

USING UV SPECTROSCOPY TO SIMULTANEOUSLY MEASURE MULTIPLE SULFUR SPECIES

APPLICATION

Analytical measurement of reduced sulfur compounds in natural gas is required at various operational stages in a gas processing plant.

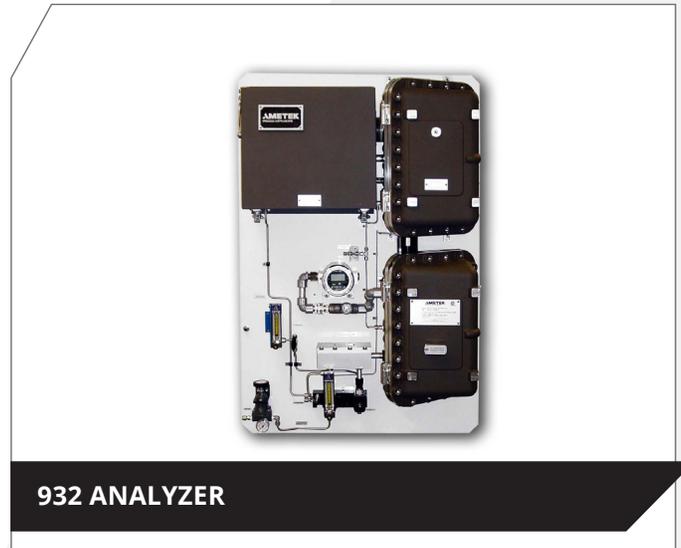
The predominant sulfur compounds of interest are hydrogen sulfide (H₂S), carbonyl sulfide (COS), methyl mercaptan (MeSH) and carbon disulfide (CS₂).

PROBLEM

By far the predominant reduced sulfur compound present in natural gas is H₂S. It can exist in the reservoir from parts-per-million (ppm) to percent levels. COS and MeSH are the next most common reduced sulfur components. They typically exist in concentrations from single-digit ppm up to 100s of ppm in quantity. Other sulfur compounds that can exist in minor concentrations (if present at all) are, in general order of relative concentration, ethyl mercaptan (EtSH), CS₂, di-methyl disulfide (DMDS), propyl mercaptan (PrSH), butyl mercaptan (BuSH), and various thiophenes.

In sour gas treatment, the primary operation is amine treating for the removal of H₂S. The remaining sulfur compounds – COS, CS₂ and the mercaptans – have only a slight affinity for absorption by amine, and largely pass through the process. The purpose of measuring the H₂S, COS, CS₂ and MeSH as discrete compounds (vs. a total of the reduced sulfurs by conversion) is the ability to optimize and troubleshoot the process. Real-time analysis and speciation of the predominant sulfur compounds has a distinct advantage. Using the additive of the primary sulfur compounds as the total reduced sulfur (TRS) accounts for approximately 95% or more of the TRS and is a consistent indication of the total.

The term “TRS compounds” has a different definition when applied to gas processing as compared to continuous emissions monitoring. Typically, in the practical world of process gas analysis, TRS refers to one of two methods.



The first is a two-step method of using a reduction catalyst to convert sulfur compounds to H₂S and measure with a H₂S specific detector, (typically lead acetate paper tape). The other method is one that individually measures the majority of the reduced sulfur compounds. These approaches include ultraviolet (UV) spectroscopy and gas chromatography (GC) using a flame photometric detector (FPD). In a process gas stream, there can be as many as 15 or more TRS compounds present. The similarity in molecular structure and low ppm/sub-ppm concentrations preclude the quantification of these sulfur compounds by any discrete analyzer. In these approaches, the term “TRS” is an approximation and it consists of the summation of only the measured species.

EQUIPMENT

While UV analyzers have been providing rapid H₂S response in pipeline gas for decades, current devices are capable of measuring H₂S, as well as COS and MeSH. Measurement of COS is important because it can hydrolyze to H₂S, while the mercaptan measurement is, in some cases, indicative of the total sulfur content of the gas.

The AMETEK 932 UV photometer used in pipeline natural gas TRS applications is a dual-beam multi-wavelength design. The light sources are hollow cathode lamps, chosen specifically for their narrow emission lines at specific and reproducible wavelengths. The sample and reference detectors are photomultiplier tubes (PMT), which yield excellent photometric accuracy and linearity. A six-filter chopper wheel allows for multiple measuring wavelengths and for the simultaneous analysis of up to five species. The

resulting narrow, precise, and reproducible emission lines are instrumental in achieving high resolution, wavelength accuracy, and wavelength precision in the spectrometer, independent of variations in the filter bandpass. These analyzers measure TRS species by determining the amount of UV radiation absorbed at specific wavelengths and amount of UV radiation absorbed at specific wavelengths and using a multiple linear regression model to determine the concentration of the individual species.

RESULT

Figure 1 depicts the results obtained during an actual process upset. The 932 UV analyzer can measure the COS, MeSH, H₂S concentrations.

The 932 analyzer is not referred to as a total sulfur analyzer. It is a multicomponent analyzer using UV spectroscopy to measure several different UV-absorbing "sulfur" compounds. It is commonly configured to measure H₂S and COS in TGT contactor overhead gas, H₂S in sulfur plant inlet gas,

and various combinations of sulfur components in other applications. It uses an optical bench designed for the simultaneous measurement of H₂S, COS and MeSH.

Since the individual species can be identified and quantified, the sum of the concentrations of the species can also be determined. This value is then the total concentration of all the sulfur species measured and is representative of the total sulfur content of the gas stream.

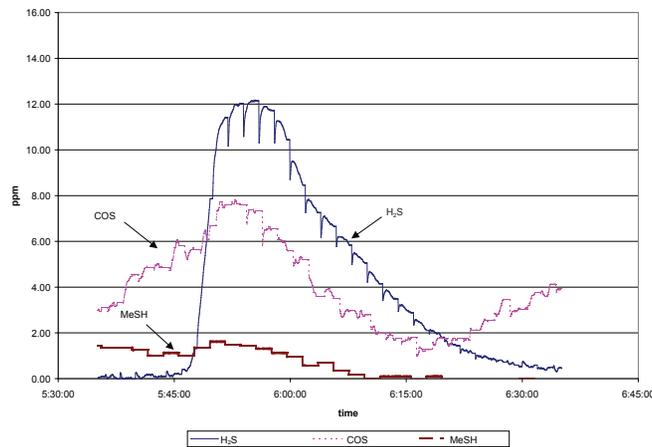


Figure 1. Results during a process upset

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