

# The Application of UV Spectroscopy to Simultaneous Measurement of Sulfur Species

## Model 932 Multi Gas Analyzer

The following information describes the analytical measurement of reduced sulfur compounds in natural gas at various operational stages in a gas processing plant. The predominant reduced sulfur compounds are H<sub>2</sub>S (hydrogen sulfide), COS (carbonyl sulfide), MeSH (methyl mercaptan) and the method discussed is UV spectroscopy using hollow cathode lamps.

### THE OCCURRENCE AND DISTRIBUTION OF REDUCED SULFUR COMPOUNDS IN NATURAL GAS / NATURAL GAS TREATING

By far the predominant reduced sulfur compound present in natural gas is H<sub>2</sub>S and it can exist in the reservoir from ppm to % levels. COS and MeSH are the next most common reduced sulfurs and they typically exist in concentrations from single digit ppm up to 100s of ppm in quantity. Other sulfur compounds, (if present at all) that can exist in minor concentrations are in general order of relative concentration; ethyl mercaptan (EtSH), carbon disulfide (CS<sub>2</sub>), di-methyl disulfide (DMDS), propyl mercaptan, butyl mercaptan, and various thiophenes.

In the process treatment of sour gas, the primary unit operation is amine treating for the removal of H<sub>2</sub>S. The remaining sulfur compounds; COS, CS<sub>2</sub> and the mercaptans have only a slight affinity for absorption by amine and largely pass through the process. The purpose of measuring the H<sub>2</sub>S, COS, MeSH and CS<sub>2</sub> as

discrete compound (vs a total of the reduced sulfurs by conversion) is to be able to optimize and troubleshoot the process. The real time analysis and speciation of the predominant sulfur compounds have a distinct advantage. Using the additive of the primary sulfur compounds as the total reduced sulfur accounts for ~95% or more of the Total Reduced Sulfur (TRS) and it is a reasonable assumption it is a consistent function of the total.

### COMPARATIVE MEASUREMENT TECHNOLOGIES FOR REDUCED SULFUR COMPOUNDS

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 all of the sulfur compounds to H<sub>2</sub>S and measure with a H<sub>2</sub>S specific detector, (typically lead acetate paper tape). The other method is one that measures, individually, the majority of the reduced sulfur compounds. These approaches include UV spectroscopy and GC using a flame photometric detector (FPD). There can be as many as 15 or more TRS compounds present in a process gas stream. The similarity in molecular structure and low ppm/sub ppm concentrations preclude the quantification of all of these sulfur compounds by any discrete analyzer. In these approaches, the term "TRS" is an approximation and it consists of the summation of the measured species.

### MEASUREMENT OF SULFUR SPECIES USING UV SPECTROPHOTOMETRY

While UV analyzers have been providing rapid H<sub>2</sub>S response in pipeline gas for almost two decades<sup>[1]</sup>, recent advances have extended the capabilities of these devices. Most notably, additional species can be measured and sensitivity has been improved. Current devices are capable of measuring both COS and MeSH as well as H<sub>2</sub>S. Measurement of the former species may be important in that it can hydrolyze to H<sub>2</sub>S, while the mercaptan measurement is, in some cases, indicative of the total sulfur content of the gas.

The AMETEK UV photometer (Model 932) used in the following pipeline natural gas TRS application is a dual beam multi-wavelength design and 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<sup>[2]</sup>. These analyzers measure these TRS species by determining the amount of

ultraviolet radiation absorbed at specific wavelengths, and using a multiple linear regression model to determine the concentration of the individual species. The ultraviolet spectra for some of the species of interest are available in various peer-reviewed technical papers produced by AMETEK.

Data presented in Figure 1 depicts the results obtained during an actual process upset. The Model 932 UV Analyzer is capable of measuring the COS, MeSH as well as the H<sub>2</sub>S concentrations .

The AMETEK Model 932 Analyzer is not referred to as a total sulfur analyzer, but rather is a multicomponent analyzer using UV spectroscopy to measure several different ultraviolet absorbing gases. It is commonly configured to measure H<sub>2</sub>S and COS in TGT Contactor Overhead gas, H<sub>2</sub>S in sulfur plant inlet gas, and for other sulfur measuring applications. It uses the same optical bench as the Model 933 (which is described in detail in a separate application bulletin) for the simultaneous measurement of H<sub>2</sub>S, 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 thus representative of the total sulfur content of the gas stream.

**Ranges**

**H<sub>2</sub>S:** 0 - 50 ppm / 0 - 500 ppm / 0 - 5% (higher ranges available)

**COS:** 0 - 500 ppm minimum range

**MeSH:** 0 - 300 ppm minimum range

**CS<sub>2</sub>:** 0 - 500 ppm minimum range

Component ranges are application specific, AMETEK requires complete application data before confirming the ranges.

AMETEK provides analyzers for a variety of process applications to simultaneously measure sulfur compounds in natural gas processing, tail gas treating and natural gas transmission applications. Further detailed information is available on request.

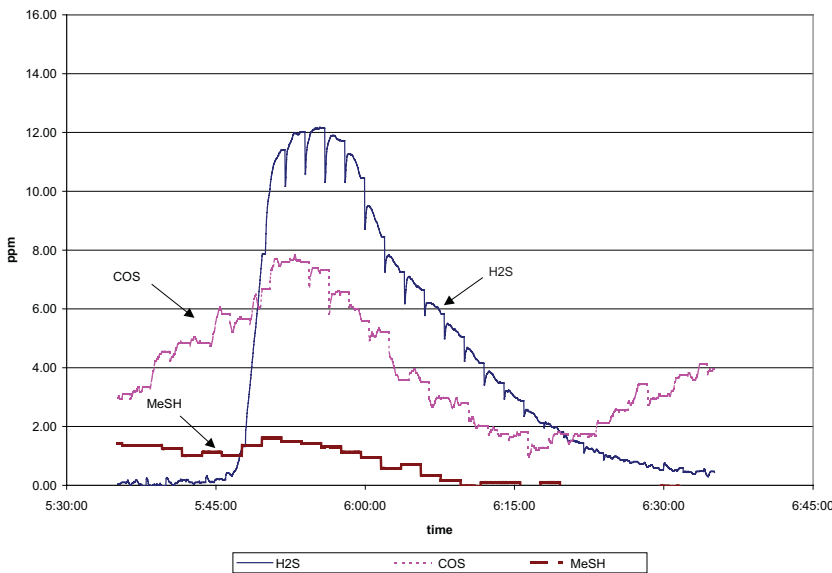


Figure 1 UV Results - Process Upset

**References:**

1. Babiuk, Ken F., "Advances in fast-response H<sub>2</sub>S Analysis", 1982.
2. Adam H. and Harris P., "The design and practical application of UV process photometers", L'analyse Industriel, Paris, France, 1996.



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