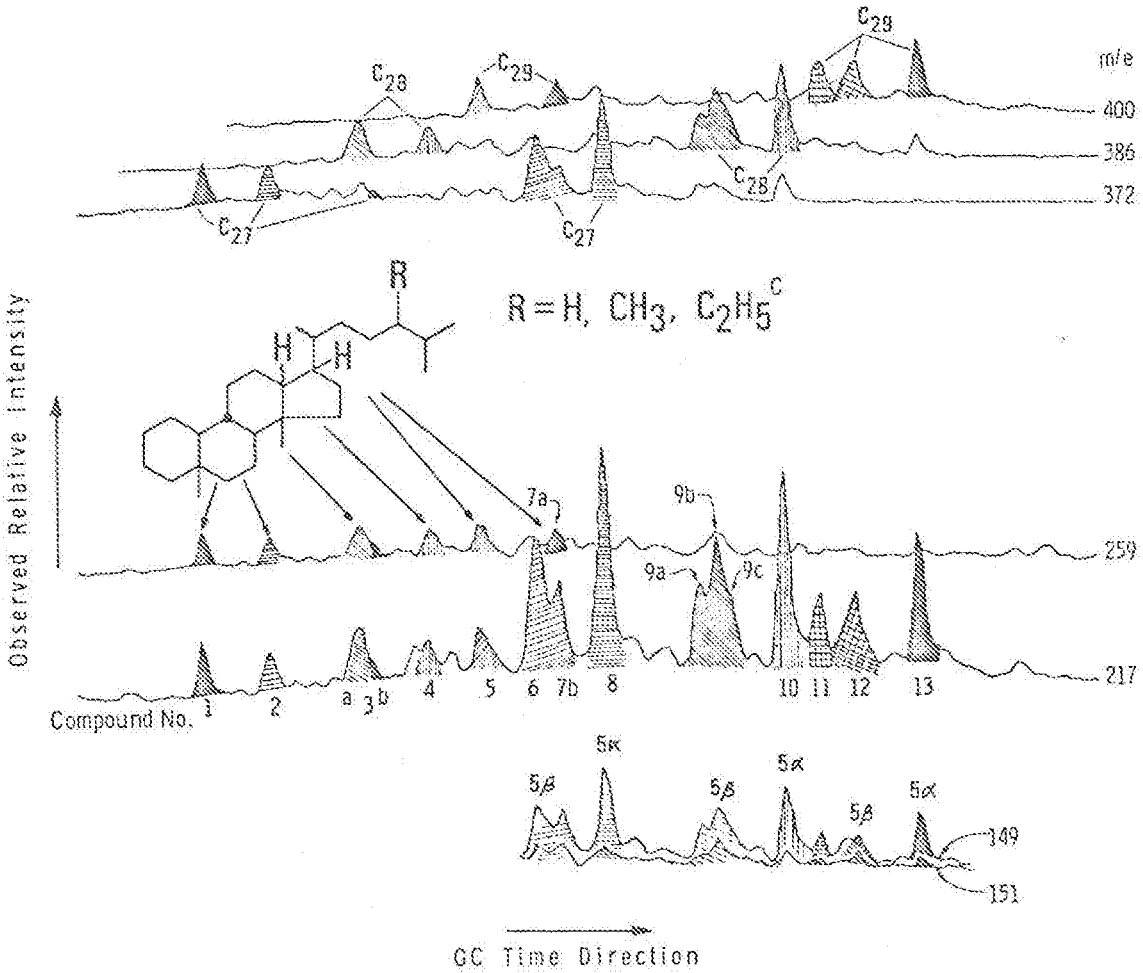


Fig. 2 Sterane map for Carneros (4) 7194–7221'—mass chromatograms.
* See Table 8 and text.
[b] INCOS computer software.
[c] See section on Rearranged Steranes: Migration in text for exact stereochemistry.

(From Seifert & Moldowan, 1978)

Mass spectra of rearranged sternes show M^+-side chain base peaks (Rubinstein et al. 1975) at m/e 257, which would correspond to large m/e 259 fragments, 50-80% of base, in saturated compounds 15 and 7a in Fig.3. The m/e 259 peake is extremely minor in the mass spectra of compounds of structure II; for example 5α - cholestane. Gross differences at m/e 189 and 287 between the spectra of compounds 15, Fig.2, and 5α - chosestane are also evident from Fig.3. Mulheirn and Ryback (1974) found that the mass spectra of seven cholestane stereoisomers (II) are virtually identical, except for an enhanced m/e 151 and m/e 218 in the 5β - and 14β - epimers, respectively. As was presented by Dr.P.Albrecht at the VIIIth International Congress on Organic Geochemistry at Moscow, May 10th 1977, the Strasbourg team has independently proved the structure pf two C_{27} rearranged steranes by synthesis, as being the (13βH, 17α H) 20R and 20S isomers.

The major steranes found in different oils are listed in Table 3 and their relative GC-MS retention times are seen in Fig. 2. In addition, the sterane map in Fig. 2 shows the determination of carbon number for various steranes and an attempt to classify 5α -and 5β -steranes by the ratio of their m/e 149 and 151 fragments m/e 149 > 151 for 5α -steranes and m/e 151 > 149 for 5β -steranes, (Toekes et al. 1968). Overlapping terpanes and sterans contribute strongly to the m/e 149 fragments generating apparent m/e 149/151 ratios masking the recognition of the true stereo chemistry of the 5α and 5β -steranes.

Seifert and Moldowan (1978), has shown, with background in other information about various oils and the molecular structure of the biomarkers may be applied to discover new migration parameters and predict moleular properties. The ratio of rearranged steranes to 5α -steranes distinguishes the various oils in their study on a sourceinput/maturation basis (parameter 5, Table 2). Superinposed large effects of migration are seen and hence they predict greater migrational mobility for rearranged steranes than for 5α -steranes. The migrationel difference is perhaps greatest between 5β - steranes and hence 17α (H)-hopanes as shown by the last parameter in Table 2. A large increase in 5β -steranes / 17α -(H)hopanes is experienced by the more migrated oil.

Table 3 Major steranes in McKittrick oils

Compound Number from Figure 9	Formula	Assignment	Skeleton	Assignment Based on:
1	$C_{27}H_{48}$	Rearranged Sterane	VII	MAP, MS[a]
2	$C_{27}H_{48}$	Rearranged Sterane	VII	MAP, MS[a]
3a	$C_{28}H_{50}$	Rearranged Sterane	VII	MAP, MS[a]
3b	$C_{27}H_{48}$	Rearranged Sterane	VII	MAP
4	$C_{28}H_{50}$	Rearranged Sterane	VII	MAP, MS[a]
5	$C_{29}H_{52}$	Rearranged Sterane	VII	MAP, MS[a]
6	$C_{27}H_{48}$	5β(H)-Cholestane	VI	MS,[a] Coinjection
7a	$C_{29}H_{52}$	Rearranged Sterane	VII	MAP
7b	$C_{27}H_{48}$	Cholestane Epimer	VI	MAP
8	$C_{27}H_{48}$	5α(H)-Cholestane	VI	MS,[a] Coinjection
9a	$C_{28}H_{50}$	24-Methylcholestane Epimer	VI	MAP, MS[a]
9b	$C_{28}H_{50}$	5β(H)-24-Methylcholestane	VI	MS,[a] Coinjection
9c	$C_{28}H_{50}$	24-Methylcholestane Epimer	VI	MAP
10	$C_{28}H_{50}$	5α(H)-24-Methylcholestane	VI	MS,[a] Coinjection
11	$C_{29}H_{52}$	24-Ethylcholestane Epimer	VI	MAP, MS[a]
12	$C_{29}H_{52}$	5β(H)-24-Ethylcholestane	VI	MS,[a] Coinjection
13	$C_{29}H_{52}$	5α(H)-24-Ethylcholestane	VI	MS,[a] Coinjection

[a]Mass spectrum.

(From Seifert & Moldowan, 1978)

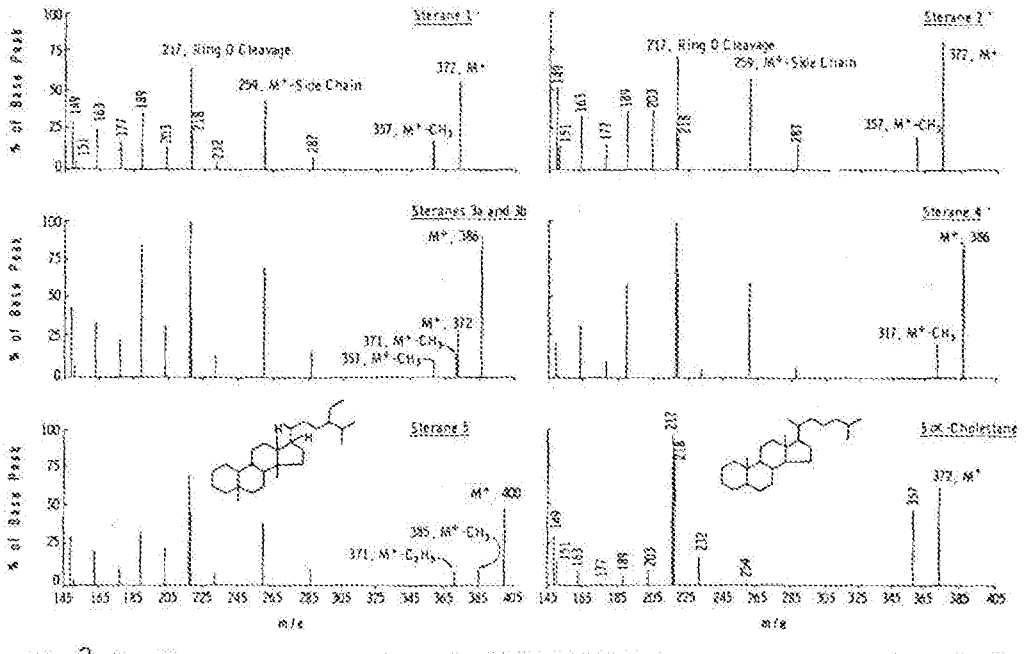


Fig. 3 Partial mass spectra from computerized GCMS-SCAN of cameros (4) 7194-7221', CA Crude.

(From Seifert & Moldowan, 1978)

By comparing various oils, they find that source input and maturation decrease 5β steranes relative to 17α(H)-hopans.

Since this study should also encounter the possibility of biodegradation of the oil found in well 34/10-1 we would like to give some background information on various work of this kind.

Since the report by Winters and Williams (1969), the interpretation of n-paraffin depletion is normally believed to be a consequence of biodegradation. Normally the nC_{12} - nC_{15}15 are first attacked while the light end and heavy end alkanes go later. Oils which contain light end n-alkanes, C_1-C_{10} and no heavy end n-alkanes might not be biodegraded, but instead be early condensates. Biodegradation often leads to production of new compounds which is normally seen as a large unresolved envelope on the gas-chromatogram of the oil.

In the years after Winters and Williams (1969) classical study, various workers have reported on the effect of biodegradation. Bailey et al., (1973), showed that the isoprendoids, pristane and phytane were metatolized after the disappearance of n-paraffins. The condensed cyclic hydrocarbons were reported unaffected. A recent report (Rubinstein et al., 1977), which also summarizes the literature, specifically deals with steranes and terpanes as being unaffected by bacteria in laboratory simulation and in natural fossil fuels. In contrast, work by Reed (1977) supports alteration of terpanes due to biodegradation. Aromatics also are shown biodegradable (Gibson, 1976). The work by Winters and Williams touched on the possiblity of optically active compounds produced by the organisms and added to the original oil. Later work by Bird et al. indeed showed the formation of sterols and squalene (1971b) and of hop-22(29)-ene (1971a) by the bacterium Methylococcus capsulatus grown in a mineral salt medium with methane as sole carbon source. The same hopene plus another isomer, hopene-1, were isolated from acidophilic bacteria, optimum growth at pH 2.6-2.8 (De Rosa et al., 1971).

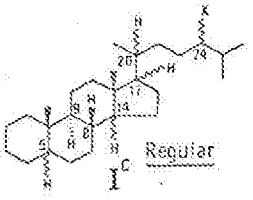
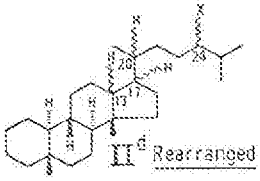
These reports give rise to a number of questions regarding petroleum triterpanes and steranes in bacterially degraded oil: Do these biomarkers, which were shown to be useful in correlation studies (Seifert, 1977; Seifert and Moldowan, 1978;Seifert, 1978) survive biodegradation ? Do bacteria synthesize steranes and terpanes in biodegraded oil? Are bacterially degraded oils richer in steranes and terpanes than undegraded oil?

To what extent can steranse and terpane biomarkers be used for correlation studies in biodegraded oil?

A resent published paper (Seifer and Moldowan 1979) gave a lot of information regarding the structure of a number of petroleum sterans which should enable us to answer some of these questions.

In order to give as much information on this problem as possible, large parts of this article is cited in the following.

Table 4. Steranes found in petroleum[a]

No.[e]	Assignment	Stereo-chemistry	No. of Carbons	Assignment Based on	Stereochemistry[b]
1	β,α-Diacholestane 20S	IIa	27	f	 I[c] Regular
2	β,α-Diacholestane 20R	IIb	27	f	
3	Unknown		28	g	
4	α,β-Diacholestane	IIc	27	h	
5	24-Methyl-β,α-Diacholestane 20S	IIa	28	h	
6	α,β-Diacholestane	IIc	27	h	
7	Unknown		27	g	
8	Unknown		28	g	
9	24-Methyl-β,α-Diacholestane 20R	IIb	28	h	a. 5α, 14α, 17α, 20R b. 5β, 14α, 17α, 20R
10	Unknown		27	g	c. 5α, 14α, 17α, 20S
11	Unknown		28	g	d. 5α, 14β, 17β, 20S or 20R
12	24-Ethyl-β,α-Diacholestane 20S	IIa	29	h	
13	24-Methyl-α,β-Diacholestane	IIc	28	h	 II[d] Rearranged
14	Coprostane 20R	Ib	27	f	
15	Cholestane 20S	Ic	27	f	
16	24-Methyl-α,β-Diacholestane	IIc	28	h	
17	Isocholestane 20S	Id	27	f	
18	Isocholestane 20R	Id	27	f	
19	24-Ethyl-β,α-Diacholestane 20R	IIb	29	h	a. 13β, 17α, 20S b. 13β, 17α, 20R
20	Cholestane 20R	Ia	27	f	c. 13α, 17β, 20S or 20R
21	24-Ethyl-α,β-Diacholestane	IIc	29	h	
22	Unknown		27	g	
23	Unknown		28	g	X = H, CH_3 OR C_2H_5
24	24-Ethyl-α,β-Diacholestane	IIc	29	h	
25	24-Methylcholestane 20S	Ic	28	i	
26	24-Methylcoprostane 20R	Ib	28	f	
27	24-Methylisocholestane 20S	Id	28	i	
28	24-Methylisocholestane 20R	Id	28	i	
29	Unknown		29	g	
30	24-Methylcholestane 20R (Ergostane)	Ia	28	f	
31	Unknown		29	g	
32	24-Ethylcholestane 20S	Ic	29	i	
33	24-Ethylisocholestane 20S	Id	29	i	
34	24-Ethylcoprostane 20R	Ib	29	f	
35	24-Ethylisocholestane 20R	Id	29	i	
36	24-Ethylcholestane 20R (Sitostane)	Ia	29	f	
37	Unknown		29	g	

[a] Identified in a Pliocene crude of 4318-ft depth from 'basin F', California.
[b] Stereochemistry at C_{24} is unresolved.
[c] Only 8β,9α stereochemistry has been found in petroleum.
[d] Stereochemistry based on ENSMINGER *et al.* (1978). Diasteranes are 8α,9β,10α.
[e] Refers to numbered mass fragmentographic peaks in Fig. 1.
[f] Available authentic standard.
[g] GC-MS data.
[h] Comparison of GCMS with those reported in ENSMINGER *et al.* (1978) for this compound or a homologue.
[i] Authentic material present in isomerizate of ergostane plus sitostane obtained from A. A. PETROV.

(From Seifert & Moldowan, 1979)

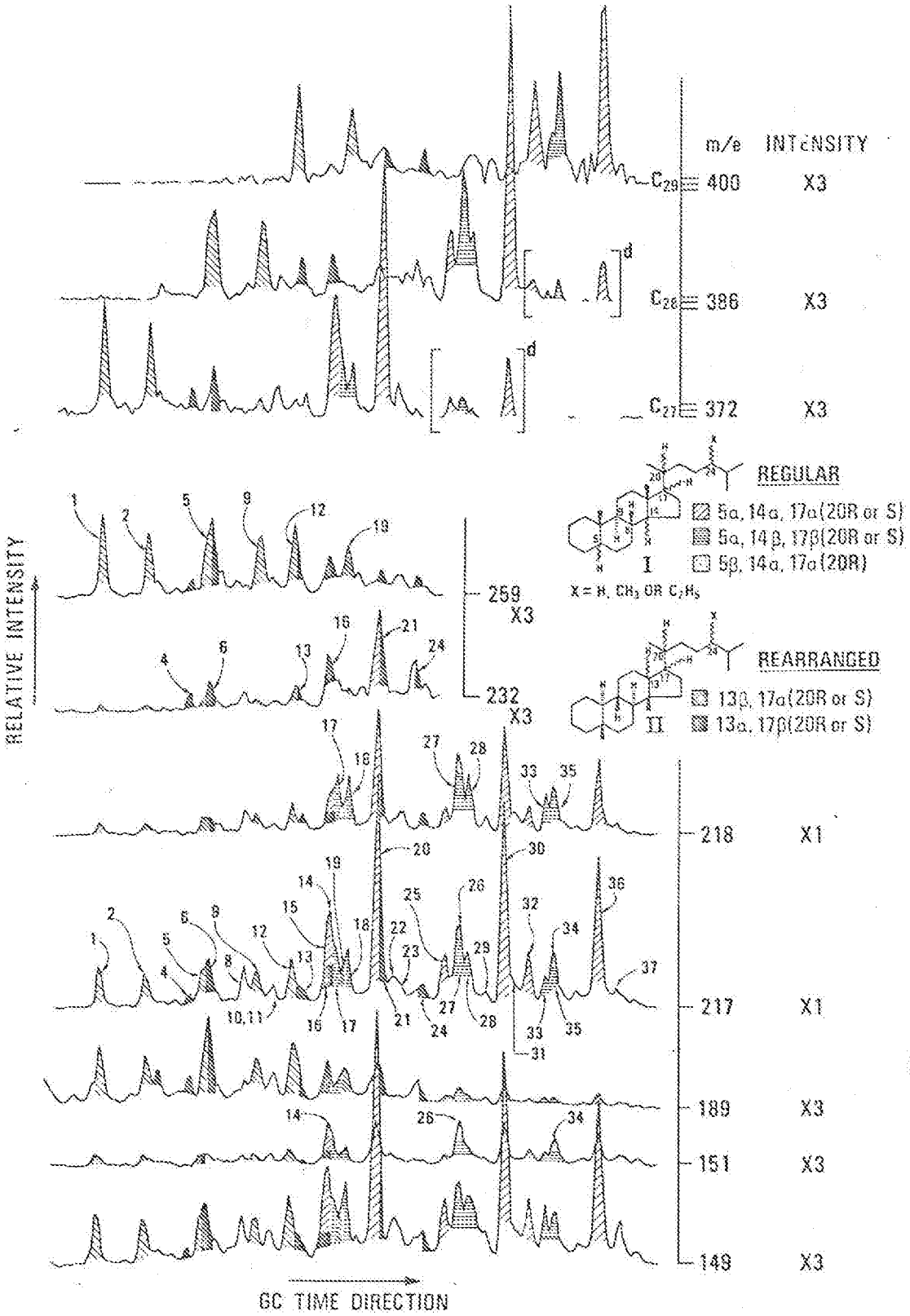


Fig. 4 Identification[a] of steranes by diagnostic ion[b] map[c] (GC-MS).

[a] See Table 4 for nomenclature by compound number. Peak shadings are symbolic and not meant to represent actual percentage composition of peaks with more than one component.
[b] Parent ions: m/e 400, 386, and 372. Fragment ions: m/e 149, 151, 189, 217, 218, 232, and 259.
[c] INCOS computer software chromatogram display for California 'basin I', Pliocene, 4318-ft crude.
[d] C_{13} contribution of M-15 fragments.

(From Seifert & Moldowan, 1979)

Sterane structure

Besides adding some new structural detail, we wish to describe an overview of sterane structure in fossil fuels using our practical GC-MS map approach (SEIFERT and MOLDOWAN, 1978). Fig. 4 depicts this new method of unraveling an otherwise complex mixture of steranes in the saturate cut of a lightly biodegraded crude in which, for practical purposes, steranes and terpanes have not been altered. Table 4 lists the precise stereochemistry. The information in Fig. 4 and Table 4 updates and supersedes all previous structural assignments (SEIFERT and MOLDOWAN, 1978). Designations of α and β refer to the configuration of the H atom. Two basic types of skeletons are present, namly, the regular steranes (Type I) and the rearranged steranes (Type II); see Fig. 4 for structures. Rescently, the latter were independently discovered by the University of Strasbourg, France, and the Chevron, Richmond, USA, groups and first simultaneously reported at the VIIIthe International Congress on Organic Geochemistry at Moscow, USSR, May 1977. The Richmond, USA group (SEIFERT and MOLDOWAN 1978) used them in oil/oil correlation studies; and the Strasbourg, France, group (ENSMINGER et al., 1978) proved their structure conclusively by synthesis. These so-called disteranes occur in two basic modes of stereochemistry (ENSMINGER et al., 1978): (1) 13β, 17α (major petroleum constituents), and (2) 13α, 17β (minor petroleum constituents, compare Fig.4): the latter possess a unique main additional diagnostic ion profile at m/e 232 (Fig. 4), which can be exploited in correlation studies. Both types of disteranes show diagnostic ion profiles at m/e 259 and 189 in addition to the ones at 217 and 149 (Fig. 4). Both range in C-number from C_{27} to C_{29} because they are diagenetically derived by rearrangement from C_{27} to C_{29} sterenes (RUBINSTEIN et al. 1975). Both possess 20R and 20S isomers (the latter eluting first for the 13α, 17β series) (ENSMINGER et al., 1978); also compare Fig. 4 and Table 4 of this paper. Most significantly, we have observed that the C_{27} 20S isomer in the 13β 17α series undergoes biodegradation at a faster rate than the 20R isomer (see later in this paper). Thus, the diasteranes, as we understand their structure at this time, are comprised of two series, 13β, 17α and 13α, 17β, six basic compounds in each. This point is conveniently illustrated by the GC-MS map-type presentation in Fig. 4 which includes the molecular ions for carbon numer identification. Additional disteranes with a methyl substituent in position 4 have been reported (ENSMINGER et al., 1978), and

Table 5. Relative mass spectral intensities[a] for diagnostic ions of steranes in cholestane isomerizate

Cpd No.[b]	Proposed Stereochemistry[c]	Relative Intensities for m/e								
		149	151	189	203	217	218	259	357	372
47	5α, 14α, 17β, 20R	44	5	2	10	100	54	1	22	18
48	5β, 14β, 17α, 20R	34	16	4	7	60	100	1	21	21
49	5β, 14β, 17α, 20S	25	16	2	13	51	100	2	10	13
50	5β, 14β, 17β, 20S	23	13	4	17	58	100	2	30	29
51	5β, 14β, 17β, 20R	44	14	3	18	86	100	2	22	23
52	5β, 14α, 17α, 20S	19	25	1	9	100	43	1	43	39
53	5α, 14β, 17α, 20R	32	5	4	19	63	100	5	19	21
54	5α, 14β, 17α, 20S	29	4	5	18	64	100	9	29	29
15[d]	5α, 14α, 17α, 20S	36	6	4	12	100	51	2	43	50
14[d]	5β, 14α, 17α, 20R	18	25	2	9	100	47	2	47	50
17[e]	5α, 14β, 17β, 20S	27	5	5	19	66	100	7	31	34
18[d]	5α, 14β, 17β, 20R	28	4	5	19	64	100	6	26	26
20	5α, 14α, 17α, 20R	34	6	3	13	100	56	2	43	50

[a] From GC–MS run at 40 eV.
[b] See Fig. 2.
[c] Based on relative GC retention times and mass spectra; see *Discussion of experimental*.
[d] From a separate GC–MS run on pure material.
[e] Mass spectrum contaminated slightly by GC–MS coelution with compound 14.

(From Seifert & Moldowan, 1979)

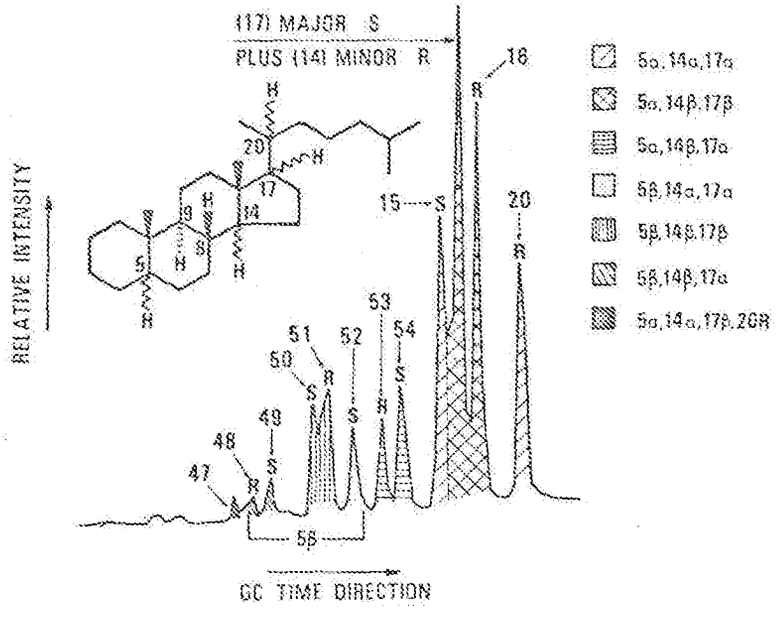


Fig. 5 Isomerizate[a] of cholestane, capillary GC–MS total ion current.[b]

(From Seifert & Moldowan, 1979)

isomers at C_{24} are expected to exist (MULHEIRN and RYBACK, 1975). The diasteranes, as will be shown later in this paper, are nore resistant to bacterial attack than the regular steranes. The bulk of the regular steranes elutes after the diasteranes (Fig. 4), although some overlap, mainly in the region of compounds 14-21 (fig. 4 and Table 4) occurs.

While the disteranes, as they occur in petroleum and are easily resolved by GC, can be described in variations at three epimeric centers (at 13, 17 and 20; see Fig. 4), other variations have not been recognized to date), the regular steranes involving five epimeric centers (5, 14, 17, 20 and 24) occur in greater varity: (1) The natural cholesterol-type skeleton, all rings trans and 20R stereochemistry; (2) natural cholesterol skeleton but 20S stereochemistry; MULHEIRN and RYBACK reported an about 10% shorter GC retention time for the C_{27} 20S isomer (1974) and described its occurrence in Rozel Point crude (1975). We now wish to report its ubiquitous occurrence in unbiodegraded fossil fuels and its isolation from a cholestane isomerizate (compund 15 in Figs. 4 and 5 obtained on Pt/C at 300°C. In analogy, we have identified the C_{28} and C_{29} 20S homologs compounds 25 and 32, Fig 4), and it is now clear that the C_{27}-C_{29} 20S epimers of the naturally derived steranes (20R) play a predominant role in fossil fuel biomarker composition. (3) 5β, 20R stereochemistry, Rings A/B cis, all other rings trans (compunds 14, 26 and 34 Fig. 4 and Table 4) characterized by m/e 151 > 149 (SEIFERT et al. 1972). (4) 14β stereochemistry, Rings C/D cis. The first report of the existence of such a compound (MULHEIRN and RYBACK 1974), namely 5α, 8β, 9α, 14β, 17α, 20R pointed out its easy diagnosis by mass spectrometry, namely, m/e 218 > 217. Its occurrence in crude oils together with its 20S epimer in a 40/60 ratio was reported later (MULHEIRN AND RUBACK 1975). We now wish to report the occurance of these two compounds in about the same ratio, as found in petroleum, in the isomerizate of cholestane (compounds 53 and 54, Fig. 5 and Table 5). In 1976 PETROV et al. reported the presence of 14β-steranes in a number of Russian crudes and coined them isosteranes. Up to this point in all reports no proof of 17β stereochemistry was delivered. We now wish to report that the predominantly occuring 14β-steranes in fossil fuels, as characterized by the m/e 218 profile in Fig. 4 all possess 14β, 17β , (20R and 20S) stereochemistry (compounds 17, 18, 27, 28, 33, 35, Table 4). This conclusion was reached by isolation of these compounds from

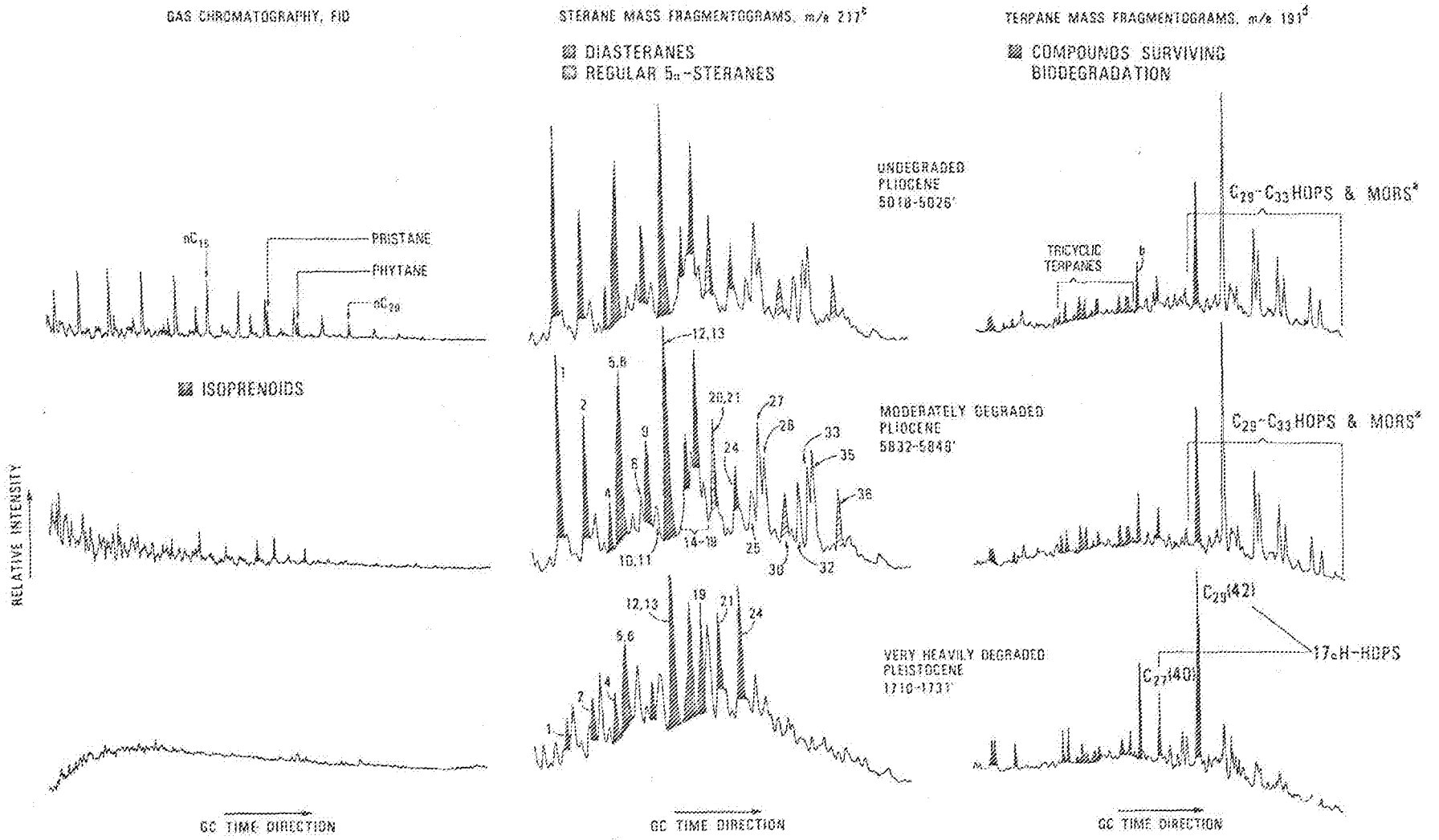


Fig. 6 Source-related Gulf Coast oils at various stages of biodegradation.

[a] Common petroleum terpanes. See Fig. 6 this paper, and SEIFERT and MOLDOWAN (1978) for identifications.

[b] 18α(H)-22,29,30-Trisnorhopane II, see WHITEHEAD (1973).

[c] See Fig. 1 and Table 4 for identification of numbered peaks.

[d] See Fig. 5 for identification of numbered peaks.

(From Seifert & Moldowan, 1979)

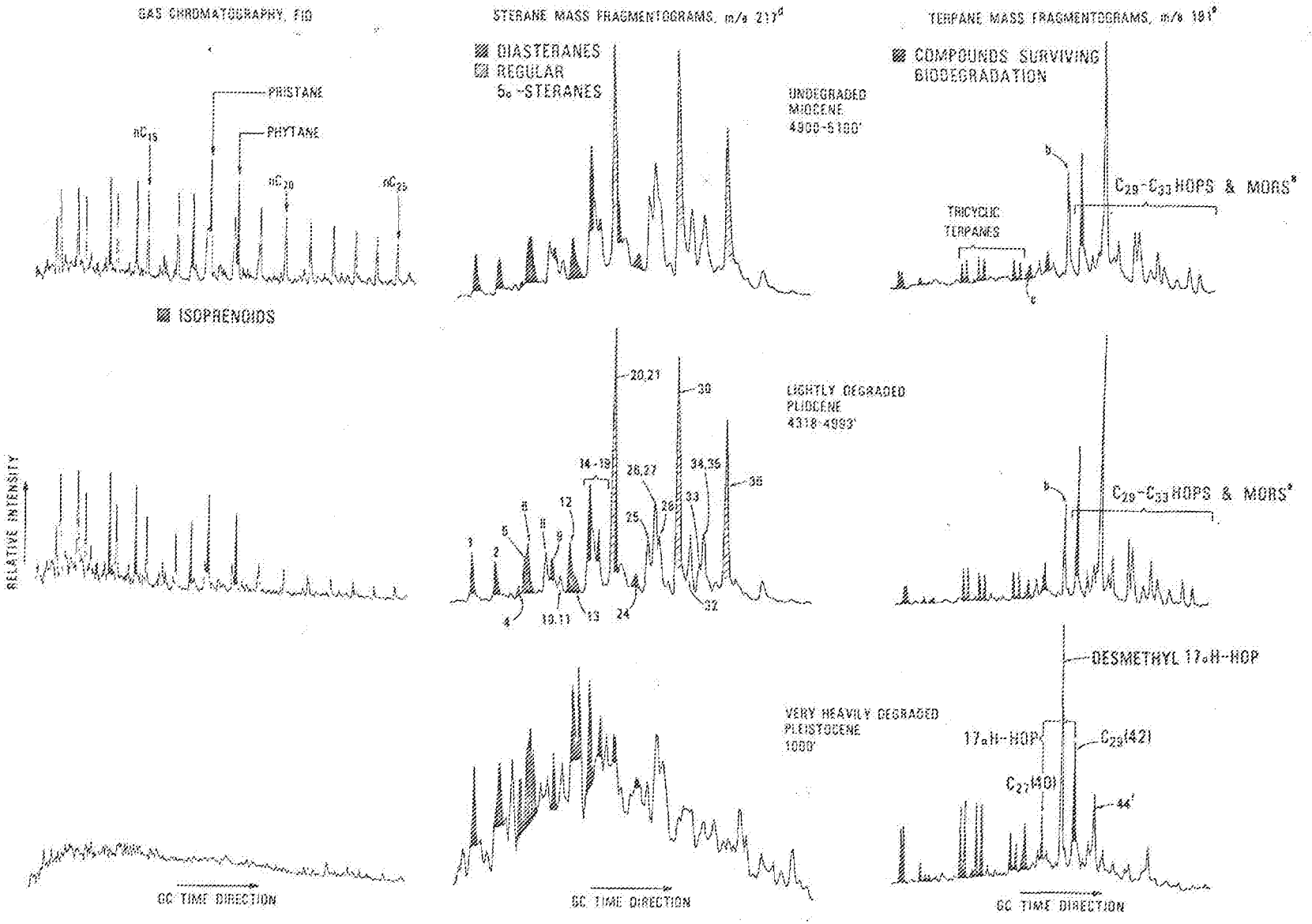


Fig. 7 Source-related California 'basin I' oils at various stages of biodegradation.

[a] Common petroleum terpanes. See Fig. 6 this paper, and SEIFERT and MOLDOWAN (1978) for identifications.

[b] 17α(H), 18α(H), 21β(H)-28,30-Bisnorhopane, see SEIFERT *et al.* (1978).

[c] 18α(H)-22,29,30-Trisnorhopane II, see WHITEHEAD (1973).

[d] See Fig. 1 and Table 4 for identification of numbered peaks.

[e] See Fig. 5 for identification of numbered peaks.

[f] Compound 44 is a C_{30} terpane of unknown structure.

(From Seifert & Moldowan, 1979)

Petrov's isomerizate (Fig. 5), MS and NMR studies (see Discussion of experimental), and coinjection with the saturate fraction, depicted in Fig. 4. The designation as "isosteranes" (PETROV et al., 1976) was retained in Table 4. Note that these 5α, 14β, 17β (C/D cis) steranes coelute with 5β, 14α, 17α (A/B cis) steranes under the conditions described in the experimental section for Fig. 4. The parallel observation of the m/e 218 ion profile (Fig. 4), diagnostic for the first, with the m/e 151 ion profile, diagnostic for the latter, allows the distinction between 5α, 14β, 17β and 5β, 14α, 17α by the GC-MS map approach. (5) The fifth and last epimeric center of practical significance, nemly C_{24}, has been discussed; epimers have been shown to occur in petroleum in various ratios (MULHEIRN and RYBACK, 1975). However, these compounds are not resolved in Fig. 4. (6) Joint occurence of 5β and 14β stereochemistry. The four possible isomers with 17α and 17β and 20R and 20S stereochemistry were found present in the isomerizate of cholestane (compounds 48-51, Fig. 5 and Table 5) in small quantities; because of the small amounts observed in the isomerizate, their presence in petroleum can neither be confirmed nor denied. An interesting feature of their mass spectral fragmentation patterns (Table 5) is a m/e 151 frament of lesser strength in the 5β, 14β compunds than in their 5β, 14α counterparts. Compound 52 appears to be 20S coprostane. (7) Finally, 5α, 14α, 17β, 20R and 20S were reported (MULHEIRN and RYBACK, 1974) to possess shorter GC retention times and one of the two (20R) appears to be compount 47, present as a trace component in the isomerizate (Fig. 5).

All steranes with the regular skeleton discussed in (1)-(7) undergo biodegradation at a faster rate than the first described diasteranes, i.e. all regular steranes were found to be totally destroyed in heavily biodegraded crudes. REED (1977) noticed a "puzzling" avsence of steranes in biodegraded seep oils from the Uinta Basin. The examples shown here support biodegradation as the cause.

Thermodynamic stability

Although is is unknown whether the isomerizate is at thermodynamic equilibrium, the comparison of its composition with that of petroleum gives rise to some interesting considerations. PETROV et al. (1976) note an increase in 14β-steranes with increasing degree of maturity; with the structural work

described in this paper, it is now lear that this statement is only true for 14ß,17ß and not for 14ß, 17ß. The latter (20R), being thermodynamically disfavored, is present in only small amounts in the isomerizate (compound 53, Fig. 2); the first (20R + 20S) are the major products of artifical and naturally occuring isomerization (compounds 18 and 17, Figs. 5 and 4). 14ß-Steranes are expected to be thermodynamically more stable than 14α-steranes, by analogy to cis-fused 8-methylhydrindane ring system which are energetically more favored than trans (DREIDING, 1954). Recent wo Δ8-11-keto steroids suggests the greater stability of the C/D cis ring juncture (PATTERNSON et al. 1977), although they are exeptions (BARNES et al. 1953). The thermodynamic unfavorability of the 14α, 17ß configuation, consistent with its near absence in the isomerizate, has been explained by a large interaction between the side chain and the 14α-hydrogen (HANACK 1965), however, conversion to 14ß-stereochemistry makes the 17ß-configuration accessible.

Next, the 20 position is free to epimerize between 20R and 20S, such that 20R + 20S pairs are observed in petroleum and in the isomerizate, independent of ring skeletal configuration (Fig. 4 and 5). While the ratio of 20R to 20S is close to unity in the C_{27} isomerizate (Fig. 5), this is not the case in the fossil fuel sample described in the Tabel 4, where 20R is much larger than 20S for C_{28} and C_{29} regular steranes, because these natural products have not progressed as far along the route to thermodynamic equilibrium as the isomerizate. The observation of only small quantities of 5ß, 14ß compounds in the isomerizate (compounds 48-51, Tabel 4 and Fig. 5) is not surprising because the cis A/B ring configuration has been shown to be thermodynamically less favored (MITRA and ELLIOTT, 1969). Therefore, their occurrence in petroleum is expected tp be limited and, thus, might easily be hidden by the predominant components described above (Fig. 4).

Effects of naturally occurring biodegradation

For biodegradation studies, three basins were selected, two from California, one from the Gulf Coast. In each basin, the oils chosen possess a common source and the undergraded oil was compared with a heavily degraded oil. The Gulf Coast Field is very large field on and around a highly faulted salt dome. All oils are produced from depths of 1500 ft to over 10 000 ft in a multitude of sands. The degree of biodegradation decreases with increasing depth. The tree oils studied are en reservoirs of young age (botton Table 6).

is paralleled by an increase in terpanes and steranes in the most degraded Gulf Coast oil by factors of 3 and 2,5, respectively. On first sight, optical rotation and group-type mass spectral analysis could easily lead tp the erroneous conclusion of sterane and terpane increase with degradation. However, the superimposition of an immaturity component is likely to be inherent in the heavily degraded oil due to its lesser depth. That is, the shallow oil is expected to possess more steranes and terpanes (SEIFERT and MOLDOWAN, 1978, Table 2) and, consequently, a higher degree of optical rotation than the deeper oils prior to biodegradation. Consequently, we also observed more degraded terpanes (12,5% Table 6) and more degraded steranes (9,7% Table 6) in the shallower oil and concurrent higher optical activity than can be accounted for by paraffin depletion alone. Figure 6 clearly shows the loss of regular steranes and terpanes. The explanation is that during biodegration the regular steranes and terpanes get transformed to a multitude of other optically active spesies, which possess mass spectral framents fitting the designed mass spectral matrix. Alteration of optically active centers provides for additional small variations. Thus, the observed high optical activity in the heavily biodegraded crude does not require bacterial synthesis of optically active species, e.g. BIRD et al. (1971), because all can be explained as being the consequence of one or more of the following: (1) paraffin depletion by biodegradation; (2) immaturity (less paraffins, more terpanes plus steranes) as starting material for biodegradation; (3) transformation of steranes and terpanes to other optically active species.

The conclusions derived from samples of the Gulf Coast are enhanced and further expanded by observing similar trends in a California basin ("basin I"), namely, on the west side of the San Joaquin Valley. Figure 4 again illustrates the survival of all steranes and terpanes in the lightly degraded oils, which is characterized by loss of n-paraffins and survival of isoprenoids. As in the Gulf Coast Basin oil, all regular steranes have been destrayed in the very heavily degraded oil, whereas diasteranes have survived (Fig. 7 bottom). In this basin, the increase in optical activity by a factor of 1,5 in the saturate fraction can be rationalized by a parallel decrease in yield (Table 6). However, the apparent increase of terpanes by mass spectral oil to 19,6% in the heavily degraded oil (Table 6) can be explained as follows:

the regular hopanes were found to be converted in the heavily degraded oil of this sequence (Pleistocene, 1000 ft) to a demethyl hopane series in which one methyl group in the A/B portion of the terpenoid ring system has been lost. This conclusion was reached by obsering (Fig. 8 compounds 39, 41, 43a and b, 45a and b, 46a and b) that the regular sequence of terpanes at ion profile m/e 177 was identical in pattern to that normally observed at m/e 191; e.g.a. C_{30} doublet on the m/e 177 profile (compounds 43a and b) possesses a doublet a m/e 205, which the regular 17α (H)-homohopane (C_{31}) would possess (except for different mass spectral fragment intensities). Because m/e 191 represents the A/B portion fo the ring, the m/e 177 fragment represents the same moiety with one less methyl group in the A/B portion of the ring skeleton. This is, perhaps the same series of biodegraded hopanes discovered by REED (1977) in a P.R. Spring Seep, Uintra Basin, Utah, who assigned methyl group loss to the C-4 position. The same effect, caused by biodegradation, is observed for our recently described 28, 30-bisnorhopane (SEIFERT et al. 1978). We find its Ring A/B demethylated C27 analog (compound 38) in the heavily degraded (Pleistocene, 1000 ft.) oil (Fig. 5). The presence of compound 38, the complete reproduction of the regular hopane series (C_{29} - C_{33}) in the demethylated series (C_{28} - C_{32}), and the destruction of regular hopanes simultaneously with the occurrence of demethylated hopanes confirm a bacterial transformation of regular hopanes into demethylated hopanes. The explanation for the apparent higher terpane value (19,6%) and for the increased optical activity in the saturate cut (2,28) in the Pleistocene oil (third entry, Table 6) in spite of near total destruction of C_{29} - C_{33} regular hopanes (bottom, Fig.7) is that the demethylated hopanes are the predominant terpanes in this oil. In fact, quantitatively speaking, the increase in optical activity by a factor of 1,5 is matched by an increase from hopanes to biodegraded hopanes by the same factor and is further matched and caused by a parallel decrease in saturate yield due to paraffin loss again by the same factor (Table 6).

The third basin (California, "basin II") examined is located in the San Joaquin Valley itself, and the oils are representative of a large number of biodegraded oils produced from this basin. All three oils are from a common source. This heavily degraded oil of "basin II", like the Pleistocene oil of "basin I", shows biogeneration of the Ring A/B

Table 6 Biological marker 'bulk' parameters in three oil groups

Basin	Age	Depth, Ft	% Saturates Based on Crude[a]	$[\alpha]_D^{25}$ of Saturates[b]	OGGT[c]			Degree of Degrad.[e]
					Paraffins[d]	Sterranes	Terpanes	
California I	Mio	4900	42.1	1.52	18.6	16.3	12.7	0
	Plio	4318	42.8	1.57	12.4	20.8	14.5	+
	Pleis	1000	26.5	2.28	2.3	12.5	19.6	++++
California II	Mio	4570	55.6	0.48	25.1	4.8	5.0	0
	Plio	3032	41.2	1.28	15.1	13.7	11.2	+
	Plio	1585	23.9	3.10	0.9	15.9	22.4	+++
Gulf Coast	Plio	5018	61.0	0.40	9.7	3.9	4.3	0
	Plio	5832	54.5	0.58	5.1	3.5	5.5	++
	Pleis	1710	43.1	1.04	0.5	9.7	12.2	++++

[a] Isolated by Tswett chromatography (SEIFERT, 1977).
[b] Taken in cyclohexane solvent.
[c] Organic geochemical mass spectrometric group-type analysis of 770–900°F saturates (%) (SEIFERT and GALLEGOS, unpublished).
[d] *n* + iso-paraffins.
[e] 0 = undegraded, + = lightly, + + = moderately, + + + = heavily, + + + + = very heavily.

(From Seifert & Moldowan, 1979)

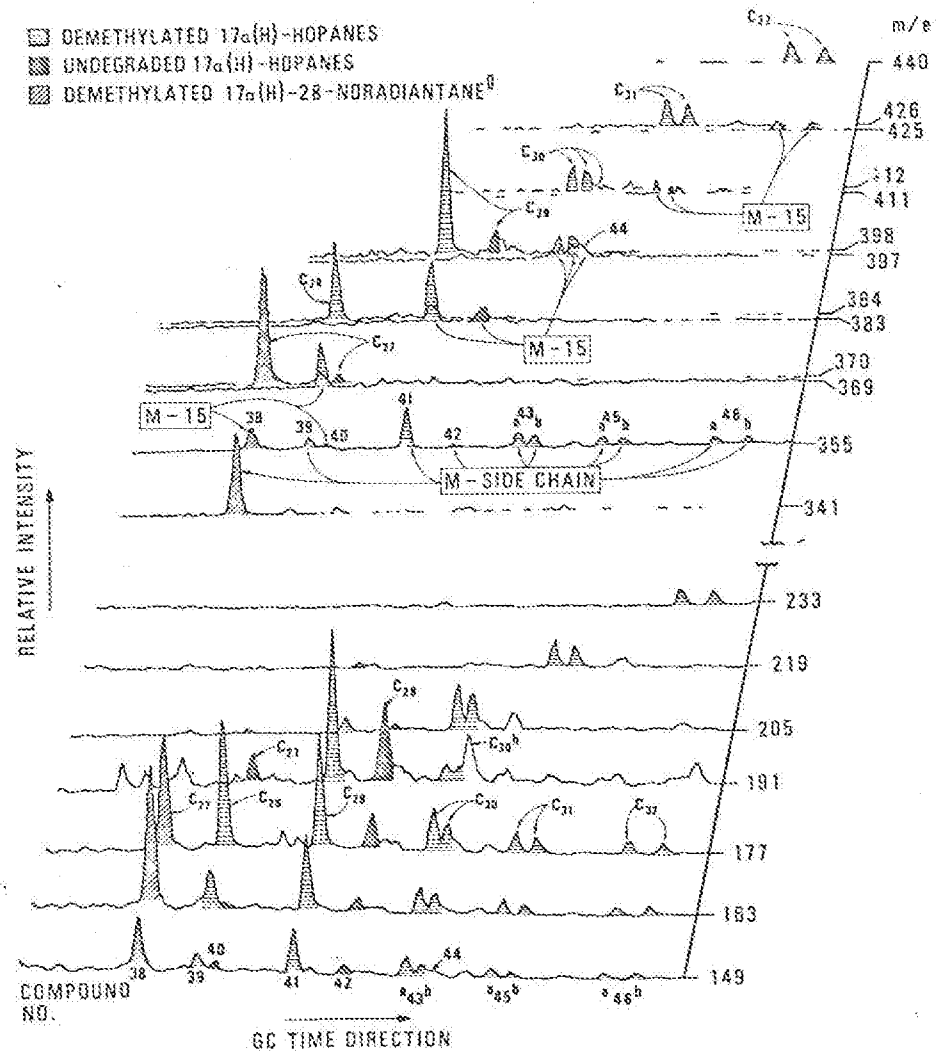


Fig. 8 Parent[a] and fragment ion[b] MAP[c] showing demethylated 17α(H)-hopanes[d] in a very heavily degraded[e] crude.[f]

[a] m/e 370, 384, 398, 412, 426, and 440.
[b] m/e 149–369, 383, 397, 411, and 425.
[c] INCOS computer software chromatogram display.
[d] Normethyl-17α(H)-hopanes via nuclear methyl group loss from Ring A or B (see text).
[e] See text and Fig. 4.
[f] California 'basin I', Pleistocene, 1000-ft depth.
[g] SEIFERT *et al* (1978).
[h] Compound 44 is a C_{30} terpane of unknown structure.

(From Seifert & Moldowan, 1979)

demethylated hopanes asevidenced by the observation of the regular sequence of m/e 177 diagnostic compounds, like in Fig. 8 all other conclusions of this basin are identical to those described for the other two basins. Table 6 (second group of three oils) shows an increase in optical activity in the saturate cut from undegraded to heavily degraded oil by a factor of 6 with a parallel yield decrease by a factor of about 2,5 and an apparent terpane increase by a factor of 4,5. The same explanation as given for the other basins appears acceptable, namely, that transformation of hopanes to demethylated hopanes plus transformation of regular steranes to other optically active species are responsible for a portion of the optical activity. However, in the case of the heavily degraded oil of California "basin II", biodegradation was not as extensive as in the Pleistocene oil of "basin I", and the 1710-ft Gulf Coast oil (Table 7) as evidenced by a substantial survival of the bacteria-resistant diasteranes. The 4,2-fold increase in C_{28} (20R) diasterane (Table 7) for heavily degraded over underdraged oil in "basin II" cannot be attributed solely to the 2,3-fold saturate depletion from paraffin loss (Tabel 6). The explanation again is a large immaturity component in the 1585 ft oil from California "basin II", requiring more steranes and terpanes (plus concurrent higher optical activity) as starting material for biotransformation. Therefore, in none of the three oil groups is there a need to invoke bacterial synthesis to explain higher optical activity in heavily degraded oils.

The situation is further elucidated by quantitative values (absolute) for individual biomarker steranes (Table 7). In all three basins an increase in individual steranes is observed going from the undegraded to the moderately or lightly degraded oil, due to a concentration effect. The most significant observation for all three sets of oils is the decrease of the C_{27}20S/C_{27} 20R ratio in the 13β, 17α diasterane series, in comparing the undergraded to the heavily degraded oil. In fact, in the Gulf Coast Basin and in California "basin I" (top of Table 7), their ratio is inverted. In the lightly or moderately degraded oils in these two basins, an enrichment of 20R relative to 20S is already indicated. This means a faster rate of biodegradation for 20S. This results supports the conclusion of PHILLIPI (1977), who postulated bacterial attack at different rates on optical antipodes to account for increased optical activity in low boiling fractions of degraded oils.

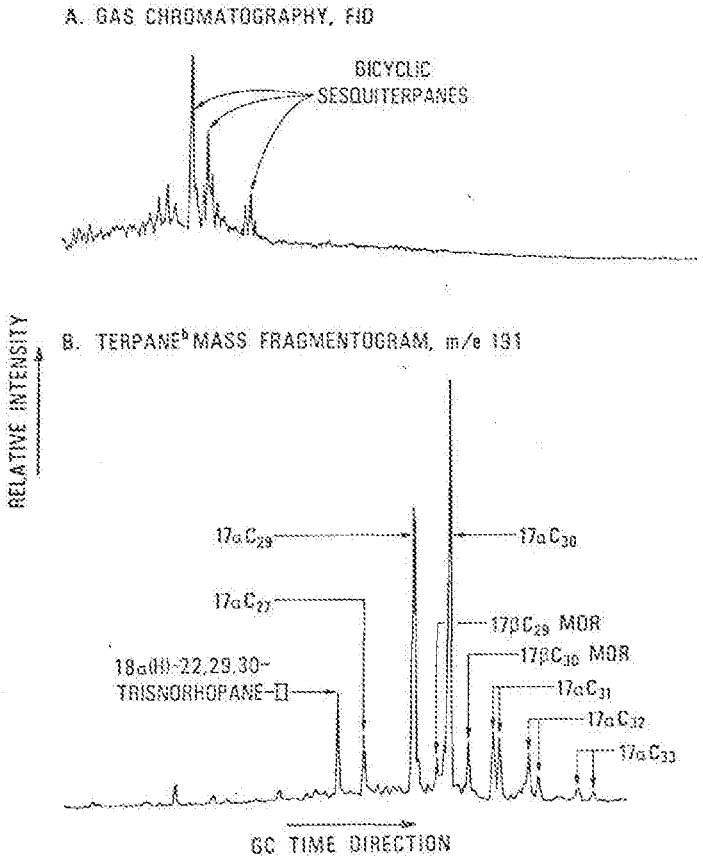


Fig. 9 An unusual heavily degraded crude.[a]

[a] Texas, Gulf Coast, Oligocene.
[b] Stereochemical labels refer to 17α(H),21β(H)-hopanes and 17β(H),21α(H)-moretanes.

(From Seifert & Moldowan, 1979)

Biodegradation of steranes and terpanes in crude oil

Table 7 Absolute quantities of selected[a] steranes in crude oils (ppm)

Basin	Age	Depth, ft	Natural Skeleton 5α: C_{27}[c] 20R (I)[d]	C_{28} 20R (I)	C_{28} 20S (I)	C_{29} 20R (I)	C_{29} 20S (I)	Natural Skeleton 5β (I)[b]: C_{28}	C_{29}	Iso Skeleton[b] 14β,17β (I)[b]: C_{28}	C_{29}	Rearranged 13β,17α: C_{27} 20S (II)[a]	C_{27} 20R (II)[b]	C_{28} 20R (II)[b]	Degree of ...gradation[d]
California I	Mio	8900	510	460	379	400	319	93	50	500	320	200	170	215	0
	Plio	4518	610	670	152	570	142	90	70	500	360	270	250	215	+
	Pleis	1000	0	0	0	0	0	0	0	0	0	78	145	100	++++
California II	Mio	4520	109	80	36	57	37	19	27	140	93	155	97	86	0
	Plio	3032	340	320	140	280	116	56	28	410	250	170	105	160	+
	Plio	1585	0	0	0	0	0	0	0	0	0	290	260	360	+++
Gulf Coast	Plio	5018	37	38	9	20	17	0	0	79	73	130	70	78	0
	Plio	5832	93	23	15	31	25	0	0	133	120	160	120	100	++
	Pleis	1710	0	0	0	0	0	0	0	0	0	38	51	58	++++

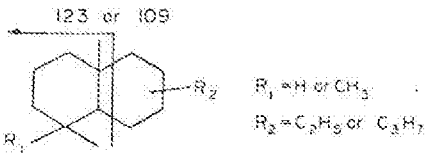
[a] Selected on the basis of model compound availability (see Table 4) and resolution from other steranes in mass chromatography (see Fig. 1). See text and Table 3 for an explanation of how calculations were performed.
[b] Values represent total of 20R + 20S epimers for each carbon number.
[c] Values are greater than true values due to overlap with a C_{29} diasterane (compound 21, Table 4).
[d] Roman numerals refer to complete stereochemical structures in Table 4.
[e] See footnote e, Table 5.

(From Seifert & Moldowan, 1979)

On first sight, one is tempted to draw a similar conclusion for C_{28} and C_{29} 20S regular steranes (Table 7) as being easier biodegradable than 20R because there is more 20S relative to 20R in the undegraded oils. However, the undegraded oils are also deeper, i.e. more mature. Returning to our discussion above on thermodynamic stabilities, it follows that the more mature oils should have undergone a greater degree of epimerization from 20R (configuration in natural product) to 20S formed during diagenesis) than the less mature ones. Thus, it is not possible to assign the subtle change in 20S/20R ratio in the regular steranes to different rates of biodegradation because it could mostly or totally be the consequence of different degrees of maturation. In the case of the 13β, 17α C_{27} diasteranes, the 20S/20R ratio changes are very drastic and are truly expected to reflect rates of biodegradation.

Figure 9 depicts an unusual biodegraded oil for which we possess no source related less degraded counterparts. This Texas Gulf Coast crude is probably related to the Loma Novia crude from South Texas described by BENDORAITIS (1974). Like Bendoraitis, we find high concentrations of bicyclic sesquiterpanes (described below) and a component in the monoaromatic fraction which displays a large m/e 365 peak. It is among the most degraded of all oils examined as evidenced by total loss of n + isoparaffins. In contrast to the oils from the three basins described above, it exhibits a total absence of all steranes and tricyclic terpanes while retaining all regular hopanes.

The phenomenon, so we speculate at present, is either related to the specific conditions of biodegradation or an unusual source or to factors unknown to us at this time. Also, unique for this oil is a high consentration of compounds with a probable bicyclic sesquiterpane structure. This assignment is made solely on the basis of their mass spectra which contain a m/e 109 or 123 base peak along with a m/e 194, 208 or 222 molecular ion compare also Fig. 4 of BENDORAITIS, 1974.



Present research activities are focused on simulating naturally occuring biodegradation processes in the laboratory, including the structural elucidation of the products of sterane degradation.

Seifert and Moldowan, 1979, sum up their results in the following

1. In crude oils, steranes and terpanes are biodegraded at a slower rate than isoprenoids and survive light to moderate biodegradation. Therefore, previously described (SEIFER and MOLDOWAN 1978) correlation approaches appear applicable to such cases.

2. In heavily degraded crudes, regular steranes are totally destroyed; diasteranes survive biodegradation; but diasterane concentration is also decreased in most cases.

3. Tricyclic terpanes survive heavy degradation in most cases and, thus can potentially serve as correlation parameters as described previously (SEIFERT, 1978).

4. The rate of biedegradation of 20S C_{27} 13β, 17α (H) diasteranes is greater that that of its 20R epimer.

5. Regular fossil fuel hopanes are transformed by biodegradation to Ring A/S demethylated hopanes in two California basins. In the three basins reported in this paper, demethylation plus n-paraffin depletion (causing biomarker enrichment) results in an increase of optical activity in heavily degraded crudes. No evidence for bacterial synthesis of normal fossil fuel steranes and terpanes was found for these three basins.

6. Ring C/D cis(14β)-steranes previously reported as predominant components in Russian crudes are now proven to possess 14β, 17β 20R and 20S stereochemistry by NMR, MS, and optical rotation. These compounds were found to be major biomarker constituents in all fossil fuels examined.

7. A cholestane isomerizate (300°C, Pt on C) was found to contain 14β, 17 20R and 20S and cholestane 20S as major components and 14 , 17 20R + 20S cholestanes + the 5-counterparts of these 20R and six compounds as minor components. Relative thermodynamic stabilities of all fossil fuel steranes are discussed.

8. A convenient overview of the complex sterane mixture in fossil fuels is deployed by the use of the GC-MS map. Ion profiles at m/e 218 characteristic for 14β,17βsteranes and that at m/e 232 diagnostic for 13α,17β diasteranes supplement the previously used profiles at m/e 259 for all disteranes (SEIFERT and MOLDOWAN, 1978) and at m/e 151 and 149 for Ring A/B stereochemistry (SEIFERT et al., 1972), rendering this method a most powerful analytical tool.

9. A method for determination of absolute quantities of individual sterane biomarkers is described. The method employs spiking with 5β-cholane plus subsequent multiple ion detection GC-MS-C. Up to 0,06% (based on crude oil) 5α-cholestane was found in lightly biodegraded crude oil.

Experimental:

The rocksamples were crushed in a centrifugal mill and extracted with DCM in soxlet apparatus for 48 hrs. The extract were then chromatographed on silica/allumina columns using hexane, benzene and methanol as eluants. The saturated hydrocarbon fractions were then tested of glascapillary GC and GC-MS and the concentration of steranes and triterpanes were found to be sufficient for further analyses. The urea/thiourea adduction which normally have to undertake for such analyses, were not performed on these samples.

Total hydrocarbons from an aliquot of the oil were isolated by allumina calumn chromatography eluting with an 80/20 mixture of petroleum ether/ toluene.

Examination by C-GC-MS:

All fraction were examined by C-GC-MS under the following conditions:

Finnigan 3200 GC-MC/6100 Data system

GC	: 10m x 0.3mm OV-1 capillary temperature programmed from 80-270 at 4^{o}/min, ca 2ml/min He
MS	: 300µ A filament emission, 70eV electron energy
Data System	: Continuous scanning and data collection from mass 50-550 every ca 1.8 seconds

Following data collection the following mass fragmentograms were generated for all samples:

a) the TIC
b) m/e 85 (acyclic alkanes)
c) m/e 191 (triterpenoid alkanes)
d) m/e 217 (steroidal alkanes in general)
   m/e 259 (rearranged steranes)
   m/e 218 (14β H-steranes)
   m/e 231 (nuclear methylated steranes)

The above suite of sterane framentograms (series d) were generated in stacked format for ease of intersample comparison.

RESULTS

a) Triterpanes

OVERALL COMPARISON OF OIL AND CORE EXTRACTS

Comparison on a visual basis of the m/e 191 framentograms between the oil and rock extracts is given in Table 8, together with general comments concerning the distributions observed.

Thus, the m/e 191 framentogram for the oil, Fig. 10, shows the presence of a C_{28} triterpane (substantiated by further mass fragmentography of m/e 163 and examination of a full mass spectrum). Such a component is almost certainly 17α H,-18α H,28,30-Bisnorhopane found in many other crude oils, including some from the North Sea. Of the extracts examined, only those from 1780m (Fig.17) and 1940m (Fig.20) (well 34/10-1) and those from 2550-65m (Fig.11) and 2730-50m (Fig.12) (well 34/10-2) show the presence of a similar C_{28} triterpane (confirmed by examination of full mass psectrum). Samples from well 34/10-2 and those at 1970 (Fig.22) and 1880m (Fig.19) (well 34/10-1) show triterpane distributions (m/e 191) characteristic of most crude oils ie, the predominance of 17αH-Triterpanes extending from C_{29} to C_{35}, but do not contain the C_{28} triterpane observed in the oil. The triterpane distribution observed for 1833m (well 34/10-1) (Fig.18) does not resemble that associated with crude oils but is more similar to those of immature sediments and shales. That from 1951m/well 34/10-1 (Fig.21) shows similarities to that of an oil but is also shown to contain a major abundance of triterpanes not of the 17αH-hopane series.

As noted above samples from 1780 and 1940m (well 34/10-1) and those from 255065m and 2730-50m (well 34/10-2) are the only extracts shown to contain the C_{28} triterpane, present in the crude oil. However, minor differences in the distribution compared with the oil are observed, in particular the presence of a minor contribution to the extract from well 34/10-1 from 17βH-homohopane, a triterpane not normally associated with oils but with more immature sediments such as those from trom the 1833 and 1951 (well 34/10-1) samples.

Table 9 shows the ratios obtained for the 17αH-C_{29}/17αH-C30 hopanes in each of the samples. As can be seen, no major trends are apparent, although the ratios closest to that for the oil are observed for samples from 1940 and 1951m (well 34/10-1).

TRITERPANE DISTRIBUTIONS FOR INDIVIDUAL SAMPLES

Crude oil well 34/10-1: The major triterpenoids present are those of the 17αH-hopane series. The relative abundance of such components are as observed for most crude oils. The presence of a major C_{28} triterpane (almost certainly 17αH, 18αH, 28, 30-bisnorhopane, see above) component is a major diagnostic feature of the oil for "fingerprint correlation purposes with triterpane distributions observed for presumed source rock extract. (Fig.10.)

Well 34/10-2:

2550-65m — The triterpanes present, although low in relative abundance, show a distribution similar to most crude oils. Furthermore, the extract can be seen to contain the C_{28} triterpane observed in the crude oil. (Fig. 11)

2730-50m — As for the extract from 2550-65m the triterpane distribution parallels that for most crude oils. Furthermore, the presence of the C_{28} triterpane in the extract shows similarities to the crude oil. (Fig. 12)

2780-95m — Again, the distribution is similar to thos observed for most crude oils. However, in contrast to the extract above the samples does not contain the C_{28} triterpane observed in the crude oil. (Fig.13)

2975-90m — The triterpane distribution observed resembles that of most crude oils. However, the sample does not contain the C_{28} triterpane observed in the crude oil. (Fog. 14)

3032-50m — As for the sample from 2975-90m. (Fig. 15).

3110-25m — As for the sample from 2975-90m. (fig. 16).

For the above suite of samples, from deeper than 2900m, several trends in the triterpane distributions with depth are apparent:

i) decrease in the ratio of $17\alpha HC_{29}/17\alpha H\text{-}C_{30}$ hopanes (see table 10).

ii) Decrease in the relative contribution of a triterpane series not of the $17\alpha H$-hopanes type but presumably of the moretane type.

iii) decrease in the relative contribution from $17\alpha H\text{-}C_{27}$ hopane.

Well 34/10-1:

1780m — The triterpane distribution observed is superimposable with that of the crude oil. However, it is not unlikely that the sample is contaminated with the oil in question (Fig.17). (Se report 0-170/1/78).

1833m — The distribution observed does not resemble that of a crude oil but of an immature sediment or shale. (Fig. 19).

1880-90m — Distribution similar to most crude oils. However, the sample does not contain the C_{28} triterpane observed in the crude oil (Fig. 20).

1940m — Distribution similar to most crude oils and the sample does contain the C_{28} triterpane observed in the oil. However, minor triterpanes are present which are not normally found in oils, but which are normally associated with immature sediments and shales. The sample is known to contain a major portion of reworked material (Fig. 20). (See report 0-170/1/78).

1951m — The triterpane distribution shows the presence of major components normally associated with immature sediments and shales (Fig. 21).

1970-85m — As for the core from 1951m (Fig. 22).

No trends are apparent in the triterpane distribution with increasing depth of sample from this suite.

b) Steranes

Comparison on a visual basis of the m/e 217, 259, 218 and 231 mass fragmentograms between the oil and rock extracts is given in Table 11 together with general comments concerning the distributions observed.

As may be seen, the correlation of the m/e 231 fragmentogram between the oil and all the rock extracts is poor. Thus, the oil appears to contain discrete nuclear methylated sterane components whereas such components were not observed in any of the extracts.

The m/e 217, 259 and 218 fragmentograms for the well 34/10-2 rock extracts and those from 1883 and 1970m well 34/10-1 show poor matches compared with oil. Good comparisons with the oil were obtained for samples 1780, 1880 and 1951m (well 34/10-1, with those for 1780 and 1940m (well 34/10-1) being the closest.

To reinforce the visual comparison, peak heights of 9 of the major components of the m/e 217 fragmentograms for each extract and the oil were measured and certain peak height ratios obtained. The 9 peaks of interest are shown on each m/e 217 framentogram. The components taken were chosen specifically to reflect specific steroidal alkane structural types. Thus, for example, components 1 and 2 are rearranged steranes, components 7 and 15 are regular steranes but having the 14βH, 17βH stereochemistry and components 11 and 17 are 24-methylcholestane and 24-Ethylcholestane respectively.

Certain peak height ratios of the components taken are presented in Table 12. Parameter 1 shows the internal distribution of rearranged steranes, parameters 5 and 8 show the relative distribution of rearranged steranes to regular steranes (reflecting both migration and maturation effects) and parameter 10 shows the internal relative distribution of regular steranes recognised as a valuable source rock/oil correlation parameter. Thus parameter 10 (Table 12 shows that the extract from 1940m (well 34/10-1) and in particular that from a core of depth 1780m (well 34/10-1) bear the closest similarity to that of the oil. Parameter 8 shows that extracts from 2975, 3032 and 3110 (well 34/10-2) and 1833 and 1970m (well 34/10-2) have far more abundant regular steranes than rearranged compared to the oil and compared to extracts from 1880, 1940 and 1951m (well 34/10-1). Overall, the closest comparison of all the parameters with those of oil are shown for the 1780m (well 34/10-1).

STERANE DISTRIBUTIONS (m/e 217)

CRUDE OIL: The distribution of steroidal alkanes obtained (and reflected in the parameter ratios, Table 12) is typical of that obtained for many crude oils. The ratio of rearranged to regular steranes (eg parameter 8, Table 12) suggests the oil to be fairly mature. (Fig. 23).

Well 34/10-2

2550-65m The distribution obtained is similar to those for many crude oils. However, as indicated in Table 12 the relative distribution of the steranes shows differences compared to the oil under study. (Fig. 24).

2730-50m As for 2550-65m. (Fig. 25)

2780-95m As for 255065m. (Fig. 26)

2975-90m — The distribution obtained suggests a major abundance of regular steranes (especially 5α-) compared to rearranged (parameter 8, Table 12) suggesting the sample to be more immature compared to the crude oil. (Fig.27).

3032-50m — As for sample from 2975-90m. (Fig. 28).

3110-25m — As for sample from 2975-90m. (Fig. 29).

The distributions obtained for the above 3 samples below 2900m show a trend in various internal steroidal alkane relative abundances with increasing depth. Thus, for example:

a) Paramter 8 (rearranged/regular 5α-sterane) shows an increase with increasing depth reflecting a greater maturity with increasing depth.

b) Parameters 7, 5 and 4 show increases with increasing depth, again presumably reflecting greater maturity with depth.

Well 34/10-1:

1780m — The distribution obtained together with the parameters presented in Table 12 are identical to those of the oil sample. (Fig.30) However, as stated above it is quite possible that this sample was contaminated with the crude oil under examination.

1833m — As for the sample from 2975m (well 34/10-2). (Fig.31)

1880-90m — The distribution obtained is similar to those for many crude oils. However, minor differences are apparent, eg, parameters 3 and 4 due to the low intensity of peak 8 compared to the oil. (Fig. 32).

1940m — As for the sample from 1880-90m (Fig. 33).

1951m As for the sample from 1880-90m. (Fig. 34)

1970-85m As for the sample from 2975m (well 34/10-2).(Fig. 34)

No clear cut trends are apparent in the steroidal alkane parameter ratios with increasing depth. However, higher values for parameters 8, 9 and 10 are apparent in the 1850-1950m section of the well, possible indicating higher sample maturity in this region.

c) Steranes v triterpanes

The relative abundance of steroidal alkanes to triterpenoid alkanes based on the m/e 217 and 191 overall signal intensities, for the oil and extracts are given in Table 13. For all the extract samples the ratio values obtained were higher than that for the oil. However, those for the 1780 and 1940m extracts (well 34/10-1) bear the closest similarity to that for the oil.

CONCLUSIONS

Based on the distributions of triterpenoid alkanes (m/e 191) and steroidal alkanes (m/e 217, 259, 218 and 231), the following conclusions may be drawn:

i) The distributions were superimposable with those of the oil (apart from m/e 231) only for the 1780m extract from well 1. However, it is possible that this sample (although a core) was to some extent contaminated with the crude oil in the well.

ii) The sample (apart from the from 1780m) showing the closest similarity to the oil was that from 1940m (well 34/10-1). However, it is believed from vitrinite reflectance measurements that the sample contained a major proportion of reworked material. (See report 0-170/1/78). Thus, it is possible that the distributions observed may not be attributable to the indigenous material in the core.

iii) The steroidal and triterpenoidal alkane fingerprints from the 2975,, 3032 and 3110m (well 34/10-2) extracts showed no similarities to those of the oil and thus cannot be considered as as source rocks for the oil in well 34/10-1.

iv) The extracts from 2550 and 2730m (well 34/10-2) showed the presence of the C_{28} triterpane observed in the oil under study. The sterane distributions for these samples suggest, surprisingly, that the hydrocarbons present are more mature than those below 2900m in the well. However, the distributions observed show major dissimalrities (Table 12) to those of the oil. This section of the well constained, however, a large proportion of reworked material. (See report 0-179/1/79.)

v) Major differences in the distributions of steroidal alkanes are apparent between the extracts for 2975m (well 34/10-2), 3032m (well 34/10-2)) 2550m (well 34/10-2), 2730m (well 34/10-2), 2780m (2311 34/10-2), 2780m (well 34/10-2),1880m (well 34/10-1), 1940m (well 34/10-1) and 1951m (well 34/10-1), the former showing major contributions from regular steranes reflecting the lesser degree of sample maturity than the latter. This might be due to a large input of reworked material in the latter.

vi) The triterpanes of sample extracts from 1883m and 1951m (well 34/10-1) exhibit distributions normally associated with immature sediments and shales.

vii) The distribution of the steranes and triterpanes in the oil from well 34/10-1 indicate the oil to be an ordinary mature oil. On the background of the GC measurements of the oil this indicate that the oil is slightly beodegraded. Most of the n-alkanes are degraded but no all, especially the low end ones.

TABLE 8

Description of samples.

	Sample Depth (m)	Description of sample
Well 34/10-2	2550-65	Extract from cuttings
	2730-50	Extract from cuttings
	2780-95	Extract from cuttings
	2975-90	Extract from cuttings
	3032-50	Extract from cuttings
	3110-25	Extract from cuttings
Well 34/10-1	1780	Extract from core, similar age to 2975m from well 34/10-2. The sample might be contaminated with oil.
	1833	Extract from core sample. GC indicate high ionmaturity (high CPI value).
	1880-90	Extract from cuttings. Probably contaminated with oil.
	1940	Extract from core.
	1951	Extract from core.
	1979-85	Extract from cuttings

TABLE 9.

VISUAL COMPARISON OF TRITERPANE MASS FRAGMENTOGRAMS FROM SAMPLES WITH THAT OF OIL

	SAMPLE DEPTH	MATCH*	COMMENTS
WELL 34/10-2	2550-65	***	C_{28} triterpane present
	2730-50	***	C_{28} triterpane present
	2780-95	*	
	2975-90	*	major differences in relative abundances
	3032-50	**	no C_{28} Triterpane
	3110-25	***	no C_{28} Triterpane
WELL 34/10-1	1780		
	1833	*	Distribution similar to those of immature shales
	1880-90	***	no C_{28} Triterpane
	1940	****	Only sample to contain C_{28} Triterpane but also contains minor 17βH-Homohopane
	1951	*	Major abundance of components other than 17αH-hopane series
	1970-85	*	Major differences in relative abundances

* matching based on 5 star basis ie ***** superimposable
**** very good match
*** good match
** some similarities
* poor match

TABLE 10

RATIO OF 17αH-NORHOPANE (D) TO 17αH-HOPANE IN OIL AND CORE SAMPLES

	SAMPLE	RATIO	COMMENTS
	OIL	0.48	major C_{28} Triterpane
WELL 34/10-2	2550-65	0.5	C_{28} triterpane present
	2730-50	?	C_{28} triterpane present
	2780-95	0.69	no C_{28} triterpane
	2975-90	0.75	-
	3032-50	0.70	-
	3110-25	0.51	-
WELL 34/10-1	1780	0.48	major C_{28} Triterpane
	1833	0.6	-
	1880-90	0.57	-
	1940	0.50	major C_{28} Triterpane
	1951	0.48	-
	1970-85	0.60	-

TABLE 11

VISUAL COMPARISON OF STERANE MASS FRAGMENTOGRAMS FROM CORE SAMPLES WITH THOSE OF OIL (E-5038)

	SAMPLE DEPTH	STERANE FRAGMENTOGRAM (m/e)				COMMENTS
		217	259	218	231	
WELL 34/10-2	2550-65	*	*	*	*	-
	2730-50	**	**	*	*	-
	2780-95	***	***	**	*	-
	2975-90	*	***	*	*	C_{29} steranes > C_{27}
	3032-50	**	*	**	*	as 2975-90
	3110-25	**	*	*	*	as 2975-90
WELL 34/10-1	1780	*****	****	****	*	superimposable apart from m/e 231
	1833	*	*	*	*	as 2975-90
	1880-90	***	***	***	*	Good match although differences in relative abundances apparent
	1940	****	****	****	*	Good match apart from m/e 231
	1951	****	?	***	*	m/e 259 signal weak but m/e 217 good match
	1970-85	*	*	*	*	as 2975-90

m/e 217 = steranes in general, 259 = rearranged steranes,
218 = 14βH, 17βH-steranes, m/e 231 = nuclear methylated steranes

matching based on 5 star basis ie ***** superimposable
**** very good match
*** good match
** some similarities
* poor match

TABLE 12

CORRELATION PARAMETERS FROM m/e 217 FRAGMENTOGRAMS

	SAMPLE/RATIO	1/2	1/7	7/8	8/9	1/11	9/11	1/14	1/17	15/17	11/17
	OIL	1.4	1.3	2.1	0.7	1.6	0.9	2.1	1.6	1.2	1.05
WELL 34/10-2	2550-65	1.05	1.2	1.1	1.1	1.2	0.83	3.5	0.65	0.4	0.56
	2730-50	1.08	1.3	1.1	0.73	1.3	1.2	1.9	1.1	0.6	0.9
	2780-95	1.3	1.0	1.3	1.3	1.6	1.0	1.5	1.2	0.9	0.7
	2975-90	1.8	0.4	3.6	0.5	0.9	1.4	0.5	0.3	0.4	0.4
	3032-50	1.4	1.0	0.9	1.3	1.0	1.0	0.9	0.5	0.5	0.5
	3110-25	1.6	1.2	0.7	1.7	1.7	1.1	1.5	0.7	0.5	0.41
WELL 34/10-1	1780	1.5	1.3	1.9	0.7	1.6	0.9	2.1	1.7	1.2	1.06
	1833	1.5	0.75	2.0	0.5	1.0	1.25	2.5	0.3	0.6	0.33
	1880-90	1.5	1.6	2.4	0.5	2.0	1.2	2.9	2.1	1.0	0.67
	1940	1.5	1.4	1.1	1.4	1.4	0.7	3.5	1.4	1.0	0.96
	1951	1.7	1.7	1.3	1.0	1.7	0.77	2.9	1.7	0.9	0.58
	1970-85	1.2	1.4	0.7	2.2	0.9	0.4	0.8	0.4	0.5	0.5
	PARAMETER	1	2	3	4	5	6	7	8	9	10

TABLE 13

RATIO OF MAJOR STERANE V MAJOR TRITERPANE COMPONENTS OF OIL AND EXTRACTS

	SAMPLE	RATIO
	OIL	3.0
WELL 34/10-2	2550-65	5.1
	2730-50	4.03
	2780-95	6.2
	2975-90	6.3
	3032-50	7.9
	3110-25	7.7
WELL 34/10-1	1780	3.7
	1833	4.3
	1880-90	9.2
	1940	3.8
	1951	4.5
	1970-85	12.9

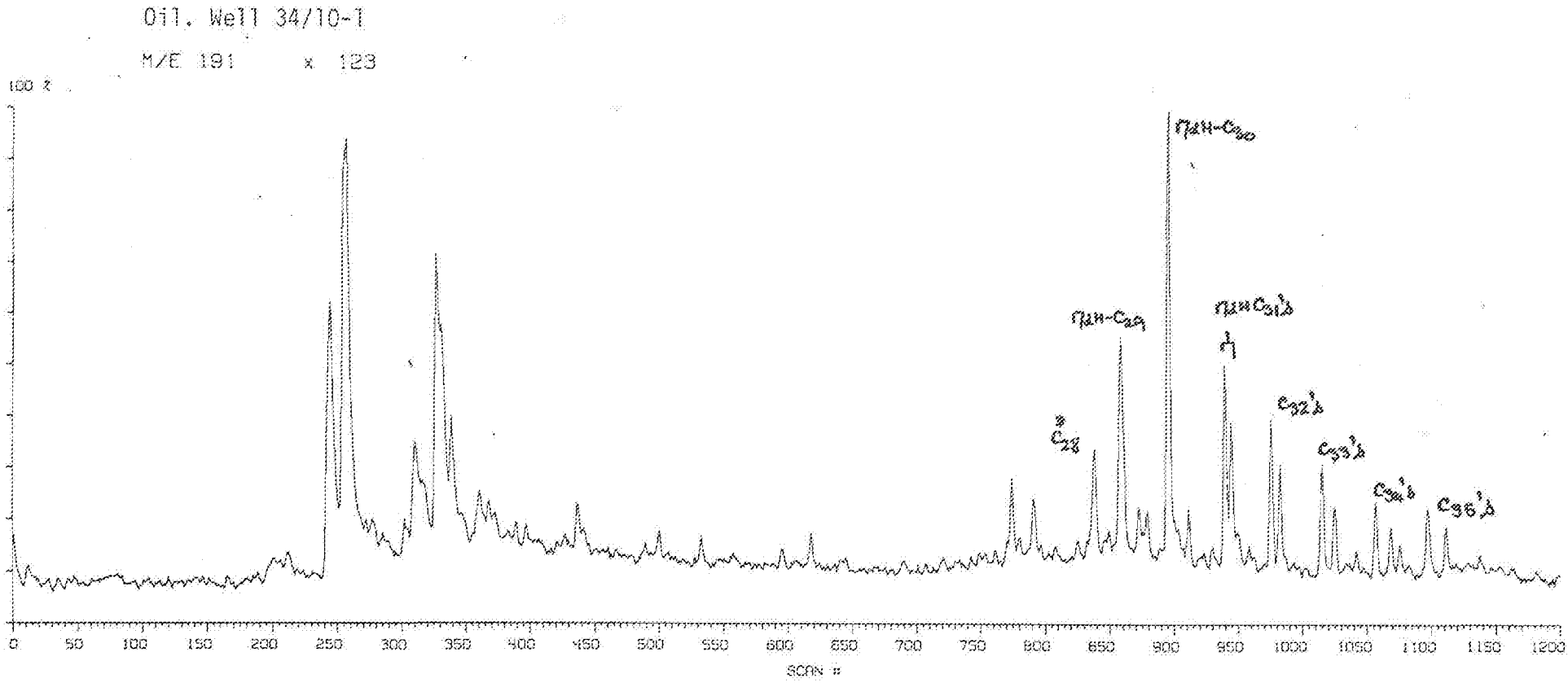

Oil. Well 34/10-1
M/E 191 x 123
100 %
nC28
nC29
nC30
nC31
C32'b
C33'b
C34'b
C36'b
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200
SCAN #

Fig. 10.

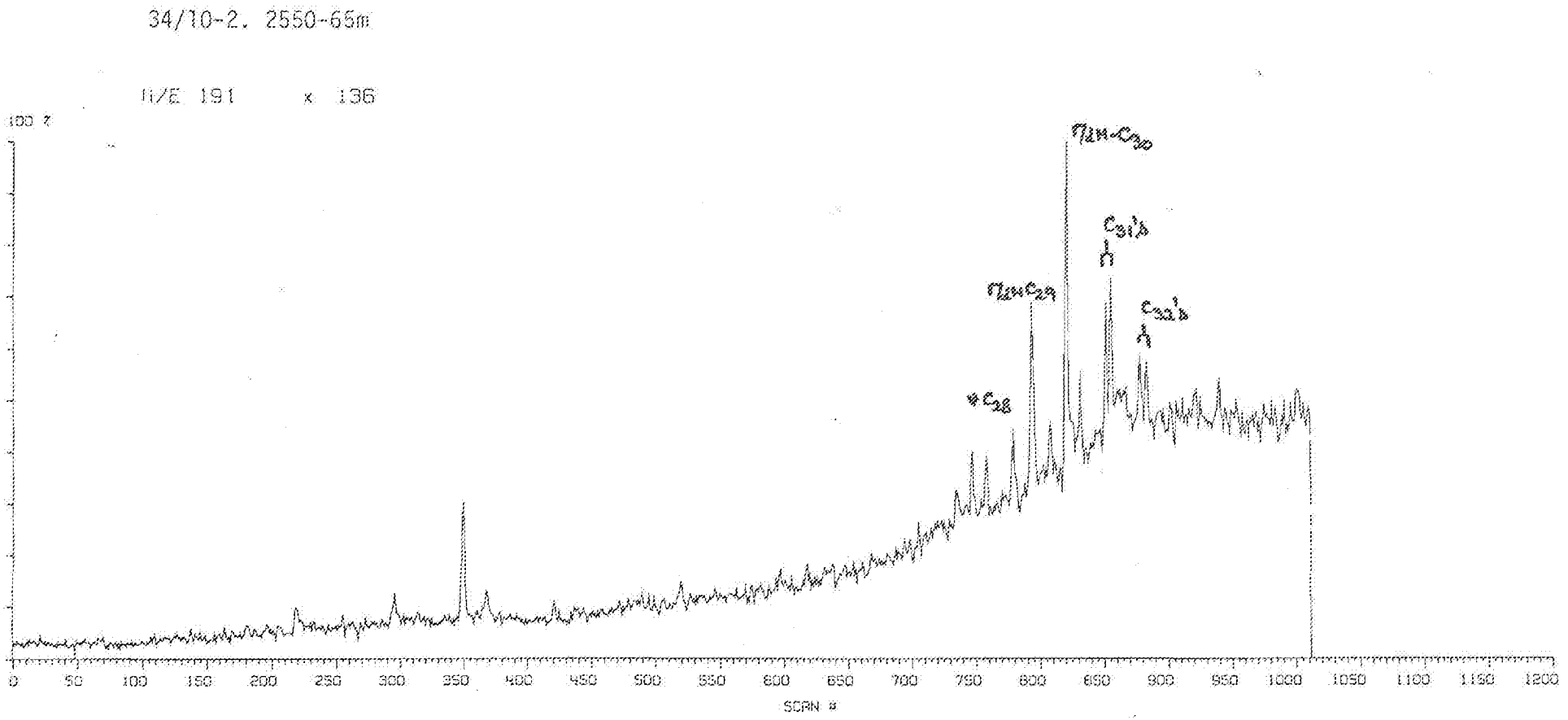

34/10-2. 2550-65m
M/E 191 x 136
100 %
nC29
nC31
nC33
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200
SCAN #

Fig. 11.

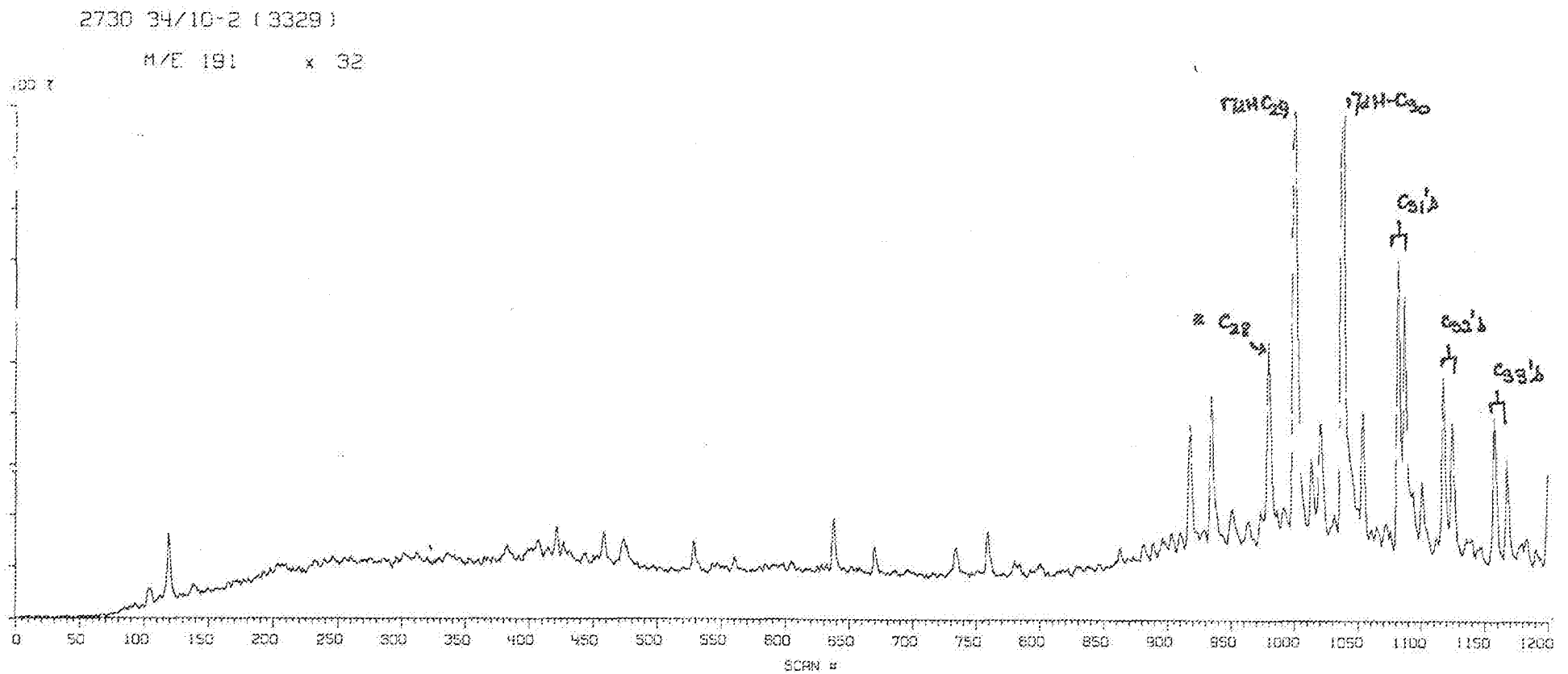

2730 34/10-2 (3329)
M/E 191 x 32
100 %
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200
SCAN #

Fig. 12.

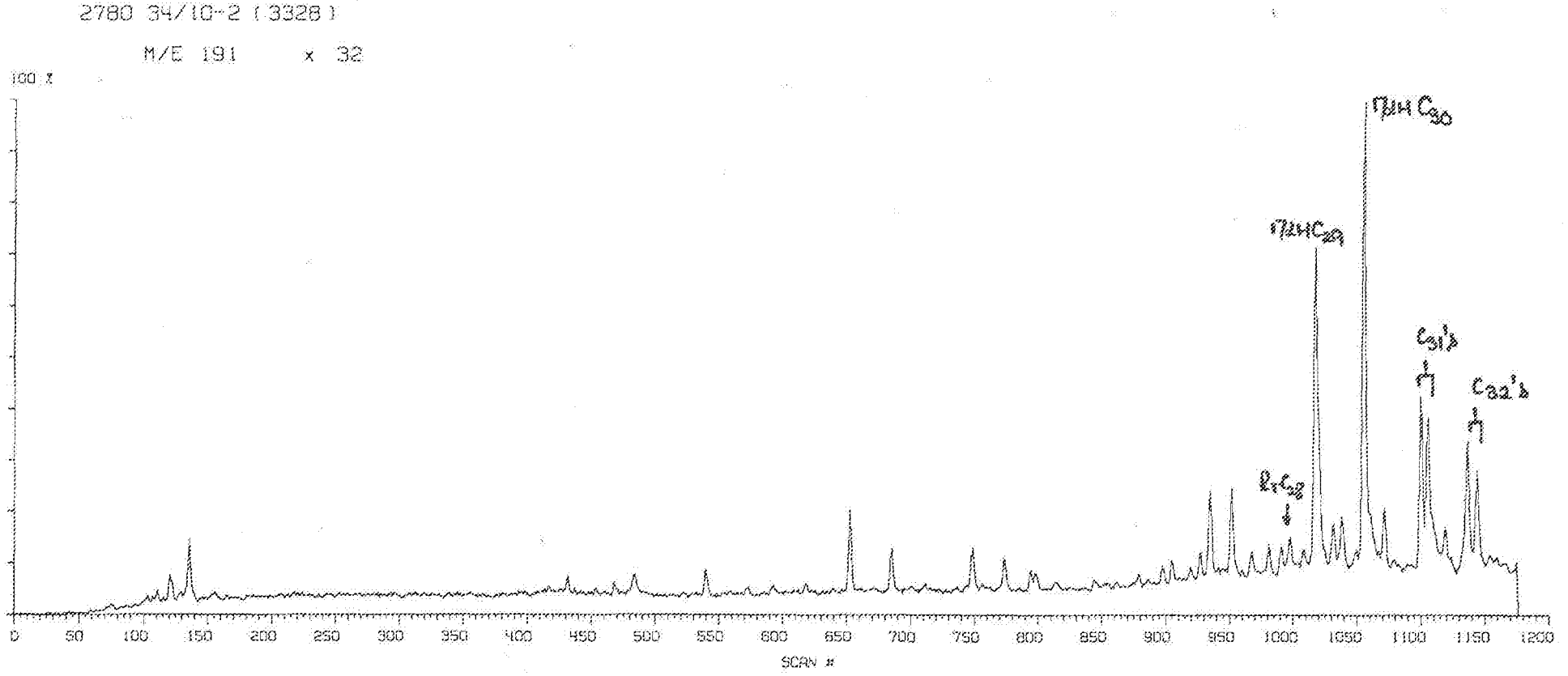

2780 34/10-2 (3328)
M/E 191 x 32
100 %
n-C_{29}
n-C_{30}
C_{31}'s
C_{32}'s
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200
SCAN #

Fig. 13.

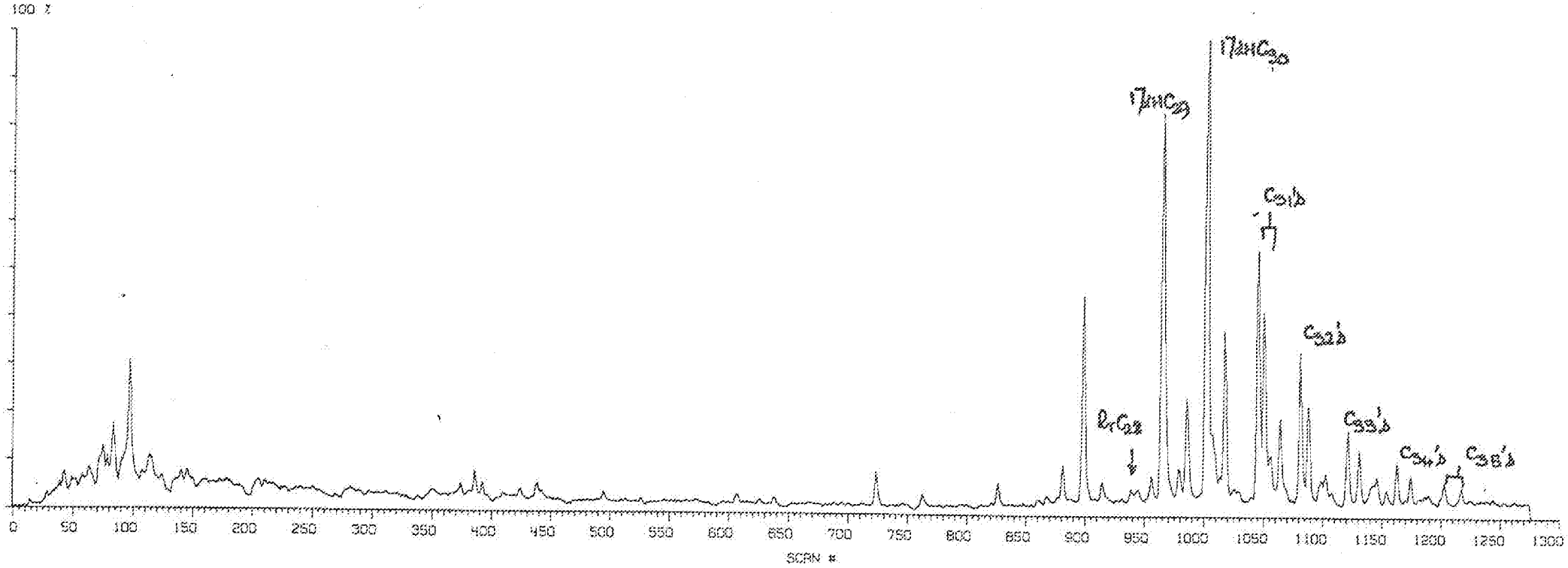

34/10-2. 2975-90m
M/E 191 x 32
100 %
17nC29
17nC30
C31's
C33's
C35's
C36's
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200 1250 1300
SCAN #

Fig. 14.

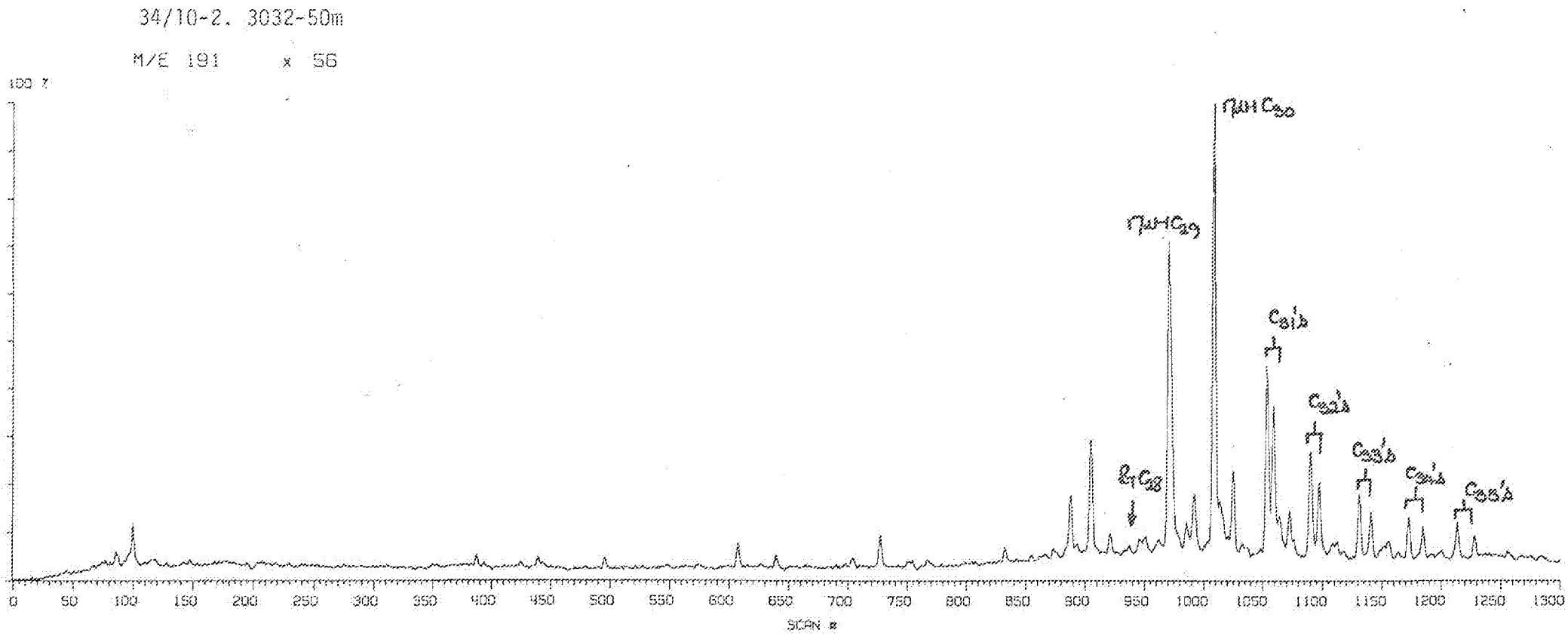

34/10-2. 3032-50m
M/E 191 x 56
100 %
nor C29
nor C30
C31 S
C32 S
C33 S
C34 S
C35 S
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200 1250 1300
SCAN #

Fig. 15.

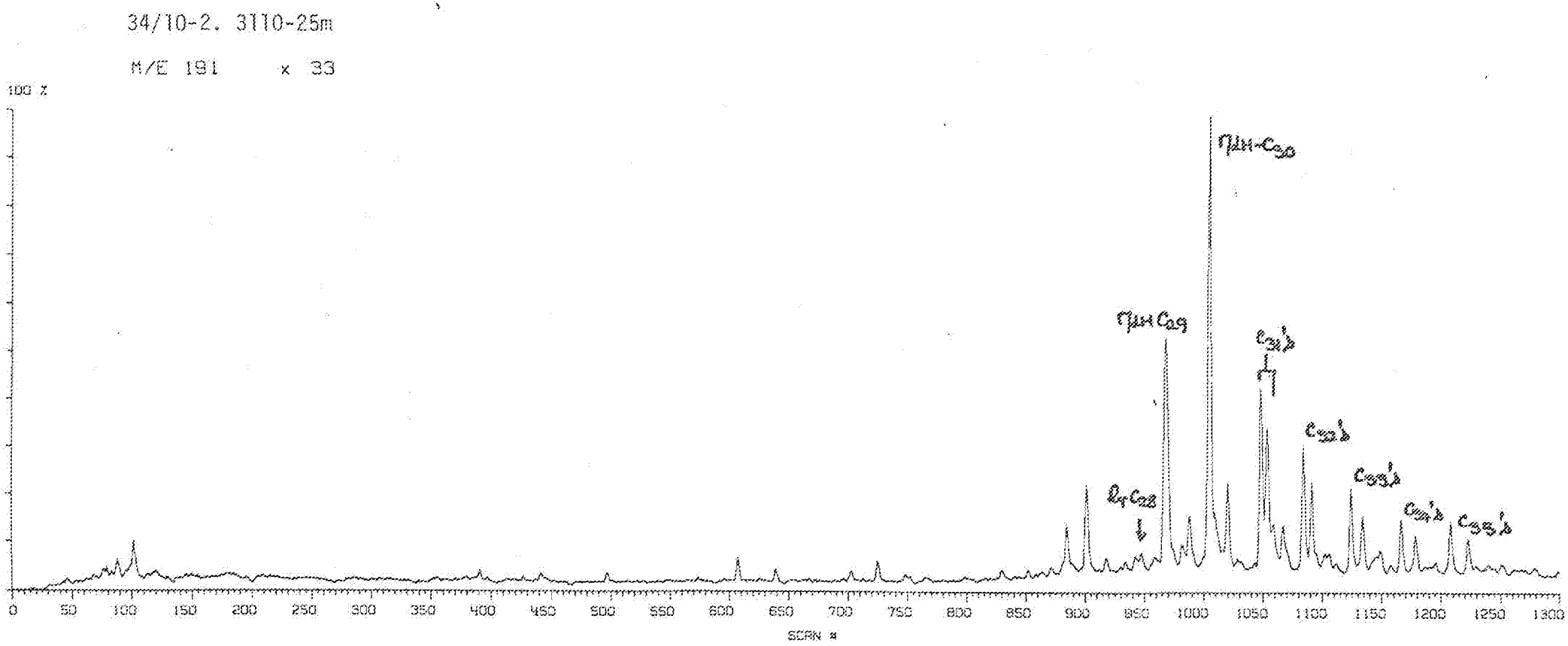

34/10-2. 3110-25m
M/E 191 x 33
100 %
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200 1250 1300
SCAN #

Fig. 16.

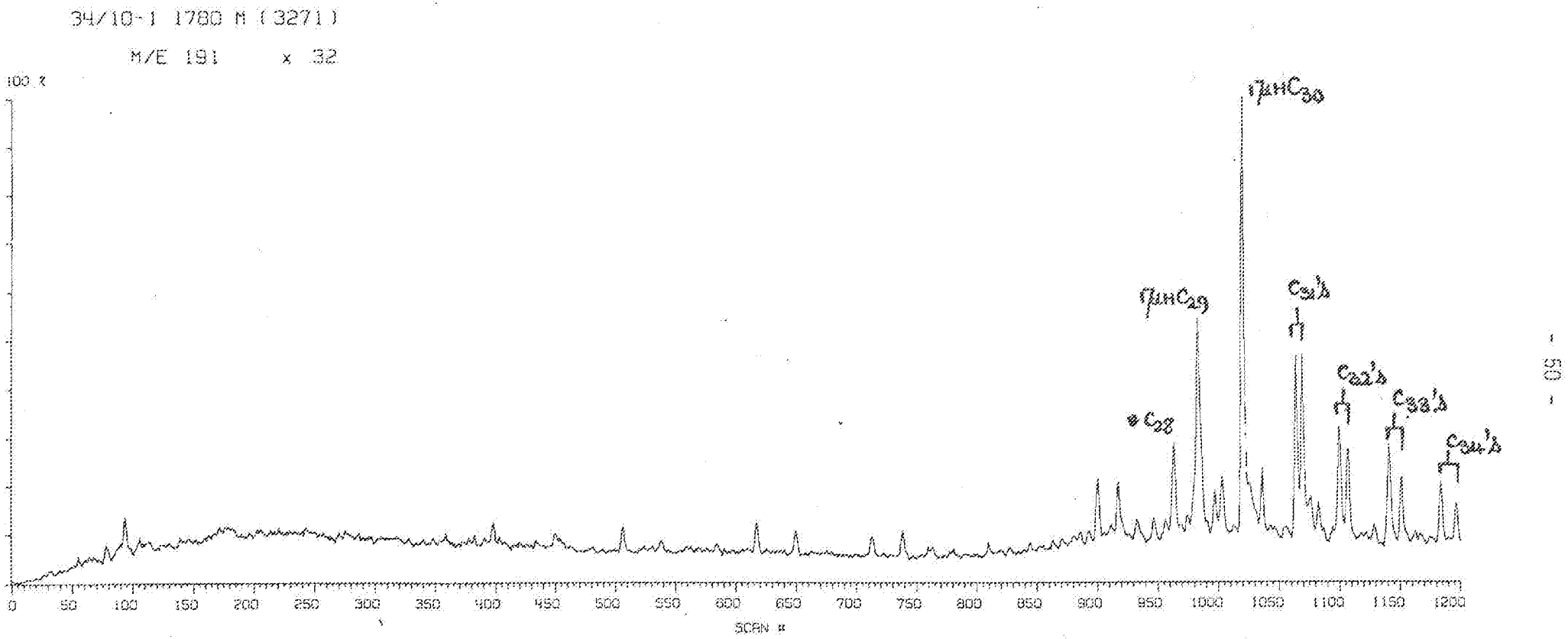

34/10-1 1780 M (3271)
M/E 191 x 32
100 %
nC29
nC30
C31's
C32's
C33's
C34's
C28
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
1150
1200
SCAN #

Fig. 17.

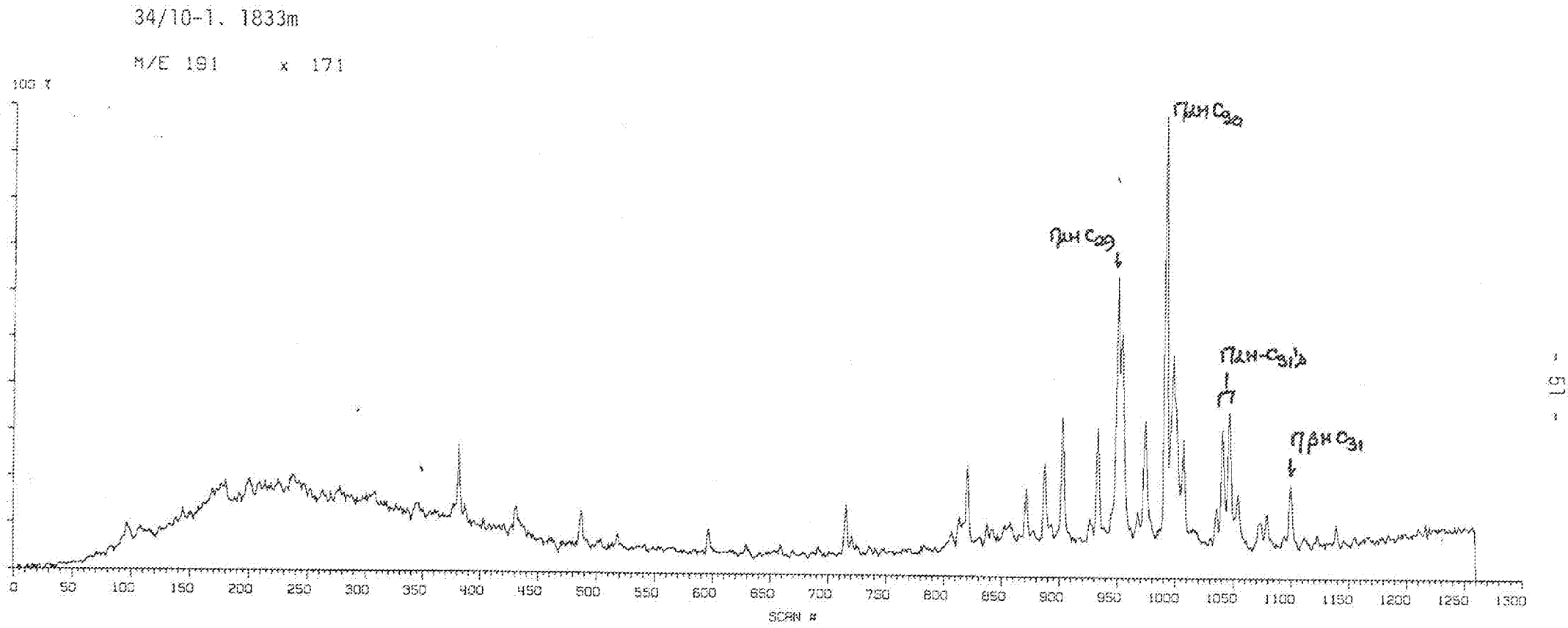

34/10-1. 1833m
M/E 191 x 171
100 %
Pan C29
Pan C30
Pan-C31b
Pan C31
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
1100
1150
1200
1250
1300
SCAN #

Fig. 18.

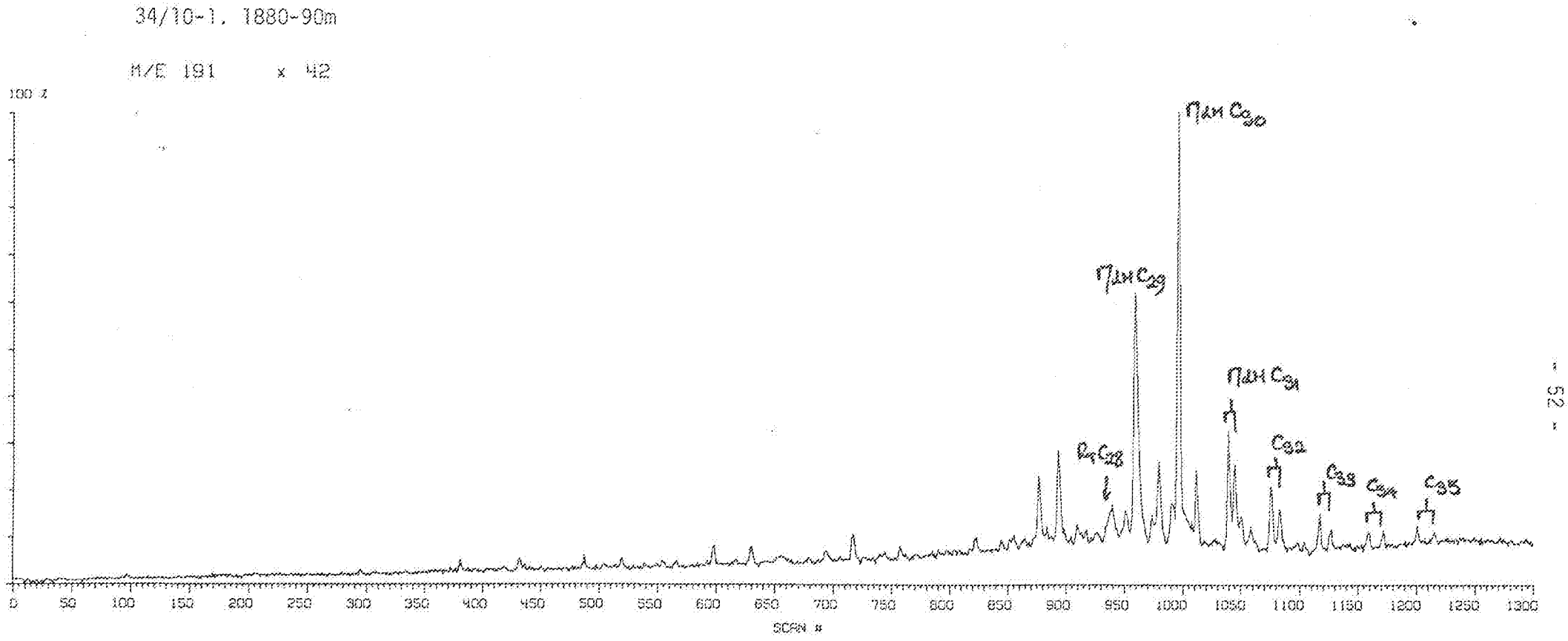

34/10-1. 1880-90m
M/E 191 x 42
100 %
nAn C30
nAn C29
nAn C31
C28
C32
C33
C34
C35
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200 1250 1300
SCAN #

Fig. 19.

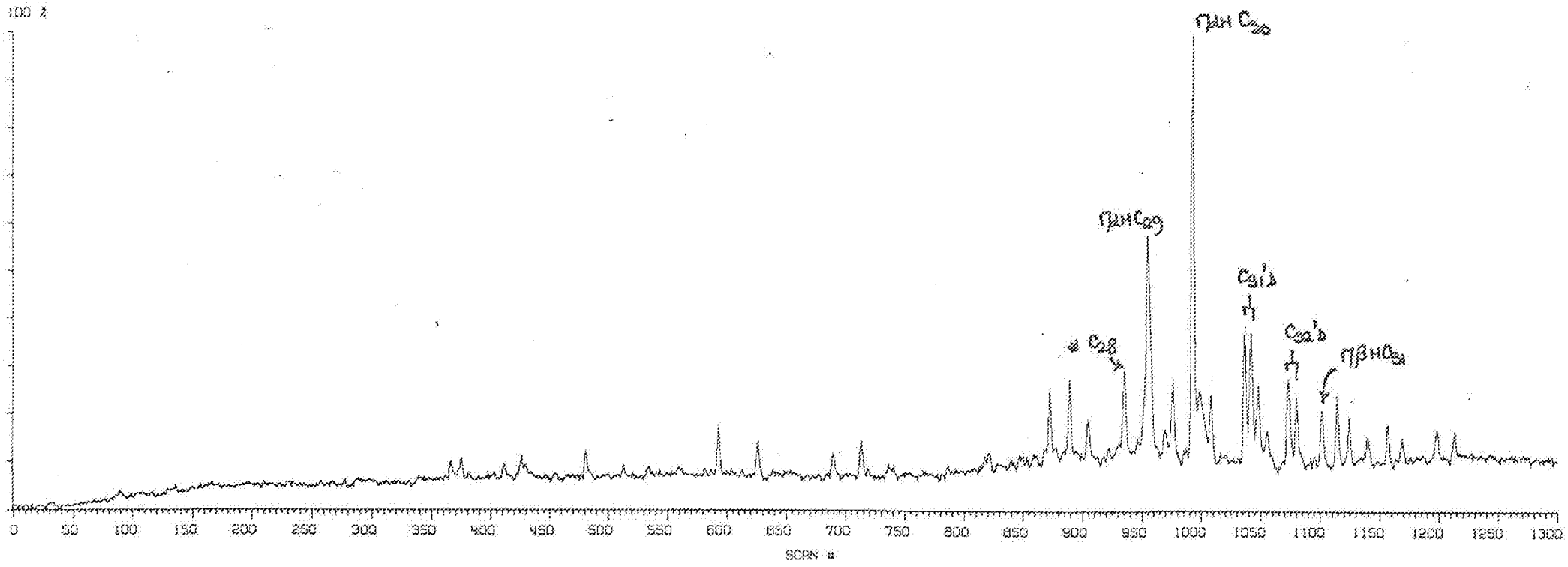

34/10-1. 1940m
M/E 191 x 96
100 %
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200 1250 1300
SCAN #

Fig. 20.

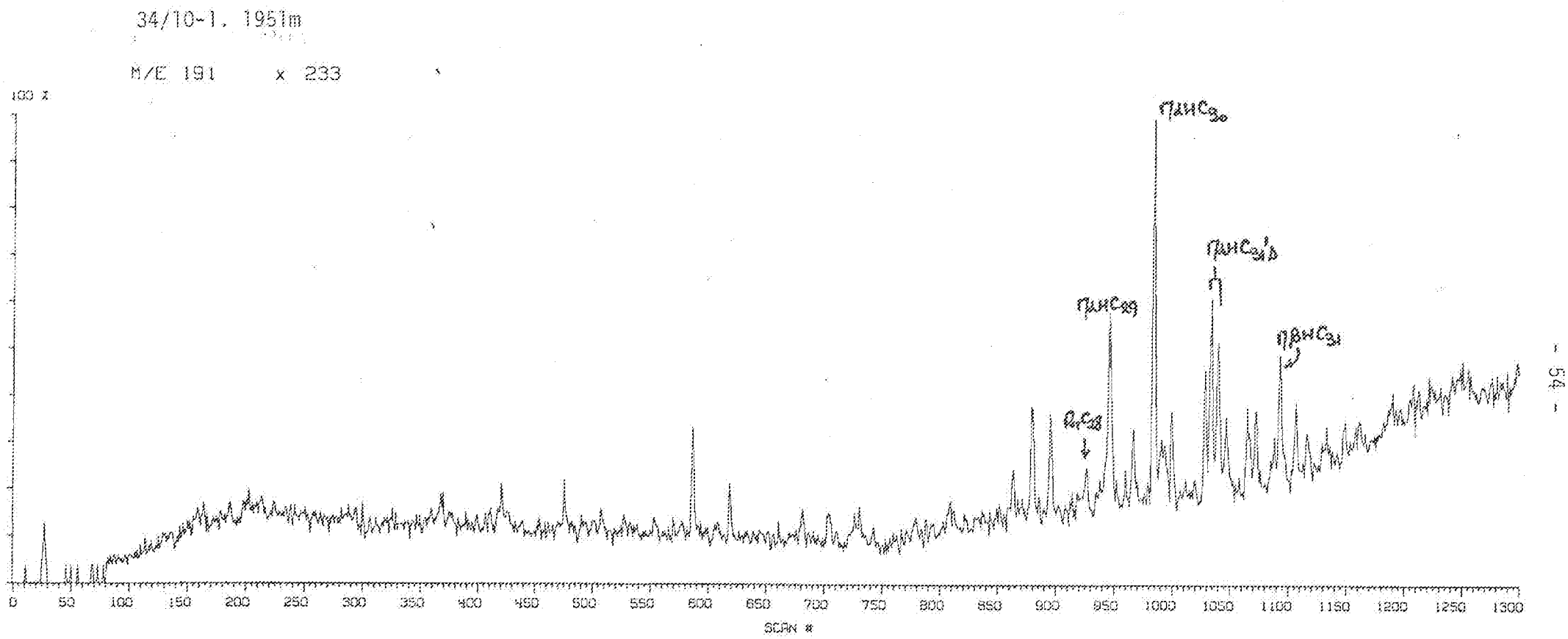
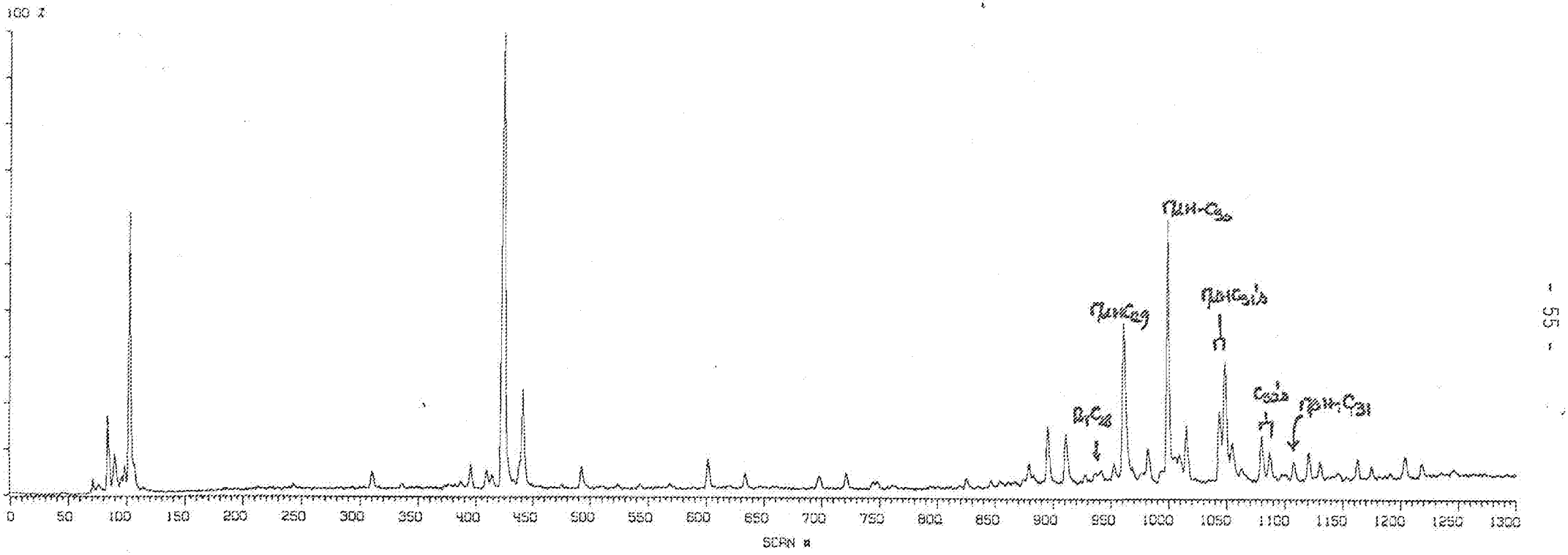

34/10-1. 1951m
M/E 191 x 233
100 %
nC29
nC30
nC31/3
nC31
nC33
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200 1250 1300
SCAN #

Fig. 21.


34/10-1. 1970-85m
M/E 191 x 45
100 %
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SCAN #

Fig. 22

Oil. 34/10-1.

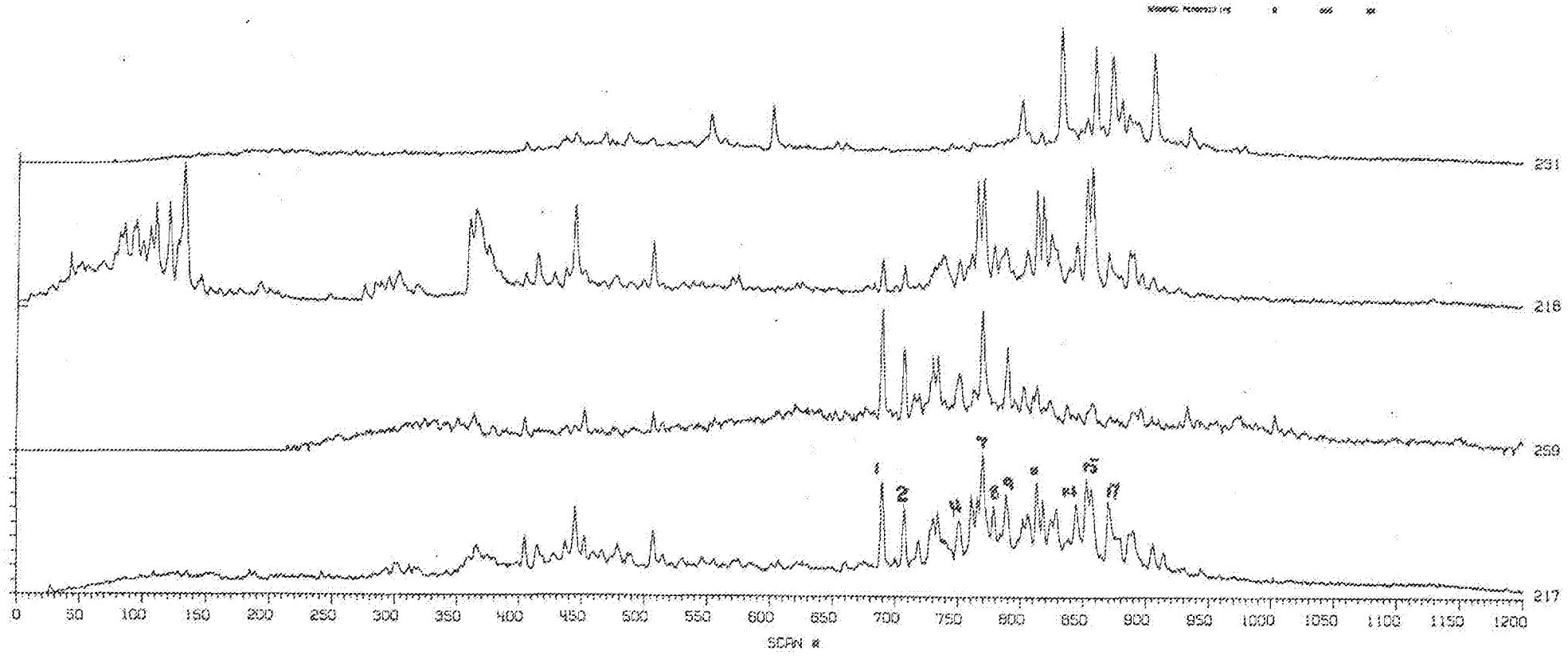
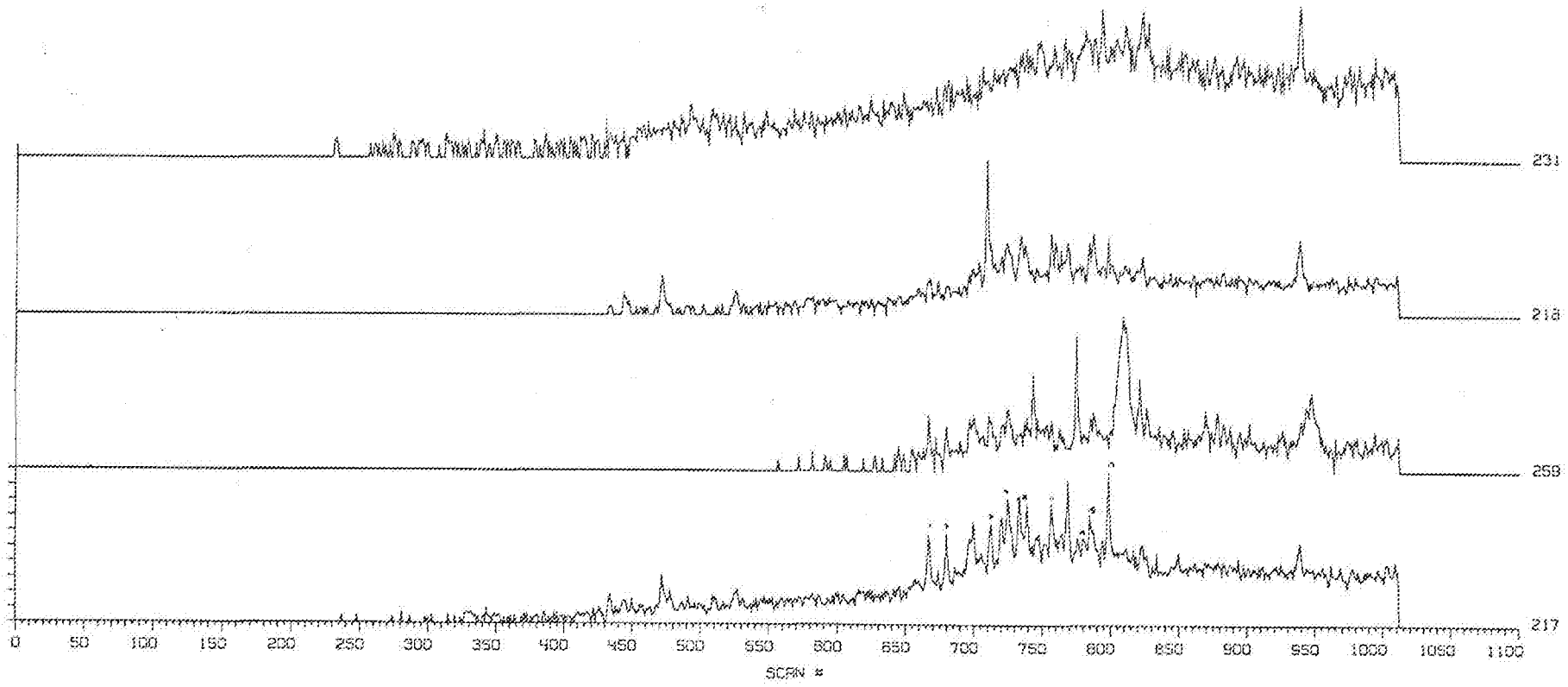


Fig. 23.


34/10-2 2550-65 (3330)
231
218
258
217
0
50
100
150
200
250
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550
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700
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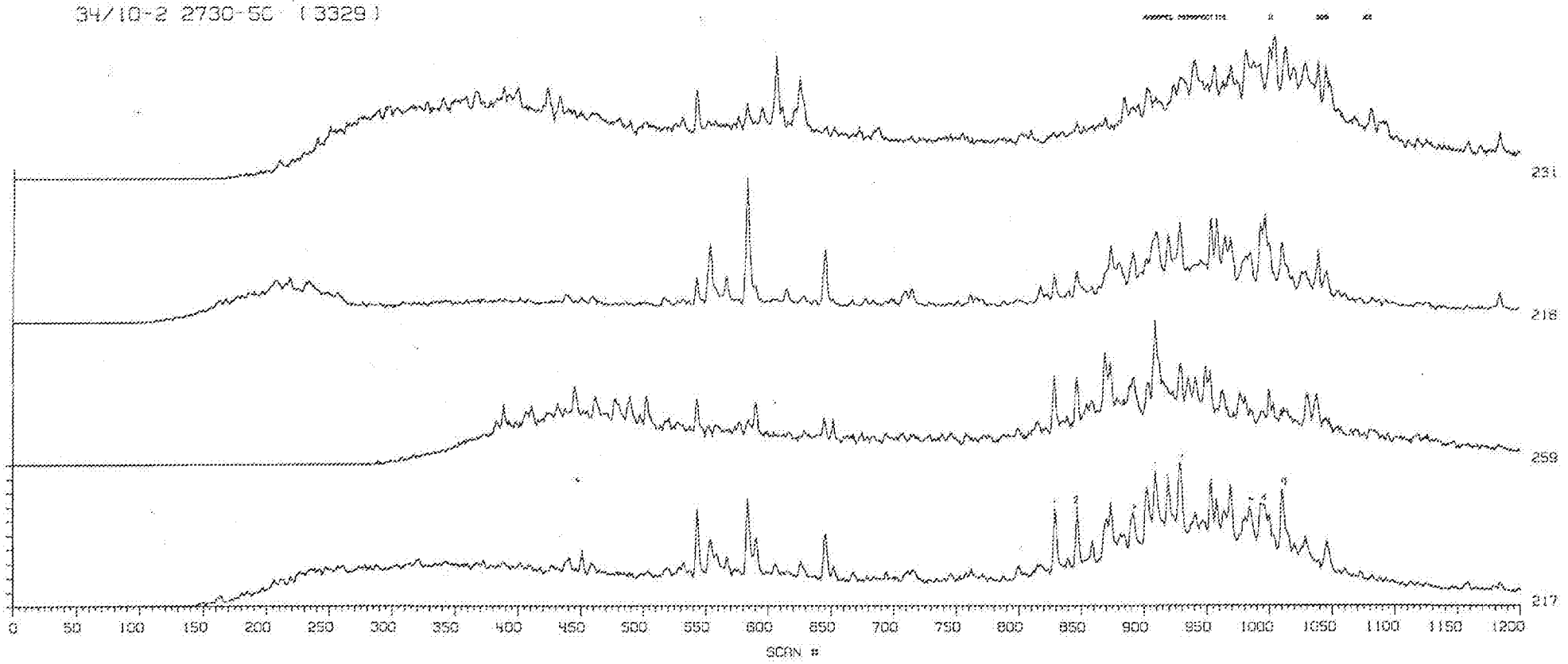
1000
1050
1100
SCAN #

Fig. 24


34/10-2 2730-50 (3329)
231
218
259
217
0
50
100
150
200
250
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350
400
450
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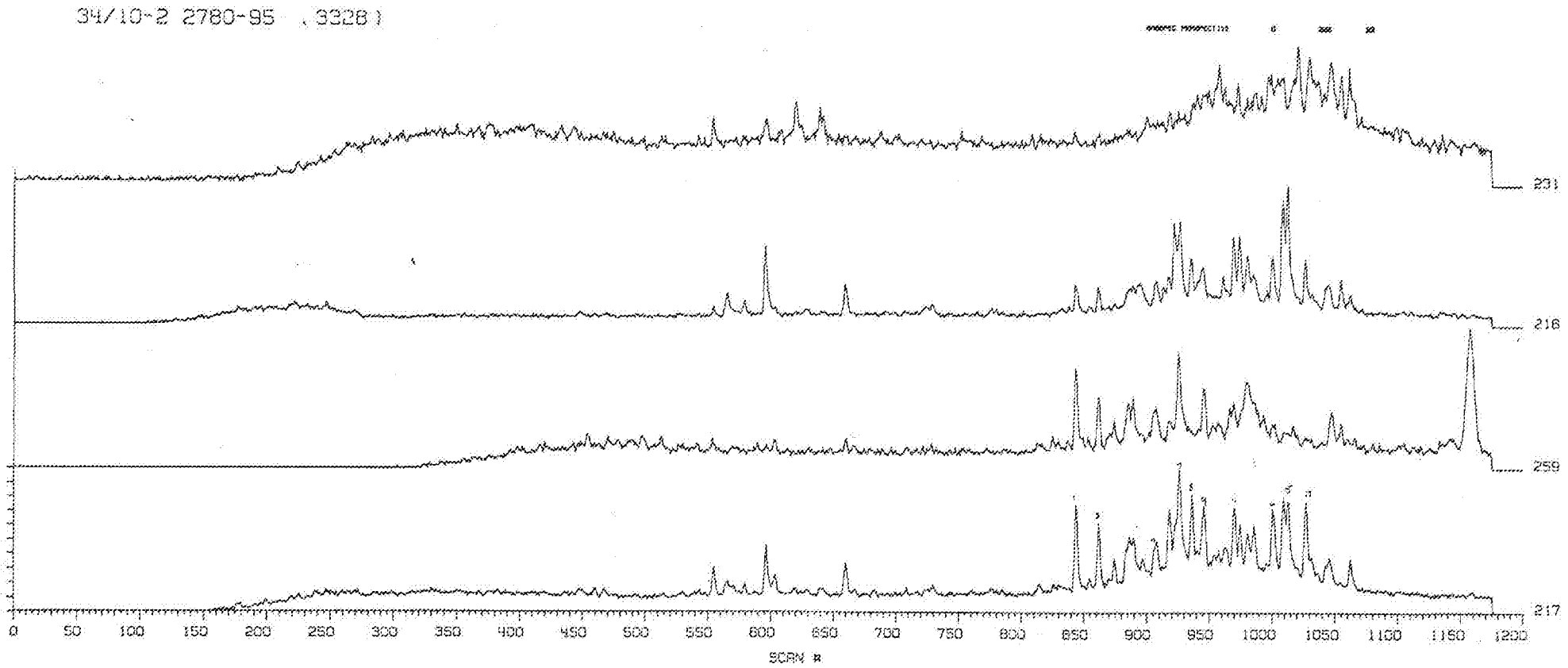
650
700
750
800
850
900
950
1000
1050
1100
1150
1200
SCAN #

Fig. 25.


34/10-2 2780-95 (3328)
231
216
259
217
0
50
100
150
200
250
300
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650
700
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850
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950
1000
1050
1100
1150
1200
SCAN #

Fig. 26

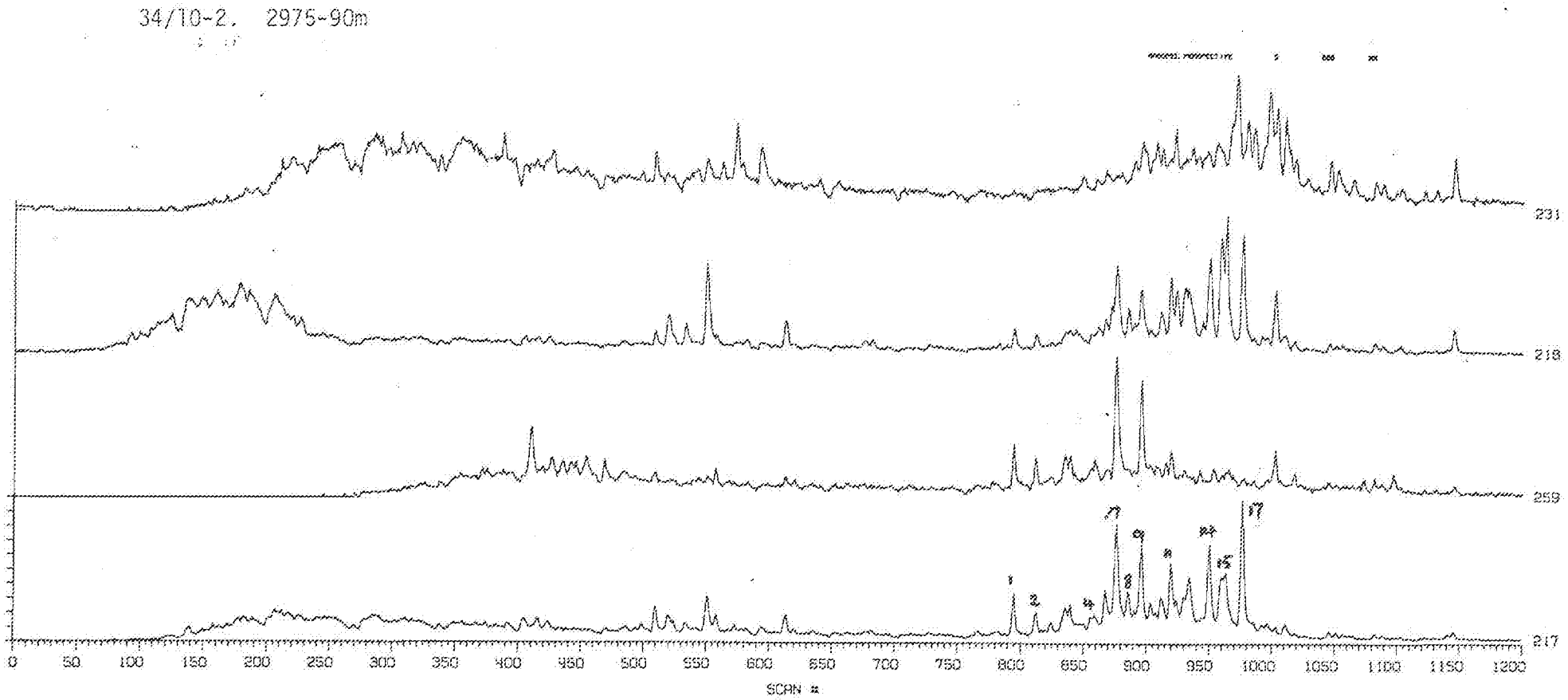
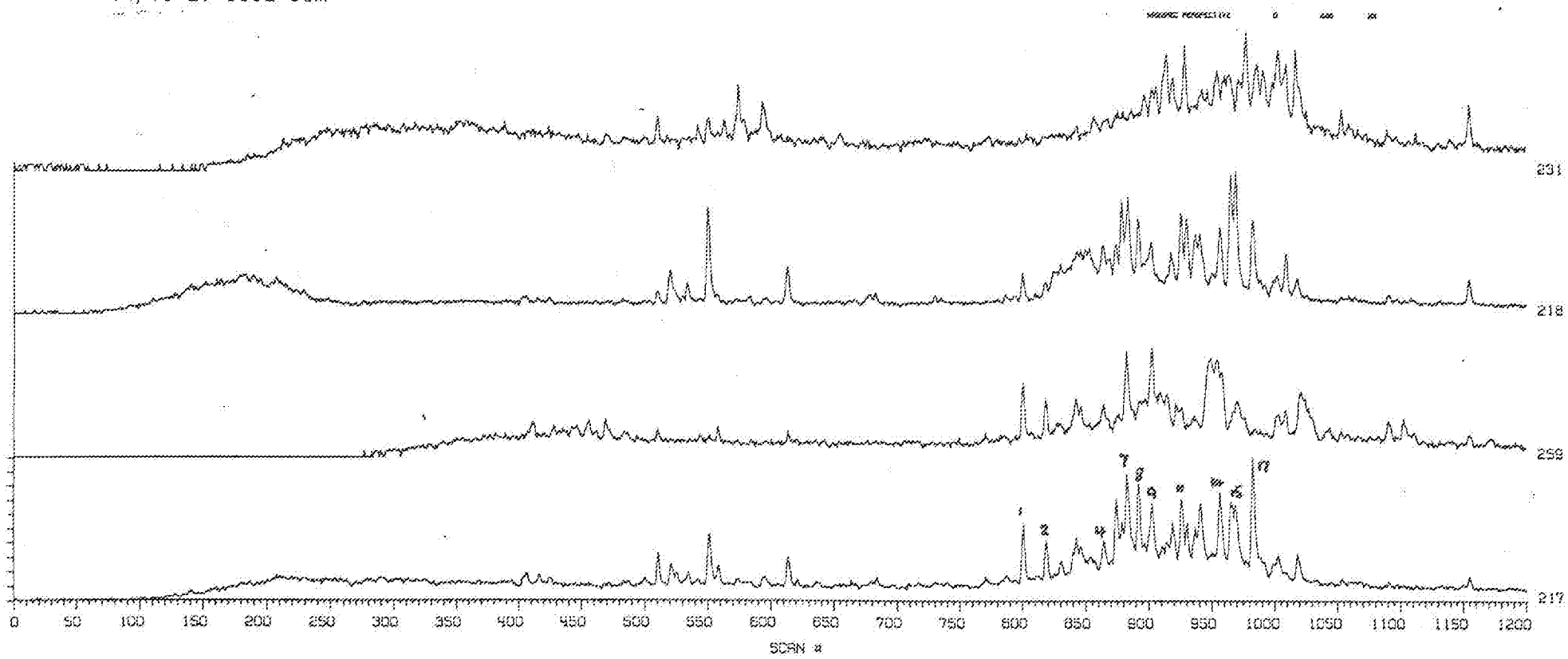

34/10-2. 2975-90m
231
218
259
217
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200
SCAN #

Fig. 27


34/10-2. 3032-50m
231
218
259
217
0
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250
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850
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1000
1050
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1150
1200
SCAN #

Fig. 28.

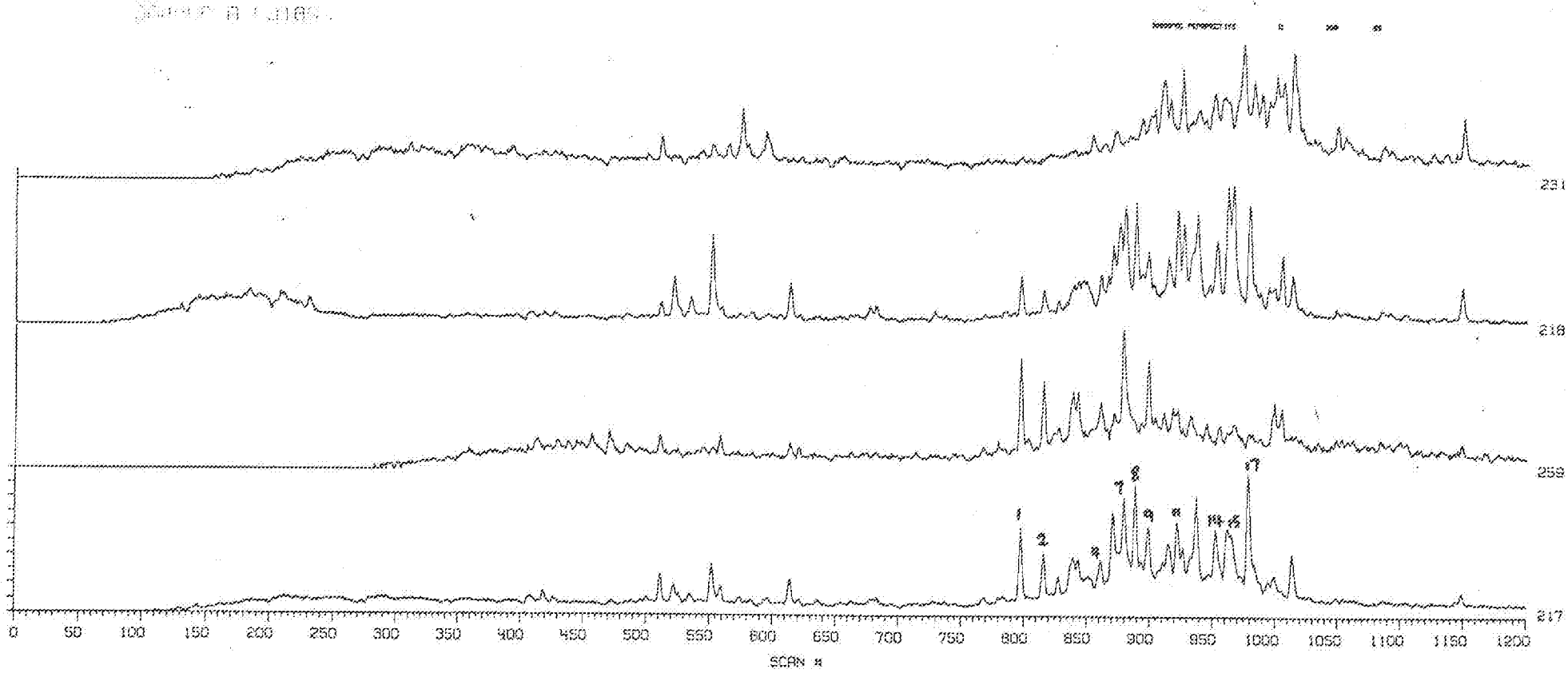
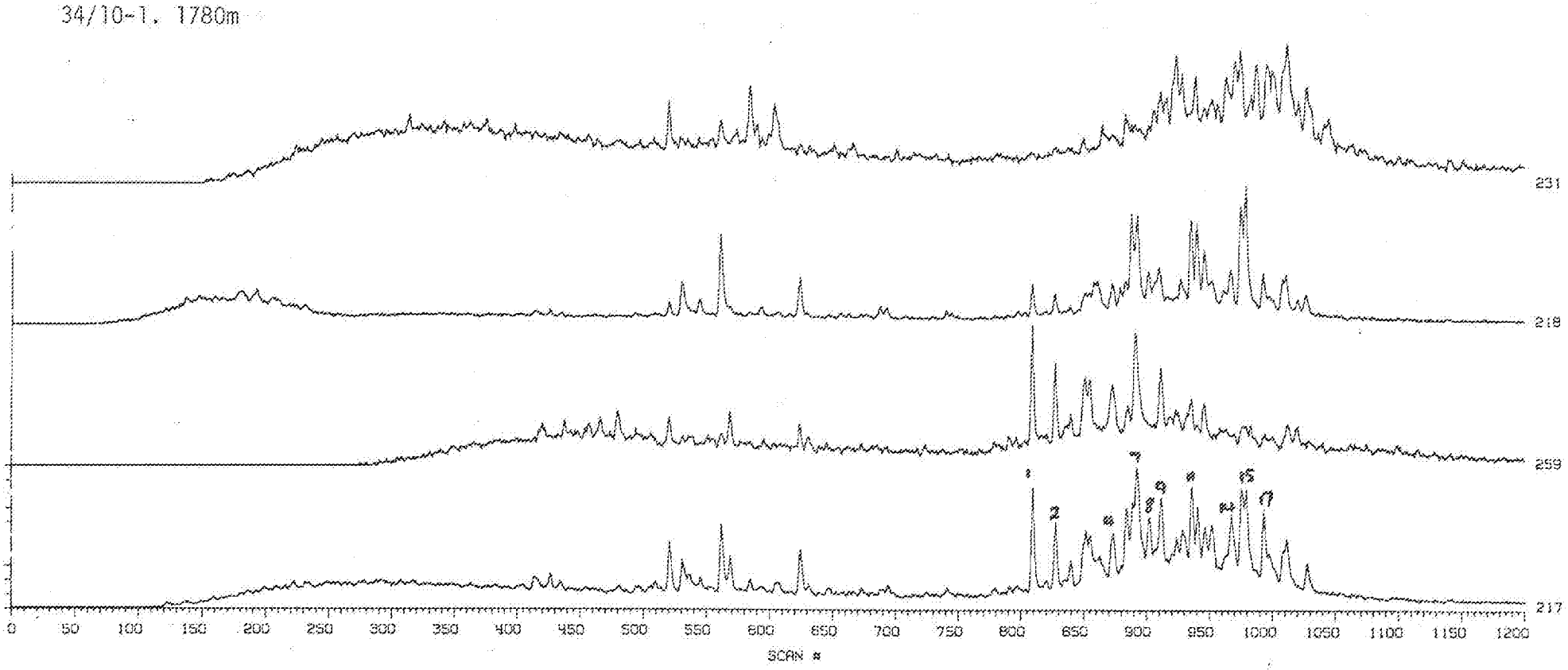

34/10-2. 3110-25m
231
218
259
217
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200
SCAN #

Fig. 29.


34/10-1. 1780m
231
218
259
217
0
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850
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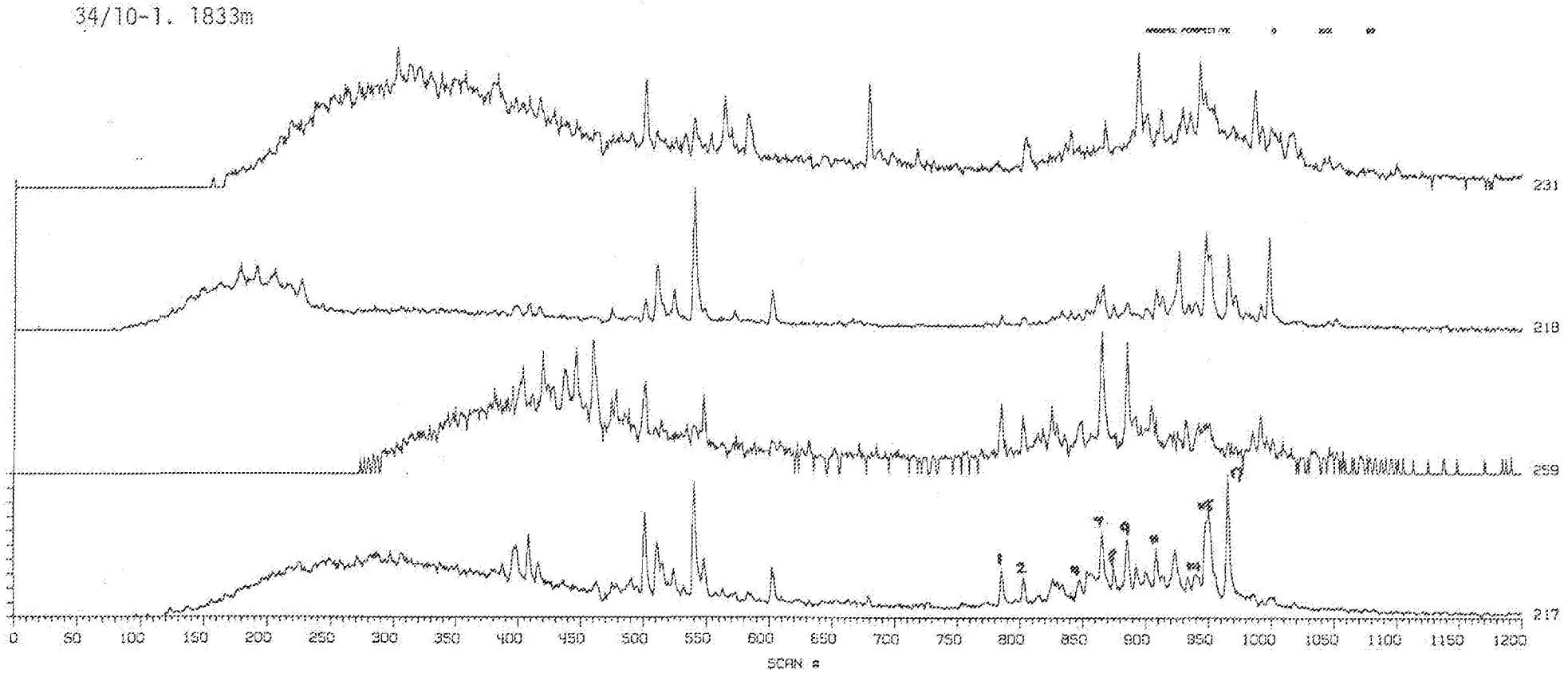
950
1000
1050
1100
1150
1200
SCAN #

Fig. 30.


34/10-1. 1833m
231
218
259
217
0
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100
150
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1050
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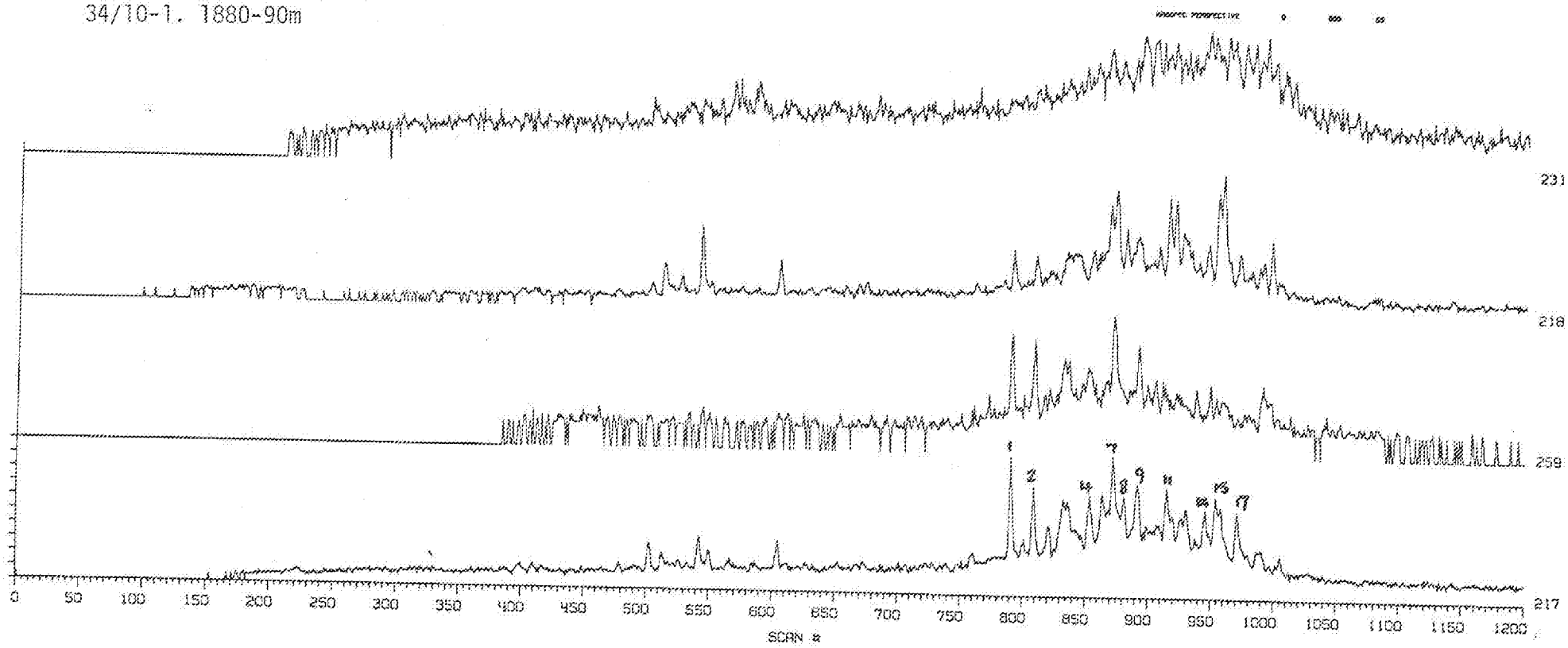
1150
1200
SCAN #

Fig. 31.


34/10-1. 1880-90m
231
218
259
217
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1150
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SCAN #

Fig. 32.

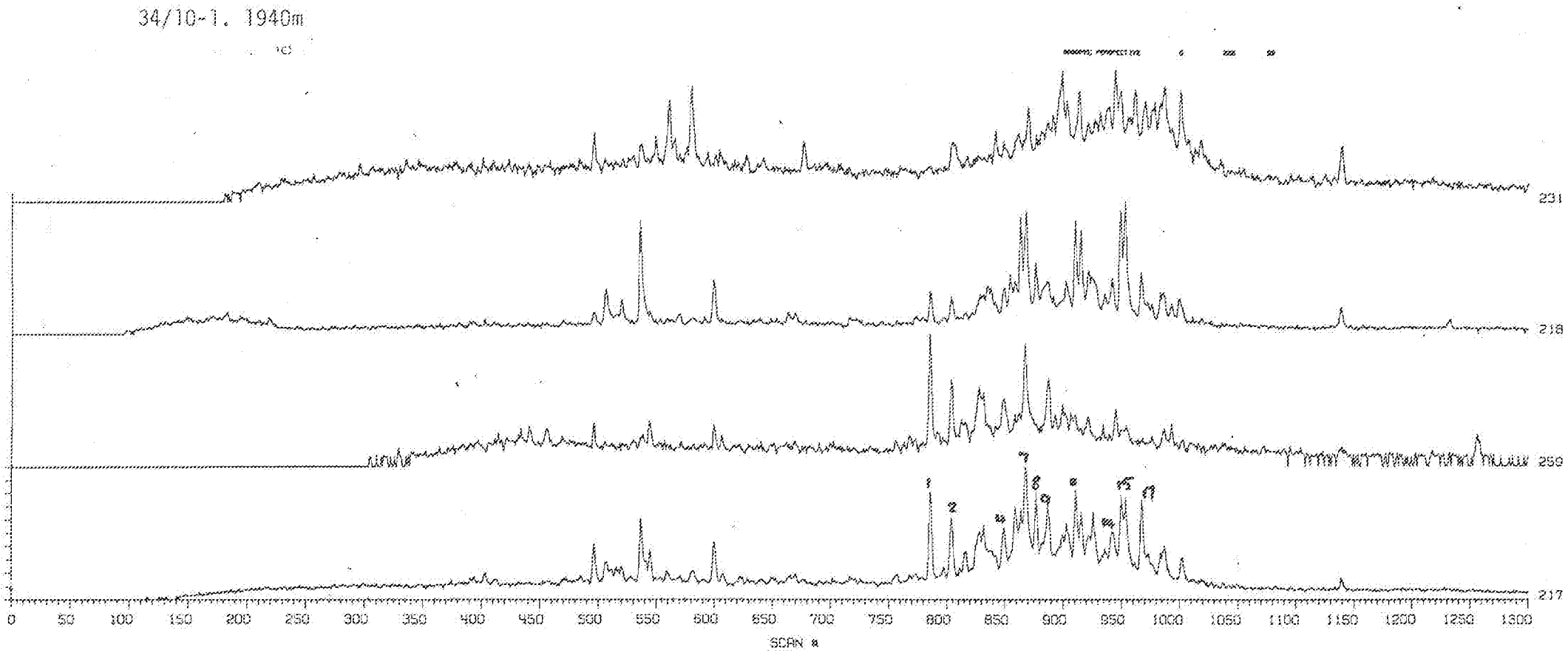
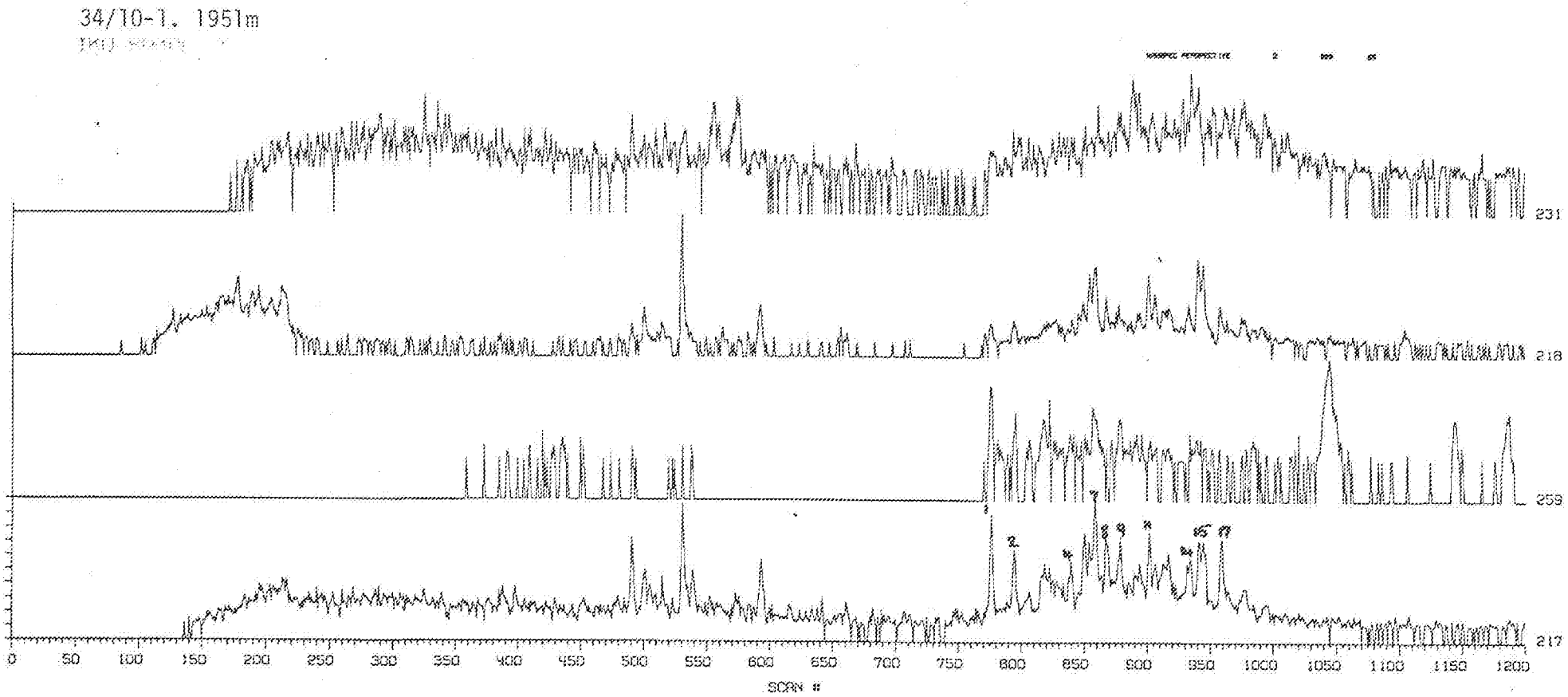

34/10-1. 1940m
231
218
259
217
0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000 1050 1100 1150 1200 1250 1300
SCAN #

Fig. 33.


34/10-1, 1951m
231
218
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217
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1150
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SCAN #

Fig. 34.

34/10-1. 1970-85m

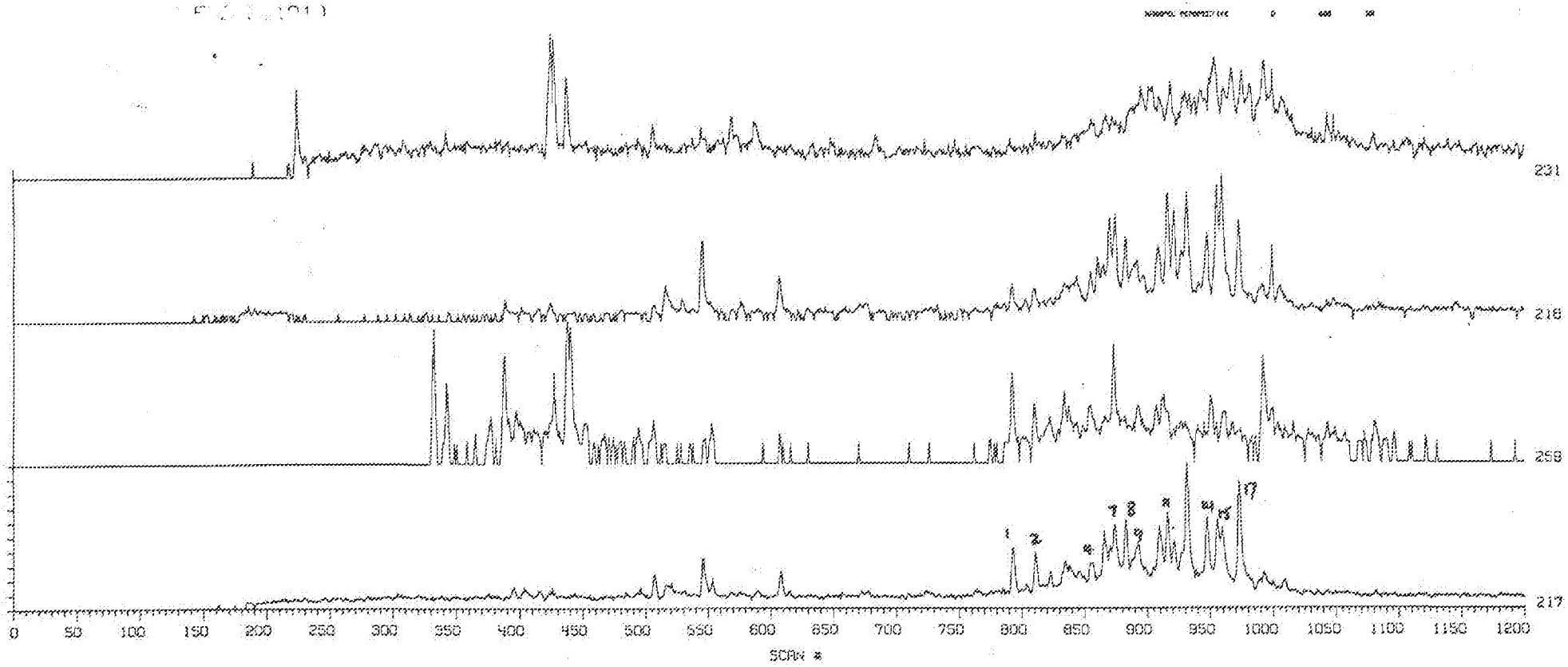

Fig. 35.

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