HOW TO ANALYSE H_2S, ALL MERCAPTANS, THT AND TOTAL SULPHUR FOR MONITORING NATURAL GAS OR GASEOUS FUELS IN METERING STATIONS

Introduction

Natural gas is colourless and odourless in its most pure form. When extracted, it can contain sulphur compounds such as H_2S and Mercaptans that when in the presence of moisture can produce sulphuric acid that can degrade the pipeline. So for reasons of public safety as well as pipeline integrity, there is a need to measure and control precisely the level of odorant species in natural gas:

- adjust the amount of sulphur molecules in the gas
- control of odorant passivation
- aids in detection of leaks

For more than 30 years, Chromatotec® has manufactured the energyMEDOR, based on the gas chromatography principles, to measure H_2S, all mercaptans, sulfides, Tetrahydrothiophene (THT) and total sulphur in natural gas. Due to the advantages of the "MEDOR" technology, a new guideline was defined, ASTM D7493-08 (as the Standard Test Method for Online Measurement of Sulphur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatograph and Electrochemical Detection). The energyMEDOR by Chromatotec® is fully compliant with this guideline.

1. Equipment Specificities

The energyMedor is able to analyse H_2S, all mercaptans, Diethyl sulfide (DES), Dimethyl sulfide (DMS), Dimethyl disulfide (DMDS), THT and total sulphur directly without convertor. In addition the internal calibration stream (permeation tube installed into the instrument) is analysed at each cycle, at very low levels (ppb-ppm). Results are thus automatically validated. No external calibration cylinders are required for operation. The energyMedor can detect total sulphur compounds thanks to a sulphur specific detector.

Please find below examples of the analysed sulphur compounds:

1. Hydrogen sulphide (H_2S)
2. Methyl Mercaptan
3. Ethyl Mercaptan
4. N Propyl Mercaptan
5. Iso Propyl Mercaptan
6. Tertiary Butyl Mercaptan
7. TetraHydroThiophene (THT)
8. Total Mercaptans (2+3+4+5+6)

We can transfer each compound and the sum of all the compounds.

1.1 Instrument requirements

o Gas supply: N2 or air

- No Flammable gases are required by the analyser.
- No need of special pre instrument filters or conditioners or traps.

o Standard pressurised gas at 1 bar or 15 PSI is required.

- energyMedor can be installed in an Ex Cabinet

1.2 Suitable for hazardous areas

The energyMEDOR, normally manufactured as a 19" rack design, has been re-packaged in a 144L IP66 rated 316 SS enclosure. The system is wall-mounted. A Z- or X-purge is installed and creates a constant positive flow of air inside the enclosure, thus making a positive pressure inside enclosure. The purge is set to prevent toxic fumes from going inside the instrument in case of hazardous leakage.

A purge controller located on the side of the analyser with visual display activates the analyser if the out-coming air flow supplied to the instrument is sufficient at minimum 2 Bars (70 psi). To be sure that there is a positive pressure inside the analyser, a pressure probe has been placed inside the instrument and the pressure value is displayed at all times on the monitor.

To be sure that the temperature inside the cabinet is adapted to the chromatographic separation of the energyMEDOR, the temperature inside the enclosure is monitored and displayed at all times. A type **CSA (US and Canada) or ATEX** certificate

is provided with this instrument. Beside the additional Z- or X-purging, the components and the operation of the instrument are mostly identical to that of our standard energyMEDOR.

An industrial computer is located inside the enclosure and has internal mouse and keyboard available in case local maintenance is required in non-hazardous conditions. The computer transmit data to a local central room via RS-485 or to an Ethernet connection. In this case, network connection between central controls located 46 meters away can be done via RS-485. Data can be sent by the computer either via 4-20 mA output or Modbus RTU protocol.

1.3 Data acquisition

Thanks to an internal or external PC (required for safety areas), it is possible to collect data with the software Vistachrom. It allows transferring concentrations, TOS calculations and status (calibrations, streams, default analyser) by the Modbus protocol to the control room.

1.4 Calculation module

This module has the capacity to perform daily averages (on 24 hours) of selected components. This information can be provided to the Modbus driver as well as the component analysis.

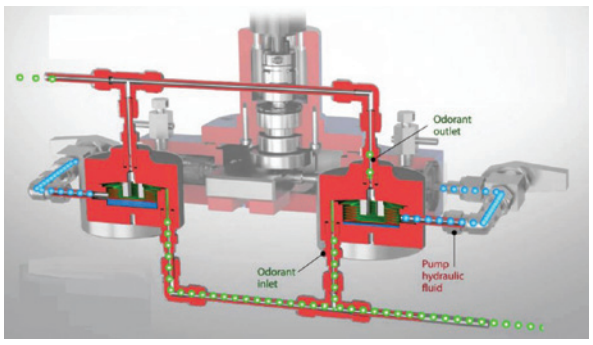
2.1 Odorization requirements

Natural gas is required to be readily detected by a person with a normal sense of smell.

The MEDOR is used for 2 applications:

Odorant verification:

The MEDOR monitors downstream (with the option of upstream, "2 streams") of the injector. The data is the actual concentration of odor present. *OR* End of line monitoring, the MEDOR provides the concentration of odorant that is present (this accounts for odor fade in the pipeline).



Odorant injection control:

The MEDOR monitors downstream (with the option of upstream, "2 streams") of the injector. The output of the MEDOR is monitored by a PLC or directly input the Odorizer via a feedback loop. The Odorizer monitors the output concentration of the MEDOR and adjusts the injection rate of odorant accordingly.

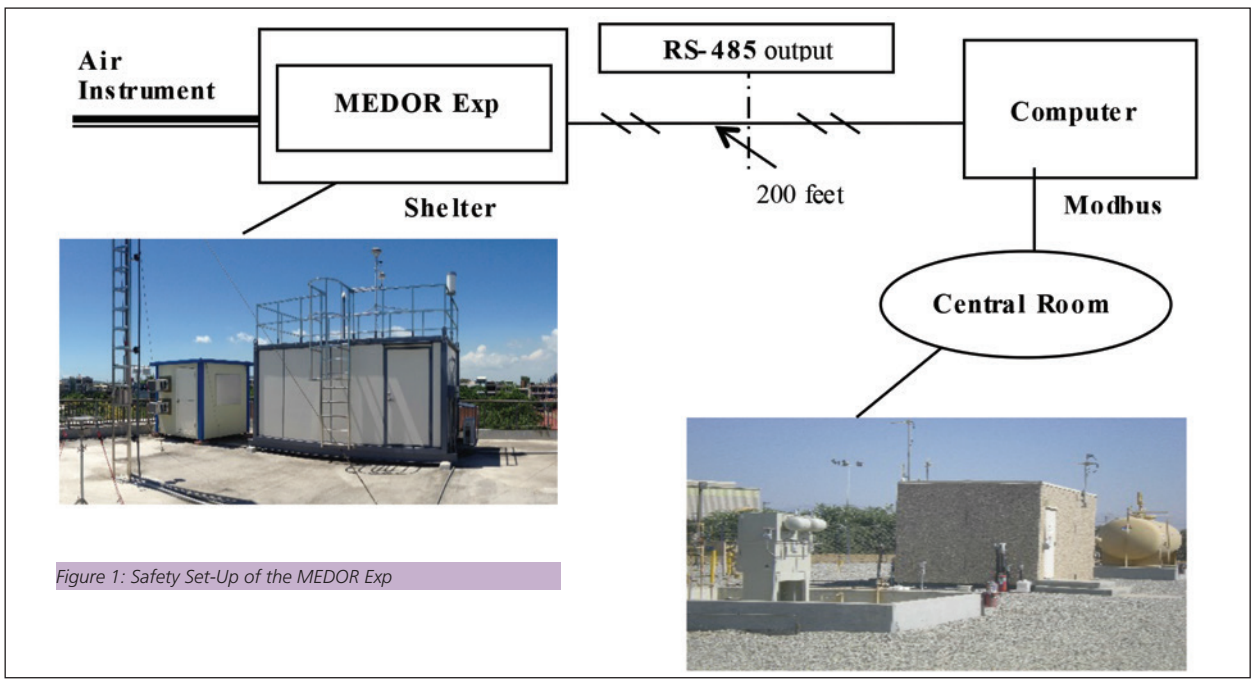


Figure 1: Safety Set-Up of the MEDOR Exp

2.1.1 Experimental results

As performance tests, an analysis of 8 compounds from external standard using DMS permeation tube as calibration has been done. Here are the results for Stability tests and Linearity tests after 20 consecutive analysis performed:

Hydrogen sulphide	H_2S
Methyl Mercaptan (MM or MTM)	CH_3-SH
Ethyl Mercaptan (EM or ETM)	CH_3CH_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)	$CH_3CH_2CH_2$-SH
TetraHydroThiophene (THT)	C_4H_8S

Table 1: List of molecules analysed during test.

2.1.1.a Repeatability results

All tests performed are defined by a European third part laboratory protocol document pertaining to analyser validation. To validate it is required to perform 20 analyses with the results in compliance with ISO 5725-2. The samples are generated from a permeation device placed in a temperature controlled oven.

Table 3 represents the criteria for compliance with UNE-EN 196739 and the obtained values using the energyMEDOR instrument. The relative reproducibility and repeatability values are much lower than values of performance criteria indicated in ISO 19739 norm. All tested compounds have a linear response (EC detector) in the trial conditions i.e. range of 0 – 5 mg/m3, THT range 0-25 mg/m³. R2 > 0.995 is obtained for all compounds. Performance criteria are in compliance with the norm.

In the Figure 2 is an example of a chromatogram obtained by energyMEDOR at around 1mg/m³ for H_2S. At the end of each chromatogram, internal CALIB composed by DMS is injected to validate automatically the sensitivity of the energyMEDOR.

2.2 Integrity Monitoring

During the extraction of raw natural gas and following processing, Midstream companies are required to track the level of H_2S and TS (Total Sulphur = H_2S + Total Organic Sulphur (TOS)). If the concentration of either exceed the required levels the Midstream provider will shut down the gathering line until the required levels are met.

For this analysis, the sample is first loaded in a loop and then injected in a column to separate H_2S from the other sulphurs.

	Concentration (mg/m³)						
	H2S	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

	Repeatability (%)		Relative reproducibility (%)	
	Performance Criteria	Obtained Value	Performance Criteria	Obtained Value
H2S	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 UNE-EN ISO 19739 and obtained values.

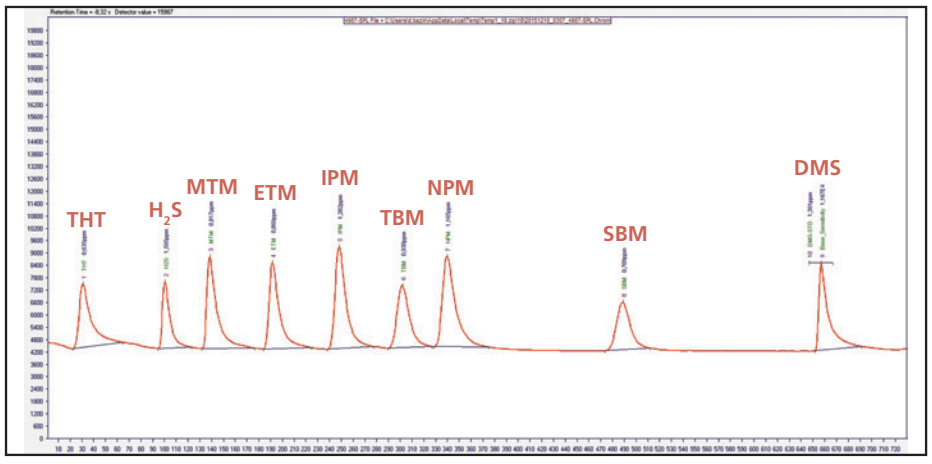


Figure 2: Typical chromatogram obtained with energyMEDOR

The instrument was sampling stagnant gas, which explains the discrepancy between the expected odorant composition (50% w/w THT and 50% w/w TBM)and its measured composition (71% w/w THT and 29% w/w TBM).

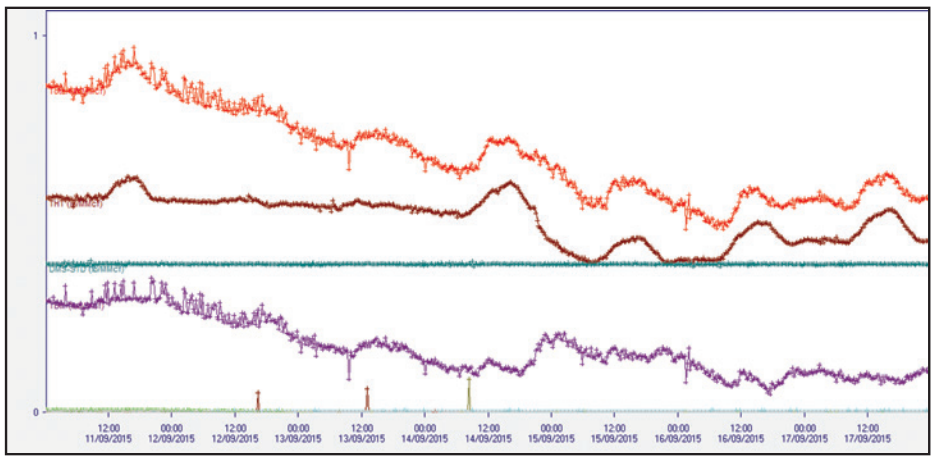


Figure 4: Trend for Natural Gas and Calibration Cylinder Constituents – Concentration in ppm

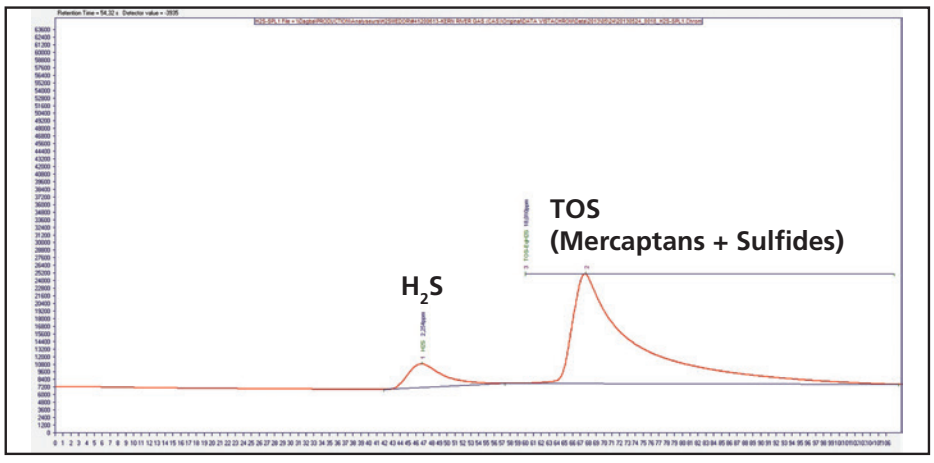


Figure 3: Analysis of H_2S, TOS and TS in two minutes – Concentration in ppm

Example of odorant concentration analysis obtained with energyMEDOR

Data provided by our US partner Consolidated Analytical Systems

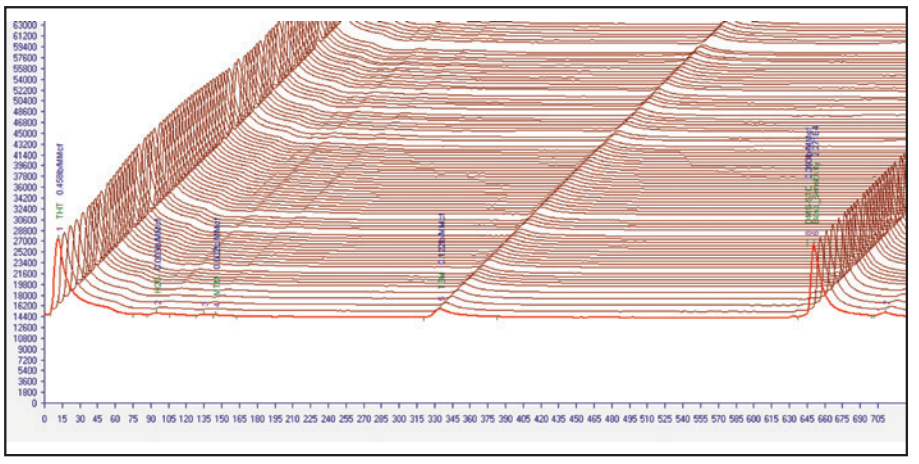


Figure 5: 3D presentation of Natural Gas and Calibration Cylinder Chromatograms.

H_2S goes through the column and is then detected by the electrochemical detector.
The sample is then back-flushed and heavy sulphur compounds are injected without separation to the detector.

In the Figure 3, a typical chromatograph is shown where two peaks can be observed. The H_2S first, then an actuation of the valve allows the sample to be black-flushed to the detector and the other sulphur compounds will then be detected. After 120 seconds, all compounds have been analysed.

CONCLUSION

The energyMEDOR® is a unique sulphur specific detector technology recognized in natural gas industry since it responds **directly** to H_2S, mercaptans and THT. It offers linearity of each sulphur component and allows to measure each components with speciation with air only.

These advantages are also suitable for other applications for Oil and Gas market like:

- **Pipeline quality control:** unodorised gas can be analysed for natural sulphur species before and during transport or storage.

- **Process monitoring – gas cleaning and desulphurization:** for sulphur removal processes, such as Natural Gas extraction, Landfill or Biogas, treatment before injection into a pipeline network requires careful monitoring and control. A detection limits as low as 1 ppb H_2S coupled with concentration based alarm thresholds offers maximum security. Thanks to an internal multiplexer, monitoring before and after treatment is possible with one analysis system.

Internal permeation system offers automatic validation of results and data with full traceability. Natural gas destined for cracking processes is then easily monitored automatically to ensure protection for catalytic plants.

- **Delivery station at interface between transport and distribution.**

- LPG: for trace of sulphur compounds measurement at ppb level for application requiring non- odorized gas (for example aerosol application).

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