



Low sulphur analysers

- Low ppb level sulphur compound analysis
- FPD, PFPD and MS(ISQ) available
- Can be combined with RGA and NGA

GAS offers custom configured GC analysers for many application fields for over 40 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.

Analysis of sulphur components in natural gas and various hydrocarbon streams is of utmost importance. Sulphur is harmful to expensive catalysts involved in downstream hydrocarbon processing, and is corrosive to equipment. The amount in finished fuel products is lowered worldwide to reduce emission. GC-(P)FPD has proven to be a stable and reliable solution for sulphur determination in many laboratories.

Figure 1. Low sulphur analyser for LPG samples (liquid injection)



Figure 2. Vaporiser for gaseous injection of LPG samples



FPD and PFPD

GAS offers Low sulphur analysers for various sample types and concentration ranges. FPD (Flame Photometric Detector) and PFPD (Pulsed FPD) are both available, providing ppm/ppb level results. Sulphur components will adsorb on active surfaces, therefore Sulfinert deactivation is applied to the full sample path, which is vital for accurate quantification.

Liquid samples

Liquid fuel samples are injected using SSL (split-splitless injector) or PTV (programmable temperature vaporiser), according to ASTM D5623. Figure 3 shows a diesel sample.

LPG samples

GAS offers 2 options for analysing LPG samples:

- gaseous injection by GSV (gas sampling valve), with prior evaporation by Vaporiser (figure 2).
- liquid injection by LSV (liquid sampling valve), using the optional Sample Securitiser for guaranteed quantitative injection (figure 1; see the LPG application note for further information). Figure 4 shows trace sulphur analysis in propylene.

Vaporiser and Sample Securitiser are Sulfinert-treated to eliminate adsorption. Covered standardised methods: see specification on page 4.

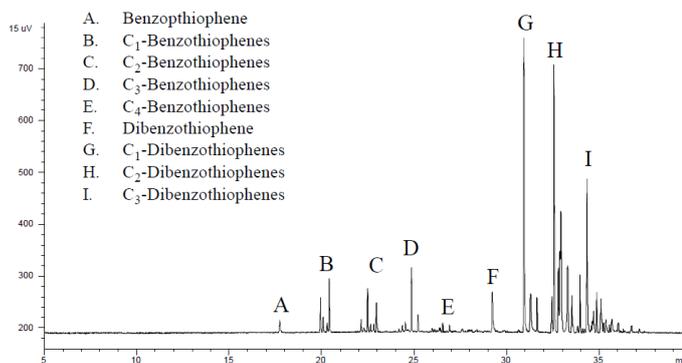


Figure 3. Low sulphur in diesel fuel (SSL-Rtx 1-PFPD)

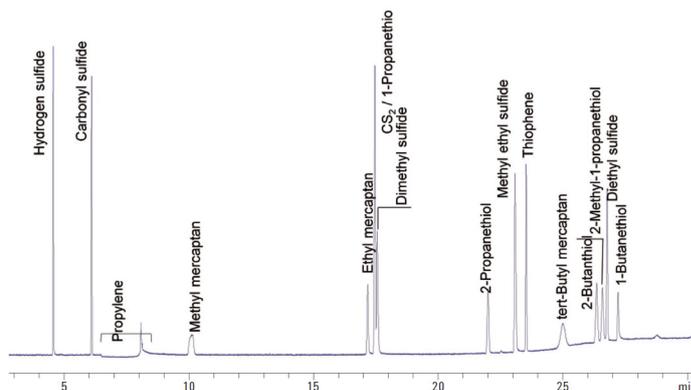


Figure 4. Low sulphur analysis in propylene (Sample Securitiser-LSV-PFPD; 1 ppm per component)

Natural gas/refinery gas samples

Natural gas, refinery gas and other gaseous samples like ethylene are injected using GSV. Figure 6, 7, 8 and 9 show chromatogram and data about linearity, sensitivity and repeatability for natural gas analysis using PFPD.

Combining methods

Low sulphur analyser is available as a single channel instrument, but can also be combined with other analysers like RGA and NGA, providing a very efficient cost/footprint solution (figure 5).



Figure 5. Extended 4 channel Natural Gas and Refinery Gas Analyser with separate low sulphur channel (FPD)

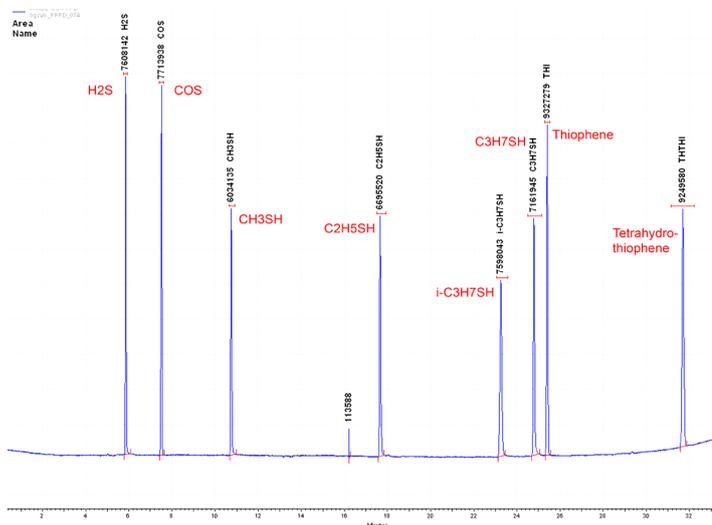


Figure 6. Calibration standard of sulphur components in N₂ (5 ppm each) (GSV-PFPD)

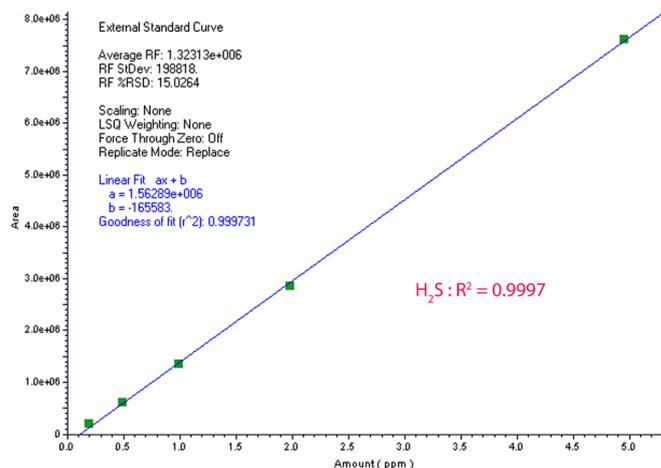


Figure 7. Linearity curve of H₂S: $r^2 = 0.9997$ (100ppb - 5 ppm) ($r^2 > 0.995$ for all components; PFPD, lineariser mode)

GC-PFPD ID	H ₂ S Area	COS Area	CH ₃ SH Area	C ₂ H ₅ SH Area	i-C ₃ H ₇ SH Area	C ₃ H ₇ SH Area	THI Area	THTHI Area
PFPD_071	7653680	7716514	6026713	6764998	7612207	7096988	9317300	9228699
PFPD_072	7575351	7695225	5928568	6794046	7631111	7204149	9296086	9213385
PFPD_073	7648397	7698897	6013745	6725392	7641811	7193838	9352864	9246370
PFPD_074	7608142	7713938	6034135	6695520	7598043	7161945	9327279	9249580
Min:	7575351	7695225	5928568	6695520	7598043	7096988	9296086	9213385
Max:	7653680	7716514	6034135	6794046	7641811	7204149	9352864	9249580
Mean:	7621393	7706144	6000790	6744989	7620793	7164230	9323382	9234509
Std Dev:	36820	10646	48880	43352	19489	48294	23569	16811
%RSD:	0.48	0.14	0.81	0.64	0.26	0.67	0.25	0.18

Figure 8. Repeatability at 5 ppm concentration level (GSV-PFPD).

Component	LOD (ppb)
H ₂ S	17
COS	18
CH ₃ SH	25
C ₂ H ₅ SH	27
i-C ₃ H ₇ SH	39
C ₃ H ₇ SH	30
THI	22
THTHI	30

Figure 9. LOD (s/n = 3 * noise) (PFPD)

Very sensitive. High selectivity

PFPD provides high sensitivity with LOD < 100ppb. Lower limits (< 20ppb) are shown when sulphur components are well-separated from the hydrocarbon matrix. Good selectivity is offered as well, however co-elution with (very) high amounts of hydrocarbons results in decreased sensitivity and therefore chromatographic separation is optimised for each standardised method.

PFPD or FPD ? or MS?

PFPD and FPD are both available; PFPD offers best sensitivity (20-30ppb) while FPD provides a cost effective solution when detection limits of 100-200 ppb are sufficient. See figure 9 and 10; note that LODs for PFPD are different in both figures due to the used conditions. When (P)FPD sensitivity is not adequate, GC-MS can provide < 1 ppb limit of detection (figure 12; see application note).

High stability. Easy operation compared to SCD

(P)FPD provides high long term stability, therefore frequent calibration and maintenance is not needed. Compared to SCD (chemiluminescence detector), (P)FPD is less expensive, easier to operate, offers better value for your money and provides a long term stable response.

Component	LOD (ppb)	
	PFPD	FPD
H ₂ S	33	176
COS	31	158
CS ₂	35	196
C ₂ H ₆ S	41	206
CH ₄ S	18	90

Figure 10. Comparison of PFPD and FPD sensitivity.

Conditions: column: Rtx-1, 60 m * 0.32 mm ID, 5 µm; sample loop: 250 µl; column flow: 2 ml/min; splitflow: 5 ml/min; test standard: 500ppb per component; (LOD based on s/n=3)

Specification

Standardised methods:

ASTM D3328	Comparison of waterborne petroleum oils
ASTM D4735	Trace thiophene in refined benzene
ASTM D5303	Trace COS in propylene
ASTM D5623	Sulphur compounds in light petroleum liquids
ASTM D6228	Sulphur compounds in natural gas and gaseous fuels
ASTM D7011	Trace thiophene in refined benzene
ISO 19739	Sulphur compounds in natural gas



Figure 11. Optional Analytical Calibration Unit (ACU) for automated multi-level calibration, using permeation tubes or dilution of calibration standard.

Configuration:

1 channel instrument based on Thermo Trace 1300 GC or CompactGC^{4.0}

Can be combined with other standardised analysers like NGA or RGA

Detectors:

Pulsed Flame Photometric Detector or Flame Photometric Detector

Sample injection:

GSV, LSV, SSL, PTV

Optional:

- Vaporiser or Sample Securitiser for LPG samples (Sulfinert-treated)
- hydrocarbon signal output on PFPD
- column effluent splitter to (P)FPD and FID for simultaneous detection of sulphur components and hydrocarbons
- Analytical Calibration Unit (ACU):
 - automatic multi-level dilution of calibration gases and/or permeation tube
- GC-MS using AEI (Advanced Electron Impact source)

Sample tubing:

Sulfinert[®] tubing for inert sample path

Application:

Custom configured analyser for the analysis of sulphur components in various gases, liquefied gases and liquid streams

Range:

25 ppb - 100 ppm (PFPD); 200ppb - 100ppm (FPD)

Detection limit:

PFPD: <25 - <100 ppb, depending on separation

FPD: < 200 ppb

MS: < 1 ppb

Selectivity:

S/C = 10⁶:1 (FPD and PFPD)

Repeatability:

< 3 % RSD or better

Sample requirements:

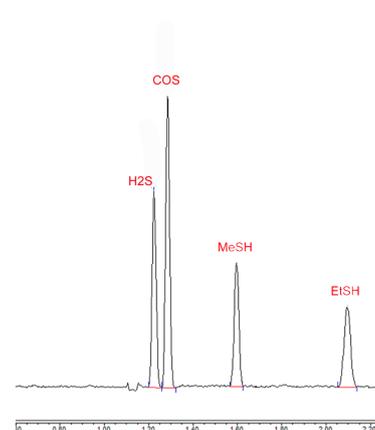
See our pre-installation guide for additional requirements



Figure 12. When (P)FPD sensitivity is not sufficient, GC-MS provides sulphur component analysis below 1 ppb, using Advanced Electron Impact source.



Figure 13, 14. PFPD is also available on 19" CompactGC^{4.0} for very fast ppb sulphur analysis in several matrices.



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