Low sulphur in various samples

Sensitivity < 20 ppb

High stability, low maintenance

Factory tuned

APPLICATION NOTE 212WA1012E

# Low sulphur analyser

ASTM D6228, D5303 D5504, D3328, D4735, D5623, D7011
UOP 791
ISO 19739

**G·A·S offers custom configured GC analysers for complex separations, data processing and reporting. We have over 35 years of experience in designing and building turnkey analysers for many application fields. Our analysers are designed to meet many accepted standard methods (like GPA, ASTM, UOP, ISO, etc.) in the Oil and Gas industry. The efficient configurations are based on proven GC technology, resulting in robust instruments with an optimal return on investment.**

**The determination of sulphur components in natural gas and various hydrocarbon streams is of utmost importance for several reasons. Sulphur is known to be very harmful to expensive catalysts involved in downstream hydrocarbon processing. Sulphur components are corrosive to equipment, and sulphur amount in finished fuel products is lowered worldwide to reduce emission. GC-(P)FPD -Gas Chromatography with (Pulsed) Flame Photometric Detector- has proven to be a very stable and reliable solution for sulphur determination in many laboratories.**


Figure 1: Low sulphur analyser with optional Sample Securitiser

Gaseous samples like natural gas and ethylene are injected using GSV (Gas Sampling Valve), according to ASTM D6228, D5303, D5504, UOP791 and ISO 19739.

LPG samples are analysed by GSV after vaporising or by LSV (Liquid Sampling Valve) using direct liquid injection. The optional Sample Securitiser is used for guaranteed quantitative injection by LSV. See figure 1 and our dedicated application note for more information.

Liquid samples like finished fuels are injected using SSL (Split injector) or PTV (Programmable Temperature Vaporiser), according to ASTM D5623.

Sulphur components very easy adsorb on active surfaces, therefore Sulfinert deactivation is applied to the full sample path, which is vital for accurate quantification.

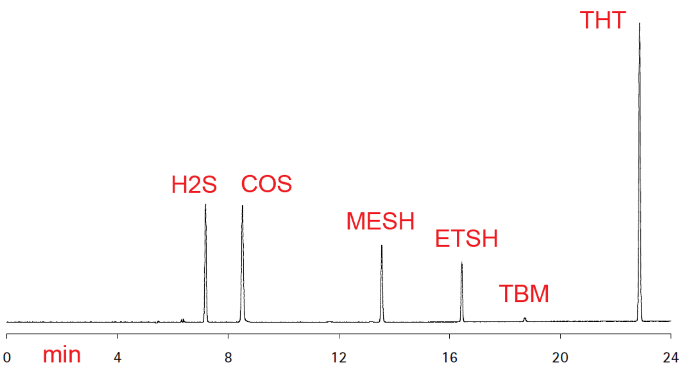


Figure 3. Low sulphur in natural gas
(GSV-Rtx 1,FPD)

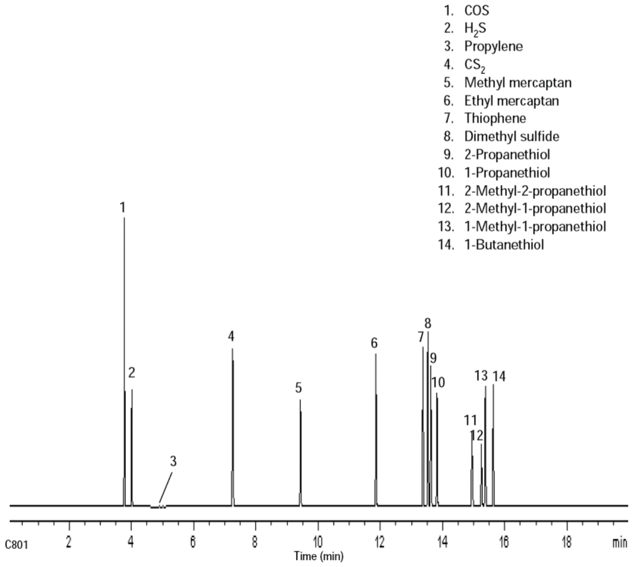


Figure 2: Low sulphur analysis in propylene
(LSV-Rt SilicaBond-PFPD; 1 ppm per component)

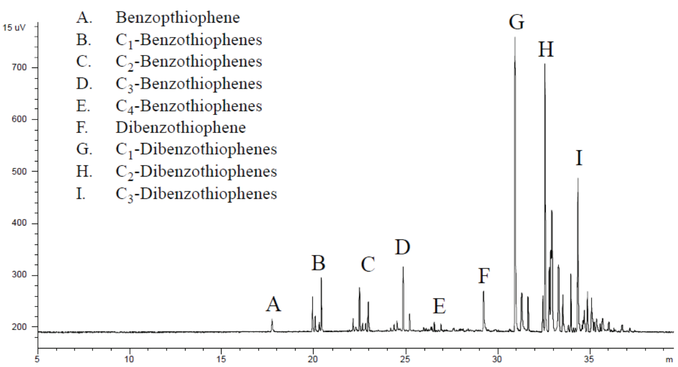


Figure 4. Low sulphur in diesel fuel
(SSL-Rtx 1-PFPD)

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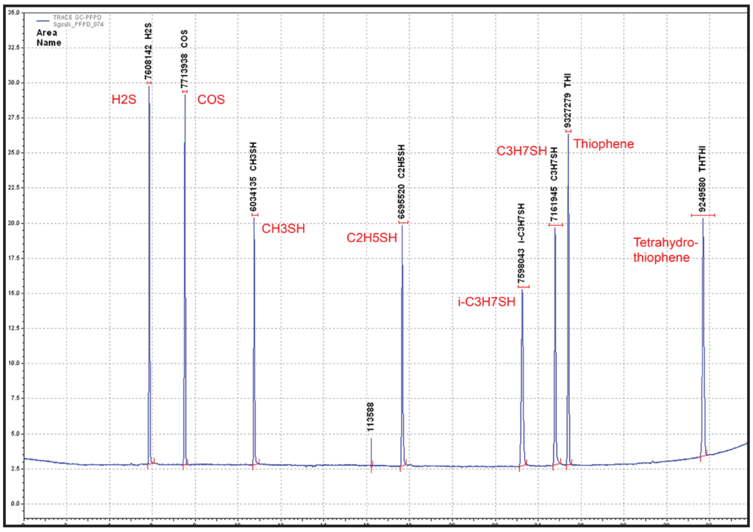


Figure 5. Calibration standard of sulphur components in $N_2$ (5 ppm each)
(GSV-Rtx 1-PFPD)

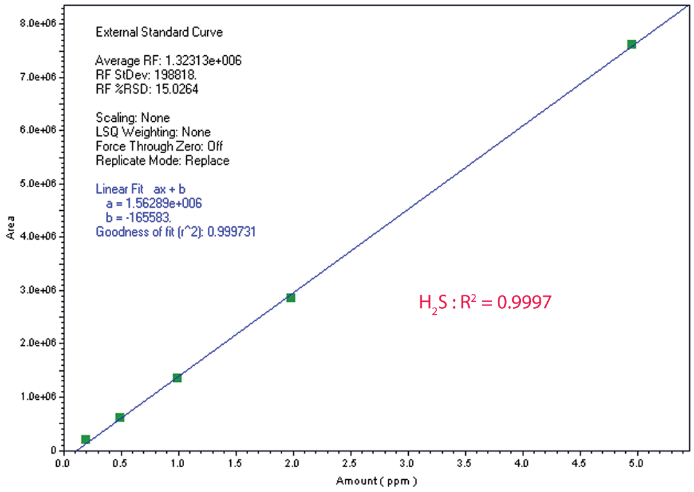


Figure 6. Linearity curve of $H_2S$: $r^2 = 0.9997$ (100ppb - 5 ppm)
($r^2 > 0.995$ for all components; PFPD, lineariser mode)

| 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).

| 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)

| | 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)

## Very sensitive. High selectivity

PFPD provides high sensitivity with LODs below 100ppb. Even lower limits (< 20ppb) are reached when sulphur components are well-separated from the hydrocarbon matrix. Good selectivity is offered as well; hydrocarbon components show no positive response. However co-elution with (very) high amounts of hydrocarbons decreases sensitivity and therefore chromatographic separation is optimised for each standardised method.

## PFPD or FPD ?

PFPD and FPD are both available; the first one shows best sensitivity (20-30ppb) and selectivity while the latter provides a more cost effective solution, with detection limits of 100-200 ppb. See figure 8 and 9; note that LODs for PFPD are different in both figures due to the used conditions.


Figure 10. Optional calibrator module for generating multi level calibration standards, using permeation tubes or using dilution of a calibration gas.

## High stability. Easy operation compared to SCD

There is no need for frequent calibration and maintenance thanks to a high long term stability. (P)FPD is easier to operate, is less expensive and the response is more stable compared to the Chemiluminescence detector.

## Combining methods

Low sulphur analysis can be combined efficiently with for example refinery gas or natural gas analysis, using a single instrument (figure 11).

# Specifications

## Standardised methods:

| Standard Designation (Committee) | D3328 (D19) | D4735 (D16) | D5303 (D02) | D5504 (D03) | D5623 (D02) | D6228 (D03) | D7011 (D16) |
|---|---|---|---|---|---|---|---|
| **Title** | Comparison of Waterborne Petroleum Oils by Gas Chromatography | Determination of Trace Thiophene in Refined Benzene by Gas Chromatography | Trace Carbonyl Sulfide in Propylene by Gas Chromatography | Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence | Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection | Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection | Determination of Trace Thiophene in Refined Benzene by Gas Chromatography and Sulfur Selective Detection |
| **Matrix** | Petroleum oils recovered from water or beaches compared to oils from suspect sources. | Refined benzene | Propylene | High methane-content gaseous fuels such as natural gas | Light petroleum liquids such as distillates, gasoline motor fuels, and other petroleum liquids with final boiling point of 230 °C or lower. | Gaseous fuels | Refined benzene |
| **Analytes** | Hydrocarbons (FID) and associated sulfur compounds (FPD) | Thiophene | Carbonyl sulfide (COS) | Speciated volatile sulfur-containing compounds such as $H_2S$, COS, $SO_2$, thiols, sulfides, thiophenes, etc. | Volatile sulfur-containing compounds; both unidentified and known individual compounds are determined. | Volatile sulfur-containing compounds; both unidentified and known individual compounds are determined. | Thiophene |
| **Range** | Qualitative only; no quantitative range is cited | 0.5 to 5.0 mg/kg | 0.5 to 4.0 mg/kg | 0.01 to 1,000 $mg/m^3$ | 0.1 to 100 mg/kg (ppm) | 0.02 to 20 $mg/m^3$ (0.014 to 14 ppmv) | 0.02 to 2.0 mg/kg |
| **Detector Cited** | FID alone, or FID with flame photometric detection | Any flame photometric detector (FPD or PFPD) | A flame photometric detector | FID and SCD in series, or other sulfur specific detector | A sulfur selective detector that produces a linear and equimolar response to sulfur compounds | Any flame photometric detector (FPD or PFPD) | Pulsed flame photometric detector, sulfur chemiluminescence detector, atomic emission detector, or any other sulfur selective detector. |
| **Detector Specification** | ▪ A flame photometric detector is cited when independent, selective detection of HC and S is desired to improve identification of oil<br>▪ Linearization of the sulfur signal is recommended | Signal-to-noise of at least 2-to-1 for 0.5 mg/kg (ppm) thiophene in benzene (4-µL injection with FPD or 1-µL injection with PFPD) | Signal-to-noise of at least 2-to-1 for 0.1 mg/kg COS in propylene | Sulfur specific detectors other than the SCD can be used provided that they have sufficient sensitivity, respond to all eluted sulfur compounds, do not suffer from interferences, and satisfy quality assurance criteria. | ▪ Linearity of $10^4$<br>▪ 5-pg sulfur/second minimum delectability<br>▪ Approximate equimolar response to sulfur<br>▪ No interference from co-eluting hydrocarbons | Any flame photometric detector calibrated in the sulfur-specific mode is used for this test method | ▪ Linearity of $10^2$<br>▪ Minimum detectable level of less than 0.02 mg/kg thiophene in benzene<br>▪ Selectivity of sulfur to carbon greater than $10^5$<br>▪ Absence of quenching that affect results |
| **PFPD Suitability** | A PFPD with increased sensitivity, equimolar sulfur response, and linear signal provides maximum information about the number, distribution, and relative concentrations of the sulfur species present for positive identification of the suspect oil. | The PFPD provides additional sensitivity, down to 0.02 mg/kg (ppm), when lower concentrations of thiophene in benzene must be measured. | Linear, equimolar response of the PFPD eliminates log/log plots, simplifies calibrations, and enables quantitation of any unknown sulfur peaks that may be present along with the COS. | The PFPD exceeds requirements for "other sulfur specific detectors", including all QA criteria. The two-signal output of the PFPD provides a simultaneous fingerprint of the hydrocarbon matrix along with the sulfur chromatogram. | Linear, equimolar response of the PFPD allows accurate quantitation of individual known and unknown sulfur compounds down to 25-ppb sulfur or lower. | Increased sensitivity of the PFPD allows quantitation of sulfur at concentrations 5 to 10 times lower than an FPD. Linear, equimolar response of the PFPD allows accurate quantitation of the sulfur content in unknowns. | Long-term stability and ease of use make the PFPD well suited for use in production facilities with limited staff, and where low detection limits are required. |

- UOP 791 and ISO 19739 are covered as well

**Configuration:** 1-4 channel instrument based on Thermo Trace 1300 GC or CompactGC4.0

**Detectors:** Pulsed Flame Photometric Detector or Flame Photometric Detector
Available injection: GSV, LSV, Split or PTV injection

**Optional:**
- Vaporiser or Sample Securitiser for LPG samples
- hydrocarbon signal output on PFPD
- simultaneous detection on FID using effluent splitter

**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:** 20 ppb - 100 ppm (PFPD); 200ppb-100ppm (FPD)

**Detection limit** <100 ppb; <20 ppb in case of well-separated sulphur components (PFPD)
< 200 ppb (FPD)

**Repeatability** < 3 % RSD or better

**Sample requirements:** See our pre-installation guide for additional requirements

**(P)FPD compared to SCD:** (P)FPD is easier to operate and offers better long term stability

Figure 11. Refinery Gas and Low sulphur analysis offered in a single instrument.

Figure 12. PFPD is also available on 19" CompactGC4.0 for fast ppb sulphur analysis in several matrices.

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P.O. Box 2148, 4800 CC Breda, The Netherlands
T: +31 (0)76 5411800 F: +31 (0)842 206757 info@gas-site.com www.gas-site.com