AC HT CNS Simdis Analyzer - Fast crude oil characterization for sulfur, nitrogen and carbon using gas chromatography.

- Fast & simultaneous analysis of C, N & S BP Distribution
- Reports boiling range 151 °C – 700 °C (C9-C90)
- Fully implemented state of art PAC SIMDIS^{xlnc} software
- PAC SeNse chemiluminescence detector

Keywords: GC, Chemiluminescence, SeNse, Sulfur, Nitrogen, Simdis

Introduction:

Crude oil at the molecular level, is composed predominantly of carbon, which can make up as much of 87% of the material. Hydrogen is another major component that makes up as much as 15% of crude oil. Other components that are found in crude in varying amounts include oxygen, sulfur and nitrogen.

In total there are about 160 crude oils on the market, and the industry often names them based on its geographical source. For example, “Brent” or “Arab light” Besides that, it is also classified based on physical characteristics and chemical composition, and these qualities are described with terms such as “sweet,” “sour,” “light,” and “heavy.” Depending on how they are categorized, they will have different price, usefulness and environmental impact.

Low sulfur crude oil is classified as “sweet.” Crude oil with a higher sulfur content is classified as “sour.” Sulfur content is considered an undesirable characteristic for both the processing and the quality of the final product. Therefore, sweet crude is typically more desirable and valuable than sour crude. West Texas Intermediate (WTI) crude oil is a good example of sweet crude oil, while oil from Canada and the U.S. Gulf Coast tends to be sour.

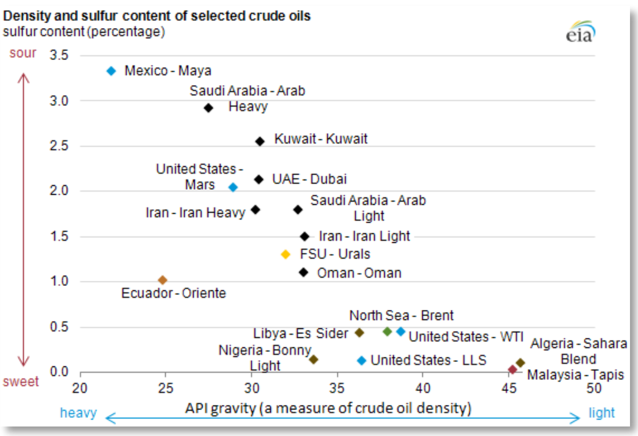

Figure 1: Sulfur content and API for various crude oils.

The value of a crude oil comes from its ability to be refined and turned into products ranging from asphalt and gasoline to lighter fluid and gases. The more valuable products that can be produced with the least effort, the higher the value of the crude for refiners but also their trading value in the marketplace will increase as ra material.

During this refinery process crude oil components containing sulfur and/or nitrogen (called heteroatomic components) can end up in the various finished products like gasoline or diesel. Depending on the amount of sulfur these products may require further processing to lower the sulfur content making sure it meets increasingly strict regulations. Furthermore, the heteroatoms may impact the performance of conversion processes due to catalyst degradation.

It is therefore of great value for refiners to know in advance how much of sulfur and or nitrogen is present in the crude and how it is distributed over its boiling range. This has become even more important with the current situation where refineries are changing their crude oil supply (or mixing different type of crude oils) more often than in the past. All related to price, market speculation and market demands regarding final product specification.

To help address this challenge, PAC has developed as a complete Turned-Key system, the "**AC HT CNS SIMDIS**" Analyzer. Adding dedicated SCD and NCD detectors to a SIMDIS, PAC created an analyzer that generates complete boiling point distribution data for hydrocarbon, sulfur and nitrogen in less than 30 minutes, without any sample preparation other than dilution.

Analysis description

Simdis is a technique used in the petrochemical industry to determine the boiling point range distribution of product like for example diesel, vacuum gasoil, lube oils and crude oil. Simdis systems equipped with specific chemiluminescence detectors for sulfur and nitrogen provide the ability to not only report the boiling point distribution of hydrocarbons, but also the boiling point distribution of sulfur and nitrogen. In addition, it will yield total sulfur and total nitrogen numbers up to 700 °C. This information is provided simultaneously after separation on one column and detection on 3 different detectors: FID (hydrocarbons), NCD (nitrogen traces) and SCD (sulfur traces).

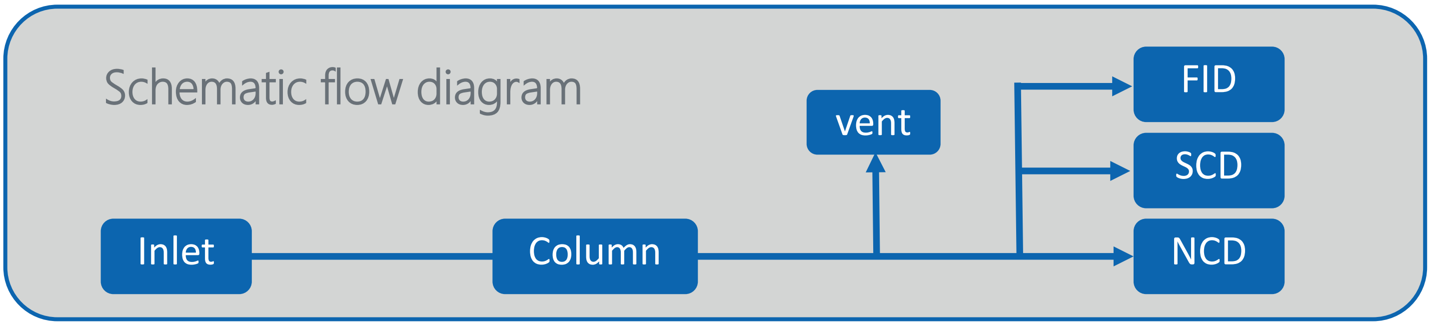

Figure 2: Schematic flow diagram of AC HT CNS Simdis analyzer

The AC HT CNS Simdis provides boiling point distribution information in the range from 151°C to 700°C (C9-C90) comparable to D7500 and D7169. To avoid detector deterioration the fraction after C90 is send to a vent.

The detector of choice for the heteroatomic molecules is a chemiluminescence detector, because of:

Selectivity The detector should be able to detect sulfur and/or nitrogen in such a complex mixture as crude, without given a response for the hydrocarbons.

Equimolarity Not all individual sulfur/nitrogen components can be separated and thus identified so quantification should be based on "sulfur or nitrogen" only, so the detector should have a true equimolar response.

Linearity Not only total concentration can vary from but also the concentration of individual components can vary a lot, one calibration should cover whole range both for individual components and total sulfur & nitrogen.

Sensitivity A very low injection volume in combination with high boiling point range and split between the detectors require a sensitive detector.

The PAC SeNse is meeting all these requirements, has an outstanding performance and long-term stability therefore the detector of choice for this application.

Just like in any standard Simdis systems, the following type of analysis need to be performed before analyzing regular samples:

BLANK

An analysis of the solvent is performed and recorded to subtract from the sample analysis. It compensates for the solvent signal, the base signal of the system, as well as column bleeding towards the end of the oven programming. Typically, cyclohexane is used a solvent, the commonly used solvent carbondisulfide is obviously not suitable for this application.

CALIBRATION ANALYSIS

To determine boiling point versus retention time relation, a calibration mixture that contains a series of n-paraffins covering the complete boiling range of C9-C90, is analyzed.

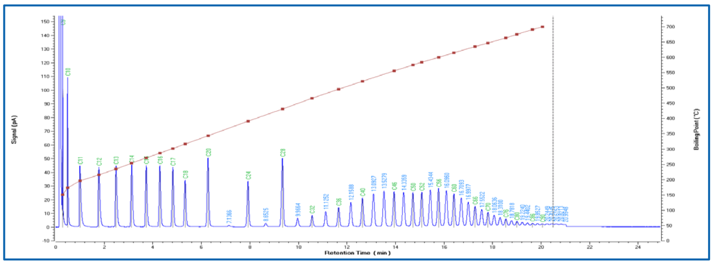

Figure 3: Boiling point calibration

REFERENCE OIL

In regular high temperature Simdis methods, like ASTM D7169, a response factor is used to calculate the % recovery (up to the last point of calibration) of the sample. This response factor is determined from the net area of the standard, the mass of the standard and the mass of the solvent. A fully eluting sample, such as "Reference oil 5010" is typically used to obtain the response factor.

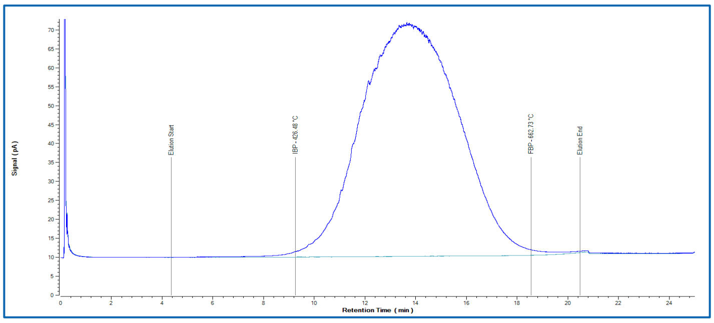

Figure 4: ASTM "Reference oil 5010"

The analysis of a "Gravimetric blend" consisting of two distillation fractions is used to check for a correct detector response

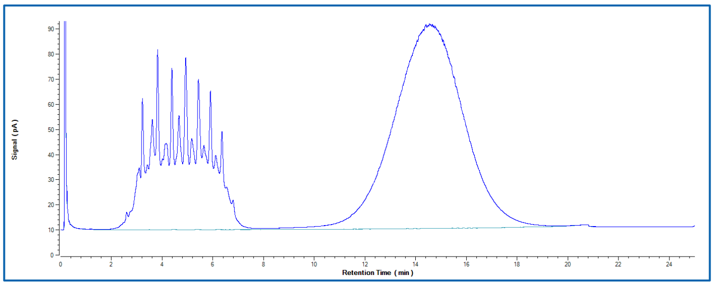

Figure 5: Gravimetric blend

For the HT CNS Simdis, analysis of a typical sample, like "Albian heavy", with known sulfur and nitrogen content yields the response factors for the 3 detectors: FID, NCD and SCD. These response factors are used to calculate the recovery of crude oil sample.

The system is validated by injection of a validation sample with not only a known sulfur and nitrogen content but also known boiling point distributions for the 3 signals.

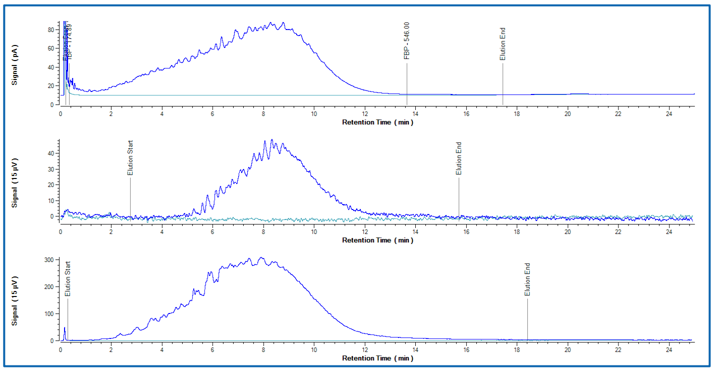

Figure 6: AC Albian heavy reference calibration

COMBINATION WITH DHA FRONT END DATA

For accurate analysis of a crude oil, the CNS SIMDIS systems needs to be combined with our unique AC DHA Front End (DHA FE) solution. This combination completes the hydrocarbon distribution profile for the fractions under C10 (BP<174°C), as this is partially lost in SIMDIS due to the overlap of the solvent (cyclo-hexane) with the low boiling fractions.

IRIS & SIMDISxInc software combines DHA and SIMDIS data into one comprehensive report with normalized carbon distribution profile over the complete boiling point range of the sample. Figures below show Traces for all channels; Carbon channel contains additional DHA FE Merged data with boiling points < 151° (n-C9).

SAMPLE ANALYSIS

Sample preparation is limited to diluting the crude oil in cyclohexane to about 2% concentration level. The below picture (figure 7) shows the typical chromatograms from a crude oil analysis.

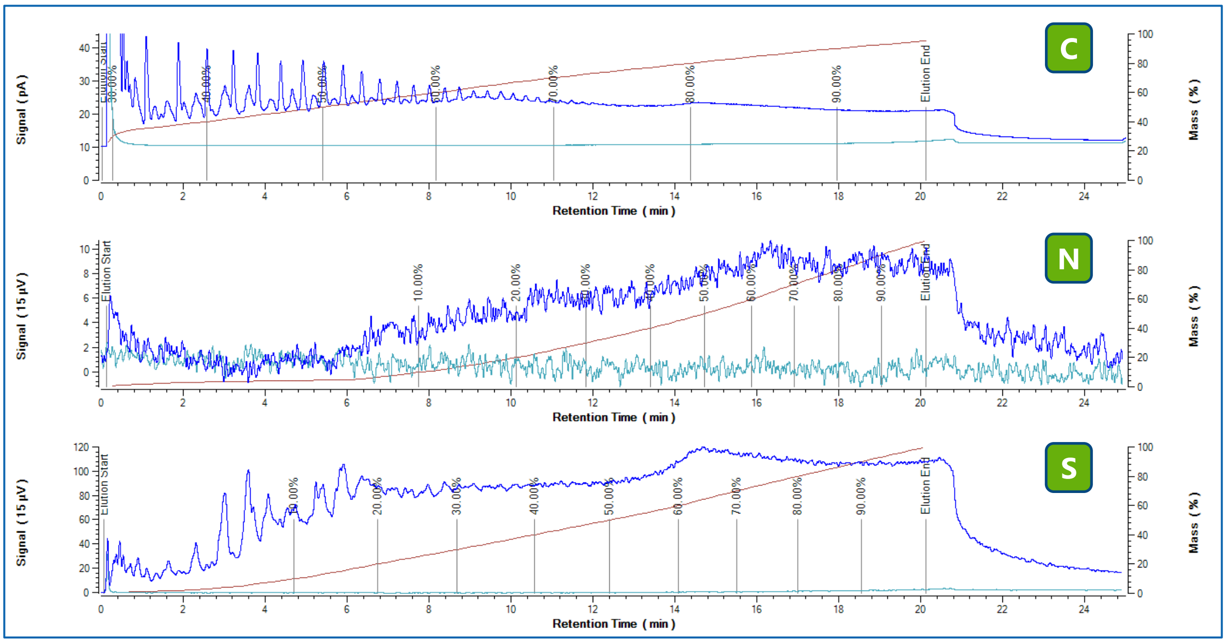

Figure 7: Typical crude oil chromatograms

Information obtained from the analysis is not only limited to the boiling distribution for the hydrocarbons, sulfur and nitrogen up to the found recovery at 700 °C. It also includes the total sulfur and total nitrogen content (up to 700 °C), and the content of sulfur and nitrogen in each customer defined carbon fraction. See figure 8.

Values of Interest (BP vs Mass) — Sulphur

Name	BP (°C)	Concentration (ppm Wt)	Concentration fraction (ppm	Recovered mass (%)	Residual mass (%)	Fraction mass (%)	Fraction S content
Naphtha	165.00	229.51	229.51	3.22	96.78	3.22	5093.54
Kerosene	270.00	900.09	670.58	12.63	87.37	9.41	2666.39
Diesel	370.00	2270.74	1370.65	31.85	68.15	19.23	10583.58
VGO	565.00	4976.94	2706.20	69.81	30.19	37.96	18295.98
Vac Residue	700.00	7129.02	2152.08	100.00	0.00	30.19	29146.01

Figure 8: Typical fraction report for sulfur channel

Figure 9 shows an overlay of three "Sulfur chromatograms" of a typical crude, where the difference in distribution can be clearly observed. The blue and purple chromatogram do not show much of response for the light fraction while the dark green chromatogram clearly shows a significant light fraction while the overall response is much lower.

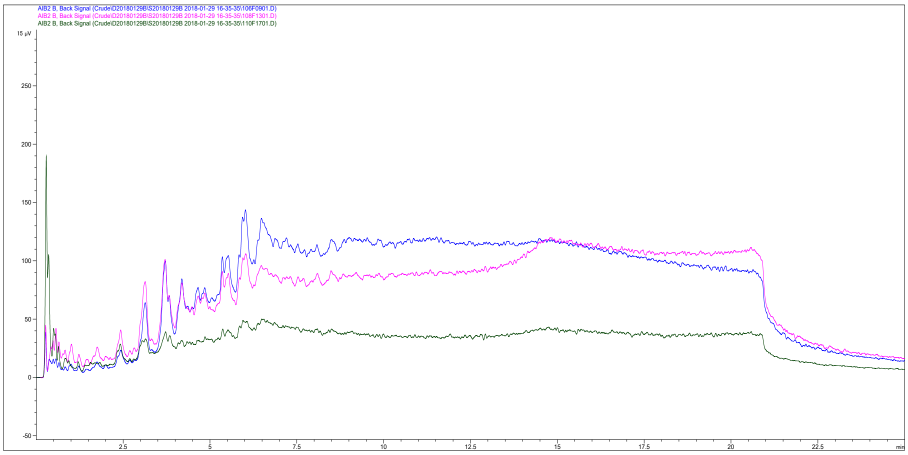

Figure 9: Overlay of 3 different crude oil sulfur chromatograms

This becomes even more obvious when the various fraction concentrations are presented in the graphs as shown below. Figures 10 & 11 show for different crudes the sulfur concentration for the various fractions as part a total sulfur content. As example the unknown crude has a low total sulfur content, however the sulfur concentration in the naphtha & kerosene fraction is at the same absolute level as for example for the Kirkurk crude, which has a much higher total sulfur concentration.

The following fractions have been defined (but are custom editable): naphtha: IBP – 165 °C, kerosene 166 – 270 °C, diesel 271 – 370 °C, vacuum gas oil 371 – 565 °C, vacuum residue 565 - 700°C.

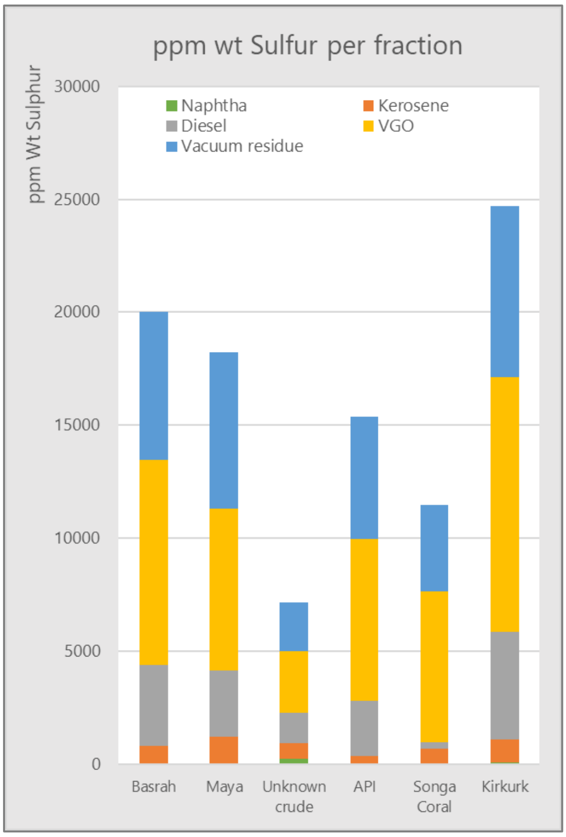

Figure 10: sulfur concentration in ppm wt for each defined fraction.

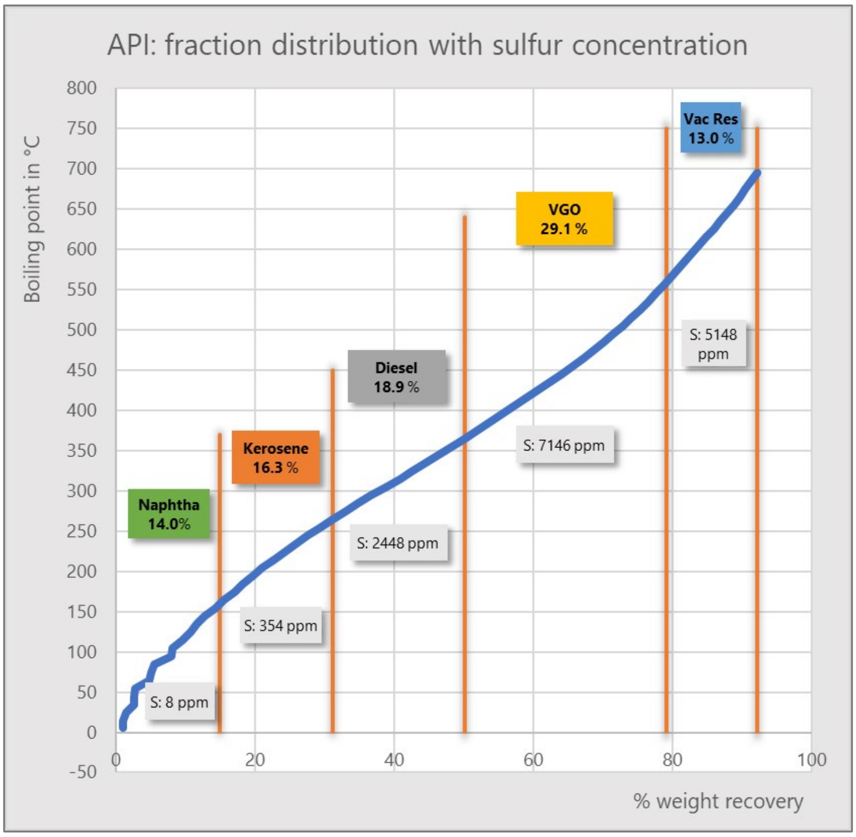

Figure 11: API crude fraction distribution and sulfur concentration per fraction

COMPARISON WITH NIST MATERIALS

To check the total sulfur concentration results, a well-established NIST 1624D standard has been analyzed. The found recovery matches well with the found total sulfur amount on the PAC HT CNS Simdis analyzer.

Total Sulfur ppm wt				
Validation material	Target	Found results (n=5)	Bias	Relative Bias (%)
NIST 1624D	3882	3819	-63	-1.6

ANALYTICAL SPECIFICATIONS

	Sulfur	Nitrogen
Application range *	200-50000 (ppmS wt)	500-50000 (ppmN wt)
Equimolarity	< 10%	< 10%
Selectivity	S/C: 5 x 10^7	S/C: 2 x 10^7
Response stability	<10%	<10%

(*) Application range Sulfur and Nitrogen depended on sulfur distribution.

Conclusion

The AC HT CNS Simdis analyzer, in combination with the AC DHA Front-end, is a powerful tool that provides refiners and crude oil traders with information about the boiling point distribution of the crude, and how much and how the sulfur and nitrogen are distributed within the crude. This information is otherwise obtained from a full Crude Assay, which involves a time consuming and costly set of tests and requires a larger amount of crude oil versus only two analysis (CNS Simdis and DHA Front-end) using less than 10 ml of sample and only 2 hours of testing time.

This allows operators to optimize the processes such as hydro-treating, cracking, etc. and predict in advance how much effort will have to be spent on desulphurization for the different fractions and products produced.

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