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Molecular Speciation of Saturates by On-Line Liquid Chromatography–Field Ionization Mass Spectrometry

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A commercial field ionization (FI) source has been successfully reconfigured to accommodate the moving belt interface for on-line liquid chromatography–mass spectrometric (LC/MS) operations. This novel combination allows us to characterize saturates with maximum chromatographic resolution and minimal sample preparation. We found that FI generates predominantly molecular ions for normal paraffins and naphthenes but fragment ions for isoparaffins. By combining these ionization characteristics with spectral editing software, we can differentiate and measure levels of naphthenes, normal paraffins, and isoparaffins with a single mass spectrometric (MS) analysis. Most importantly, the normal and isoparaffins split can be measured directly by MS without the need of using gas chromatography (GC). This new LC/MS approach has been evaluated using saturates fractions generated by urea adduction of a lube basestock. Material balance of FI results for the fractions from this separation was in good agreement with that calculated from gravimetric measurement. The normal paraffin measurement by FI agrees well with that by GC. Comparisons with results obtained by the conventional ASTM (American Society for Testing and Materials) high-voltage electron–ionization (EI) method were favorable.

Introduction

On-line liquid chromatography/mass spectrometry (LC/MS) provides an effective means for the characterization of complex high-boiling hydrocarbon mixtures.^{1–4} It combines the separation capabilities of high performance liquid chromatography (HPLC) and the molecular level characterization capabilities of mass spectrometry (MS). Low-voltage electron ionization (LV/EI) and chemical ionization (CI) have been used for aromatic hydrocarbon type analysis of heavy oils because these techniques produce molecular ions for aromatic compounds with minimal fragmentation. Hsu and co-workers demonstrated that by using ring-type separation of liquid chromatography with a moving belt LC/MS interface, low-voltage EI and CS₂ charge exchange (CS₂/CE) provide compound type distributions of aromatic hydrocarbons.^{1,2,4} Nevertheless, these low-energy ionization processes are not suitable for analyzing saturated hydrocarbons because they have higher ionization potentials than aromatic hydrocarbons and are not ionized. Increasing the energy even slightly above that required to ionize saturated hydrocarbons results in significant fragmentation due to low appearance potential of fragment ions, making measurement based on molecular ions impractical.

The conventional MS technique for the characterization of saturated hydrocarbons is high voltage (70 V) EI. The distributions of paraffins and 1- to 6-ring naphthenes (cycloparaffins) are calculated from the intensities of the various fragment ions representative of each compound type. The calculations use precalibrated “sensitivity matrices” which are established based on two factors: (1) the average carbon number estimated from the distribution of low abundance molecular ions of normal paraffins and (2) the normal paraffins/isoparaffins ratio estimated from molecular to fragment ion intensities.^{5,6} Ideally, an ionization technique yielding only molecular ions of the saturates would allow us to determine not only the distribution of compound types but also the carbon number distribution within each type.

Field ionization (FI) and field desorption (FD) have been used for obtaining molecular ions of saturates with little fragmentation.^{7–10} Both FI and FD employ an emitter made of a fine wire to which a high electric potential (8–12 kV) is applied relative to the counter electrode (cathode –2 to –4 kV). In FI, samples are

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(1) Hsu, C. S.; Qian, K.; McLean, M. A.; Aczel, T.; Blum, S. C.; Olmstead, W. N.; Kaplan, L. H.; Robbins, W. K.; Schulz, W. W. *Energy Fuels* **1991**, *5*, 395–398.

(2) Qian, K.; Hsu, C. S. *Anal. Chem.* **1992**, *64*, 2327–2333.

(3) Hsu, C. S.; Qian, K. *Energy Fuels* **1993**, *7*, 268–272.

(4) Hsu, C. S.; Qian, K.; Robbins, W. K. *J. High Resolut. Chromatogr.* **1994**, *17*, 271–276.

(5) Hastings, S. E.; Johnson, B. H.; Lumpkin, H. E. *Anal. Chem.* **1956**, *28*, 1243–1247.

(6) 1994 *Annual Book of ASTM Standards*, Volume 05.02, ASTM Method D2786-86.

(7) (a) Beckey, H. D. *Field Ionization Mass Spectrometry*; Pergamon Press: Oxford, England, 1971. (b) Prokai, L. *Field Desorption Mass Spectrometry*; Marcel Dekker: New York, 1990.

(8) Mead, W. L. *Anal. Chem.* **1968**, *40*, 743–747.

(9) Scheppele, S. E.; Grizzle, P. L.; Greenwood, G. J.; Marriott, T. D.; Perreira, N. B. *Anal. Chem.* **1976**, *48*, 2105–2113.

(10) Scheppele, S. E.; Hsu, C. S.; Marriott, T. D.; Benson, P. A.; Detwiler, K. N.; Perreira, N. B. *Int. J. Mass Spectrom. Ion. Phys.* **1978**, *28*, 335–346.

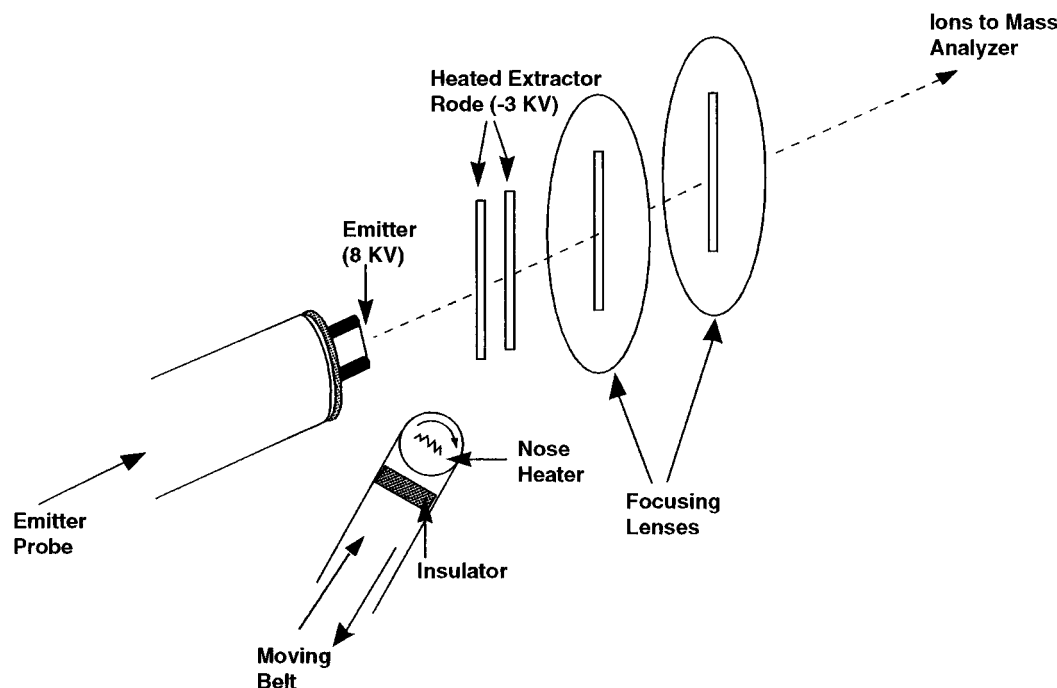


Figure 1. Schematic diagram of the field ionization ion source with a moving-belt LC/MS interface.

introduced as a gas phase through a heated glass inlet system or direct insertion probe. Gaseous molecules close to the emitter are subjected to a high electric field which leads to electron loss through quantum mechanical tunneling. In FD, samples are deposited onto the emitter directly and are ionized on or near the emitter surface without vaporization. In addition to the process of field ionization, other ionization processes such as cation attachment and dimerization may also occur.¹¹

FI and FD are currently practiced with off-line HPLC. For example, Buduszynski combined FIMS with off-line HPLC for the molecular characterization of heavy petroleum.^{12,13} Malhotra and co-workers used off-line HPLC and FIMS to characterize vacuum residua.¹⁴ Although off-line HPLC removes interfering aromatic compounds from saturated hydrocarbons prior to MS analysis, it requires time-consuming preparative work (isolation, solvent removal, injection, etc.) and a rather large amount of sample. It is therefore advantageous to couple FIMS on-line with LC. While the emitter loading characteristic of FD does not lend itself to on-line operations, the FI injection in a continuous mode can be accomplished by an appropriate volatilization interface. We have modified a FI/FD source of our VG-70 VSE mass spectrometer for operation with a moving belt LC/MS interface and applied this technique to the characterization of the heavy saturated hydrocarbons in high-boiling petroleum and synthetic hydrocarbon fractions.¹⁵

Experimental Section

On-line LC/MS data were collected with a VG-70 VSE double-focusing mass spectrometer equipped with a moving-

belt interface for transporting LC effluent. VG's FI/FD ion source was reconfigured to make it compatible with the moving-belt interface. To allow access of the moving-belt probe, a set of the screening plates was replaced with a single plate and the metal piece originally used for mounting a direct chemical ionization (DCI) probe contacts was removed. Contacts for the moving-belt nose heater were fabricated and were mounted onto two of the thicker metal pieces on the ion source. Ceramic spacers electrically insulated the moving-belt contacts. Other small adjustments were made, such as repositioning parts on the FI source, to accommodate the moving belt interface. The moving-belt assembly was retracted slightly (a few millimeters) away from the source to prevent arcing between the source and the probe. The distance of the emitter from the nose heater was about 1.5 cm. Figure 1 displays the schematic of the FI moving belt system.

All experiments were conducted at a resolving power of the mass spectrometer set at 1000. The FI emitters were activated 10 μm tungsten wires purchased from Linden Chromspec (Auf dem Berge 25D 2803 Leeste, Germany). The moving belt was operated at a speed of 2 cm/s with the nose heater set at ~ 2.3 A (~ 310 °C). The scanning speed was 1 s/decade (1.65 s from m/z 900 down to 20) with a 1 s interscan delay. The FI/FD ion source was heated to 200 °C. The optimal heating current through the FI emitter was empirically determined to be 20 mA during scanning and 30 mA for cleaning, during the interscan delay (see below).

The details of the HPLC conditions were described elsewhere.¹ In this work, the saturates are eluted from a dinitroanilinopropyl (DNAP) silica column with hexane pumped at a flow rate of 1.5 mL/min.

Several sample types were used to characterize the LC/FIMS performance. A synthetic wax, Polywax 500, was used to optimize FI conditions for carbon number distributions. A blend of model compounds—*n*-dotriacontane, *n*-octacosane 3-ethyltetracosane, squalane, cholestane, and *n*-nonadecylcyclohexane—was used to establish the sensitivities for naphthenes and for normal and isoparaffins. A set of related saturates samples was used to study compound types more broadly. The sample set consists of the saturates fraction of an S150N

(11) Hsu, C. S. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1997**, 42, 390–393.

(12) Boduszynski, M. M. *Energy Fuels* **1987**, 1, 2–11.

(13) Boduszynski, M. M. *Energy Fuels* **1988**, 5, 597–613.

(14) Malhotra, R.; McMillen, D. F.; Tse, D. S.; St. John, G. A.; Coggiola, M. J.; Matsui, H. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1989**, 34, 330.

(15) Hsu, C. S.; Blum, S. C.; Liang, Z.; Grosshans, P. B.; Robbins, W. K. U.S. Patent 5,644,129 (1997).

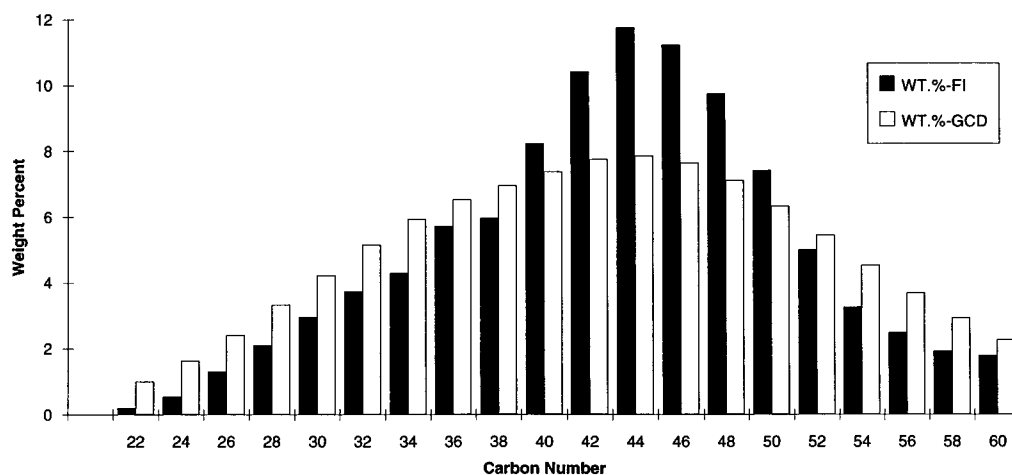


Figure 2. Comparison of carbon number distribution of Polywax 500 determined by LC/FIMS and by gas chromatographic (GC) distillation with flame ionization detection.

lube basestock, the dewaxed oil isolated from this fraction by urea adduction, and the corresponding wax. For comparison, high-voltage (70 V) EIMS type analysis (ASTM D2786) was performed on this sample set using a Hewlett-Packard mass selective detector (MSD) equipped with a Brunfeldt all-glass heated batch inlet system. The FI results for the normal paraffins were also compared to the values measured by gas chromatographic flame ionization detection (GC-FID).

Results and Discussion

FI sensitivities can vary substantially among different types of compounds as well as among different molecules of the same type.¹⁶ Furthermore, FI source conditions can affect relative sensitivities of different compounds. A normal paraffin mixture (Polywax 500) was selected to determine FI optimal conditions that give a carbon number distribution closest to that obtained from GC-distillation (GCD) analysis. The mixture was introduced into the FI source either by a direct insertion probe or through the moving belt.

In these experiments, two types of heating current were applied to the emitter. One is called scan-in-progress (SIP) current during data acquisition which provides thermal energy to prevent molecules from adsorbing on the emitter. The other type of current is called flash current which is higher than the SIP current and is applied between scans to remove high-boiling species condensed on the emitter. Without the use of flash current, signal enhancement of higher mass ions can occur due to field desorption phenomenon.^{17,18} At 20 mA SIP current and 30 mA flash current, the carbon number distribution of Polywax 500 obtained by FI is closest to that obtained by GC distillation (GCD), shown in Figure 2¹⁹. These conditions were considered optimal and chosen for subsequent LC/FIMS experiments.

With VG's current FI source design, the optimal SIP current was fixed (not programmable) during the scan. Both high and low carbon number species show slightly lower abundance than those of midrange carbon number

species. However, this distortion does not seriously affect the determination of average carbon number of the mixtures. For high carbon number species, two effects can influence their apparent carbon number distribution. The "adsorption effect" results from higher boiling point larger molecules condensed onto the emitter and ionized by field desorption.^{7,17,18} This effect will increase the peak intensities of high carbon number (i.e., high mass) species and can be significantly reduced by raising the emitter flash current between scans. In doing so, however, the apparent carbon number distribution is shifted downward below that determined by gas chromatographic distillation (GCD). Thermal decomposition does not seem to play an important role because no significant increase in low m/z ions is observed. Therefore, we attributed this shift to the preferential condensation of heavier molecules onto cold spots on other source components near the moving-belt nose heater. The longer the distance between the nose heater and the emitter, the greater is this condensation effect. Raising the temperature of the heater inside the extractor, the only other heating element in the ion source, did not significantly reduce this effect. Moreover, higher temperatures can lead to more fragmentation of the molecular ions of normal paraffins. Fortunately, these two opposing effects (adsorption to increase ion yield and condensation to decrease ion yield) can be balanced to achieve experimental conditions where the carbon number distribution of a compound series can be determined without significant distortion. For low carbon number species, some are lost during vaporization on the moving belt for solvent removal. These compounds also contribute less to FI spectra because they have a smaller tendency to adsorb on the emitter than higher carbon number species.

Our next objective was to determine the FI sensitivities of different types of molecules in the saturate fraction of oils. We measured the sensitivities of six compounds representative of paraffin and naphthene types: *n*-dotriacontane, *n*-octacosane, 3-ethyltetracosane, squalane, cholestane, and *n*-nonadecylcyclohexane. Under conditions optimized for normal paraffins (200 °C source temperature, 20 mA SIP current and 30 mA flash current), the molar sensitivities of normal paraffins and naphthenes were found to be comparable

(16) Schulz, C.; Chowdhury, S. K.; Blum, S. C. *Anal. Chem.* **1993**, *65*, 1426–1430.

(17) Ryska, M.; Kuras, M.; Mostecky, J. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *16*, 257–267.

(18) Kuras, M.; Ryska, M.; Mostecky, J. *Anal. Chem.* **1976**, *48*, 196–198.

(19) Ferris, S. W. *Handbook of Hydrocarbons*; Academic Press: New York, 1955.

Table 1. Relative Molar Sensitivity of Six Model Compounds in FIMS (Normalized to *n*-Nonadecylcyclohexane)

compound	rel molar sensitivity based on	
	molecular ions	alkyl ions
<i>n</i> -dotriacontane	1.00 ± 0.12	0.06 ^a
<i>n</i> -octacosane	1.03 ± 0.11	0.06 ^a
3-ethyltetracosane	0.05 ± 0.008	0.65 ± 0.07
squalane	0.03 ± 0.006	0.74 ± 0.04
cholestane	1.00 ± 0.16	0
<i>n</i> -nonadecylcyclohexane	1.00	0

^a Obtained from mass spectrum of pure compound.

(Table 1). However, isoparaffins undergo significant fragmentation, resulting in more than an order of magnitude reduction in sensitivity when only molecular ions are measured. This is illustrated by the mass spectra in Figure 3 of a normal paraffin, *n*-octacosane, and an isoparaffin, squalane (2,6,10,15,19,23-hexamethyltetracosane). Figure 4 shows how the spectrum from the mixture of the six compounds noted above contains molecular ions from the normal paraffins and naphthenes as well as alkyl fragment ions mainly from the isoparaffins.

Individual compound measurements showed that fragmentation of the naphthenes, i.e., cholestane and *n*-nonadecylcyclohexane, was minimal (<2%). Normal paraffins fragment to varying degrees than naphthenes (15% fragment ions relative to molecular ions in the Polywax experiments), yielding mainly the *m/z* 29 and 43 ions at a ratio of approximately 2 to 1. Excluding the fragment ions, the molar sensitivities of the two normal paraffins are practically identical to those of the two naphthenes. The intensities of the molecular ions of the isoparaffins, on the other hand, were only about 4% relative to those of the normal paraffins on a molar basis. Alkyl ions (C_{*n*}H_{2*n*+1}) make up most of the fragment ions. The sum of the intensities of the alkyl ions (i.e., *m/z* 43 for squalane, *m/z* 29, 71, and 337 for 3-ethyltetracosane) for isoparaffins are about 0.70 relative to the intensity of the molecular ion of *n*-nonadecylcyclohexane on a molar basis. Although various degrees of fragmentation are expected for different isoparaffins, based on data from a number of 650–1050 °F saturate fractions, ions below C₇H₁₅ (*m/z* 99) make up more than 80% of the total alkyl fragment ions.

Since the intensities of fragment ions from normal paraffins are small compared to those from isoparaffins, the amounts of isoparaffins and normal paraffins can be estimated. First, the weight percent of paraffins and naphthenes can be calculated from the molecular ions of the corresponding series. In this calculation, the weight percent of paraffins is mainly due to normal paraffins because isoparaffins contribute little to the molecular ion region. The amount of isoparaffins can then be calculated from the alkyl fragment ions by assuming that the total moles of alkyl ions represent total moles of isoparaffins and that the carbon number distribution from the isoparaffins can be estimated from the molecular ion data. With these assumptions, the weight percentage of isoparaffins can be calculated from eq 1 by comparing with the 1-ring naphthenes:

$$\text{wt \% (iP)} = \frac{\text{wt \% (1-ring)} f_s \sum I_{\text{alkyl}} M_A(\text{iP})}{\sum I_{\text{1-ring}} M_A(\text{1-ring})} \quad (1)$$

where wt % (iP) is the weight percentage of isoparaffins, *f_s* is the sensitivity factor of normal paraffins relative to that of isoparaffins from alkyl fragments, wt % (1-ring) is the weight percentage of 1-ring naphthenes calculated from the molecular ions, $\sum I_{\text{alkyl}}$ is the sum of intensities of all alkyl ions from isoparaffins, and $\sum I_{\text{1-ring}}$ is the sum of intensities of all molecular ions from 1-ring naphthenes, and *M_A*(iP) and *M_A*(1-ring) are the average molecular weights of isoparaffins and 1-ring naphthenes, respectively.

In the 650–1050 °F boiling range, an isoparaffin boils at the same temperature as a normal paraffin with ~2 fewer carbons;¹⁸ i.e., the average carbon number of isoparaffins is two carbon units higher than that of normal paraffins in this boiling range. Similarly, the average carbon number of 1-ring naphthenes is also about 2 carbon units higher than that of normal paraffins. Therefore, *M_A*(iP) and *M_A*(1-ring) are about the same and can be canceled out.

To further simplify eq 1, ¹³C contributions are excluded from the terms of sum of ion intensities. About 80% or more of the total alkyl ions are C₂–C₇ alkyl ions. Less than 10% of these ions contain ¹³C isotopes. Furthermore, the error introduced by neglecting ¹³C alkyl ions is compensated by also neglecting the contribution of molecular ions containing two ¹³C isotope in $\sum I_{\text{1-ring}}$. From the two model compounds studied, *f_s* ≈ 1/0.7 = 1.4. Because the average carbon number is ~30 for 1-ring naphthenes in the 650–1050 °F fractions, a factor of 1.33 will account for the ¹³C contribution of the molecular ions essentially canceling out the sensitivity factor. Equation 1 can be rewritten as

$$\text{wt \% (iP)} = 1.4 \times \text{wt \% (1-ring)} \frac{\sum I_{\text{alkyl}}}{(\sum I_{\text{1-ring}} \times 1.33)}$$

which reduces to

$$\cong \text{wt \% (1-ring)} \frac{\sum I_{\text{alkyl}}}{\sum I_{\text{1-ring}}} \quad (2)$$

where wt % (iP) and wt % (1-ring) are the weight percentages of isoparaffins and 1-ring naphthenes, $\sum I_{\text{alkyl}}$ and $\sum I_{\text{1-ring}}$ are the sums of the intensities of alkyl fragment ions and 1-ring naphthene molecular ions containing only ¹²C isotope.

In the above equation, all molecular ions of paraffins are assumed to be derived from normal paraffins, and all alkyl ions from isoparaffins. However, for more accurate quantitation of normal paraffins and isoparaffins, the alkyl ions derived from normal paraffins should be corrected from the isoparaffins value, whereas molecular ions due to isoparaffins should also be corrected from the normal paraffin value. As mentioned previously, normal paraffins produce 15% fragmentation relative to the abundance of molecular ions (including ¹³C ions). For 650–1050 °F fractions, the average carbon number of normal paraffins is ~30, the total intensity of fragment ions from normal paraffins relative to that of molecular ions is therefore 15% × (1 + 30 × 1.1%) = 20%. Hence, to calculate the intensity (*I_{np}*) of alkyl ions due to normal paraffins, simply multiply the total intensity of ¹²C molecular ions of paraffins (predominantly normal paraffins) by 0.2.

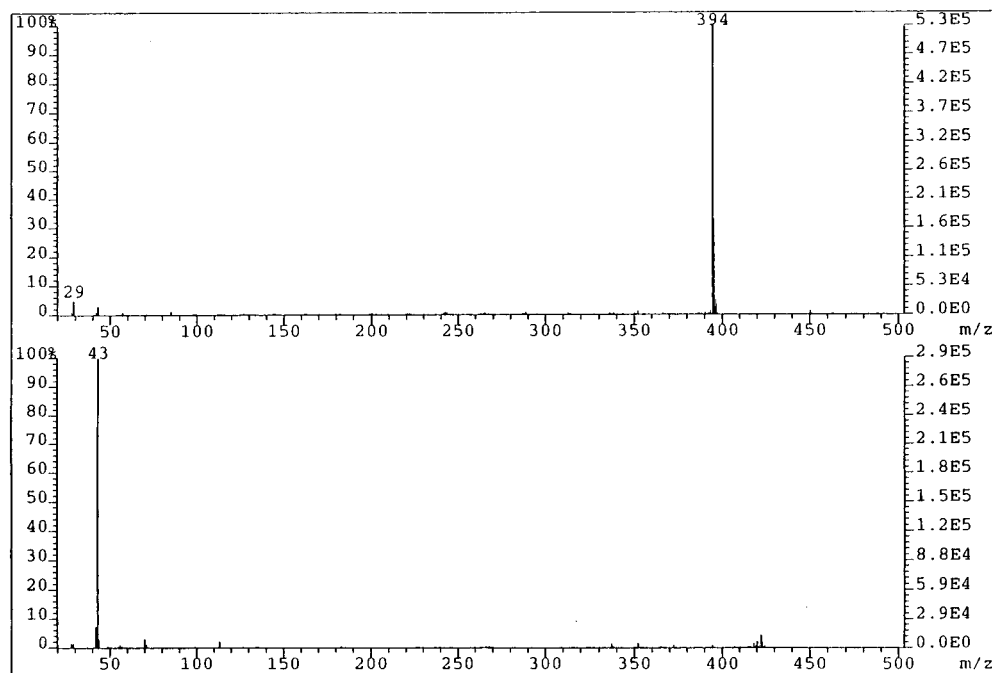


Figure 3. Field ionization mass spectra of *n*-octacosane (top) and squalane (bottom).

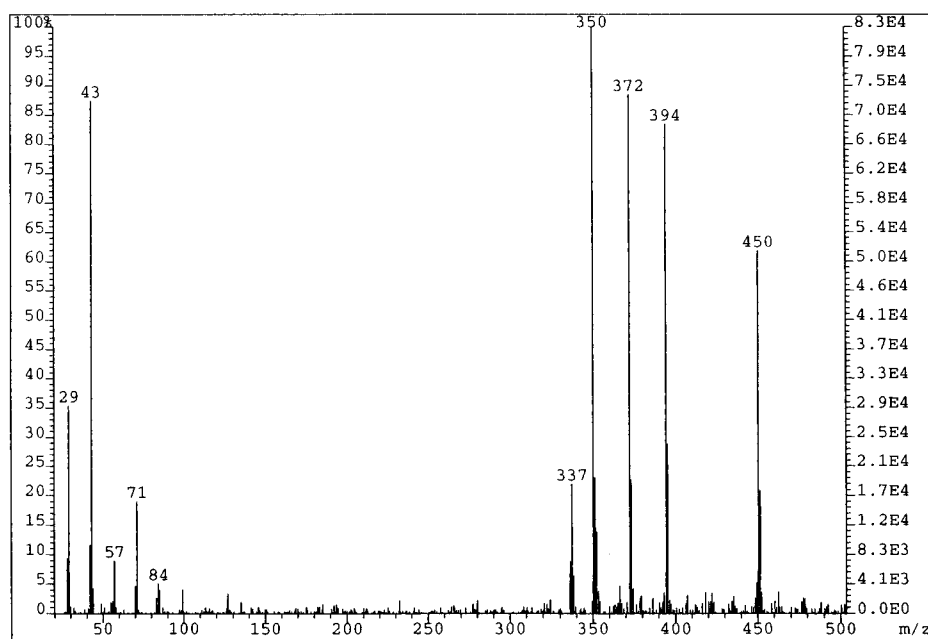


Figure 4. Field ionization mass spectrum of a mixture of *n*-dotriacontane, *n*-octacosane, 3-ethyltetracosane, squalane, cholestane, and *n*-nonadecylcyclohexane.

wt %(iP) =

$$\text{wt \% (1-ring)} (\sum I_{\text{alkyl}} - 0.2 \sum I_{\text{P}}) / \sum I_{\text{1-ring}} \quad (3)$$

On the other hand, to get the intensity (I_{IP}) due to isoparaffin molecular ions, multiply the total intensity of alkyl ions by 0.04. The normal paraffin value is then adjusted as

$$\text{wt \% (nP)} = \text{wt \% (P)} (\sum I_{\text{P}} - 0.04 \sum I_{\text{alkyl}}) / \sum I_{\text{P}} \quad (4)$$

where wt %(nP) is the weight percentage of normal paraffins, wt %(P) is the weight percentage of all paraffins, and $\sum I_{\text{P}}$ is the total intensity of ^{12}C molecular ions of all paraffins.

When normal paraffins are present in less than 5%, the correction for the contribution of molecular ions of 1-ring naphthenes containing two ^{13}C isotopes becomes necessary to quantify normal paraffins more accurately. After all of the corrections, the weight percentages of all saturated compound types are then renormalized to 100%.

Equations 3 and 4 allow us to perform type analysis of saturates fractions including quantitation of both normal paraffins and isoparaffins directly by MS. We have analyzed a set of lube basestock saturates samples by this technique, which include a saturates fraction, a dewaxed oil obtained from this fraction by urea adduction, and the recovered wax.

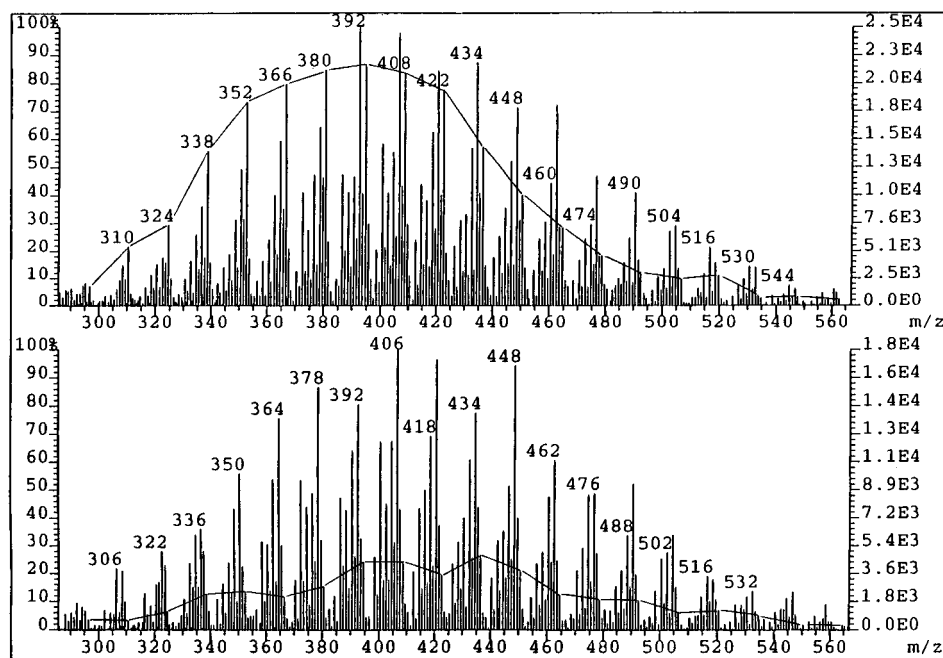


Figure 5. Field ionization mass spectra of molecular ion regions of whole saturates fraction (top) and the dewaxed oil (bottom). Molecular ions of paraffins are connected by lines for clarity.

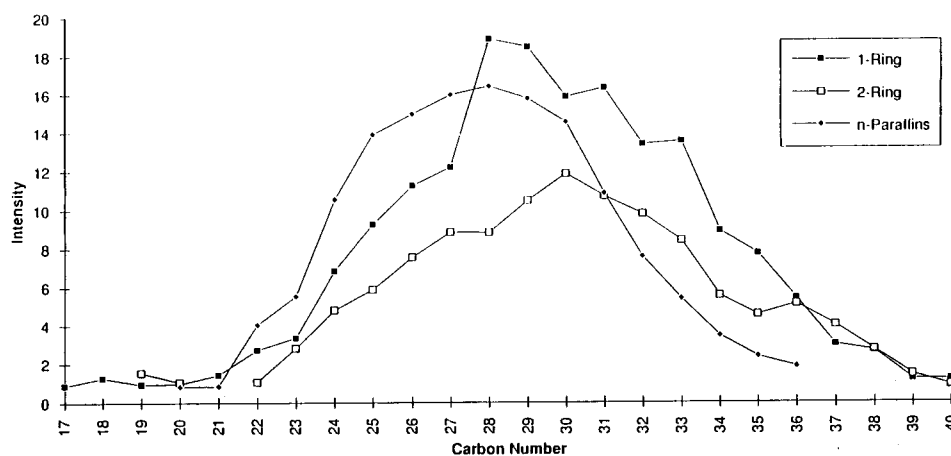


Figure 6. Carbon number distribution of normal paraffins, 1-ring naphthenes, and 2-ring naphthenes in the S150N saturates fraction.

Table 2. Normal Paraffin Concentrations Measured by GC and LC/FIMS (in Weight Percent)

	whole saturates	dewaxed oil	wax
LC/FIMS	14.7	3.2	58.2
GC ^a	13.3	1.0	54.0

^a Normal paraffins and isoparaffins obtained by GC are peaks above the envelopes of the chromatogram.

Table 3. Comparison of Measured and Actual Concentrations of Standard Compounds Added into the Dewaxed Oil in the Standard Addition Experiments (in Weight Percent, Average of Three Measurements)

compound added	measured concn		actual concn
	by LC/FIMS	by EIMS (ASTM)	
cholestane (4-ring naphthene)	8.0	18.9	9.6
nonadecylcyclohexane (1-ring naphthene)	7.0	6.4	9.0

In Figure 5, the mass spectra of the molecular ion region of the whole saturates fraction and the dewaxed oil are shown. It can be seen that the intensities of molecular ions from paraffins (m/z 338, 352, 366, 380,

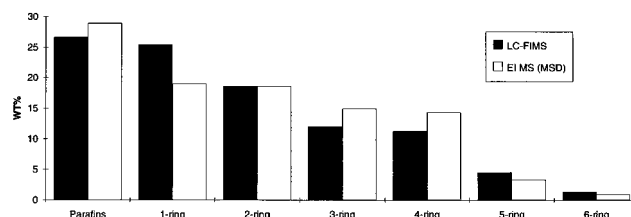


Figure 7. Weight percent distributions of paraffins/naphthene types in a dewaxed oil measured by LC/FIMS and by ASTM D2786-86 EIMS with GC and a direct insertion probe.

etc.) in the dewaxed oil are much lower than those in the whole fraction. Figure 6 shows carbon number distributions of three representative types, normal paraffins, 1-ring naphthenes, and 2-ring naphthenes, extracted from the mass spectrum of the whole saturates fraction. Notice that the average carbon number of the series increases with the ring number. The average carbon numbers of normal paraffins, 1-ring naphthenes, and 2-ring naphthenes shown are 27.9, 29.6, and 30.0, respectively.

Table 4. Weight Percentages of Paraffin/Naphthene Types in the Dewax Sample Suite

sample	nP ^a	iP ^a	1-ring Naph	2-ring Naph	3-ring Naph	4-ring Naph	5-ring Naph	6-ring Naph	2- to 6-ring Naphthenes
whole fraction	14.7	27.4	21.4	14.2	9.2	8.1	3.5	1.5	36.5
dewaxed oil	3.2	23.6	25.4	18.6	12.0	11.2	4.5	1.3	47.8
dewaxed oil (adjusted) ^b	2.4	18.0	19.4	14.2	9.3	8.6	3.4	1.0	36.5
wax (adjusted) ^c	13.8	5.7	3.7	0.5	0	0	0	0	0.5
dewaxed oil + wax (adjusted) ^d	16.2	23.7	23.1	14.7	9.3	8.6	3.4	1.0	37.0

^a nP = normal paraffins and iP = isoparaffins. ^b The adjusted values of the dewaxed oil are the normalized values multiplied by 0.764 (recovery rate, see text). ^c The adjusted values of the recovered wax are the normalized values multiplied by 0.236 (the weight percent that removed as wax from the saturates fraction). ^d The sum of the adjusted percentages of the dewaxed oil and the recovered wax for material balance.

At the present time, no existing techniques can provide accurate quantitation for all saturate compound types in a 650–1050 °F boiling fraction of petroleum. We obtained the quantitation of normal paraffins by GC for comparison with the FI results. Table 2 lists the concentrations of normal paraffins of the separate lube basestock sample suite measured by GC and LC/FIMS. In the whole saturates fraction, GC measured 13.3% of normal paraffins, compared with 14.7% by FI. In the recovered wax, GC gave 54.0% of normal paraffins, while FI showed 58.2%. For these two samples, GC and FI measurements on normal paraffins are in good agreement. In the dewaxed oil, the normal paraffins measured by GC and FI are 1.0% and 3.2% respectively. The difference is probably due to the fact that for FI, the correction for isoparaffins is only accurate to ~1% absolute, whereas for GC, the measurement of small paraffin peaks on a big isoparaffins and naphthenes envelope reduces the accuracy of measurements. Overall, the comparison suggest that the normal paraffin values by FI agree with those by GC.

We also compared the compound type distribution of a dewaxed oil obtained by FI with that by the ASTM D2786 high-voltage EIMS method, shown in Figure 7. The values of paraffins, 2-ring, 5-ring, and 6-ring naphthenes are in good agreement. The differences in the rest of the types are all within ~5% in absolute weight percentage, the kind of difference in results (reproducibility) typically obtained at different laboratories by the ASTM method.⁵

In order to evaluate the accuracy between the two methods among the types that show differences, we conducted two simple standard addition experiments. Either *n*-nonadecylcyclohexane or cholestane was added into the dewaxed oil in a ratio of 1 to 10. The concentration of each standard compound measured by FI and EI is compared with its actual concentration to identify which technique gives better quantitative results. As suggested in Table 3, FI produces more accurate results than the ASTM EI method for the types that these two methods do not agree.

Returning to the lube basestock suite, the FI results of the recovered wax show 58.2% normal paraffins, 24.1% isoparaffins, and 15.5% 1-ring naphthenes. The 2- to 6-ring naphthenes are basically untouched by urea adduction; therefore, these multi-ring naphthenes can be used as internal standards for material balance. The

weight distributions by FI for the whole saturates fraction, the dewaxed oil, and the recovered wax are shown in Table 4. The totals of weight percentages of multi-ring naphthenes for the whole fraction and dewaxed oil are 36.5% and 47.8% respectively. Because these multi-ring naphthenes are not removed in the dewaxing process, one can use these two numbers to calculate the amount of material recovered in the dewaxed sample. We find $100 \times 36.5/47.8 = 76.4\%$ recovered; the actual recovery rate is 74.7%. When the normalized weight percentages of 2- to 6-ring naphthenes in the dewaxed oil are multiplied by 76.4%, their values matched closely with those of the whole fraction. Because the wax recovered represents 23.6% of the whole fraction, the weight percentages of paraffins and 1-ring naphthenes in the wax have been adjusted accordingly. The adjusted percentages of paraffins/naphthenes in the wax are added back to those of the dewaxed oil. Their sums agree well with the percentages of corresponding paraffin/naphthene types in the whole fraction; which is a strong indication of the accuracy of the LC/FIMS technique.

Conclusion

We have successfully reconfigured a commercial field ionization (FI) source to accommodate the moving-belt interface for on-line LC operations. The on-line technique eliminates tedious and time-consuming preparative methods and reduces sample size for better chromatographic separation. This novel combination generates molecular ions for normal paraffins and naphthenes but significantly fragments isoparaffins. By combining these molecular and fragmentation characteristics, we can quantify the distribution of saturated hydrocarbons in 650–1050 °F boiling range oils into naphthenes, normal paraffins, and isoparaffins with a single MS analysis.

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