PAC | Application Note

Analysis of Ultra low Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence according to ASTM D5504

- Ultra low detection limits
- Excellent Sensitivity, Repeatability & Linearity
- Robust Solution using AC SeNse detector

Keywords: SeNse, Sulfur, Natural gas,

INTRODUCTION

This application note describes the determination of speciated volatile sulfur-containing compounds in high methane content gaseous fuels such as natural gas, using the novel PAC SeNse detector. The SeNse detector is highly sensitive to sulfur response, linear, equimolar, and no interference or quenching from co-eluting hydrocarbons are observed.

Many sources of natural and petroleum gases contain sulfur compounds that are odorous, corrosive, and poisonous to catalysts used in gaseous fuel processing. Low ppm amounts of sulfur odorants are added to natural gas and LP gases for safety purposes. Some odorants are unstable and react to form compounds having lower odor thresholds. Quantitative analysis of these odorized gased ensures that odorant injection equipment is performing to specification. Fuel gases are also used in energy production or are converted to new products using catalyst that are poisoned by excessive sulfur in the feed gas. Industry frequently requires measurement of sulfu in these fuel type gased to protect their catalyst invesments.

INSTRUMENTAL

The sample is introduced on the analytical column by switching the sample loop in the carrier gas stream. The thick phase methyl silicone capillary column separates the trace sulfur components from the matrix and each other in a temperature-programmed run. The capillary column is coupled to a dual plasma furnace where the sulfur compounds are combusted to SO_2. Sulfur dioxide is reduced, in the presence of excess hydrogen to various reduced sulfur species. These species are transferred to a reaction cell. Ozone is added to the reaction cell where it reacts with the reduced sulfur species to create exited state sulfur dioxide. Relaxation of sulfur dioxide to the ground state releases a photon. The emitted light is measured using a photomultiplier tube and converted to a voltage.

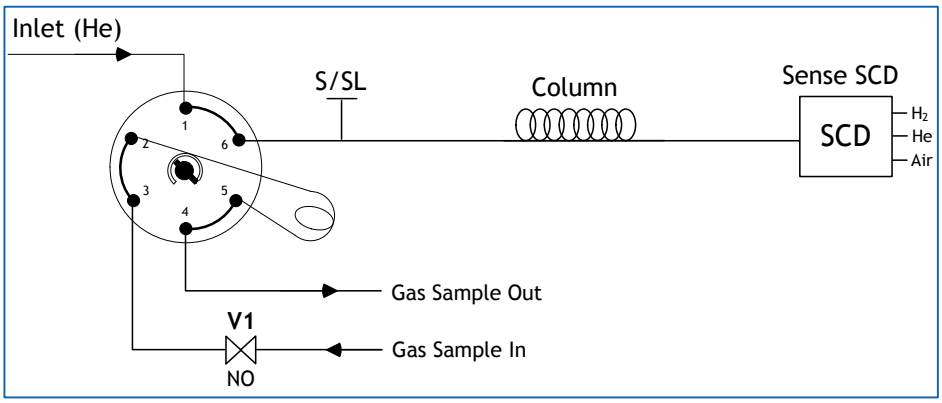

Figure 1: Plumbing diagram for Sulfur Compounds in Natural Gas and Gaseous fuels analyzer according ASTM D5504 using PAC SeNse detector.

VALIDATION

The system and methodology of the AC ASTM D5504 Ultra low Using PAC SeNse detector are thoroughly tested for separation efficiency, repeatability, Equimolarity, detection levels, response linearity and recovery.

SEPARATION EFFICIENCY

Chromatographic conditions are optimized to obtain adequate separation of the common Sulfur compounds. As shown in figure 2, the column provides baseline separation for Hydrogen sulfide and carbonyl sulfide at 35°C initial oven temperature (no cryogenic cooling required).

REPEATABILITY

Area (concentration) and retention time are the two primary measurements in gas chromatography. The precision in which they are measured ultimately determines the validity of the generated quantitative data. Retention time and area precision require that all parameters (temperatures, pressure, flow, injection) are controlled to exacting tolerances. Furthermore, the inertness of the flow path can considerably affect area precision, especially for active Sulfur components at low levels.

RETENTION TIME REPEATABILITY

ASTM D5504 stated: *"Chromatographic parameters must be capable of obtaining retention time repeatability of 0,05 min (3s) throughout the scope of this analysis"*.

Retention time repeatability is measured for 8 consecutive runs for a calibration standard blend diluted to 500 ppb single peak (figure 3). Retention time repeatability of the sulfur components is calculated in table 1.

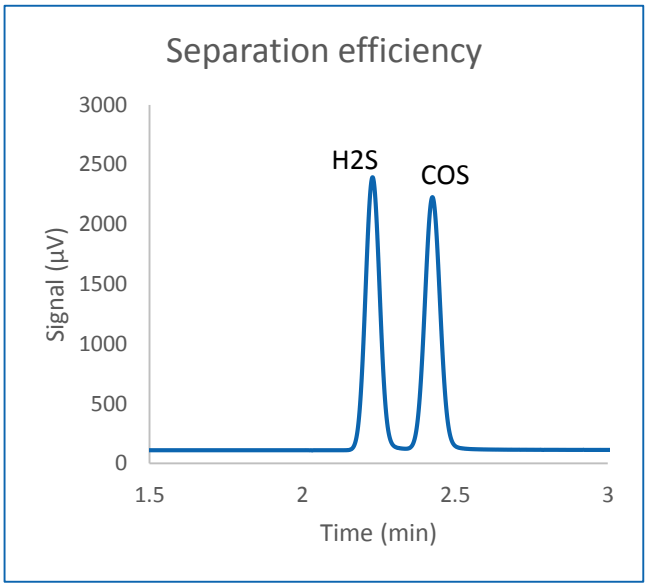

Figure 2: Calibration gas (~ 10 ppm single compound).

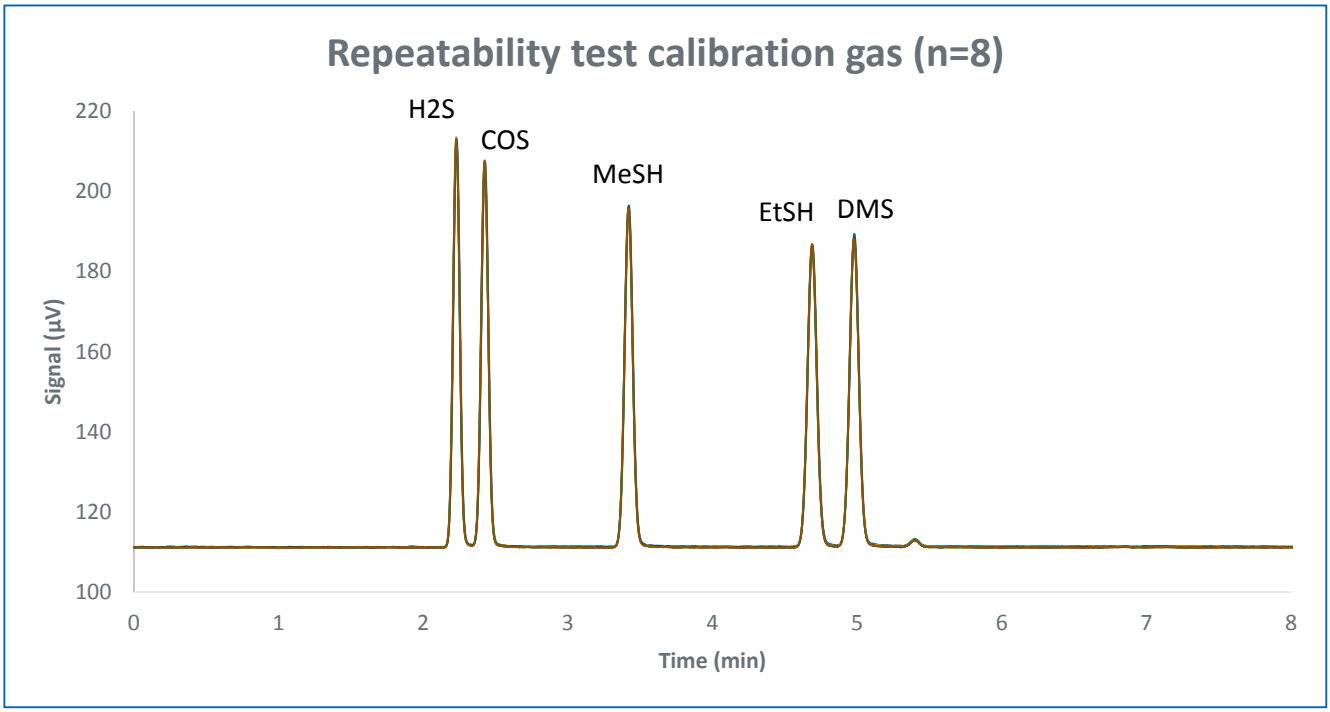

Figure 3: Repeatability overlay of 8 consecutive runs of calibration gas diluted to ~ 500 ppb.

Run	Retention time (minutes)				
	Hydrogensulfide	Carbonyl sulfide	Methyl Mercaptane	Ethyl Mercaptane	DMS
1	2.232	2.428	3.423	4.692	4.982
2	2.231	2.426	3.422	4.690	4.981
3	2.230	2.426	3.421	4.690	4.981
4	2.229	2.425	3.420	4.689	4.979
5	2.230	2.426	3.420	4.690	4.980
6	2.230	2.426	3.421	4.690	4.980
7	2.231	2.426	3.421	4.690	4.981
8	2.230	2.425	3.420	4.689	4.980
Average	2.230	2.426	3.421	4.690	4.981
MIN	2.229	2.425	3.420	4.689	4.979
MAX	2.232	2.428	3.423	4.692	4.982
stdev	0.0009	0.0009	0.0011	0.0009	0.0009
RSD	0.04%	0.04%	0.03%	0.02%	0.02%

Table 1. Retention time repeatability of 8 consecutive runs of calibration gas diluted to ~ 500 ppb.

CONCENTRATION REPEATABILITY

Concentration repeatability according ASTM D5504-12 is measured for 8 consecutive runs for a calibration standard blend diluted to ~ 500 ppb single peak. Repeatability is compared with the precision statement of the method.

Very good repeatability values are obtained (table 2).

The repeatability standard deviation obtained on the analyzer is compared with the values mentioned in the precision statement. The analyzer complies easily with the precision statement for Hydrogen Sulfide, Carbonyl Sulfide and Methyl Mercaptane.

Run	Concentration (ppm)				
	Hydrogensulfide	Carbonyl sulfide	Methyl Mercaptane	Ethyl Mercaptane	DMS
1	0.471	0.455	0.456	0.482	0.476
2	0.466	0.449	0.455	0.478	0.467
3	0.469	0.449	0.453	0.475	0.470
4	0.471	0.454	0.454	0.476	0.470
5	0.473	0.454	0.455	0.479	0.470
6	0.466	0.451	0.455	0.479	0.472
7	0.468	0.450	0.456	0.480	0.471
8	0.471	0.456	0.452	0.483	0.472
Average	0.469	0.452	0.455	0.479	0.471
MIN	0.466	0.449	0.452	0.475	0.467
MAX	0.473	0.456	0.456	0.483	0.476
RSD	0.52%	0.60%	0.33%	0.55%	0.58%
repeatability stdev measured	0.0024	0.0027	0.0015	0.0026	0.0027
repeatability stdev method	0.10	0.06	0.10	-	-

Table 2: Repeatability of a standard blend by GSV introduction (500 ppb)

LINEARITY

The linearity of response for the analyzer is verified by creating dynamic dilutions of a certified calibration gas. The dilutions are prepared by combining the calibration gas (sulfur compounds in nitrogen) and dilution gas (pure nitrogen) using two separate mass flow controllers.

Concentrations from ~ 10 ppm down to 10 ppb have been created and analyzed on the AC D5504 Ultra Low system. Calibration lines have been prepared for Hydrogen Sulfide (H2S), Carbonyl Sulfide (COS), Methyl Mercaptane (MeSH), Ethyl Mercaptane (EtSH) and DMS. All calibration lines have a linearity correlation > 0.9999.

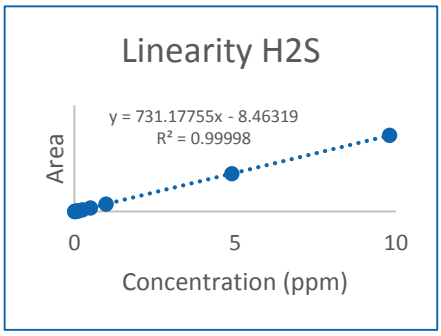

Figure 4: Linearity Plot H2S

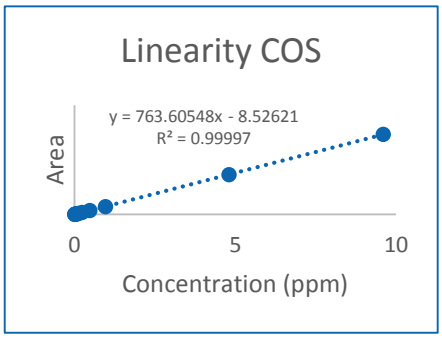

Figure 5: Linearity Plot COS

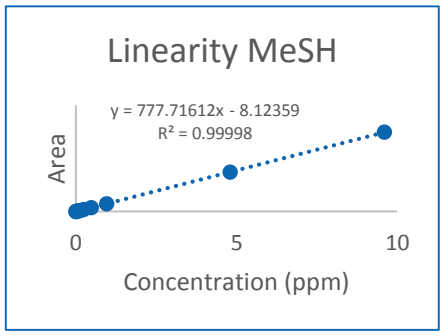

Figure 6: Linearity Plot MeSH

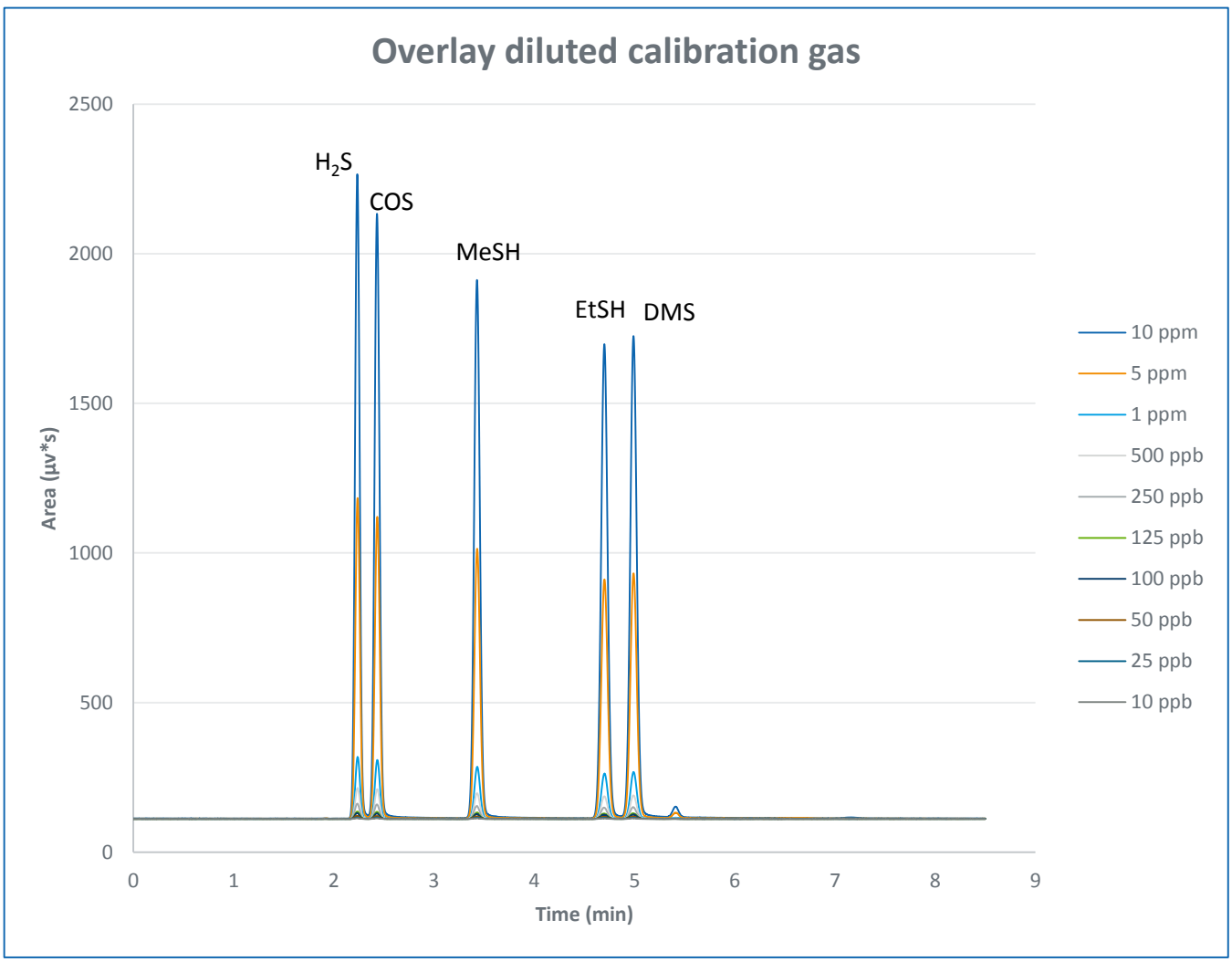

Figure 7: Overlay diluted Calibration gas

DETECTABILITY

Detection limit is calculated according the next formula. The calculations are based on a ~ 50 ppb diluted calibration gas. Results are listed in Table 3.

$$LOD = \left(\frac{3 * c * N}{A}\right) * W * 60$$

Where:

LOD = Limit of detection (ppm mol)

c = Concentration of component of interest (ppm mol)

N = Noise (peak to peak) (µV)

A = Area of peak of interest (µV * s)

W = Width of peak at half height (minutes)

To verify the calculated detectability of the AC D5504 Ultra low system, the calibration gas is diluted (as described above under "linearity") down to 5 ppb level and analyzed on the system.

Component	Noise (µV)	Area (µV*s)	Conc. (ppb)	Width (min)	LDL (ppb)
Hydrogen sulfide	0.2	33.4	49	0.0542	2.9
Carbonyl sulfide	0.2	34.6	48	0.0580	2.5
Methanethiol	0.2	34.1	48	0.0656	3.3
Ethanethiol	0.2	34.8	50	0.0785	4.1
Dimethyl Sulfide	0.2	37.5	50	0.0792	3.8

Table 3: Detection limit calculation

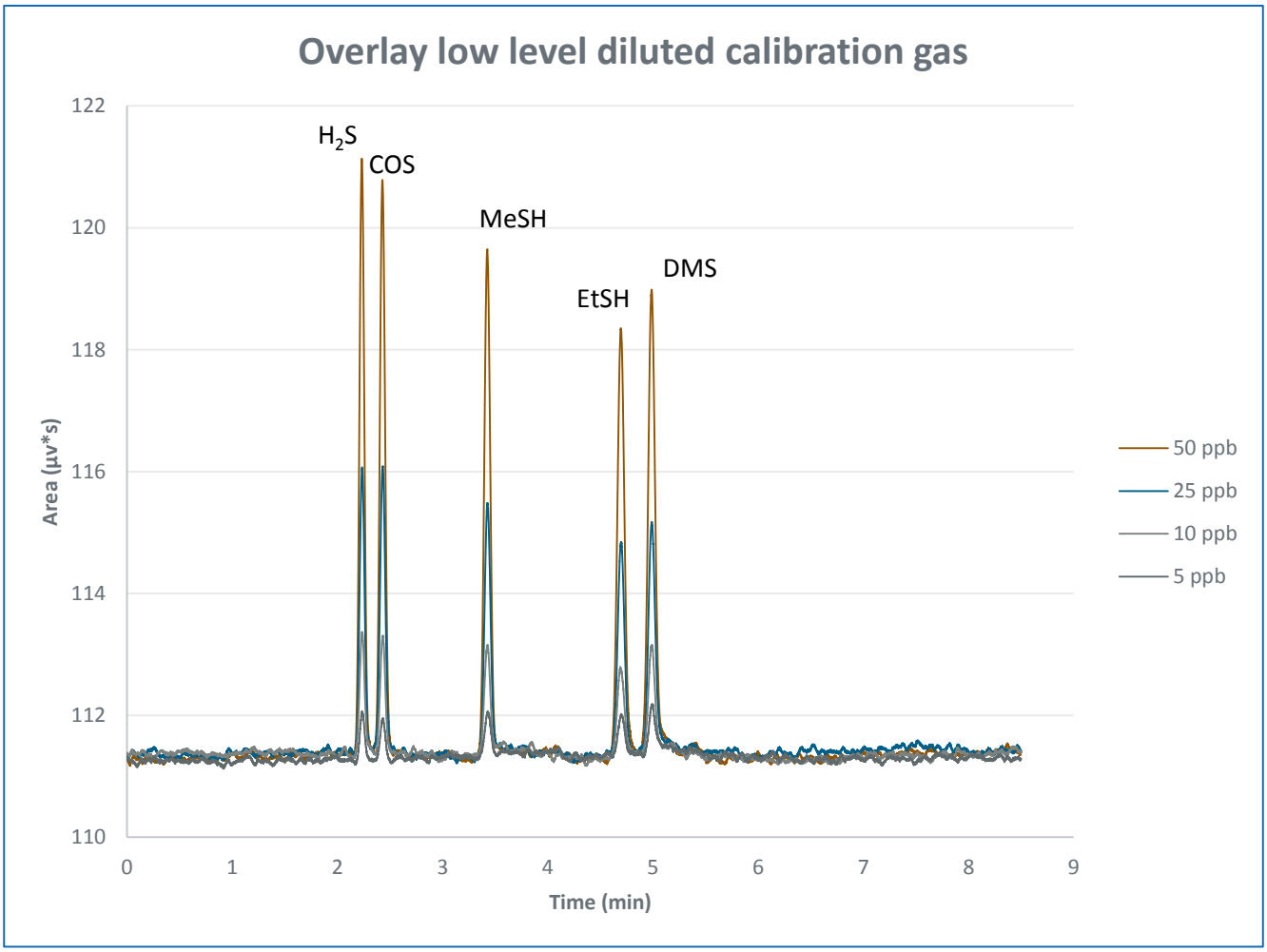

Figure 8: Overlay low level diluted Calibration gas

EQUIMOLARITY

The SCD is an equimolar detector; therefore, all sulfur compounds are assumed to produce equivalent response as sulfur. The response factors for all calibration components in the calibration gas are calculated and displayed in table 4. The response factor of each single sulfur compound are within 5% of the response factor for hydrogen sulfide.

Component	Concentration ppm	Average Area	RF	Deviation RF to H2S
Hydrogen Sulfide	0.49	343	0.001429	0.00%
Carbonyl Sulfide	0.48	353	0.001359	-4.92%
Methyl Mercaptan	0.48	350	0.001370	-4.11%
Ethyl Mercaptan	0.50	351	0.001425	-0.29%
Dimethyl Sulfide	0.50	366	0.001368	-4.27%

Table 4: Response factor calculation at 0.50 ppm Sulfur level

Natural gas

A natural gas sample (taken from the local distribution network) is analyzed using the Ultra low D5504 system. The main peak is THT (Tetra Hydro Thiophene) which is added to the natural gas network as odor component by the supplier at ~18 mg/m^3. The measured concentration is 4.55 ppm mol THT, which complies with 16.99 mg/m^3.

Zoomed in on the baseline, various sulfur compounds (i.a. DMS) are determined at single digit ppb levels.

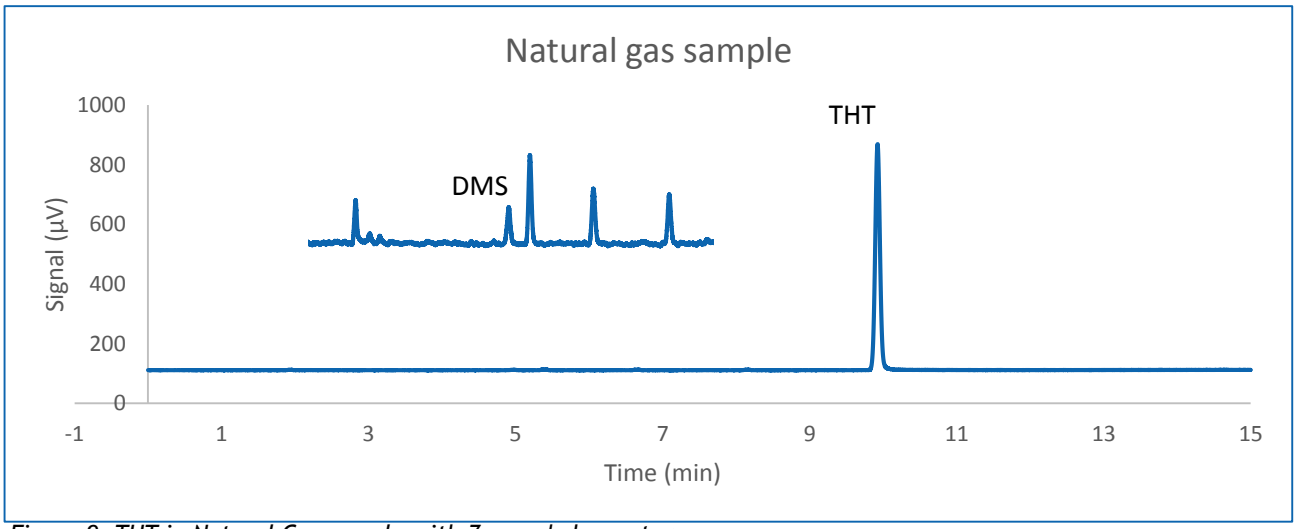

Figure 9: THT in Natural Gas sample with Zoomed chromatogram

CONCLUSION

The AC D5504 Ultra Low analyzer is a dedicated solution for accurate determination of Sulfur compounds in Natural gas and Gaseous Fuels. Its performance not only meets but exceeds ASTM D5504 requirements, ensuring the best quality data that can be used to estimate effects of Sulfur compounds in Natural Gas and Gaseous Fuels.

The application with the novel AC SeNse detector, already well known for its stability and ruggedness, makes the AC D5504 Ultra Low very robust and easy to use in routine environments. The AC Ultra Low D5504 analyzer provides low detection levels (down to ~ 5 ppb), excellent repeatability, stability, Equimolarity and recovery values every time.

Ordering information	Description
CCG6104A	ASTM D5504 Ultra Low Sulfur System, 120V 7890GC
CCG6104C	ASTM D5504 Ultra Low Sulfur System, 230V 7890GC
CCG6104.100	Kit, Spares & Consumables for ASTM D5504 Ultra Low Sulfur analyzer on 7890GC
99.10.040	Calibration gas, Sulfur, without regulator (H2S, COS, MeSH, EtSH, DMS – 10 ppm Mol)
99.10.014	Pressure regulator, for Sulfur calibration gas, inert
CCG6199	Permeation Device, build-in for Sulfur analyzer on 7890GC

Table 5: AC ASTM D5504 ordering guide

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer® , DHA, SimDis, NGA, Hi-Speed RGA and Customized instruments.