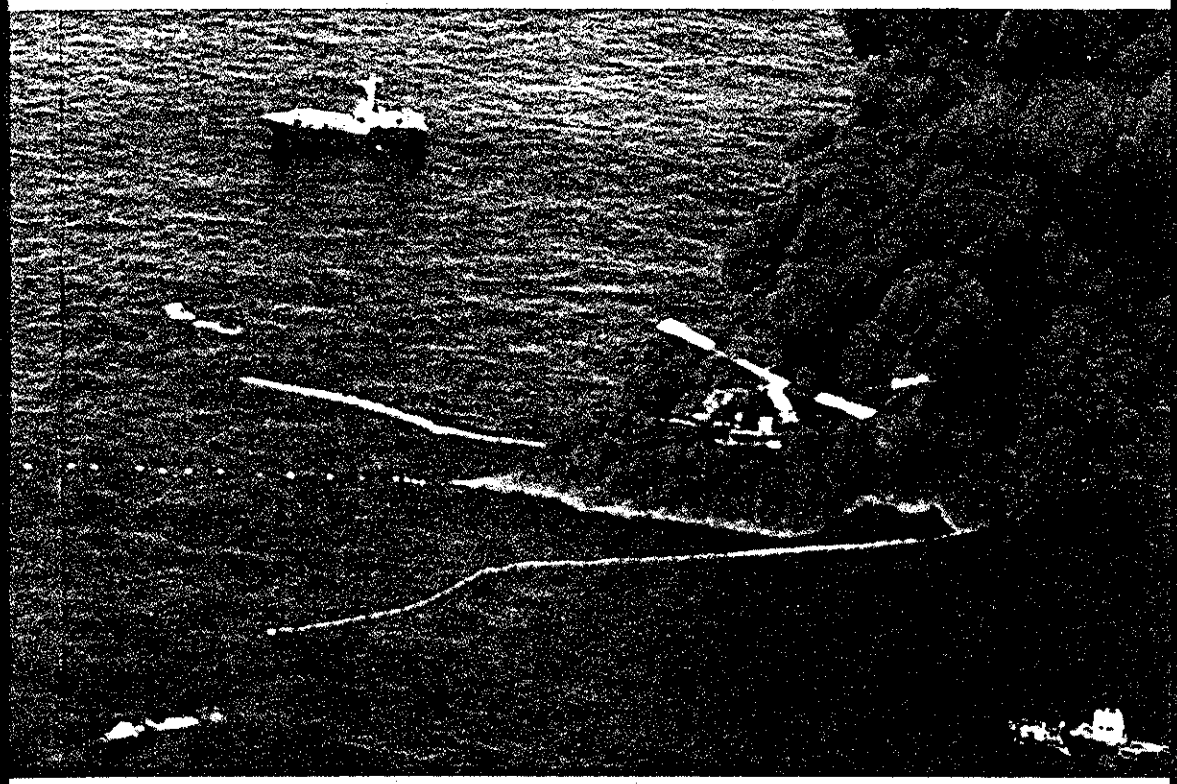
VOLUME 1

PROCEEDINGS OF THE SEVENTEENTH ARCTIC AND MARINE OIL SPILL PROGRAM (AMOP) TECHNICAL SEMINAR

COMPTE RENDU: 17e COLLOQUE TECHNIQUE DU PROGRAMME DE LUTTE CONTRE LES DÉVERSEMENTS D'HYDROCARBURES EN MER ET DANS L'ARCTIQUE (AMOP)



JUNE 8-10, 1994
VANCOUVER, BRITISH COLUMBIA

DU 8 AU 10 JUIN, 1994
VANCOUVER (COLOMBIE-BRITANNIQUE)

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QUANTITATIVE OIL ANALYSIS METHOD

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Assessing the petroleum damage to environment and natural resources (water, soil, and biological resources) caused by accidental release of crude or refined oil requires the design of appropriate and reliable chemical analytical methods for oil samples collected in the study area. The analytical data and results will provide essential information to document oil exposure pathways, to determine extent and degree of oiling, to evaluate the long-term impact of spilled oil, to estimate recoverability of the injured resources, and to suggest effective clean-up strategies.

Analytical methods and techniques for oil analysis have made major advances in recent years and the development continues. Modern techniques include gas chromatography (GC), mass spectrometry (MS), infrared spectroscopy (IR), ultraviolet (UV) and fluorescence spectroscopy, supercritical fluid chromatography (SFC); and hyphenated techniques such as GC/MS, GC/FTIR, SFC/GC etc. Among these techniques, high resolution capillary GC/FID and GC/MS are the most important and most widely-used techniques for oil separation, characterization and identification.

Many people consider the analytical methods for oil spill study be the same or similar as for any other spill of other hazardous materials. For example, some U. S. Environmental Protection Agency (EPA) methods (such as EPA method 602 for volatile aromatic compounds and Method 610 for priority polycyclic aromatic hydrocarbons) have been used for oil spill assessment [1]. However, these methods are traditionally used for industrial waste and hazardous waste analysis, not for oil analysis. Due to the extremely complicated chemical composition and very different chemical nature of petroleum as compared to other hazardous materials, the data generated by these methods often lack chemical specificity for oil and are inadequate for assessing the impact of the spilled oil on the environment and insufficient for interpreting the fate and behaviour of oil in the environment [2].

Very recently, ASTM has proposed standard test methods for oil spill identification and for determination of low level total petroleum hydrocarbons in water, waterborne oil, and sediments. It is definitely a good practice, although these methods are still under consideration and have not received all approvals required to become ASTM standard methods.

In recent years, the Emergencies Science Division (ESD) of Environment Canada has conducted projects to investigate various counter-measures in responding to oil spills. One of the important elements in these projects is to develop the quantitative oil analytical methods. Described below are the detailed procedures of an oil chemical analysis method developed in our laboratory. Since 1992, this method has been successfully applied to analyze hundreds of oil samples with various forms,

natures and concentrations, including crude oil, weathered oil, burned oil, lube oil, sediments, water samples, biosamples, and legal samples [3-6]. Numerous data have demonstrated this method to be effective, reliable and specific, and can be used as an important elements of future technical guidance documents.

OBJECTIVES OF OIL CHEMICAL ANALYSIS

Two objectives of oil chemical analysis are :

--To characterize the environmentally important constituents (such as toxic PAHs and their alkylated homoloques) in oil, and to determine their concentrations;

--To characterize the major (such as n-alkanes and isoprenoids) and minor (such as biomarker triterpane and sterane compounds) constituents in oil. These oil constituents can be valuable indicators of weathering degree and fate of spilled oil in environment. They can be used for oil source identification and oil-oil matching, and to determine their concentrations as well.

For long-term assessment, it is especially important to know the composition of oil residue and the changes in its chemical characteristics as a result of physical, chemical, and biological degradation processes.

Table 1 lists important petrogenic target compounds and compound classes. An appropriate selection of target analytes will help to achieve the two objectives described above. The types and concentrations of specific oil constituents in environmental samples are dictated by the nature of the spilled oil. Each oil has a

different "fingerprint" and compound distribution. For crude oil, the distribution depends greatly on its geological source; for weathered oil, the distribution depends on not only the weathering conditions, but the time of weathering (short-term or long-term). Some low molecular weight targets in heavily weathered oil samples may be lost and some degradation-resistant compounds may be built up at the same time because of the weathering effects. This results in significant changes in chemical composition and concentration.

As Table 1 shows, the target compounds include: n-alkanes (n-C8 to n-C40) plus selected isoprenoids (pristane and phytane); PAHs and their alkylated homologues; biomarker compounds triterpanes and steranes. Sometimes the volatile C2- through C5-benzenes, and polar phenols and polar heterocyclic PAHs may be included as well.

The n-alkanes and isoprenoids are generally considered to be nontoxic. These target analytes are not particularly useful in oil source determination, but they are valuable for tracing the spilled oil, useful for studying the fate of spilled oil, and can provide information on the degree of weathering of the sample. Figure 1 shows the n-alkane distribution chromatograms of ASMB oil, California oil, and Orimulsion oil by GC/FID and GC/MS. It can be readily seen from Figure 1 that these three oils are different, not only due to their different distribution modes and profiles, but also due to significantly higher concentration of branched saturates relative to normal alkanes in California oil. As for Orimulsion oil, even no noticeable n-alkanes is seen from its GC/FID chromatogram and GC/MS n-alkane distribution chromatogram.

The five groups of alkylated PAH homologues (alkyl naphthalenes, alkyl phenanthrenes, alkyl dibenzothiophenes, alkyl fluorenes, and alkyl chrysenes) are very important target analytes. Unlike the 16 EPA-defined priority PAH compounds, these homologuous series are very useful in oil spill assessment. This is because: (1) These alkylated PAH homologues are the most abundant PAH compounds in oil, and they persist for relatively greater periods of time than their parent compounds. Other 4- and 5-ring PAHs are very minor constituents of most crude oils, or are not even detected in many oil samples. (2) Different oils have different distribution profiles of alkylated PAH homologues. They are more valuable than the parent PAHs in fingerprinting the weathered and spilled oil, distinguishing between sources of hydrocarbons in the environment, and providing information on the extent and degree of oil weathering and degradation. (3) Reporting values of alkylated PAH homologues more truly reflects the composition of PAHs in oil than using data on parent PAH compounds. The PAH composition changes caused by weathering and degradation can be more easily detected and traced as well. Figure 2 shows the alkylated PAH homologue distributions of ASMB oil and NOBE oil (Newfoundland Offshore Oil Burn Experiment oil, a type of western oil used specifically for this experiment). These two oils come from very similar origins, but exhibit distinguishing PAH signatures, especially the abundances and relative ratios of alkyl dibenzothiophenes. The distinctive character of each oil, as evidenced by the alkylated PAH homologue distributions, is apparent. If only 16 priority PAH compounds were the target analytes, such differences of composition between two oils would not be evident.

Figure 3 shows the preferential loss of certain alkylated PAH homologues in a highly-weathered NOBE oil (collected after NOBE burn test) compared to the unweathered crude oil. Figure 4 depicts graphically the alkylated PAH fingerprints of the weathered ARROW oil, and three 22-year-old spilled ARROW oil samples S-6, S-a and S-9, illustrating the effect of field weathering on PAH composition. The loss of alkylated PAH compounds is very apparent. Conducting such analyses over time and at different locations having different exposures will provide essential information on the long-term impact of spilled oil.

For oil-impacted environmental samples in which identification and characterization of n-alkanes and alkylated PAHs is different or even impossible due to long-term heavy weathering, determination of biomarker compounds, triterpanes and steranes, becomes not only useful, but necessary. Studies on separation and identification of biomarker compounds from oil samples have greatly increased in recent years [7-14]. This is because: (1) triterpane and sterane compounds are unique for each oil, therefore they have great importance in recognition of the oil source from either neighbouring or different geographical areas; (2) they are highly degradation-resistant compounds in comparison to the aliphatic and aromatic compounds; (3) calculation based on hopane analysis to estimate percent of oil depletion can provide a more accurate representation of the degree of oil degradation than the traditional aliphatic/isoprenoid hydrocarbon ratio, and greatly improves the ability to resolve biodegradation differences between sites. Figure 5 shows hopane and sterane distribution chromatograms of three crudes (ASMB oil, NOBE oil, and California oil).

ASMB oil and NOBE oil are of similar origins and both are light oil. Califonia oil is much heavier than ASMB oil and NOBE oil (the API gravity for California oil and ASMB oil are 15 and 37, respectivily). Even by eyeball comparison, these three oils can be readily distinguished by the distribution profiles and the relative amount of hopanes and steranes.

DEFINITION OF KEY COMPONENT GROUPS

Some key component groups used in oil analysis are defined as follows:

-TSEM: Total Solvent Extractable Material, consists of all the hydrocarbons extracted from sediment samples (expressed as mg/g sample). TSEM supplies a same basis for determination and comparison of relative composition of aliphatics, aromatics, asphaltenes plus polars in samples;

-GTPH: Total Petroleum Hydrocarbons determined by the Gravimetric method;

-TPH: Total GC-detectable Petroleum Hydrocarbons, are the sum of all resolved and unresolved distillable hydrocarbons detected by GC. The unresolved hydrocarbons appear as the "envelope" or hump area between the solvent baseline and the curve defining the base of resolvable peaks;

-GCRTPH: GC Resolvable Total Petroleum Hydrocarbons, is the sum of the GC resolvable saturated hydrocarbons and GC resolvable aromatic hydrocarbons. The difference between TPH and GCRTPH is the GC unresolvable total petroleum

hydrocarbons;

-Asphaltenes + Polars: the difference between TSEM and GTPH. They are retained on the silica gel column, and removed prior to further analysis;

-GC undetectable high molecular weight (MW) hydrocarbons: the difference between GTPH and TPH, represents the high MW hydrocarbons retained on the GC column and undetected by the GC;

-Total alkanes: the sum of GC resolvable n-alkanes from n-C8 to n-C40 plus pristane and phytane;

-(C8+C10+C12+C14)/(C22+C24+C26+C28): this n-alkane ratio is very useful for evaluating the extent and degree of oil weathering.

PROTOCOL

Figure 6 shows the summary of the oil analytical method. This protocol allows detailed analysis of hydrocarbons in crude oil, weathered oil, sediments, or any other oil-impacted environmental samples.

1. Extraction

1.1 Sediment Sample Extraction.

Homogenize the sediment sample with a solvent-rinsed stainless steel spatula. Add 10-50 grams (depending on how much oil the sample contains) of the

sample to a 250 mL solvent-rinsed Erlenmeyer flask, and mix with 5-50 g of sodium sulphate (depending on the water content of the sample). If the sample has excessive moisture, additional amounts of sodium sulphate are added.

Spike sediment sample with the surrogates, and mix using a solvent-rinsed steel spatula.

Add 60 mL of 1:1 (v/v) hexane/methylene chloride, cover with aluminium foil. Place the Erlenmeyer flask in an ultrasonic bath, and extract for 30 minutes using sonication.

Decant extract into a 250 mL beaker.

Repeat the extraction with methylene chloride (2 x 60 mL) and extend the extraction time to 45 minutes for the final extraction. If there is visible colour in the third extract, additional extraction should be performed.

Combine the extracts, and dry by adding 3-5 grams of sodium sulphate and stirring with a clean glass rod for a few minutes.

Filter the extract with Gelman type A/E glass fiber filter. Rinse filter thoroughly with methylene chloride after filtration.

Concentrate extract to appropriate volume by rotary evaporation at 40-50 ^{0}C or by nitrogen blowdown.

1.2 Oil samples are directly dissolved in hexane at a concentration of 50 mg/mL, and spiked with the appropriate surrogate compounds.

1.3 Water samples are extracted according to EPA method 3510.

1.4 Determination of total solvent-extractable materials (TSEM) by gravimetric method: An aliquot of the extract is placed in a small accurately preweighed vial and blown to dryness by nitrogen. The residue is weighed until the weight is constant. This is an important and necessary step that enables reporting the data on the total solvent-extractable materials weight basis.

2. Fractionation

Place 3.0 grams of activated silica gel into a 30 mm x 10.5 mm ID chromatographic column plugged with glass wool. Tap to settle the silica gel, and add 0.5 cm anhydrous sodium sulphate.

Pre-elute the column with 20 mL of hexane. discard the eluent. Just prior to exposure of the sodium sulphate layer to the air, quantitatively transfer 0.4 mL (approximate 20 mg oil) onto the column using an additional 3 mL of hexane to complete the transfer. Discard this 3 mL eluent. To avoid overloading the column, it is suggested no more than 40 mg of oil be placed on the column.

2.1 Saturates

Just prior to exposure of the sodium sulphate to the air, elute the column with 12 mL of hexane. Collect the effluent in a centrifuge tube and label this fraction "F1".

F1, the saturated hydrocarbon fraction, is used for determination of n-alkane distribution and total saturated hydrocarbons, and for analysis of biomarker compounds.

2.2 Aromatics

Elute the column with 15 mL of 1:1 (v/v) benzene/hexane, collect the eluent in a centrifuge tube, and label this fraction "F2".

F2, the aromatic fraction, is used for analysis of PAHs and alkylated PAH homologues.

2.3 Polars

Elute the column with 15 mL of methanol, collect the eluent in a centrifuge tube, and label this fraction "F4".

2.4 Total Petroleum Hydrocarbons (TPH)

Combine half of F1 and F2, and label this composite fraction as "F3". this fraction is used for analysis of total petroleum hydrocarbons.

2.5 Concentrate the fractions using nitrogen blowdown technique. The concentrated extracts are spiked with the appropriate quantities of internal standard compounds and then made up to appropriate pre-injection volume (PIV) 0.5 to 1.0 mL. To achieve lower quantitation limit, the PIV may be reduced to 0.25 mL, but the extract should

never be blown dry to prevent loss of the volatile compounds and to prevent the precipitation of the high molecular weight hydrocarbons.

2.6 Gravimetric determination of percentages of saturates, aromatics, and polars

Use accurately preweighed vials instead of centrifuge tubes to collect the saturate fraction, aromatic fraction, and polar fraction. Blow these 3 fractions to dryness by nitrogen separately. The residues are weighed three times for gravimetric weights of saturates, aromatics and polars. The percentages of the saturates, aromatics and polars in oil sample (at TSEM basis) can be estimated using the following equations:

$$\%\ Saturates = \frac{W_1}{TSEM}\ x\ 100 \qquad (1)$$

$$\%\ Aromatics = \frac{W_2}{TSEM}\ x\ 100 \qquad (2)$$

$$\%\ Polars = \frac{W_3}{TSEM}\ x\ 100 \qquad (3)$$

The difference between TSEM and the sum of saturates, aromatics and polars are mainly accounted for by the aspheltenes.

2.7 Gravemetric determination of aspheltenes

The asphaltenes (defined as either n-pentane insoluble or n-hexane insoluble)

can be readily determined according to the ASTM method D-893, or using the following procedure:

Wash Gelman type A/E glass fiber filters (or Whatman GF/A glass microfiber filters) with mathylene chloride, air-dry them and weigh them individually.

An aliquot of the extract is placed in an accurately preweighed flask and blown to dryness by nitrogen. The residue is weighed until the weight is constant.

Add 20 mL of hexane to the dried residue. The asphaltenes, which are insoluble in hexane and adhere to the wall of the flask, will form suspension when the flask is exposed to ultrasound for 5-10 min. Filter the suspension through the cleaned filter placed over a funnel. Rinse the flask and the filter with 20 mL of hexane. Air-dry and weigh the filter. The difference from its initial weight is the mass of the asphaltenes.

3. Capillary Gas Chromatography (GC/FID and GC/MS) Analysis

3.1 Calibration

Prior to analysis work, the chromatographic system must be calibrated.

Prepare calibration standards at a minimum of 5 concentration levels for each component of interest from stock standard solution. One of the standards should be at a concentration near, but above, the minimum detection limit, and the other concentrations should correspond to the expected range of concentrations found in real samples. A range of 1.0 to 100 µg/mL, 0.1 to 20 µg/mL, and 0.1 to 20 µg/mL is

recommended for the n-alkanes, target PAHs, and triterpanes and steranes, respectively.

Analyze each calibration standard and tabulate peak area response against concentration for each compound and internal standard, and calculate relative response factors (RRF) for each compound using Equation 4:

$$RRF = \frac{AC_{IS}}{A_{IS}C} \qquad (4)$$

where: A = Response for the target analyte

A_{IS} = Response for the internal standard

C_{IS} = Concentration of the internal standard

C = Concentration of target analyte

A five response factor calibration is established demonstrating the linear range of the analysis.

The average RRF used for calculation of the TPH value is defined as an average of the five point averages of the individual analyte response factors. The analytes include C8 through C40 n-alkanes, and pristane and phytane.

The working calibration curve or RRF should be verified on each working day by the measurement of one (mid-level) or more calibration standards. If the response for any target analyte varies from the predicted response by more than 20%, the test must be repeated using a fresh calibration standard.

3.2 Identification of petroleum hydrocarbons

F1, F2, and F4 can be also used for detailed identification of petroleum hydrocarbons. The identification of compounds will be based on their mass spectra, comparison of GC retention time with standards, certain distribution patterns, and calculation of Retention Index (RI) values and comparison with literature RI values.

3.3 F3 and F1 Analysis for TPH and individual saturates by GC/FID

The analysis of TPH and individual saturates (C8 through C40, plus pristane and phytane) is performed by high resolution capillary GC/FID using the following conditions:

Instrument: Hewlett Parkard 5890 GC or equivalent

Column: 30m x 0.32 mm ID DB-5 or equivalent fused silica column (0.25 µm film thickness)

Detector: FID

Autosampler: HP 7673 or equivalent

Inlet: Splitless

Gasses: Carrier: Helium, 2.5 mL/min, nominal

Make-up: helium, 27.5 mL/min

Detector air and hydrogen: 400 and 30 mL/min

Injection volume: 1 µL

Injector temperature: 290 ^{0}C

Detector temperature: 300 ^{0}C

Temperature program: 50 ^{0}C for 2 min, then 6 ^{0}C/min to 300 ^{0}C, hold 16.7 min. The total run time is 60 minutes

Daily calibration: Alkane standard mixture

Prior to sample analysis, a five point response factor calibration is established demonstrating the linear range of the analysis.

3.4 F2 analysis for target PAHs and alkylated PAH homologues

Target PAHs and alkylated PAH homologues are analyzed by GC/MS in the selected ion mode (SIM). Table 2 lists the selected characteristic ions used for analysis of target PAHs and alkylated PAH homologues. The GC/MS conditions are the following:

Instrument: Hewlett Parkard 5890 GC/5972 MS or equivalent

Column: 30m x 0.25 mm ID DB-5 or HP-5 or equivalent fused silica column (0.25 µm film thickness)

Autosampler: HP 7673 or equivalent

Inlet: Splitless

Gasses: Carrier: Helium, 1.0 mL/min, nominal

Injection volume: 1 µL

Injector temperature: 290 ^{0}C

Detector temperature: 300 ^{0}C (transfer line temperature)

Temperature program: For target PAHs, 90 ^{0}C for 1 min, then 25 ^{0}C/min to 160 ^{0}C, then 8 ^{0}C/min to 290 ^{0}C and hold 15 min. The total run time is 35 min;

For alkylated PAH homologues, 50 ^{0}C for 2 min, then 6 ^{0}C/min to 300 ^{0}C, hold 11.7 min. The total run time is 55 minutes.

Daily calibration: SRM 1491 standard

Prior to sample analysis, a five point response factor calibration is established demonstrating the linear range of the analysis.

3.5 F1 analysis for triterpanes and steranes

The biomarker compounds triterpanes and steranes are analyzed by GC/MS in the selected ion mode (SIM). The selected characteristic ion for triterpanes are m/z 191 and 177, and for steranes are m/z 217 and 218. The GC/MS conditions are the following:

Instrument: Hewlett Parkard 5890 GC/5972 MS or equivalent

Column: 30m x 0.25 mm ID DB-5 or HP-5 or equivalent fused silica column (0.25 μm film thickness)

Autosampler: HP 7673 or equivalent

Inlet: Splitless

Gases: Carrier: Helium, 1.0 mL/min, nominal

Injection volume: 1 µL

Injector temperature: 290 ^{0}C

Detector temperature: 300 ^{0}C (transfer line temperature)

Temperature program: 50 ^{0}C for 2 min, then 6 ^{0}C/min to 300 ^{0}C, hold 16.7 min. The total run time is 60 minutes.

Daily calibration: Hopane and sterane standard mixture

Prior to sample analysis, a five point response factor calibration is established demonstrating the linear range of the analysis.

4. Quantitation

4.1 Quantitation of individual analytes

Quantitation of individual compounds is based on the integration area or integrated abundance by using the internal standard method.

The equation used to calculate the analyte of interest in sample is the following:

$$Concentration\ (\mu g/g) = \frac{A\ x\ W_{IS}\ x\ D\ x\ 2}{A_{IS}\ x\ RRF\ x\ W} \qquad (5)$$

where: A = Response for the analyte in the sample, units may be in area counts or peak height;

A_{IS} = Response for the internal standard in the sample, unit same as A;

W_{IS} = Amount (μg) of internal standard added to the sample;

D = Dilution factor. If no dilution made, D=1, dimensionless;

W = Weight of sample loaded to clean-up column, gram;

2 = As described in "Fractionation" section, F1 and F2 are divided in half for analyses, so the final concentration of individual analytes should be multiplied by the volume factor of 2.

RRF = Response factor of the target analyte relative to the internal standard, which is obtained from measurement of calibration standards

4.2 Quantitation of Total Petroleum Hydrocarbons (TPH)

To calculate the concentration of TPH in the sample, the area response attributed to the petroleum hydrocarbons must be determined. This area include all of the resolved peaks and unresolved "envelope". This total area must be adjusted to remove the area responses of the internal standards. surrogates and GC column bleed.

Column bleed is defined as the reproducible baseline shift that occurs during temperature programming of the GC. To determine this area, a methylene chloride blank injection should be analyzed at the beginning of the analysis and after every 10 samples. This baseline is then set at a stable reproducible point just before the solvent peak. This baseline should be extended horizontally to the end of the run. The area for the blank run must be subtracted from the actual sample run.

In the HP 3655 "Chempc" software, the total area response attributed to the TPH can be readily obtained using "Manual Integration" and "Draw Baseline" functions.

Calculation of the TPH value can be accomplished using the following equation:

$$TPH\ (\mu g/g) = \frac{A_{TPH}\ x\ W_{IS}\ x\ D\ x\ 2}{A_{IS}\ x\ RRF_{TPH}\ x\ W} \qquad (6)$$

where: A_{TPH} = the corrected area of the sample chromatogram

RRF_{TPH} = average relative response factor of all target n-alkanes

W_{IS}, D, A_{IS}, W, and 2 have the same definitions as in Equation 4

It should be noted that to each sample, a specific amount of o-terphenyl (OTP) is added. The recovery of the surrogate is monitored in each sample using the response of 5-α-androstane internal standard added to fraction F1 and F3. The percent recovery of OTP is calculated using Equation 6:

$$OTP\ recovery\ (\%) = \frac{A_{OTP}\ x\ W_{IS}}{A_{IS}\ x\ W_{OTP}\ x\ RRF_{OTP}} \qquad (7)$$

where: A_{OTP} = Integration area of 5-α-androstane

W_{OTP} = µg of OTP added to the sample

RRF_{OTP}= Response factor of OTP relative to 5-α-androstane

4.3 Quantitation Notes

It is important to note that the RRFs used for quantitation of alkylated PAH homologues should be directly obtained from the corresponding alkylated PAH

standards if they are commercially available. Traditionally, the RRFs of the parent PAH compounds are used for quantitation of alkylated PAH homologues. However, unacceptable errors may be introduced by this way. For example, it was found from our work that 30% to up to 150% error may be introduced if C1-, C2-, C-3, C4-naphthalenes are quantified using the RRF obtained from the parent naphthalene standard.

For the purpose of quality control, the laboratory that uses this method should maintain performance records to define the quality of data that is generated. Also, the quality control procedures have to be followed (for example, followed with each analytical batch --approximately 10 samples, one blank, one check standard, and one standard oil should be analyzed.

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Table 1 Petroleum Fingerprinting Analyte List

Aliphatic hydrocarbons

1. Normal Alkanes
   - n-C8
   - n-C9
   - n-C10
   - n-C11
   - n-C12
   - n-C13
   - n-C14
   - n-C15
   - n-C16
   - n-C17
   - n-C18
   - n-C19
   - n-C20
   - n-C21
   - n-C22
   - n-C23
   - n-C24
   - n-C25
   - n-C26
   - n-C27
   - n-C28
   - n-C29
   - n-C30
   - n-C31
   - n-C32
   - n-C33
   - n-C34
   - n-C35
   - n-C36
   - n-C37
   - n-C38
   - n-C39
   - n-C40

2. Isoprenoid Compounds
   - Priatane
   - Phatane

Target PAHs

- Naphthalene
  - C1-naphthalene
  - C2-naphthalene
  - C3-naphthalene
  - C4-naphthalene
- Phenanthrane
  - C1-Phenanthrene
  - C2-Phenanthrene
  - C3-Phenanthrene
  - C4-Phenanthrene
- Dibenzothiophene
  - C1-Dibenzothiophene
  - C2-Dibenzothiophene
  - C3-Dibenzothiophene
- Fluorene
  - C1-Fluorene
  - C2-Fluorene
  - C3-Fluorene
- Chrysene
  - C1-Chrysene
  - C2-Chrysene
  - C3-Chrysene
- Biphenyl
- Acenaphthylene
- Acenaphthene
- Anthracene
- Fluoranthene
- Pyrene
- Benz(a)anthracene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Benzo(e)pyrene
- Benzo(a)pyrene
- Perylene
- Indeno(1,2,3-cd)pyrene
- Dibenz(a,h)anthracene
- Benzo(ghi)perylene

Biomarker Compounds

1. Triterpanes
   - Tricyclic terpanes
   - Tetracyclic terpanes
   - Pentacyclic terpanes
     - $C_{27}H_{46}$ (T_S)
     - $C_{27}H_{46}$ (T_M)
     - $C_{28}H_{48}$
     - $C_{29}H_{50}$
     - $C_{30}H_{52}$
     - $C_{31}H_{54}$
     - $C_{32}H_{56}$
     - $C_{33}H_{58}$
     - $C_{34}H_{60}$
     - $C_{35}H_{62}$

2. Steranes
   - C_{27} 20R/S-Cholestanes
   - C_{28} 20R/S-Ergostanes
   - C_{27} 20R/S-Stigmastanes

Surrogates and Standards

1. Surrogates
   - o-Terphenyl
   - d10-Acenaphthene
   - d10-Phenanthrene
   - d12-Benz(a)anthracene
   - d12-Perylene

2. Internal Standards
   - 5-α-Androstane
   - d14-Terphenyl
   - C30 ββ-Hopane

3. QC Standards
   - SRM 1491
   - n-alkane standards
   - Triterpane & Sterane std

Table 2 GC/MS Analysis for PAHs and Alkyl PAH Homologues

Compounds	Target Ion/Qualifying Ions
Naphtalene	128/127/64
C1-Naphthalenes	142
C2-Naphthalenes	156
C3-Naphthalenes	170
C4-Naphthalenes	184
Phenanthrene	178/176
C1-Phenanthrenes	192
C2-Phenanthrenes	206
C3-Phenanthrenes	220
C4-Phenanthrenes	234
Diobenzothiophenes	184
C1-Dibenzothiophenes	198
C2-Dibenzothiophenes	212
C3-Dibenzothiophenes	226
Fluorene	166
C1-Fluorenes	180
C2-Fluorenes	194
C3-Fluorenes	208
Chrysene	228/114
C1-Chrysenes	242
C2-Chrysenes	256
C3-Chrysenes	270
Biphenyl	154/153/76
Acenaphthylene	152/151/76
Acenaphthene	153/154/76
Anthracene	178/176
Fluoranthene	202/101
Pyrene	202/101
Benz(a)anthracene	228/114
Benzo(b)fluoranthene	252/126
Benzo(k)fluoranthene	252/126
Benzo(e)pyrene	252/126
Benzo(a)pyrene	252/126
Perylene	252/126
Indeno(1,2,3-cd)pyrene	276/138
Dibenz(a,h)anthracene	278/138
Benzo(ghi)perylene	276/138
d10-Acenaphthene	164
d10-Phenanthrene	188
d12-Benz(a)anthracene	240
d12-Perylene	264
d14-Terphenyl	244

CAPTIONS

Figure 1 Comparison of alkane distribution chromatograms (GC/FID and GC/MS) of ASMB oil (1A and 1B), California oil (1C and 1D), and Orimulsion oil (1E and 1F).

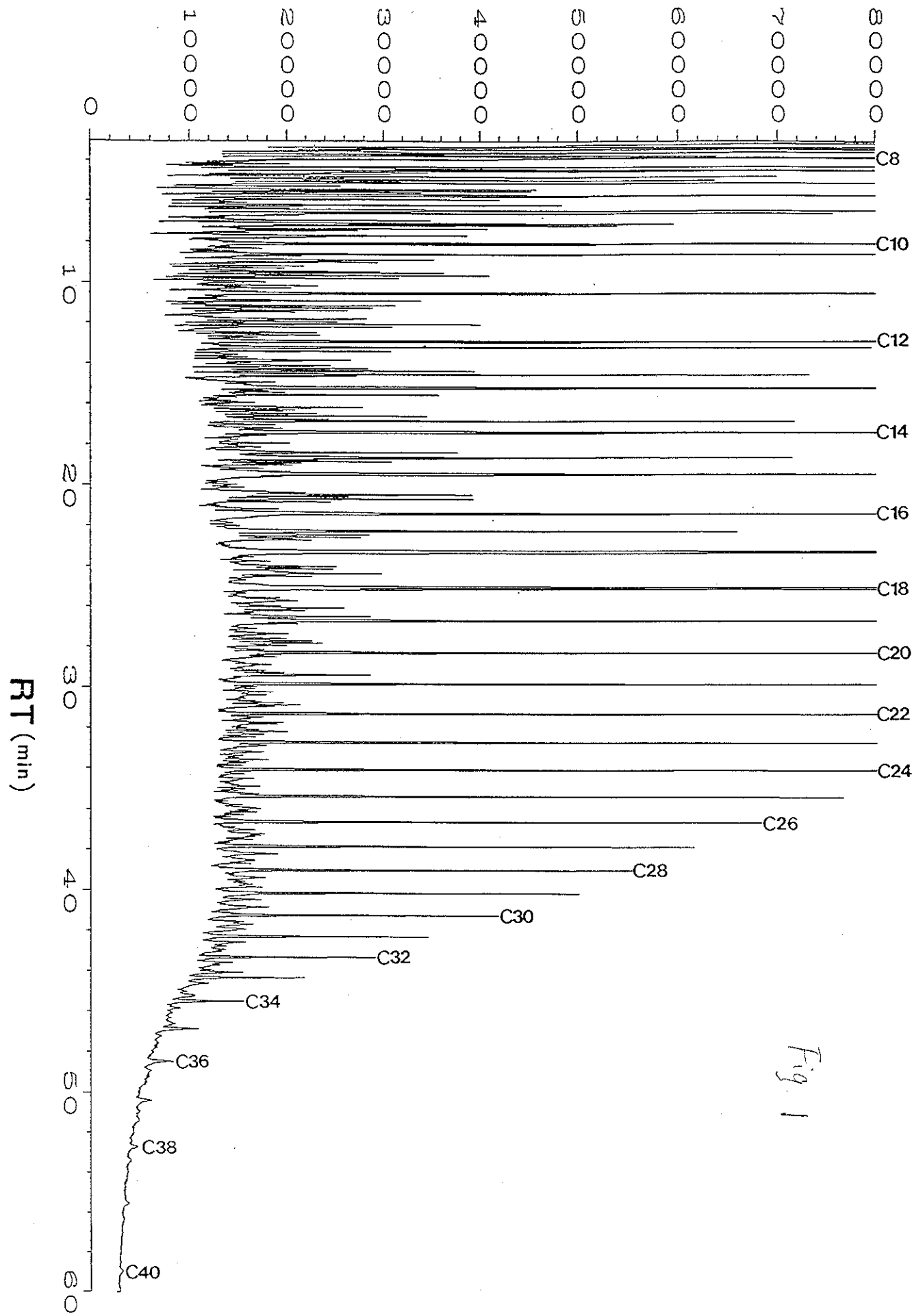
Figure 2 Comparison of alkylated PAH homologues distribution of ASMB oil and NOBE oil. Y axis: normalized abundance (C2-P=1.00). N, P, D, F, and C represent naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene, respectively. 0, 1, 2, 3, and 4 represent carbon numbers in alkylated PAH homologues.

Figure 3 Alkylated PAH homologue distribution in unweathered and weathered NOBE oil illustrating the preferential loss of certain alkylated PAH homologues in weathered NOBE oil.

Figure 4 PAH fingerprints of the weathered source oil (A), S-6 (B), S-A (C), and S-9 (D) illustrating the effects of weathering on PAH compositions.

Figure 5 Comparison of hopane (m/z 191) and sterane (m/z 217 and 218) distribution of ASMB oil (5A and 5B), NOBE oil (5C and 5D), and California oil (5E and 5F).

Figure 6 Summary of oil chemical analysis protocol.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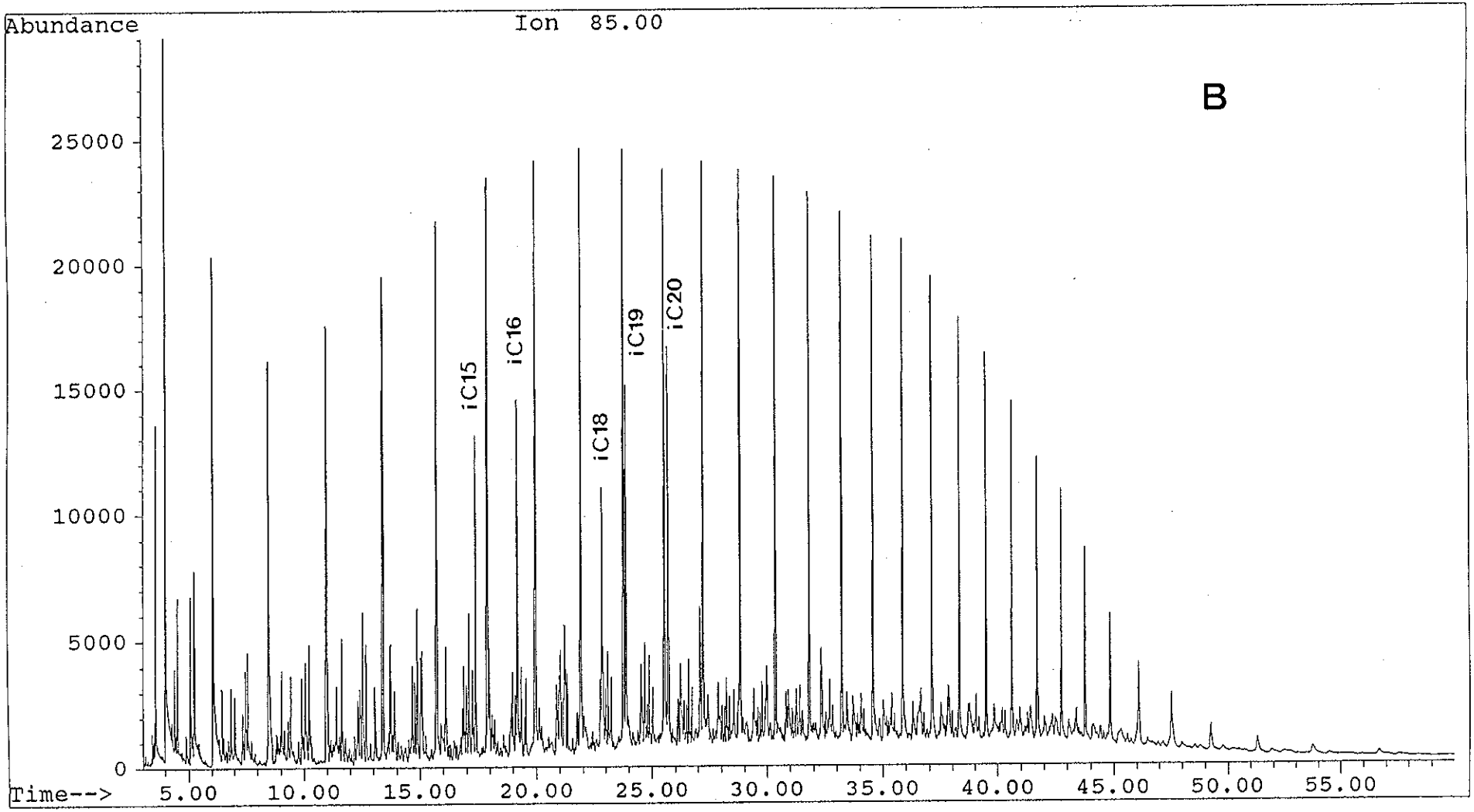
300000
400000
500000
600000
700000
800000
RT (min)
10
20
30
40
50
60
C8
C10
C12
C14
C16
C18
C20
C22
C24
C26
C28
C30
C32
C34
C36
C38
C40

Fig 1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20000
15000
10000
5000
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iC15
iC16
iC18
iC19
iC20
Time-->
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20.00
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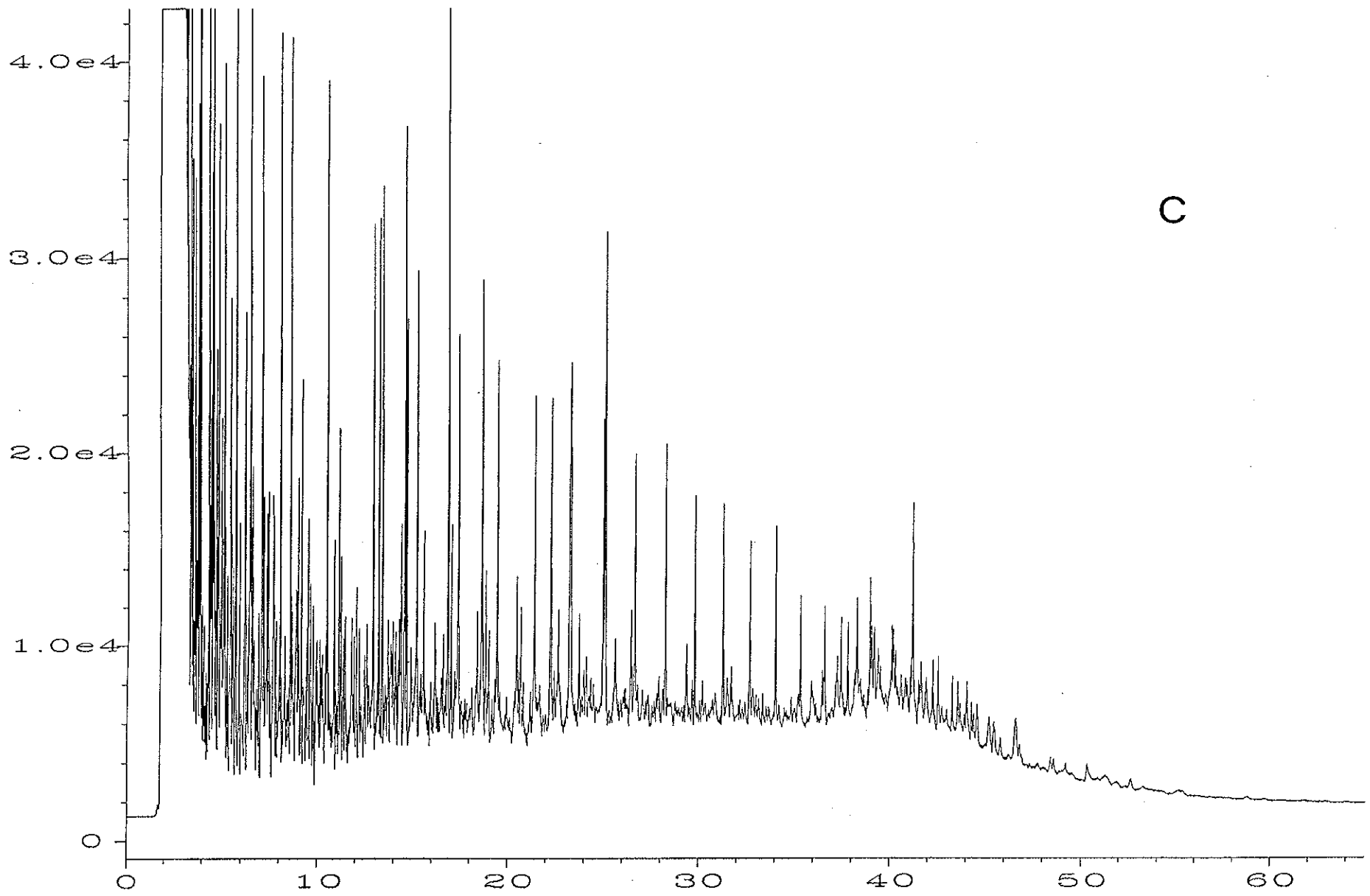
30.00
35.00
40.00
45.00
50.00
55.00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2.0e4
1.0e4
0
0
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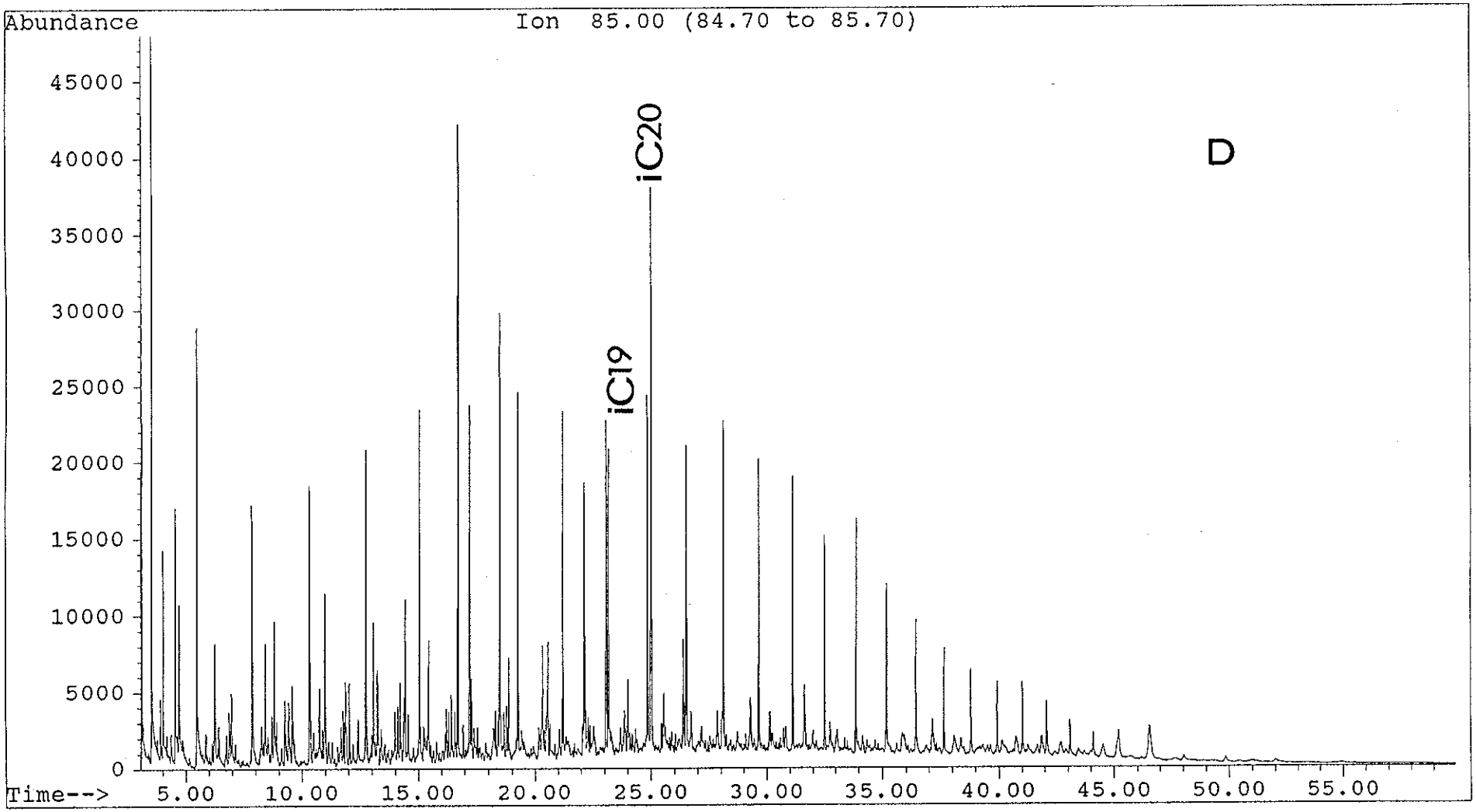
20
30
40
50
60
C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30000
25000
20000
15000
10000
5000
0
iC19
iC20
D
Time-->
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00

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0
10
20
30
40
50
60
m

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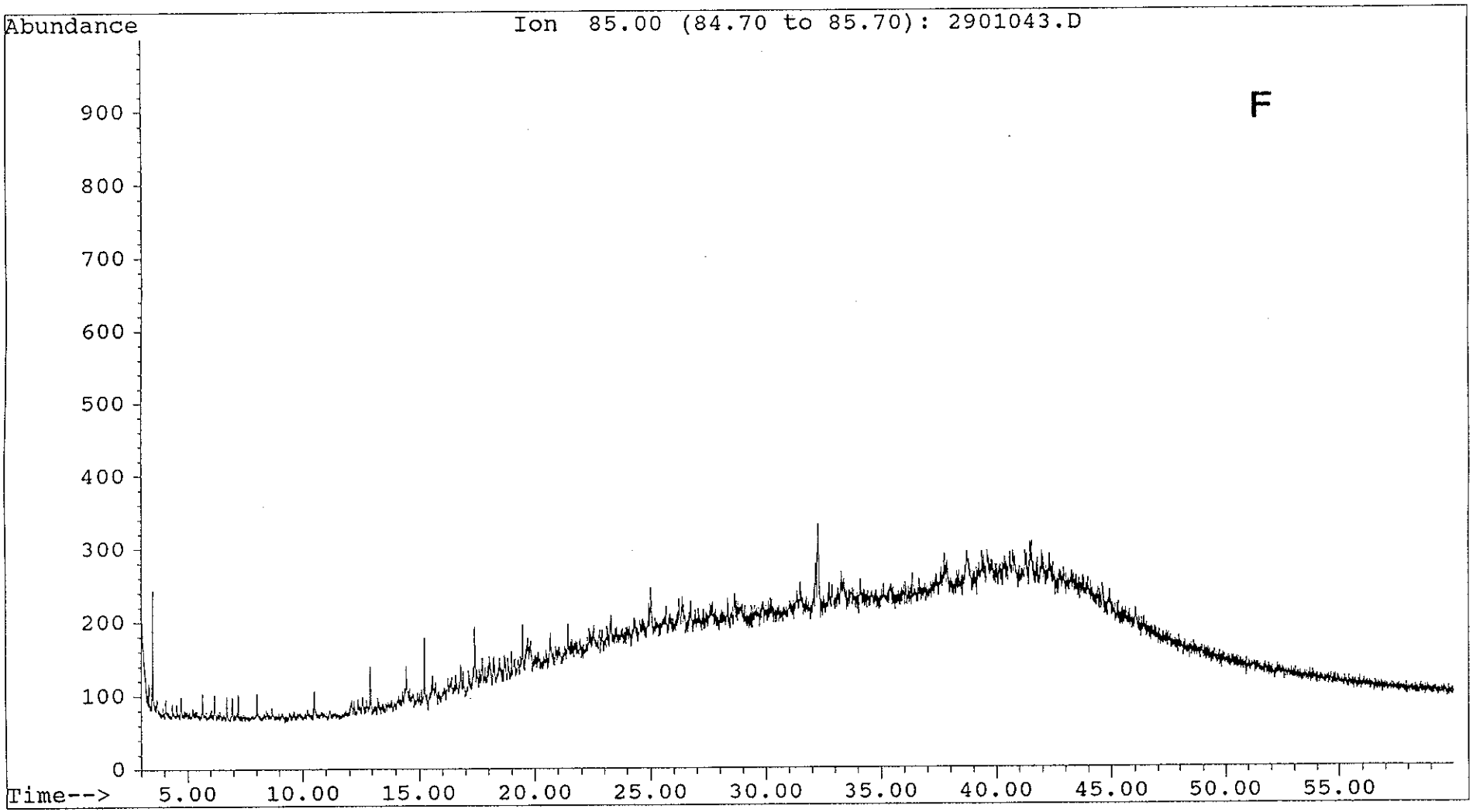


Fig 2. Comparison of Alkylated PAH Homologue Distribution of ASMB Oil and NOBE Oil

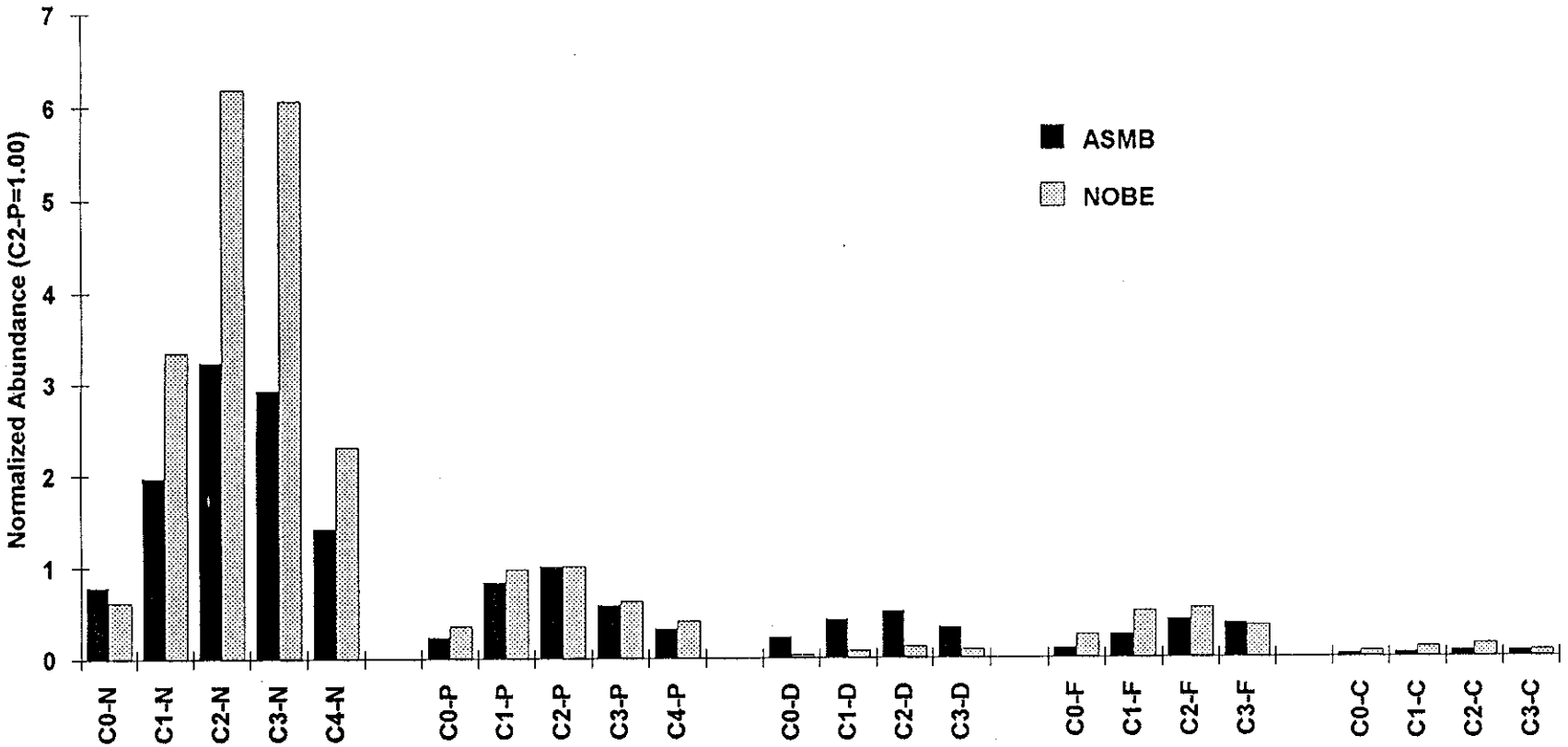


Fig 3. Alkylated PAH Homologue Distribution in Unweathered and Weathered NOBE Oil

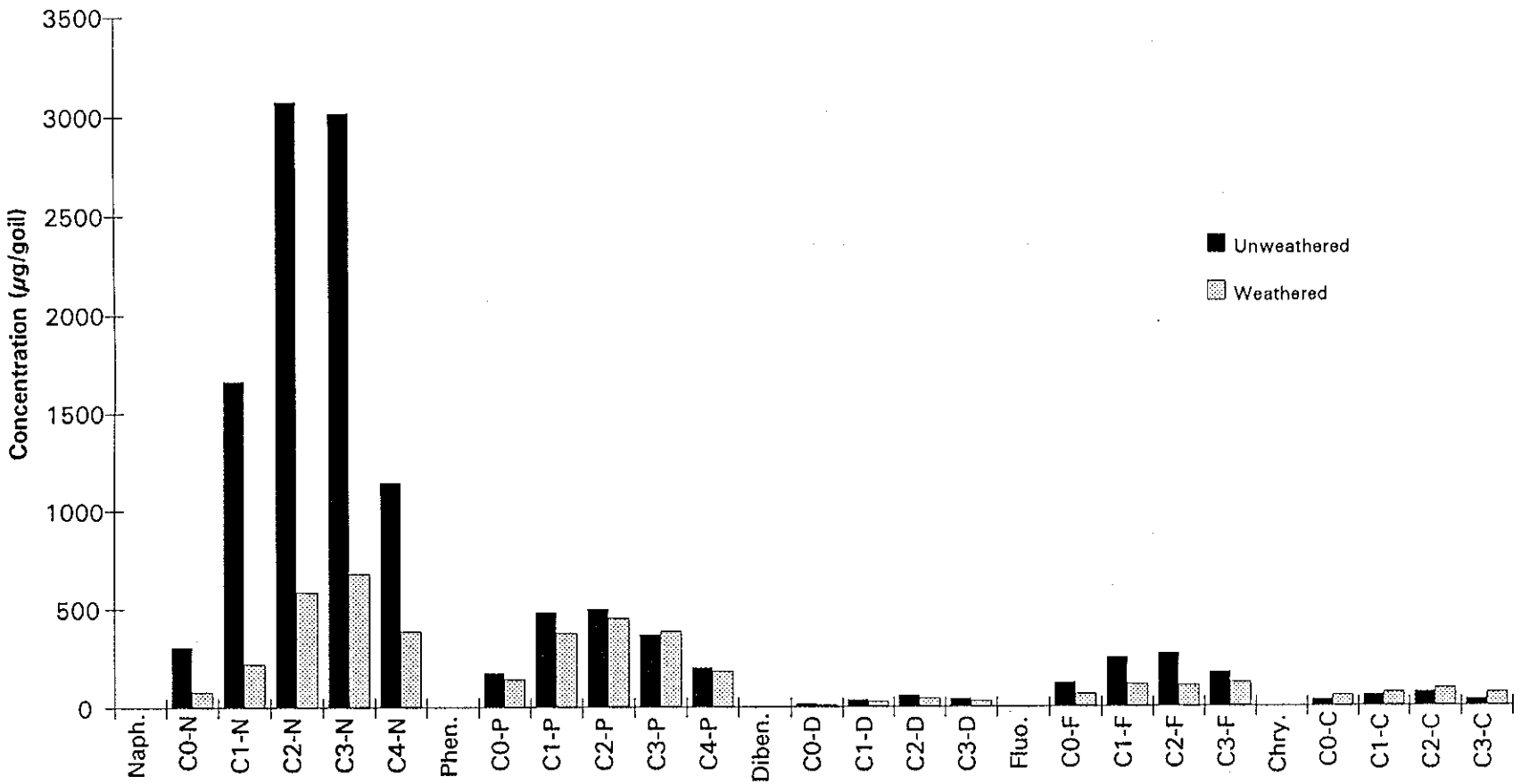


Figure 4 PAH Distribution of the Source Weathered Oil (A), S-6(B), S-A(C), and S-9(D)

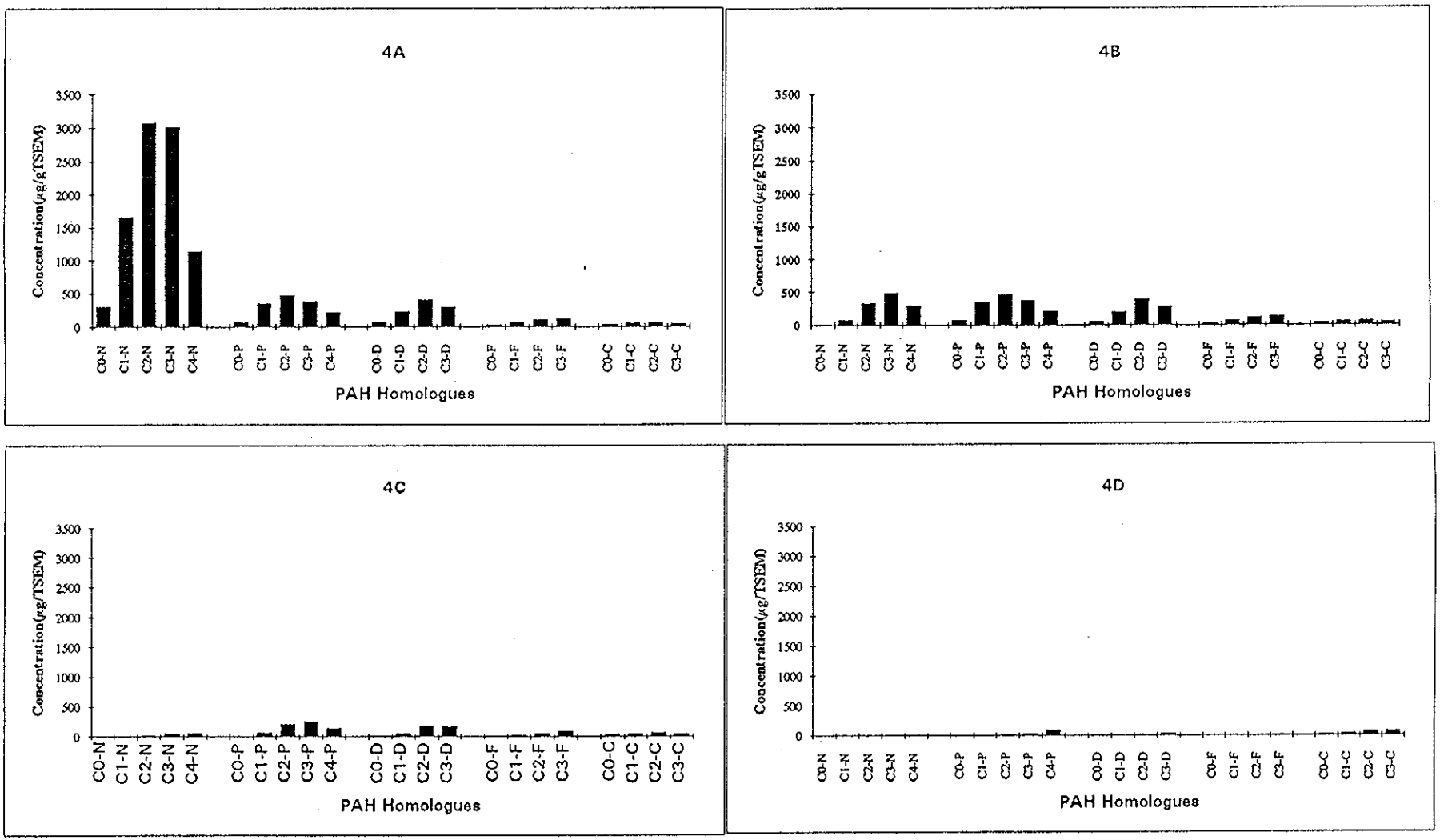
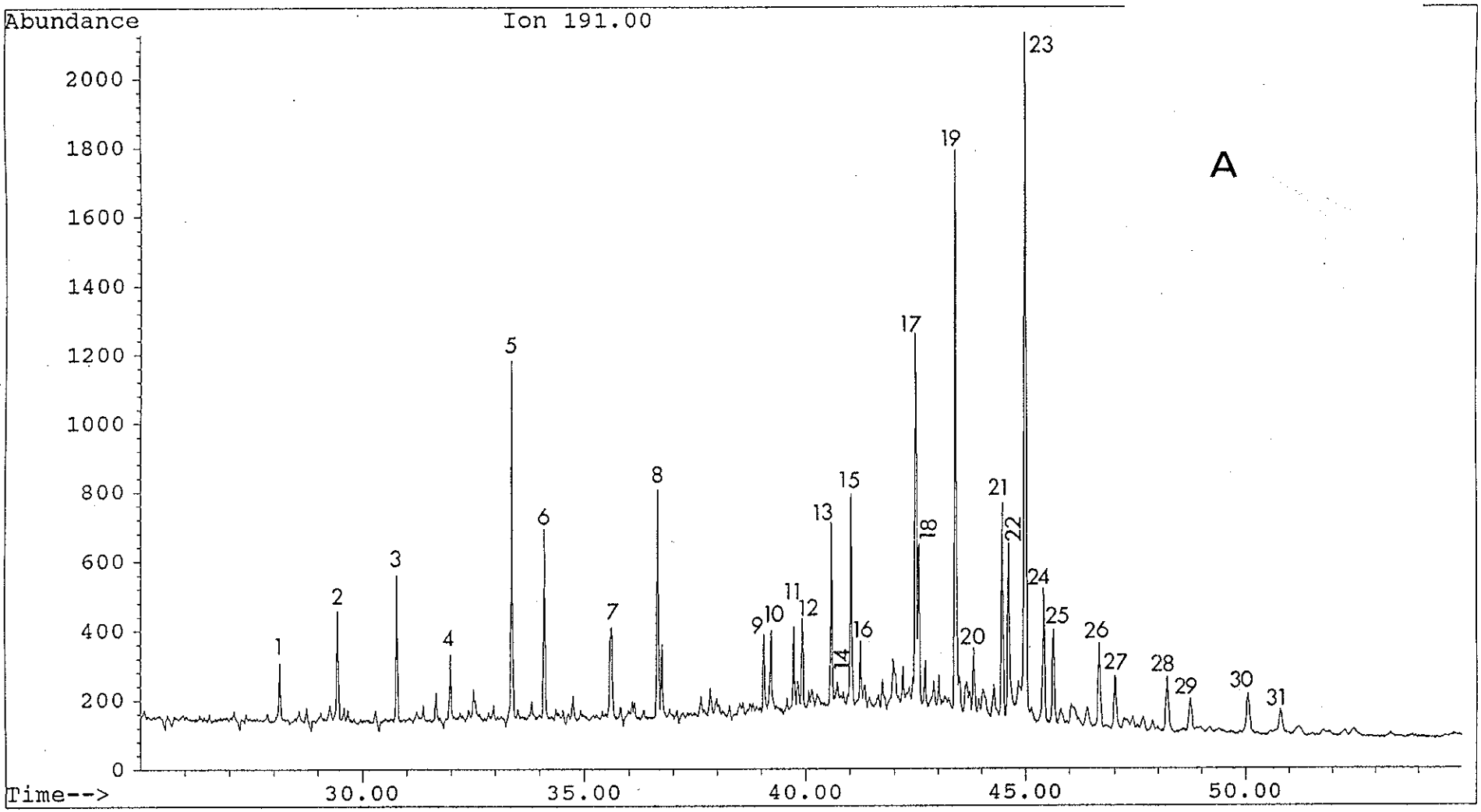


Fig. 5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1400
1200
1000
800
600
400
200
0
Time-->
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40.00
45.00
50.00
1
2
3
4
5
6
7
8
9
10
11
12
13
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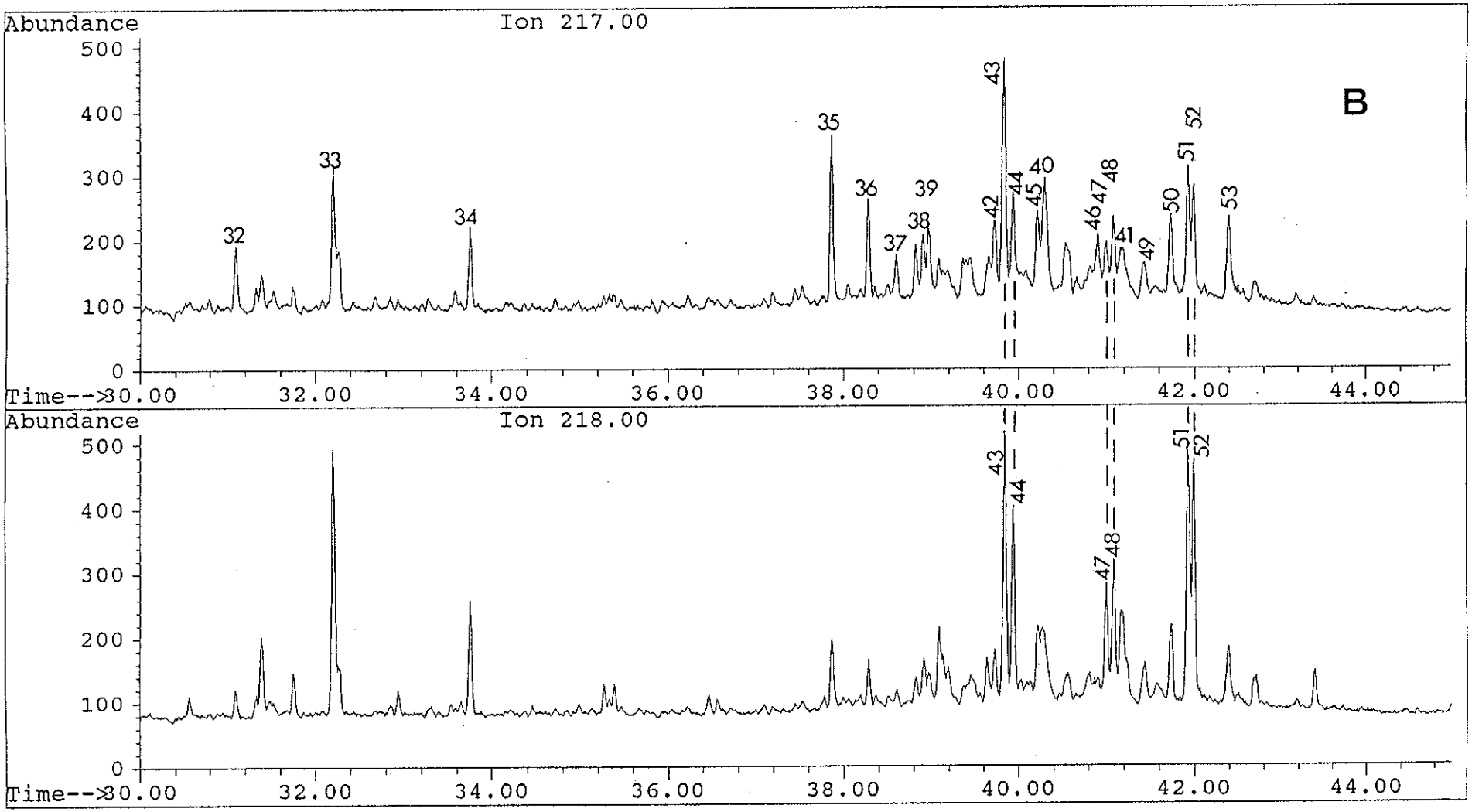
28
29
30
31
A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200
100
0
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33
34
35
36
37
38
39
42
43
44
45
40
46
47
48
41
49
50
51
52
53
Time--> 30.00
32.00
34.00
36.00
38.00
40.00
42.00
44.00
Abundance
Ion 218.00
500
400
300
200
100
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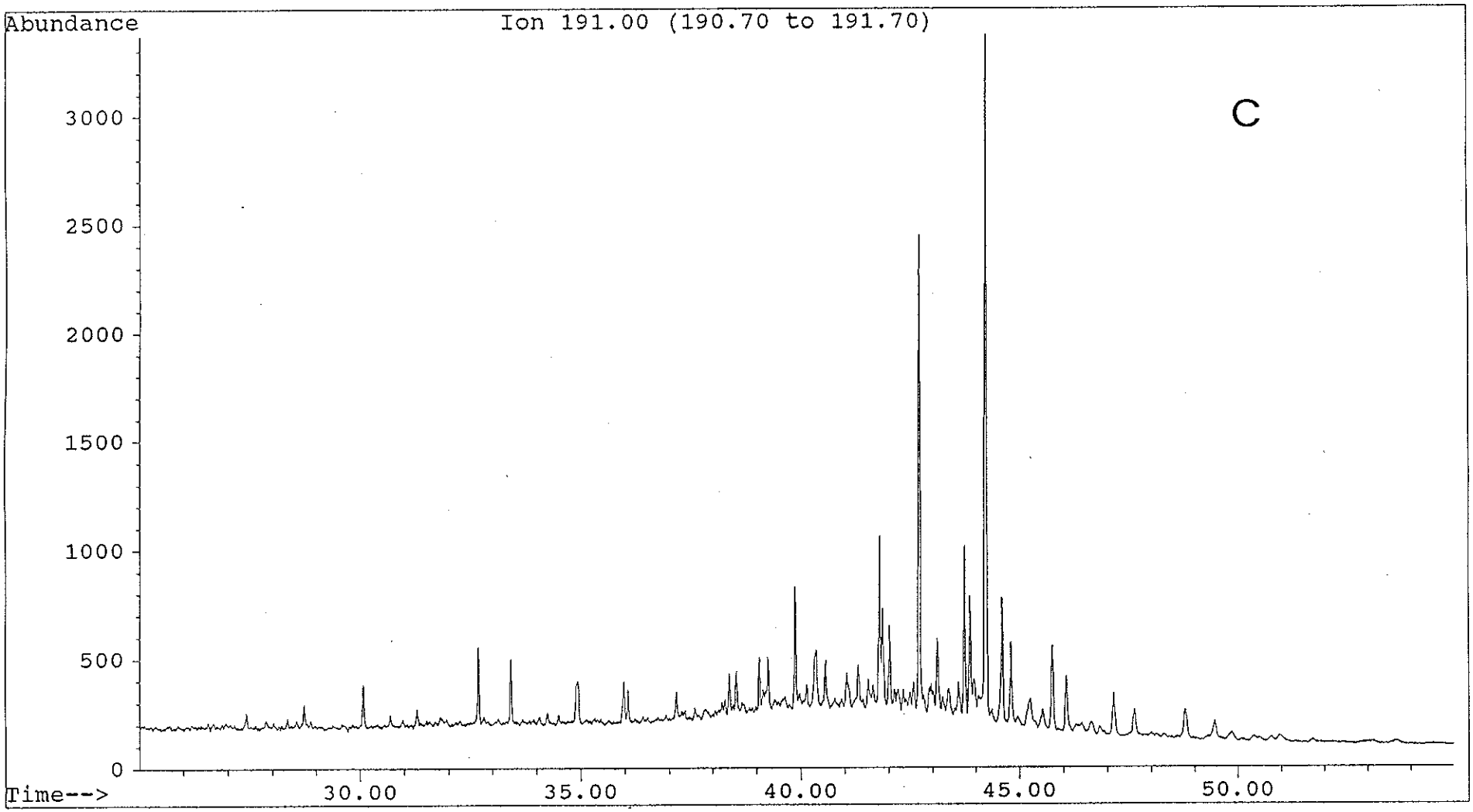
40.00
42.00
44.00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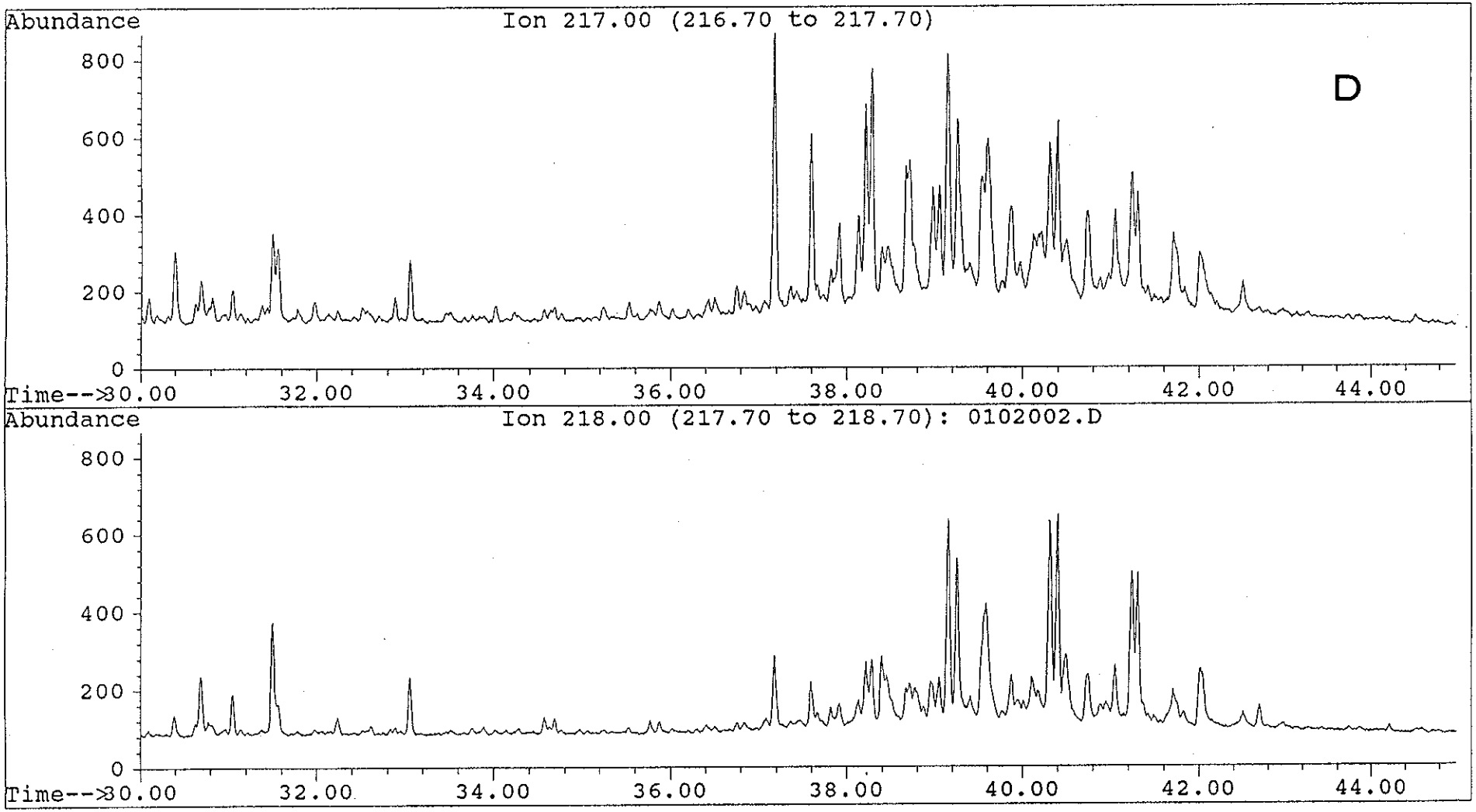
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200
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38.00
40.00
42.00
44.00
Abundance
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200
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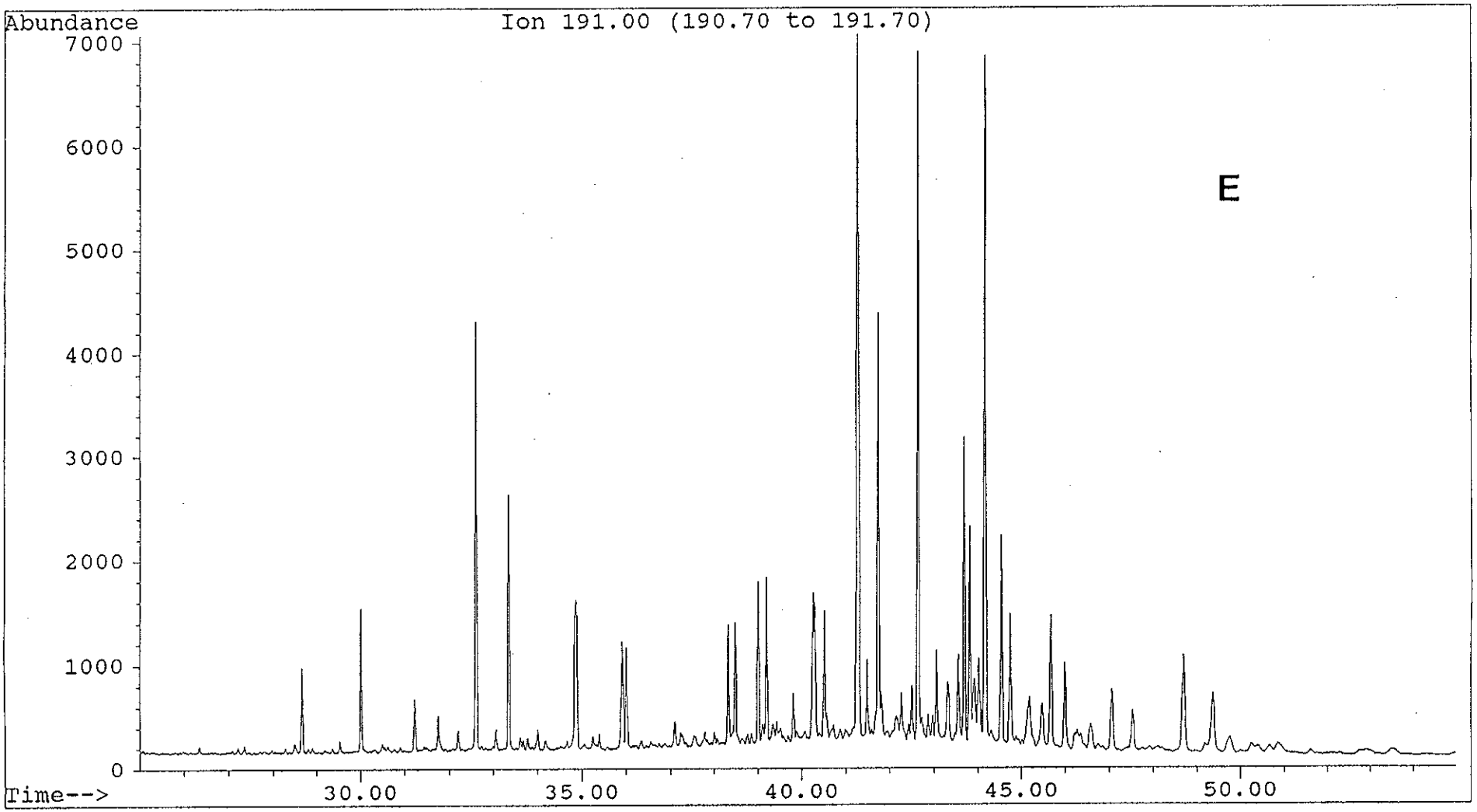
44.00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4000
3000
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Time-->
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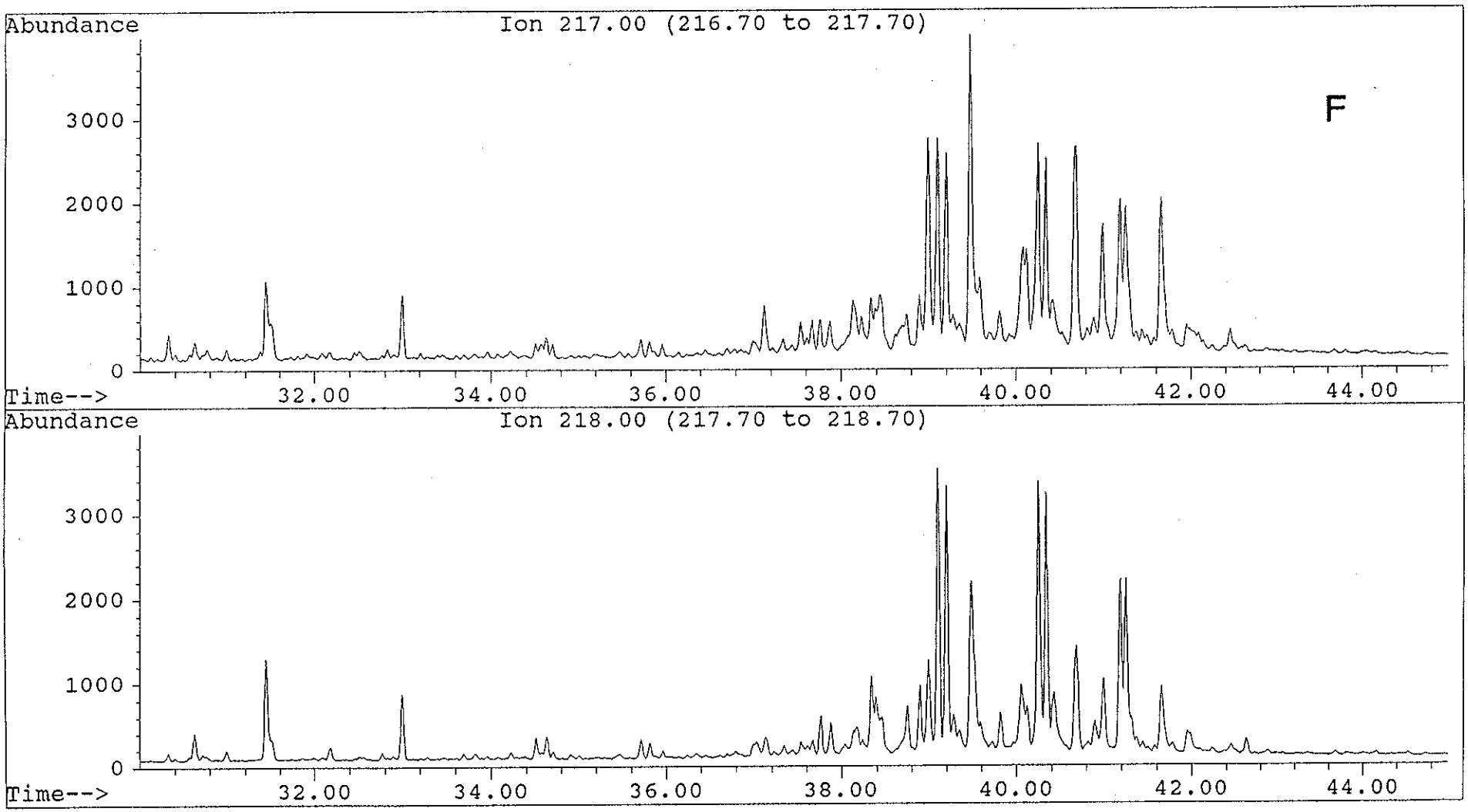
35.00
40.00
45.00
50.00
E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3000
2000
1000
0
Time-->
32.00
34.00
36.00
38.00
40.00
42.00
44.00
Abundance
Ion 218.00 (217.70 to 218.70)
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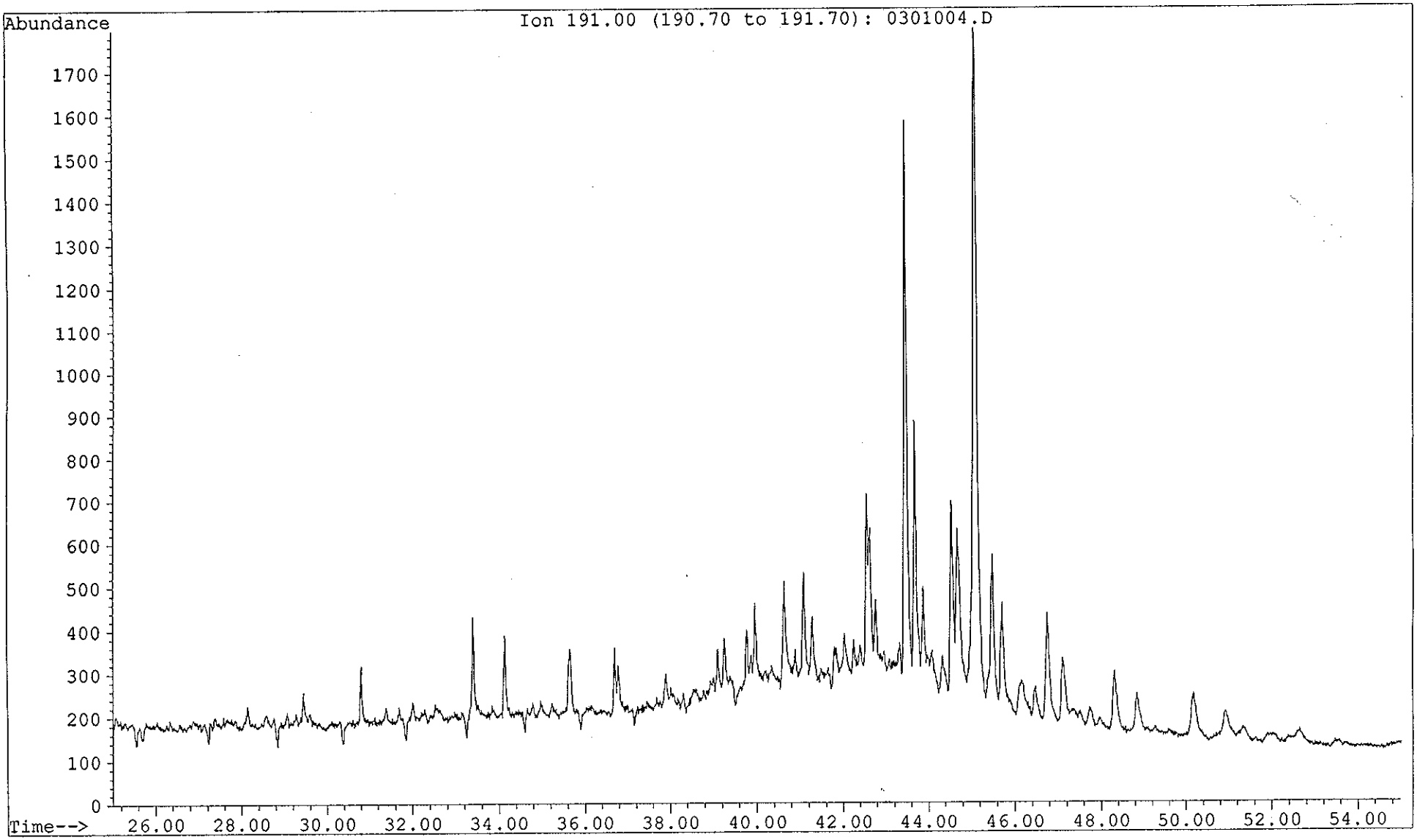

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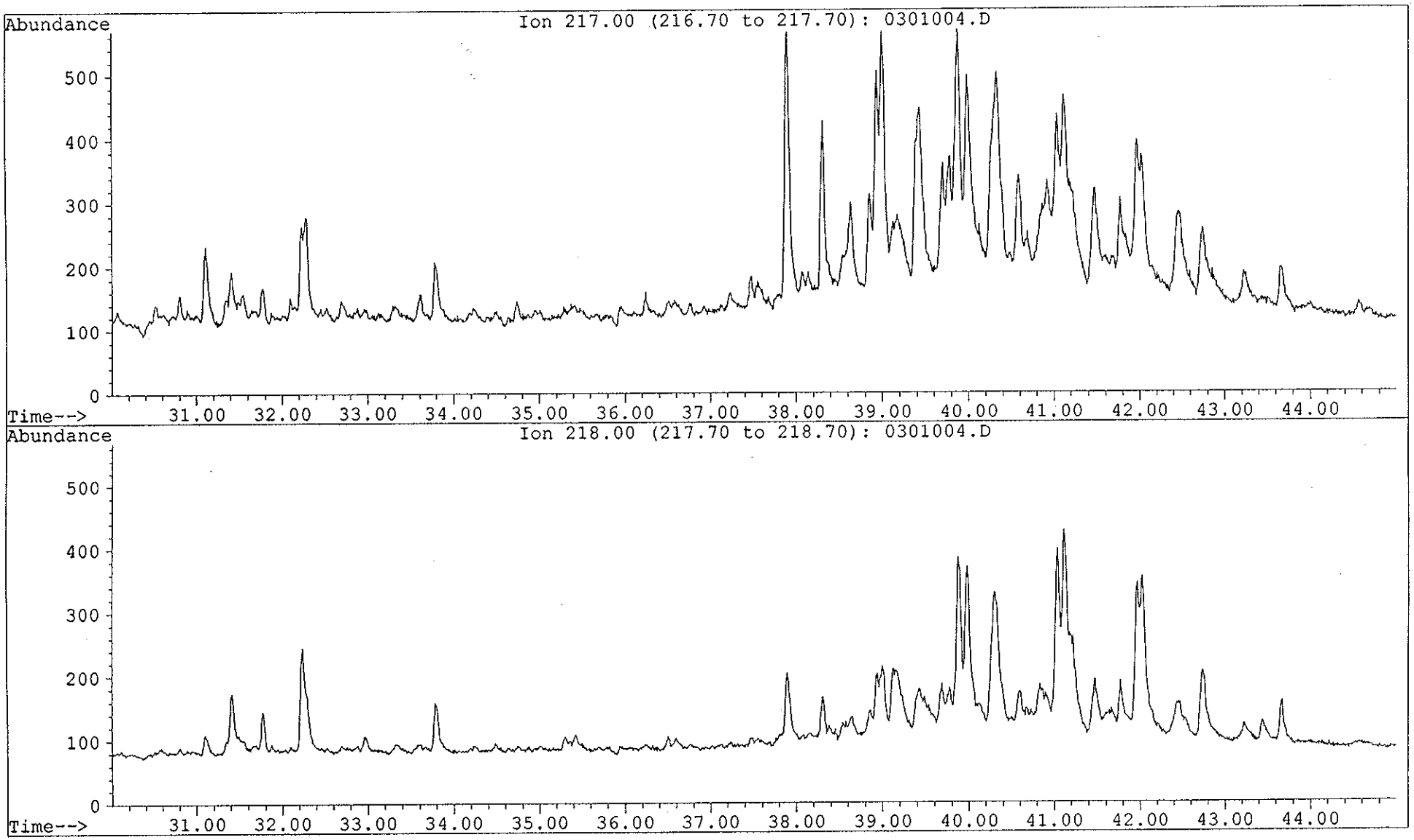

Fig 6. Diagram of Oil Analysis Protocol

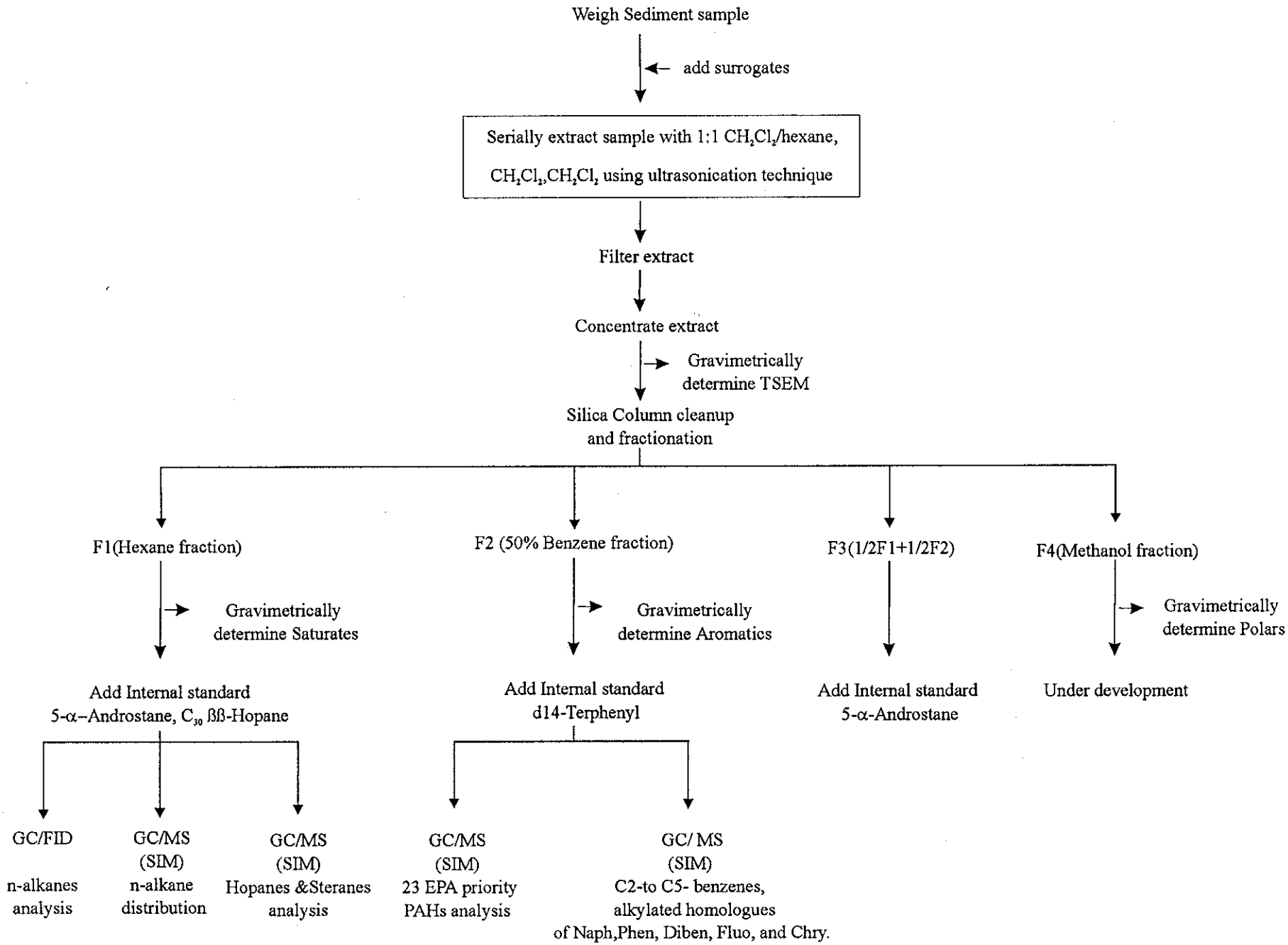

Fig 7. Diagram of Oil Analysis Protocol