

A HAZARDOUS ROAD TO SUCCESS

Chromatotec have established themselves in the Forefront of Sulphur Analysis in Hazardous Areas. Their latest Enhancement of their MEDOR range has Augmented their Rapid Rise in this Expanding Market

Most natural gas production and exploitation sites are considered to be hazardous areas. This is certainly the case when it comes to Liquefied Petroleum Gas (LPG) sites. It is vital to avoid creating any areas, within the sites, in which the atmosphere contains flammable gas. The need to comply to stringent safety and environmental regulations and the associated cost and constraints associated with compliance, need to be factored in, when calculating a site's profitability.

Natural gas is a natural resource present on the earth which can vary in composition depending on the location of its extraction. In order to maximise the use and value of natural gas, it is necessary to control its composition. Even if it is composed mainly of methane, natural gas contains some traces of Sulphur compounds which can affect its quality as well as having dramatic effects during its transportation (for example: pipe corrosion). Therefore, companies that work with natural gas need to control the level of Sulphur compound impurities, as well as adding specific Mercaptans to make it odourant and easily detectable in cases of leakage.

For over 30 years, Chromatotec® has manufactured the MEDOR® instruments, which are based on gas chromatography principles, to measure H_2S , all Mercaptans, Sulphides, Tetrahydrothiophene (THT) and Total Sulphur in natural gas or gaseous fuels. Thanks to



MEDOR ex CSA – Odorization site in USA



LNG Terminal application

the advantages of the "MEDOR"® technology and its ubiquitous deployment in the USA, American customers have defined a new guideline based on the solution: ASTM D7493-08 "Standard Test Method for Online Measurement of Sulphur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatograph and Electrochemical Detection".

As the MEDOR® analyser only needs between 5 to 60 mL/min of nitrogen or zero air to operate, the development of an ATEX solution was a catalyst in expanding Chromatotec's® position in the hazardous areas market. It all started in 2009 with the development of an ATEX and CSA certified Purge solution to operate in hazardous areas zone I and II. Chromatotec® managed to overcome the main limitation, which is the use of an important flow of purge gas (from 30 to 60 L/min of nitrogen or air) which is not always available on site. The second phase, which started on January 2017, was to develop and produce an ATEX solution using a "d" type enclosure which does not need any purging gas. This solution can be implemented in area zone I and II depending on each customer's specific needs.



H_2S Thermal Powerplant Application

This solution was developed, whilst keeping in mind the need to attain the certifications necessary for the various different parts of the world – such as CSA for North America. Now Chromatotec® is the only manufacturer to provide Sulphur analysers developed to require only 5 to 60 mL/min of zero air or nitrogen for operation including internal automatic calibration. In addition MEDOR® instrumentation technology is some of the most sensitive that is capable of detecting without pre-concentration and without any convertor down to 1 ppb of individual Sulphur compounds.

Other technologies require at least two gases to operate and/or a convertor to convert Sulphur compounds into H_2S or SO_2 depending on the detector. It can be a problem for some operators to use hydrogen cylinders in hazardous areas, the risk of leaks prohibits their use. Convertors are not 100% efficient for all compounds and the efficiency decreases over time which creates potentially critical errors of measurement.

A specific product in the MEDOR® range named energyMEDOR® allows the speciation and measurement of sulfur compounds in different matrix (natural gas, LPG...). The equipment specifications are given here:

The energyMEDOR® is capable of analysing individual Sulphur compounds and Total Sulfur with direct measurement. In addition the internal calibration stream (permeation tube installed into the instrument) is analysed at the end of every analysis, at a very low concentration level (ppb or ppm). Results are thus automatically validated. No external calibration cylinders are required for operation and calibration. The energyMEDOR® can detect Total Sulphur compounds thanks to its Sulphur Specific Detector (SSD).

A list of possible sulphur compounds to measure is given below:

1. Hydrogen sulphide (H₂S)
2. Methyl Mercaptan
3. Ethyl Mercaptan
4. N Propyl Mercaptan
5. Iso Propyl Mercaptan
6. Tertiary Butyl Mercaptan
7. TetraHydroThiophene (THT)
8. Total Mercaptans (as sum of 2+3+4+5+6)
9. Total Sulphur (as sum of 1+2+3+4+5+6+7)

Every component and the sum of them can be transferred to a data logger through a specific communication protocol (e.g. Modbus, 4-20mA outputs...).

To operate, the instrument specifications are:

- Gas supply: N₂ or zero air
- energyMedor® can be installed either in 19" rack or in an ATEX Cabinet type "p" or "d".

An industrial computer is located inside the enclosure and has an internal mouse and keyboard available in case local maintenance is required. The computer transmits data to a local central room via RS-485 or via an Ethernet connection. In cases of long distances between the instruments and the local central room, the network connection can be routed via RS-485. Data can be sent by the computer either via 4-20 mA output or Modbus RTU protocol.

Thanks to this internal PC, it is possible to collect data with Vistachrom software. The software permits the transference of concentrations, Total Organic Sulfur (TOS) calculations and status (calibrations, streams, default analyser) via the Modbus protocol to the control room.

A calculation module is available and has the capacity to perform concentration daily averages (on 24 hours) on selected components.

The Odourisation of natural gas is an important application for which the energyMEDOR® is a key product.

For safety reason, natural gas is required to be readily detected by a person with a normal sense of smell. Therefore, the MEDOR® solution needs to be as sensitive as the human nose.

To demonstrate its sensitivity, some performance tests have been carried out. Analysis of 8 Sulphur compounds from external certified standards have been performed. Below are shown the results obtained for the stability tests and linearity tests after 20 consecutive analysis were executed on the following components:

Table 1: List of molecules analyzed during the test

Hydrogen sulphide	H ₂ S
Methyl Mercaptan (MM or MTM)	CH ₃ -SH
Ethyl Mercaptan (EM or ETM)	CH ₃ CH ₂ -SH
Dimethyl Sulphide (DMS)	CH ₃ -S-CH ₃
(iso) 2-Propyl Mercaptan (IPM)	(CH ₃) ₂ -CH-SH
ter Butyl Mercaptan (TBM)	(CH ₃) ₃ -C-SH
(N) 1-Propyl Mercaptan (NPM)	CH ₃ CH ₂ CH ₂ -SH
TetraHydroThiophene (THT)	C ₄ H ₈ S

All tests performed are part of a protocol document pertaining to analyser validation and are defined by a European third party laboratory. To validate the instrument, it is required to perform 20 analysis and to obtain results in compliance with ISO 5725-2. The samples are generated from different standards.

The relative reproducibility and repeatability values are much better than performance criteria values as defined in the ISO 19739 norm. All tested compounds have a linear response (to SSD) in the trial conditions (i.e. range of 0 – 5 mg/m³ for most Sulphur compounds and THT range 0-25 mg/m³) with a R² > 0.995 for all compounds. So the conclusion was that the performance criteria are in compliance with the norm.

Table 2: Concentrations obtained for H₂S, MM, EM, IPM, TBM, THT and DMS STD over 20 measurements

	Concentration (mg/m ³)						
	H ₂ S	MM	EM	IPM	TBM	THT	DMS STD
Mean	3,16	9,06	6,02	8,05	5,18	27,20	6,04
SD	0,011	0,031	0,072	0,048	0,031	0,146	0,021
Relative Error (%)	1,50	0,84	0,21	2,06	0,96	0,51	0,19
Repeatability (%)	0,72	0,68	2,38	1,20	1,21	1,07	0,71
Reference concentration	3,11 (+/-4%)	9,14 (+/-4%)	6,01 (+/-4%)	8,22 (+/-4%)	5,13 (+/-4%)	27,06 (+/-4%)	6,03 (+/-10%)

Table 2 (above) summarises the different results obtained by compound.

Table 3 represents the criteria for compliance with the ISO 19739 norm and the obtained values using the energyMEDOR® instrument.

	Repeatability (%)		Relative reproducibility (%)	
	Performance criteria	Obtained value	Performance criteria	Obtained value
H ₂ S	3	0,72	25	1,50
MTM (or MM)	2	0,68	10	0,84
ETM (or EM)	4	2,38	30	0,21
IPM	10	1,20	20	2,06
TBM	7	1,21	25	0,96
THT	4	1,07	20	0,51

An example of a chromatogram obtained with the energyMEDOR® for the measurement of H₂S at around 1 mg/m³ is shown in Figure 1 below.

At the end of each chromatogram, a validation of results is carried out by injecting and analysing the DMS from the internal calibration device certified (permeation tube).

Another application for the natural gas market is related to Integrity Monitoring. During the extraction of raw natural gas and following processing, midstream companies are required to track the level of H₂S and TS (Total Sulphur = H₂S + Total Organic Sulphur (TOS)). If the concentration measured exceeds the required level, the midstream companies must shut down the

gathering line until the measurements are displaying the required concentration levels again.

For these analysis, the sample is first loaded into a loop and then injected in an analytical column to separate H₂S from the other Sulphur compounds (shown in Figure 2).

To expand the applications of the MEDOR®, a specific sampling module has recently been developed by Chromatotec®. It can inject extremely low volumes (from 0.1 to 1 µL) into MEDOR® autoGC for LPG analysis (Propane and butane), which is directly connected in the sampling module inlet. It is then vapourised and injected into the MEDOR® directly. Other applications for heavier liquid hydrocarbons, like condensate or gasoline, are

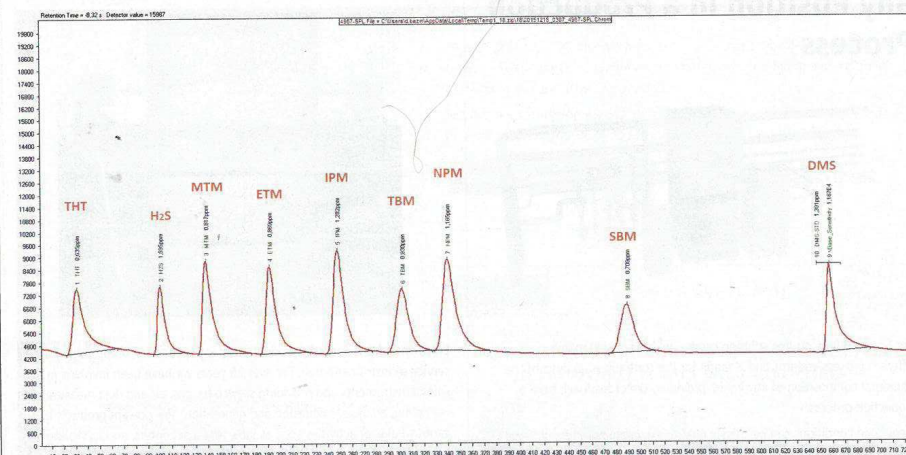


Figure 1: Typical chromatogram obtained with energyMEDOR

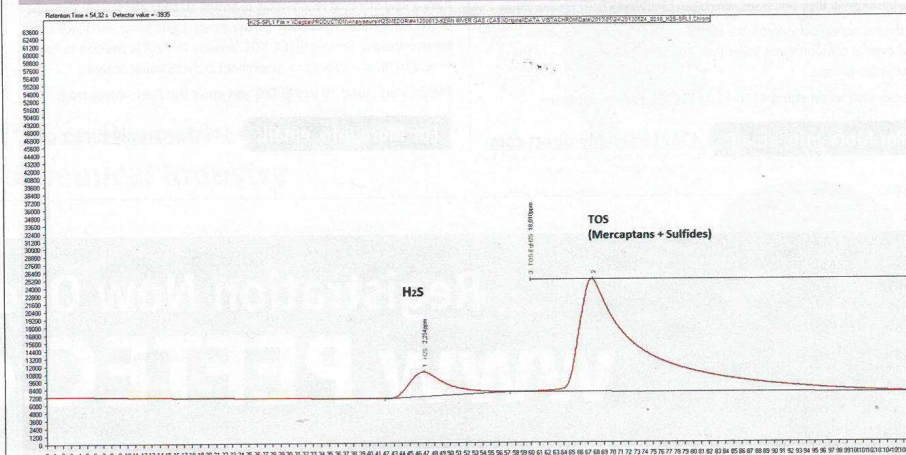


Figure 2: Analysis of H₂S, TOS and TS in two minutes



Medor under Quality Control

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A New Solution for Getting Real-time Feedback from any Position in a Production Process



The Epsilon Xflow on-line solution can be incorporated in many different process streams and is made for the continuous analysis of the elemental composition of any liquid, providing direct feedback from a production process.

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Envicontrol is a scientific product company specialised in the sale and service of instrumentation. For over 25 years we have been involved in the sale of instruments and providing service for gas, air and dust measurement (sampling, analysis, calibration and generation). We present products in various fields of activities such as labs, research centers, air monitoring networks, industries and meteorology. To ensure to meet the needs of our customers we have a broad range of manufacturers, with whom we have a long-standing relationship, to ensure stability and quality. Amongst others we represent following manufacturers: Opsis (stack and fence-line measurements), Synspec (BTEX, VOC in water and air) in addition to Palas (Fine dust measurement and generation) and ABB water analysis.

Please visit stand 10 at PEFTEC and meet the Envicontrol team.

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Next Generation Gas Analysers on show at PEFTEC



Servomex, will be demonstrating its innovative next-generation analysers on stand 100 at PEFTEC 2017.

Visitors to the stand will see all the performance and cost benefits of the analysers, which are ideal for the power generation, hydrocarbon processing and environmental monitoring sectors, including:

The SERVOTOUGH Laser 3 Plus range – compact TDL analysers optimized for combustion, process control and ammonia slip applications

The SERVOPRO MonoExact DF150E and DF310E – oxygen analysers combining reliable trusted measurements with an intuitive touchscreen interface

The new SERVOPRO MultiExact 4100 – a sophisticated multi-gas analyzer offering four simultaneous gas stream measurements and advanced digital communications

Barb Marshik, Market Sector Manager for Power will be giving a talk on 'Emissions Reduction by Combustion and Post Combustion Control Strategies', and other Servomex experts will be on hand to provide information and advice.

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