

Analysis of Light Crude Oil Using Gas Chromatography—High Resolution Time-of-Flight Mass Spectrometry

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1. Introduction

Crude oil is a very complex mixture of organic compounds including aliphatic, aromatic and heterocyclic compounds. Analysis of oil is complicated not only by the enormous number of multi-functional components, but also by the large variation in compound concentrations.^{1,2} High performance time-of-flight mass spectrometry (TOFMS) is an ideal instrumental technique for the analysis of complex matrices such as crude oil. Fast acquisition rates, non-skewed data, broad mass analysis ranges and comprehensive detection using TOFMS greatly facilitate characterization of petroleum samples. Classification of oil components (e.g., saturates, aromatics, etc.) is simplified with the instrument's high resolving power and advanced software features. Sulfur and nitrogen containing species that cause emission problems during combustion are of particular interest. These heteroatomic species can poison metal catalysts even at very low concentrations. Identification and robust characterization of these low-level materials can be very difficult because of the matrix effects associated with oil samples; however, high performance TOFMS with resolving powers up to 50,000 can help alleviate this problem. In this study, various light crude oil samples were analyzed for aromatic, polycyclic aromatic hydrocarbon and heterocyclic compounds. These compounds were characterized using a combination of elemental formula determinations with exact mass calculations and spectral library similarity searches. High performance TOFMS provided a comprehensive profile of samples and facilitated the search for these compounds in light crude oil.

2. Experimental Conditions

Samples

Crude oil can be classified according to extraction location, density (light or heavy) and sulfur content (sweet or sour). Samples analyzed in this study included Arabian, Nigerian, Basra and South Louisiana Light crude oil standards. Standards (100 mg/mL in hexane) were diluted (500 μL \rightarrow 1500 μL) and placed in MS vials for analysis.

Experimental

A LECO Pegasus[®] GC-HRT high resolution mass spectrometer was used for these analyses (Figure 1). It was equipped with an Agilent Technologies 7890A GC System and 7693 Autosampler.



Figure 1. LECO Pegasus GC-HRT with Folded Flight Path (FFP) Technology.

At the heart of the Pegasus GC-HRT is its state of the art Folded Flight Path[™] (FFP[™]) mass analyzer (Figure 2) which consists of a set of periodic lenses sandwiched between two gridless mirrors. Ions are introduced into the mass analyzer via orthogonal acceleration (A), reflected through the analyzer and returned to a detector (D) located near the ion source. An onboard data acquisition system Kinetic Algorithmic Data Acquisition System (KADAS) allows for ultra-fast capture of high resolution spectra.

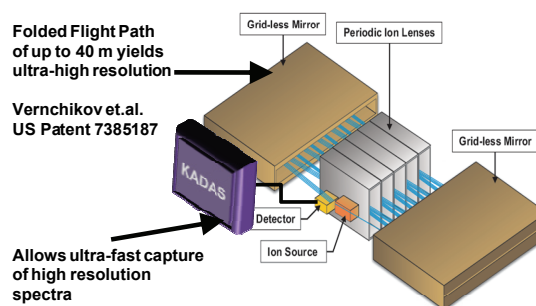


Figure 2. Pegasus GC-HRT FFP Mass Analyzer.

The Pegasus GC-HRT can be operated in three modes (Figure 3): Nominal Mode ($R = 1000$ at $m/z = 219$ FWHM), High Resolution Mode ($R = 25,000$ at $m/z = 218.985080$) and Ultra-High Resolution Mode ($R = 50,000$ at $m/z = 218.985080$). GC and MS instrument parameters are listed below.

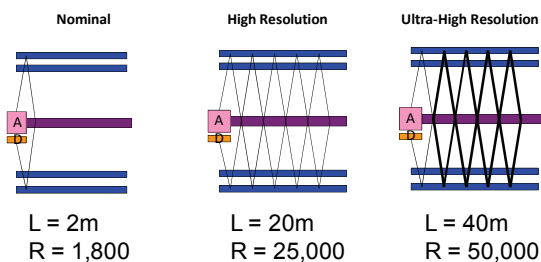


Figure 3. LECO Pegasus GC-HRT Operating Modes.

GC

Instrument: Agilent 7890A
 Column Type: Restek Rxi-5 MS (30 m x 0.25 mm x 0.25 μ m)
 Injection: Split 25:1, 1 μ L
 Inj. Temp.: 300°C
 Oven: 40°C (1 min) to 260°C at 2.5°C/min to 320°C at 10°C/min (5 min)
 Carrier Gas: He, 1.00 mL/min constant flow

MS

Spectrometer: LECO Pegasus GC-HRT
 Ion Source: LECO EI
 Polarity: Positive (70 eV)
 Flight Path: High Resolution Mode (R=25,000) and Ultra-High Resolution Mode (R=50,000)
 Acquisition: 6 spectra/second
 m/z Range: 50–580 High Resolution Mode, 80–300 Ultra-High Resolution Mode
 Calibration: PFTBA

3. Results

The desired instrument characteristics for resolution of components and robust elemental composition assignments of compounds in petroleum include high mass resolving power and mass accuracy values below 1 ppm.³ LECO's Pegasus GC-HRT meets these requirements but also provides a comprehensive sample profile coupled with high quality spectral data in a single acquisition.

High resolution mode (L = 20m, R = 25,000) analysis of crude light oil samples (South Louisiana, Nigerian, Basra and Arabian) resulted in the analytical ion chromatograms (AICs) shown in Figure 4. This report will focus on the Arabian and Nigerian oil samples. Paraffins (C₉ to C₂₈) in the Arabian light sample are shown in Figure 5. An extracted ion chromatogram (XIC) with some substituted benzene molecules (C₈H₁₀, C₉H₁₂, C₁₀H₁₄, C₁₁H₁₆, C₁₂H₁₈; RBDE = 4) in this sample is shown in Figure 6.

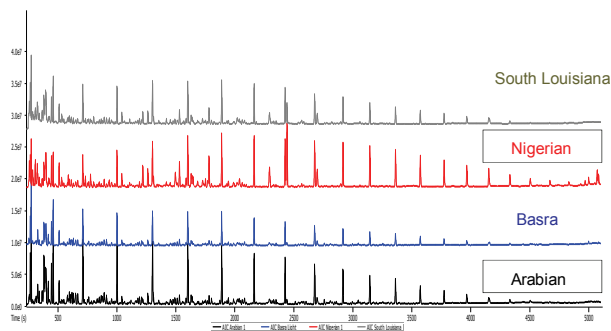


Figure 4. AICs for South Louisiana, Nigerian, Basra and Arabian light crude oil.

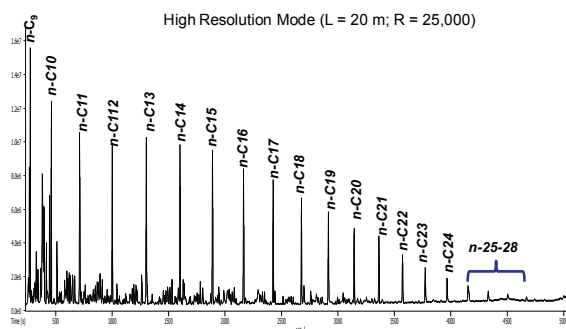


Figure 5. AIC showing paraffins in Arabian light crude oil.

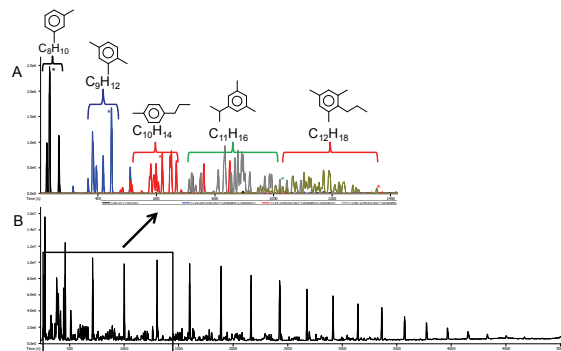


Figure 6. AIC (B) and XIC (A) showing substituted benzene molecules in Arabian light crude oil.

Representative benzene compounds in the sample included: *m*-xylene, 1,2,4-trimethylbenzene, *p*-propyltoluene, 1,3-dimethyl-5-propylbenzene and 1,3,5-trimethyl-2-propylbenzene. Mass spectral data for *m*-xylene and 1,2,4-trimethylbenzene are shown in Figures 7 and 8. Mass accuracy values for the molecular ion and M-CH₃ fragment of *m*-xylene were 0.27 and -1.1 ppm respectively. A spectral similarity search of the Peak True (deconvoluted) mass spectrum for *m*-xylene against the NIST library yielded a similarity score of 979 out of a possible 1000 points. Mass accuracy values for the molecular ion and M-CH₃

fragment of 1,2,4-trimethylbenzene were 1.65 and 0.86 ppm. The spectral similarity score for this compound was 949/1000. Spectral data, mass accuracy values and spectral similarity scores for *p*-propyltoluene, 1,3-dimethyl-5-propylbenzene and 1,3,5-trimethyl-2-propylbenzene are displayed in Figure 9.

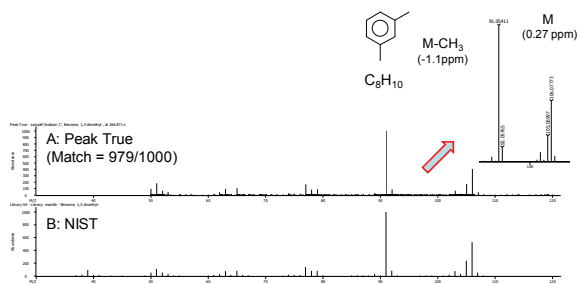


Figure 7. Peak True (A) and NIST library (B) mass spectra for *m*-xylene.

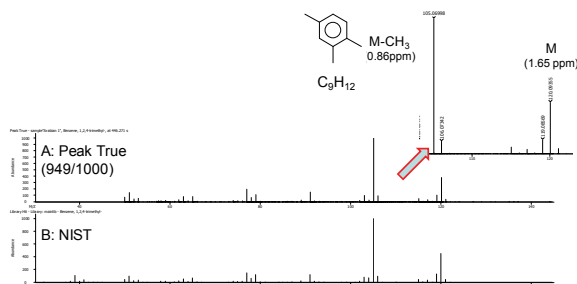


Figure 8. Peak True (A) and NIST library (B) mass spectra for 1,2,4-trimethylbenzene.

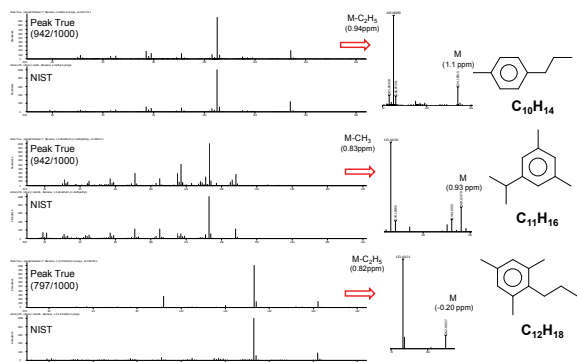


Figure 9. Peak True and NIST library mass spectra for *p*-propyltoluene (Top), 1,3-dimethyl-5-propylbenzene (Middle) and 1,3,5-trimethyl-2-propylbenzene (Bottom).

The Arabian light crude oil also contained a significant number of polyaromatic hydrocarbons (PAHs) and heterocyclic sulfur compounds (Figures 10 and 11). The mass accuracy values for PAHs and sulfur heterocycles ranged from -0.72 to 1.03 ppm and 0.36 to 1.12 ppm respectively (Tables 1 and 2).

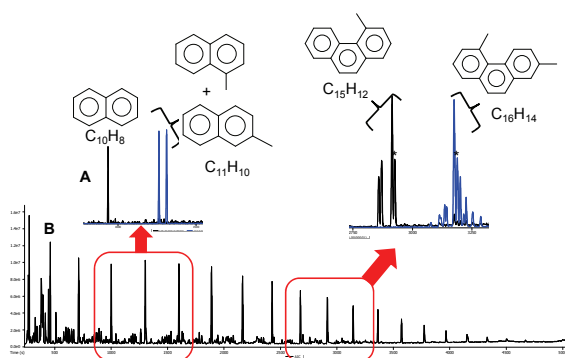


Figure 10. AIC (C) and XICs (A and B) showing PAHs in Arabian light crude oil.

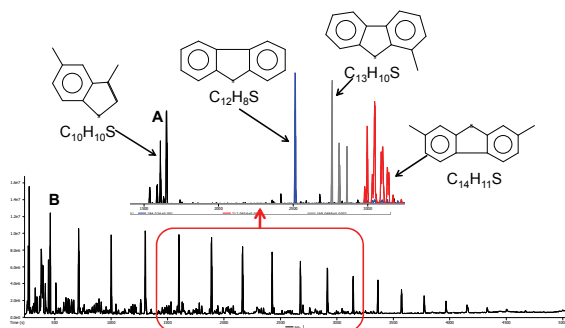


Figure 11. AIC (B) and XIC (A) showing sulfur heterocycles in Arabian light crude oil.

Table 1. Mass accuracy values for PAHs in Arabian light crude oil.

Name	Formula	Calculated ion <i>m/z</i>	Observed ion <i>m/z</i>	Mass Delta (Da)	Mass Accuracy (ppm)
Naphthalene	C10H8	128.06205	128.06196	-0.00009	-0.72
1-Methylnaphthalene	C11H10	142.07770	142.07772	0.00002	0.13
2-Methylnaphthalene	C11H10	142.07770	142.07765	-0.00005	-0.36
4-Methylphenanthrene	C15H12	192.09335	192.09355	0.00020	1.03
2,3-Dimethylphenanthrene	C16H14	206.10900	206.10903	0.00003	0.14

Table 2. Mass accuracy values for sulfur heterocycles in Arabian light crude oil.

Name	Formula	Calculated ion <i>m/z</i>	Observed ion <i>m/z</i>	Mass Delta (Da)	Mass Accuracy (ppm)
3,5-Dimethylbenzo[b]thiophene	C10H10S	162.04977	162.04983	0.00006	0.36
Dibenzothiophene	C12H8S	184.03412	184.03428	0.00016	0.86
4-Methyldibenzothiophene	C13H10S	198.04977	198.04997	0.00020	1.00
3,7-Dimethyldibenzothiophene	C14H12S	212.06542	212.06566	0.00024	1.12

Enhanced selectivity was observed when operating the Pegasus GC-HRT in ultra-high resolution mode. Analysis of the Nigerian light crude oil sample resulted in a clean extraction of over 50 alkyl substituted benzenes with formulas C₈H₁₀, C₉H₁₂, C₁₀H₁₄, C₁₁H₁₆ and C₁₂H₁₈ from the data (Figure 12). Excellent mass accuracy values were obtained for both molecular and fragment ions as shown for *m*-cymene (Figure 13). The average mass accuracy for the molecular ions and fragments of these compounds was 0.45 ppm (Table 3). PAHs were also present in this sample (Figure 14). The average mass accuracy values for the PAHs in Arabian light crude oil was 0.50 ppm (Table 4).

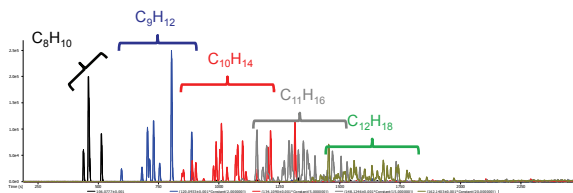


Figure 12. XIC of alkyl substituted benzene compounds in Nigerian light crude oil.

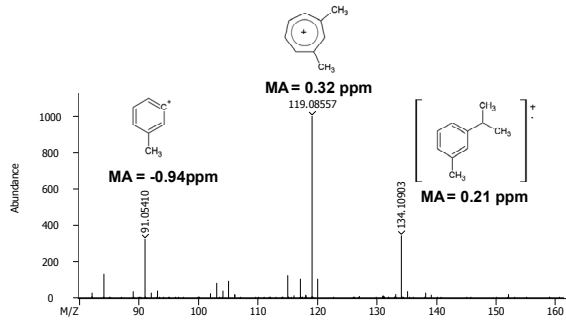


Figure 13. Peak True mass spectrum of m-cymene in Nigerian light crude oil showing structures and mass accuracy values for parent and fragment ions.

Table 3: Mass accuracy values for substituted benzenes in Nigerian light crude oil.

Formula	R.T. (s)	Quant Masses	Quant S/N	Area	Observed Ion m/z	Mass Accuracy (ppm)
CB8H10	438.776	91.0541	59	4521761	106.07769	-0.11
CB8H10	459.665	91.0541	140	14625822	106.07769	-0.11
CB8H10	513.194	91.0541	4	5137957	106.07768	-0.20
CB9H12	596.054	105.0699	21	1005072	120.09341	0.48
CB9H12-CH3 fragment ion						
CB9H12	680.81	91.054	1	1836884	120.09339	0.32
CB9H12	703.618	105.0699	75	3704556	120.09341	0.48
CB9H12	712.475	105.0699	34	1769075	120.09342	0.57
CB9H12	729.053	105.0699	64	3170530	120.09343	0.65
CB9H12	754.061	105.0699	27	1358828	120.0934	0.40
CB9H12	803.387	105.0699	145	7409182	120.09345	0.82
CB12-CH3 fragment ion						
CB9H12	886.701	105.0699	213	3103580	120.09344	0.73
CB12-CH3 fragment ion						
CB10H14	852.73	105.0699	40	569692	134.10899	-0.09
CB10H14	889.004	119.0856	224	849399	134.10902	0.14
CB12-CH3 fragment ion						
CB10H14	904.034	119.0856	192	724093	134.10906	0.43
CB10H14	977.317	119.0856	32	306056	134.10889	-0.83
CB10H14	988.225	105.0699	93	1338261	134.10899	-0.09
CB11H16	1003.189	105.0699	54	1060767	134.10903	0.21
CB10H14	1010.71	119.0856	182	4091267	134.10901	0.06
CB10H14	1033.081	105.0699	39	585565	134.10898	-0.16
CB10H14	1068.994	119.0856	114	755864	134.10899	-0.09
CB10H14	1077.21	119.0856	193	1293055	134.10897	-0.24
CB10H14	1097.578	119.0856	208	1333078	134.10903	0.21
CB10H14	1111.292	119.0856	51	343154	134.10879	-1.58
CB10H14	1202.412	119.0856	142	963926	134.10897	-0.24
CB10H14	1213.536	119.0855	207	1365778	134.10896	-0.31
CB10H14	1314.366	119.0855	239	1582443	134.10895	-0.39
CB11H16	1156.84	148.1248	117	269104	148.12478	0.86
CB11H16	1243.935	133.1011	11	58111	148.12479	0.93
CB11H16	1263.29	133.1012	39	201405	148.12473	0.53
CB11H16	1270.285	119.0856	41	271130	148.12466	0.05
CB11H16	1288.477	119.0855	34	252569	148.12478	0.86
CB11H16-CH5 fragment ion						
CB11H16	1300.535	119.0856	68	633317	148.12478	0.86
CB11H16	1328.018	105.0699	83	273549	148.12476	0.73
CB11H16	1349.116	119.0855	58	422279	148.12473	0.53
CB11H16	1364.955	119.0855	69	459065	148.12471	0.39
CB11H16	1397.343	119.0856	20	417325	148.12478	0.86
CB11H16	1469.677	133.1012	10	650529	148.12473	0.53
CB11H16	1505.302	133.1012	8	292706	148.12485	1.34
CB11H16	1530.2	133.1012	7	247184	148.1247	0.32
CB11H16	1583.441	133.1012	5	185658	148.12488	1.54
CB11H16	1734.259	133.1012	100	982695	148.12461	-0.28
CB12H18	1453.821	119.0855	13	280272	162.14029	-0.07
CB12H18	1544.796	98.1089	191	436404	162.14029	-0.07
CB12H18	1559.319	119.0856	8	233606	162.14044	0.85
CB12H18	1568.254	133.1012	4	151080	162.14023	-0.44
CB12H18	1603.382	162.1402	5	40346	162.14022	-0.51
CB12H18	1613.02	104.0621	55	97615	162.14035	0.30
CB12H18	1695.61	119.0856	10	212284	162.14025	-0.32
CB12H18	1711.242	85.1009	77	549243	162.14043	0.79
CB12H18	1741.918	133.1013	84	287770	162.14033	0.17
CB12H18	1777.644	119.0856	57	133289	162.1404	0.60
CB12H18-CH7 fragment ion						
CB12H18	1789.243	104.0621	27	96219	162.14039	0.54
CB12H18	1860.328	111.1169	58	96983	162.14037	0.42
CB11H16-CH5 fragment ion						
CB12H18					133.10114	-0.23
CB12H18-CH7 fragment ion						
CB12H18					119.08562	0.57

PAH's (Figure 14), as well as, various naphthenes and heteroatomic compounds (Figure 15) were also present in the Nigerian sample. Average mass accuracy values for the PAH's and heteroatomic species were 0.50 ppm and 0.91 ppm respectively (Tables 4 and 5).

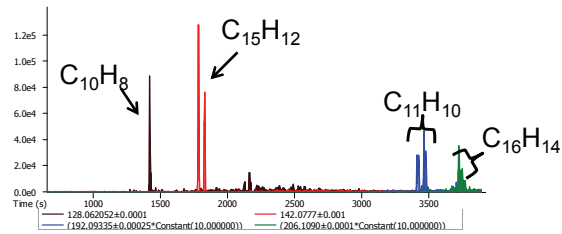


Figure 14. PAHs in Nigerian light crude oil sample.

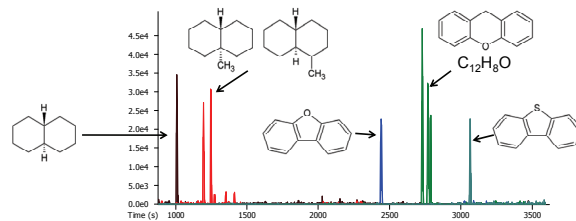


Figure 15. Naphthenes and heteroatomic compounds in Nigerian light crude oil sample.

Table 4. Mass accuracy values for PAHs in Nigerian light crude oil.

Formula	R.T. (s)	Quant Masses	Quant S/N	Area	Calculated Ion m/z	Observed Ion m/z	Mass Accuracy (ppm)
C10H8	1420	128.0622	558	3224070	128.06205	128.06216	0.85
C11H10	1782	142.0777	458	3857656	142.07770	142.07771	0.06
C11H10	1829	141.0699	464	2404022	142.07770	142.07771	0.06
C15H12	3413	192.0934	18	95431	192.09335	192.09344	0.46
C15H12	3425	192.0935	18	103283	192.09335	192.09355	1.03
C15H12	3464	192.0935	30	151527	192.09335	192.09352	0.88
C15H12	3478	192.0934	20	117862	192.09335	192.09340	0.25
C16H14	3686	206.1092	12	37819	206.10900	206.10924	1.16
C16H14	3725	206.109	35	134022	206.10900	206.10905	0.23
C16H14	3739	206.109	15	57339	206.10900	206.10900	-0.01
C16H14	3751	206.109	17	61190	206.10900	206.10901	0.04
C16H14	3804	206.1088	4	39588	206.10900	206.10879	-1.03

Table 5. Mass accuracy values for Heteroatomic compounds in Nigerian light crude oil sample.

Name	Formula	R.T. (s)	Quant S/N/Area	Calculated Ion m/z	Observed Ion m/z	Mass Accuracy (ppm)	
Naphthalene, decahydro-, trans-	C10H18	1008.629	220	976132	138.14030	138.14029	-0.09
trans-4a-Methyl-decahydro-naphthalene	C11H20	1195.751	14	955301	152.15595	152.15607	0.78
5-Methyl-decahydro-naphthalene	C11H20	1246.583	19	1487602	152.15595	152.15613	1.17
Dibenzofuran	C12H8O	2440.991	358	84869	168.05697	168.05729	1.93
Unknown	C13H10O	2731.536	43	98468	182.07262	182.07283	1.17
9H-xanthene	C13H10O	2769.36	73	11535	182.07262	182.07274	0.68
Unknown	C13H10O	2787.54	51	50359	182.07262	182.07241	-1.13
Dibenzothiophene	C12H8S	3064.946	180	38501	184.03412	184.03419	0.37

4. Conclusions

This study demonstrates the utility of high performance time-of-flight mass spectrometry for the comprehensive analysis of light crude oil samples. In addition to the increased resolution, the Pegasus GC-HRT provides the ability to acquire full mass range spectra without sacrificing sensitivity. This is beneficial for detecting not only target compounds (e.g., paraffins, aromatics, PAHs, etc.), but also heteroatomic contaminants (e.g., dibenzothiophene, dibenzofuran, 9H-xanthene). Saturated, aromatic, and heterocyclic compounds were identified using spectral similarity searches against existing nominal mass libraries together with highly accurate m/z parent and fragment ions for robust elemental formula determination. The Pegasus GC-HRT is an indispensable tool for the analysis of complex crude oil samples.

5. References

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³Shi Q, Hou D, Chng KH, Xu C, Zhao S and Zhang Y, *Energy Fuels* **2010**, *24*, 2545-2553.