PYROLYSIS-GC×GC-QTOF FOR THE IMPROVED CHARACTERIZATION OF CRUDE OIL

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1. Introduction

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-mass spectrometry (py-GC×GC-MS) 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 spite of the enhanced separation power offered by GC×GC, complexity is such that complete resolution is often not possible. The use of High Resolution Mass Spectrometry (HRMS) 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 different crude oils and the advantages arising from using a QTOF detector for speciation of heteroatoms such as sulfur-containing compounds.

2. Experimental

Samples

	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

Instrument

- CDS 5200 Pyrolyzer
- Agilent 7890B GC
- Zoex ZX2 thermal modulator
- Agilent 7200B QTOF detector.

Method

Pyrolysis at 700°C for 15 s.

Inlet: 300°C. Split ratio 400:1. Flow: 0.7 mL/min. Oven : 40°C (5 min) at 4°C/min to 320°C.

Modulation period: 8 s. Hot jet pulse: 350 ms. QTOF: EDR mode, 50 Hz.

GC × GC configuration

Agilent J&W HP-5ms primary column (30 m, 0.25 mm, 0.25 µm) × deactivated fused silica loop (1 m, 0.1 mm) × SGE BPX-50 secondary column (1.8 m, 0.10 mm, 0.10 µm).

3. Results

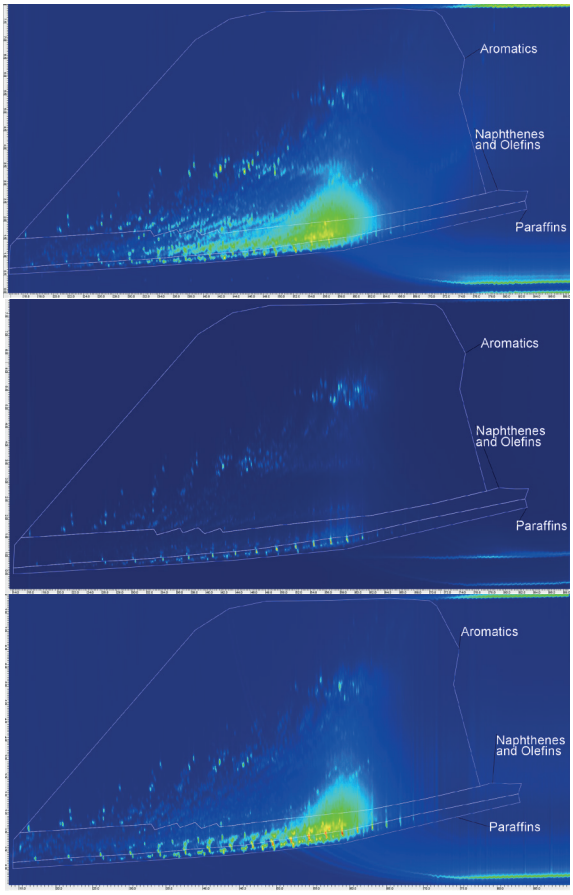

Fig. 1 –py-GC×GC-QTOF chromatograms of crude oil samples A (top), B (middle) and C (bottom).

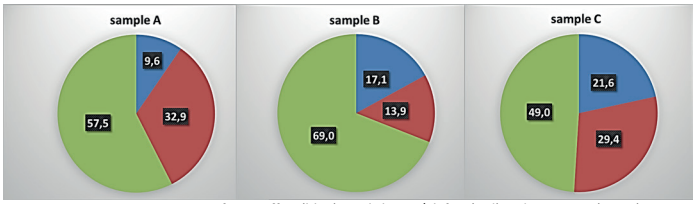

Fig. 2 – TIC percent response for paraffins (blue), naphthenes/olefins (red) and aromatics (green).

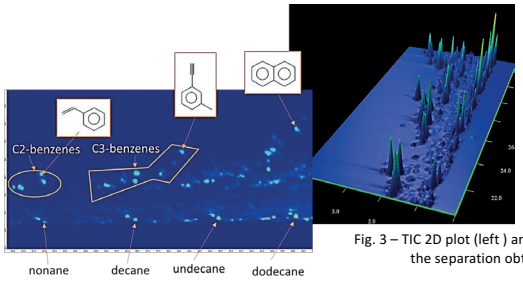

Fig. 3 – TIC 2D plot (left) and 3D view (right) of the separation obtained for sample B.

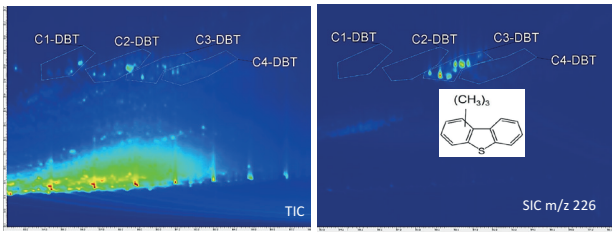

Fig. 4 – TIC 2D plot (left) and Selected Ion Chromatogram (right) with template showing the location of dibenzothiophene (DBT) groups with different degree of alkyl-substitution for sample A.

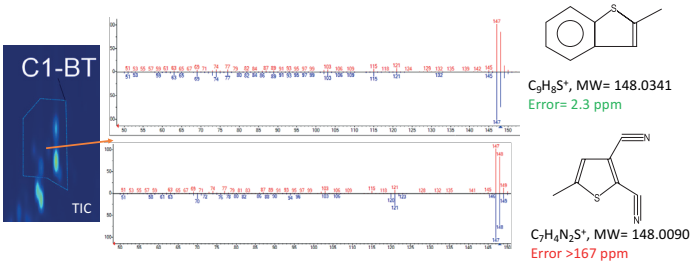

Fig. 5 – Example of confident identification of a minor sulphur compound of molecular mass 148.0338 m/z with uncertain library search thanks to accurate mass and formula generation.

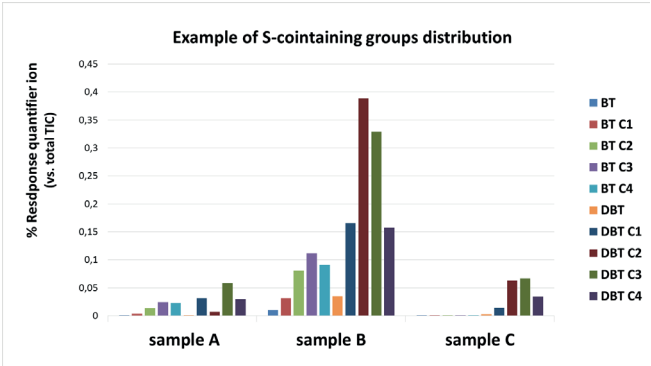

Fig. 6 – Distribution of some benzothiophenes (BTs) and di benzothiophene (DBTs) groups. The quantifier is the molecular ion, the response is expressed as percent of the total TIC signal.

4. Conclusions

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