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Re: MC-252 Spill Chemistry

Introduction

One (1) emulsified oil sample and two (2) water/ oil samples (Table 1) collected by Entrix and USCG personnel were received at the Louisiana State University Response laboratory on 26 and 28 April 2010, respectively. The samples were extracted or diluted and fingerprinted immediately after being logged in and assigned a DES/RCAT identification number. After discussing with NOAA personnel as to which parameters were needed, it was determined oil fingerprint, % moisture, ignitability, and specific gravity be analyzed. Sample 2010118-01 consisted of a thin oil layer on water, so an oil fingerprint was the only analysis performed. Sample 2010119-02 consisted of a thin oil layer on water and was a subsample from the original riser fluid sampling event. NOAA Senior Scientist Bill Lehr requested LSU perform a dispersibility test on sample 2010119-02 to determine the efficacy of dispersing with Corexit 9500. A skimmer oil sample, 20101166-01), was characterized as a highly viscous, brown oil. The two (2) source samples displayed fingerprint patterns similar to a light South Louisiana crude oil with normal alkanes ranging from nC-10 to nC-31 and moderate concentrations of aromatic compounds. The skimmer spill sample displayed a fingerprinting pattern similar to a highly weathered crude oil with normal alkanes ranging from nC-10 to nC-31 and low concentrations of aromatic compounds. The skimmer oil sample contained

moderate levels of heavy asphaltenes, while the riser oil samples contained little asphaltenes. Moderate levels of biomarker where present in the riser and skimmer oil samples. Biomarker trace matching indicated the oils came from a similar source.

Table 1. Sample Identifications and LSU Identifications

Entrix ID	Collection Site	Date/Time	LSU ID#
Skim -oil	MC-252	4/24/10 1800	2010116-01
Riser Fluid	MC-252	4/27/10 0449	2010118-01
Riser Fluid	MC-252	4/27/10 0449	2010119-02

METHODOLOGY

The emulsified oil sample (1 g) was transferred to a 40-milliliter (ml) extraction vial and diluted with dichloromethane (DCM) to a final volume of 30 ml. Sodium sulfate Na_2SO_4 was added to the sample and shaken to remove water from the solvent extract. The riser fluid water samples were prepared by placing sample in a separatory funnel and extracted with 30-ml of DCM. The DCM extract was passed through a sodium sulfate funnel to remove trace amounts of water.

The samples were then transferred, using separate disposable pipettes, into 2 mL autosampler vials and capped with a PTFE/Aluminum crimp cap. A reference oil standard, South Louisiana Crude, was analyzed from oil collected from a local refinery. The extracted oil samples and reference oils were analyzed on a Hewlett Packard 5890 Series II Gas Chromatograph coupled with a Hewlett Packard 5971 Series Mass Selective Detector operated in selected ion monitoring mode.

RESULTS AND DISCUSSION

Below are the analytical results and observations for the riser fluid oil sample (2010119-02):

After reviewing the analytical data from analysis of the Mississippi Canyon 252 (MC-252) riser oil sample, several conclusions can be made about the source oil. The unweathered oil is highly aliphatic and contains a moderate amount of aromatics. The viscosity and water content appears to be significantly lower than the skimmer sample. Due to small sample size LSU was unable to determine water content, viscosity, or density. This means the following:

1) respiratory and dermal protection should be worn when dealing with fresh oil

2) the high levels of aromatic components should allow responders to readily burn oil

3) weathering characteristics of the oil suggest the window of opportunity is approximately 24-36 hours after initial surfacing

4) initially, fresh oil will be acutely toxic to aquatic species and marine mammals but toxicity will decrease as the degree of weathering increases

5) loss of aromatic components to weathering will increase emulsification of the oil

6) biological degradation will be most effective if the oil is dispersed prior to emulsification

7) adhesion of weathered oil to sand, sediment, and grasses will be the main cause of shoreline damage

8) oil globules and tarballs will be persistent weeks to months after initial landing

Below are the analytical results and observations for the riser fluid oil sample (2010118-01):

The oil dispersibility test was setup according to standard EPA shaker flask protocol. Pictures from the test are attacked to this document. Oil was rotated on an orbital shaker for approx. 10 minutes with Corexit 9500. Looking at the Dispersed oil jpg, you can see the fresh oil easily dispersed at 200 orbitals per minute (opm). The oil was initially shaken at 50 opm and increased at 50 opm increments. The fresh oil had no problem dispersing at the 50, 100, and 150 opm increments. This oil does not require much energy to initiate dispersion with Corexit 9500. At the end of test, rotation was stopped and the flask was allowed to rest for 5 minutes. The Static-5 minute jpg shows approximately 40-50% of the oil remaining on the surface. The percent dispersion was calculated using gravimetric analysis. Looks like this fresh oil may not require a great deal of energy to disperse and should remain dispersed as long as the currents keep the oil droplets in motion. Injection of dispersant may be a desirable alternative for removal of all or some of the oil from the surface. Using the Coast Guard's flow estimate (200,000 gallons oil per day), approximately 7.3 gpm (10,500 gallons per day) of Corexit 9500 would have to be injected into the well head to obtain a 1:20 dispersant to oil ratio. The ratio may have to be adjusted to suit changing conditions or flows.

Below are the analytical results and observations for the skimmer oil sample (2010116-01):

- Specific Gravity = 0.978

- Ignitability- a 7-8 mm slick was placed in a 250-ml pyrex beaker and exposed to a high temperature torch. The oil slick popped and sputtered for approximately 5 minutes (high water content). At 6 minutes the oil began to ignite with exposure to a constant flame. The flame was removed at 7 minutes and the slick failed to burn without an external heat source. The slick was reignited and allowed to burn for an additional 2 minutes and flame was removed. As before, the flame on the slick

extinguished and had to be reignited with an additional heat source. It is out opinion that this oil will be difficult to ignite and sustain a continuous burn.

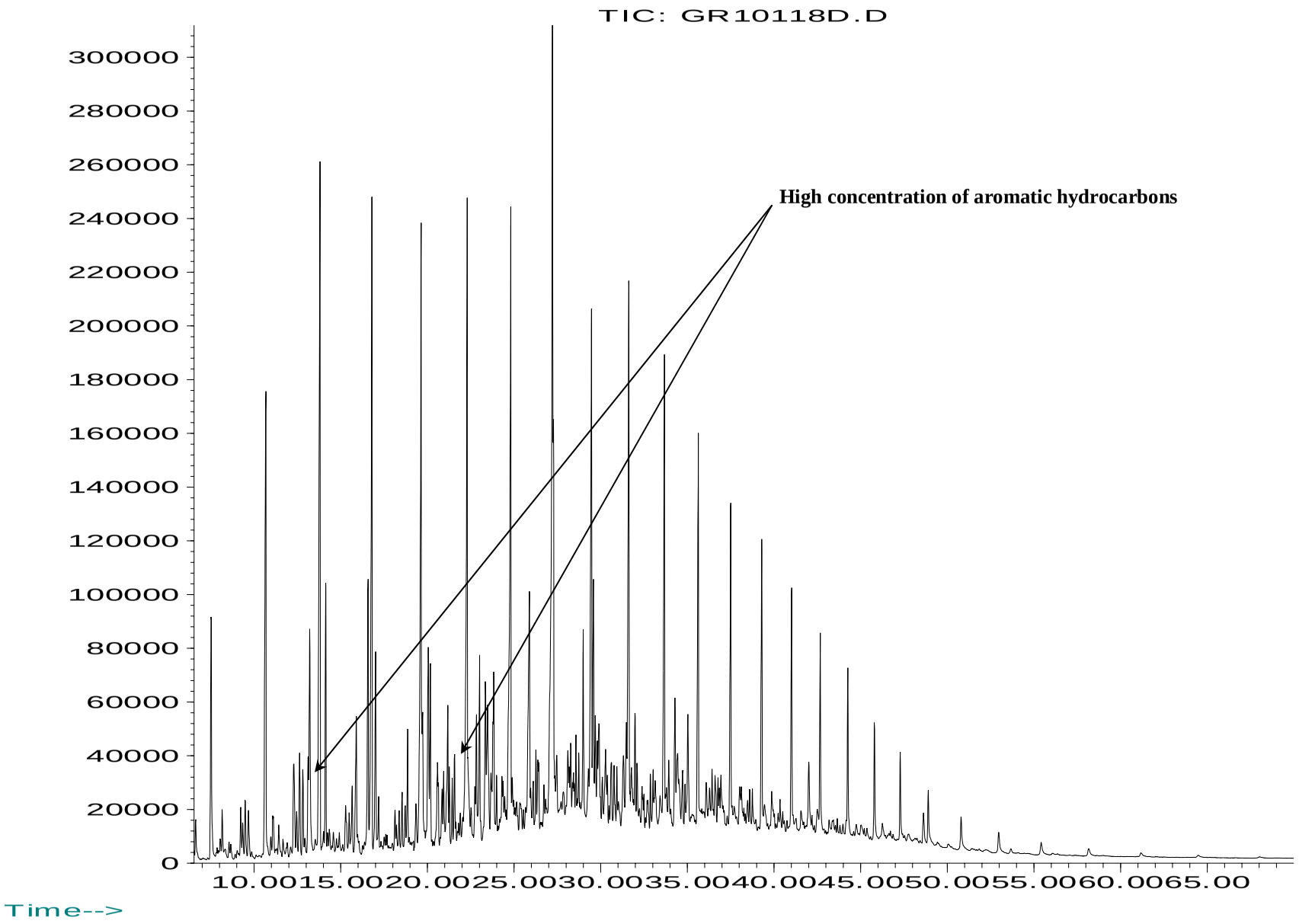
- Water content = 50-60% by volume

- The fingerprint analysis indicated the sample is a low aromatic, high aliphatic oil with a high concentration of asphaltenes. The asphaltene conc. is within the 25-50% range, by volume.

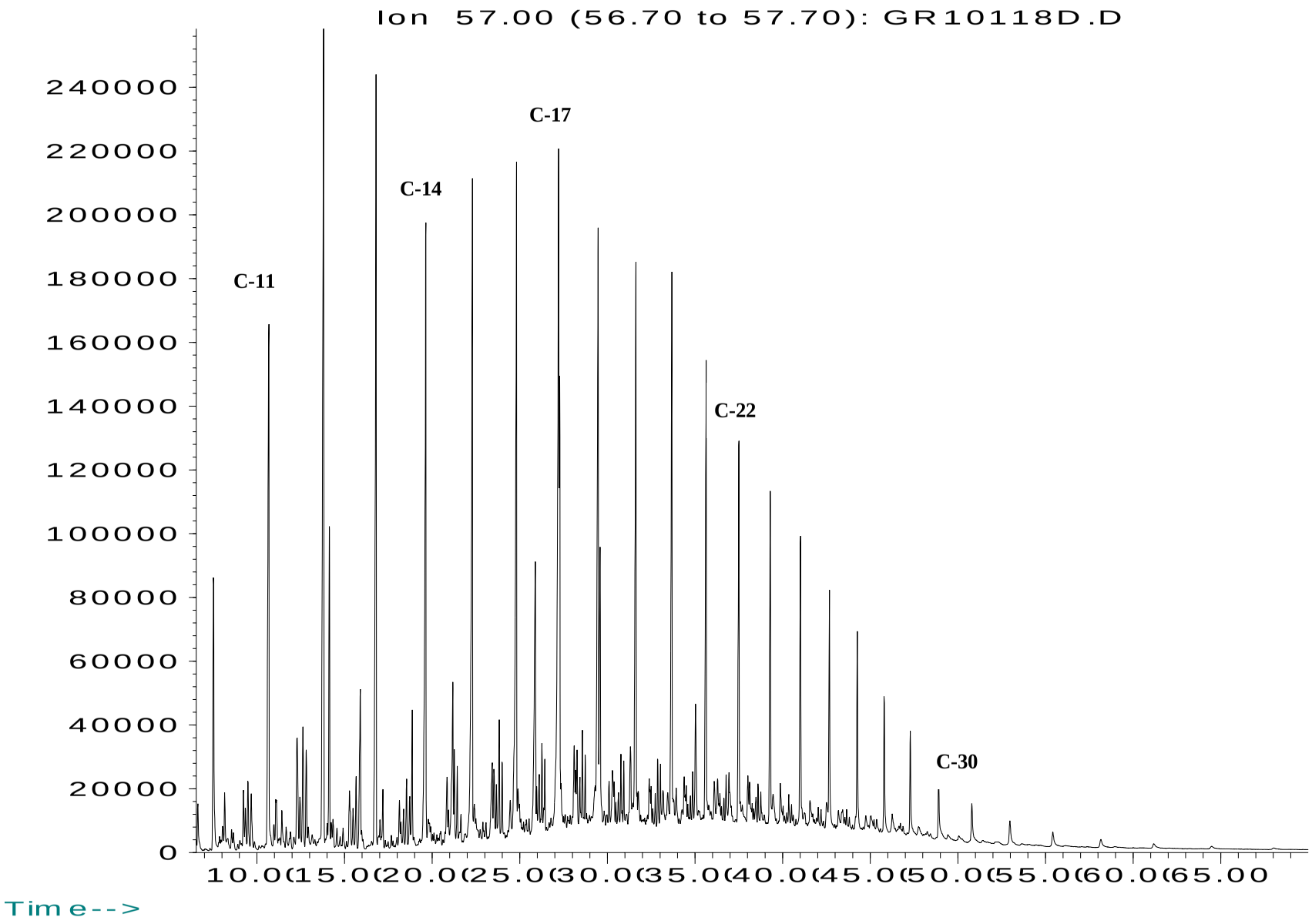
The skimmer oil sample displayed a fingerprint typical of a highly weathered South LA crude oil, but contained high levels of asphaltenes and solids, which is not typical of most South LA crudes in this region. LSU feels this sample may not be representative of the weathered open-water samples and responders should be aware of this prior to using information in fate and trajectory models. It's possible the skimmer slop holding tank may have contained additional oils or oil residues.

Attached are chromatograms showing comparative analysis of the highly weathered skimmer oil and the fresh riser source oil. As you can see there is a significant difference in their chemical composition. Visual observations of the two oils show a remarkable change in physical state over time. If the skimmer oil is truly representative of this weathered South LA crude oil the significant adhesiveness of the weathered oil should pose a hazard to shoreline inhabitants and vegetation.

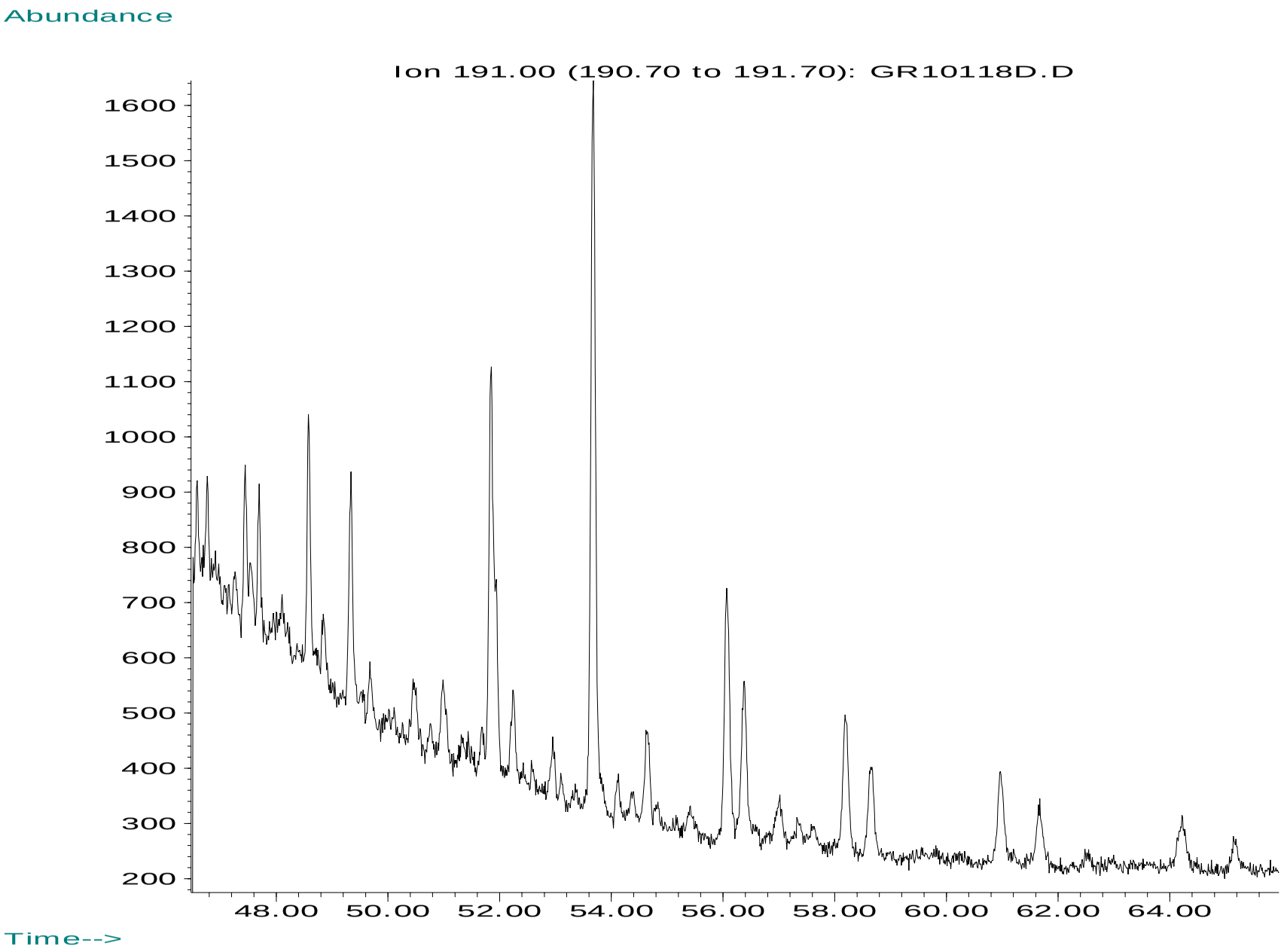
MC-252 Source Oil - Total Ion Chromatogram



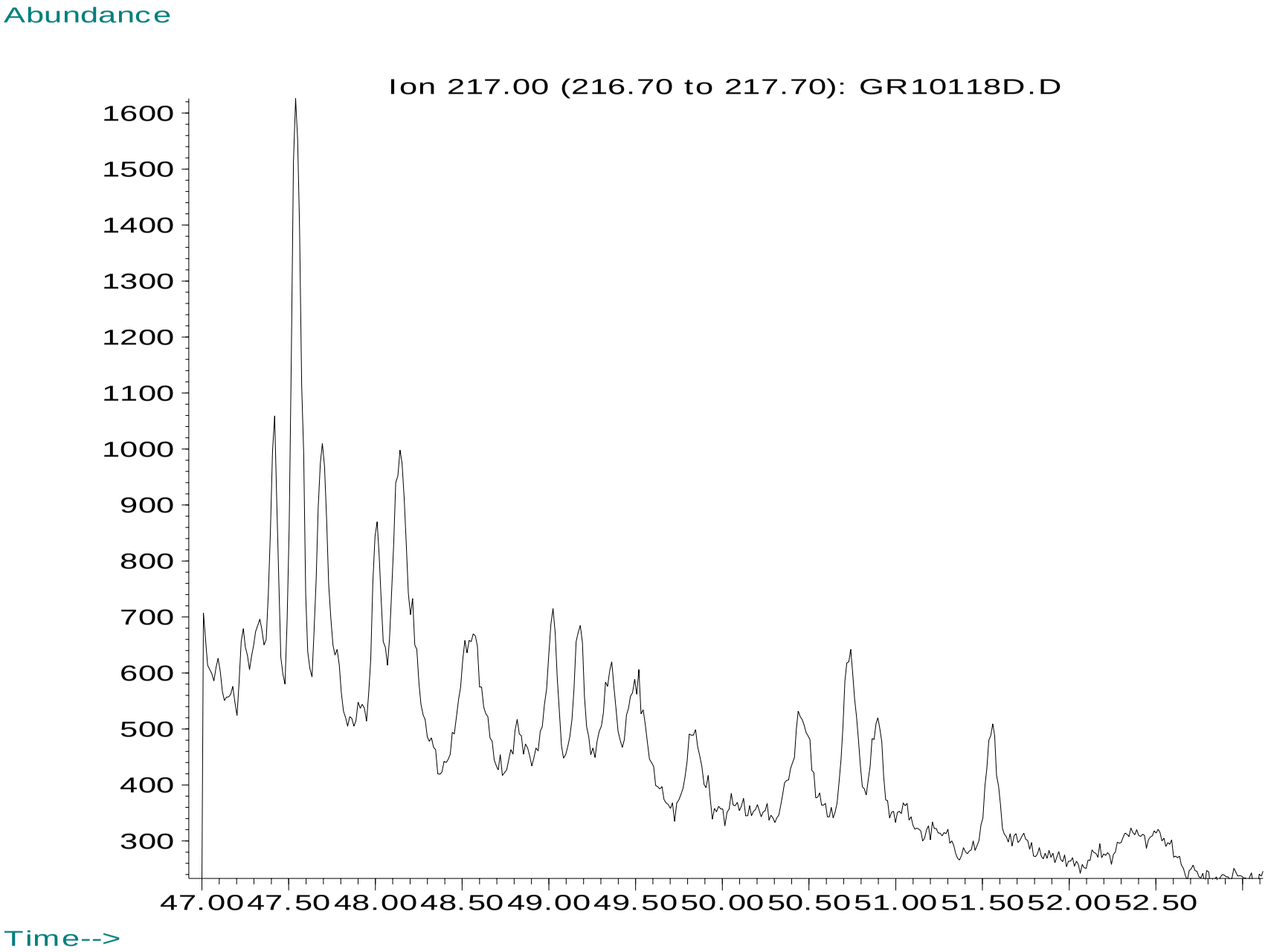
MC-252 Source Oil - Aliphatic Components



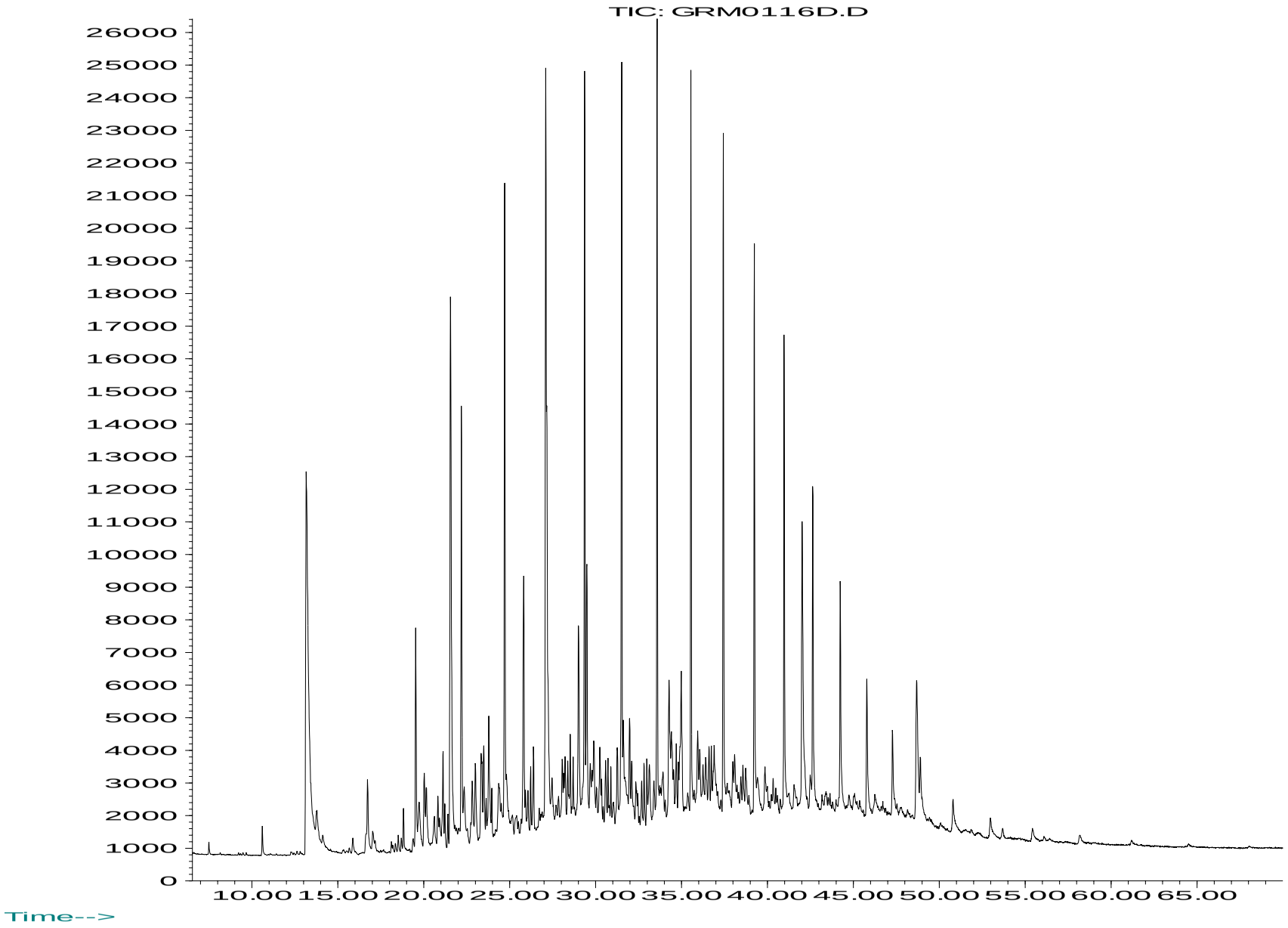
MC-252 Source Oil - Biomarkers



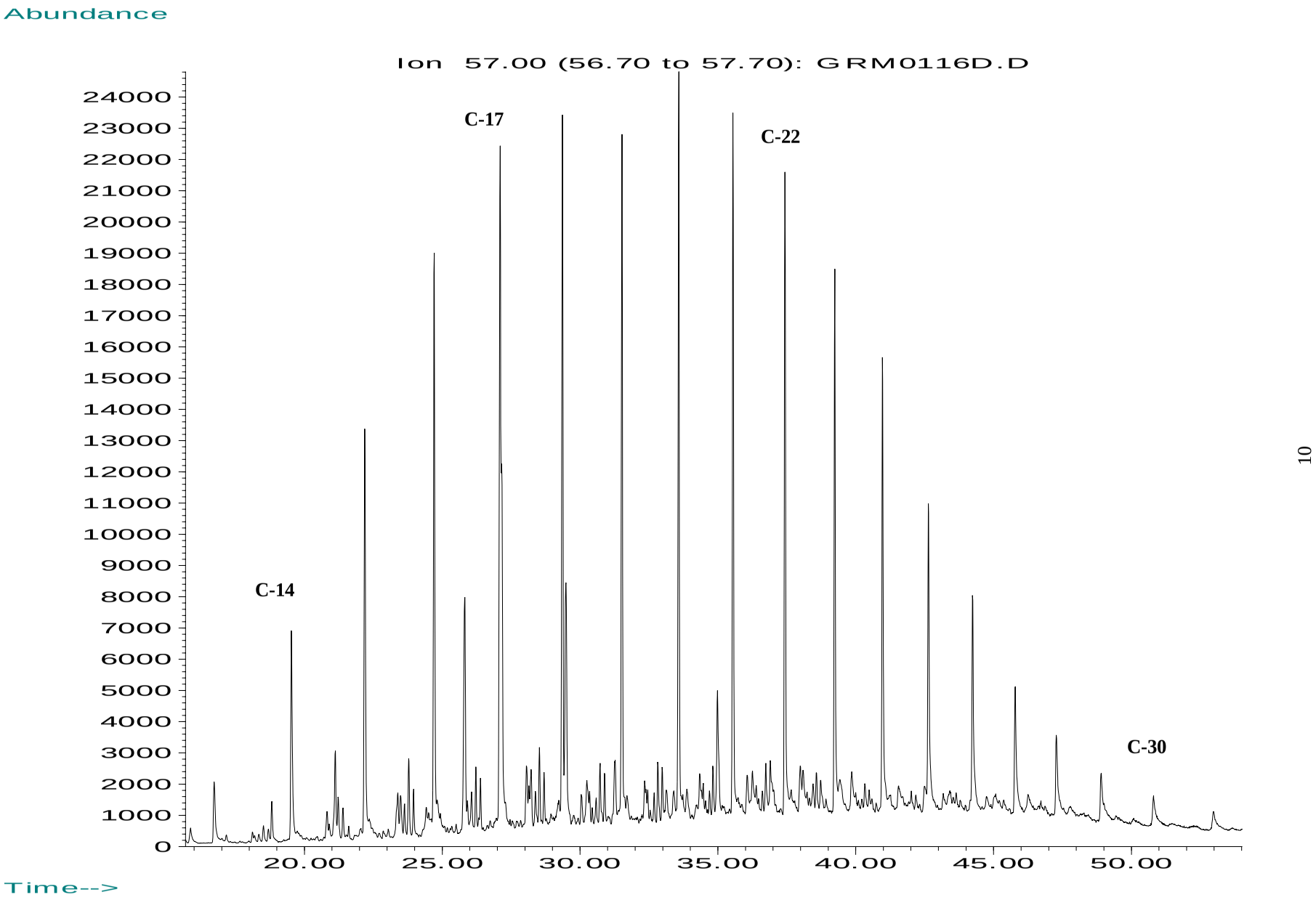
MC-252 Source Oil - Biomarkers



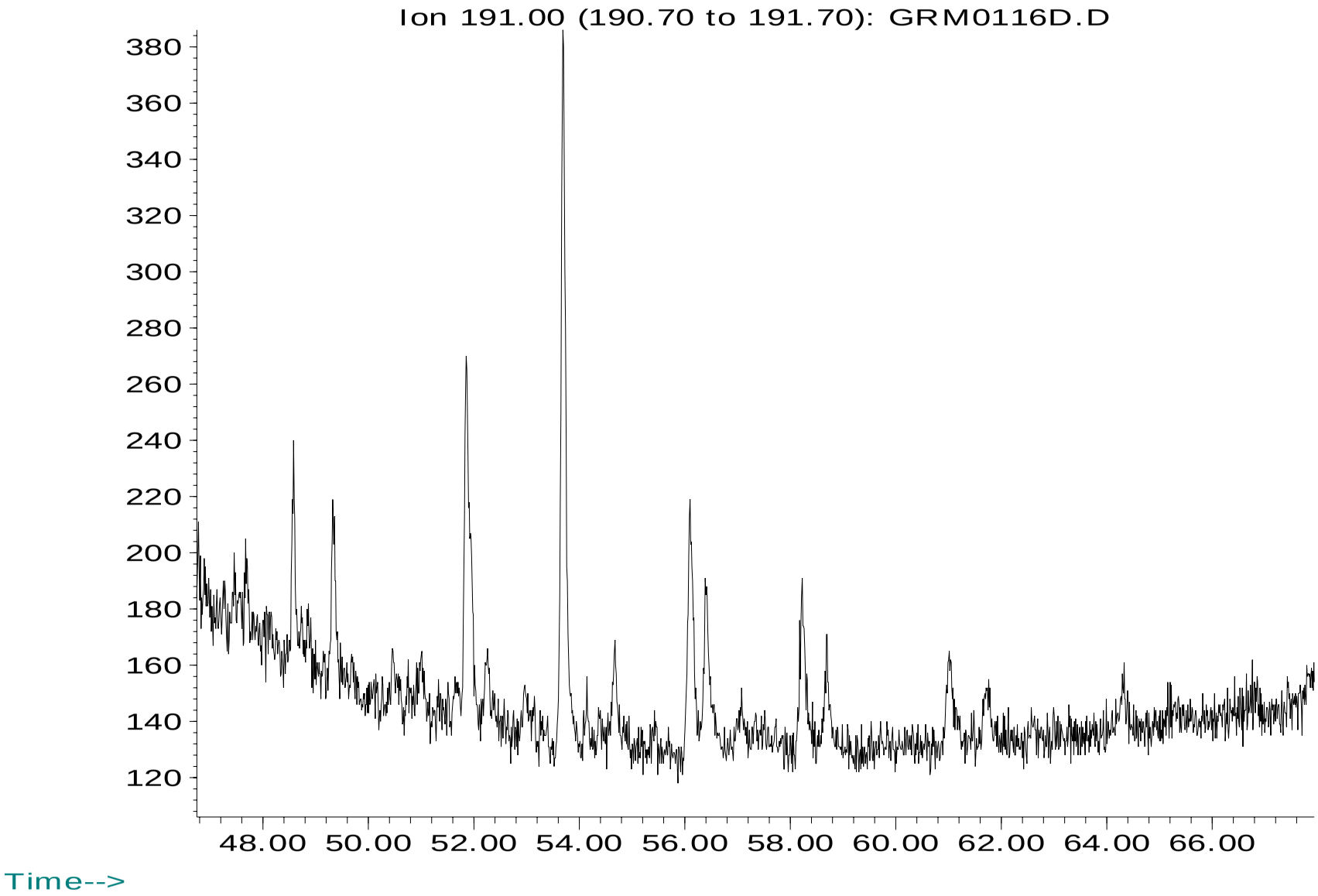
MC-252 Skimmer Oil - Total Ion Chromatogram



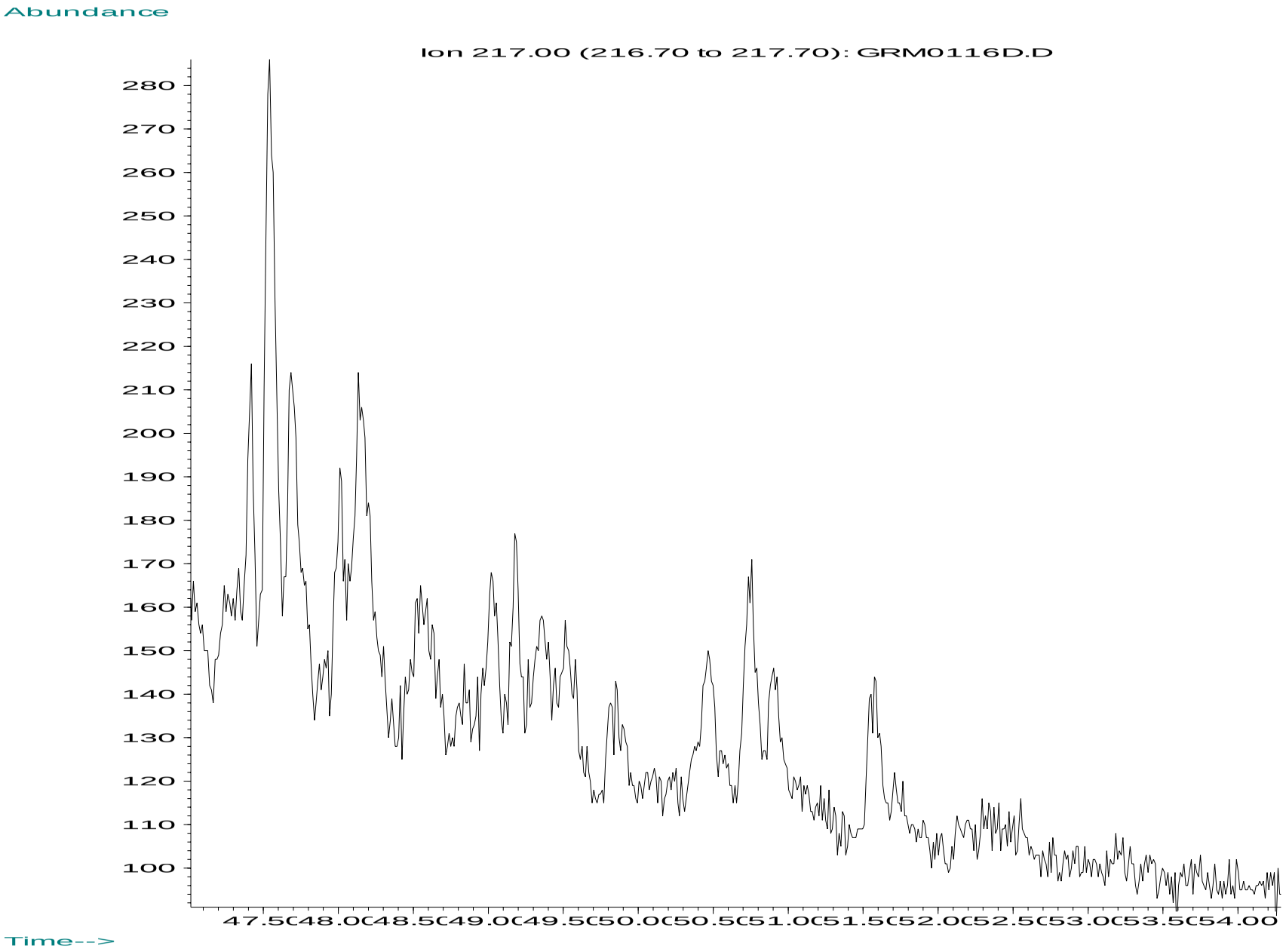
MC-252 Skimmer Oil - Aliphatic Components



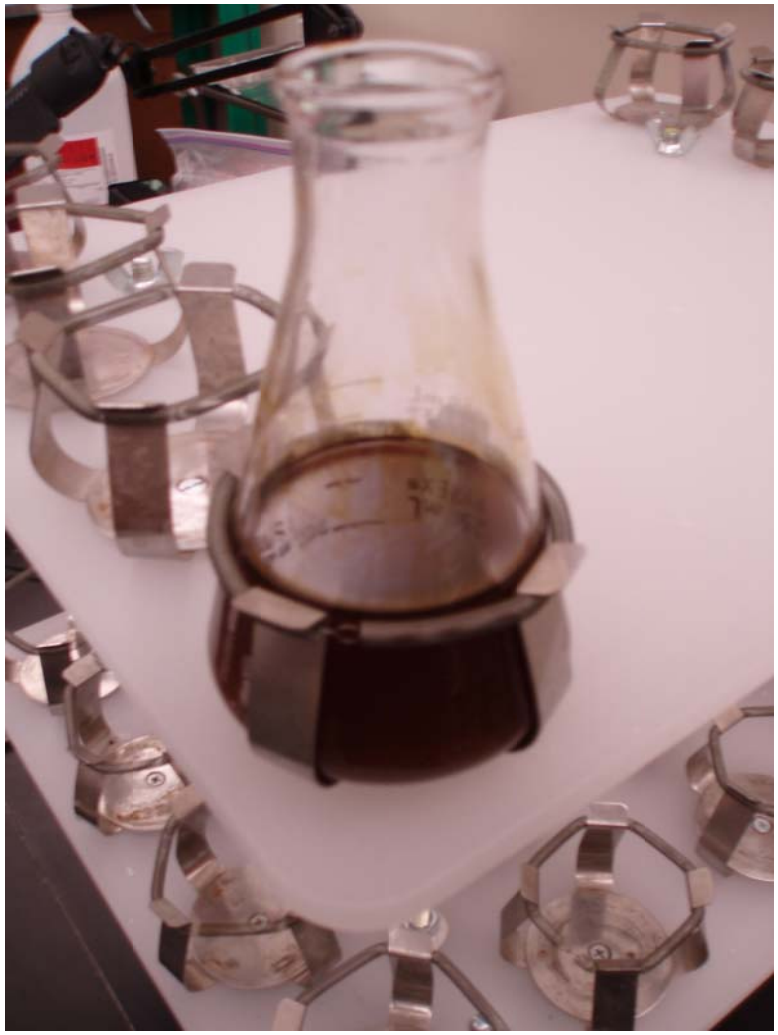
MC-252 Skimmer Oil - Biomarkers



MC-252 Skimmer Oil - Biomarkers



DISPERSED OIL



STATIC- 5 MINUTE