

# 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<sub>2</sub>S, 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<sub>2</sub>S 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<sub>2</sub>S or SO<sub>2</sub> 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 (H<sub>2</sub>S)
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: N<sub>2</sub> 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 <sub>2</sub> S                                    |
| Methyl Mercaptan (MM or MTM)   | CH <sub>3</sub> -SH                                 |
| Ethyl Mercaptan (EM or ETM)    | CH <sub>3</sub> CH <sub>2</sub> -SH                 |
| Dimethyl Sulphide (DMS)        | CH <sub>3</sub> -S-CH <sub>3</sub>                  |
| (iso) 2-Propyl Mercaptan (IPM) | (CH <sub>3</sub> ) <sub>2</sub> -CH-SH              |
| ter Butyl Mercaptan (TBM)      | (CH <sub>3</sub> ) <sub>3</sub> -C-SH               |
| (N) 1-Propyl Mercaptan (NPM)   | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -SH |
| TetraHydroThiophene (THT)      | C <sub>4</sub> H <sub>8</sub> 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/m<sup>3</sup> for most Sulphur compounds and THT range 0-25 mg/m<sup>3</sup>) with a R<sup>2</sup> > 0.995 for all compounds. So the conclusion was that the performance criteria are in compliance with the norm.

Table 2: Concentrations obtained for H<sub>2</sub>S, MM, EM, IPM, TBM, THT and DMS STD over 20 measurements

|                         | Concentration (mg/m <sup>3</sup> ) |              |              |              |              |               |               |
|-------------------------|------------------------------------|--------------|--------------|--------------|--------------|---------------|---------------|
|                         | H <sub>2</sub> 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 <sub>2</sub> 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 H<sub>2</sub>S at around 1mg/m<sup>3</sup> 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 H<sub>2</sub>S and TS (Total Sulphur = H<sub>2</sub>S + 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 H<sub>2</sub>S 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

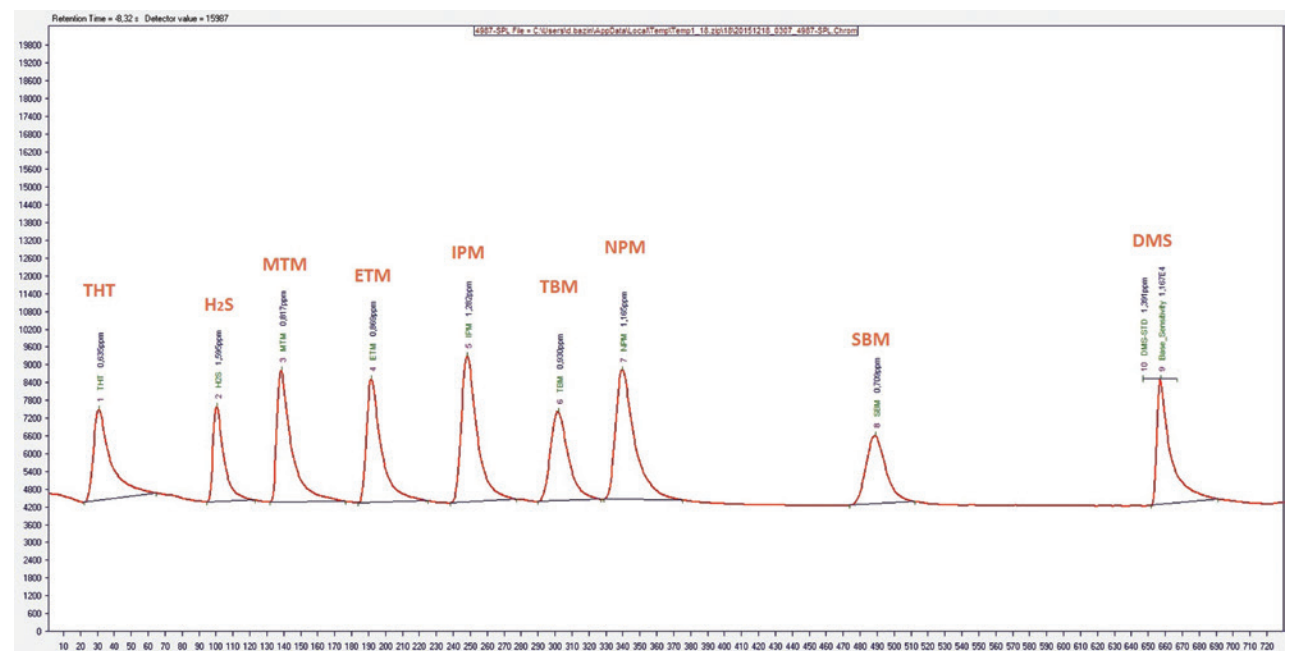


Figure 1: Typical chromatogram obtained with energyMEDOR

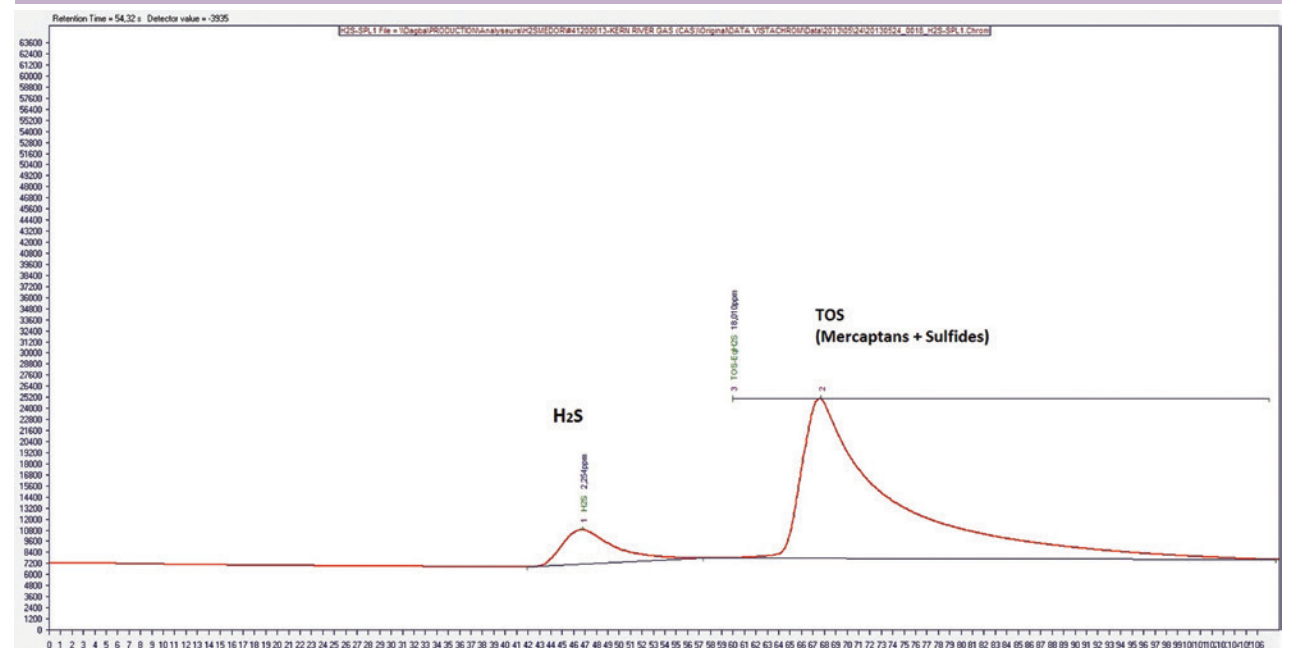
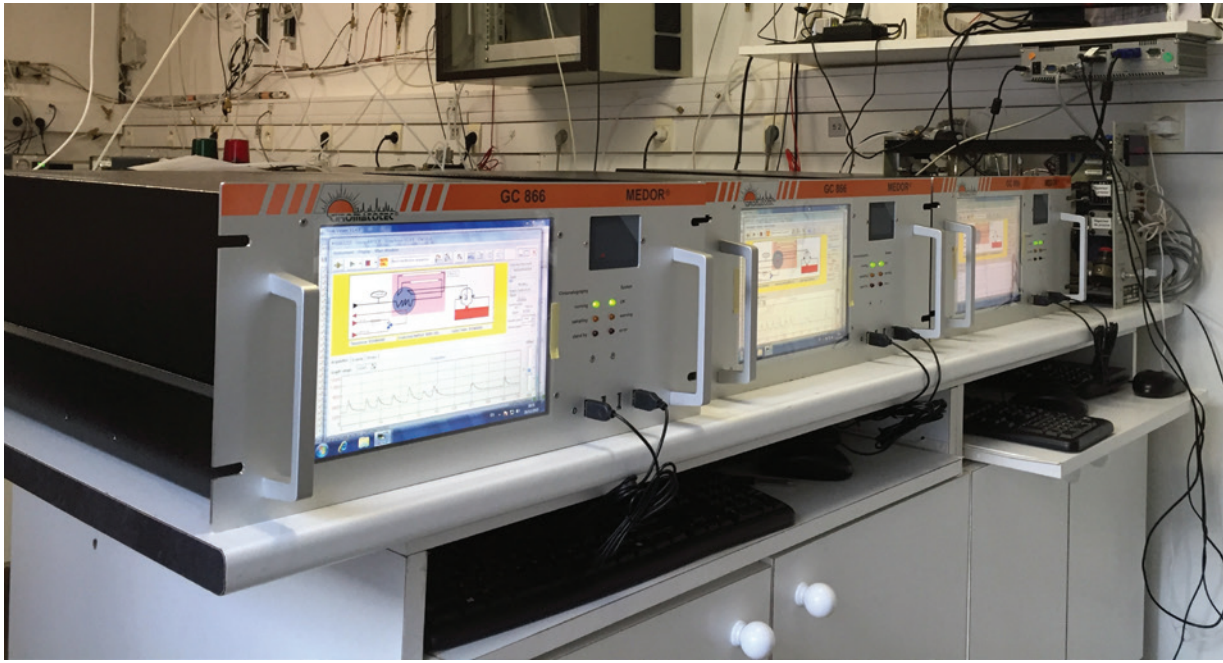


Figure 2: Analysis of H<sub>2</sub>S, TOS and TS in two minutes



*Medor under Quality Control*

also available; as soon as they can be vapourised in the heated sampling module it is possible to analyse them with MEDOR®.

### Conclusion

There is a clear global demand for analysing Sulphur compounds with speciation in the oil and gas field but also on other markets, with markets under expansion in industries like shale gas, Biogas, odour and CO<sub>2</sub> in beverage. There is no reason to believe that this will not be the case for the foreseeable future.

Certifications of compliance are also a key issue for Chromatotec 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 facilitates expanding 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's® 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.

### Author Contact Details

Franck Amiet - President and CEO, Jean-Philippe Amiet - M. Sc. Export Project Manager, Mickaël Gezat - Project Manager, CHROMATOTEC

• 15 rue d'artiguelongue - Saint-Antoine 33240 Val de Virvée France • Tel 0033 (0)5 57 94 06 26 • Email: info@chromatotec.com • Web: www.chromatotec.com

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