



APPLICATION NOTE 212WA1012A

Low sulfur analyser

ASTM D6228, D5303 D 5504, D3328, D4735, D5623, D7011 UOP 791 ISO 19739

About G·A·S

Global Analyser Solutions 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. We invite you to take advantage of our latest hardware, software and column technologies to achieve the best possible results.

Our analysers are designed to meet many accepted standard methods (like ASTM, UOP, ISO, etc) in the Oil and Gas industry. The efficient hardware configurations are based on proven GC technology, resulting in rigid instruments with an optimal return on investment. The GAS Low sulfur analysers are customised solutions for the determination of several sulfur components in Natural Gas and various hydrocarbon streams.

Introduction

The determination of sulfur components in Natural Gas and various hydrocarbon streams is of utmost importance for several reasons. Sulfur is known to be very harmful to expensive catalysts involved in downstream hydrocarbon processing. Sulfur components are corrosive to equipment, and there is a wordwide trend in lowering the sulfur amount in finished fuel products to reduce emission.

GC-PFPD -Gas Chromatography with Pulsed Flame Photometer Detection- has proven to be a very stable and reliable solution for sulfur determination in many laboratories. G.A.S offers several low sulfur analysers for various streams. For gaseous streams like Natural Gas and ethylene the system is equipped with GSV (Gas Sampling Valve), and meets ASTM D6228, D5303, D5504, UOP791 and ISO 19739. LPG samples are analysed using vaporiser and GSV or using LSV (Liquid Sampling Valve) for direct liquid injection. The optional Pressure Facility can be used for guaranteed quantitative injection. See our dedicated application notes for more information. Liquid samples like finished fuels are injected using SSL (Split injector) or PTV (Programmable Temperature Vaporiser), according to ASTM D5623. Each method describes the optimal separation column to avoid detector quenching due to co-elution of sulfur components and major hydrocarbon peaks. Sulfur components adsorb very easy on active surfaces, therefore Sulfinert deactivation is applied to the sample path as much as possible, which is vital.





Figure 1: Low sulfur analyser with optional Pressure Facility



Figure 2: Low sulfur analysis in Propylene

Applications



Figure 3. Detection of trace level sulfur in Natural Gas









- Total sulfur in gasoline.

- Dual channel output (hydrocarbon signal as well)

Easy calibration due to equimolar response

Selective, sensitive, long term stable, uniform response

The PFPD provides high sensitivity: the detection limit is lower than 100ppb. Even lower limits are reached in case of well-separated peaks: better than 20 ppb. It offers good selectivity as well, and the detector shows no positive response on hydrocarbon components. However co-elution with (very) high amounts decreases sensitivity for the co-eluting sulfur component, and therefore the chromatographic separation is optimised for each standardised method by column choice and GC conditions. Besides the sulfur output, PFPD offers a hydrocarbon signal as well, to monitor the carbon content. Due to its good long term stability, minimal calibration and maintenance is required. It is easier to operate, costs less, and the response is more stable compared to the Chemiluminescence detector. The PFPD has an equimolar response, which means that the detector signal only depends on the amount of sulfur, and independent of the compound used for calibration. This greatly simplifies the quantitation of unknown sulfur components.



Figure 6. The optional MK5 Calibrator equipped with permeation tubes is used for multilevel calibration of low sulfur at ppm/ppb level



Figure 7. Low sulfur analysis based on GC-PFPD is available on CompactGC as well



Specifications

FEATURES & **BENEFITS**

- * Robust and reliable analysis of sulfur in various samples
- * Selective and sensitive (<20 ppb, depending on separation)
- * High long term stability, low maintenance costs
- * Factory tuned for required standardised method * On site installation and familiarisation

Standardised methods:

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 ₂ S, 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 Linearization of the sulfur signal is recommended	Signal-to-noise of at least 2-to-1 for 0.5 mg/kg (ppm) thiophene in benzen (4-µL injection with FPD or 1-µL injection with PFPD)	Signal-to-noise of at least 2-10-1 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 5-pg sulfur/second minimum delectability Approximate equimolar response to sulfur No interference from co-eluting hydrocarbons	Any flame photometric detector calibrated in the sulfur-specific mode is used for this test method	 Linearity of 10² Minimum detectable level of less than 0.02 mg/kg thiophene in benzene Selectivity of sulfur to carbon greater than 10⁵ 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 corcentrations 5 to 10 times lower than an FPD. Linear, equimolar response of the PFPD allows accurate quartitation 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, ISO 19739

Configuration:	1-3 channel instrument based on Thermo Trace or CompactGC and PFPD. Available injection types: GSV,				
	LSV, Split or PTV injection.				
Optional:	- Vaporiser or Pressure Facility 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 sulfur components in various gases, liquefied gases and				
	liquid streams				
Range:	100 ppb - 100 ppm				
Detection limit	<100 ppb; <20 ppb in case of well-separated sulfur components				
Repeatability	< 3 % RSD				
Sample requirements:	See our pre-installation guide for additional requirements.				

