Stripped Sour Water Analysis

Applied Analytics Application Note No. AN-027

Application Summary

Analytes: **H_2S** (hydrogen sulfide), **NH_3** (ammonia)

Detection Technology: **OMA-300 Process Analyzer**

Process Stream: **stripped sour water**

Introduction

In the context of petrochemical refining and wastewater treatment, water containing H_2S is referred to as "sour." The sulfide loading lends an unpleasant odor and makes the water corrosive. Additionally, the presence of H_2S in certain water pipes can serve as an indicator of equipment problems, e.g. heat exchanger leaks.

In a refinery, sour water must be cleaned of its sulfide content before being recycled or released to the environment. This cleaning process is known as "stripping" because it flows gas (air or steam) through the sour water to strip H_2S and NH_3 out of the water. To verify that the sour water is being effectively stripped, online analysis is required in the stripped water stream.

The OMA system applies the power of dispersive UV-Vis absorbance spectroscopy to this analysis. In applications where the water is too dark or dirty to transmit a light signal, Applied Analytics utilizes our expertise in headspace sampling design, thus providing a proven analytical solution for water streams where other analyzers have failed.

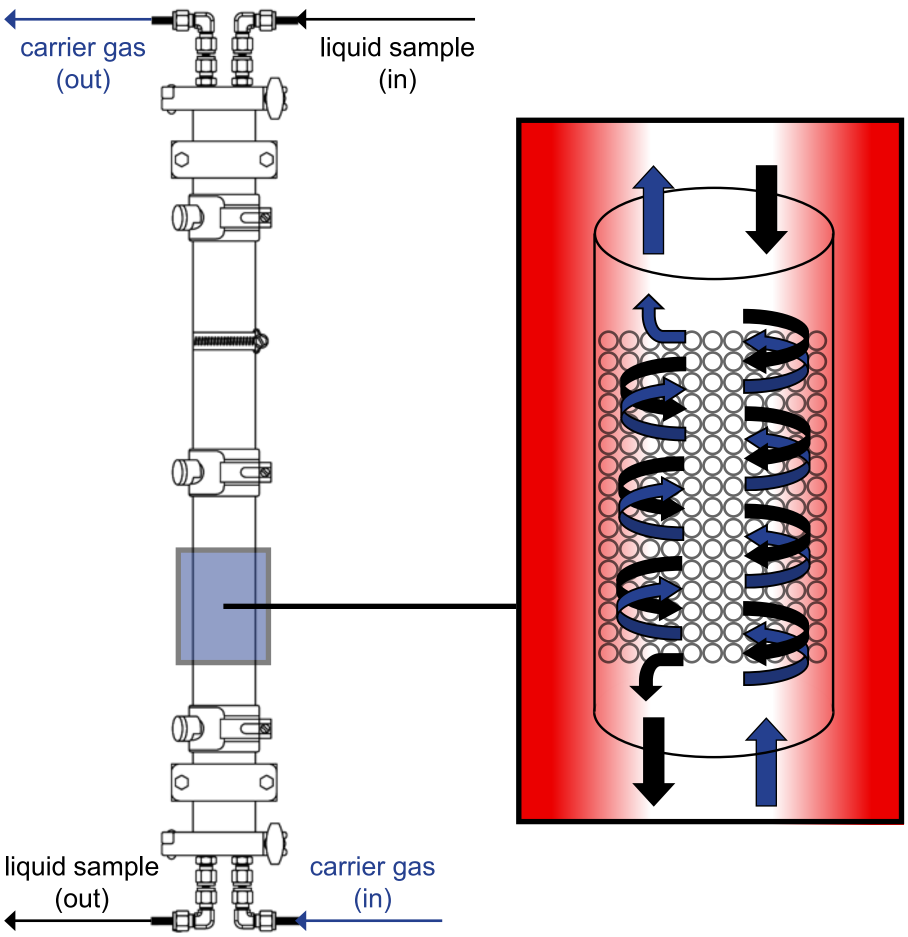
OMA Benefits

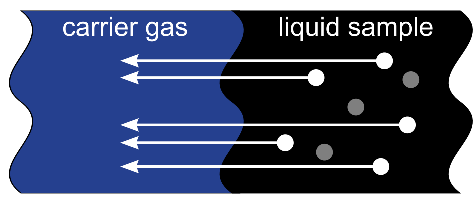
- Continuously measures H_2S and NH_3 concentrations in water using dispersive UV-Vis absorbance spectrophotometer
- Totally solid state build with no moving parts — modern design for low maintenance
- Capable of analyzing opaque/dirty water using headspace sampling option
- Fully automated using Auto Zero to normalize spectrophotometer on zero-analyte process water
- Decades of field-proven performance in diverse water compositions

The Headspace Solution for Opaque Sour Water

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 water 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 water, the headspace system uses a temperature-controlled column (24" high by 2" diameter). 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.





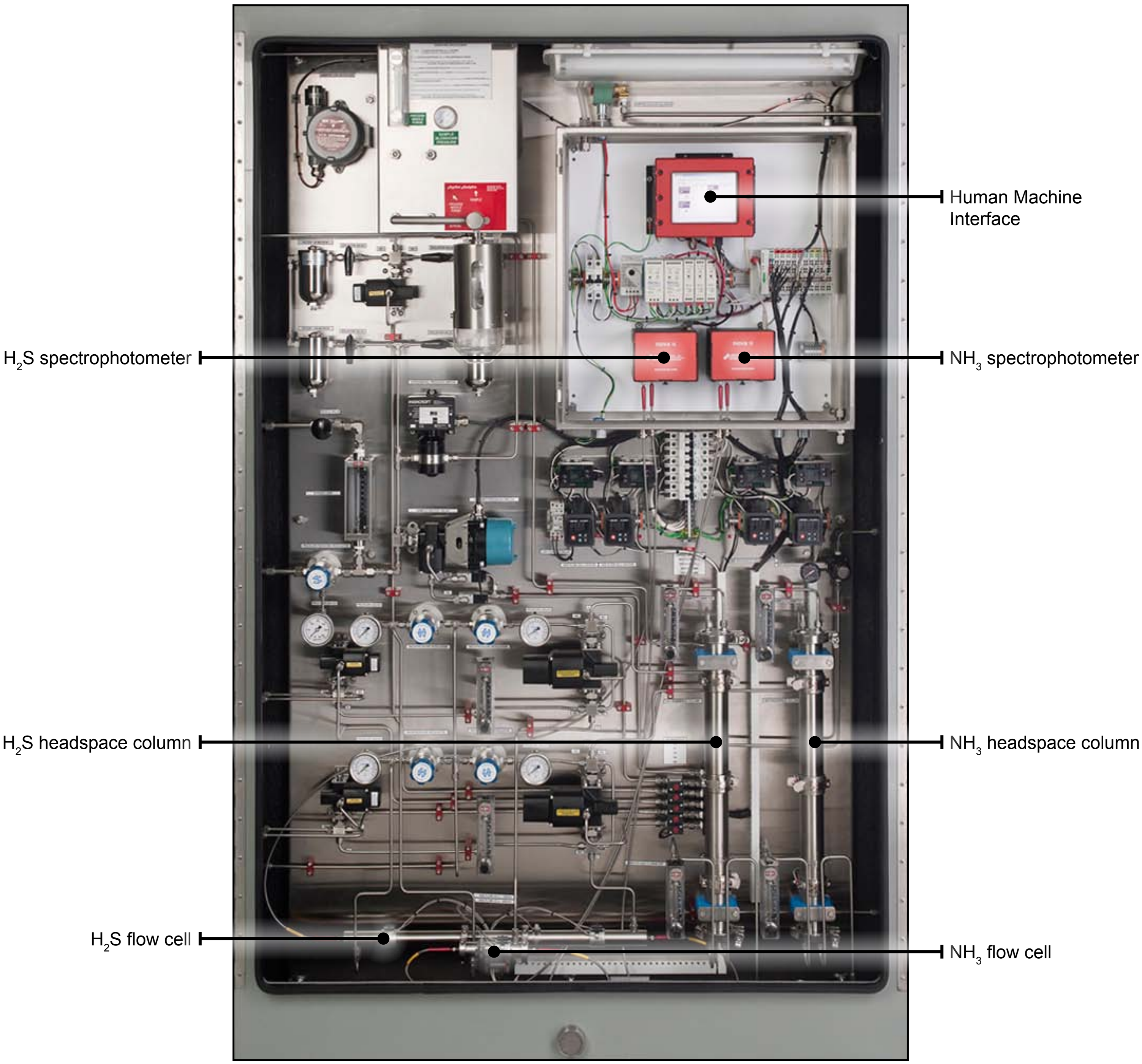
= Raschig rings for maximizing surface area within the column for interaction between liquid and gas. Common in distillation, these rings allow for much more efficient mass transfer.

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 the analyte 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).

The OMA Double Headspace System for H_2S and NH_3

Measuring H_2S and NH_3 simultaneously in the effluent water from a stripping operation requires twofold application of the headspace principle, since the two analytes have different Henry's Law constants.

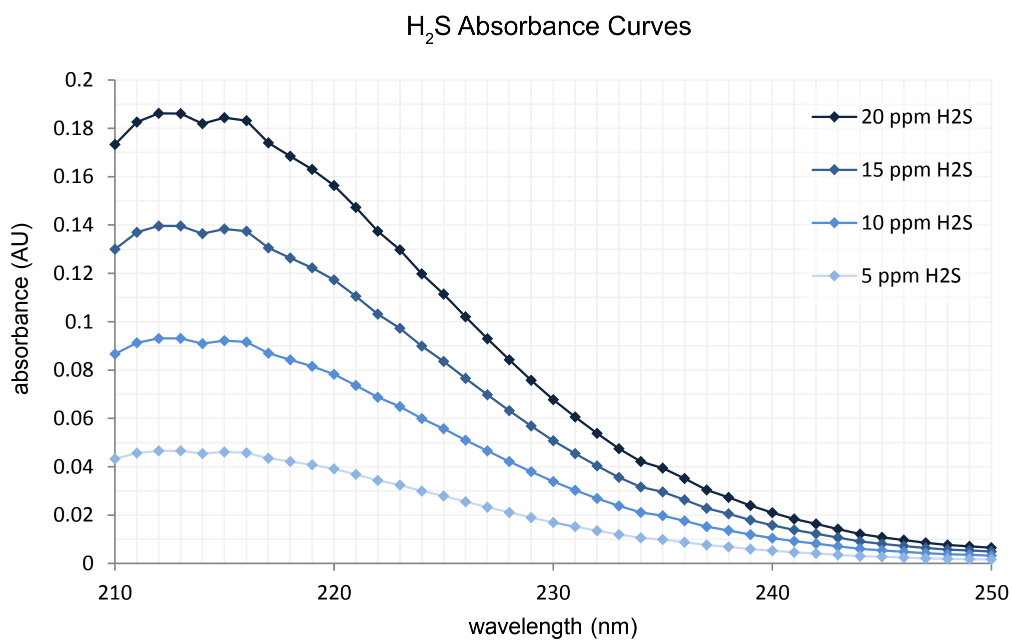
The double headspace system uses two separate headspace columns, each with a corresponding optical flow cell for the emerging headspace gas. The H_2S column is held at a temperature optimized for H_2S stripping, while the NH_3 column is held at a different temperature optimized for NH_3 stripping. Each column feeds the headspace gas into a dedicated flow cell with a specialized optical path for the analyte.



Absorbance Curves and the Power of Collateral Data

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:

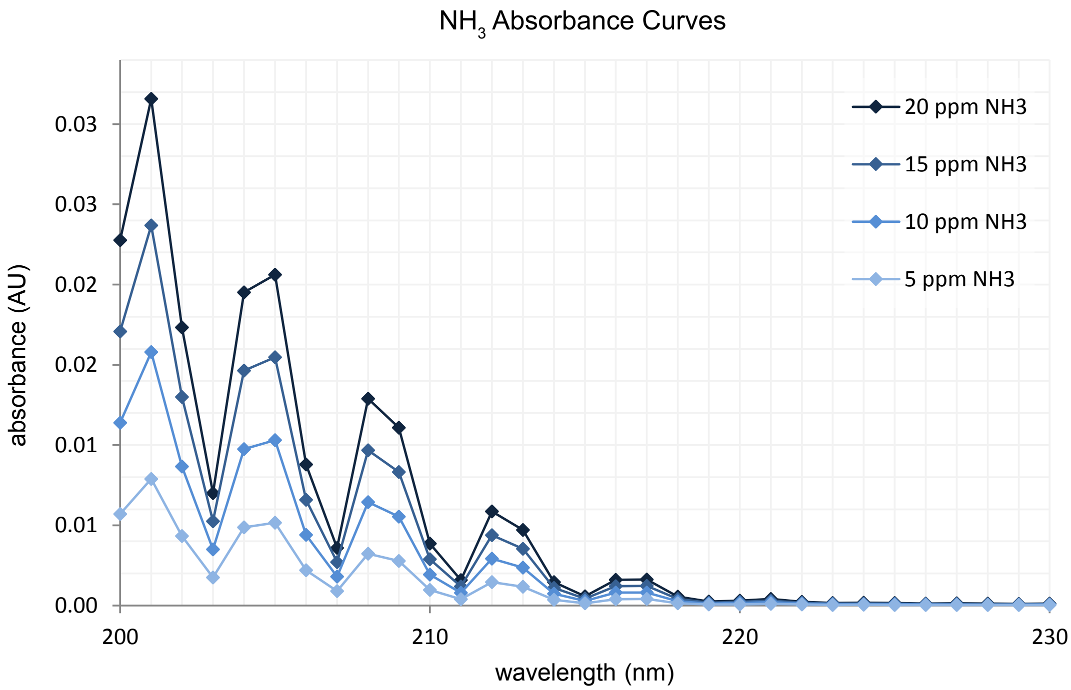


In the spectra above, each diamond represents a single photodiode and data point. The spectrophotometer measures absorbance at each integer wavelength within the 200-800 nm UV-Vis range and produces an H_2S absorbance curve.

After being calibrated on a full spectrum of pure H_2S, the OMA knows the absorbance-concentration correlation for each measurement wavelength. The system averages 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.

The same principle is used in the NH_3 measurement:



As with the H_2S calibration explained above, the NH_3 analysis is calibrated on a full spectrum of standard NH_3 solution. In the double headspace configuration, each analyte has its own flow cell with path length specialized for the concentration range.

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The specifications below represent performance of the OMA-300 Process Analyzer in a typical stripped sour water application.

For technical details about the OMA-300 Process Analyzer, see the data sheet:
http://www.a-a-inc.com/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
	NH_3	0-10 ppm: ±0.5 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 Process Analyzer Data sheet	http://www.a-a-inc.com/documents/AA_DS001A_OMA300.pdf
Advantage of Collateral Data Technical Note	http://www.a-a-inc.com/documents/AA_TN-202_CollateralData.pdf
Headspace Sample Conditioners Brochure	http://www.a-a-inc.com/documents/Headspace.pdf

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