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CONDENSATES

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ABSTRACT

Condensate samples were heated under a stream of nitrogen at 200 °C. Then the samples were treated with 5-A or S-115 molecular sieve to remove normal alkanes. Next the samples were refluxed with Zeolite 13X molecular sieve with n-pentane as solvent to adsorb fused-ring biomarkers. The adsorbed biomarkers then were released by Soxhlet extraction. Four groups of commonly used biomarkers, namely tricyclic and pentacyclic terpanes, tetracyclic steranes, mono-aromatic steranes, and tri-aromatic steranes are dramatically enriched in the released zeolite (ZA) fraction. This method overcomes the difficulty encountered in analysts of fused-ring biomarkers in condensate and other biomarker depleted samples.

INTRODUCTION

Condensates are liquid hydrocarbons dissolved in production natural gas: they are separated when the gas reaches surface or shallow subsurface positions (Tissot and Welte; 1984). Under reservoir pressure and temperature, liquid hydrocarbons can be dissolved in natural gas and the solution is in a gaseous state. Upon reaching the surface where temperature, and more importantly pressure, are decreased, the liquid hydrocarbons will separate from the gas as liquid condensates. Another similar situation is natural gas dissolved in oil. With large amounts of gas and light hydrocarbons are dissolved in oil, the asphaltenes and heavy components of oil can be precipitated from the oil (as what happens in the

geochemical laboratory where we use n-pentane or iso-octane to precipitate asphaltenes from oil or rock extract samples), resulting in light, condensate-like oils.

The lighter the hydrocarbons, the easier they can be dissolved in gas in the reservoir. Therefore, most condensates are dominated by light hydrocarbons ($C_5 - C_{15}$) with high API gravity and very low concentrations of C_{15+} hydrocarbons. The characteristics of condensates make organic geochemical biomarker analyses very difficult; especially for GC/MS analysis of cyclic biomarkers, such as the commonly used tricyclic and pentacyclic terpanes, tetracyclic steranes, and aromatic steranes. These biomarkers are mostly C_{19} to C_{35} fused-ring naphthenes or aromatized naphthenes, which provide very useful information about the depositional environment, maturity of source rocks and petroleum, and biodegradation and migration of petroleum. Biomarker distribution and concentration are also good tools for oil-oil and oil-source rock correlations. The concentrations of fused-ring biomarkers in most condensates are so low that they are often masked by normal alkanes, other single-ring, long chain hydrocarbons, and biodegraded complex compounds. As a result, most biomarker analyses using standard procedures with whole condensate or fractions of condensate give very poor results.

A method of biomarker enrichment for condensates has been developed to overcome the difficulty of condensate biomarker analysis. Dimmler and Strausz (1983) and Armanios *et al* (1994) reported methods using several kinds of molecular sieves to enrich pentacyclic triterpanes from oils and source rock extracts, but they did not apply the methods to condensate samples or to analysis of steranes and aromatic steranes. We decided to try a few different condensate samples to enrich four groups of commonly used biomarkers:

- Tricyclic and pentacyclic terpanes (base peak m/z 191.1800);
- Tetracyclic steranes (base peak m/z 217.1956);
- Tetracyclic mono-aromatized steranes (base peak m/z 253.1956);
- Tetracyclic tri-aromatized steranes (base peak m/z 231.1174).

If our method works, it could become a universal biomarker enrichment method for all liquid petroleum samples for all groups of commonly used biomarkers.

EXPERIMENTAL

Two natural gas condensates were chosen for the experiment. Sample #R738015 is a natural gas condensate from a unknown field in the Gulf Coast area and will be called sample #1 hereafter in this report. Sample #94097005 is another condensate from well

McCune #1, Winters Sandstone reservoir, San Joaquin Basin, California and will be called sample #2 hereafter in this report.

About 1 gram condensate samples were taken for analysis. First, the samples were heated in a sand bath at 200 °C under nitrogen flow for about 4 hours. This step removed almost all compounds lighter than C₁₅. Then the samples were treated with 5-A (pore size 5 Å) or S-115 molecular sieve for at least 24 hours at room temperature to remove C₁₅₊ normal alkanes.

Next, the samples were treated with Zeolite 13X to adsorb the target biomarkers. Zeolite 13X is a kind of molecular sieve with size 13 Å micro holes which are approximately the size of three to five fused-ring molecules and too big for chain or single-ring molecules. Those chain and single-ring molecules could also be adsorbed but might be later washed out by solvent rinsing. One of the manufacturers for this product is Coast Engineering Laboratory in Redondo Beach, California. The 13X molecular sieve was first conditioned at 400 °C for 36 hours. Then about 25 grams of 13X were added to the remaining sample with 50 ml of n-pentane as solvent. The mixture was refluxed for 2 hours, filtered and quickly washed with 50 ml of n-pentane. The solvent (with the sample in it) was reduced to about 50 ml under a stream of nitrogen and another 25 grams of 13X molecular sieve was added and the mixture again refluxed for another 2 hours. Filtration and washing with 50 ml n-pentane yielded the ZNA fraction which is the non-biomarker (or Zeolite Non-Adsorbed) fraction. Biomarkers are adsorbed on the 13X molecular sieve. The two fractions of 13X were Soxhlet extracted with iso-octane for about 36 hours. The extract, reduced *in vacuo* and filtered through silica with n-pentane yielded the ZA fraction which is the biomarker (or Zeolite Adsorbed) fraction.

The initial sample, the sample after heating, the ZNA fraction and the ZA fraction were analyzed with a Perkin-Elmer AutoSystem Gas Chromatograph. The ZA fraction was then analyzed with a VG 7035 double-focusing magnetic Gas Chromatography-Mass Spectrometer using a routing biomarker SIM (Single Ion Monitoring) analysis program to collect m/z 191.1800, 217.1956, 231.1174, and 253.1956 ion chromatograms, respectively. The results are discussed in the following section.

RESULTS AND DISCUSSION

The ZA fractions of the two samples recovered are about 15 to 41 mg (from about 1 gram initial samples, Table 1), about 1.5 to 4 % of initial samples. Light hydrocarbons, normal alkanes, and other chain and single-ring compounds were successfully removed. It is possible that some biodegraded complex compounds were also partially removed with biomarkers (if any) concentrated in the ZA fraction.

Figures 1a and 2a are the gas chromatograms of condensate samples #1 and #2, respectively before any treatment. It can be seen that both samples contain abundant low molecular weight hydrocarbons but very little high molecular weight compounds (range of common biomarkers). The peak marked Pr is a C₁₉ isoprenoid (pristane) and the peak marked Ph is a C₂₀ isoprenoid (phytane). The peak (or the position where the peak normally elutes) marked 30H is hopane which is a C₃₀ pentacyclic triterpane, a very common biomarker which is not evident in the initial (untreated) sample.

Table 1. Condensate Biomarker Enrichment Experiment Initial Data

Sample #	#1 R738015	#2 94097005
Location	Gulf Coast	San Joaquin Basin, CA
Initial Amount (mg)	1100	1375
After Heating @ 200 °C (mg)	312	109
% of Initial Amount	28.36	7.93
ZNA Fraction (Zeolite Non-Adsorbed,	181.5	54.1
% ZNA of Initial Amount	16.50	3.93
ZA Fraction (Zeolite Adsorbed, mg)	41.9	15.6
% ZA of Initial Amount	3.81	1.13

Figures 1b and 2b are the gas chromatograms of condensate samples #1 and #2, respectively after heating under nitrogen flow at 200 °C. It can be seen that most light compounds (less than C₁₅) in the samples were evaporated, leaving pristane (Pr) and phytane (Ph) as almost the lightest compounds. Again the concentration of hopane (30H) is still too low and is masked by hundreds of unknown compounds which are mostly long chain with zero to one ring at the end of the chain. There are also a lot of biodegraded complex compounds. Those compounds are responsible for the big humps in the chromatograms and give the heated samples waxy characteristics.

Figures 1c and 2c are the gas chromatograms of the ZNA fractions (the non-biomarker fractions) of samples #1 and #2, respectively after Zeolite 13X adsorption. It can be seen that pristane (Pr), phytane (Ph), and other isoprenoids remained in this fraction. Hopane (30H) and other fused-ring biomarkers are not in this fraction (or are in very low concentrations).

Figures 1d and 2d are the gas chromatograms of the ZA fractions (the biomarker fractions) of samples #1 and #2, respectively after Zeolite 13X adsorption and then release from the 13X by extraction. It can be seen clearly that hopane (30H) and other pentacyclic triterpanes are enriched while pristane (Pr), phytane (Ph) and other isoprenoids are not (or are in very low concentrations) in this fraction. The other three groups (steranes, mono-aromatic and tri-aromatic steranes) of biomarkers can not be seen very clearly in these gas chromatograms. However, they can be seen very clearly in the GC/MS SIM chromatograms in Figure 3 and 4.

Figures 3 and 4 are the GC/MS chromatograms of the ZA fractions (the biomarker fractions) of samples #1 and #2, respectively after Zeolite 13X adsorption and then released from the 13X by extraction. Four groups of biomarkers are shown clearly here as in chromatograms of "regular" oils or rock extract samples. Since the condensate percolated through source rocks and reservoir rocks, or was extracted by gas from the source rocks and regular crude oils, those biomarkers can carry the information about source organic matter, environment of deposition, maturity, migration, and biodegradation. They are also good tools for correlations. The results of sample #2 are not as good as sample #1, because sample #2 was extremely depleted in biomarkers at the outset.

CONCLUSIONS

The method developed provides an effective analysis of condensate biomarkers. Condensates do have high molecular weight biomarkers; at least some condensates can be treated and then analyzed for biomarker study and yield abundant useful information. The method can also be used for analysis of highly mature oil and source rock samples and other biomarker depleted samples.

Further development of the method will simplify the process, test if the method is good for bicyclic terpanes and hexacyclic terpanes, and test if the method affects the ratios of some biomarkers (such as mono- to triaromatic steranes) which are used by geochemists for investigating maturity, environment, correlations, and other geochemical parameters.

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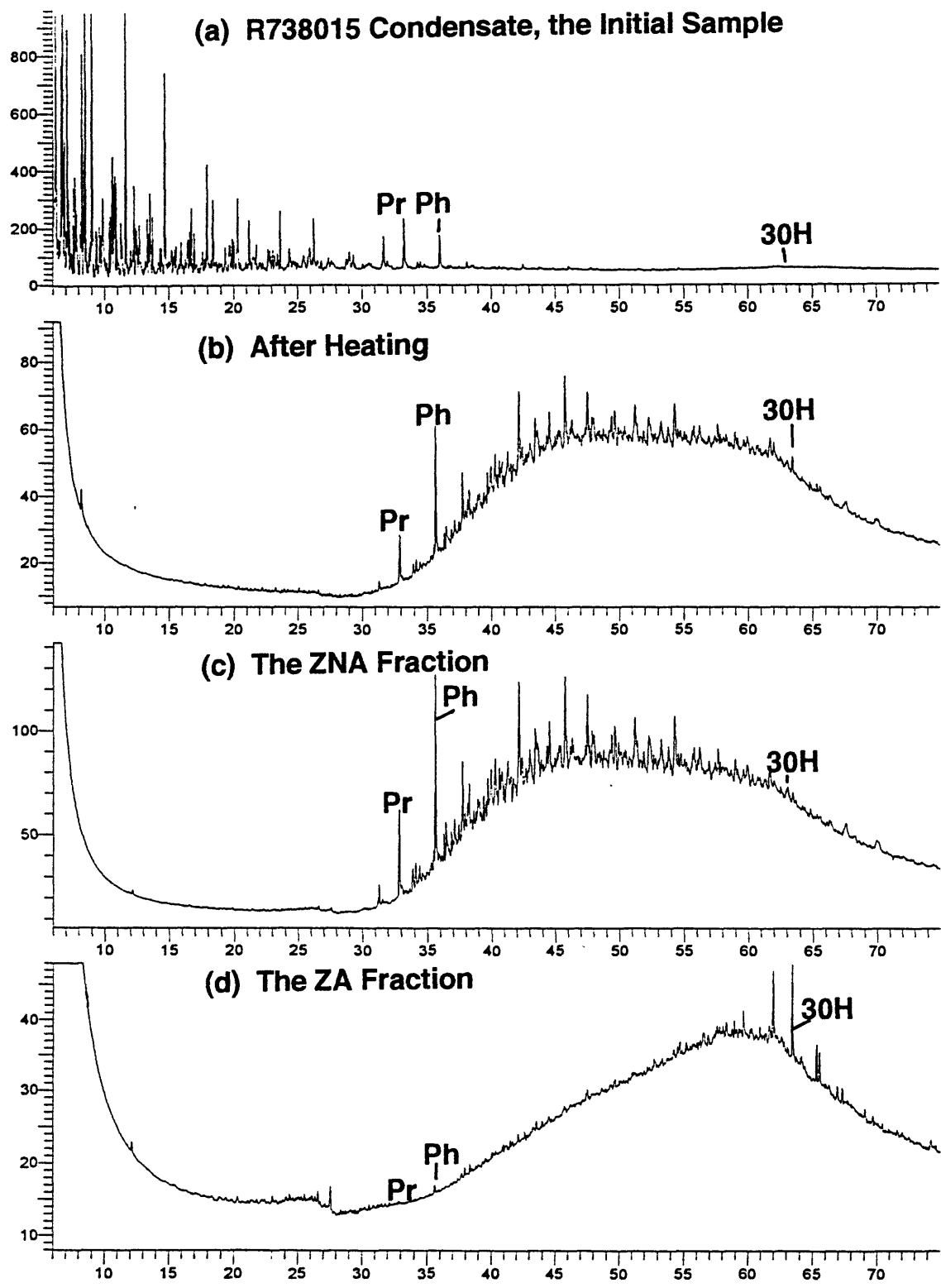


Figure 1. Sample #1 at different stages of processing: (a) the whole oil before any treatment; (b) after heating at 200 °C for 4 hours; (c) the zeolite non-adsorbed fraction; and (d) the zeolite adsorbed fraction, fused-ring biomarkers enriched.

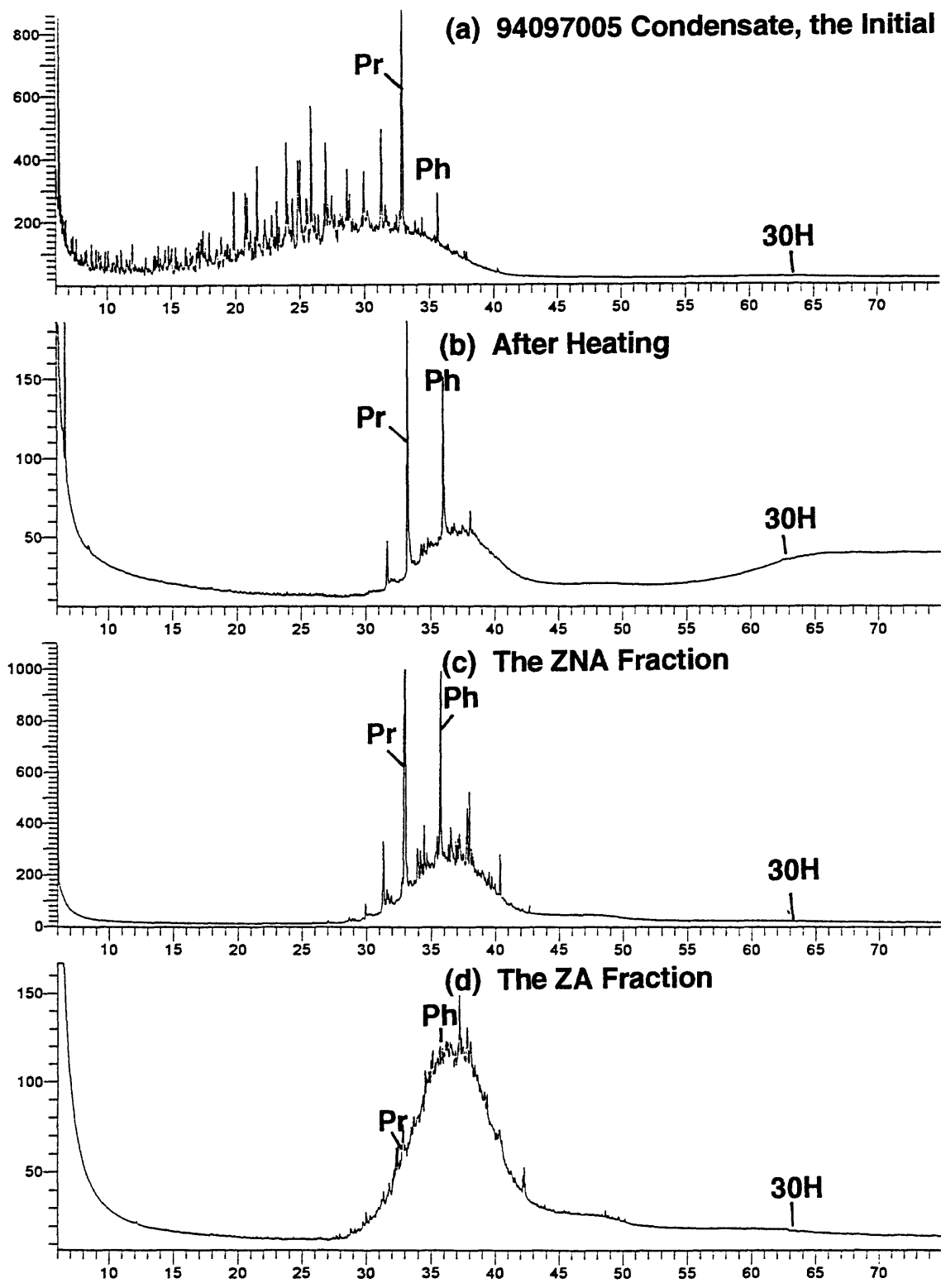


Figure 2. Sample #2 at different stages of processing: (a) the whole oil before any treatment; (b) after heating at 200 °C for 4 hours; (c) the zeolite non-adsorbed fraction; and (d) the zeolite adsorbed fraction, fused-ring biomarkers enriched.

R738015 Condensate, Fused-ring Biomarkers

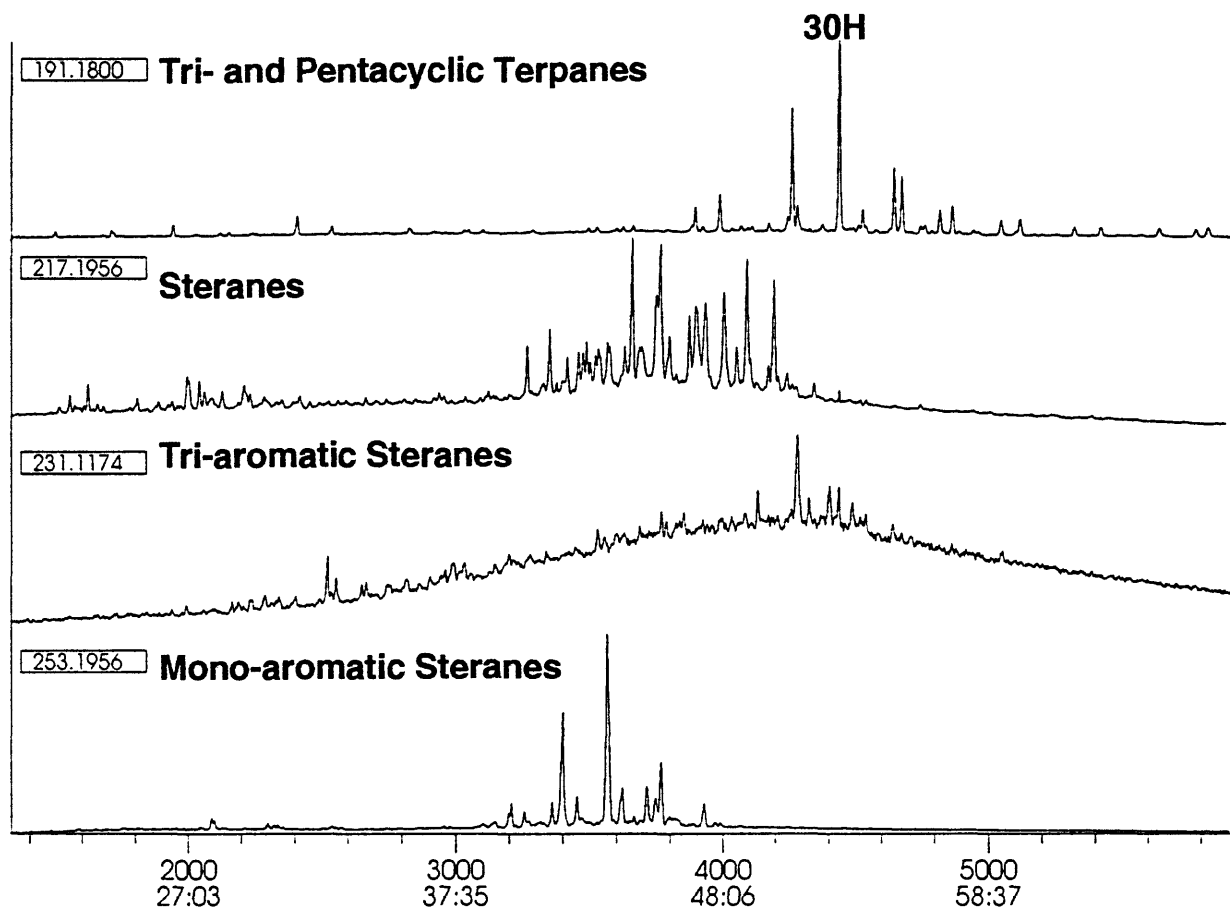


Figure 3. The GC/MS Chromatograms of commonly used fused-ring biomarkers in Sample #1.

94094005 Condensate, Fused-ring Biomarkers

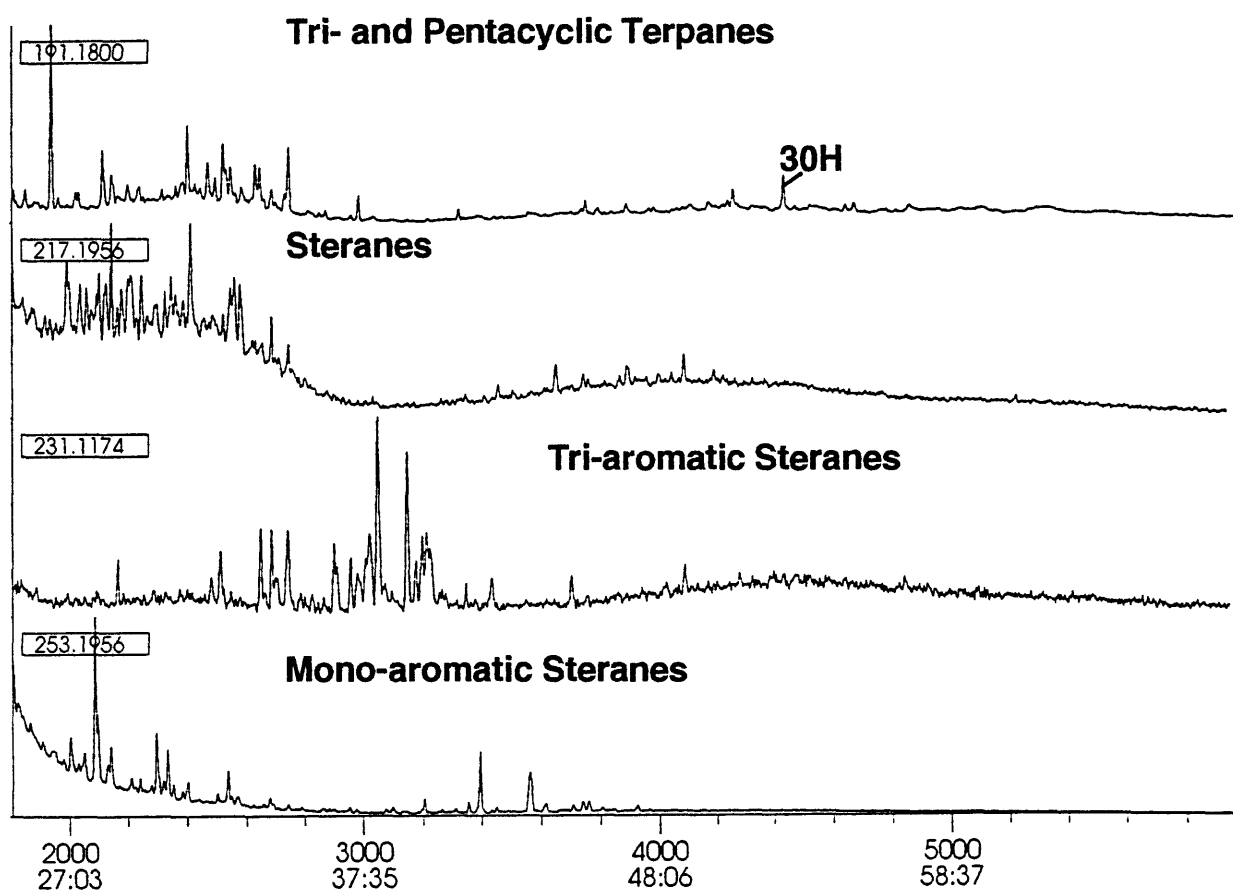


Figure 4. The GC/MS Chromatograms of commonly used fused-ring biomarkers in Sample #2.