Application Note: 420050

Analysis of Hydrogen Sulfide in gas by XVI+ according to ASTM D4084

Introduction

Hydrogen Sulfide (H_2S) is a colorless gas with a strong odor and is extremely poisonous. It is often referred to as sewer gas. High concentrations of H_2S are often found in petroleum and natural gas and are of major concern during the drilling of oil wells. Employees as well as people in surrounding cities need to be protected against this hazardous gas.

H_2S is corrosive to steel and therefore is a potential cause of damage within the refinery process. Not only is the H_2S introduced into the process by the feed, but at several steps in the process H_2S may be formed. For example, hydrotreating is used to desulfurize the feedstock, the sulfur being convereted into H_2S. Refineries therefore need to measure the H_2S content in the feedstock as well as at several steps in the process.

Principle of operation

Thermo Electron Corporation introduces the next generation of their trace level Total Sulfur Analyzer; model XVI+. This analyzer uses the Lead Acetate Tape principle. This detection method is based upon the darkening of the tape by sulfur. A very low detection limit can be obtained by injecting a larger volume of sample (accumulation effect). The Lead Acetate detection method is the only detection system which can determine H_2S without any interference, while providing a low limit of detection.

The XVI+ typically comes as an oxyhydro or hydro analyzer. For this particular application the analyzer is equipped with a direct H_2S option, for which the oven is bypassed. To have a constant level of humidity the gas is let through a humidifier. Finally the gas reaches the detection chamber (red flowpath in figure 1).

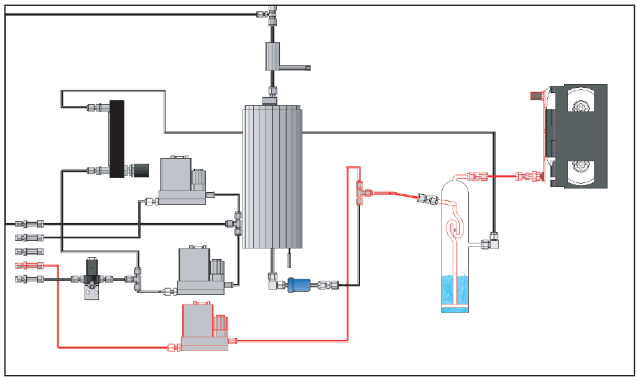

Figure 1. Flowpath XVI+ analyzer

The reaction of the H_2S with the Lead Acetate tape is:

$$H_2S + Pb(CH_3COO)_2 \xrightarrow{H_2O} PbS + 2\,CH_3COOH$$

The PbS forms a dark brownish stain on the white tape. Light illuminating the tape is reflected due to the white color. The photo diode detects the reflected light. Less light is reflected when the color of the tape changes from white to brown, due to H_2S. The rate of this reaction (meaning the rate of color change) is proportional to concentration of H_2S in the sample. The concentration of H_2S in the sample is determined by comparing the rate of color change to those of a set of samples with known concentrations of H_2S. Figure 2 shows a typical detector response. The red lines indicate the start and end point of the rate of color change calculation. The ThEuS software calculates the rate of color change at each measurement and calculates the amount of H_2S present in the sample by referring it to one or more calibration standards.

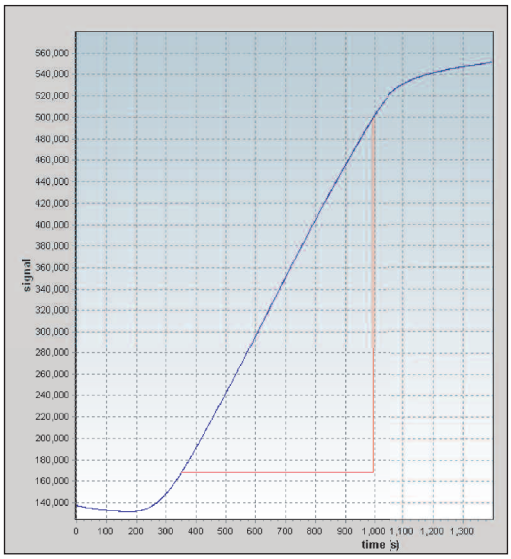

Figure 2. Typical response

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Calibration

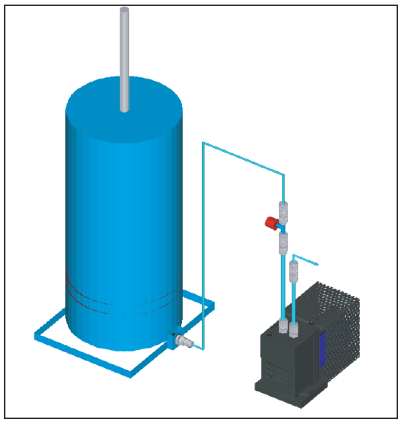


Figure 3. Gas Calibration Kit

The calibration of the XVI+ analyzer is done by using the gas calibration kit (figure 3).

The total volume of the cylinder is 10 L. The dilution gas is argon and while filling the cylinder with the dilution gas a certain amount of either 1 ppm/v of 2000 ppm/v H_2S gas is injected to get the calibration gas mixture with the desired concentration. A membrane pump feeds the gas mixture to the mass flow controller. The mass flow controller guarantees a stable and reproducible sample gas flow.

ASTM D4084 does not suggest a calibration range. Instead samples must be within 25% of the response of a reference standard with a known concentration of H_2S. However, the applicable concentration range is from 0.1 to 16 part per million by volume (ppm/v). In this application note we describe setting up calibration curves for this concentration range. We divide the concentration range into 3 parts. Table 1 lists the calibration ranges. Range I is out of the applicable concentration range of the ASTM D4084, but we include it in this application note to illustrate the sensitivity, linearity and reproducibility in the ultra-low range too.

RANGE I	RANGE II	RANGE III
0.1 ppb	20 ppb	1 ppm
0.3 ppb	50 ppb	2 ppm
0.5 ppb	100 ppb	6 ppm
1.0 ppb	200 ppb	12 ppm
2.0 ppb	600 ppb	18 ppm
5.0 ppb	1000 ppb	
10.0 ppb		

Table 1. Calibration ranges

Each calibration range is measured at a specific analyzer setting. Table 2 lists the system settings for each calibration range.

	RANGE I	RANGE II	RANGE III
Stock gas	1 ppm/v	2000 ppm/v	2000 ppm/v
Tape advance	Each standard	Each replicate	Each replicate
Flow	120 mL/min	24 mL/min	10 mL/min
Integration time	120 seconds	120 seconds	30 seconds

Table 2. System settings

Results

The data for calibration range I, II and II are listed in table 3, table 4, table 5 respectively. The calibration curves for each range are shown in graph 1, graph 2 and graph 3.

CONCENTRATION	AREA	RSD (%)
0.1 ppb	1549	11.34
0.3 ppb	3539	6.03
0.5 ppb	5538	2.67
1.0 ppb	9584	1.83
2.0 ppb	23484	2.70
5.0 ppb	50016	2.16
10.0 ppb	94540	1.05

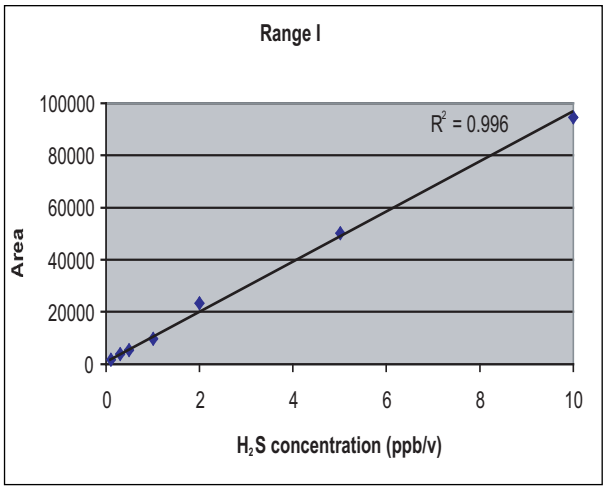
Table 3. Calibration data for range I

CONCENTRATION	AREA	RSD (%)
20 ppb	19106	7.18
50 ppb	69560	3.84
100 ppb	173916	2.30
200 ppb	362252	4.40
600 ppb	922519	0.49
1000 ppb	1489222	0.48

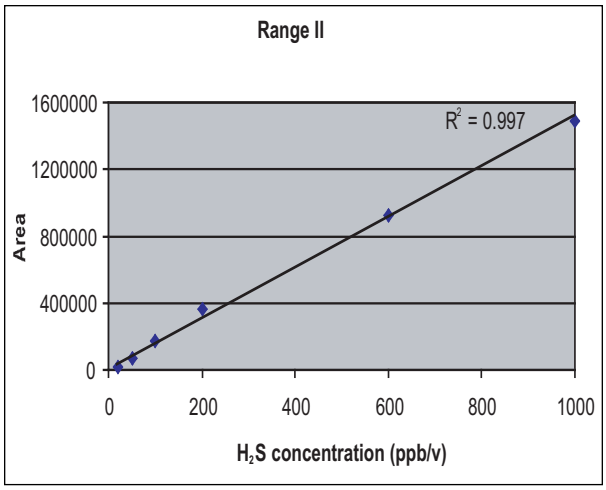
Table 4. Calibration data for range II

CONCENTRATION	AREA	RSD (%)
1 ppm	132726	2.09
2 ppm	302746	1.35
6 ppm	790980	1.12
12 ppm	1337654	1.28
18 ppm	1550259	1.44

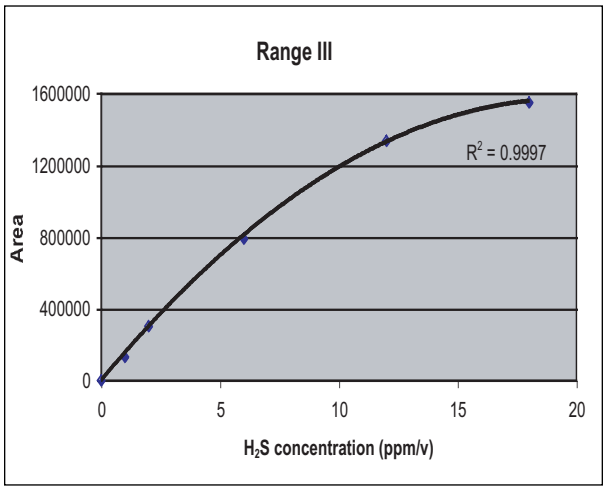
Table 5. Calibration data for range III



Graph 1. Calibration curve for range I



Graph 2. Calibration curve for range II



Graph 3. Calibration curve for range III

Discussion

Data processing described in the ASTM D4084 is very labor intensive. For this application we have used ThEuS computer software for signal processing. The software automatically calculates the rate of color change and enables data reprocessing in a very easy way.

The reproducibility requirements stated in the ASTM D4084 is not very strict. Instead we identify a good reproducibility if the relative standard deviation of the replicates is lower than 5%.

The calibration curve of Range I is linear and the relative standard deviation (RSD) is lower than 5% for concentration higher or equal to 0.5 ppb/v. Concentration levels lower than 0.5 ppb seem to have a higher RSD than 5% at these system settings.

The calibration curve of Range II is linear and the RSD is lower than 5% for concentrations higher or equal to 50 ppb/v. Concentration levels lower than 50 ppb/v seem to have a higher RSD than 5% at these system settings.

The calibration curve of Range III is not linear across the whole range. The response of the analyzer follows a second order line in this concentration range. All calibration gas mixtures in this range are measured with the RSD lower than 5%.

Conclusion

Thermo Electron XVI$^+$ analyzer is very well suited for the scope of the ASTM D4084. The sensitivity at sub-ppb level of the XVI$^+$ is very good and exceeds the sensitivity requirements of the ASTM D4084. The response of the analyzer at higher levels tends to follow a second order line.

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