# H$_2$S, COS
Arsine, phosphine
in ethylene and propylene

- highly sensitive : **< 1 ppb**
- single method, single run
- automatic calibration via permeation tubes
- GC-MS with AEI source for ultra low detection limits

AN 236WA0821D

GAS offers custom configured GC analysers for many application fields for over 45 years. GAS analysers are designed to meet many standardised methods from GPA, ASTM, UOP, ISO, EN and others. The efficient configurations are based on proven GC technology, resulting in robust instruments with an optimal return on investment.

H_2S, COS, arsine and phosphine are extremely damaging to downstream catalyst in hydrocarbon processing. Presence in ppb level in ethylene and propylene streams can poison the downstream precious metal catalyst in polymer plants. Low level detection of these contaminants offer olefin producers the ability to soothe these impurities.

Figure 1. Schematic diagram
H_2S, COS, arsine, phosphine analyser
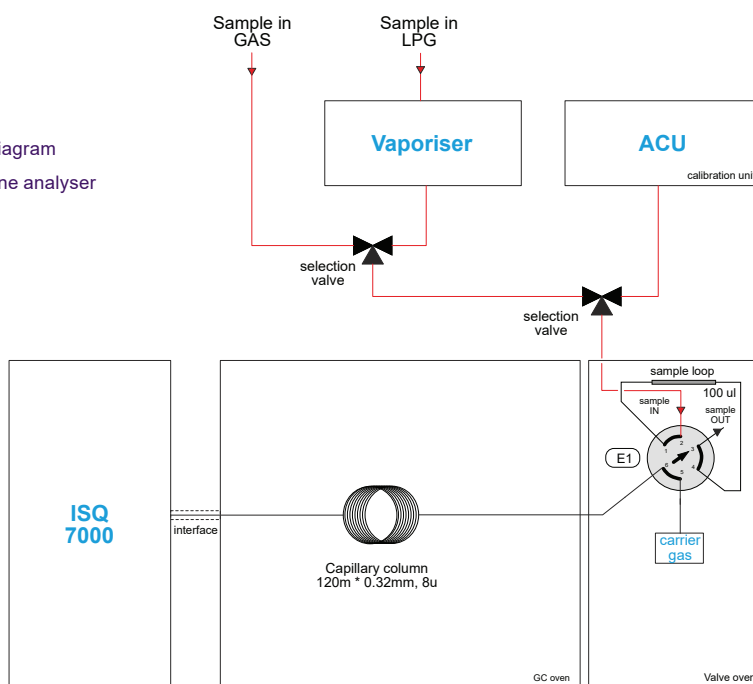
Instrument

Figure 1 shows the schematic diagram of the analyser. The gas sample is injected using GSV (Gas Sampling Valve) on a column with high chromatographic resolution, to resolve significant matrix peaks from the impurities of interest. Liquefied samples are vaporised first by the optional GAS Vaporiser (figure 8) or by prior transfer to a Tedlar bag. The active compounds necessitates an inert pathway to avoid adsorption.

ISQ 7610 GC-MS + Advanced Electron Ionisation

The ISQ 7610 GC-MS system delivers highest sensitivity, and with the optional Advanced Electron Ionisation (AEI) source, detection limits are driven down further to reach the required limits for the components of interest. Acquisition was performed in SIM mode (Selected Ion Monitoring) at masses 33, 34, 60, 76 and 78. Achieved LOD's are below 1 ppb.

Calibration

Permeation tubes with H_2S, COS, arsine and phosphine were placed in the GAS ACU (Automatic Calibration Unit, figure 9) to obtain low level calibration gases in concentration range 2-50 ppb. Multi-level calibration curves are automatically provided by ACU and Chromeleon MS data system.

Figure 2. GC 1600 with valve oven and ISQ 7610 mass spectrometer with and AEI source (Advanced Electron Ionisation).
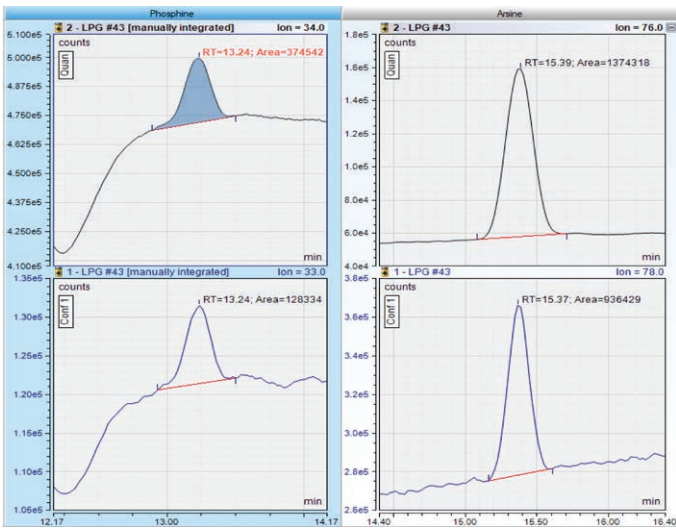
Figure 3. Mass chromatograms of arsine and phosphine, 10 ppb level

Results - Arsine & phosphine

10 ppb and 3-4 ppb calibration gases were prepared using permeation tubes and dilution by mass flow controllers (Automatic Calibration Unit). Nitrogen was used as dilution gas. Figure 3 shows mass chromatograms of 10 ppb for both components, while figure 4 represents 4 ppb arsine and 3 ppb phosphine.

The selected quantitation masses were 76 and 78 for arsine and 33 and 34 for phosphine. For both components detection limits below 1 ppb were found (100 ul gas injection).

Repeatability was 4,8 %RSD for arsine and 3,2 %RSD for phosphine (n=10, 10 ppb concentration level).

Figure 5 displays the linearity of this method. The recorded R^2 for both components was 0.998 (2-50 ppb concentration range).
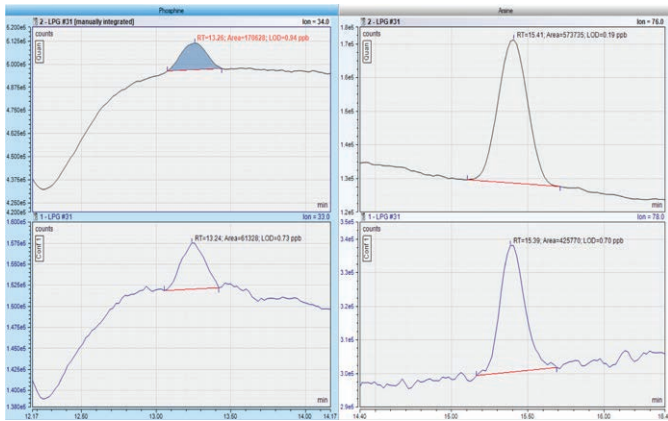

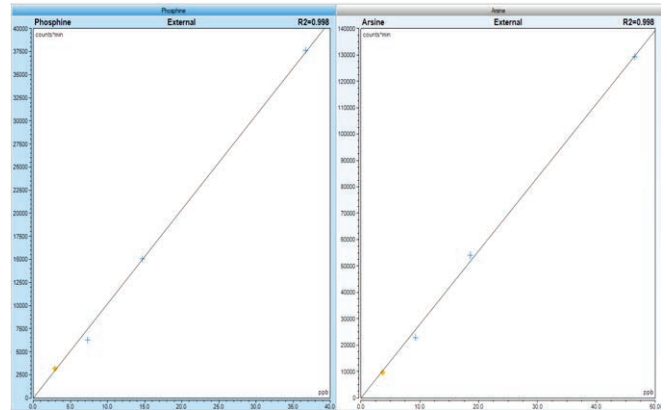Figure 4. Mass chromatograms of arsine and phosphine, resp. 4 and 3 ppb

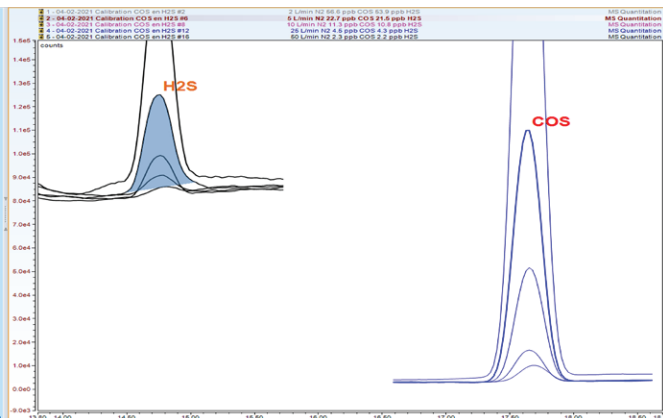Figure 5. R^2=0.998 for arsine and phosphine (2-50 ppb)

Figure 6. Overlay of 5 H$_2$S/COS concentration levels:
H$_2$S: 2.2, 4.3, 10.8, 21.5 and 53.9 ppb
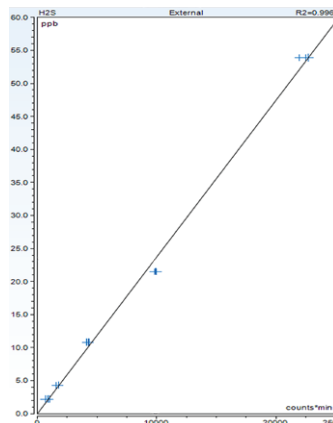COS: 2.3, 4.5, 11.3, 22.7 and 56.6 ppb

Figure 7. Calibration curve for H$_2$S.
Range= 2.2-53.9 ppb.
H$_2$S: R^2=0.996
COS: R^2=0.999

Results - H$_2$S & COS

Figure 6 and 7 show chromatograms and calibration curve of 2-50 ppb H$_2$S and COS. Quantitation masses were 33, 34 (H$_2$S) and 60 (COS)

Results were obtained in cooperation with SGS Nederland B.V. Vlissingen, Mr. K. Spaas and Mr. J. Verkuil.

Specification

Application:	Custom configured analyser for combined analysis of hydrogen sulphide, carbonlyl sulphide, arsine and phosphine in ethylene and propylene
Configuration:	1 channel analyser based on Thermo GC 1600 and ISQ 7610 Quadrupole MS with AEI (Advanced Electron Impact source)
Injection type	GSV (Gas Sampling Valve), 100 ul.
Optional:	- Vaporiser to evaporate liquefied samples to gas samples without discrimination (figure 8)
	- ACU (Automatic Calibration Unit) with permeation tube and mass flow controller dilution system for automated preparation of multi-level calibration gases (figure 9)
	- LSV and Sample Securitiser when liquid injection of LPG is preferred (figure 10)
	- Stop flow valve
Sample tubing:	Sulfinert® tubing for inert sample path (active components)
Sample requirements:	See our pre-installation guide for additional requirements
Analysis time:	35 minutes
Minimum detectability:	below 1 ppb for H_2S, COS, arsine and phosphine
Linearity (2-50 ppb):	Arsine, phosphine: $R^2=0.998$
	H_2S: $R^2=0.996$
	COS: $R^2=0.999$
Repeatability:	< 5 % RSD
Data systems:	Chromeleon CDS

Figure 8. GAS Vaporiser

Figure 9. Automatic Calibration Unit (ACU) with permeation tube and MFC dilution system

Figure 10. Optional Sample Securitiser for LPG injection as a liquid

Global Analyser Solutions

Turnkey customised
GC & GC-MS solutions

iS·X ACADEMY
Xpert center for chromatography

Expert & education centre
Learn from the Xperts!

SampleQ

Fully automated solutions
for sample preparation

GAS, IS-X, IS-X Academy & SampleQ are INTERSCIENCE brandings