Sustainable mobility| New energies| Responsible oil and gas

Chemometric methods applied to FT-ICR/MS data: comprehensive study of aromatic sulfur compounds in Gas Oils

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Context

- Depending on process used for Gas Oils (GO) production, several types of sulfur compounds are found in GO
- **Some aromatic sulfur compounds** contained in GO are **very refractory** to hydrotreatment (HDT)
- **APPI(+)-FT-ICR/MS** provides advanced characterization of refractory aromatic sulfur compounds for each type of GO[1]
- FT-ICR/MS analysis generate **big datasets** and require **chemometric methods** (PCA and HCA) to extract **information**

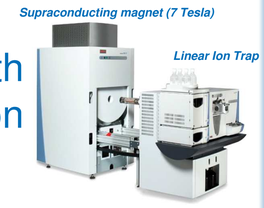
Material and Methods

Samples

23 GO from various processes* (SR, LCO, GOCK, HOIL, HYVAHL, MIX, HDT) considering 6 replicates

Experimental set-up

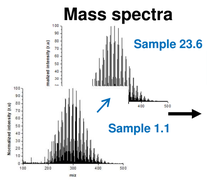
LTQ FT-ICR/MS Ultra ThermoFisher Scientific 7T used with *Atmospheric Pressure Photo-Ionization* APPI(+) ion source. 70 scans x 4 µ scans @200k



HRMS Data processing

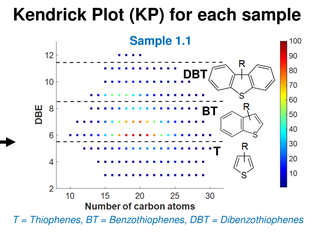
Identified compounds : $C_cH_hS_s$ with key parameters: **DBE** (aromaticity, from 1 to 25) and **nC** (number of carbon atoms – alkylation length, from 1 to 50)

Full workflow

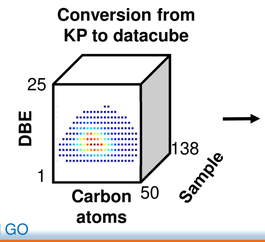


Sulfur compounds peaks list of all samples

Sample	m/z	Formula	DBE	nC	Relative Intensity (%)
1.1	162,049806	C10 H10 S1	6	10	0,0906
…			…	…	…
23.6	332,159396	C23 H24 S1	12	23	0,1359



T = Thiophenes, BT = Benzothiophenes, DBT = Dibenzothiophenes



Unfolding datacube according to DBE values

DBE	DBE 1			…			DBE 25		
nC	1	…	50	1	…	50	1	…	50
Sample 1.1	x(1,1)	…	x(1,50)	…	…	…	…	…	x(1,1250)
…	…	…	…	…	…	…	…	…	…
Sample 23.6	x(138,1)	…	x(138,50)	…	…	…	…	…	x(138,1250)

138x1250 matrix

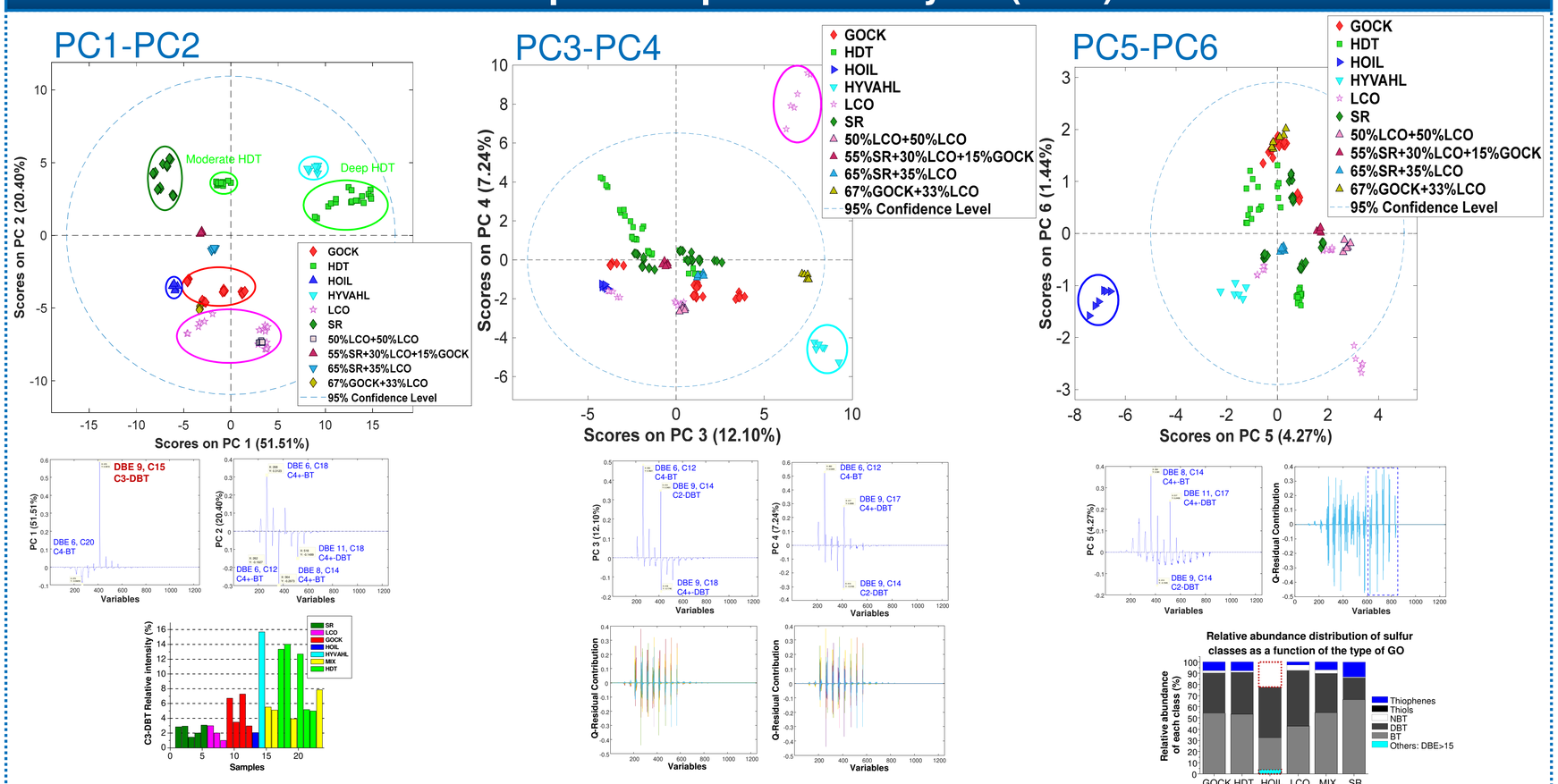
Chemometric data processing

Variables used: compounds **relative intensities**. Pre-processing: **mean-centering**. MIX samples were used as validation samples in PCA

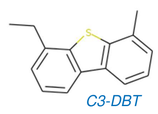
*SR: Atmospheric Distillation GO, LCO: Fluid Catalytic Cracking GO, GOCK: coking GO, HOIL/HYVAHL: catalytic hydrocracking GO, MIX: mixed GO blends, HDT: hydrotreated GO

Results and Discussion

Principal Component Analysis (PCA)



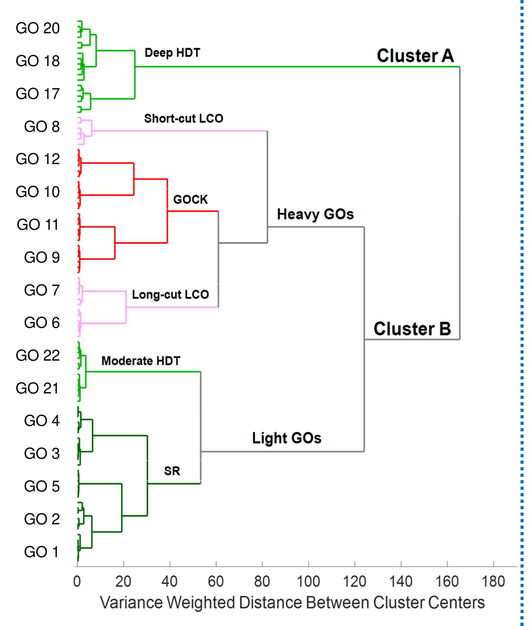
- Satisfying **replicates grouping**
- **GO grouping** depending on native process and **HDT severity speciation**
- **MIX-validation samples** located with respect to **original mix proportions**
- **C3-DBT** is mainly expressed over PC1: known to be **very refractory**[2] to HDT
- PC3, PC4 and PC5 extracted **unique** samples and **corresponding key variables**
- Loadings analysis correlated to **GO macroscopic properties**



C3-DBT

Hierarchical Cluster Analysis (HCA)

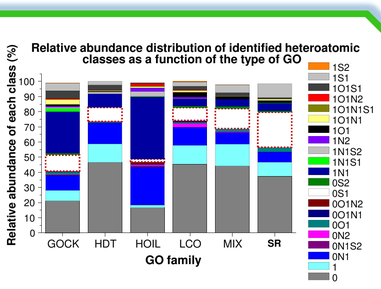
Ward's distance



- Light and heavy GO clustering
- GO with **similar characteristics** clustered together
- **HDT severity** speciation
- **Unique LCO sample** highlighted from other

Conclusions and perspectives

- **New workflow to generate datacube from Kendrick Plots issued from various samples**
- **GO clustering depending on native process observed with PCA and HCA**
- **Consistent location of mixed samples compared to original samples**
- **C3-DBT is a key variable, very refractory to HDT and highlighted among 1250 initial variables**
- **Perspectives: Data fusion first considering all identified families in APPI(+) and then 3 FT-ICR/MS ionization modes datasets**



[1] Purcell, J. M. et al. Atmospheric pressure photoionization fourier transform ion cyclotron resonance mass spectrometry for complex mixture analysis. *Analytical chemistry,* **2006**, *78*, 5906–5912.

[2] Morales-Valencia, E. M et al. Kinetic Assessment of the Simultaneous Hydrodesulfurization of Dibenzothiophene and the Hydrogenation of Diverse Polyaromatic Structures. *ACS Catalysis,* **2018**, *8*, 39263942.