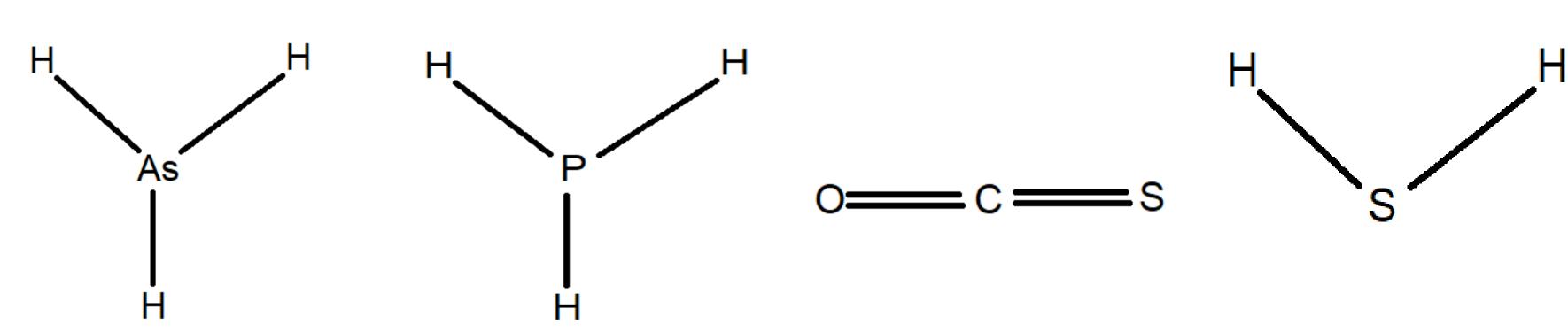# SHIMADZU

Trace level determination of AsH$_3$, PH$_3$, COS and H$_2$S in Propylene by using GC-MS

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1. Introduction

Arsine (AsH$_3$), Phosphine (PH$_3$), Carbonyl Sulfide (COS), and Hydrogen Sulfide (H$_2$S) are compounds present as impurities (Figure 1) in petroleum products and their derivatives. They contribute to the corrosion of facilities and the inhibition of catalytic reactions, leading to the deterioration of product quality. High purity propylene is used as feedstock to produce polypropylene and the quality of the monomer is critical for successful polymerization. The presence of trace amounts of AsH$_3$, PH$_3$, COS, and H$_2$S can have detrimental effects on the catalyst and product yield. To maximize the lifetime of the catalyst, propylene producers need to monitor AsH$_3$, PH$_3$, COS and H$_2$S at the lowest possible concentration levels.

Shimadzu GCMS-QP2020 NX (Figure 2) single quadrupole system with vaporizer and Gas sampling valve (GSV) was used to simultaneously determine AsH$_3$, PH$_3$, COS and H$_2$S impurities in propylene at trace levels.

Figure 1. Structure of AsH$_3$, PH$_3$, COS and H$_2$S

2. Materials and methods

2-1. Procedure

Individual standard of about 500 ppb for AsH$_3$, PH$_3$, COS and H$_2$S in balance Helium was procured for the study. The standard was further diluted to prepare the linearity concentration levels as mentioned in Table 1.

Table 1. Linearity standards preparation

Sr. no	Linearity Conc. (Mol-ppb)	AsH$_3$	PH$_3$	COS	H$_2$S
1	5	✓	✓	✓	NA
2	10	✓	✓	✓	NA
3	25	✓	✓	✓	NA
4	50	✓	✓	✓	✓
5	100	✓	✓	✓	✓
6	250	NA	NA	NA	✓
7	500	NA	NA	NA	✓

✓ – Applicable.   NA – Not Applicable

The liquified petroleum sample was passed through the vaporizer to eliminate the sample condensation effects. Then the sample was introduced into Shimadzu GCMS-QP2020 NX single quadrupole system automatically through GSV equipped with 1mL loop. Sulfinert® treated parts were used to ensure inert sample path for trace level analysis.

Plot column was used for simultaneous determination of these impurities in propylene matrix. The concentrations of targeted contaminants are determined against multi-point external standard calibration curve. The standard and samples were analyzed under identical conditions and injection volumes.

Figure 2. Shimadzu GCMS-QP2020 NX

2-2. Analytical Conditions

The analysis was carried out on Shimadzu GCMS-QP2020 NX with GSV and liquid sample vaporizer as per the conditions given in Table 2.

Table 2. Analytical conditions

Chromatographic parameters
- Column : Plot (50 m x 0.32 mm I.D. x 10.0 μm)
- Injection Temp : 80 ^{0}C
- Injection Mode : Split
- Split Ratio : 1:5
- Carrier Gas : Helium
- Flow Control Mode : Column flow
- Column Flow : 1.5mL/min
- Total Program Time : 35.00 min
- Column Temp. Program : Rate (^{0}C /min)   Temperature (^{0}C)   Hold time (min)

Rate (^{0}C /min)	Temperature (^{0}C)	Hold time (min)
	40.0	10.00
1.50	50.0	3.00
10.00	150.0	5.33

- GSV temperature : 80 ^{0}C
- Vaporizer temperature : 100 ^{0}C

Mass Spectrometry parameters
- Ion Source Temp. : 150.0 ^{0}C
- Interface Temp. : 150.0 ^{0}C
- Ionization Mode : EI (Electron Ionization)
- Acquisition Mode : SIM
- AsH$_3$ m/z : 76, 78
- PH$_3$ m/z : 34
- COS m/z : 60
- H$_2$S m/z : 34

3. Results

The analysis of of AsH$_3$, PH$_3$, COS, and H$_2$S was carried out as per the method shown in Table 2 and Selective Ion Monitoring (SIM) chromatogram of 50 ppb standard mixture acquired using this method is shown in Figure 3
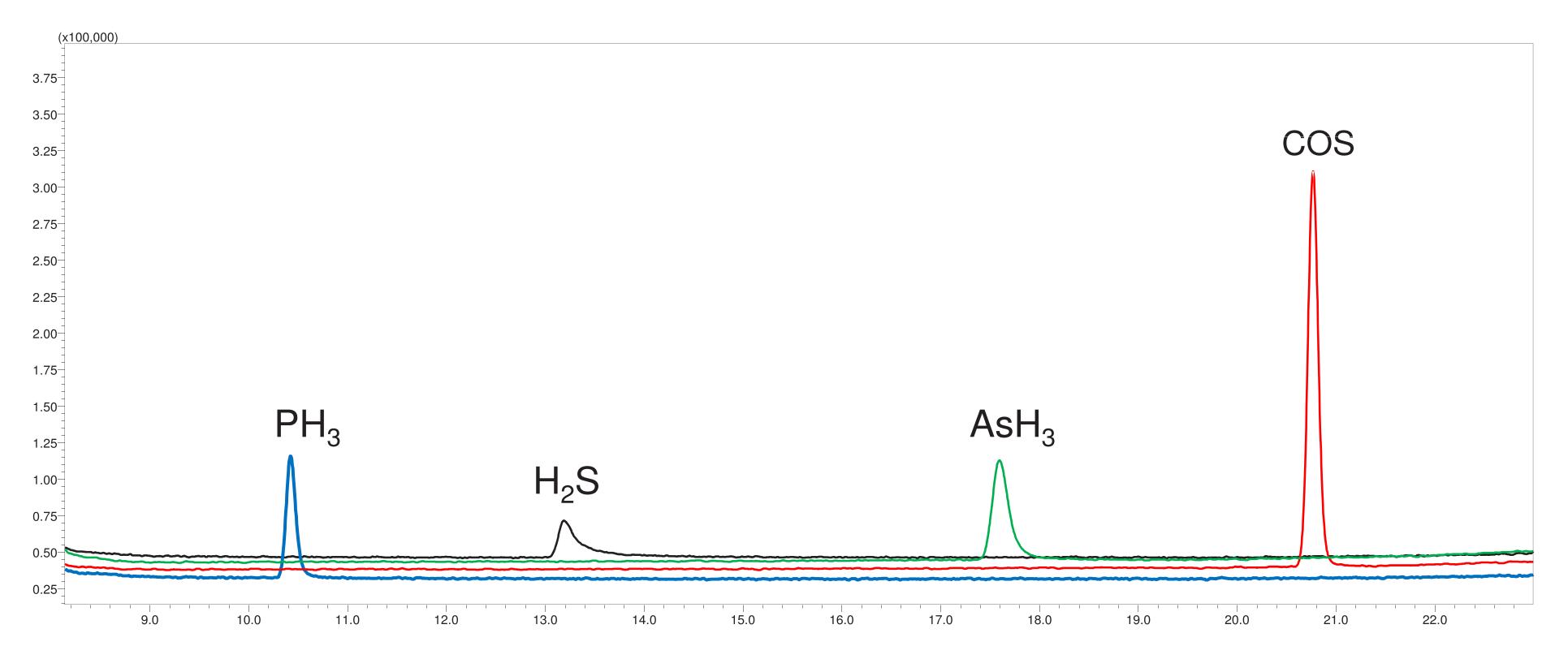

Figure 3. SIM chromatogram for 50 mol-ppb standard

The Relative Standard deviation (RSD) for three replicate injections of AsH$_3$, PH$_3$, COS at 5 mol-ppb and H$_2$S at 50 mol-ppb was found to be less than 5%. Linearity was plotted at concentration level ranging from 5 to 100 mol-ppb for AsH$_3$, PH$_3$, COS and from 50 to 500 mol-ppb for H$_2$S. For all target components, the regression coefficient (r^2) ≥ 0.995 was obtained (refer Figure 3 to 6). The limit of detection (LOD) and limit of quantitation (LOQ) were determined based on S/N ratio. Statistical evaluation of the data showed that the method was selective, sensitive and reproducible (refer Table 3).
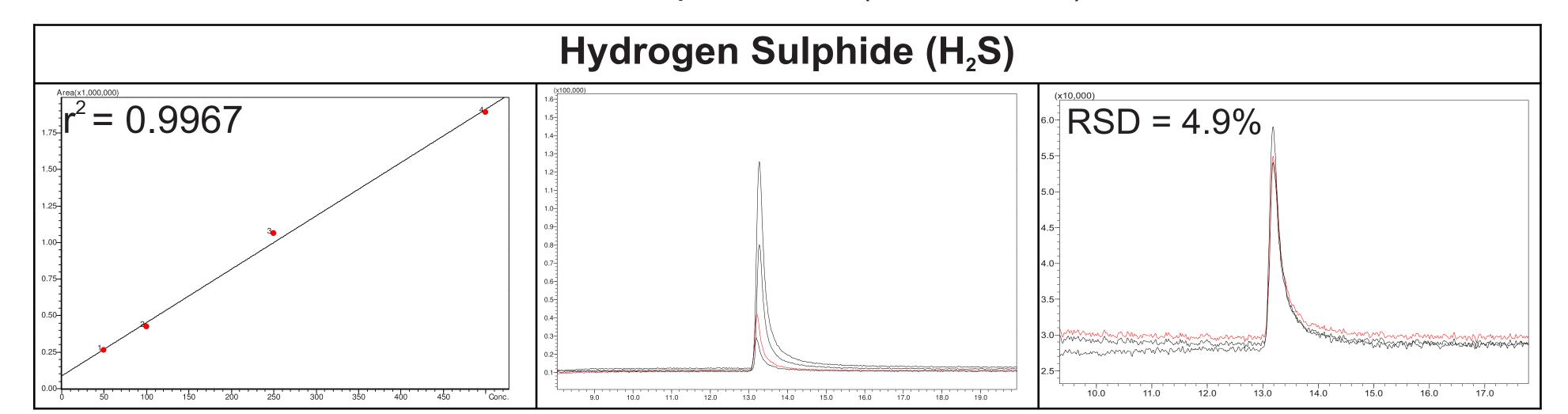
Hydrogen Sulphide (H$_2$S)

Figure 3. Calibration curve, linearity overlay graph and precision overlay at 50mol-ppb for H$_2$S
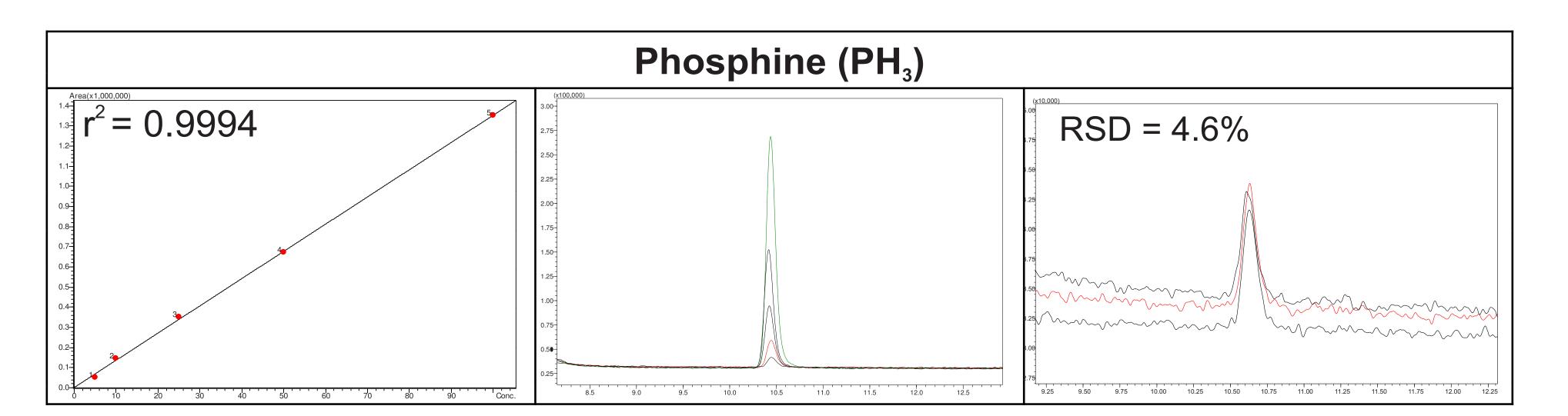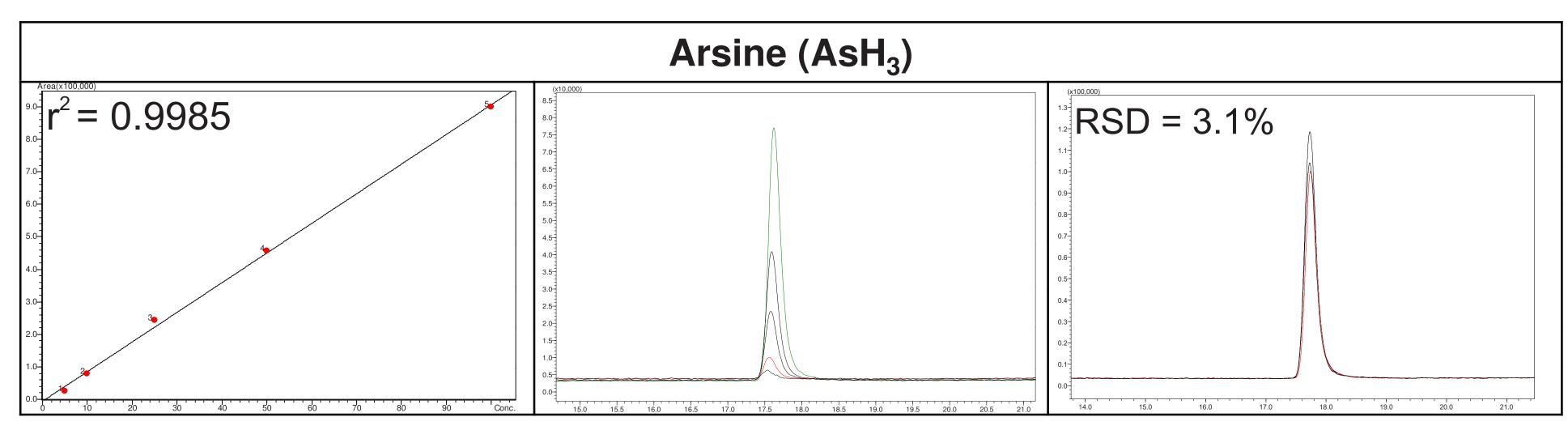
Phosphine (PH$_3$)

Figure 4. Calibration curve, linearity overlay graph and precision overlay at 5mol-ppb for PH3

Arsine (AsH$_3$)

Figure 5. Calibration curve, linearity overlay graph and precision overlay at 5mol-ppb for AsH$_3$
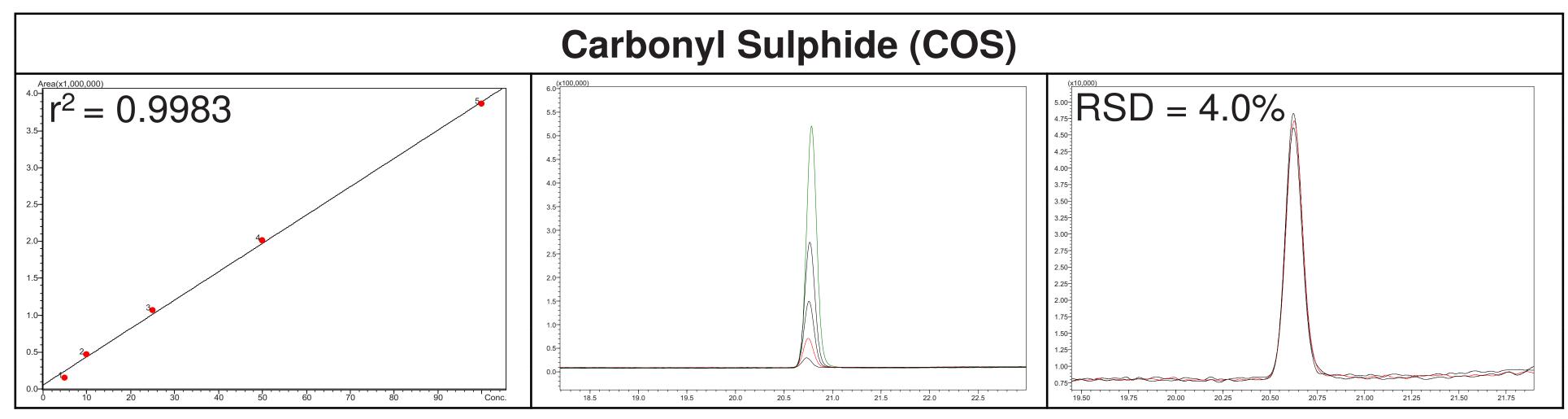
Carbonyl Sulphide (COS)

Figure 6. Calibration curve, linearity overlay graph and precision overlay at 5mol-ppb for COS

Table 3. Analytical Results

Name	m/z	Linearity range (mol-ppb)	r^2	Precision		*LOQ (**S/N=10) (mol-ppb)	*LOD (**S/N=3) (mol-ppb)
				Conc. (mol-ppb)	%RSD (n=3)		
PH$_3$	34	5 – 100	0.9994	5	4.6	3.6ppb	1.2ppb
H$_2$S	34	50 – 500	0.9967	50	4.9	18ppb	6ppb
ASH$_3$	76	5 – 100	0.9985	5	3.1	1.2ppb	4.1 ppb
COS	60	5 – 100	0.9983	5	4.0	0.1ppb	0.4 ppb

*LOD/LOQ are determined based on the values obtained from GCMS Solutions software.
** Noise calculation method used is ASTM with interval of 0.5mins.

4. Conclusion

The GCMS-QP2020 NX is an advanced gas chromatograph mass spectrometer which provides highest sensitivity in its class through its unique design and superior noise reduction technology, thereby enabling ultra trace level determination of low molecular weight compounds like AsH$_3$, PH$_3$, COS and H$_2$S in propylene sample.