THE VERSATILITY OF TIME-OF-FLIGHT MASS SPECTROMETRY FOR THE INVESTIGATION OF PETROLEUM DERIVED MATRICES – FROM MIDDLE DISTILLATES TOWARD VACUUM RESIDUES

Petroleum derived matrices are very challenging to analyze in a comprehensive manner and a single analytical techniques mostly fails to cope with all different chemical and physical properties such as isomeric complexity, boiling point range or polarities of such matrices. Therefore, a wide range of analytical standard techniques have to be applied and combined to ensure the comparability and quality of the different feedstock and products. Nevertheless, mass spectrometry became a key technology in this field and is applied alone or in hyphenation with other mainly chromatographic techniques to investigate the qualitative and quantitative composition of petroleum matrices. Time-of-flight mass spectrometry (TOFMS) is maybe the most versatile mass spectrometric technique, since it combines a high acquisition rate with high mass resolution and accuracy as well as the capability to acquire full mass spectral information.

All these aspects makes TOFMS very versatile for combination with a wide range of chromatographic and thermal separation techniques as well as ionization techniques. This manuscript will focus on some of these hyphenations with the aim to cover the full boiling point range starting from middle distillates towards vacuum residues based on time-of-flight mass spectrometry (e.g. LECO Pegasus GC×GC-TOFMS and GC×GC-HRT platforms).

The analysis of middle distillates and next generation fuels with comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry:

Comprehensive two-dimensional gas chromatography (GC×GC) has matured over the last 20 years as a key technology for the analysis of volatile petroleum derived matrices. Middle distillates with a boiling range of 165 – 350 °C are well suited for GC×GC and in industry mainly robust flame ionization detectors are applied as detection system allowing straight forward quantification. However, in most cases the separation power of GC×GC is not sufficient for full resolution of individual compounds or even compound classes within middle distillates. The application TOFMS overcomes this obstacle and the fast acquisition frequency together with full spectral information allows a selective separation

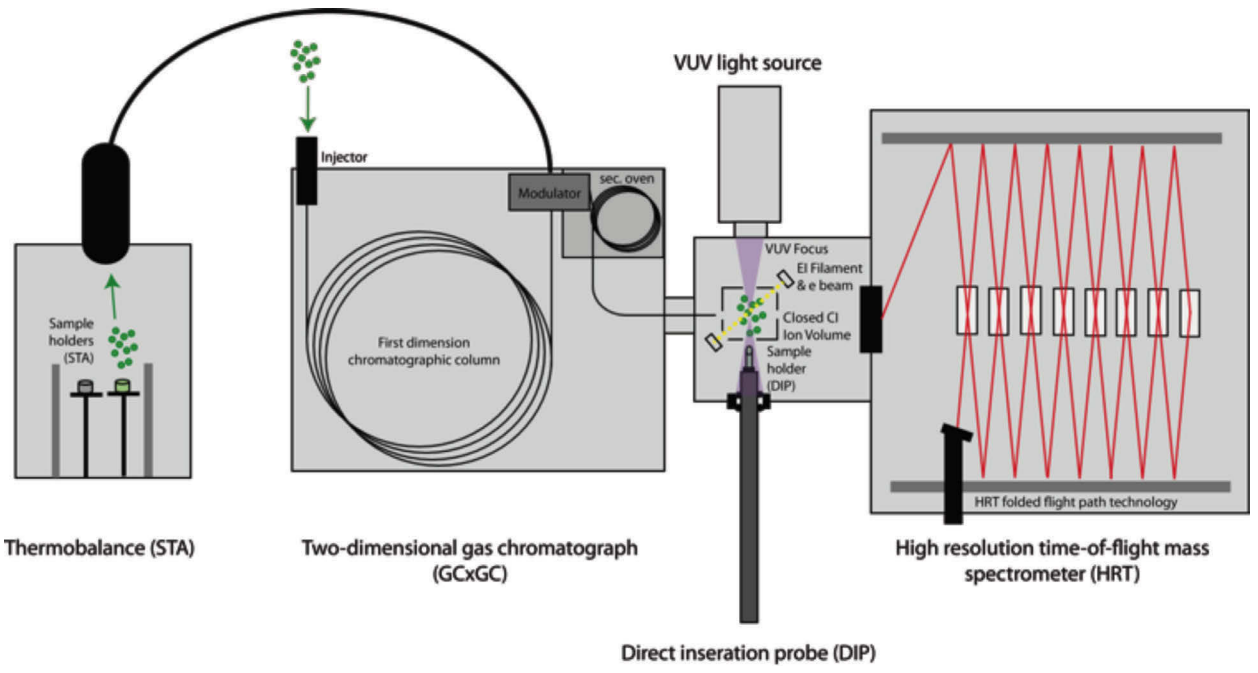

Figure 1: Schematic of a combined analytical system based on a LECO Pegasus GCxGC-HRT.

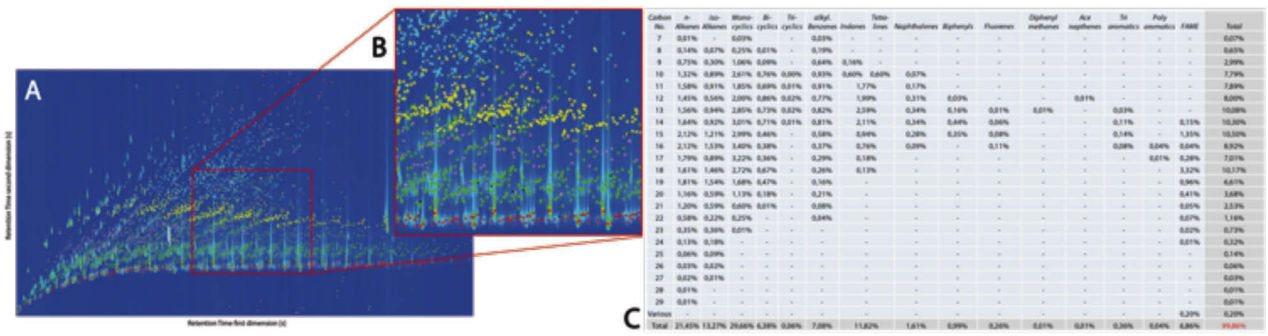

Figure 2: Middle distillates could be analyzed almost comprehensively by GC×GC-TOFMS. (A): Due to the combination of a two dimensional separation with mass spectral information for each peak a classification of compound classes and carbon number could be achieved. (B): The selectivity of TOFMS allows a differentiation of overlapping compounds classes. (C): Peak data could be used for an absolute quantification of individual compound and an assignment to compound classes and carbon numbers.(Sample: B5 Diesel fuel)

of compound classes. A straightforward deconvolution with spectral and retention information in two dimensions can be used to specify compounds according to their chemical class as well as carbon number. This scripting and classification approach is based on a typical elution pattern of compound classes over the two-dimensional separation plane as well as the investigation of typical spectral features of a 70 eV nominal mass fragmentation pattern. The quantification is more challenging than with FID but could be solved with a sophisticated calibration, which benefits from the linear response of the homologues of a compound class with increasing carbon number over the complete boiling point range of middle distillates. About 99 % of the injected middle distillates matrix could be associated to more than 15 compound classes and its carbon number. Quantification could be done in m/m % and due to the high selectivity of the method, different EN Methods could be addressed with a single analysis.[1]

The implementation of TOFMS makes the method also very robust to changes in the composition of the matrix. Most EN Methods are specified for certain concentration ranges and compositions of the middle distillates and could fail for uncommon or modern matrices in the range of middle distillates. An example could be modern fuels based on HVO or oxyblends with either an unbalanced composition or non-fossil composites. In such cases, the usually applied "mean" calibration of these standard methods in combination with non-selective detection systems will lead to substantial miss quantification. Highly selectivity GC×GC-TOFMS will allow also the quantification of such matrices with a high degree of reliability.[2]

Extending the range of GC×GC-TOFMS for the analysis of heavy petroleum derived matrices – light crude oil and heavy fuel oil.

The volatility and thermal stability of the compounds are the most limiting constraints for the application of GC×GC-TOFMS. Technical limitations, such as the temperature limits of the injection or detection method, as well as the thermal stability of the polar phases applied for GC×GC have to be considered. In addition, also the complexity of the matrices in terms of compound classes as well as isomeric composition is increasing with increasing boiling point and could overcome the selectivity of GC×GC-TOFMS. The targeted boiling point range also includes more feedstock and intermediates matrices, which are also not fully specified in terms of their chemical composition compared to their derived fully refined products. Therefore, the "conventional" GC×GC-TOFMS method has to be adjusted towards higher temperatures and adapted for the higher complexity. However, the necessary adaptions often have contrary effects. e.g. shortened columns which are operating close to their temperature limit provide less separation while the complexity of the matrix will increase. To compensate for such a decrease in selectivity but also to cope with new compound classes, high resolution and accurate mass time-of-flight mass spectrometry (HRT) becomes the preferred detection system.

Modern HRT systems are ideal for the application to GC×GC due to their high acquisition speed and sensitivity but also provide enough resolution and mass accuracy to allow identification and differentiation of compound classes based on the obtained elemental composition information and fragmentation information. With this approach GC×GC-TOFMS could be further extended towards the boiling point limit and typical matrices such as light crude oils or heavy fuel oils. The HT-GC×GC-TOFMS/HRT approach allows a similar classification as for middle distillates but also includes additional compound groups such as nitrogen and sulfur containing species, which are found in crudes and intermediate matrices. The high mass accuracy and resolution also enables the differentiation of species such as oxygenated species, which are eluting in the same area but also often show a similar fragmentation pattern as some pure hydrocarbon species. Besides differentiation, elemental compositions could be derived for the majority of mass spectral fragments. The introduction of accurate mass derived plots like Kendrick mass defect or double bounds equivalent allow a straight forward visualization and direct comparison of even very complex matrices. For the vaporizable part of the matrix a similar itemization according to carbon number and compound class could be achieved as for middle distillates. Absolute quantification is also possible if standard materials are available to generate group specific response curves. A very detailed relative comparison based on abundance signals is always possible and allows the identification of changes within the matrix.[3]

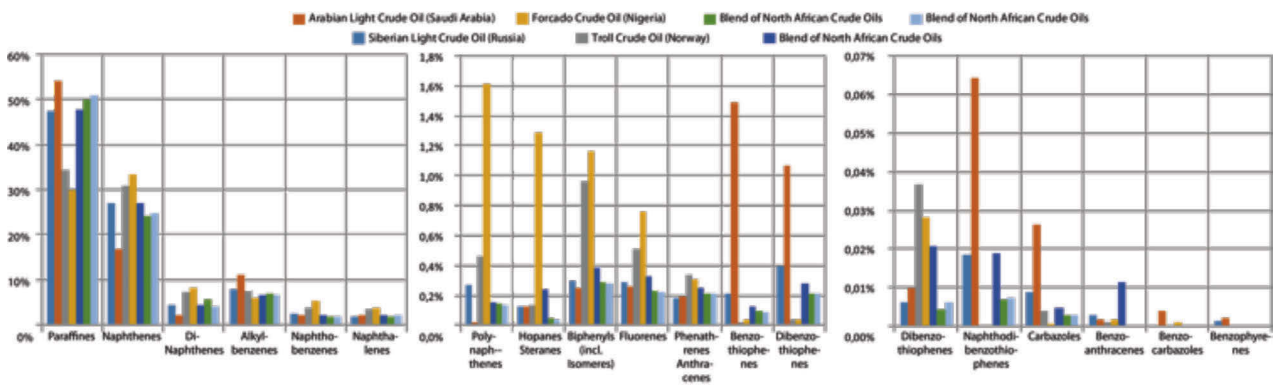

Figure 3: Comparison of different crude oils and blend based on a detailed chemical analysis obtained by GCxGC-TOFMS. The assignment to the compound classes was confirmed by accurate information obtained by high-resolution time-of-flight mass spectrometry.

The two-dimensional approach could be further extended and combined with basic specification methods for petroleum to derive and predict fundamental parameters for refining. Based on the GC×GC-TOFMS/HRT a high temperature two-dimensional simulated distillation (2DSimDist) could be established. Virtual boiling point cuts are generated and conferred to the chromatographic plane. The quantitative information is similar to the standard 1D approach but a much more detailed qualitative and quantitative itemization according to the compound classes is achieved.

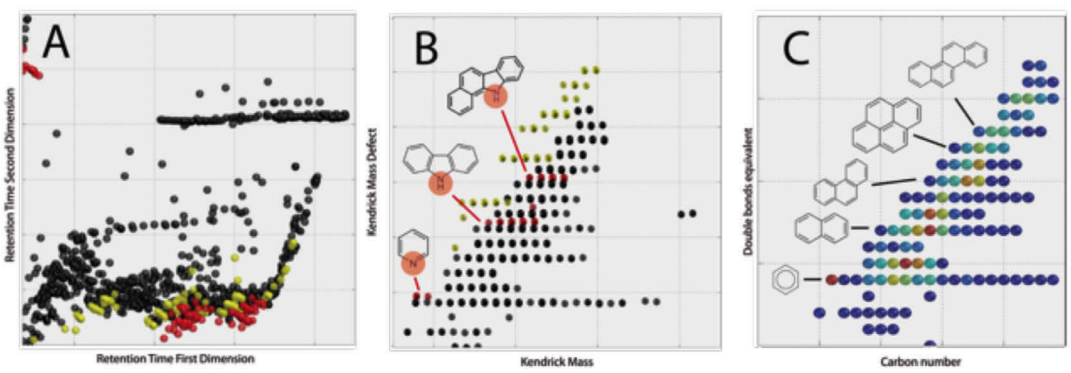

Figure 4: Accurate mass information could be also transformed into elemental formula information for compound class assignment (A), Kendrick mass defect calculation (B) or double bond equivalent information (C). The isomeric information achieved due to chromatographic resolution could be included. E.g. Color coding in plot C reflects the number of detected isomers. (Sample: Heavy fuel oil)

Applying high resolution and accurate mass spectrometry for matrices towards the atmospheric boiling point limit and above – Vacuum residues.

At some point GC will reach it temperature limit and for some compound classes thermal degradation will start before they are volatilized and in such cases GC×GC will no longer be applicable and direct mass spectrometric methods could be an alternative. The HR-TOF technology already discussed in combination with its gas phase ionization sources offers some possibilities to deal even with such heavy matrices and e.g. thermal analysis (TA) can be applied as introduction method for the HRT. For the given approach TA methods are generally divided into setups working under a defined atmosphere at pressures ranging from sub-ambient to increased pressure like thermogravimetry (TG) and methods working under highly reduced pressure such as direct insertion probe (DIP). However, TA only provides temperature resolved fundamental physical data like weight loss or heat consumption. Selective chemical information can be only derived from subsequent evolved gas analysis (EGA). In this respect, an appropriate ionization technique is essential for an in-depth chemical description. Electron impact (EIMS) and photoionization mass spectrometry (PIMS) are particularly well suited for Evolved Gas Analysis (EGA). Both techniques can be used for a wide range of compound classes ("universal ionization") and are not very prone to produce ionization artefacts. In particular, PIMS allows the determination of the molecular signatures (i.e. intact organic molecules) derived from desorption-, pyrolysis- and combustion-processes. If EI is applied, a pre-separation step is indicated to reduce the complexity of the spectral information. Thermal gravimetric analysis (TGA) and direct insertion probe (DIP) were directly hyphenated to the existing ion source of the HRT system. TGA-HRMS analysis for heavy crude oil enabled the separation of components due to their boiling point under atmospheric conditions. Higher temperatures will lead to a thermal fragmentation of the residual substances. The thermal processes within the thermo balances could be separated and homologous series for pure hydrocarbons as well as heteroatom-containing molecules are assigned for the rearrangement, evaporation and pyrolysis steps. The validity of the chemical fingerprints are further enhanced due to an implemented modulation-GC separation step.

DIP-HRT allowed the introduction of sample material directly into the ion source, where a temperature gradient could be applied. The low pressure in the ion source increases the volatility of high boiling components and reduces the effective boiling point, which leads to non-destructive volatilization.[4] Results for DIP-CI-HRT and DIP-SPI-HRT showed the advantage of a less destructive ionization technique, especially if no preceding chromatographically separation could be applied.

Conclusion:

The time-of-flight mass spectrometry platforms described show a high versatility for the investigation of petroleum-derived matrices. In combination with two-dimensional gas chromatography an unmatched selectivity could be achieved for the analysis of middle distillates and the same approach can be extended towards higher boiling matrices. A decrease in chromatographic resolution can be counterbalanced due to the application of high resolution and accurate mass time-of-flight mass spectrometry. For non-volatile matrices and residues direct mass spectrometric techniques like thermal balances and direct insertion probes are available for these high esolution time-of-flight platforms. Optional soft gas phase ionization techniques further promote a more detailed investigation.

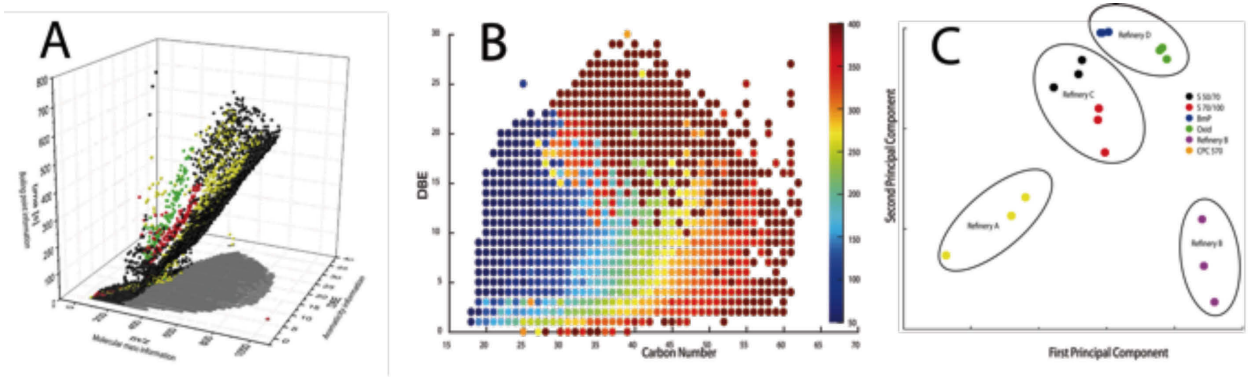

Figure 5: Analysis of Bitumen by DIP-HRT. (A): Three-dimensional illustration of the bitumen sample. Each dot represents a confirmed mass signal. The color-coding illustrates the assignment to a chemical species (heteroatoms) based on the calculated elemental composition. (B): Two-dimensional illustration of the first occurrence temperature for the evaporation compounds. Accurate mass information allows an calculation of double bond equants and carbon numbers. (C): The DIP-HRT approach also allows a quantitative comparison of different samples. Samples could be grouped according to their chemical composition.

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