

High-resolution MS coupled to Photoionisation-GC×GC for Petrochemicals Characterisation

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The trend in shifting focus from petrochemical refining to the downstream industry brings new analytical challenges for advanced characterisation of feedstocks, including structural elucidation of hydrocarbons, heteroatom impurities and functional biomarkers in petroleum products. Comprehensive GC (GC×GC) as a separation technique coupled with high resolution (HR) MS is almost invariably required to tackle such complex matrices. Soft ionisation coupled to GC×GC-HRMS can add several other dimensions on top of GC×GC separation for in-depth elucidation. A new generation soft-ionisation technique, photoionisation (PI) has shown to enhance analyte speciation by providing superior data on both molecular ions and structurally significant fragment ions at low-energy PI mass spectra.

Introduction

The analysis of hydrocarbon classes as well as heteroatom impurities in different feedstock has long been an established practice in chemical industries as this information is used as input feed vector to calculate the cracking value of the feedstock, processability evaluation and also as indication for predicting possible fouling. The majority of those low-to-middle distillate feedstock is easily amenable via GC using classic gas or liquid sample introduction techniques. However, the sheer number of compounds in such distillate petrochemical samples quickly exceeds the available peak capacity of single-column GC techniques [1]. Consequently, the use of multidimensional separation techniques is essential. Despite the superior separation achieved by GC×GC, the identification of individual compounds in complex petrochemicals remains challenging where the majority of compounds in a hydrocarbon class displays similar skeleton-spectra at conventional EI (70 eV) ionisation energies. Moreover, new generation feedstock, like pyrolysis oil from mixed plastic waste, often brings complexities, as those are highly abundant with heavily branched alkanes, alkenes, olefins and diolefins together with numerous groups of heteroatom (O, N, S, and Cl etc.) impurities.

Although mass spectral fragmentation is useful for molecule identification via

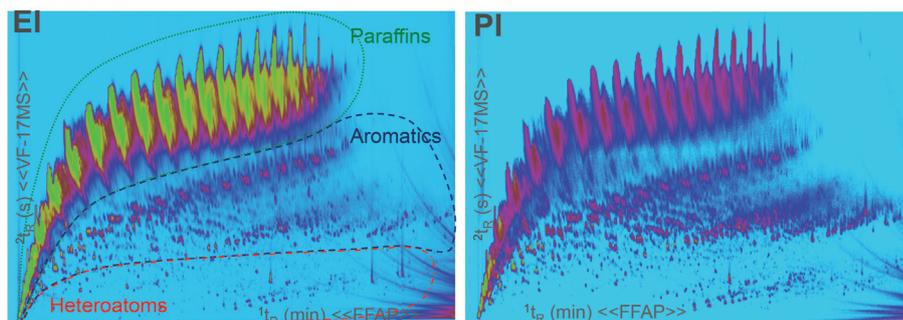


Figure 1: GC × GC-TOF/MS contour plots of pyrolysis oil sample for EI and PI revealing selectivity towards different ion sources as visualised by 2D plots using reverse phase column configuration ($1t_R$: first dimension retention time; $2t_R$: second dimension retention time).

comparison of fragmentation patterns to spectral libraries, for many chemical classes, particularly for hydrocarbons, identification of compounds with isomeric structure or alkyl series is often ambiguous due to lack of molecular ion information [2]. One of the major approaches to ensure high yields of molecular ions is lowering ionisation energies (or soft ionisation) by providing minimal excess internal energy to the compounds resulting in limited or no fragmentation. Among several soft-ionisation techniques available for GC-MS like field ionisation (FI), chemical ionisation (CI), cold EI, variable ionisation [3], increasingly popular studies support the view that photoionisation (PI) may become a major universal and standard soft ionisation technique [4]. The enhanced sensitivity and selectivity stemming from the dramatic reduction in fragmentation at low energies

in PI greatly increases the number of compounds identified, permitting effective comparisons and chemical fingerprinting of petrochemicals. High resolution and tandem mass spectrometry are very often and effectively used in conjunction with gas chromatography as mass spectrometers with high resolving power becoming more and more available, affordable and popular. The correct usage of three virtues: resolving power, sensitivity and high data acquisition speed creates the opportunity for novel GC×GC methods with improved reliability and lower detection and quantitation limits for both targeted and non-targeted analyses.

In this study, the application of photoionisation (PI) coupled with GC×GC-HRTOF-MS was evaluated. This soft-ionisation technology was shown to enhance analyte speciation by providing superior

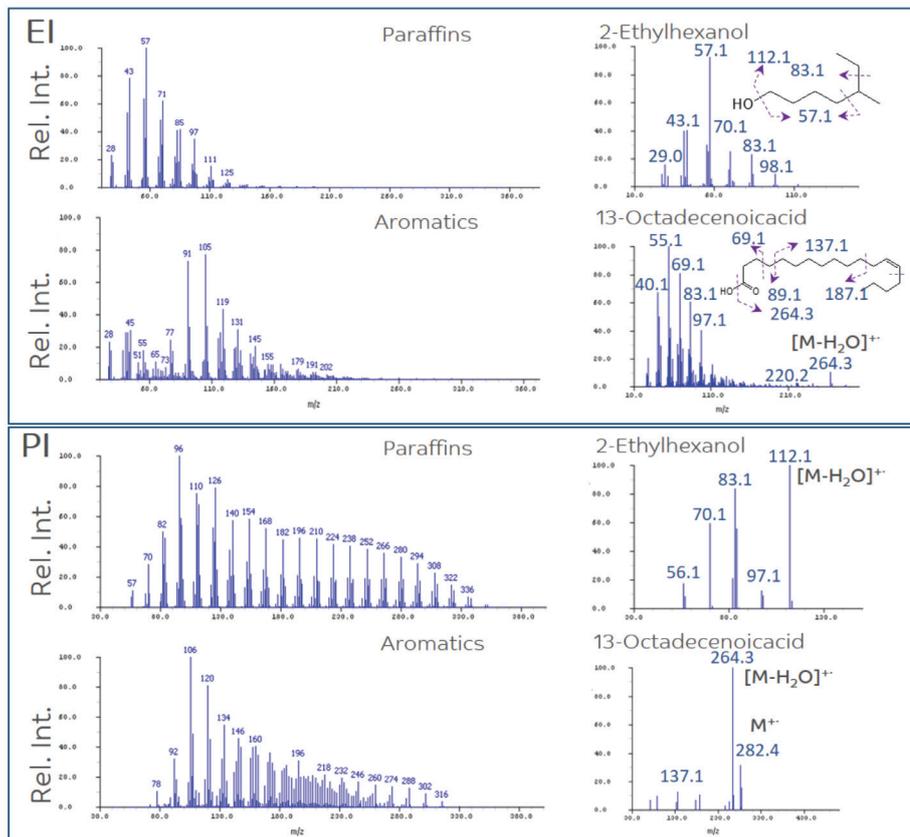


Figure 2: Mass spectra revealing ionisation impact on alkane and aromatic classes specified in Figure 1, as well as for compound specific ionisation impact of EI and PI.

data on both molecular ions and structurally significant fragments in low-energy (10.8 eV) PI mass spectra.

Experimental

Reverse and normal phase GC×GC column setups comprised of an Agilent 7890B gas chromatograph equipped with a split/split-less injector at 300°C were used to analyse pyrolysis oil (pyoil) from mixed plastic waste. Helium was used as the carrier gas in constant flow mode with a flow rate of 1.3 mL min⁻¹. The order of columns in reverse phase GC×GC was- 1st column: 30 m polar, Zebron ZB-FFAP; and 2nd column: 3.7 m polar, Agilent VF-17ms. The chromatographic analysis commenced with an oven temperature at 60 °C for 1 min; then programmed at 2°C min⁻¹ up to 260°C; and held there for 5 min. Normal phase configuration was as follows: 1st column: 30 m apolar, Rxi® 1Sil MS; and 2nd column: 2 m polar, Rxi® 17Sil MS. Analysis commenced with an oven temperature at 60°C for 0.2 min; then programmed at 2°C min⁻¹ up to 280°C; and held there for 5 min. Modulation was performed with a cryogenic thermal loop modulator ZX-1 (ZOEX Corporation, USA) with a modulation time of 16 s and 7 s for reverse and normal phase, respectively.

An EI/PI combination ion-source (JEOL, Japan) was used to ionise chromatographically separated compounds eluted in ion-block. A deuterium lamp (L7293; Hamamatsu, Japan) was used for photon emission in PI with a maximum energy output of 10.78 eV at 118 nm. A time-of-flight mass spectrometer (AccuTOF GCv 4G, JEOL, Japan) was used to acquire data at a mass resolution of >10,000 FWHM. Data processing and visualisation was done based on GCImage (v-2.6, ZOEX Corporation, Houston, U.S.A.) and mMass software (V.3, open source).

Results and Discussion

Figure 1 shows the contour plots obtained from EI and PI for a pyrolysis oil sample. In the reverse phase GC×GC condition developed in this study, first dimension separation was based on polarity and second dimension separation on volatility. It allowed a nice separation for the majority of the heteroatoms by stripping off those polar compounds from the major apolar hydrocarbons. EI and PI contour plots revealed that although the majority of the chemical classes were ionised by both EI and PI, relative intensity indicated more selectivity of PI towards aromatic and heteronate compounds than paraffinic and naphthenic ones. Noteworthy to mention is that commonly two types of PI are used - single photon ionisation (SPI) and resonance enhanced multi-photon ionisation (REMPI). Among those, SPI is considered as relatively universal and REMPI is selective mainly towards aromatics. Current PI configuration is based on SPI, thus a universal selectivity was observed covering both paraffinic as well as poly-aromatic compounds.

The comparison of cumulative global mass spectra of a pyrolysis oil for EI and PI (Figure 2) revealed exhaustive fragmentation in EI leading to the smaller fragments of homologous series of butyl, pentyl, hexyl (m/z 57, 71, 85, respectively) etc, together with corresponding alkenyl and alkynyl carbocations (loss of 2H or 4H, respectively) with limited or no presence of molecular ions for paraffins. For aromatic zone, a series of fragments at m/z 91, 105, 119, and 133 and so on, signified cleavage of C–C bond next to methyl substituted alkylbenzene ring (mono-, di-, tri-, tetra-methyl, respectively). For both paraffinic and aromatic zones, prominent ions in EI spectrum were odd-mass fragment ions. On the other hand, PI not only retained the molecular ions but also

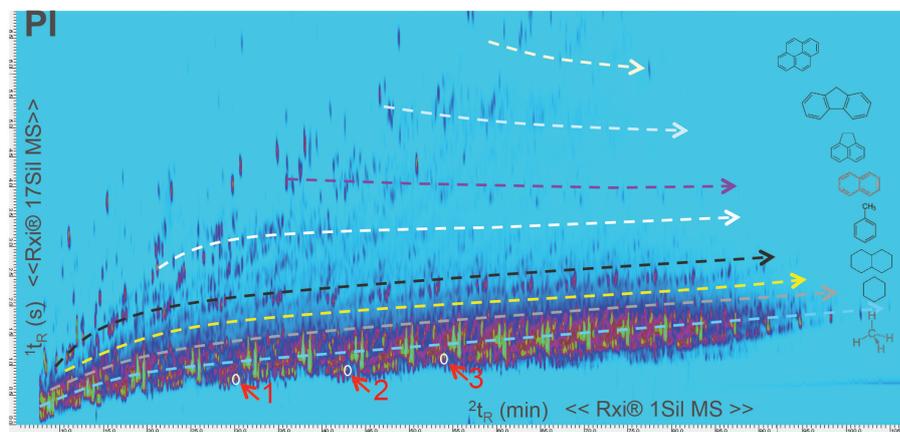


Figure 3: GC×GC TOF/MS contour plots of pyrolysis oil sample for PI revealing elution patterns of hydrocarbon group types as visualised by 2D plots using normal phase column configuration (t_R : first dimension retention time; $2t_R$: second dimension retention time).

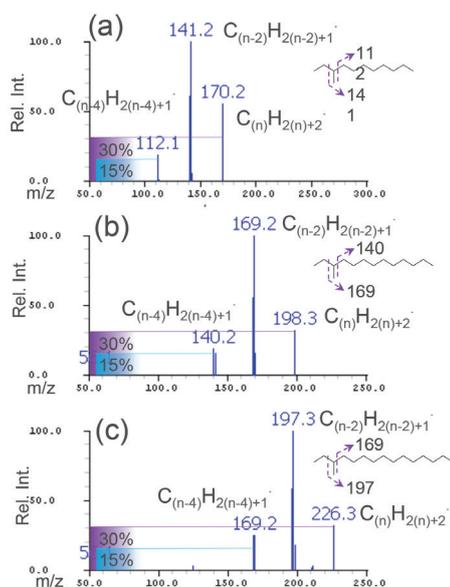


Figure 4: Mass spectra of 3-methyl isoparaffins (a-C12, b-C14, and c-C16 pointed in Figure 3) confirming the fragmentation hypothesis presented. Pattern recognition of major fragments enables scripting to identify/extract the information on isomers.

exhibited significant even-mass fragment ions. These characteristic even-mass fragment ions could be generated either from the molecular ions or corresponding to naphthenic and aromatic rings, or from the secondary carbocation at C–C bond adjacent to tertiary carbon atom followed by a hydrogen rearrangement. In PI, the absorption of photon by a gaseous molecule resulted in molecular radical cation as the primary product. Fragment ions might be generated as a result of absorption of a photon by a primary photo-dissociation product, neutral loss from the radical ions, and ionic fragmentation during photoionisation step.

Mass spectral patterns of selected heteroatoms (2-Ethylhexanol, 2-EH; and 13-Octadecenoic acid, 13-OA) for EI and PI are presented in Figure 2. 2-EH, a primary alcohol, exhibited small or nonexistent molecular ion by EI. Moreover, cleavage of the C–C bond resulted in series of ions corresponding to alkyl chain breaking. However, PI fragmentation resulted dehydrated molecular ion ($M-H_2O$) as a base peak. This agrees with previous literature referring to dehydration of alcohols by the hot surface of the ion-source system [2]. PI also exhibited loss of ethylene, propylene, butylene, etc. as a result of McLafferty rearrangement. For 13-OA, PI exhibited both molecular (M) as well as dehydrated molecular ion ($M-H_2O$) as base peak. However, EI, though

retaining lower amount of dehydrated molecular ion, mainly exhibited series of ions corresponding to alkyl chain breaking, making the identification indecisive. Similarly, by retention of molecular ions and other structurally important ions by using PI, identification of several other classes of heteronates including, alcohols, acids, ketones, nitriles, phenols, thiols etc were confirmed.

For conventional group type analysis, classic normal phase column configuration is preferable as typical structured pattern of separation for several groups of hydrocarbons including n paraffins, iso paraffins, monocyclic, dicyclic, polycyclic saturated, and aromatic compounds etc, could be easily achieved (Figure 3). GC×GC being widely orthogonal compared to 1D GC separation, compounds were separated in the first dimension based on volatility and in the second dimension based on polarity. Therefore, the molecular mass, one of the most selective information, is highly related to the elution order of the corresponding compound. On the other hand, along the second axis relatively apolar saturated alkanes were eluted first followed by saturated and aromatic cyclics with increased polarity.

The fragmentation pattern for n-paraffins and isoparaffins at EI generally reveals clusters of peaks 14 mass unit apart representing loss of $(CH_2)_nCH_3$ with limited or no presence of molecular ion. In contrast, the superficial fragmentation achieved by PI greatly simplified mass spectra with reduced background noise as well as enhanced molecular ions for hydrocarbons. For paraffinic compounds, PI retained molecular ions and predominant ions signified the probability of cleavage at lower state of excitement, revealing the branching position. The structured elution pattern of branched alkanes in GC×GC revealed several mono-, di-, and heavily branched alkanes for pyrolysis oil.

Elution of 3-methyl alkanes belonging to C12, C14, and C16 is shown in Figure 3. Corresponding PI mass spectra agrees with the postulated structures as shown in Figure 4. Further, the fragmentation pattern of 3-methyl alkanes can be generalised as follows for the 3 major fragments: 1. molecular ions- $C_{(n)}H_{2(n)+2}$; 2. base peaks- $C_{(n-2)}H_{2(n-2)+1}$; 3. daughter ions- $C_{(n-4)}H_{2(n-4)+1}$ as shown in Figure 4. Such pattern recognition of the classes or even sub-classes of hydrocarbons followed by weighing out the patterns (relative intensity 30%, 100% and 15%, respectively) can potentially

be used to design scripting for isomeric species identification and extraction of other relevant information from PI.

PI also resulted in dominant molecular ion ($M+$) and the ions at m/z 82 and 68 for alkylcyclohexanes and alkylcyclopentanes respectively, related to the corresponding ring. Methyl-substituted isomers were tentatively identified by the presence of molecular ions and predominant ions at m/z 96, 110, 124 and 138 for alkylcyclohexane and at m/z 82, 96, 110 and 124 for alkylcyclopentane corresponding to the C–C cleavage of the alkyl chain from methyl substituted ring. For bi-cyclic and polycyclic naphthenics as well as aromatic compounds, PI resulted exclusively molecular ions; thus EI remains advantageous to elucidate isomeric species by providing molecular ions as well as structurally important fragment ions.

Chromatographic resolution achieved by GC×GC can be synergised by soft-ionisation, and can further be enhanced by coupling high resolution (HR) MS to extract useful information from molecular ions. Depending on the mass resolving power used, HRMS has the ability to resolve

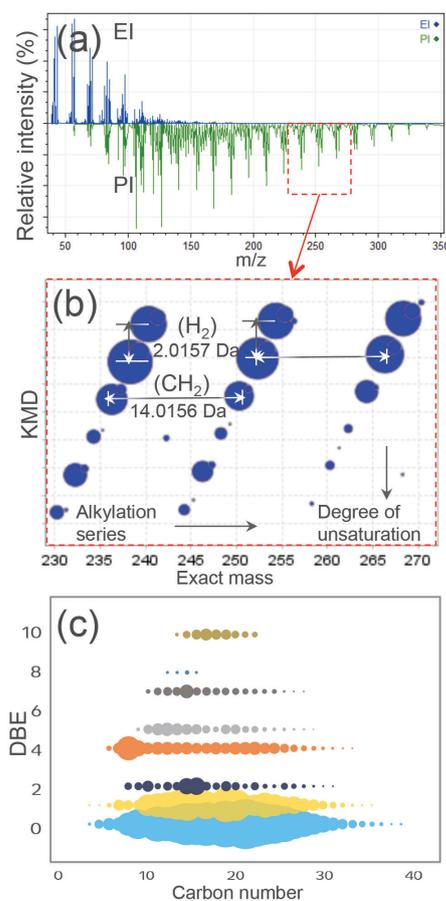


Figure 5: Cumulative global mass spectra obtained from EI and PI for pyrolysis oil sample (a); Kendrick Mass Defect (KMD) plot for zoomed area of PI revealing alkylation and double bond equivalent (DBE) series (b); and carbon number vs DBE plot (c).

very narrow mass differences between isobars, eg, C₃ vs SH₄ (0.0034 Da), CH₂ vs N (0.0126 Da), and CH₄ vs O (0.0364 Da) (required resolving power at m/z 300 of 89 000, 24 000, 8400, respectively). It is highly unlikely that such isobars occupy the same 2D time space in GC×GC; thus, resolving power requirement would be much lower. GC×GC PI HRMS with prominent molecular ions can add several other dimensions on top of two dimensional chromatographic separation. Added dimensions could be: 1) near unambiguous mass determination; 2) detection of heteroatom classes; 3) degree of unsaturation; 4) carbon number characterisation; and 5) elemental compositions. These could be used for improved visualisation and characterisation of petrochemicals. As shown in Figure 5, a significant retention of molecular ions could be achieved in PI compared to EI. Cumulative spectra achieved through PI-HRMS could further be treated to generate

Kendrick Mass Defect (KMD) plot to reveal and compare the distribution of alkyl series and abundances of classes with different degrees of saturation. In addition, m/z to C:H ratio, carbon number to C:H ratio, or m/z to DBE etc. could be plotted for improved visualisation of data.

In conclusion, PI plays a greater role in isomeric species identification of paraffinic and heteronate compounds as it generates molecular ions as well as structurally important fragment ions. However, for bicyclic, or polycyclic naphthenic, and monoaromatic compounds, EI still remains advantageous. GC×GC Soft-ionisation (PI) followed by high resolution MS analysis enables confirmation of structures/ formulae as well as improved visualisation of data.

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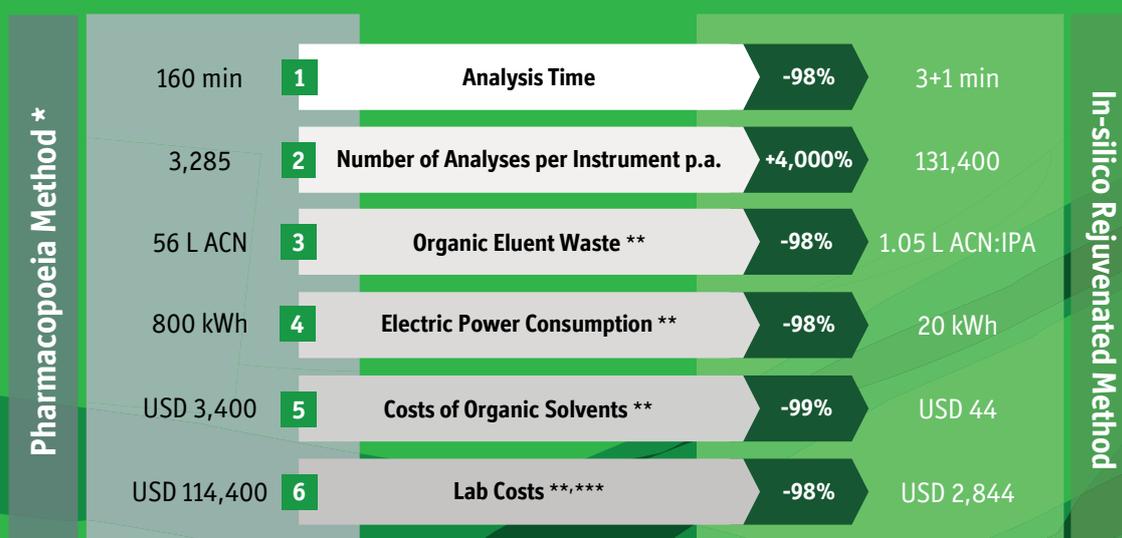
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