

HYDROGEN-FREE SULPHUR SPECIFIC ANALYSER CERTIFIED FOR HAZARDOUS AREA ZONE I AND II USING "D" TYPE ENCLOSURE

Most of natural gas production and exploitation sites are considered as hazardous area. This is as well the case for Liquefied Petroleum Gases (LPG) sites. It means that any flammable atmosphere must be avoided. It is very important to keep in mind this constraint for the providers of solution to valorise these resources.

Natural gas is a natural resource present on the earth which can vary in composition depending on the place it is extracted.

In order to use and valorise 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 and can have dramatic effects for its transportation (e.g. corrosion of the pipes). Therefore, companies that work with natural gas control the level of sulphur compound impurities as well as adding specific Mercaptans to make it odorant and easily detectable in case of a leak.

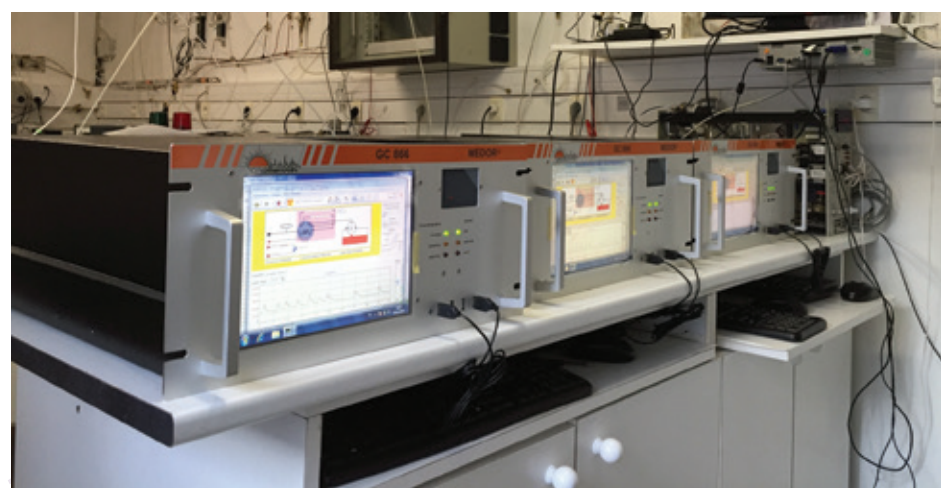
For more than 30 years, Chromatotec® has manufactured the MEDOR® instruments, based on the gas chromatography principles, to measure H₂S, all Mercaptans, Sulphides, Tetrahydrothiophene (THT) and Total Sulphur in natural gas or gaseous fuels. Thanks to the advantages of the "MEDOR"® technology and its large 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 from 5 to 60 mL/min of nitrogen or zero air to operate, the development of an ATEX solution was an evidence to expand Chromatotec® position on hazardous areas market. It started in 2009 with the development of a Purge solution. These solutions are ATEX and CSA certified to operate in hazardous areas zone I and II. Nevertheless, the main limitation 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. Then, the second step 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 customers need.

This solution was developed keeping in mind the possibility to get the certification necessary for other areas in the world – such as CSA for America. Now Chromatotec® is the only manufacturer to provide sulphur analyser with speciation requiring only 5 to 60 ml/min of zero air or nitrogen for operation including internal automatic calibration. In addition MEDOR® technology is one of the most sensitive instrument capable to detect 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 H₂S or SO₂ depending on the detector. It can be a problem for some customers to use hydrogen cylinders in hazardous areas, the risk of leaks remaining a mental barrier to their use. Convertors are not efficient at 100% for all compounds and the efficiency decreased over the time which create important error in the measurements.

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



The energyMEDOR® is able to analyse individual Sulphur compounds and Total Sulphur with direct measurement as described below. In addition the internal calibration stream (permeation tube installed into the instrument) is analysed at the end of every analysis, at very low concentration level (ppb or ppm). Results are thus automatically validated. No external calibration cylinders are required for operation. 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)

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:

o Gas supply: N₂ or zero air

o 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 internal mouse and keyboard available in case local maintenance is required. The computer transmit data to a local central room via RS-485 or via an Ethernet connection. In case of long distance between the instruments and the local central room, network connection can be done via RS-485. Data can be send 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 the software Vistachrom. The software allows transferring concentrations, Total Organic Sulphur (TOS) calculations and status (calibrations, streams, default analyser) by 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 where 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 done. Analysis of 8 Sulphur compounds from external certified standards have been done. Below are shown the results obtained for the stability tests and linearity tests after 20 consecutive analysis performed on the following components:

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

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

Table 1: List of molecules analysed during the test

Table 2 here above summarise the different results obtained per compound.

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

Table 3 represents the criteria for compliance with 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

Table 3: Comparison between performance criteria in compliance with ISO 19739 and obtained values.

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 of 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.

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

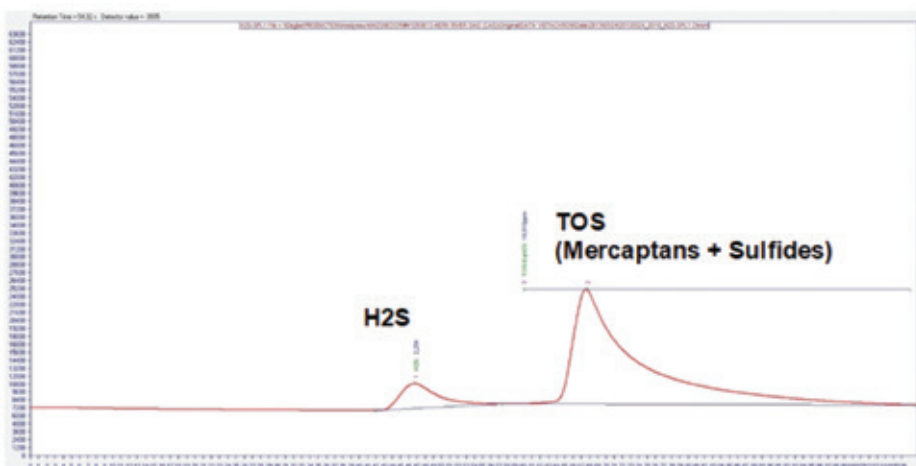


Figure 1: Typical chromatogram obtained with energyMEDOR

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

Another application for natural gas market is related to the 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 exceed the required levels, the Midstream companies must shut down the gathering line until the measurement are showing 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 species (shown in Figure 2).



To expand the applications of the MEDOR®, a specific sampling module has been developed by CHROMATOTEC® to inject extremely low volume (from 0.1 to 1 µL) into the autoGC. LPG analysis (Propane and butane), which is directly connected in the sampling module inlet. Then it is vaporised and injected into the MEDOR® directly. Another application is for high concentration up to low %: thanks to the very low volume injected the MEDOR® instrument is not disturbed.

Other applications for heavier liquid hydrocarbon like condensate or gasoline are also available; as soon as they can be vaporised in the heated sampling module it is possible to analyse them with MEDOR®.

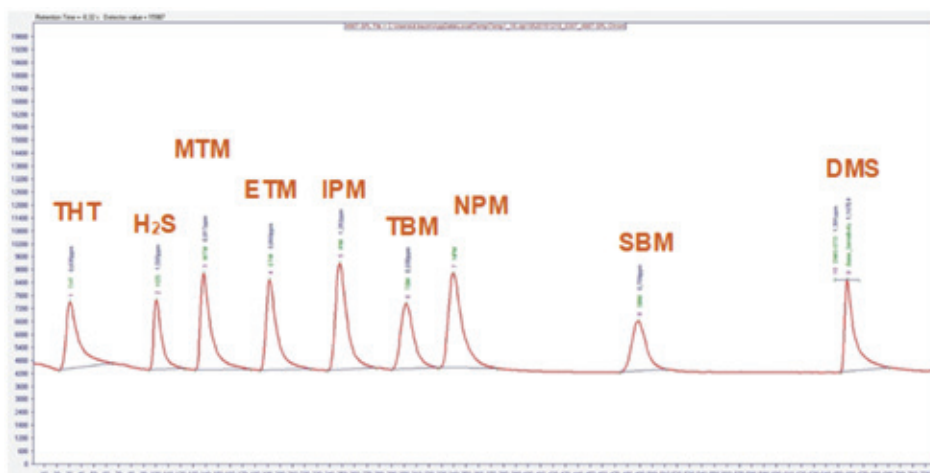


Figure 2: Analysis of H₂S, TOS and TS in two minutes

Conclusion

There is a clear global tendency for analysing Sulphur compounds with speciation in the oil and gas field but also on other markets, with a demand under expansion in industries like shale gas, Biogas, odour and CO₂ in beverage. This should remain important in coming years.

Certifications are also a key issue for the company as it is important to continue to invest in these processes to validate the technologies for specific fields and applications. Chromatotec® investments in Ex d applications and sampling module development allow to extend the scope of its MEDOR® solution.

The diversifications of the processes and the need for efficiency improvements result in customers looking for customised and performant solutions. These specific needs are at the base of Chromatotec® evolution.

Chromatotec®'s energyMEDOR® appears to be the best alternative for these applications since it only needs a small amount of nitrogen or zero air to operate its Sulphur Specific Detector. This certified solution has been designed to operate in zone I and II and can be used with 230V, 115V and 24V power supply making it quite unique on such type of market.

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