GLOBAL™ ANALYSER SOLUTIONS G·A·S

Low Sulphur analyser using SCD

- very sensitive: < 10 ppb
- high linearity: 10^4
- ASTM D5303, D5504, D5623, D7011
- automatic calibration via permeation tubes

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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.

Sulphur component are inherently present in many products derived from fossil sources like natural gas and crude petroleum, or are added later for safety reasons. Sulphur species are corrosive and will harm expensive production catalyst, and have effect on the ecosystem. Therefore frequent measurement at low ppb levels in various matrices is of high importance.

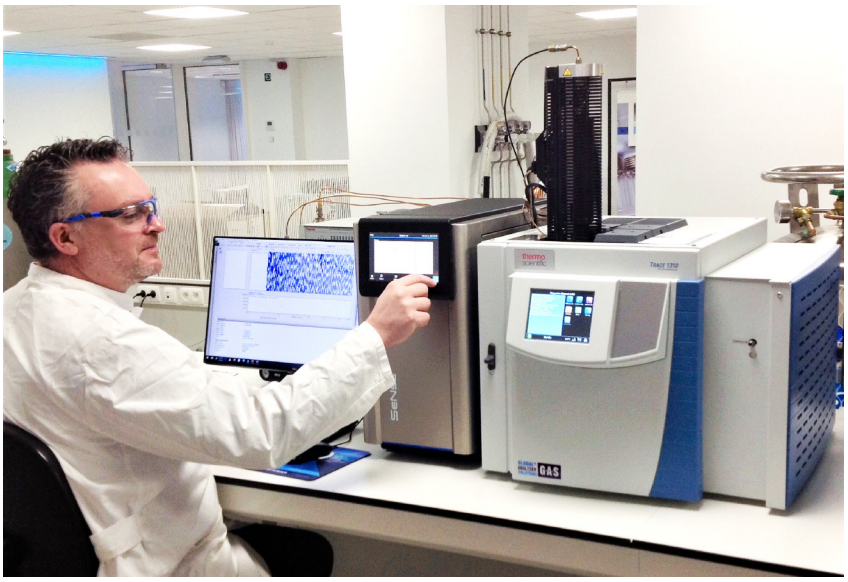

Figure 1. Trace GC1310-SCD

Overview

GAS offers a range of detectors for sulphur analysis, like Thermal Conductivity Detector (TCD), (Pulsed) Flame Photometric Detector (P)FPD, Sulphur Chemiluminescence Detector (SCD) and Mass Spectrometer. Required sensitivity, selectivity, linearity and sample matrix determine the final optimal configuration. This application note describes SCD, which is mandatory for ASTM D5504 (natural gas and gaseous fuels) and D5623 (light petroleum liquids). SCD shows excellent linearity and sensitivity, and has low interference from hydrocarbon matrices. See figure 2 for an overview.

Detector	LOD	Linearity	Selectivity	Equimolar response
TCD	low ppm	10^4	-	-
FPD	100-200 ppb	10^{2-3}	+	+
PFPD	< 25 ppb	10^{2-3}	++	+
SCD	< 10 ppb	10^4	+++	++
MS	< 1 ppb	10^4	++++	-

Figure 2. Detectors for sulphur analysis. Overview properties

Principle

The complete sample matrix is oxidised at 700-900 °C, whereby sulphur species react to SO_2. After reduction with hydrogen, the sulphur species react with ozon, produced by an on-board generator to form SO_2 * (excited state). During decay to the ground state, light is emitted and detected by a photomultiplier. This chemiluminescent emission is selective for sulphur and is proportional to the amount in the original sample.

Analyser configuration

Despite the excellent quenching behaviour, sulphur species have to be separated form high concentration matrix peaks using specific chromatographic columns. When various samples types have to be analysed, often 2 columns with different selectivity are present in the analyser.

SCD shows high linearity up to a few hundreds ppm level. In case higher concentrations are requested as well, a TCD can be added to cover the complete concentration range (figure 4).

Results

Figure 3 shows the chromatogram of 19 sulphur components at 50 ppm level. The standard was injected by GSV (Gas Sampling Valve) with 100 ul sample volume. Figure 4 demonstrates TCD results when high ppm and % levels are requested as well. Figure 5 proves SCD repeatability below 2 % RSD. The limit of detection of SCD is < 10 ppb.

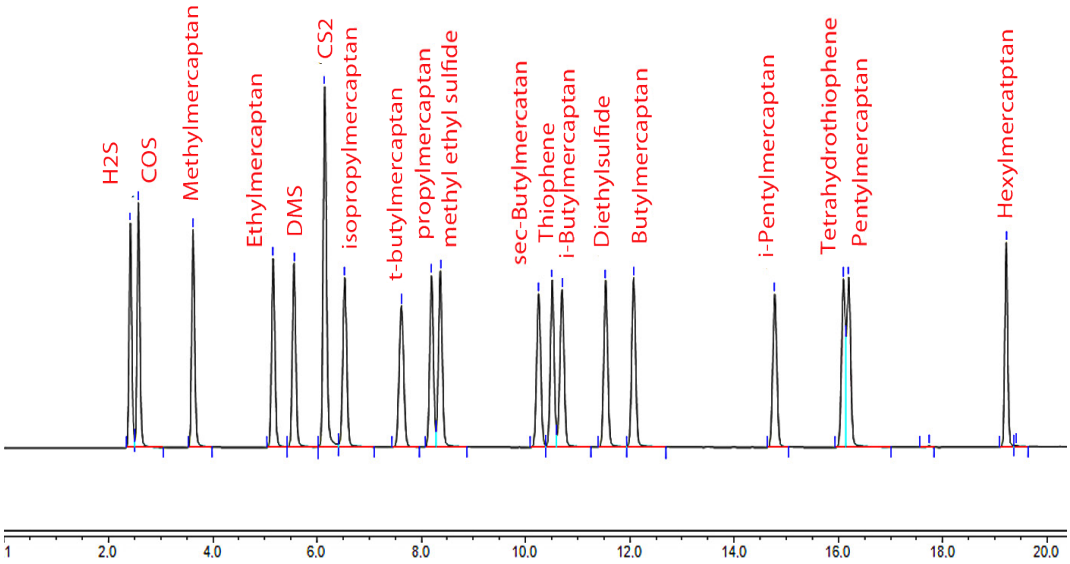

Figure 3. SCD chromatogram of 19 sulphur components at 50 ppm. LOD: <10 ppb

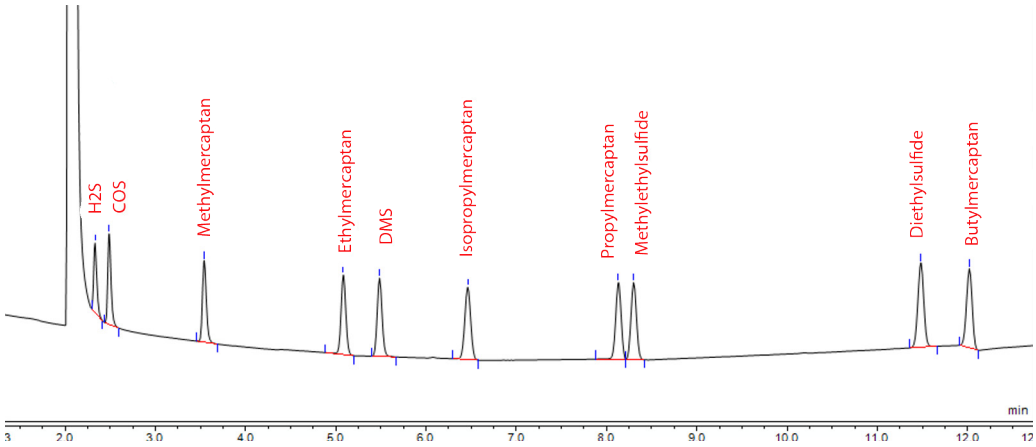

Figure 4. Sulphur components in N2, 1000 ppm level, TCD. SCD and TCD in a single instrument deliver full concentration range sulphur analysis from low ppb to high %

		SCD_Analog								
		Hydrogen st	Carbonyl su	Methylmerc	Ethylmercaj	Dimethyl su	Carbon disu	isopropylme	t-Butylmerc	Propylmerc
1	*Standard #1 RXI5 SCD*	*3,6874*	*4,0727*	*4,4627*	*4,1639*	*4,5140*	*4,2905*	*3,8226*	*4,0010*	*3,9325*
2	Standard #1 RXI5 SCD	3,7639	4,1543	4,4519	4,1102	4,4990	4,3018	3,8128	3,8877	3,8404
3	Standard #1 RXI5 SCD	3,7639	4,1549	4,6258	4,2509	4,5051	4,4148	3,8407	3,9668	3,9207
4	Standard #1 RXI5 SCD	3,7815	4,2382	4,5410	4,3249	4,6672	4,3232	3,8106	3,9650	3,8389
5	Standard #1 RXI5 SCD	3,7949	4,1282	4,5888	4,2110	4,4520	4,2963	3,8210	3,8675	3,8486
6	Standard #1 RXI5 SCD	3,8573	4,0180	4,5517	4,3061	4,4985	4,3065	3,7293	3,8953	3,8742
Maximum		3,8573	4,2382	4,6258	4,3249	4,6672	4,4148	3,8407	4,0010	3,9325
Average		**3,7748**	**4,1277**	**4,5370**	**4,2278**	**4,5226**	**4,3222**	**3,8061**	**3,9305**	**3,8759**
Minimum		3,6874	4,0180	4,4519	4,1102	4,4520	4,2905	3,7293	3,8675	3,8389
Standard Deviation		0,0550	0,0758	0,0686	0,0828	0,0740	0,0467	0,0391	0,0539	0,0414
Relative Standard Deviation		**1,46%**	**1,84%**	**1,51%**	**1,96%**	**1,64%**	**1,08%**	**1,03%**	**1,37%**	**1,07%**

		Methyl eth	sec-Butylm	Thiophene	i-Butylmerc	Diethyl sull	Butylmercz	i-Pentylme	Tetrahydro	Pentylmerc	Hexylmerc
1	*Standard #1 RXI5 SCD*	*4,3212*	*3,6767*	*3,9028*	*3,7198*	*4,2941*	*4,0425*	*3,8636*	*3,3801*	*3,6260*	*2,9274*
2	Standard #1 RXI5 SCD	4,2042	3,6476	3,8827	3,6485	4,2209	3,9748	3,9697	3,4647	3,5908	2,9458
3	Standard #1 RXI5 SCD	4,3263	3,7547	4,0061	3,6455	4,2476	4,0513	4,0105	3,4206	3,5459	3,0352
4	Standard #1 RXI5 SCD	4,2237	3,7196	3,9550	3,7650	4,2008	4,0284	3,9228	3,3638	3,5607	2,9625
5	Standard #1 RXI5 SCD	4,2701	3,6011	3,9115	3,6892	4,1568	3,8831	3,9415	3,4097	3,5507	3,0548
6	Standard #1 RXI5 SCD	4,1959	3,6828	3,9373	3,6577	4,0798	3,9641	3,9739	3,4838	3,5178	2,9740
Maximum		4,3263	3,7547	4,0061	3,7650	4,2941	4,0513	4,0105	3,4838	3,6260	3,0548
Average		**4,2569**	**3,6804**	**3,9326**	**3,6876**	**4,2000**	**3,9907**	**3,9470**	**3,4204**	**3,5653**	**2,9833**
Minimum		4,1959	3,6011	3,8827	3,6455	4,0798	3,8831	3,8636	3,3638	3,5178	2,9274
Standard Deviation		0,0578	0,0537	0,0442	0,0474	0,0746	0,0637	0,0507	0,0468	0,0379	0,0507
Relative Standard Deviation		**1,36%**	**1,46%**	**1,12%**	**1,29%**	**1,78%**	**1,60%**	**1,28%**	**1,37%**	**1,06%**	**1,70%**

Figure 5. SCD repeatability report by Chromeleon data system

Specification

Application:	Custom configured analyser for low level sulphur components in various matrices like natural gas and hydrocarbon streams.
Standardised methods:	ASTM D5303, D5504, D5623, D7011
Configuration:	1 channel analyser based on Thermo GC 1300 and PAC SeNse
Injection type	GSV (Gas Sampling Valve), LSV (Liquid Sampling Valve).
Optional:	- Vaporiser to evaporate liquid LPG quantitative to a gas sample (figure 6) - ACU (Automatic Calibration Unit) with permeation tube and mass flow controller dilution system for automated preparation of multi-level calibration gases (figure 7) - Sample Securitiser for LSV (figure 8) - 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 10 ppb
Linearity:	4 decades
Repeatability:	< 2 % RSD
Response stability:	2% over 2 hours; 3% over 24 hours
Data systems:	Chromeleon

Figure 6. GAS Vaporiser for gas injection of liquified gases

Figure 7. Automatic Calibration Unit (ACU) with permeation tube and MFC dilution system

Figure 8. Sample Securitiser for liquid injection of liquefied samples

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