Global Analyser Solutions

Low level sulphur analyser

- Low ppb level sulphur compound analysis
- For gaseous, liquid and liquefied petroleum samples
- FPD or PFPD. SCD and Mass Spectrometer optional
- Can be combined with RGA, NGA and other analysers

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AN8WA0923H

Global Analyser Solutions

GAS offers custom configured GC analysers for many application fields for over 50 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, highly productive 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 Figure 1. Low sulphur analyser for LPG samples (LSV injection)

Figure 2 Low level sulphur analyser based on CompactGC$^{4.0}$ equipped with gas sampling valve (GSV) and PFPD (LOD 20 ppb)

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, for instance for sulphur components in diesel.

LPG samples

GAS offers 2 options for analysing LPG samples:

- gaseous injection by GSV (gas sampling valve), with prior evaporation by Vaporiser (figure 11).
- 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 3 shows trace sulphur analysis in propylene. Vaporiser and Sample Securitiser are Sulfinert-treated to eliminate adsorption. Covered standardised methods: see specification on page 4.

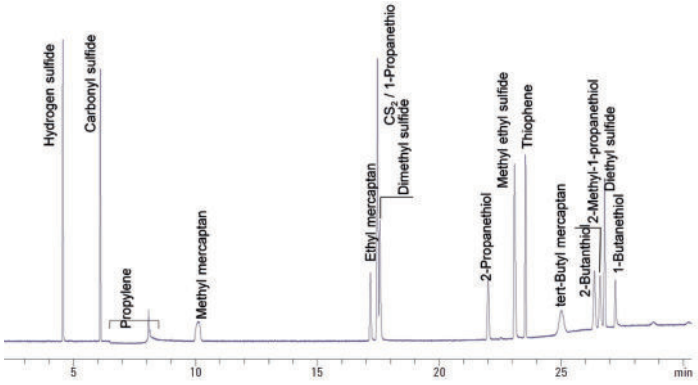

Figure 3 Low sulphur analysis in propylene (Sample Securitiser-LSV-PFPD; 1 ppm per component)

Figure 4 Permanent gas analyser with added low sulphur channel

Gaseous samples

Natural gas, refinery gas and other gaseous samples like ethylene are injected using a gas sampling valve (GSV). Figure 5, 6, 7 and 8 show chromatograms and data about linearity, sensitivity and repeatability for natural gas analysis using 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 and sample type.

Component	LOD (ppb)
H2S	*17*
COS	*18*
CH3SH	*25*
C2H5SH	*27*
i-C3H7SH	*39*
C3H7SH	*30*
THI	*22*
THTHI	*30*

Figure 8 LOD (s/n = 3 * noise) (PFPD, chromatogram figure 5)

PFPD or FPD ?

PFPD and FPD both offer excellent long term stability. PFPD offers best sensitivity (20-30ppb; figure 8) while FPD provides a cost effective solution when detection limits of 100-200 ppb are sufficient. See figure 8 and 9; note that LODs for PFPD are different in both figures due to the used conditions.

	LOD (ppb)	
Component	**PFPD**	**FPD**
H2S	33	176
COS	31	158
CS2	35	196
C2H6S	41	206
CH4S	18	90

Figure 9 Comparison of PFPD and FPD sensitivity. Conditions: column: Rtx-1, 60 m * 0.32 mm ID, 5 um; sample loop: 250 ul; column flow: 2 ml/min; splitflow: 5 ml/min; test standard: 500ppb per component; (LOD based on s/n=3)

Combining methods

Low sulphur analyser is available as a single channel instrument, or can be added to other analysers like RGA and NGA, providing a very efficient cost/footprint solution (figure 4).

Alternatives to FPD en PFPD

Figure 10 shows a comparison of GC detectors for sulphur analysis. When TCD, FPD or PFPD do not offer the required sensitivity, SCD (Sulphur Chemiluminescence Detector) provides 10 ppb detection limit. With MS (Mass Spectrometer) with Advanced Electron Impact (AEI) source even lower limits are achieved: below 1 ppb.

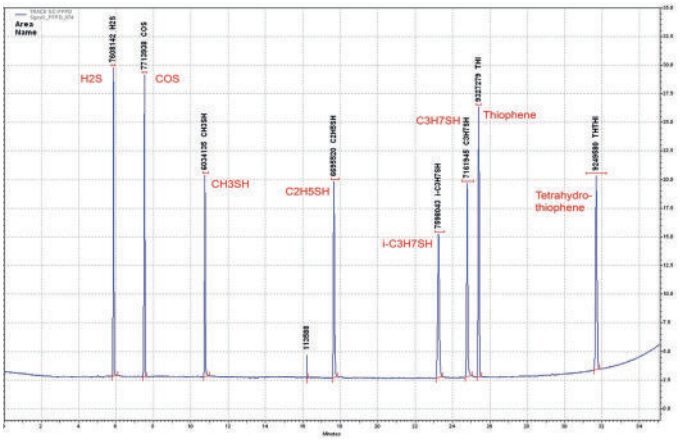

Figure 5 Calibration standard of sulphur components in N_2 (5 ppm each) (GSV-PFPD)

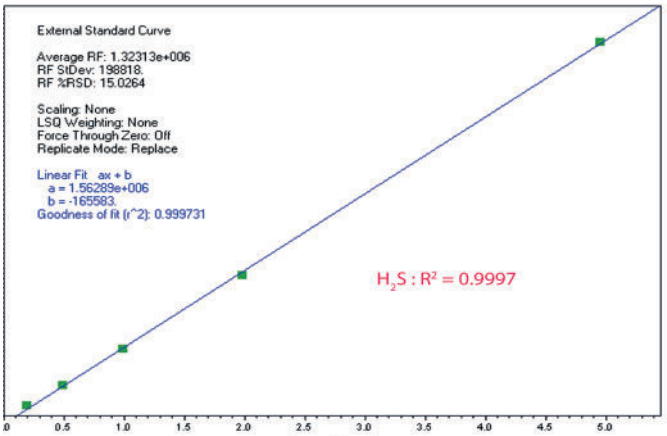

Figure 6 Linearity curve of H2S: r2 = 0.9997 (100ppb - 5 ppm) (r2 > 0.995 for all components; PFPD, lineariser mode)

GC-PFPD ID	H2S Area	COS Area	CH3SH Area	C2H5SH Area	i-C3H7SH Area	C3H7SH 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 7 Repeatability at 5 ppm concentration level (GSV-PFPD)

Detector	LOD	Linearity	Selectivity	Equimolar response
TCD	low ppm	10^4	-	-
FPD	100-200 ppb	10^{2-3}	+	+
PFPD	< 20 ppb	10^{2-3}	++	+
SCD	< 10 ppb	10^4	+++	++
MS-AEI	< 1 ppb	10^4	++++	-

Figure 10 Comparison of GC detectors for sulphur analysis

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

Configuration:	1 channel instrument based on Thermo Trace GC 1600 (fig 1) or CompactGC$^{4.0}$ (fig 2) Can be combined with other standardised analysers like NGA or RGA
Application:	Custom configured analyser for the analysis of sulphur components in various gases, liquefied gases and liquid streams
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) - column effluent splitter to (P)FPD and FID for simultaneous detection of sulphur components and hydrocarbons - Analytical Calibration Unit (ACU) (figure 13) for automatic multi-level dilution of calibration gases and/or permeation tube - GC-MS using AEI (Advanced Electron Impact source) - SCD (Sulphur Chemiluminescence Detecor)
Sample tubing:	Sulfinert® tubing for inert sample path
Range:	20 ppb - 100 ppm (PFPD); 200ppb - 100ppm (FPD)
Detection limit:	see figure 10
Selectivity:	S/C = 10^6:1 (FPD and PFPD)
Repeatability:	< 3 % RSD or better
Sample requirements:	See the pre-installation guide for additional requirements

Figure 11 Vaporiser for gaseous injection of LPG samples

Figure 12 iConnect FPD provides easy detector replacement

Figure 13 Analytical Calibration Unit (ACU) for dilution of calibration gases or permeation tubes

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