Petroleum derived matrices are very challenging to analyze in a comprehensive manner and a single analytical technique 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.

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.
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 fractionation 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 ppm % 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 mass quantification. Highly selectivity GC×GC-TOFMS will allow also the quantification of such matrices with a high degree of reliability.[2]

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 straightforward 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]

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 isometric 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 adaptations 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 pressure intermediate time-of-flight mass spectrometry (HRT) becomes the preferred detection system.

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 confirmed to the chromatographic plane.

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 ionization.[A] Results for DIP, C3H5R and DIP-SpHR-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 resolution 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

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Pro-ASTM Centrifuges Combine Accuracy, Strength and Style

Centurion Scientific (UK) have been global leaders in the production of benchtop centrifuges since the 1980’s. The company prides itself on using only the most robust and best quality components that make up their centrifuges.Whilst design is important to Centurion, they recognise the importance of functionality and reliability, their centrifuges have both in abundance and they also minimise noise levels to ensure that their instruments are seen but not heard. Centurion’s Pro-ASTM range is specifically designed to meet the needs of labs within the hydrocarbon processing sector, whilst adhering to Centurion’s tradition of combining strength with a striking and contemporary design. Such is their confidence in Pro-ASTM, a 3 year warranty is standard on all models. Pro-ASTM Centrifuges are all heated types and operate from ambient temperatures to 90 degrees Celisus. These units are part of a wide range that can be operated via basic LED buttons to a Premium 155 mm version, with a touch screen format. Models are available on a bench with a trolley, which means the instrument takes up no work area as this unit can be stored underneath the bench. Users can also opt for a floor standing combined unit with castors, which allows them to operate the centrifuge on any sturdy, level surface, this can be wheeled anywhere within the lab – and stored under the bench. Pro-ASTM centrifuges are equipped with imbalance, overheat and over-speed detection devices, lid closure, barrier rings and exhaust areas to ensure maximum safety for operators. Labs needing to work with ASTM D1295, D1796, D1996, D2273, D1996, D2273, D2709, D2711, D4007, D5546, D893, D895, D906, ITMS 791 Methods 3000, 3003, 3004, 3101, 3121, 5861, API 2543, 2548, ISO 3734, 9030, DIN 51793 and NF M 07-020 need look no further! The Centurion team listened to their customers when designing Pro-ASTM. The customers wanted a centrifuge that was easy and safe to use, accurate, quiet, flexible with sample assistance, fast pelleting and avoided initial sample side deposits – and Centurion can now give them just what they want, backed up by an expert service team.

New UHPLC guard cartridges deliver ultimate protection for 1.8 μm Raptor columns

Raptor 1.8 μm LC columns unleashed superior Raptor performance on UHPLC analyses, and now Restek has released EXP UHPLC guard column cartridges made specifically for Raptor 1.8 μm columns. These new guards provide extreme protection from particulates and matrix contamination, extend the lifetime of already rugged and long-lasting Raptor columns, and are proven to withstand the same UHPLC pressures as their analytical column counterparts. UltraShield filters are available for filtering out particulates, minimizing extra column volume, and maximizing sample throughput when using SPE, SLE, or other extensive sample preparations—but new Raptor EXP UHPLC guard column cartridges are an especially valuable alternative when using dilute-and-shoot or other minimal sample preparation techniques. Further extend the life of your 1.8 μm Raptor UHPLC columns today at www.restek.com/raptor

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New cloud point option for diesel fuel analysis

Cloud point is the temperature at which wax crystals are first observed in the liquid sample upon cooling under prescribed conditions. It is an important physical property for estimating diesel fuel performance under cold temperatures since wax formation can cause flow performance issues such as fuel filter clogging. The ASTM D975, Specification for Diesel Fuels, specifies the manual cloud point testing method D2500 as the referee method. Although the manual method maintains its significance from its history and its position as the referee method, it is a heavily time/labour consuming test, and the judgement of the cloud point is highly dependent on the operator’s skill which often times can result in poor precision and accuracy. In the latest version (2975-17a), the ASTM committee has approved the addition of D7683 Standard Test Method for Cloud Point of Petroleum Products (Small Test Jar Method) as an alternative to the manual method.

Tanaka Scientific’s MPC models which automatically run cloud point tests according to D7683 offers simple and precise measurements. Compared to the manual method, testing time is reduced by more than 50%, and sample volume by 90%. Pour point can also be measured simultaneously according to ASTM D6749 on the same sample. Precision is significantly improved due to automation. Furthermore, the MPC models allow for 1 °C test intervals for pour point and 0.1 °C intervals for cloud point which helps the user achieve even more precise results. Model MPC-1025 uses advanced refrigerant-free cooling technology without the need for connection to an external refrigerated chiller which saves lab space and eliminates maintenance of refrigerant and coolant.

For More Info, email: 45201pr@reply-direct.com


