

Presence of Oleanane in Oil as Evidence of Contamination*

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Abstract

Biomarkers are normally utilized in petroleum geochemistry to identify the stratigraphic origin of crude oil and thermal maturity of associated source rock (Head, 2003). In petroleum geochemistry, biomarkers are most useful to understand generation and thermal maturity of petroleum (Hunt, 1996). Biomarkers are helpful for the reason that they keep most of the original skeleton of carbon which is the natural product and this resemblance of structure reveals further information concerning their origins and other compounds. Whereas proteins and carbohydrate structures are destroyed during diagenesis, biomarkers are not destroyed. The alteration of an enormous amount of the biochemical precursor compounds from existing creatures into biomarkers produces a vast set of compounds present in crude oils that contain different structures. Further, by extensive diversity of geological ages and conditions in which oil has been created, each crude oil reveals an exclusive biomarker (Wand et al., 2004). Amongst them, the efficient utilization of 18 α (H)-oleanane biomarker as age indicator for source deposition is of great significance. There is a long list of works that concludes Tertiary age of the source rock using high oleanane index in the oil (eg. Diasty and Moldowan, 2013; Cortes et al., 2013).

Presence of 18 α (H)-oleanane in oil is a well-documented indicator for terrestrial organic input (Wang et al., 2011; Ishiwatari et al., 2013; Alias et al, 2012). This is because 18 α (H)-oleanane is a land plant diagnostic biomarker derived from the angiosperms recorded in Cretaceous and younger sediments. Therefore, presence of this compound in crude oil sets an age constraint for the petroleum system. However, to understand the effectiveness of such a constraint, it is also necessary to study if it can be incorporated in the oil during migration or in the reservoir itself. Since the reservoirs in Cretaceous or younger horizons are deposited in angiosperm-dominated environments, it is possible that they are also rich in specific oleanane. When oil migrated through or trapped in these reservoirs, it is possible that the trapped oil is contaminated with the same oleanane. In this situation, presence of such oleanane neither indicates the Tertiary-Cretaceous age, nor indicates the terrestrial input ([Figure 1](#)). However to date, it has not been confirmed that oleanane in oil is migrated from the source rock. It has also not been tested if this biomarker can be incorporated into the reservoir.

Presence of oleanane in source rock indicates much information, but all applications regarding source rock become accurate if oleanane is truly found in source rock instead of reservoir rock. If oleanane contaminates oil in the reservoir, then the age inference for source rock becomes totally wrong and misleading. This present work is focused on testing if oleanane in the reservoir can contaminate trapped oil or not. The work is also extended using *Ligustrum Lucidium* as the source of oleanene to contaminate gasoline.

Method

The method that has been used for this study is carried out using two sources of oleanane: using a standard of 18 α (H)-oleanane and by using *Ligustrum Lucidium*. The purpose of both methods is to determine the reliability of 18 α (H)-Oleanene as an age indicator of source deposition. Analysis of samples is measured by using Gas Chromatography-Mass Spectrometry (GC-MS).

First the solubility test of 18 α (H)-oleanane in saline water is measured. 0.5 ml of 18 α (H)-oleanane was mixed with 2 ml of 3.5% Saline water. Standard 18 α (H)-oleanane is first identified in m/z191 fragmentogram of GC-MS using selected ion monitoring method (SIM). The detection and concentration of 18 α (H)-oleanane in saline water was also tested using m/z191 fragmentogram of GC-MS. Next, contamination of 18 α (H)-oleanane in gasoline is tested using the Benchtop Permeability System. This part of the research is carried out following core-flooding test. Sequence of the test is shown in [Figure 2](#).

Benchtop Permeability System (BPS-805) is a manually operated system aimed at simple liquid permeability tests. Synthetic core with measurable porosity and permeability was used to test the possibility of contamination. First, a mixture of saline water and oleanane was injected into the core. When the core was saturated with the mixture, gasoline was added into the core. This gasoline displaces saline water that is already present ([Figure 3](#)).

An accumulator was used for the gasoline. A syringe pump was used to displace the gasoline at a constant rate of 0.5 cc/min into the core. A beaker was placed under the sample collector for collecting the displaced gasoline. An overburden pressure of 1000 psi was applied around the core to confine the core inside the core holder using a hydraulic pump.

The core was saturated with the mixture of 18 α (H)-oleanane and saline water under vacuum. The amount of the supplied mixture was made in excess of the pore volume. The pore volume of the core was calculated from the measured porosity (20%) and bulk volume of core. The core was placed inside the core holder; gasoline was injected at room temperature.

Finally, solubility of test of oleanene using source *Ligustrum Lucidium* was carried out. The methodology of research by using *Ligustrum Lucidium* is shown in [Figure 4](#). 100 ml of gasoline was mixed with 15 gm *Ligustrum Lucidium* leaves. The presence of oleanene in gasoline has been tested in GC-MS using SCAN mode. Saline water of 3.5% salinity was treated with *Ligustrum Lucidium* leaves. 700 ml of saline water with 35 gm of *Ligustrum Lucidium* leaves. We placed this mixture in oven at 60° C for few days, then we took saline water and examined using GC-MS. [Figure 5](#) has been shown the procedure of this experiment.

In this research, the results have been analyzed with GC-MS. Analysis of the sample was carried out using a Hewlett-Packard GC-MS (HP6890 series GC with an HP19091S-433) (length 30 m, internal diameter 250 μ m, film thickness 0.25 μ m). The samples are taken in labeled small vials which are about 2 ml. Acquisition modes used in this experiment are SCAN and SIM. For SCAN mode, in oven the equilibration time is 3 minute and oven program is first set at 40° C then 6° C/minute to 200° C and then 3° C/ minute to 290° C. For SIM mode, in oven the equilibration time is 3 minute and oven program is first set at 40° C then 5° C/ minute to 325° C. The size of column is 30 m x 0.25 μ m x 0.25 μ m and the temperature for the analysis is 40° C-360° C.

The procedures for detection of the samples in SCAN and SIM mode are generally as follows. A 1 μ L sample was injected into the injection port set at 40° C with a split ratio of 50:1. The column was operated in a constant flow mode using 2 ml/min in SCAN mode and 1.1685 ml/min in SIM mode of helium as carrier gas. The column temperature was initially maintained at 40° C before increasing to 360° C. In SCAN mode the identification of compound was achieved based on the matching mass spectrum in the spectral library while in the SIM mode the identification of compound was achieved by comparing retention time with standard sample.

Results

The mixture of gasoline and 18 α (H)-oleanane which has been collected from core is discussed in this section. Here we also discuss the result of analysis of oleanane extracted from *Ligustrum Lucidum* in saline water and gasoline. Standard 18 α (H) oleanane is first run in GC-MS to note retention time for further use. In [Figure 6](#) it is shown that the standard of 18 α (H)-oleanane has been detected at retention time 50.64 with 70,000 ppm abundance. As shown in [Figure 7](#), at retention time 50.64 there is no peak of 18 α (H)-oleanane which means that 18 α (H)-oleanane is not soluble in saline water.

In [Figure 8](#), pure gasoline has also been analyzed in GC-MS using SIM to verify whether gasoline contains any contamination of 18 α (H)-oleanane. As shown in [Figure 8](#), at retention time of 50.64 there is no peak of 18 α (H)-oleanane which shows that 18 α (H)-oleanane is not present in gasoline. After core flooding, the fluid is analyzed in three sets. As shown in [Figure 9](#), [Figure 10](#), and [Figure 11](#) the occurrence of 18 α (H)-oleanane can be seen at retention time 50.64 with an abundance range of 300 to 800 ppm. Results suggest that if oleanane is present in the core, then it can be dissolved in gasoline. All three random samples of core flooded fluid show presence of oleanane ([Figure 12](#)).

In [Figure 13](#) we combine 18 α (H)-oleanane, gasoline and the core gasoline sample, which indicates that at retention time 50.64, standard of 18 α (H)-oleanane and core gasoline sample shows peaks, while gasoline does not have any peak at this retention time. The combined result of 18 α (H)-oleanane in saline water and gasoline are shown in [Table 1](#).

Although results suggest 18 α (H)-oleanane is not soluble in water, it can definitely remain with water in suspension and can also remain mixed with reservoir sediments. Standard oleanane mixed with saline water is first used to fill the pore spaces of the core. The core is then flooded with gasoline and results show gasoline is contaminated with 18 α (H)-oleanane. Results thus confirm both objectives of this study.

An attempt has also been made to test if 18 α (H)-oleanane can contaminate gasoline directly from the *Ligustrum Lucidum* source. However, we know that 18 α (H)-oleanane is generated from the source only after catagenesis. The present study thus focuses on checking whether oleanane

from *Ligustrum Lucidum* is soluble in gasoline or not. As we know (Rullkötter , 1994; Haven, 1988), oleanene can be transformed into oleanane, so in the case where oleanene is soluble in gasoline, we have more confirmation on the possibility of contamination directly from the source. Oleanene has been identified in SCAN mode of GC-MS, and is found insoluble in saline water.

This result is the same as 18 α (H)-oleanane in saline water. Both oleanene and 18 α (H)-oleanane are insoluble in water. The presence of 18 α (H)-oleanane is seen at retention time 56.44 ([Figure 14](#)). The combined result of oleanene in gasoline and saline water can be seen in [Table 2](#). Combined results of standard 18 α (H)-oleanane and its *Ligustrum Lucidum* source suggest that the presence of oleanane in oil does not necessarily come from the source rock. It can be incorporated in petroleum in the reservoir.

Conclusions

The conclusions drawn in view of the objective of this research are:

- Both 18 α (H)-oleanane and its source oleanene are insoluble in water.
- 18 α (H)-oleanane can be introduced in oil as contamination in the reservoir. Therefore, presence of such 18 α (H)-oleanane in oil neither indicate the Tertiary-Cretaceous age nor indicate the terrestrial input of the source rock.
- As of today, the presence of 18 α (H)-oleanane in oil is believed to be a source indicator of oil fields. However, our study reveals that the presence of oleanane may not be a good age indicator for the source of these oils.

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Cretaceous-Tertiary

Unknown Age

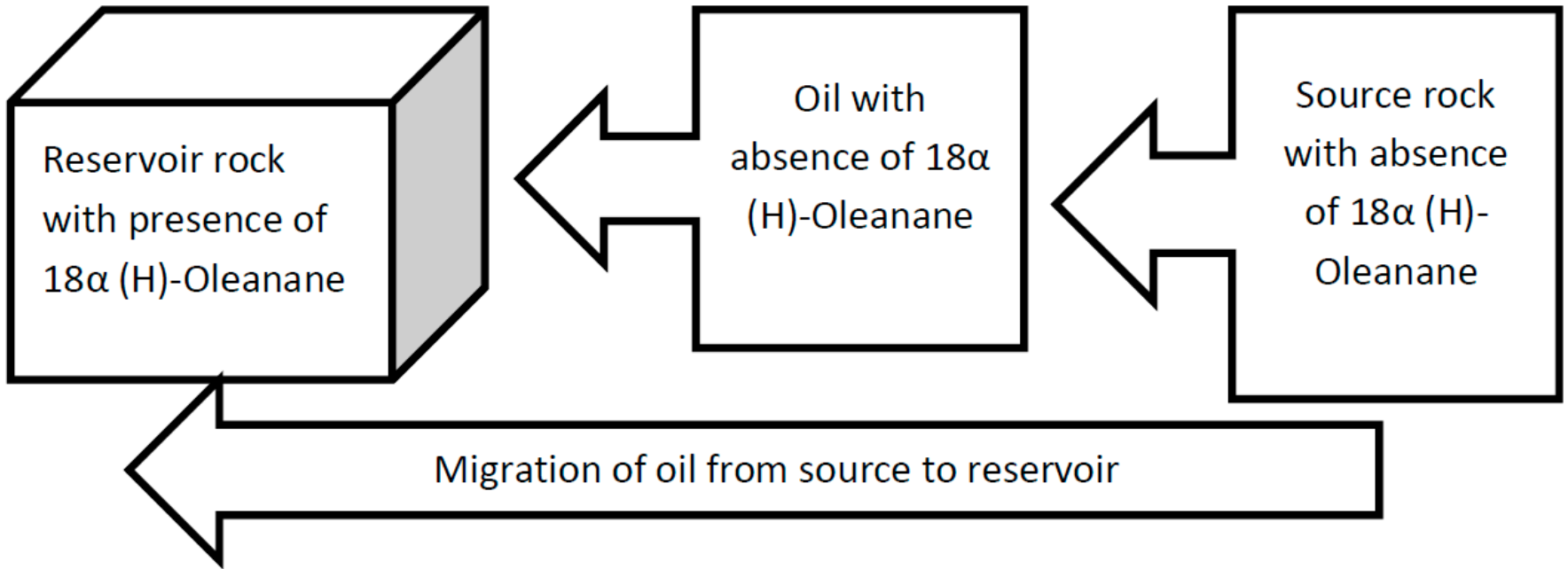


Figure 1. Migration of oil from source to reservoir.

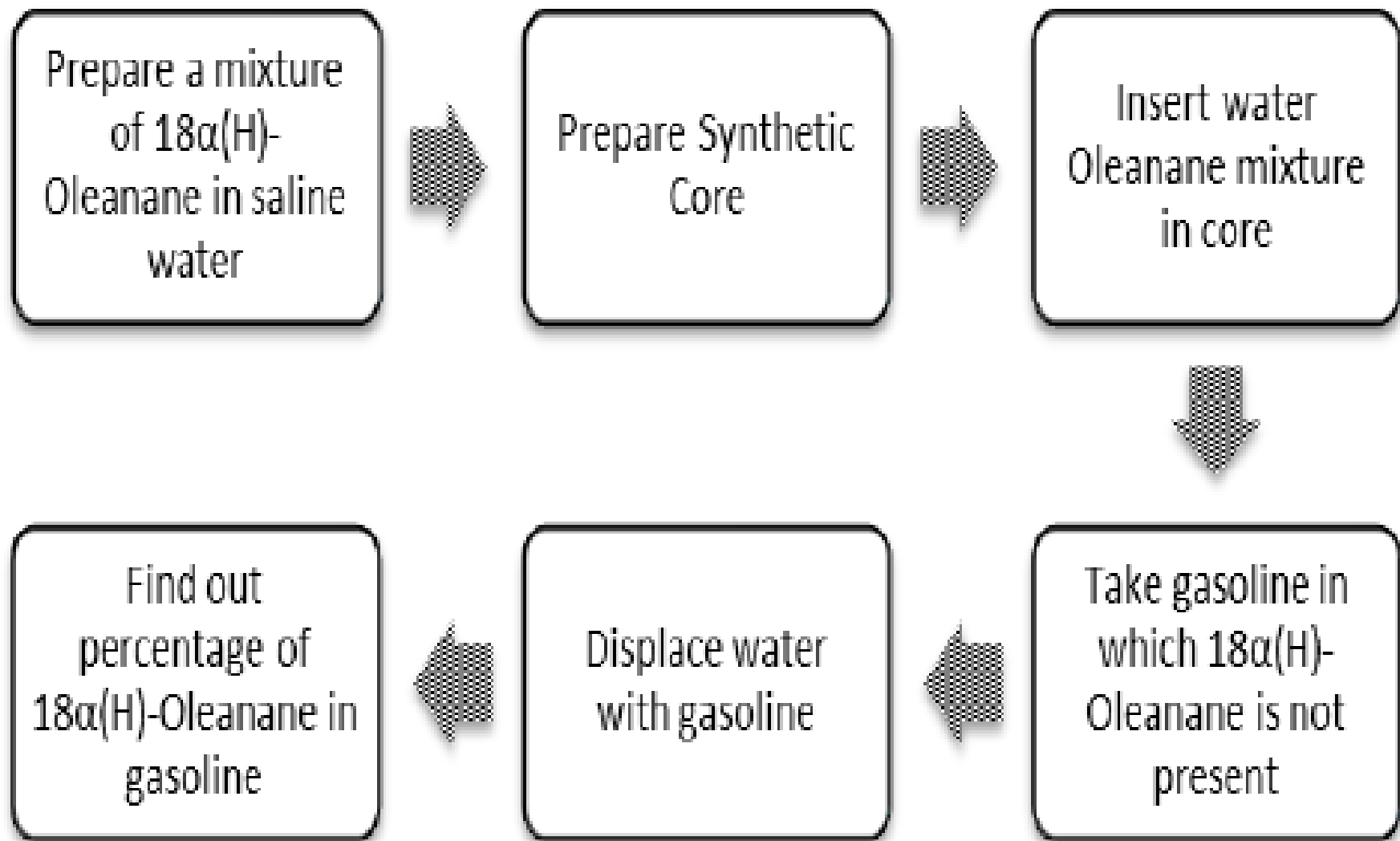


Figure 2. Shows the sequences in methodology for the experiment.

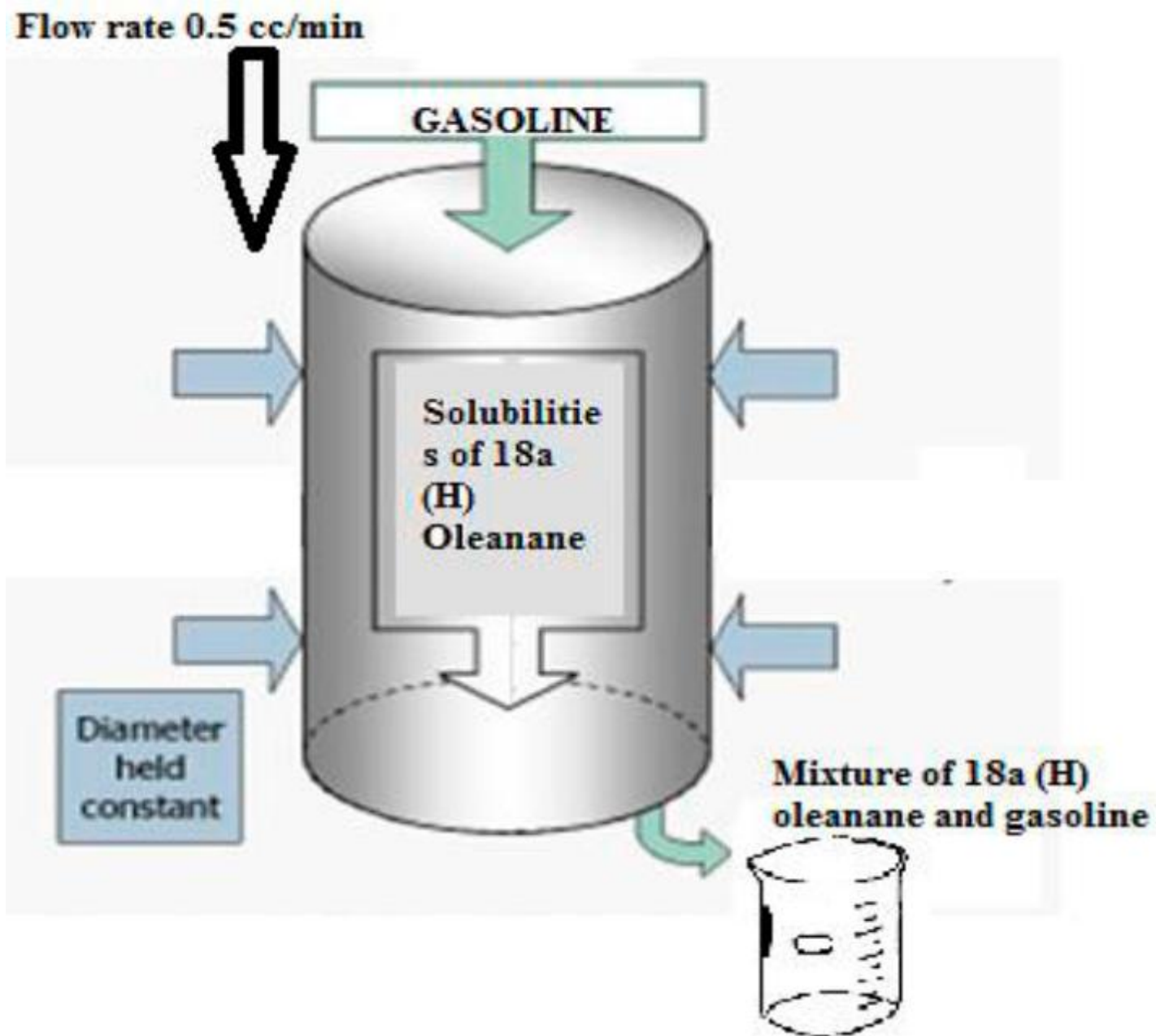


Figure 3. Gasoline displacement of 18 α (H)-oleanane.

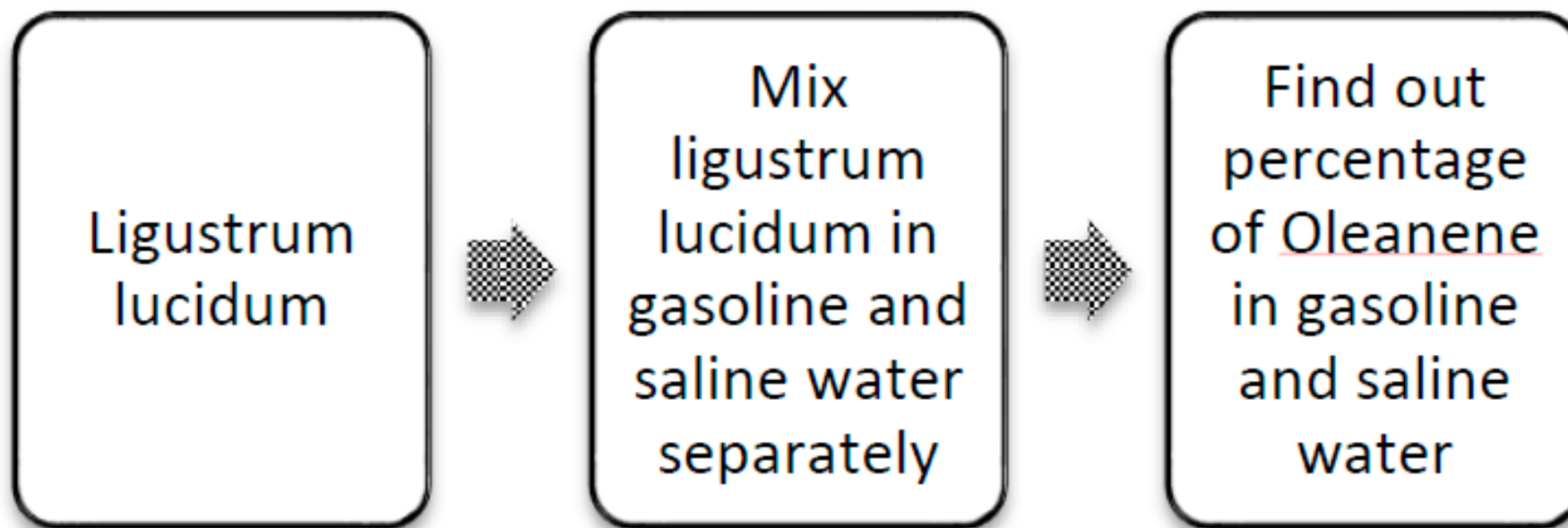


Figure 4. Diagram showing the sequences in methodology for the experiment.

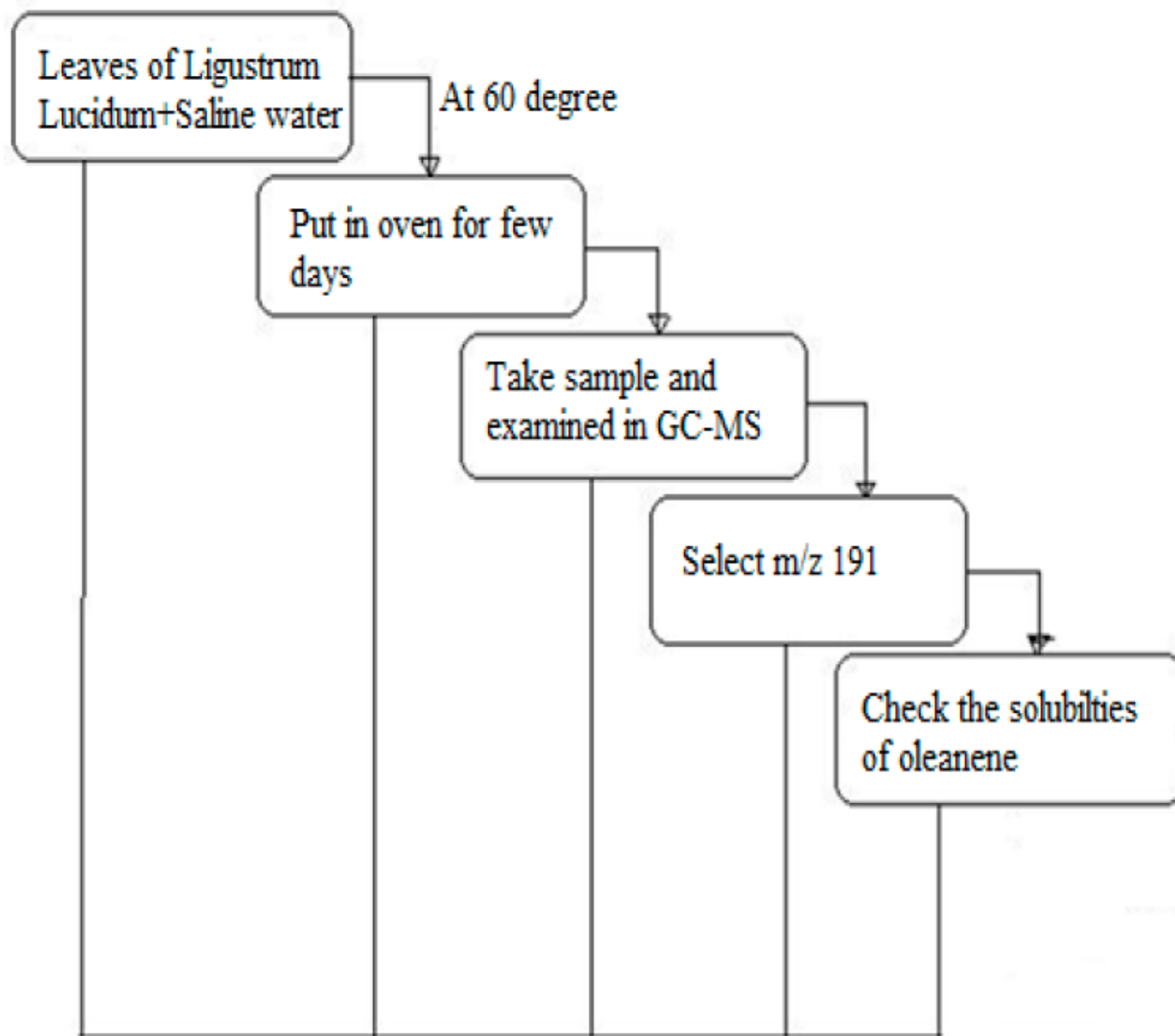


Figure 5. Detection procedure of oleanene in saline water.

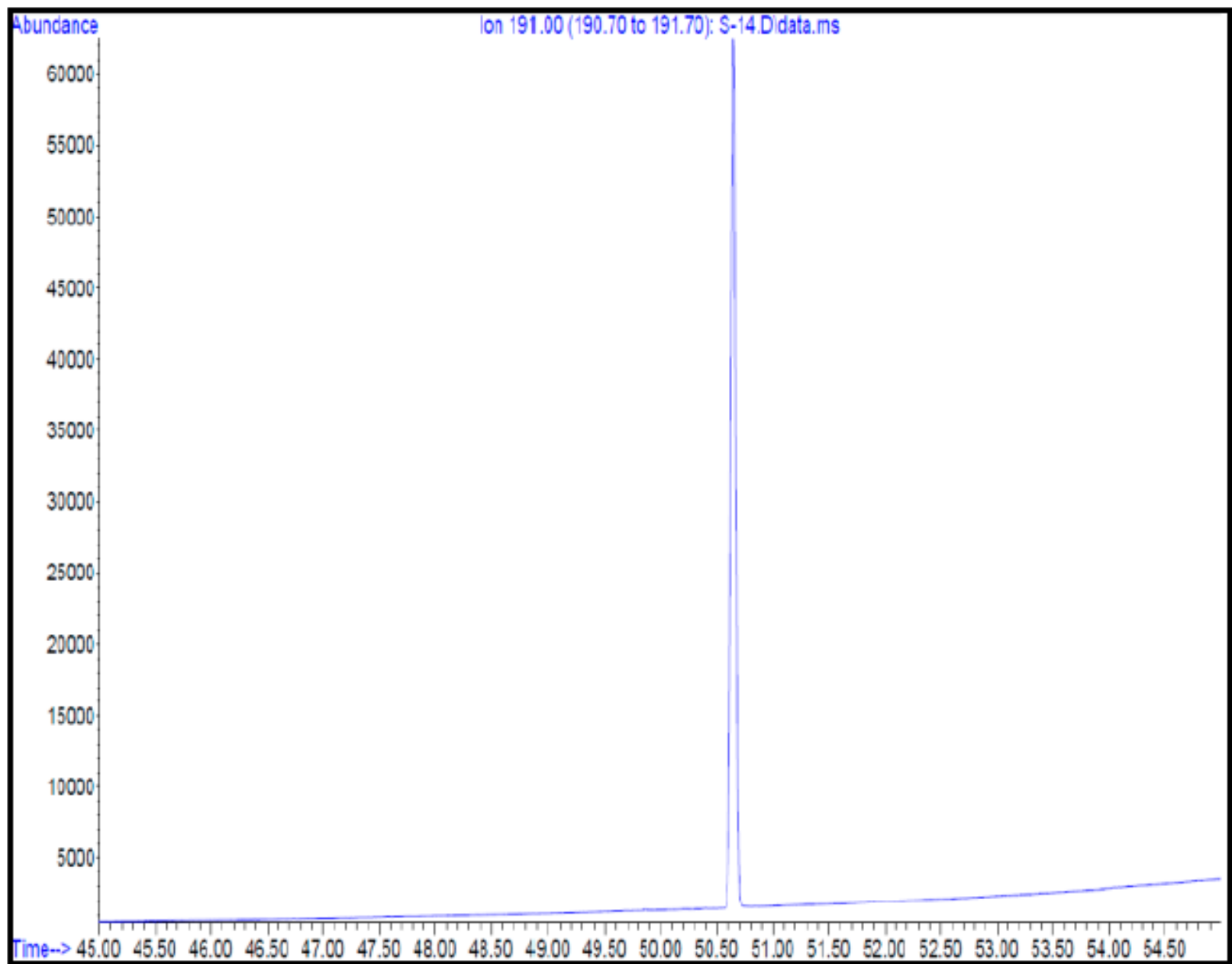


Figure 6. m/z 191 of $18\alpha(H)$ -oleanane.

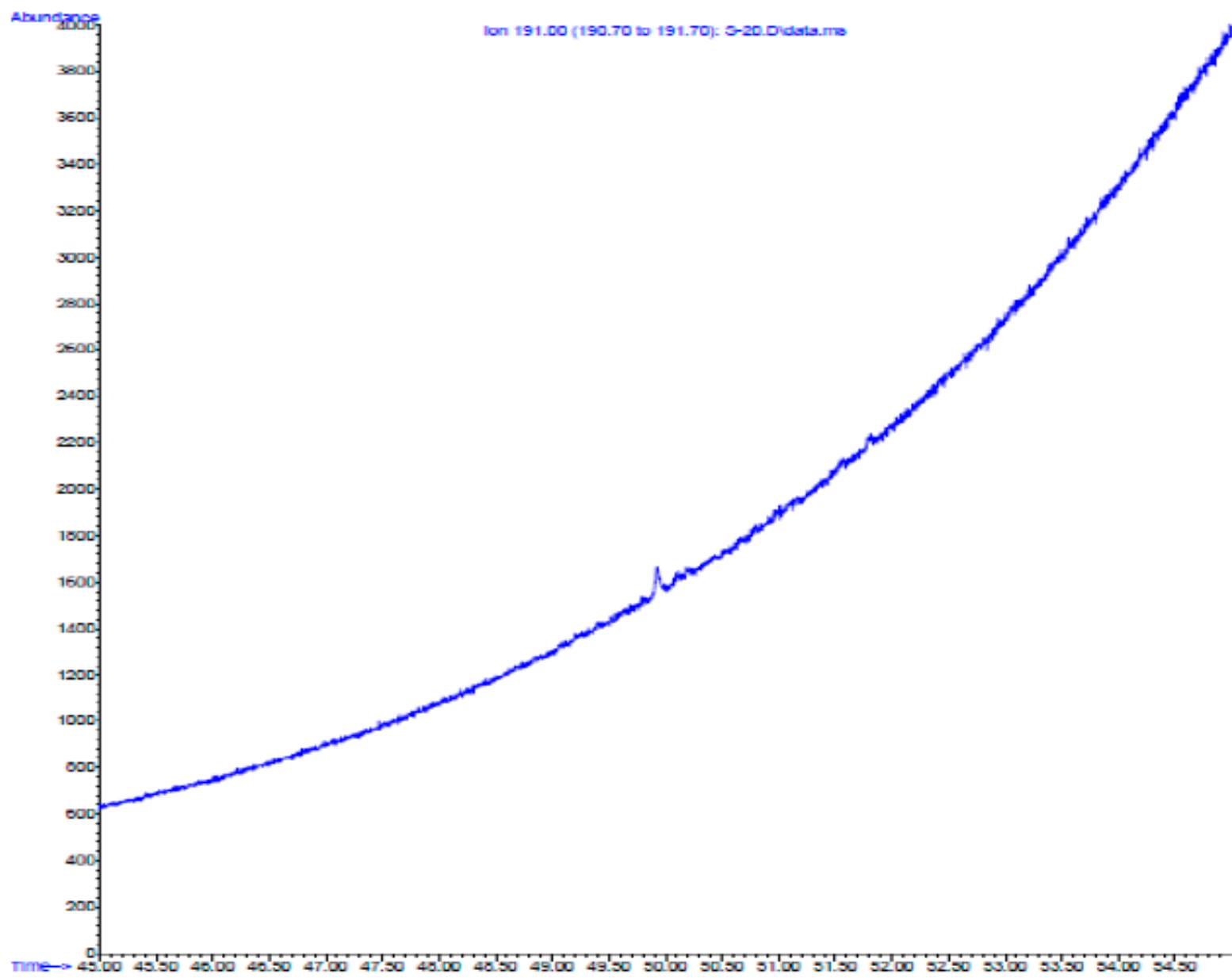


Figure 7. m/z 191 of 18 α (H)-oleanane in saline water.

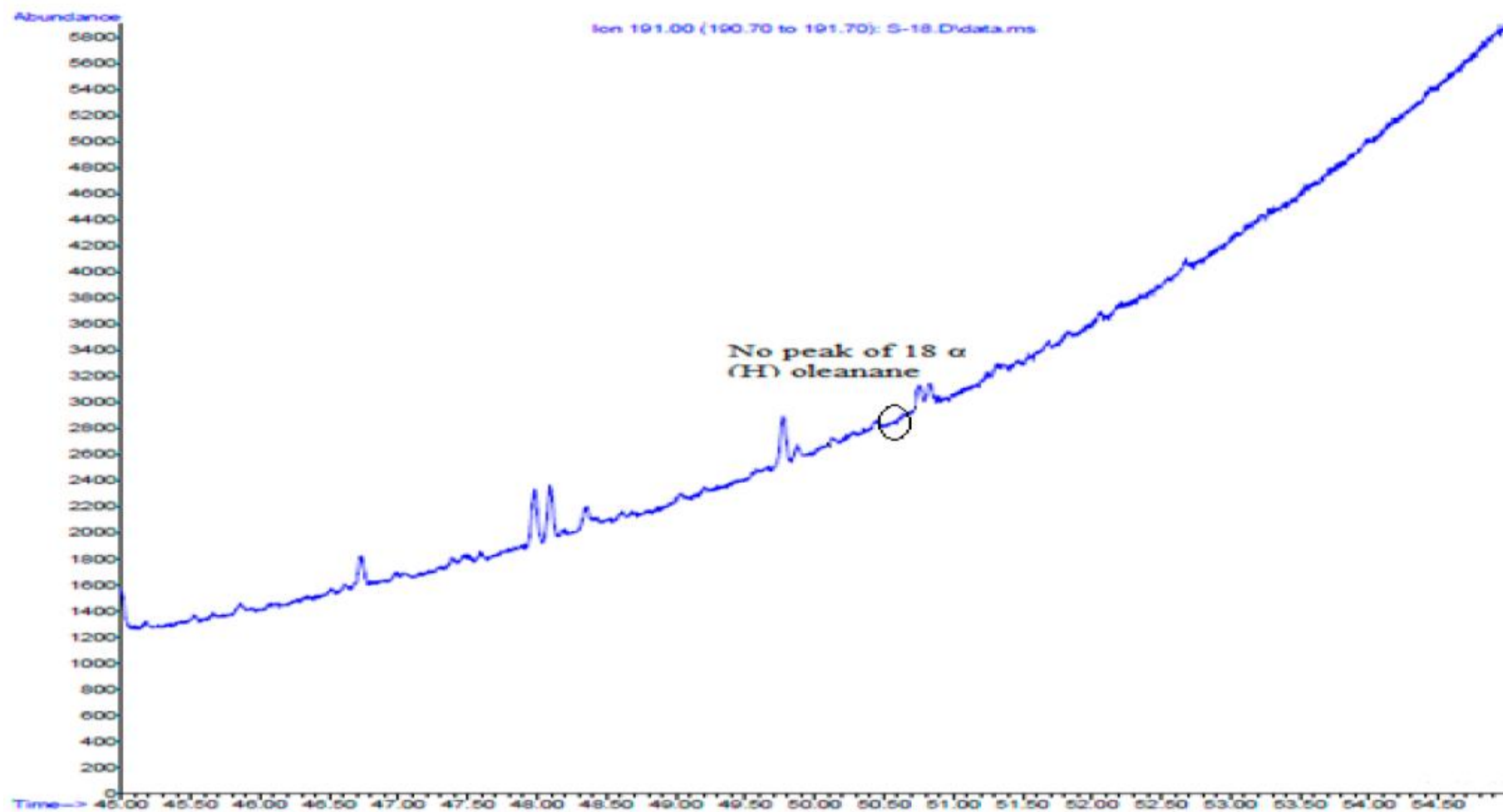


Figure 8. m/z 191 of Gasoline.

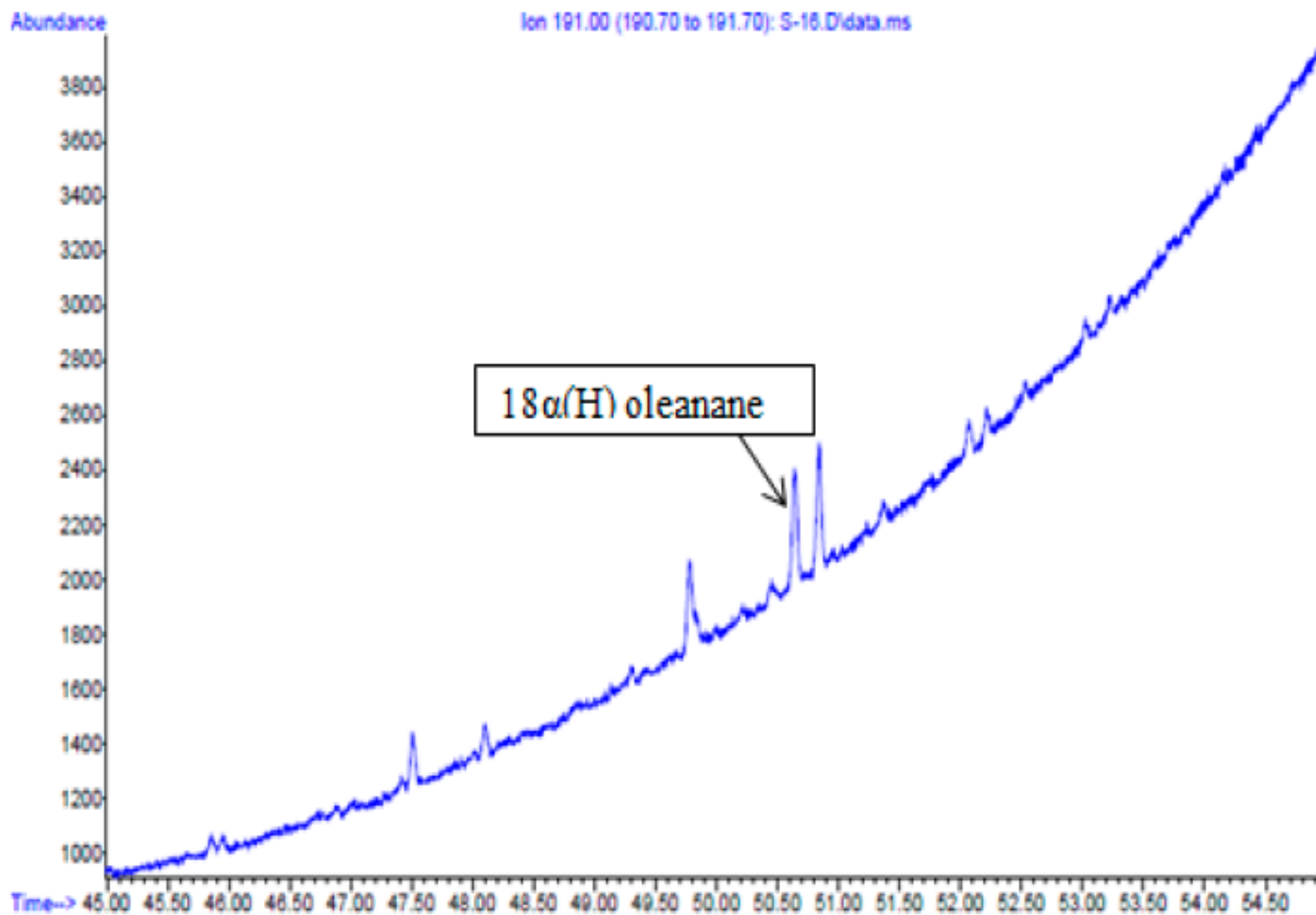


Figure 9. m/z 191 of core gasoline sample 1.

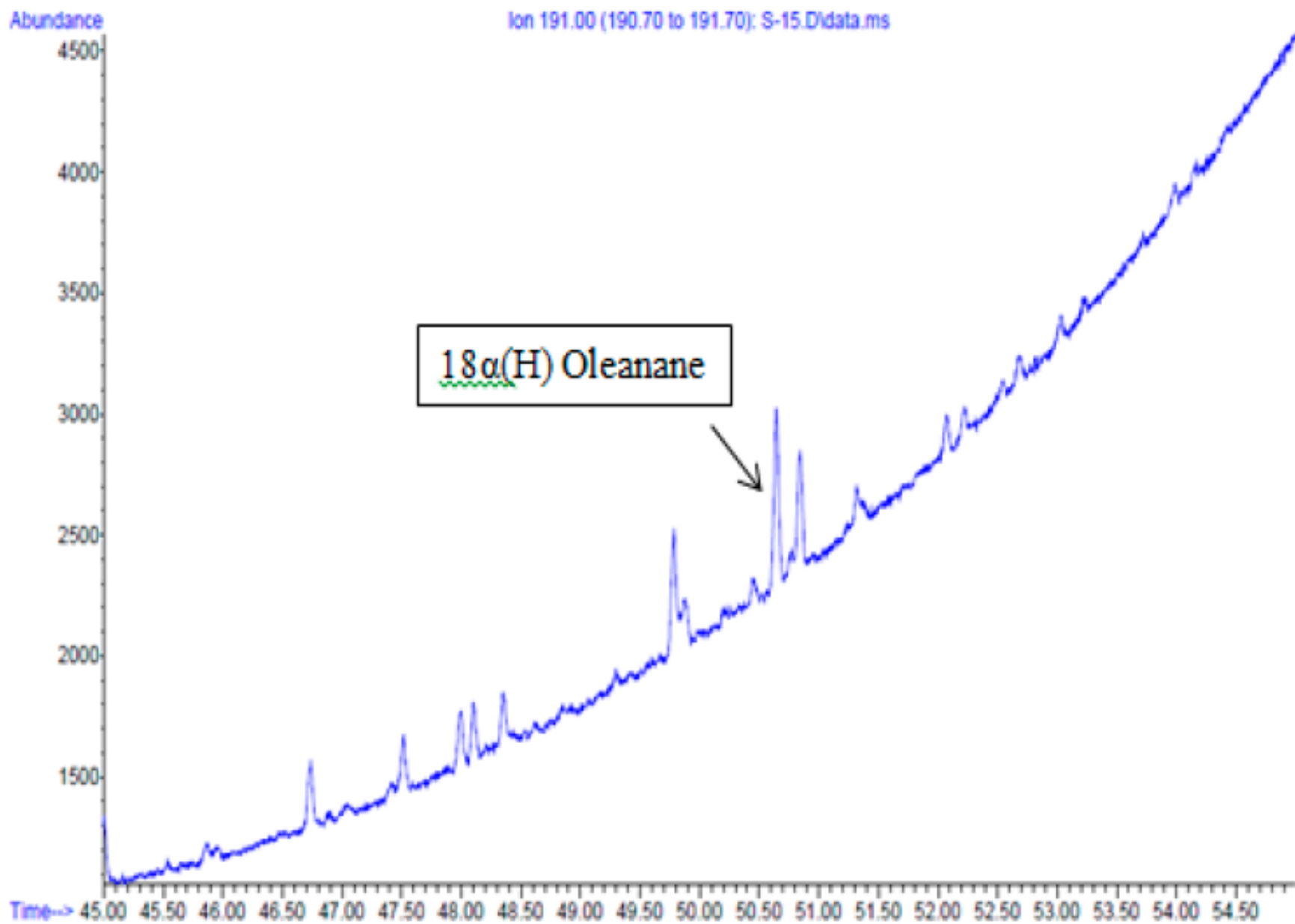


Figure 10. m/z 191 of core gasoline sample 2.

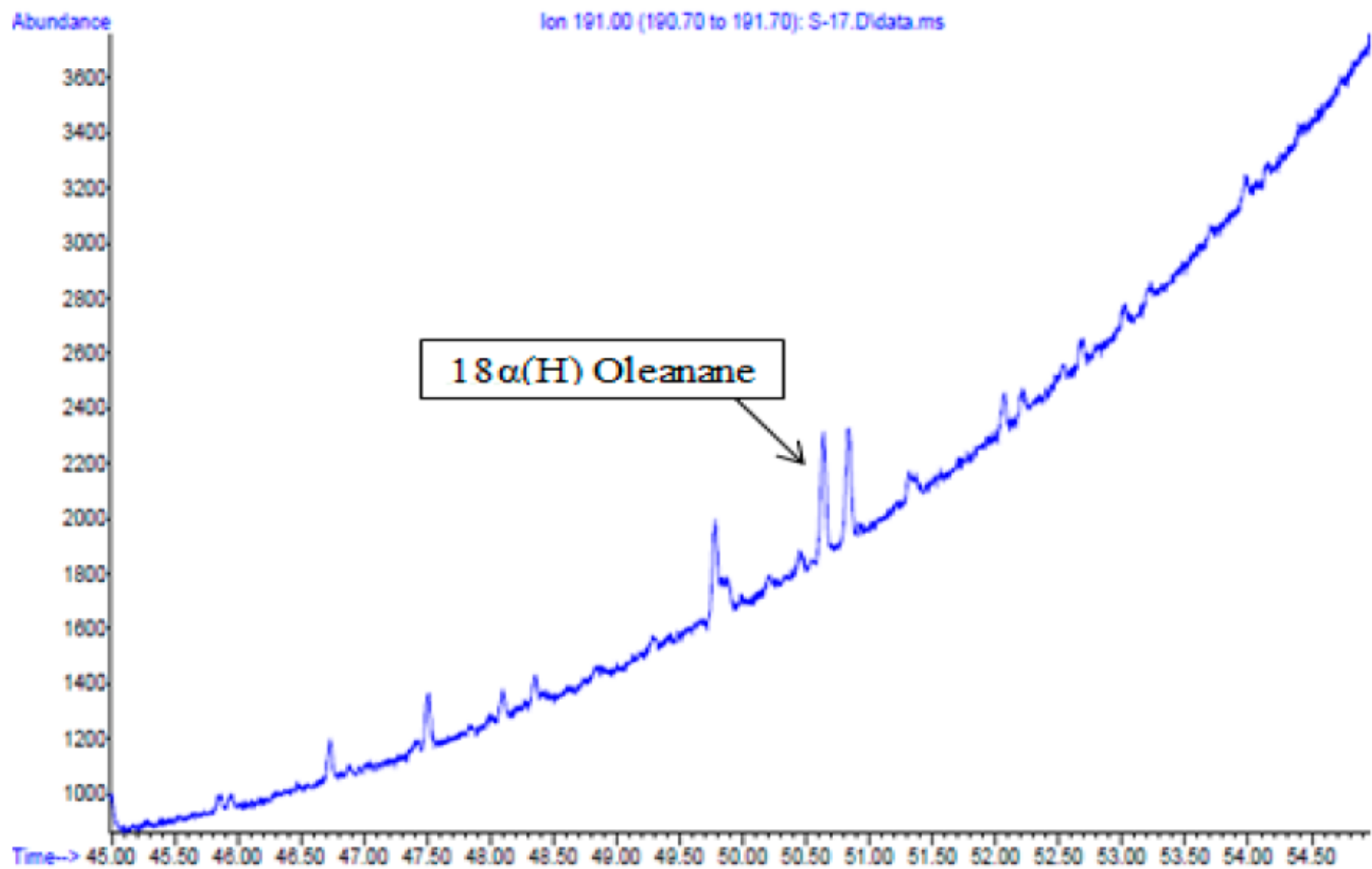


Figure 11. m/z 191 of core gasoline sample 3.

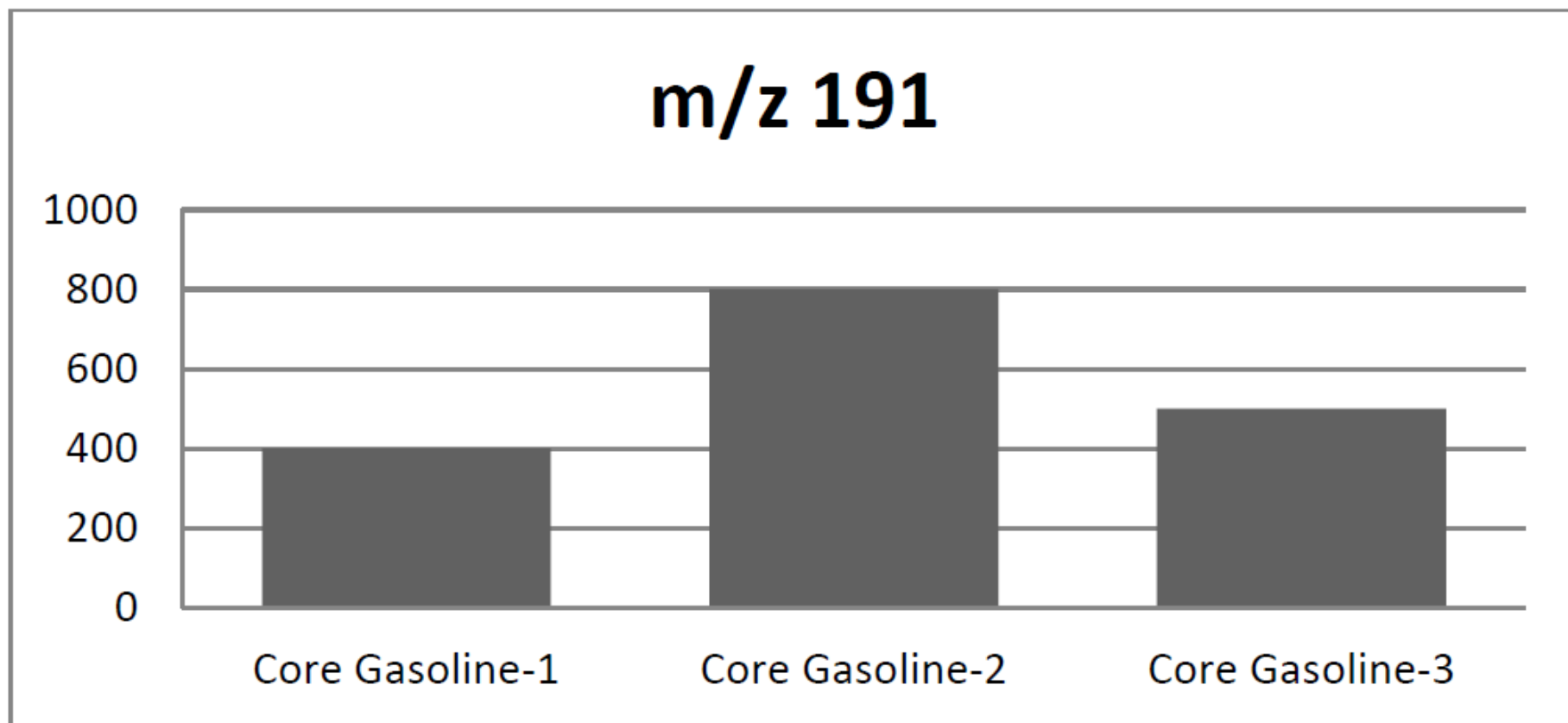


Figure 12. Solubilities of 18 α (H)-oleanane in core gasoline.

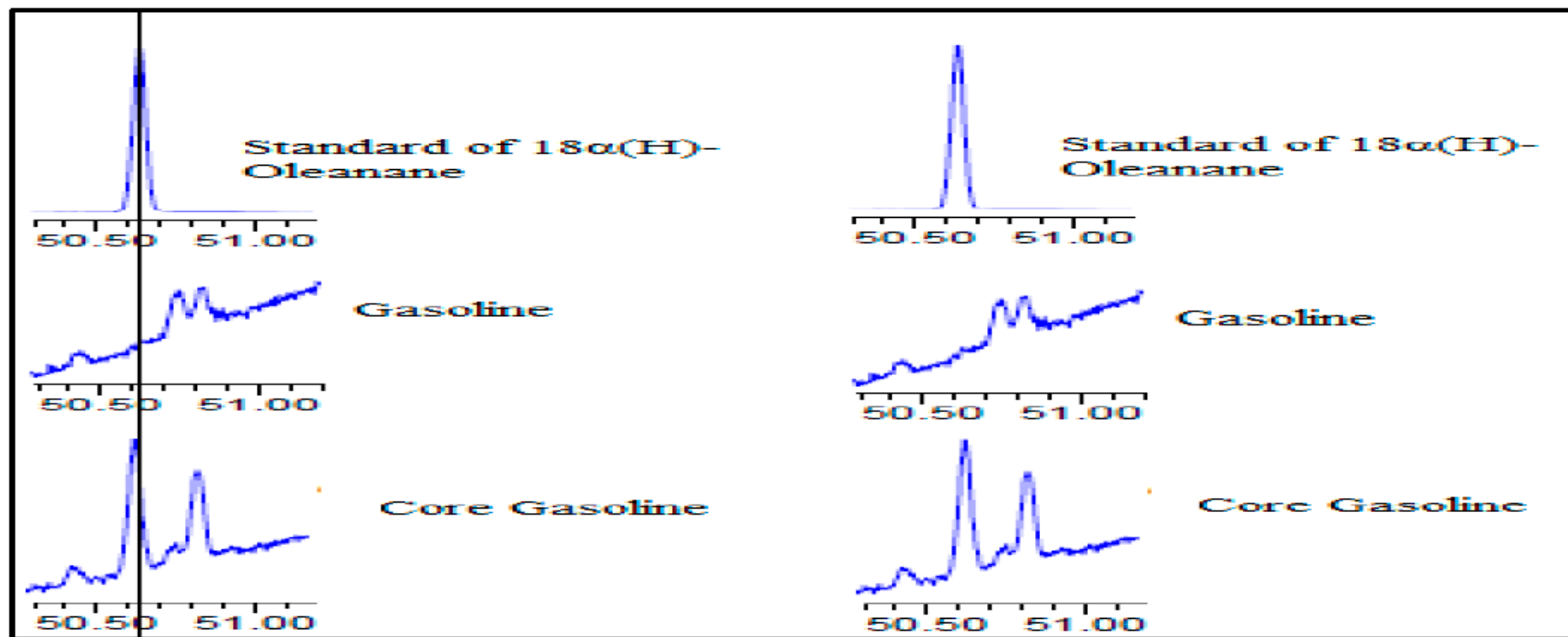


Figure 13. Comparison of 18α(H)-oleanane, gasoline and core gasoline at retention time 50.64.

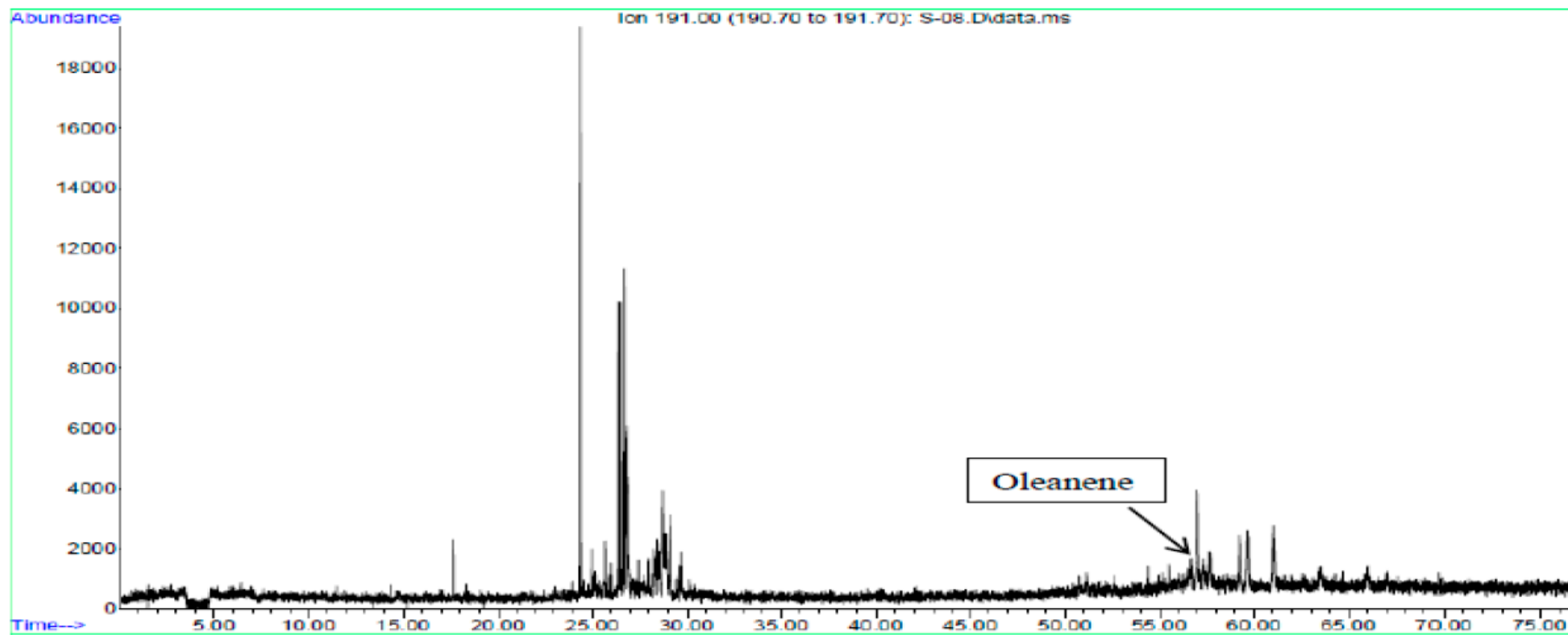


Figure 14. Ligustrum lucidum in gasoline.

Parameter	Standard of 18α(H)-Oleanane	18α(H)-Oleanane in Saline water	18α(H)-Oleanane in gasoline (Core Gasoline 2)
Abundance (m/z 191)	70000	No Abundance	800
Retention time (m/z 191)	50.64	No peak	50.64
Concentration unit (m/z 191)	100%	No Concentration	1.29 %

Table 1. 18 α (H)-oleanane in saline water and gasoline.

Abundance	Gasoline	Ligustrum Lucidum+Gasoline	Ligustrum Lucidum+Saline water
Oleanene	No abundance	700ppm	No Abundance

Table 2. Comparison of pure gasoline with Ligustrum Lucidum.