

High-Throughput Analysis Method for Hydrocarbons Profile using LDTD-HRMS system

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Introduction

Hydrocarbons C20 to C80 are usually analyzed by GC-MS systems using the Electron Ionization (EI) mode since LC-MS does not properly ionize this type of molecule. To increase the sample throughput, the Laser Diode Thermal Desorption (LDTD) technology shows promising results for the ionization and analysis of this molecular group. Luxon combined with a High-Resolution Mass Spectrometer (HRMS) is used to analyze hydrocarbon chains from commercial oil. The Luxon-HRMS is a rapid analysis approach in which molecules are thermally desorbed and then are channeled, using a carrier gas, to a corona discharge region for ionization prior to detection via a mass spectrometer. C20, C26, C40 and C50 straight-chain alkanes are used to validate the ionization process.

We propose to perform a quick hydrocarbon profile evaluation using Laser Diode Thermal Desorption High Resolution Mass Spectrometry (LDTD-HRMS).

Luxon Ionization Source

The Luxon Ion Source® (Figure 1) is the second-generation sample introduction and ionization source based on the LDTD® technology for mass spectrometry. Luxon Ion Source® uses Fiber-Coupled Laser Diode (Figure 2) to obtain unmatched thermal uniformity providing more precision, accuracy and speed. The process begins with dry samples which are rapidly evaporated using indirect heat. The thermally desorbed neutral molecules are carried into a corona discharge region. High efficiency protonation and strong resistance to ionic suppression characterize this type of ionization and is the result of the absence of solvent and mobile phase. This thermal desorption process yields high-intensity molecular ion signal in less than 1 second sample-to-sample and allows working with very small volumes.



Figure 1 - Luxon Ion Source®



Figure 2 - Schematic of the Luxon Ionization Source

Sample Preparation Method Standard

2 µL of Eicosane (1.3 mg/mL), Hexacosane (1.4 mg/mL), Tetracontane (0.65 mg/mL) and Pentacontane (0.15 mg/mL) in toluene are spotted into 96-LazWell™ plates and evaporated to complete dryness. Luxon-HRMS analysis is done after a complete evaporation.

Sample

2 µL of commercial oil is diluted in toluene at 1 ppm, spotted into 96-LazWell™ plates and evaporated to complete dryness. Luxon-HRMS analysis is done after a complete evaporation.

LDTD-HRMS Parameters

LDTD

Model: Phytronix, T-960

Carrier gas: 3 L/min (air)

Laser pattern: 3 second ramp to 45% power

MS/MS

Model: Q-Exactive™, Thermo Scientific

Ionization: APCI (Positive)

Scan mode: 200 to 1200 m/z

Results and Discussion

Hydrocarbon Ionization process

During the desorption process, a dehydrogenation occurs on the LazWell™ plate surface to generate a double bond. The alkene formed is transferred via the carrier gas and ionized by the corona discharge. Figure 3 shows the dehydrogenation process.

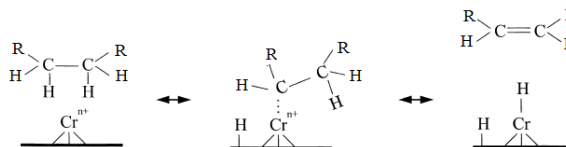


Figure 3 – Dehydrogenation process standard analysis

Five successive wells are desorbed in the same MS file (Blank, C20, C26, C40 and C50). The mass spectrum and exact mass extraction are acquired. Results are reported in Table 1 and in Figure 4.

Table 1 – Exact mass detected of standard solution

Standard	Theoretical Mass (M-2+H)	Experimental results (M-2+H)
C20	281.320825	281.32049
C26	365.414725	365.41466
C40	561.633825	561.63382
C50	701.790325	701.79015

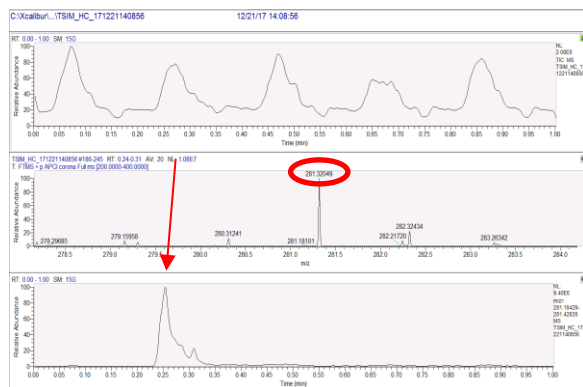


Figure 4 – C20 standard desorption

Oil sample profile analysis

Commercial oil is diluted with toluene at 1 ppm and analyzed by Luxon-HRMS. The **Figure 5** shows the exact mass profile. The analysis of the High-Resolution mass spectrum highlighted two different profile distributions.

To evaluate the profile structures, the exact mass is extracted, and peak areas are reported. The major profile (Profile 1) is composed of the highest hydrocarbon peaks of the same unsaturation number (6) from all the sub-profile distributions. Profile 2 shows the unsaturation distribution of molecules having 27 carbon atoms. A similar unsaturation distribution is observed for all alkenes (C20, C21, C22, ...).

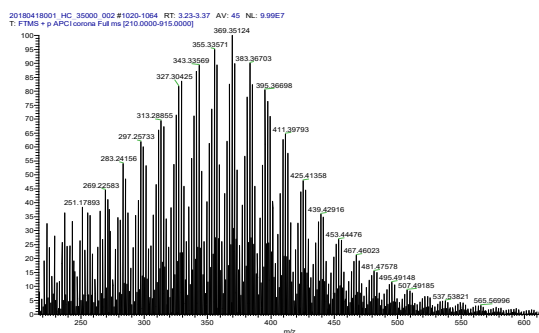


Figure 5 – Commercial oil exact mass profile

Profile 1 - Hydrocarbon distribution of 6 degrees of unsaturation

Using the accurate mass spectra acquired and an elemental composition tool, molecules having an unsaturation degree of 6 are reported. **Figure 6** shows the peak area profile of this group. **Table 2** shows the empirical formula and exact mass.

Table 2 – Results table of Profile 1

	Formula		Exact Mass	Peak area
	C	H	M - 2 + H	X 10 ⁶
C17	17	25	229.195625	178
C18	18	27	243.211275	264
C19	19	29	257.226925	291
C20	20	31	271.242575	328
C21	21	33	285.258225	399
C22	22	35	299.273875	509
C23	23	37	313.289525	598
C24	24	39	327.305175	727
C25	25	41	341.320825	779
C26	26	43	355.336475	836
C27	27	45	369.352125	911
C28	28	47	383.367775	789
C29	29	49	397.383425	691

C30	30	51	411.399075	569
C31	31	53	425.414725	416
C32	32	55	439.430375	312
C33	33	57	453.446025	244
C34	34	59	467.461675	183
C35	35	61	481.477325	134
C36	36	63	495.492975	101
C37	37	65	509.508625	75
C38	38	67	523.524275	59
C39	39	69	537.539925	43

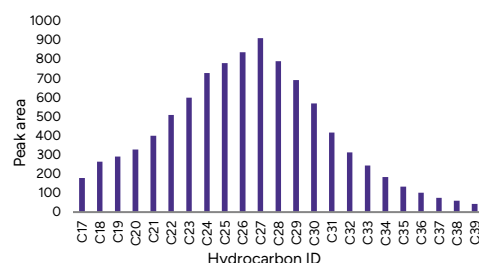


Figure 6 – Peak distribution of Profile 1

Profile 2 - Unsaturation profile

Using the accurate mass detected and the elemental composition tool, molecules having 27 carbons with different unsaturation degrees are reported. **Figure 7** shows the peak area profile of this group. **Table 3** shows the empirical formula and calculated exact mass.

Table 3 – Results table of Profile 2

	Formula		Exact Mass	Peak area
	C	H	M - 2 + H	X 10 ⁶
Unsat. 15	27	27	351.211275	17
Unsat. 14	27	29	353.226925	39
Unsat. 13	27	31	355.242575	40
Unsat. 12	27	33	357.258225	73
Unsat. 11	27	35	359.273875	154
Unsat. 10	27	37	361.289525	229
Unsat. 9	27	39	363.305175	369
Unsat. 8	27	41	365.320825	541
Unsat. 7	27	43	367.336475	727
Unsat. 6	27	45	369.352125	911
Unsat. 5	27	47	371.367775	784
Unsat. 4	27	49	373.383425	455
Unsat. 3	27	51	375.399075	16
Unsat. 2	27	53	377.414725	5
Unsat. 1	27	55	379.430375	2

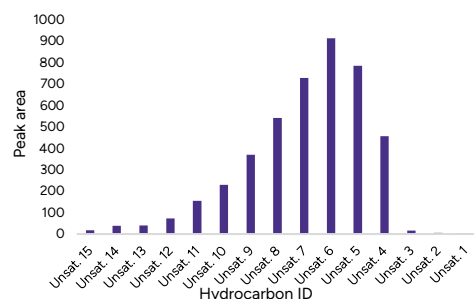


Figure 7 – Peak distribution of Profile 2

Conclusion

Luxon Ion Source combined with a Q-Exactive system allows ultra-fast (**8 seconds per sample**) analysis of hydrocarbon (C20 to C80) in different petroleum samples.