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PYROLYSIS-GC×GC-QTOF FOR IMPROVED CHARACTERIZATION OF CRUDE OILS.

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Crude oil consists of an extremely large amount of compounds covering a wide range of volatility and chemistry. This makes detailed composition characterization highly challenging.

Pyrolysis coupled to comprehensive two-dimensional gas chromatography-high resolution mass spectrometry (py-GC×GC-HRMS) is a very powerful technique for the characterization of complex, heavy matrices such as crude oils. The two-dimensional resolution provides enhanced separation of the pyrolysis products, leading to improved classification for groups and individual analytes. Additionally, the 2D pyrograms make sample comparison easier and more informative. In addition, high resolution and accurate mass can deliver extra selectivity and identification power, especially for compounds with heteroatoms (e.g. N, S, O).

Here we show the use of py-GC×GC for improved characterization and comparison of crude oils and the advantages arising from HRMS detection for speciation of heteroatoms such as sulfur-containing compounds.

Experimental details

Samples: three different crude oils of different origin. These were analyzed directly by pyrolysis at 750°C for 15 seconds.

	Type	Origin	Density (°API)	Sulfur content (%, w/w)
Sample A	HOOPS	Texas, USA	31.4	1.00
Sample B	Arabian	Saudi Arabia	31.1	2.48
Sample C	Vasconia	Colombia	24.2	0.56

All measurements are performed with a CDS Pyroprobe 5200 coupled to an Agilent 7890B GC equipped with a Zoex ZX2 cryogen-free thermal modulator and an Agilent 7200B QTOF Detector. The QTOF is operated in Extended Dynamic Range (EDR) acquisition mode and the maximum acquisition speed of 50 Hz. All 2D data are visualized and processed with the GC Image HR software package

Results

Fig. 1 shows the 2D separation obtained for the crude oils. As can be seen, the two-dimensional chromatographic separation allows for the efficient separation of different chemical groups fully co-eluting on the non-polar primary column and are hereby effectively separated based on polarity on the second dimension.

The 2D plots include a template designed to outline the distribution of the main aliphatic and aromatics hydrocarbons groups. The amount of each group is clearly different in the 3 samples: sample B is mostly aromatic, with significant paraffinic content and very low in naphthenes; samples A and C are mostly naphthenic but sample C has more paraffins while being clearly poorer in aromatics. These differences are illustrated in Fig. 2.

Fig. 1
TIC 2D plots for crude oil A (top), B (middle) and C (bottom)

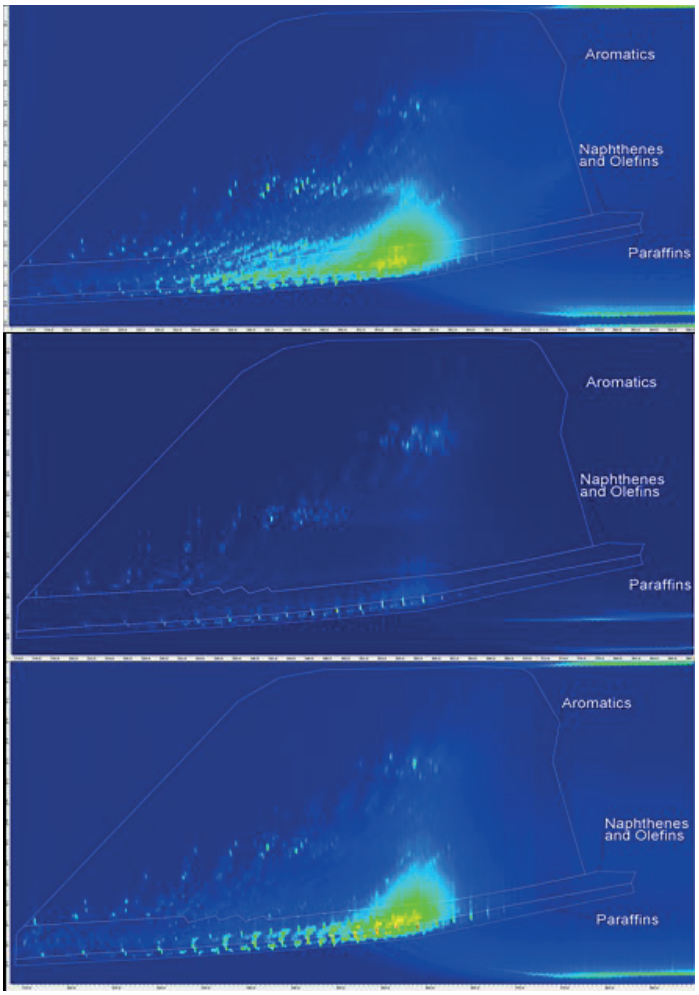
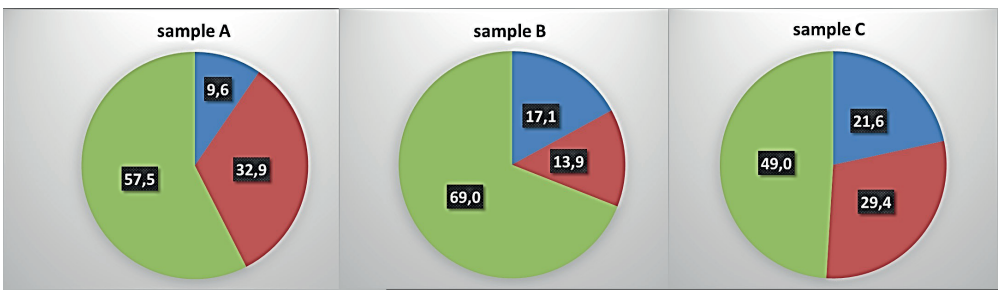


Fig. 2
TIC percent response for paraffins (blue), naphthenes/olefins (red) and aromatics (green).



Thanks to the enhanced resolution it is also possible to detect discrete differences down to individual-compounds level. Fig. 3 shows an example of how the *Compare Images* tool of the GC Image software can be used to create differential images that highlight visually sample differences in response in a quick, simple way.

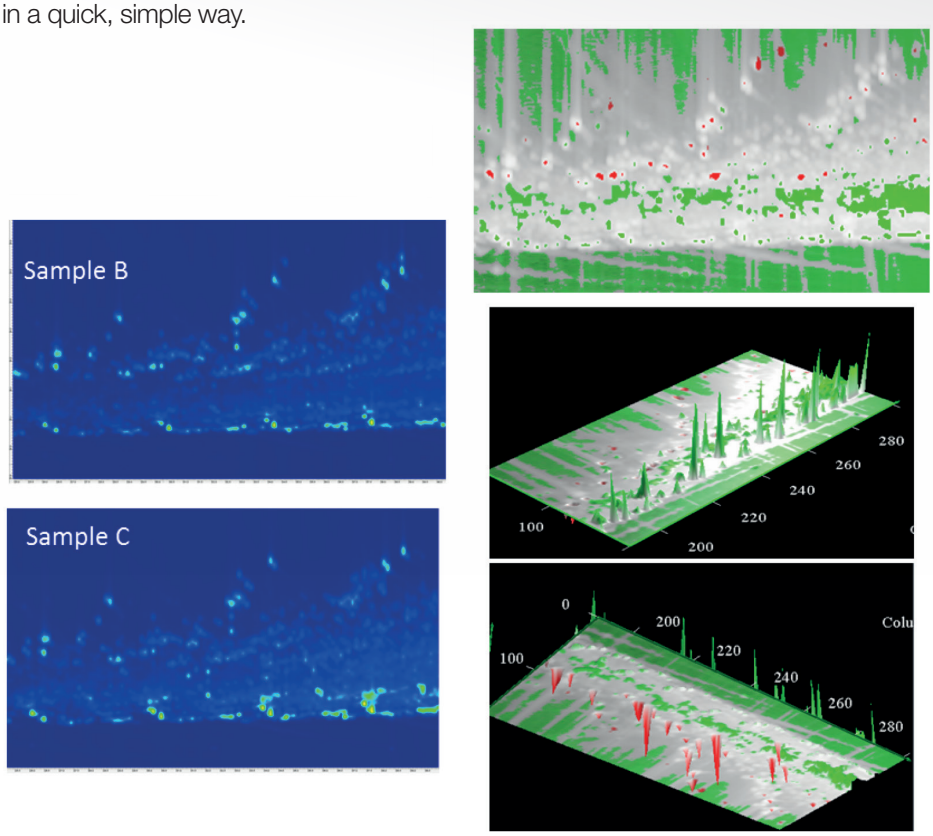


Fig. 3
Zoom-in of a complex area (left) and relative differential image (sample B as reference) with corresponding 2D views (right). The green and red areas refer to higher and lower responses, respectively.

Given their high relevance for the petrochemical industry, we focus on evaluating the presence of sulphur-containing compounds of potential interest. Fig. 4 shows as an example part of a template that indicates the location of the dibenzothiophenes with different degree of alkyl-substitution, constructed by looking for the masses corresponding to the specific molecular formulas. The figure shows the example for dibenzothiophenes with 3 methyl groups. These are fully separated by the large aliphatic signal on the secondary column, making detection and identification (and potentially quantification) much easier and more accurate. Numerous isomers are present, differing only on the position of the alkyl-substitutions. Some blobs are fully co-eluting on the primary column and, given the fact that the MS spectra will be close to identical, can be resolved and distinguished as different compounds only thank s to the enhanced two-dimensional resolving power.

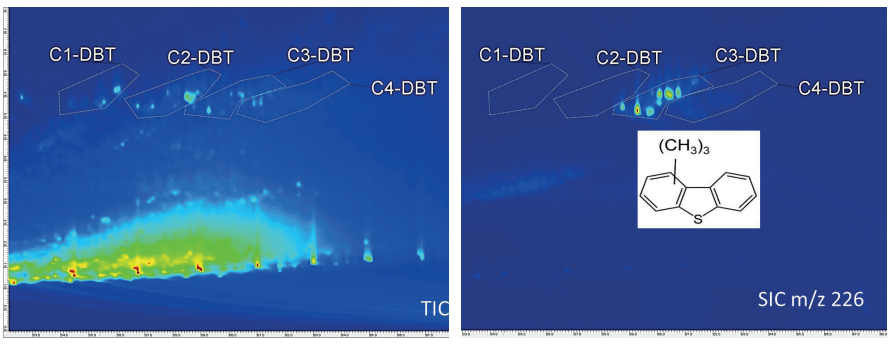
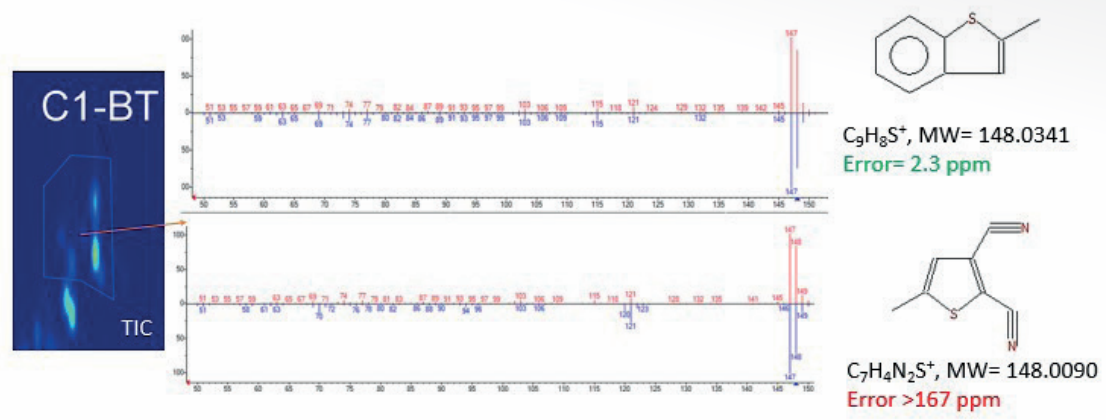


Fig. 4
TIC 2D plot (left) and Selected Ion Chromatogram (right) with template showing the location of dibenzothiophene (DBT) groups with different degree of alkyl-substitution for sample A.

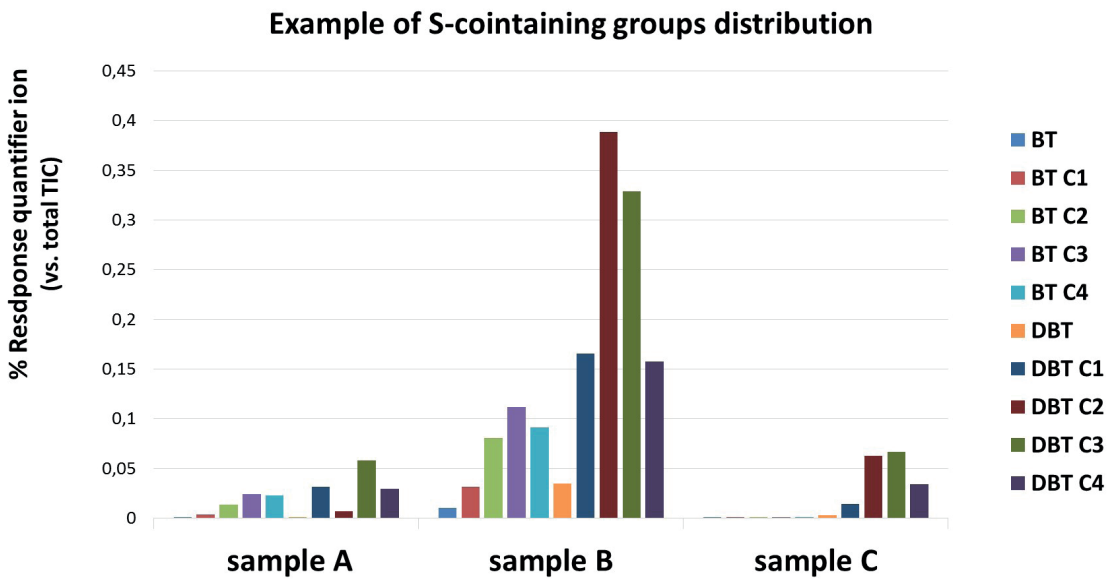
Mass accuracy is used to link high resolution spectra with a specific formula and obtain identity confirmation. An example is shown in Fig. 5, where the ambiguous library search result obtained for an S-containing molecule is integrated by formula generation to give high confidence identification.

Fig. 5
Example of confident identification of a minor sulphur compound of molecular mass 148.0338 m/z with uncertain library search thanks to accurate mass and formula generation.



The template is applied to all samples for automated identification and quantification of the target chemical groups selected as test. Fig. 6 summarize the percent response results obtained. The samples are now differentiated based, not only on their total different sulphur content, but also on the specific (sub-)groups or individual compounds (Fig. 7) to provide a much more detailed and accurate characterization.

Fig. 6
Distribution of some benzothiophenes (BTs) and di benzothiophene (DBTs) groups. The quantifier is the molecular ion, the response is expressed as percent of the total TIC signal.



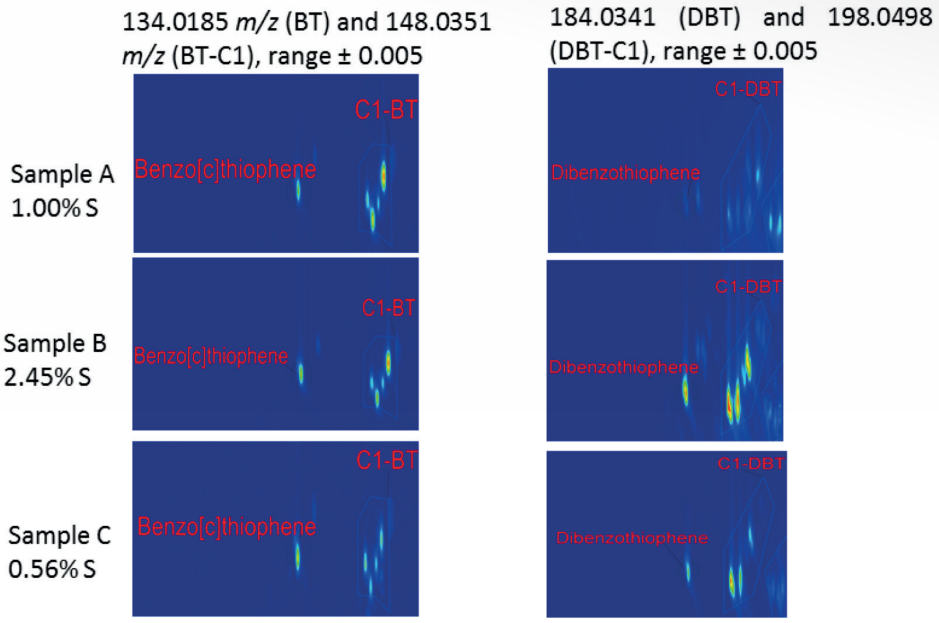


Fig. 7
Distribution of some benzothiophenes (BTs) and di benzothiophene (DBTs) groups in the three samples.

CONCLUSIONS

- Pyrolysis-GC×GC-QTOF is a very powerful technique for in-depth characterization of complex, heavy matrices such as crude oil.
- 2D patterns allow for easier target identification and profiling of unknowns and are remarkably effective for group analysis and fingerprinting.
- HRMS detection grants enhanced selectivity and allows for more confident identity confirmation (targets) or tentative identification (unknowns).
- HRMS detection is especially powerful for the characterization of heteroatomic compounds.