PAC | Application Note

Analysis of Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection according to ASTM D5623.

- **Fast Analysis in <30 Minutes**
- **Excellent Sensitivity, Repeatability & Linearity**
- **Robust Solution using PAC SeNse detector**
- **No Matrix Interference**

Keywords: SeNse, Sulfur, Gasoline,

INTRODUCTION

This application note describes the determination of volatile sulfur-containing compounds in light petroleum liquids (gasolines) 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.

Gas Chromatography with sulfur selective detection provides a rapid means to identify and quantify sulfur compounds in various petroleum feeds and products. Often these materials contain varying amounts and types of sulfur compounds. Many sulfur compounds are odorous, corrosive to equipment, an inhibit or destroy catalysts employed in downstream processing. The ability to speciate sulfur compounds in various petroleum liquids is useful in controlling sulfur compounds in finished products and is frequently more important than knowledge of the total sulfur content alone.

INSTRUMENTAL

The sample is introduced by either the liquid sampling valve (LSV) or by syringe (ALS) into the split/splitless inlet. 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 produced in the ozonator 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.

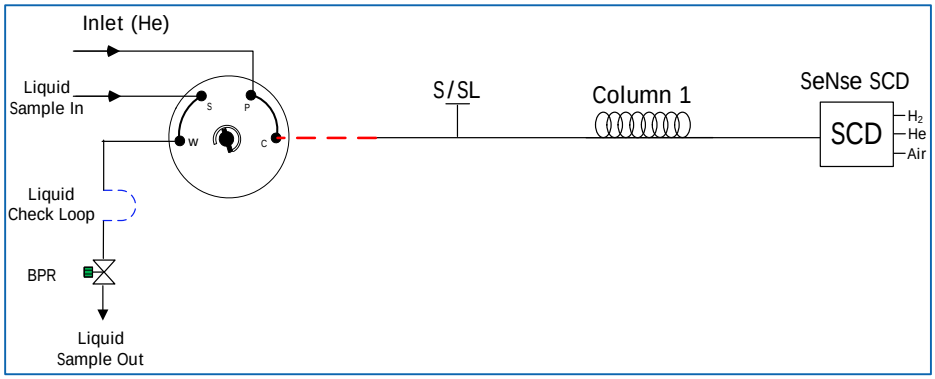

Figure 1: Plumbing diagram for Sulfur Compounds in Light Petroleum Liquids analyzer according ASTM D5623 using PAC SeNse detector (with optional LSV)

VALIDATION

The system and methodology of the AC D5623 analyzer Using PAC SeNse detector are thoroughly tested for separation efficiency, repeatability, response linearity, recovery and detection levels.

SEPARATION EFFICIENCY

Chromatographic conditions are optimized to obtain adequate separation of the common Sulfur compounds. Analytical Controls delivers two dedicated liquid samples to validate the peak identification according D5623. The composition of the samples are mentioned in table 1. The elution profiles are pictured in Figure 2 and 3.

Component ID #	Peak ID mix #	Components
1	1	Ethanethiol
2	2	Dimethylsulfide
3	1	Carbon Disulfide
4	1	2-Propanethiol
5	1	2-methyl-2-propanethiol
6	1	1-Propanethiol
7	2	Ethylmethylsulfide
8	1	2-Butanethiol
9	2	Thiophene
10	1	2-Methyl-1-propanethiol
11	2	Diethylsulfide
12	1	1-Butanethiol
13	2	Dimethyldisulfide
14	2	2-Methyl Thiophene
15	2	3-Methyl Thiophene
16	2	Diethyldisulfide
17	2	Benzothiophene
18	2	3-Methylbenzothiophene

Table 1. Calibration components ASTM D5623

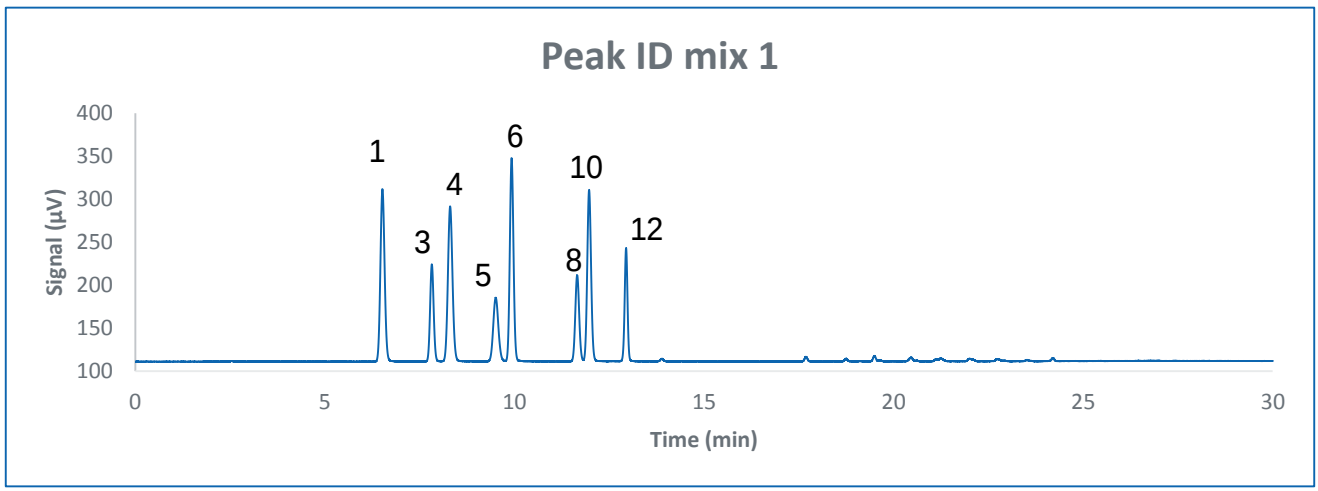

Figure 2: Peak ID mix 1 (AC part # 00.02.612)

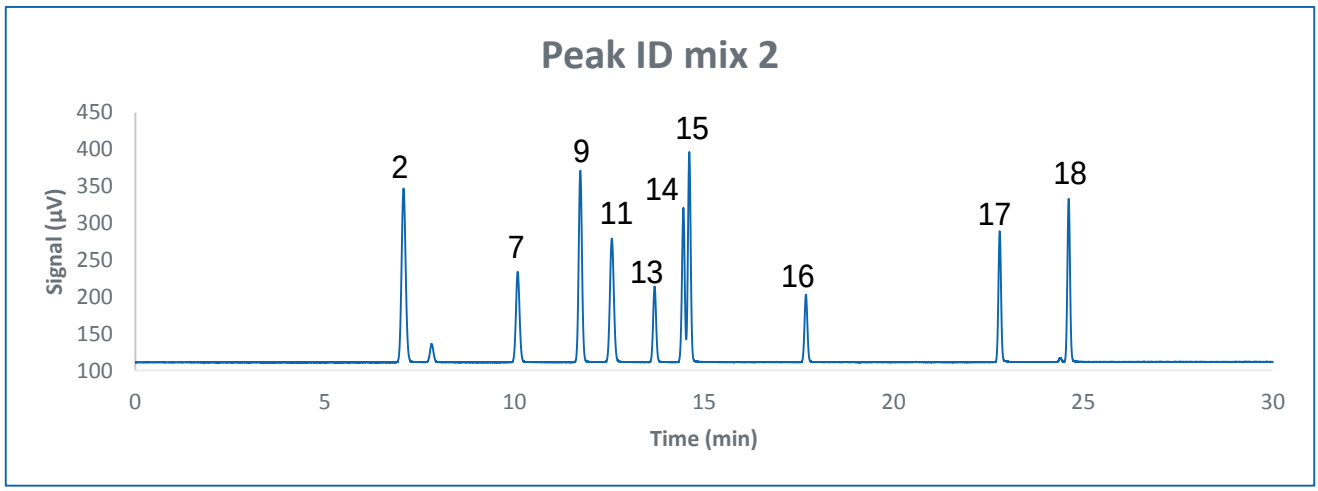

Figure 3: Peak ID mix 2 (AC part # 00.02.613)

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 D5623 stated: *"the system must be sufficiently reproducible to obtain retention time repeatability of 0,05 min (3s) throughout the scope of this analysis."*

Retention time repeatability is measured for 10 consecutive runs for a standard blend (peak ID mix 2) by ALS (figure 4). Retention time repeatability of the sulfur components is calculated in table 2.

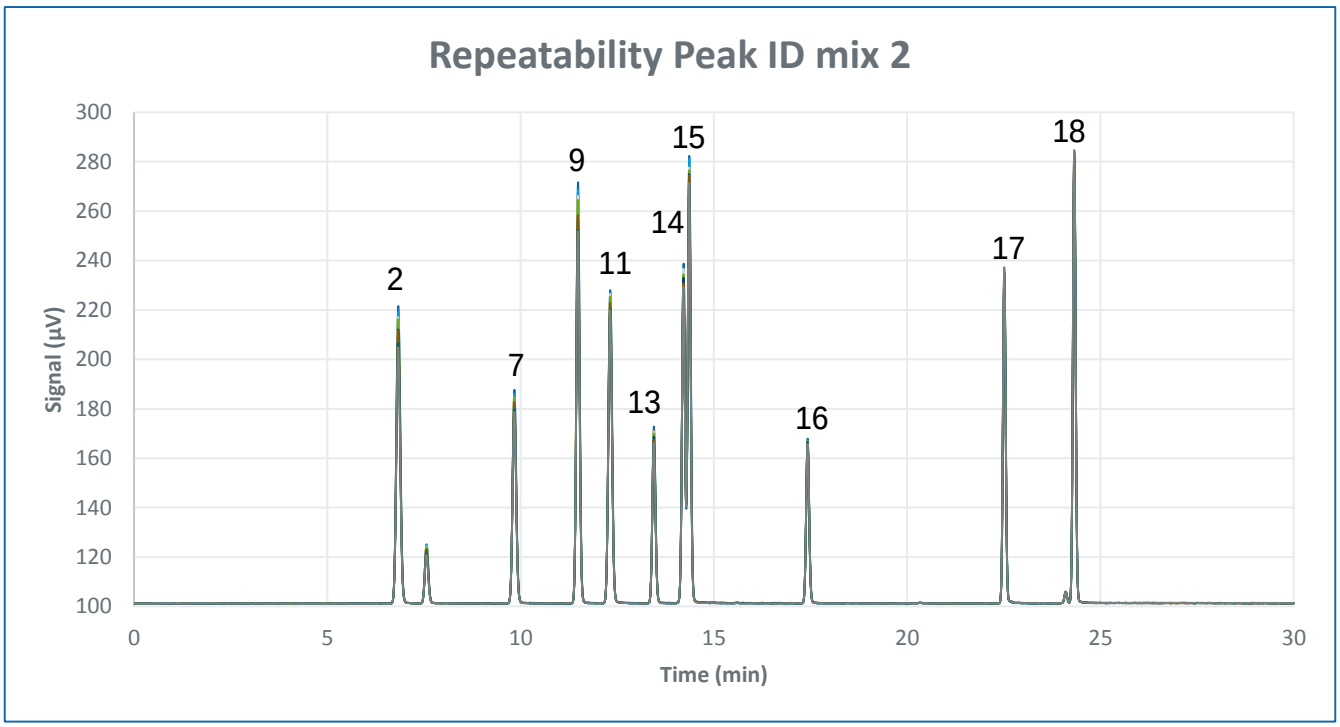

Figure 4: Repeatability overlay of 10 consecutive runs of peak ID mix 2 in ASTM D5623 ALS injection.

Component	Retention time												
	1	2	3	4	5	6	7	8	9	10	Avg	MIN	MAX
Dimethyl Sulfide	6.835	6.835	6.835	6.834	6.835	6.835	6.835	6.835	6.834	6.834	6.835	6.834	6.835
Carbon disulfide	7.566	7.566	7.568	7.566	7.565	7.567	7.565	7.566	7.566	7.565	7.566	7.565	7.568
Ethylmethyl Sulfide	9.838	9.837	9.838	9.838	9.838	9.838	9.838	9.838	9.838	9.838	9.838	9.837	9.838
Thiophene	11.484	11.483	11.484	11.483	11.483	11.483	11.483	11.483	11.482	11.483	11.483	11.482	11.484
Diethylsulfide	12.318	12.318	12.318	12.317	12.318	12.318	12.318	12.318	12.316	12.317	12.318	12.316	12.318
Dimethyl Disulfide	13.447	13.448	13.448	13.447	13.447	13.448	13.448	13.449	13.447	13.448	13.448	13.447	13.449
2-Methyl Thiophene	14.215	14.215	14.214	14.213	14.214	14.214	14.213	14.213	14.212	14.213	14.214	14.212	14.215
3-Methyl Thiophene	14.363	14.363	14.362	14.361	14.362	14.362	14.361	14.361	14.361	14.361	14.362	14.361	14.363
Diethyldisulfide	17.425	17.426	17.425	17.424	17.425	17.425	17.425	17.424	17.424	17.425	17.425	17.424	17.426
Benzothiophene	22.513	22.513	22.513	22.512	22.513	22.512	22.513	22.512	22.512	22.512	22.513	22.512	22.513
3-Methyl benzothiophene	24.323	24.323	24.323	24.322	24.323	24.323	24.322	24.322	24.323	24.323	24.323	24.322	24.323

Table 2. Retention time repeatability of a Peak ID mix 2 in ASTM D5623 by ALS introduction

RECOVERY / REPEATABILITY

Concentration repeatability and recovery for the AC D5623 analyzer is measured for 10 consecutive runs for a NIST reference sample. The NIST Standard Reference Material 2299, Sulfur in Gasoline, was used. The total sulfur in gasoline is 13.6 ± 1.5 µg/g based on analyses by isotope dilution thermal ionization mass spectrometry (IDTIMS). Homogeneity testing was performed using X-ray fluorescence spectrometry.

Reproducibility and repeatability standard deviation is calculated according the precision statement of ASTM D5623. Average recovery of total sulfur (12.35 ppm S) is well within the Reproducibility value of the method. Repeatability standard deviation of Total sulfur as well single component (Thiophene) are also well within the precision statement of ASTM D5623.

Run	Total Sulfur ppm S	Thiophene ppm S
1	12.62	6.40
2	12.13	6.34
3	11.99	6.35
4	12.27	6.34
5	12.46	6.28
6	12.29	6.39
7	12.42	6.23
8	12.16	6.41
9	12.68	6.35
10	12.45	6.41
Average	12.35	6.35
MIN	11.99	6.23
MAX	12.68	6.41
stdev	0.22	0.06
RSD	1.77%	0.92%
Target	13.60	
$r_{method\ limit}$	2.96	1.97
$R_{method\ limit}$	7.07	
$r_{method\ stdev}$	1.06	0.70
$R_{method\ stdev}$	2.53	

Table 3. Recovery and repeatability values of NIST 2299 reference material

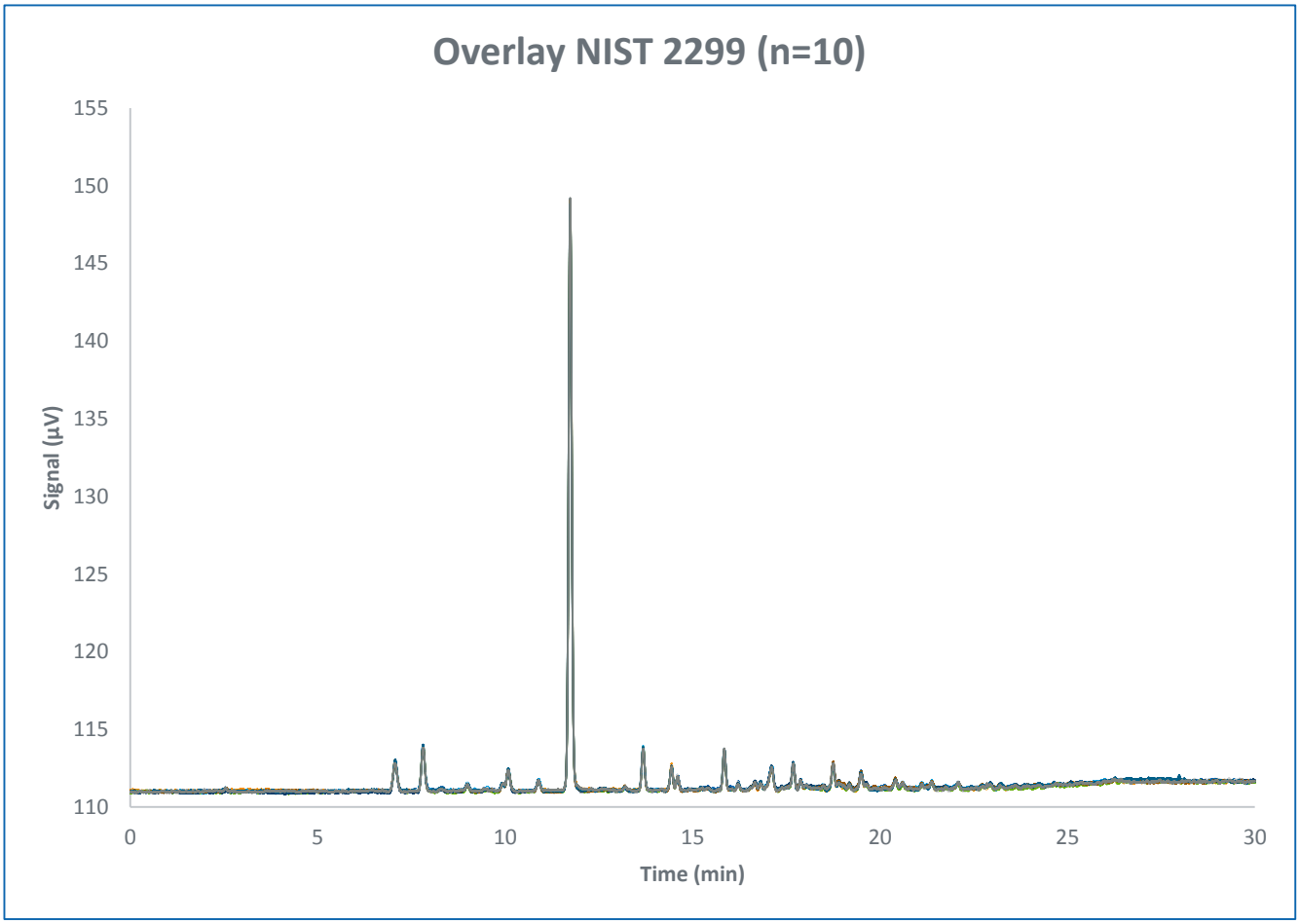

Figure 5: Repeatability overlay of 10 consecutive runs of NIST 2299 in ASTM D5623 ALS injection.

LINEARITY

The linearity of response for the analyzer is verified by measuring solutions of tert-butyl disulfide in varying concentrations. The solutions are prepared by creating dilutions of tert-butyl disulfide in iso-octane from 30 ppb to 100 ppm Wt S.

Correlation coefficient (R^2) of the tested sulfur compound over three orders of magnitude is better than 0.9999.

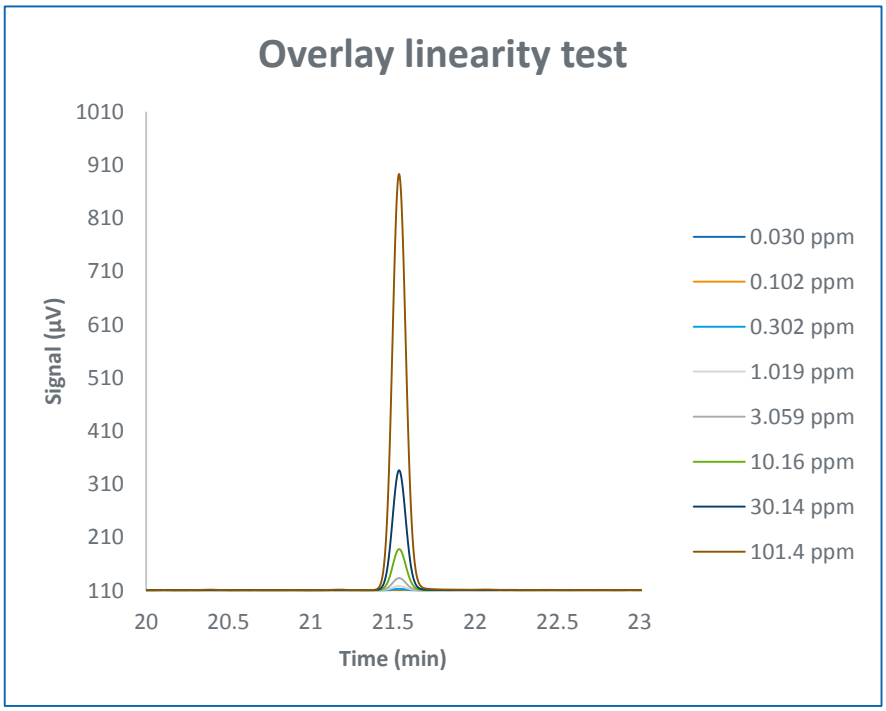

Figure 6: Linearity overlay of 30 ppb to 100 ppm tert-Butyl Disulfide

Conc. ppm S	Average Area	Response factor
0.03	1.4	2.14E-02
0.102	4.7	2.15E-02
0.302	14.0	2.16E-02
1.019	46.3	2.20E-02
3.059	134.8	2.27E-02
10.158	459.6	2.21E-02
30.147	1351.0	2.23E-02
101.402	4650.3	2.18E-02
	Average	2.19E-02
	stdev	4.24E-04
	RSD	2%

Table 4. Response factor values of tert-butyl disulfide over three order of magnitude

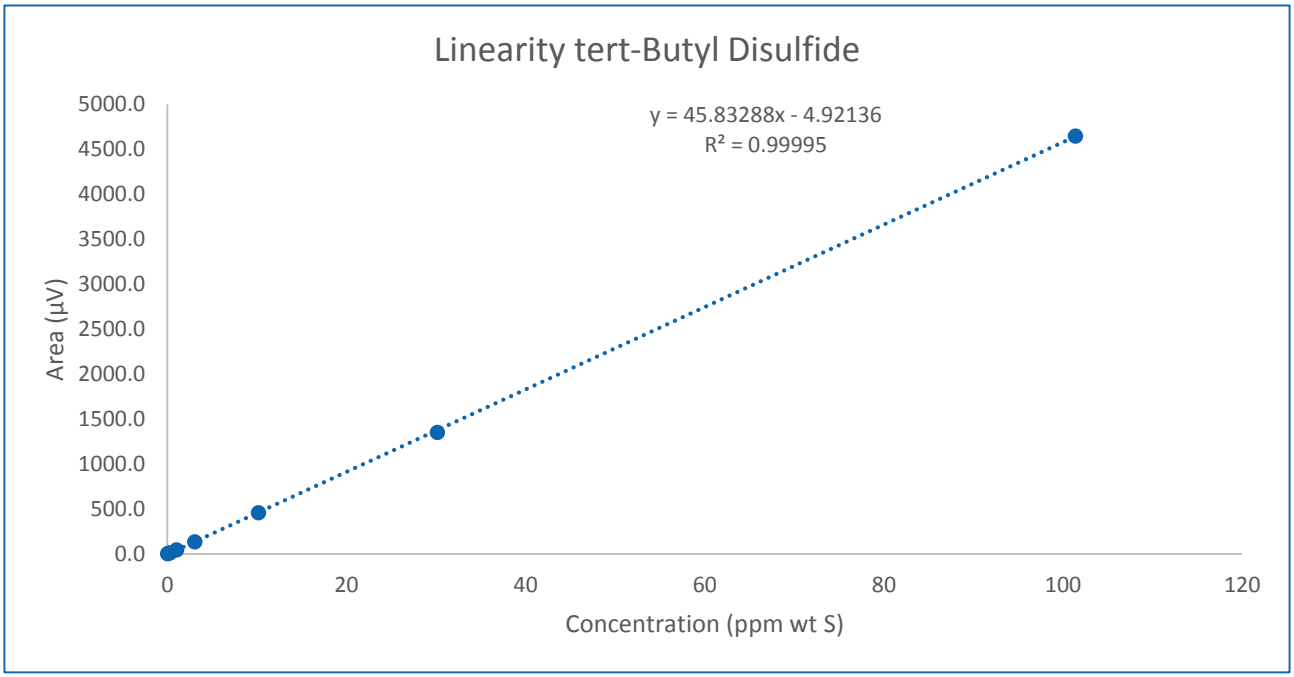

Figure 7: Linearity overlay of 30 ppb to 100 ppm tert-Butyl Disulfide

DETECTABILITY

Detection limit is calculated according the next formula. The calculations are based on a diluted SeNse check standard at ~ 10 x LDL. Results are listed in Table 5. A calculated LDL of ~ 50 ppb with split 1:10, 1 µl injection is obtained.

To verify the calculated detectability of the AC D5623 system, the SeNse check mix diluted to ~ 40 ppb / ~ 100 ppb is displayed in figure 8. At 40 ppb all components can clearly be differentiated form the baseline.

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

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)

Component	Noise (µV)	Area (µV*s)	Conc. (ppm)	Width (min)	LDL (ppmV)
Thiophene	0.15	20.1	0.443	0.0937	0.056
DiEthylSulfide	0.15	17.7	0.411	0.0869	0.054
DiMethylDiSulfide	0.15	20.0	0.430	0.0888	0.052
4-MethylThiazole	0.15	43.5	0.957	0.0938	0.056

Table 5: Detection limit calculation

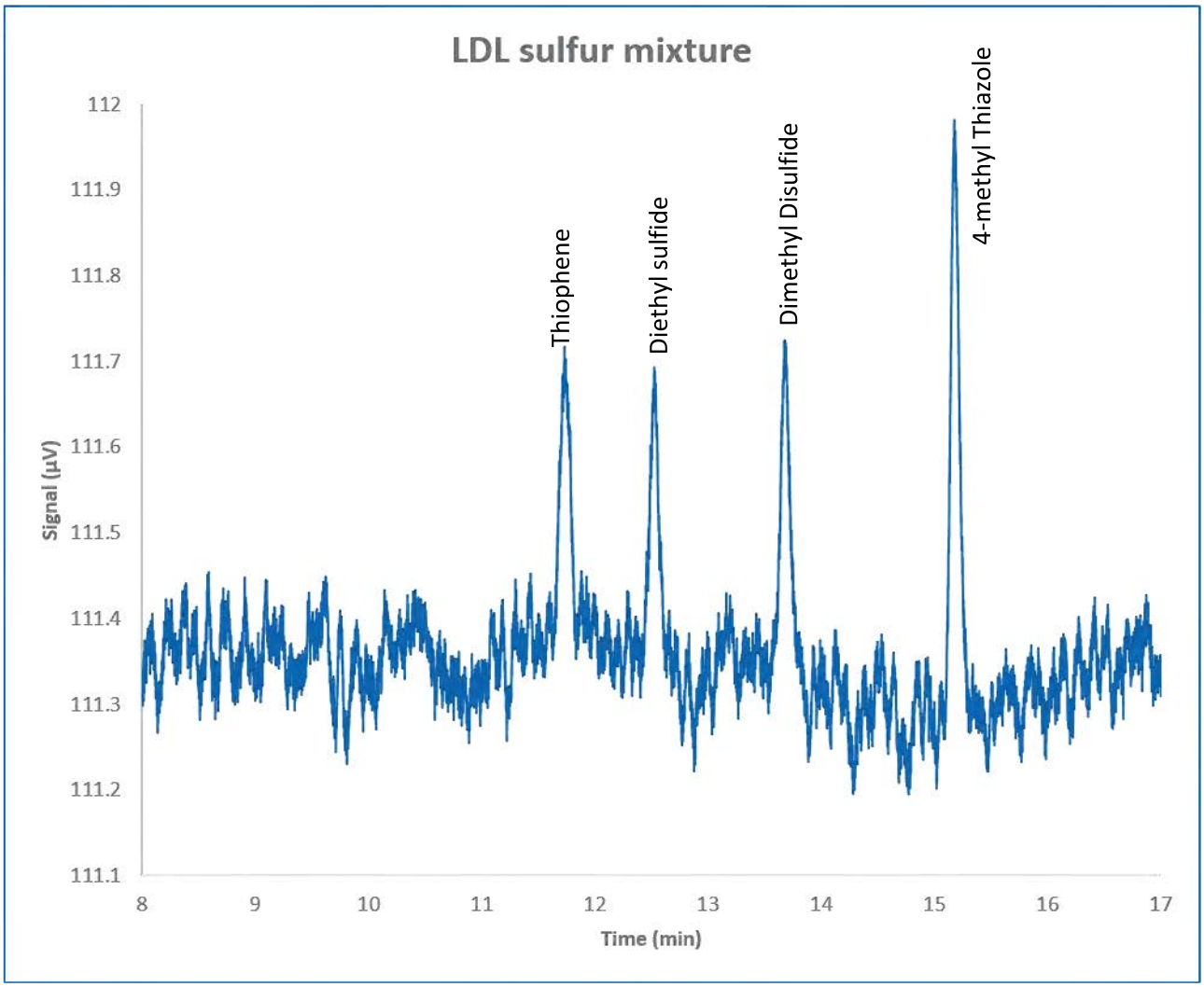

Figure 8: Chromatogram of SeNse check mix diluted to ~ 40 ppb / 100 ppb

CONCLUSION

The AC D5623 analyzer is a dedicated solution for accurate determination of Sulfur compounds in light petroleum liquids. Its performance not only meets but exceeds ASTM D5623 requirements, ensuring the best quality data that can be used to estimate effects of Sulfur compounds in light petroleum liquids.

The application with the novel AC SeNse detector, already well known for its stability and ruggedness, makes the AC D5623 system very robust and easy to use in routine environments. The AC D5623 analyzer provides low detection levels (down to ~ 30 ppb), excellent repeatability, stability, Equimolarity and recovery values every time.

Ordering information	Description
CCG6100A	ASTM D5623 Sulfur System, 120V 7890GC
CCG6101A	ASTM D5623 Sulfur System, incl. LSV, 120V 7890GC
CCG6100C	ASTM D5623 Sulfur System, 230V 7890GC
CCG6101C	ASTM D5623 Sulfur System, incl. LSV, 230V 7890GC
CCG6100.100	Kit, Spares & Consumables for ASTM D5623 Sulfur analyzer on 7890GC
CCG6101.100	Kit, Spares & Consumables for ASTM D5623 Sulfur, incl. LSV analyzer on 7890GC

Table 5: AC D5623 Ordering Information

Ordering information	Description
CCG6102A	ASTM D5504 / D5623 Sulfur System, incl. GSV, 120V 7890GC
CCG6103A	ASTM D5504 / D5623 Sulfur System, incl. GSV and LSV, 120V 7890GC
CCG6101C	ASTM D5623 Sulfur System, incl. LSV, 230V 7890GC
CCG6102C	ASTM D5504 / D5623 Sulfur System, incl. GSV, 230V 7890GC
CCG6102.100	Kit, Spares & Consumables for ASTM D5504 / D5623 Sulfur analyzer on 7890GC
CCG6103.100	Kit, Spares & Consumables for ASTM D5504 / D5623 Sulfur, incl. LSV analyzer
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 6: Mixed Configurations

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.