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Deducing molecular compositions of petroleum products using GC-field ionization high resolution time of flight mass spectrometry

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Abstract

GC-field ionization high resolution time of flight mass spectrometry provides three-dimensional separations of complex mixtures. The first dimension is the gas chromatography retention time. This dimension can be either a boiling point scale or relative polarity scale depending on the type of GC column used in the separation. The second dimension is the molecular weight. This dimension is achieved by soft ionization of molecules and measurement of m/z values of largely singly charged species. The third dimension arises from chemical mass defects associated with heteroatom content and degree of unsaturation. This dimension is established by high resolution and accurate mass capabilities. Highly detailed compositional information can be obtained when the three-dimensional separation is applied to petroleum products. Quantitative applications of the approach require careful response factor calibrations.

Keywords: Field ionization; Time of flight; Hydrocarbon; Kendrick mass; Multi-dimension separation

1. Introduction

The petroleum industry is among the earliest industries which used mass spectrometry (MS) to gain compositional information when the technology was first commercialized more than a half century ago [1–4]. MS for petroleum characterization has evolved significantly over the past several decades. The progress of the technology in petroleum characterization has been mostly driven by the need to build effective models for refinery optimization and the need for exploring new hydrocarbon resources. In the 1950–60s, MS analyses of petroleum were largely performed using 50–70 eV electron ionization. The technique fragments hydrocarbon molecules and produces hydrocarbon type information based on characteristic fragmentation patterns of hydrocarbon families. Petroleum compositions were characterized at best only in terms of average compositions of boiling point fractions. Early models resorted to techniques that generate a relatively small number of group types [5]. Starting from the 1970s, soft ionization (or non-fragmentation ionization) gained increasing popularity for petroleum analysis for primarily two reasons. First, it greatly simplifies mass spectra by eliminating fragmentation ions. Second, it enables measurement of molecular weight or carbon number distribution of hydrocarbon types. The soft ionization methods commonly used in the early days include low voltage electron ionization (LVEI) [2,6], chemical ionization (CI) [7–9] and field ionization (FI) [10–13]. These soft ionization methods when combined with high resolution mass spectrometry and chromatographic separation enabled detailed characterization of petroleum samples [14,15].

In the past decade, more progress has been made in mass spectrometric characterization of petroleum. Novel soft ionization methods, such as electrospray ionization (ESI) [16,17], atmospheric pressure photo ionization (APPI) [18], atmospheric pressure chemical ionization (APCI) [18,19] and matrix assisted laser desorption ionization (MALDI) [20] have been explored for hydrocarbon analysis. Each ionization method allows characterization of different and sometimes unique assemblies of petroleum molecules. Ultra-high resolution mass spectrometry offered by the high magnetic field Fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS) enabled complete resolution and identification of petroleum molecules in the gas oil range [16,21–25]. In the same time frame, a breakthrough was achieved by combining gas chromatographic

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separation with soft ionization and high resolution MS, most notably, the combination of GC-field ionization and high resolution time of flight mass spectrometry (GC-FI-HR TOF MS) [10,11]. The technique has gained a larger role in recent years for petroleum analysis due to its relatively low cost and great amount of information obtainable by the technique. The GC-FI-TOF combination allows resolution of very close mass overlaps (e.g., C_3/SH_4 ∼3.4 mDa) that can only be resolved by using ultra-high resolution mass spectrometry. In addition, it offers the ability to resolve isomeric overlaps that cannot be achieved by MS alone. The technique provides highly detailed information of petroleum products across a wide boiling point range.

Recently, the two-dimensional nature of chromatography-soft ionization-MS has been recognized and utilized in complex mixture analysis. Examples include liquid chromatography (LC)-ESI-MS [33], supercritical fluid chromatography (SFC)-ESI-MS [26], SFC-FI-MS [10], GC-FI-MS [27] and GC-photon ionization (PI)-MS [28]. In these cases, MS serves as the second dimension of the separation to the chromatographic retention time. In this paper, we demonstrate that when high resolution MS is applied, for example in GC-FI-TOF MS, a third dimension can be established based on chemical mass defects associated with heteroatom content and degree of unsaturation. This dimension can be made orthogonal to the molecular weight when exact masses are converted into the Kendrick mass scale [29]. Detailed molecular information of petroleum products can be deduced from the multi-dimensional separation.

2. Experimental

2.1. Sample

The petroleum sample discussed in this paper is a total liquid product (TLP) from a catalytic cracking experiment. A majority of the compounds in the sample have boiling points between those of n-C_6 and n-C_{30} paraffins.

2.2. GC-FI-TOF MS

The GC-FI-TOF MS experiments were carried out on a Micromass GCT instrument equipped with a field ionization capability. The instrument set up has been previously described [11] and will only be briefly mentioned here. In sample analysis, about 1 μl of the TLP was injected via a Split/SplitLess (SSL) injector with a split ratio of 50:1. The temperature of the GC-TOF interface is maintained at 350 °C. Initial GC oven temperature is typically controlled at 35 °C and ramped to 350 °C at 10 °C/min to assure the separation of low boiling species and the elution of high boiling molecules. Unless otherwise specified, all data discussed in this paper were collected on a 60 m DB-17 HT with 0.25 μm film thickness and 0.25 mm ID (J&W Scientific). Several other GC columns of different polarities were explored including DB-1 HT, DB-35 and DB-Wax. These three columns are 30 m long, 0.25 μm film thickness and 0.25 mm i.d.

The FI emitter is made by CarboTech, consisting of a 10 μm tungsten wire onto which carbon microneedles (10–100 nm) have been grown. The FI emitter is carefully aligned with the end of the GC capillary column so that effluent molecules pass near the tips of the carbon dendrites. The emitter (at ground voltage) is about 1.5 mm away from a pair of extraction rods held at high potential (−12 kV), producing very high electric fields ($\sim 10^{-7}$ to 10^{-8} V/cm) around the tips of the carbon dendrites. The FI emitter current was typically set at 0 mA during a scan. The emitter is flashed by a current of 12 mA during an inter-scan cycle (0.2 s) to regenerate the emitter.

Ions generated by FI are accelerated and focused into a pusher region of the TOF. A voltage pulse of 960 V is applied, ejecting ions orthogonal to the original ion path. The ion packet drifts through a TOF with an effective path length of 1.2 m. A reflectron reflects ions back to a dual micro channel plate detector. Ion arrivals are recorded using a time to digital converter (TDC) with a sampling rate of 3.6 GHz. The voltage pulse was applied at a frequency of 30 kHz. A full spectrum is generated every 33 μS. The mass range was normally set at 50–800 Da. The scan duration time or spectrum accumulation time is 1 s (i.e., every "scan" is an accumulation of 30 thousand spectra).

2.3. Calibration and accurate mass measurement

The calibration mixture contains heptacosa, pentafluorobenzene, hexafluorobenzene, pentafluoroiodobenzene, pentafluorochloro benzene, perfluorotrimethylcyclohexane, xylene and acetone. The exact masses of the reference compounds can be found in a previous publication [11]. The calibrants were introduced into the ion source via a batch inlet and were pumped out after the calibration. In some of the experiments, pentafluoro iodobenzene (m/z 293.896) was introduced as an internal mass calibration compound during data acquisition.

2.4. Data visualization

The 3D and 2D data visualization was created using IGOR Pro 4.0 from WaveMetrics Inc.

3. Results and discussion

Both gas chromatography and mass spectrometry have been extensively used in the analysis of petroleum products. Petroleum molecules are separated by GC based on a combination of volatility and polarity of analytes. Depending on the type of GC column used, hydrocarbon molecules can be separated into boiling point lumps, such as that in simulated distillation, or into different compound classes. Due to limited chromatographic resolution, the latter is often used in combination with mass spectrometry either using a high energy ionization technique or soft ionization technique. Fig. 1 shows a GC total ion chromatogram (TIC) and a selected ion (m/z 212) chromatogram (SIC) of a total liquid product generated from a catalytic cracking experiment. Evidently, the TIC is not completely resolved due to the presence of a large number of molecules and isomers. However, the SIC shows resolution of three components, $C_{15}H_{32}$ (paraffin), $C_{16}H_{20}$ (C_6 naphthalene) and $C_{13}H_{10}S$ (C_2 dibenzothiophene). For low mass ions, identifications can be proposed based on the nominal mass and expected relative

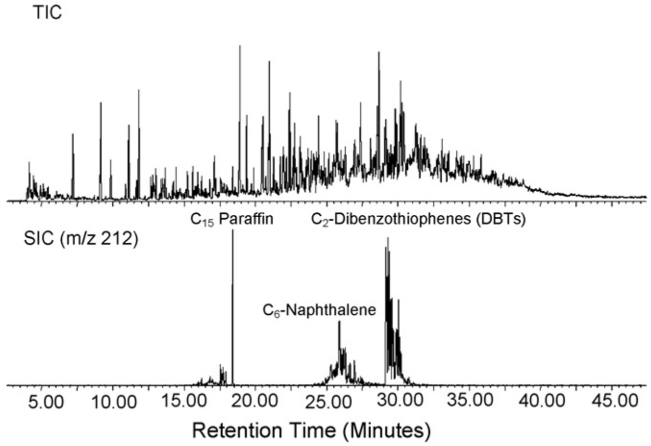

Fig. 1. Total ion chromatogram (TIC) and selected ion (*m/z* 212) chromatogram (SIC) of a total liquid petroleum product from a catalytic cracking experiment.

retention times of the species that fit the molecular weights. As will be shown later, high resolution MS and accurate mass measurements assure the identifications have high confidence. Quantification can be made based on peak area and relative response factor of each of the species. Ideally, SICs can be generated for all the other masses and can generate compositions for select hydrocarbon families. In reality, as mass increases, the chromatographic resolution decreases rapidly and not all components can be resolved by chromatography.

Soft ionization enabled MS to be used as a separation tool to resolve hydrocarbon molecules into molecular weight lumps. Here the term “lump” is used since MS does not resolve isomers. Low resolution MS does not even resolve nominal mass overlaps (or isobars). Commonly used soft ionization techniques that are compatible with GC include LVEI, FI and PI. In this work, FI is used to generate unique parent ions and their isotopic peaks as molecules elute from the GC separation. For petroleum samples, isotopic peaks are mostly from ^{13}C contributions since the number of heteroatoms (S, N and O) in a molecule is relatively low (typically less than 2). Fig. 2 illustrates the soft ionization of a C_{40} normal paraffin in comparison with that obtained by 70 eV electron impact. The latter generates extensive fragment ions that are not unique to the molecule. In fact, *m/z* 43, 57, 71, 85, etc., are the common fragments of all paraffins and were used in hydrocarbon type analysis (such as the Robinson method [30]). On the other hand, FI produced only $C_{40}H_{82}$ and its ^{13}C isotopes. For hydrocarbon samples, only singly charged species were produced by FI. Consequently, the value of mass to charge ratio (*m/z*) is equal to the monoisotopic molecular weight of the hydrocarbon species. Molecular weight and *m/z* are used interchangeably in this paper.

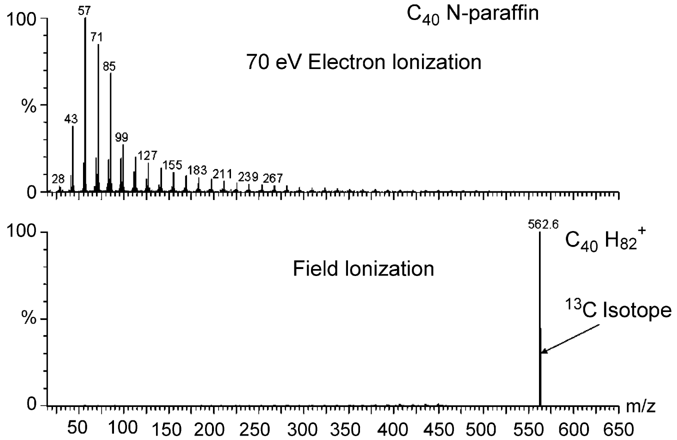

Fig. 2. Ionization of a C_{40} normal paraffin by 70 eV electron impact and field ionization.

When plotting molecular weight against retention time, GC-FI-TOF MS data show two-dimensional separations. Fig. 3 shows the contour maps (retention time (RT), molecular weight (MW) and relative abundance) of GC-FI-TOF MS data of the TLP product using 4 GC columns with varying degree of polarities (DB-1HT (a), DB-35 (b), DB 17HT (c) and DB-Wax (d)). The color scheme is indicative of relative intensities of the mass peaks. DB-1HT is a non-polar high temperature column containing 100% dimethyl polysiloxane. The non-polar column has been extensively used for simulated distillation work due to its high upper temperature limit. Here hydrocarbon molecules are largely eluted based on their volatility or boiling point (BP). One obvious advantage of the DB-1 column is that its retention time scale can be conveniently converted into a boiling point scale by using normal paraffins as boiling point markers. The disadvantage is that it offers limited separation of hydrocarbon classes as shown in Fig. 3(a). Even with this non-polar column, visible separation between saturate hydrocarbons and aromatics has been observed. This separation is mainly due to distinct BP differences between saturate hydrocarbons and aromatics for given molecular weights. By increasing polarity of the GC column, larger separations between hydrocarbon classes were observed. DB-Wax Fig. 3(d) is the most polar column containing polyethylene glycol (PEG). It exhibits the largest separation of aromatic lumps among all the columns. The DB-Wax, however, has a temperature limitation (250 °C upper limit) which prevents it from detecting high boiling molecules existing in the sample. Both DB-35 (Fig. 3(b)) and DB-17HT (Fig. 3(c)) are moderately polar columns containing 35 and 50% phenyl polysiloxane, respectively. Increased separation between hydrocarbon classes were observed in comparison with DB-1HT. The DB-17HT also has an upper temperature limit of 400 °C allowing the separation of high boiling petroleum molecules. The data discussed in the following sections were derived using the DB-17HT column.

One way to deconvolute boiling point and polarity effects is to realign GC retention times mathematically so that all normal paraffins of different carbon numbers have the same or similar “retention time” [27,28]. Here we simply fit the retention time–molecular weight function of *n*-paraffin molecules into a fourth order polynomial curve. Coefficients of retention time correction were applied to all data. Thus, the GC retention time scale was converted into a relative polarity scale which is near orthogonal to the boiling point of normal paraffins. Fig. 4 shows the effect of this transformation for the DB-17HT column. Here MS (molecular weight) is perceived as the first dimension separation and relative polarity is the second dimension separation. The pattern of the data resembles that of two-dimensional GC

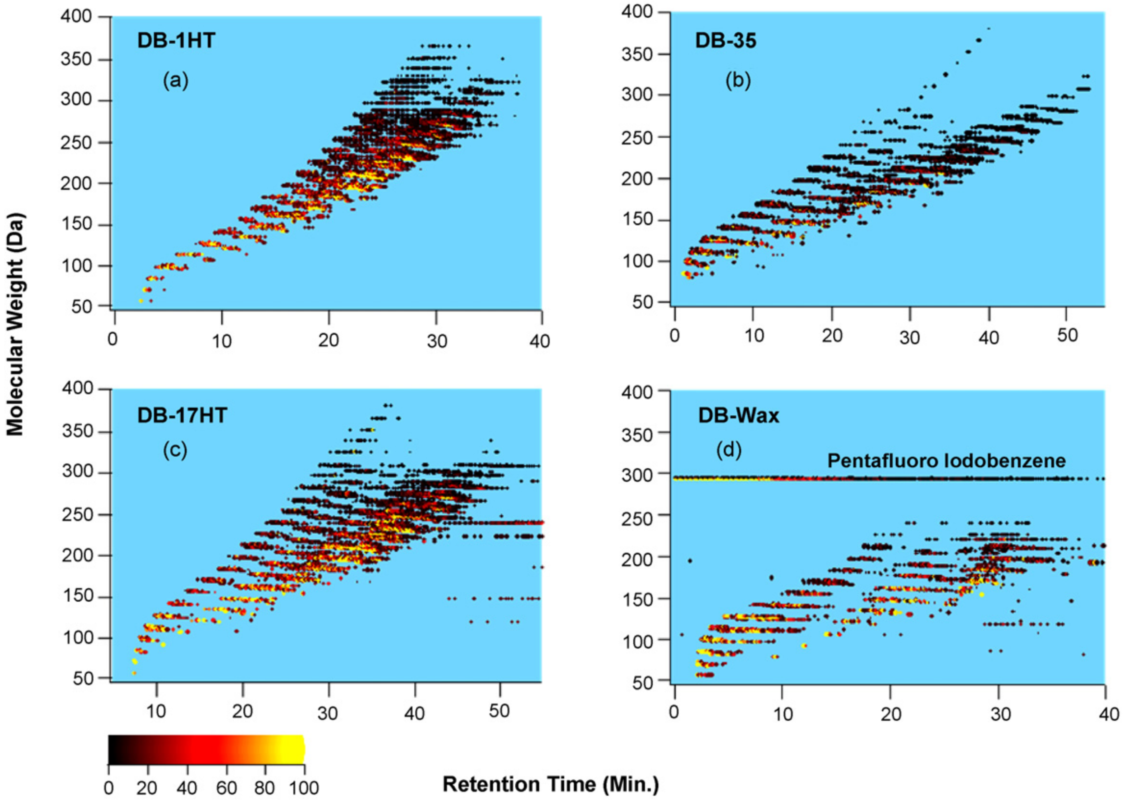

Fig. 3. 2D contour maps of GC-FI-TOF data using four different GC columns (a) 30 M DB-1HT, (b) 30 M DB-35, (c) 60 M DB-17HT and (d) 30 M DB-Wax. The solid trace at *m*/*z* ~300 shown in (d) is due to the presence of an internal mass calibration compound (pentafluoroiodobenzene, *m*/*z* 293.896). Since FI generates singly charged species, the value of mass to charge ratio (*m*/*z*) is equal to the monoisotopic molecular weight of the hydrocarbon species. Thus, *y*-axis can be considered a molecular weight scale.

data where the first dimension is created by a non-polar boiling point separation. Average mass spectra of saturates, monoaromatics and polyaromatics can be conveniently grouped by their relative polarities. The grouping simplifies data interpretation and processing by eliminating ambiguities in structure assignments. Fig. 4 also suggests incomplete resolution of molecules in the polyaromatic region by just polarity and nominal mass (molecular weight) separations.

The third dimension arises from the high resolution and accurate mass measurement of molecular ions. TOF-MS provides

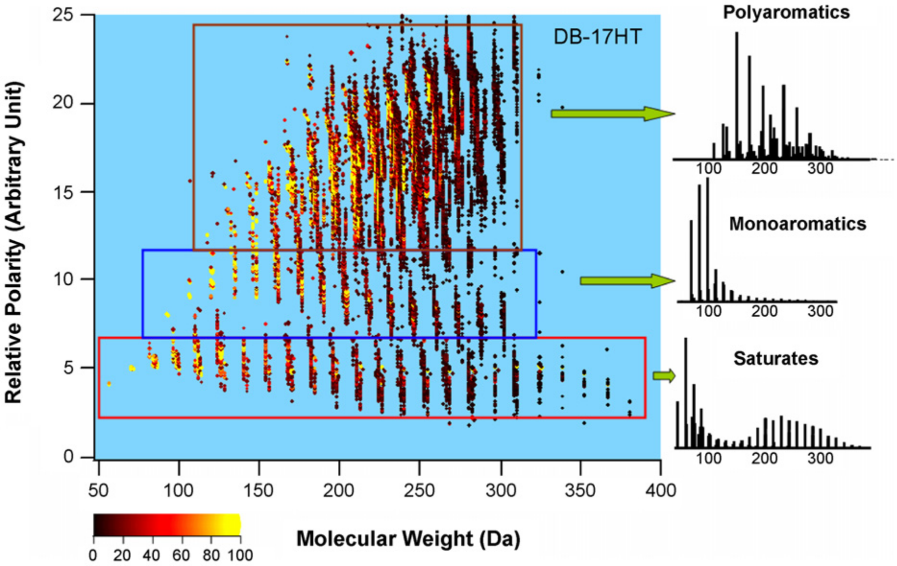

Fig. 4. A 2D contour map of 60 M DB-17HT after forcing n-paraffin retention time to be around 5 min. The effect of boiling point is decoupled from that of molecular polarity. The *y*-axis now represents relative polarity of hydrocarbon molecules.

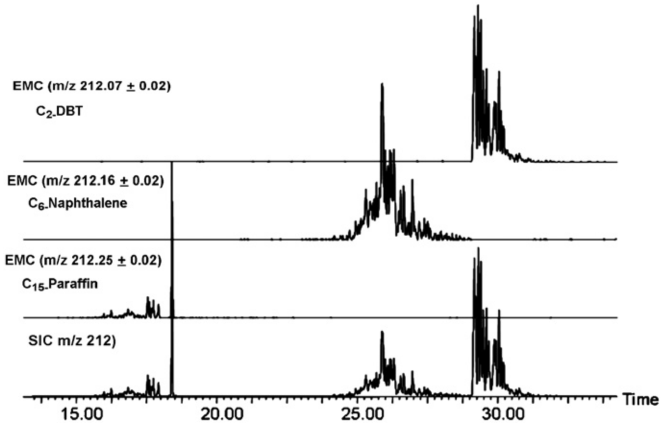

Fig. 5. Exact mass chromatograms further separate nominal mass overlaps.

an average resolving power of 5000 and mass accuracy of less than 5 ppm [11]. This feature enables differentiation of hydrocarbon classes with certain nominal mass overlaps but different exact masses. Fig. 5 shows the separation of nominal mass overlaps from Fig. 1 by displaying data in an exact mass chromatogram (EMC). The nominal masses of $C_{15}H_{32}$, $C_{16}H_{20}$ and $C_{13}H_{10}S$ are identical (*m/z* 212). The exact masses of the three are 212.253, 212.159 and 212.065, respectively. These differences are the result of C/H_{12} (93 mDa) and C_2H_6/S (91 mDa) doublets, respectively. The use of EMC with a narrow mass window (±0.02 Da) resolved the three species.

The decimal points of the exact masses are typically referred to as mass defects in the mass spectrometry community. They are due to the non-integer values of various elements in the IUPAC scale where the atomic weight of ^{12}C exactly equals 12. In this scale the atomic weights of ^{13}C, H, S, N and O are 13.0034, 1.007825, 31.97207, 14.00307 and 15.99491, respectively. Consequently homologous series of the same core structure will have different mass defects as CH_2 changes as illustrated in Table 1. One simple but highly effective way to unify mass defects for a hydrocarbon family is to convert IUPAC mass (Mass) scale into Kendrick mass (K_Mass) scale [29,31,32] by Eq. (1) where the mass of $^{12}CH_2$ is defined to be exactly 14.00000. Kendrick mass defect (KMD) is defined as the difference between nominal mass (N_Mass) and K_Mass by Eq. (2). Each homologous series will have a unique mass defect regardless of alkyl chain length as shown in Table 1.

$$\text{K\_Mass} = \text{Mass} \times \left(\frac{14}{14.01565}\right) \tag{1}$$

$$\text{KMD} = 1000 \times (\text{N\_Mass} - \text{K\_Mass}) \tag{2}$$

Here N_Mass is defined as the integer mass from combinations of integer atomic weight of C (12), H (1), S (32), N (14) and O (16), etc.

Very commonly MS analyzes petroleum in terms of general chemical formula,

$$C_cH_{2c+Z}S_sN_nO_o$$

where Z is the referred to as the hydrogen deficiency (*Z*-number); *c* the carbon number; *s*, *n*, and *o* are the number of heteroatoms X (e.g., S, N and O) in a molecule, respectively. "*Z*X" is often used as a short hand notation for a compound class. For examples, $Z = -6$ represents alkylbenzenes and isomers, −10S represents benzothiophenes and isomers, −15N represents carbazoles and isomers.

KMD of various compound classes can be calculated from "*Z*X" via the following equation

$$\begin{aligned}\text{KMD} = 1000 \times [&(Z \times (1 - F \times 1.007825)\\ &+ s \times (32 - 31.97207 \times F)\\ &+ n \times (14 - 14.00307 \times F) + o\\ &\times (16 - 15.99491 \times F)]\end{aligned} \tag{3}$$

where $F = 14/14.01565 = 0.99888$.

Table 1
Exact masses of representative compound classes in IUPAC and Kendrick mass scales

	Paraffins	Benzenes	Chrysenes	Dibenzo thiophenes	Carbazoles	Fatty acids	Vanadyl porphyrins
Z-number	2	−6	−22	−16	−15	0	−28
Heteroatoms				S	N	O_2	N_4VO
Carbon Number							
IUPAC							
1	16.031					46.006	
10	142.172	134.110				172.147	
20	282.329	274.266	258.141	296.159	279.199	312.303	
40	562.642	554.579	538.454	576.472	559.512	592.616	655.358
100	1403.581	1395.518	1379.393	1417.411	1400.451	1433.555	1496.297
Carbon Number							
Kendrick							
1	16.013					45.954	
10	142.013	133.960				171.954	
20	282.013	273.960	257.853	295.828	278.887	311.954	
40	562.013	553.960	537.853	575.828	558.887	591.954	654.626
100	1402.013	1393.960	1377.853	1415.828	1398.887	1431.954	1494.626
KMD	−13	40	147	172	113	46	384

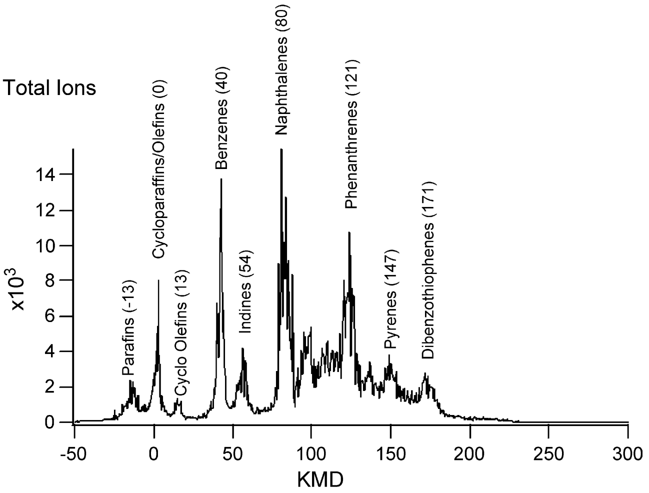

Fig. 6. A KMD total ion chromatogram. KMD values of major hydrocarbon families are given in parentheses.

A list of KMD values for hydrocarbons, mono-sulfur and di-sulfur compounds are given in Table 2. The fact that each hydrocarbon family has a unique KMD value allows us to construct a KMD chromatogram similar to the total ion chromatogram where the sum of total ions is plotted against retention times. Here the sum of total ions is plotted against KMD values as shown in Fig. 6. Major compound classes can be easily recognized based on their unique KMD values listed in Table 2.

Fig. 6 also indicates that KMD cannot completely resolve all hydrocarbon families due to limited mass resolution. Since all of the components in a petroleum sample can be grouped into 14 families according to their N_Mass, it is convenient to group KMDs by their nominal mass classes (Z^*-class) first. By doing so, some compound classes have very close KMDs will be placed into different Z^*-classes and resolved. In this work, we define the Z^*-class of an ion as the reminder of its N_Mass divided by 14, minus 14, or the modulus of (N_Mass/14 − 14). Each nominal mass yields a Z^* value between −1 and −14. Z^* numbers of various hydrocarbon families can be found in Table 2. Note that several homologous series can share the same Z^* value, for example, paraffins ($Z=2$), naphthalenes ($Z=-12$), dibenzothiophenes ($ZX=-16S$), naphtheno chrysenes ($Z=-26$) and thiopheno dibenzothiophenes ($ZX=-20S_2$) all have the same Z^* value of −12.

Now let us apply the three-dimensional (3D) separation (Polarity, MW and KMD) to the $Z^*=-12$ class. A total of 5 hydrocarbon families or homologous are resolved in the 3D space as shown in Fig. 7(a). The color scale is indicative of KMD values. For the convenience of analysis, projections to 2D surfaces of MW-KMD, Polarity-KMD and MW-Polarity are presented in Fig. 7(b–d), respectively. KMD resolves ions into four major clusters with KMD values around −13, 80, 170 and 260, respectively. Fig. 7(c) shows MS separate these ion clusters into homologous series (members with a repeating mass of CH_2 unit). Fig. 7(d) shows ion cluster with KMD of 170 is made of two groups ions separated in the polarity scales. In reference to Table 2, ions with KMD of −13, 80 and 260 are identified as paraffins, naphthalenes and thiopheno dibenzothiophenes, respectively. The two groups of ions with KMD around

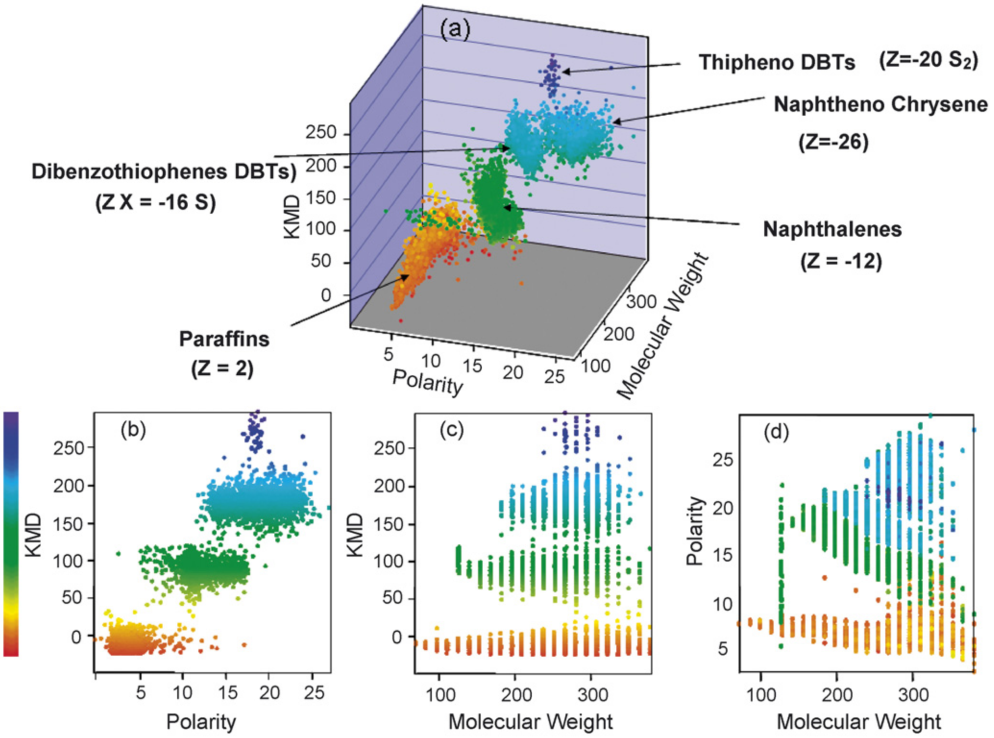

Fig. 7. (a) A three-dimensional plot of the GC-FI-TOF data (nominal mass class $Z^*=-12$); projections to 2D surfaces, KMD-Polarity (b), KMD-MW (c) and Polarity-MW (d).

Table 2
Z^* number and KMD values of petroleum homologous (ZX)

Z^*	KMD	Z	X	Possible homologues
−2	13	−2		Dicycloparaffins
−2	107	−16		Fluorenes
−2	198	−20	S	Dinaphtheno DBTs
−4	27	−4		Tricycloparaffins
−4	117	−8	S	Benzothiophanes
−4	121	−18		Phenanthrenes
−4	211	−22	S	Benzo DBTs
−6	40	−6		Benzenes
−6	131	−10	S	Benzothiophenes (BTs)
−6	134	−20		Acephenanthrenes
−6	221	−14	S_2	Thiophenobenzothiophenes (TBT)
−6	224	−24	S	Naphthenobenzo DBTs
−8	54	−8		Indanes/styrenes
−8	144	−12	S	Naphtheno BTs
−8	147	−22		Pyrenes
−8	234	−16	S_2	Dithiofluorenes
−8	238	−26	S	Pyrenothiophenes
−10	67	−10		Indenes
−10	157	−14	S	Dinaphtheno BTs
−10	161	−24		Chrysenes
−10	248	−18	S_2	Dithioindenes
−10	251	−28	S	Chrysenothiophenes
−12	−13	2		Paraffins
−12	80	−12		Naphthalenes
−12	171	−16	S	Dibenzothiophenes (DBTs)
−12	174	−26		Naphtheno chrysenes
−12	261	−20	S_2	Thiopheno DBTs
−14	0	0		Cycloparaffins/olefins
−14	90	−4	S	Thiophenes (Ts)
−14	94	−14		Bi-phenyls
−14	184	−18	S	Naphtheno DBTs
−14	188	−28		Benzopyrenes

170 are due to dibenzothiophenes (KMD = 171) and naphtheno chrysenes (KMD = 174). The mass difference between the two homologous series is 3.4 mDa which cannot be resolved by TOF MS. Note the KMD scale is orthogonal to the molecular weight scale (Fig. 7(c)). It is not orthogonal to the polarity scale (Fig. 7(b)) since KMD is determined by the chemical structures and heteroatom content of the molecules. By applying the same strategy to all Z^* classes, a detailed hydrocarbon composition can be determined for the whole petroleum sample.

4. Conclusions

We illustrated a three-dimensional separation of a petroleum sample by GC-FI-HR TOF mass spectrometry. Gas chromatography provides separation of hydrocarbon molecules by boiling point or polarity. Mass spectrometry plays two roles here. First, it provides separation of molecules by their molecular weight. Second, high resolution and accurate mass analysis provide a third dimension by Kendrick mass defect. The KMD scale is orthogonal to the molecular weight, but not orthogonal to the chromatographic separation. KMD can be conveniently used to identify compound classes. Detailed petroleum compositions can be effectively visualized and processed by the multi-dimensional approach.

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References

[1] H.E. Lumpkin, Anal. Chem. 30 (1958) 321.
[2] F.H. Field, S.H. Hastings, Anal. Chem. 28 (1958) 1248.
[3] H.E. Lumpkin, B.W. Thomas, Anal. Chem. 23 (1951) 1738.
[4] R.A. Brown, Anal. Chem. 23 (1951) 430.
[5] S.M. Jacob, B. Gross, S.E. Voltz, V.W. Weekman, AIChE J. (1976) 701.
[6] C.E. Schmidt, R.F. Spreacher, B.D. Bratts, Anal. Chem. 59 (1987) 2027.
[7] C. Allgood, Y.C. Ma, B. Munson, Anal. Chem. 63 (1991) 721.
[8] C. Allgood, Y. Lin, Y.C. Ma, Munson, B. Org. Mass Spectrom. 25 (1990) 497.
[9] I. Dzidic, M.D. Balicki, H.V. Hart, Fuel 67 (1988) 1155.
[10] K. Qian, J.W. Diehl, G.J. Dechert, F.P. DiSanzo, Eur. J. Mass Spectrom. 10 (2004) 187.
[11] K. Qian, G.J. Dechert, Anal. Chem. 74 (2002) 3977.
[12] Y. Bricker, Z. Ring, A. Iacchelli, N.P.M.R. McLean, C. Fairbridge, R. Malhortra, M.A. Coggiola, S.E. Yong, Enegry Fuels 15 (2001) 23.
[13] Y. Bricker, Z. Ring, A. Iacchelli, N. McLean, R. Malhortra, M.A. Coggiola, S.E. Yong, Energy Fuels 15 (2001) 996.
[14] C.S. Hsu, K. Qian, Energy Fuels 7 (1993) 268.
[15] T. Aczel, S.G. Colgrove, L. Lan, ASTM Spec. Tech. Publ. 1019 (1989) 159.
[16] K. Qian, R.P. Rodgers, C.L. Hendrickson, M.R. Emmett, A.G. Marshall, Energy Fuels 15 (2001) 492.
[17] D.L. Zhan, J.B. Fenn, Int. J. Mass Spectrom. 194 (2000) 197.
[18] D.B. Robb, R.C. Thomas, A.P. Bruins, Anal. Chem. 72 (2000) 3653.
[19] C.S. Hsu, G.J. Dechert, W.K. Robbins, E.K. Fukuda, Enegry Fuels 14 (2000) 217.
[20] M. Millan, B. Mahtab, F. Karaca, T.J. Morgan, A.A. Herod, R. Kandiyoti, Catal. Today 109 (2005) 154.
[21] K. Qian, W.K. Robbins, C.A. Hughey, H.J. Cooper, R.P. Rodgers, A.G. Marshall, Energy Fuels 15 (2001) 1505.
[22] A.G. Marshall, R.P. Rodgers, Acct. Chem. Res. 37 (2004) 53.
[23] C.A. Hughey, R.P. Rodgers, A.G. Marshall, C.C. Walters, K. Qian, P. Mankiewicz, Org. Geochem. 35 (2004) 863.
[24] C.A. Hughey, R.P. Rodgers, A.G. Marshall, K. Qian, W.K. Robbins, Org. Geochem. 33 (2002) 743.
[25] C.A. Hughey, C.L. Hendrickson, R.P. Rodgers, A.G. Marshall, Energy Fuels 15 (2001) 1186.
[26] J.D. Pinkston, S.B. Marapane, G.T. Jordan, B.D. Clair, J. Am. Soc. Mass Spectrom. 13 (2002) 1195.
[27] F.C.-Y Wang, K. Qian, L.A. Green, Anal. Chem. 77 (2005) 2777.
[28] S. Mitschke, W. Welthagen, R. Zimmermann, Anal. Chem. 78 (2006) 6364.
[29] E. Kendrick, Anal. Chem. 35 (1963) 2146.
[30] C.J. Robinson, Anal. Chem. 43 (1971) 1425.
[31] C.A. Hughey, C.L. Hendrickson, R.P. Rodgers, A.G. Marshall, K. Qian, Anal. Chem. 73 (2001) 4676.
[32] C.S. Hsu, K. Qian, Y.C. Chen, Anal. Chim. Acta 264 (1992) 79.
[33] X.-J. Li, P.G.A. Pedrioli, J. Eng, D. Martin, E.C. Yi, H. Lee, R. Aebersold, Anal. Chem. 76 (13) (2004) 3856.