Measuring Hydrogen Sulfide in Crude Oil

Applied Analytics Application Note No. AN-009

Application Summary

Analyte(s): **hydrogen sulfide**

Detector: **OMA-300 Process Analyzer w/ Headspace Sample Conditioner**

Process Stream: **crude oil**

Typical Measurement Range: **0-100 ppm**

Introduction

Crude oil with low sulfur content ("sweet crude") is coveted because it is more easily processed into usable gasoline. By contrast, sour crude contains a significant H_2S concentration and requires more expensive processing. Online H_2S analysis is required to determine how much processing a specific feed of crude oil will require and to differentiate different crudes by their commercial value.

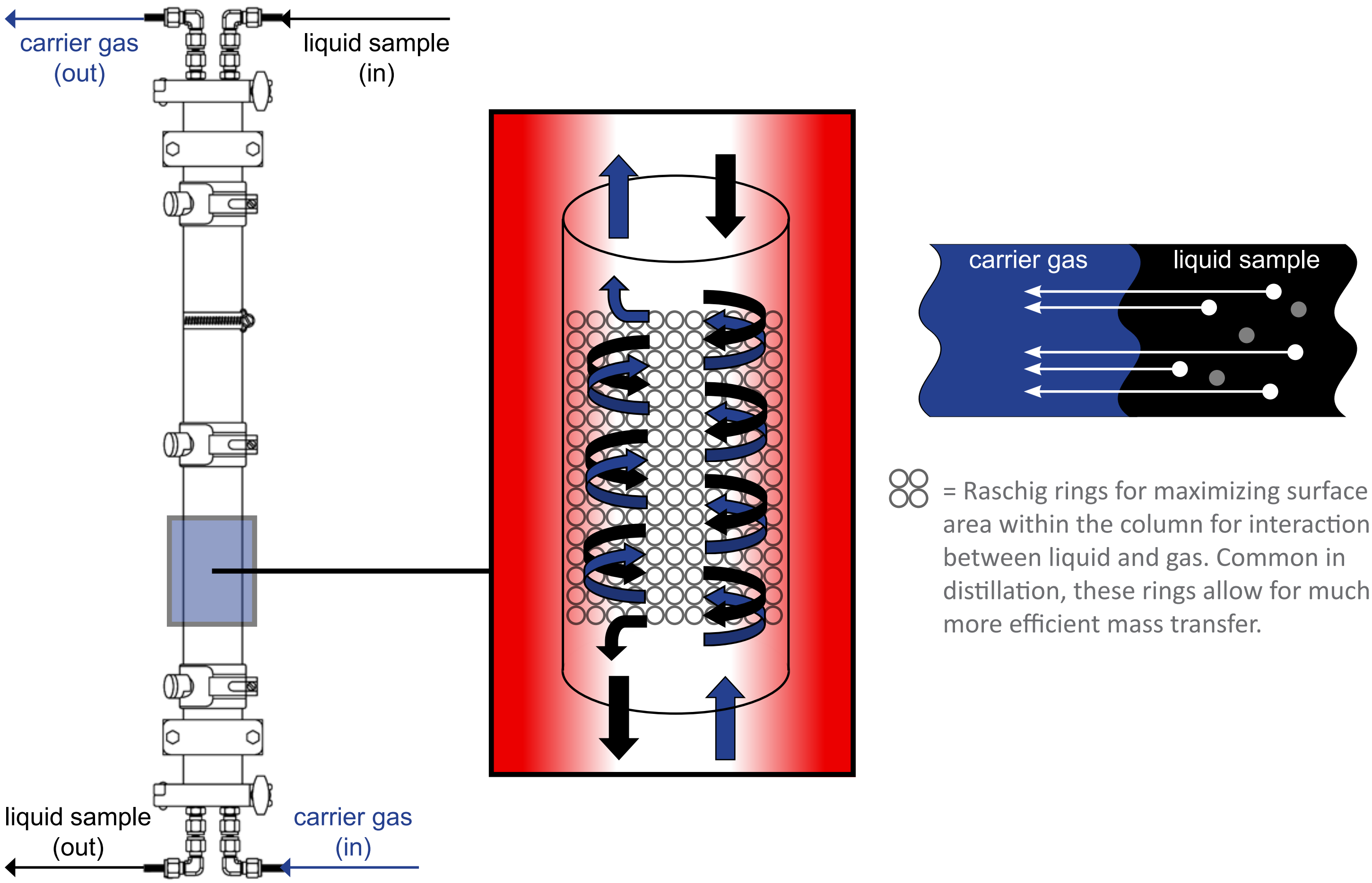
The composition of oil presents significant challenges to direct optical analysis. These challenges include aromatic hydrocarbons and/or phenols which absorb heavily in the UV range and act as spectroscopic interferents, particulates which scatter light, and the opacity of heavier crudes (too dark to transmit a light signal and will not allow optical analysis).

The OMA system uses a 'headspace' sample conditioning system to circumvent the opacity of crude oil and continuously measure H_2S concentration in the stream with proven reliability. The operating principle of the system is Henry's Law: part of the liquid sample is evaporated into 'headspace gas'— a vapor-phase sample that is totally representative of the liquid composition and can be analyzed very easily using UV spectroscopy.

Headspace Sampling & Henry's Law

Henry's Law states that the amount of a certain gas dissolved in a solution at a given temperature is directly proportional to the partial pressure of that gas above the solution. The major implication of this for crude oil analysis is that, given certain constant conditions, the chemical composition of the headspace gas correlates directly to the composition of the opaque liquid sample. The conditions which must remain constant (temperature, pressure, carrier gas flow rate, and liquid sample flow rate) are all held constant by the headspace system.

To create a representative vapor-phase sample from the liquid crude, the headspace system uses a temperature-controlled column (12" high by 2.5" diameter application dependent). The opaque liquid sample flows in from the top while carrier gas (typically nitrogen) flows in from the bottom. The carrier gas picks up the molecules that evaporate from the liquid sample and carries them out of the column and into the flow cell for optical analysis. The system is calibrated by correlating the H_2S concentration in the flow cell (gaseous sample) to the H_2S concentration of a standard liquid crude oil sample.

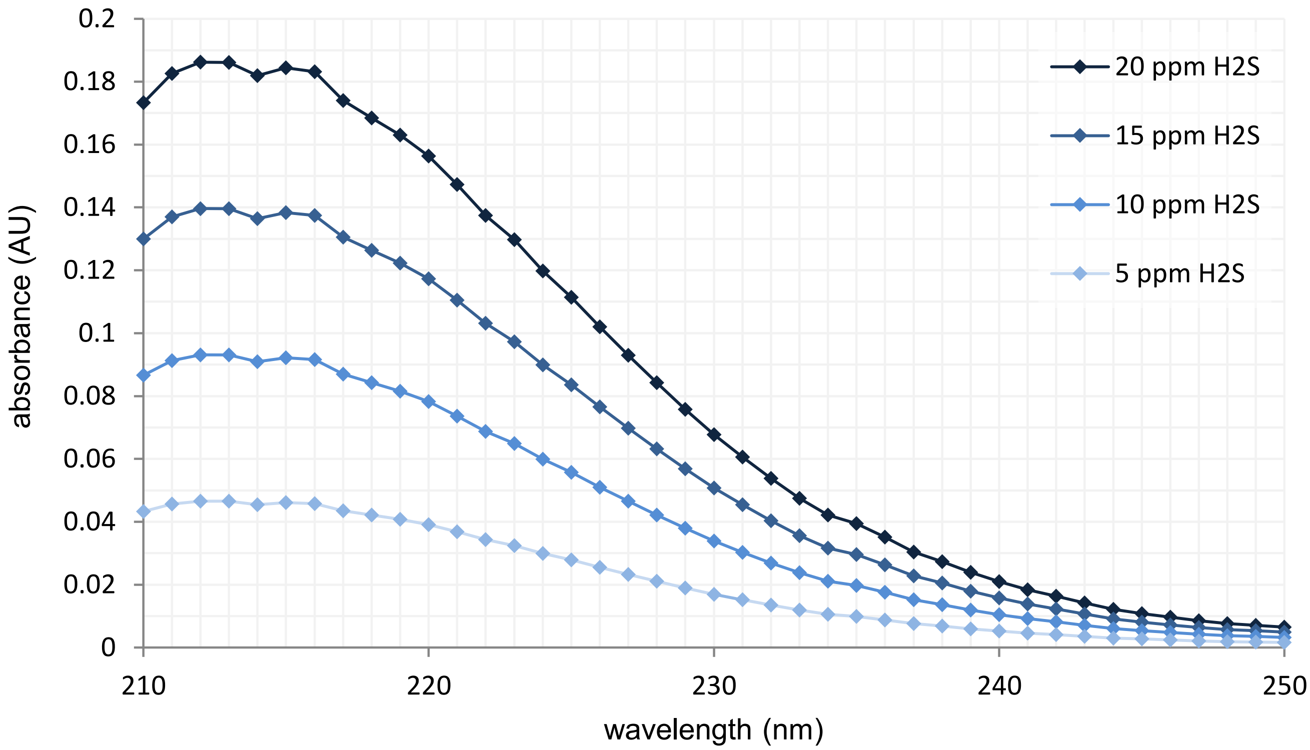


The held temperature determines the partial pressure mix of compounds in the headspace gas. This allows us to hold the temperature of the column at a point where we get an extremely useful vapor-phase sample that contains H_2S but very low levels of interfering compounds like aromatics and phenols (due to the difference in Henry's law constants between the analyte and the interfering compounds).

H_2S Absorbance Curve

Any single photodiode measurement is vulnerable to noise, signal saturation, or unexpected interference. This susceptibility to error makes a lone photodiode data point an unreliable indicator of one chemical's absorbance.

As accepted in the lab community for decades, the best way to neutralize this type of error is to use collateral data in the form of 'confirmation wavelengths,' i.e. many data points at many wavelengths instead of a single wavelength:

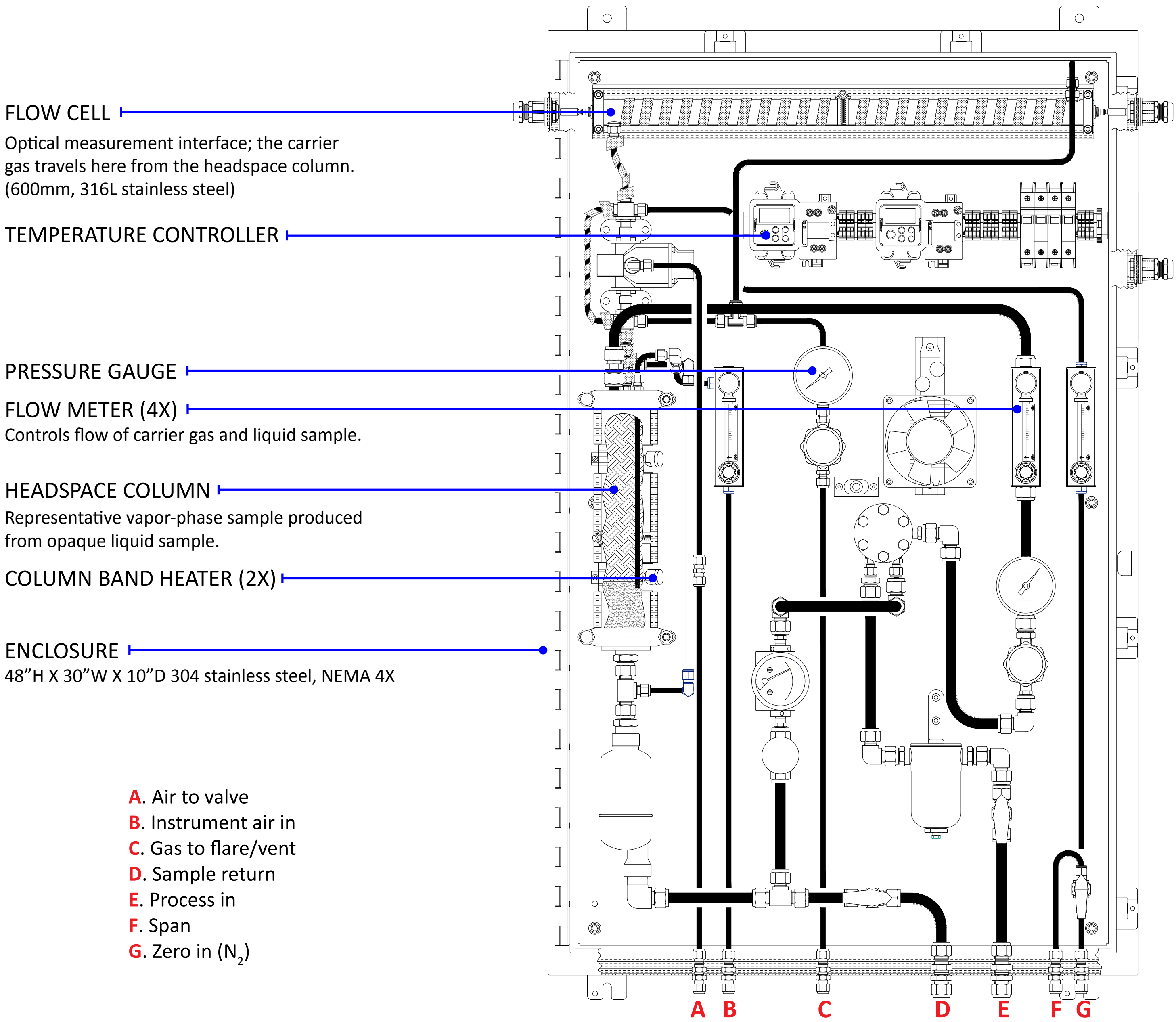


In the figures above, each diamond represents a single photodiode and data point. The nova II registers absorbance at each integer wavelength within the measurement wavelength region and produces an H_2S absorbance curve. After being calibrated on a full spectrum of pure H_2S, the OMA knows the absorbance-concentration correlation for each measurement wavelength; the system can average the modeled concentration value from each wavelength to completely eradicate the effect of noise at any single photodiode.

The OMA visualizes the H_2S absorbance curve in this manner and knows the expected relation of each data point to the others in terms of the curve's structure. This curve analysis enables the OMA to automatically detect erroneous results at specific wavelengths, such as when a single photodiode is saturated with light. The normal photometer, with a single data point, is completely incapable of internally verifying its measurement.

Headspace Sample Conditioning System Technical Details

The standard headspace SCS design is detailed below. The design will vary to suit the needs of the measurement application.



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The specifications below represent performance of the OMA-300 Process Analyzer in a typical crude oil application.

For technical details about the OMA-300 Process Analyzer, see the data sheet:
http://aai.solutions/documents/AA_DS001A_OMA300.pdf

All performance specifications are subject to the assumption that the sample conditioning system and unit installation are approved by Applied Analytics. For any other arrangement, please inquire directly with Sales.

Application Data		
Performance Specifications		
Accuracy	*Custom measurement ranges available; example ranges below. Accuracy specifications represent headspace gas sample analysis validated with span gas.*	
	H_2S	0-10 ppm: ±1 ppm 0-100 ppm: ±1% full scale or 1 ppm* 0-10,000 ppm: ±1% full scale
		*Whichever is larger.

Further Reading

Subject	Location
OMA-300 H2S Analyzer Brochure	http://aai.solutions/documents/OMAH2S.pdf
OMA-300 Process Analyzer Data sheet	http://aai.solutions/documents/AA_DS001A_OMA300.pdf
Advantage of Collateral Data Technical Note	http://aai.solutions/documents/AA_TN-202_CollateralData.pdf
Multi-Component Analysis Technical Note	http://aai.solutions/documents/AA_TN-203_MultiComponentAnalysis.pdf

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