



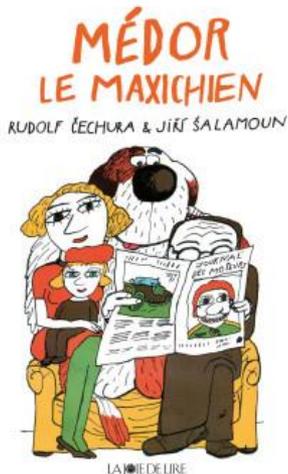
# MEDOR<sup>®</sup> technology and applications



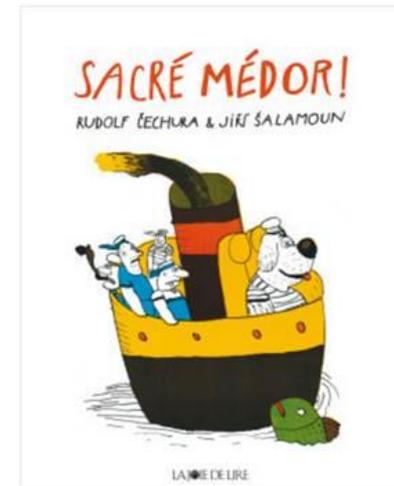
# Origin of the name MEDOR®

Based on:

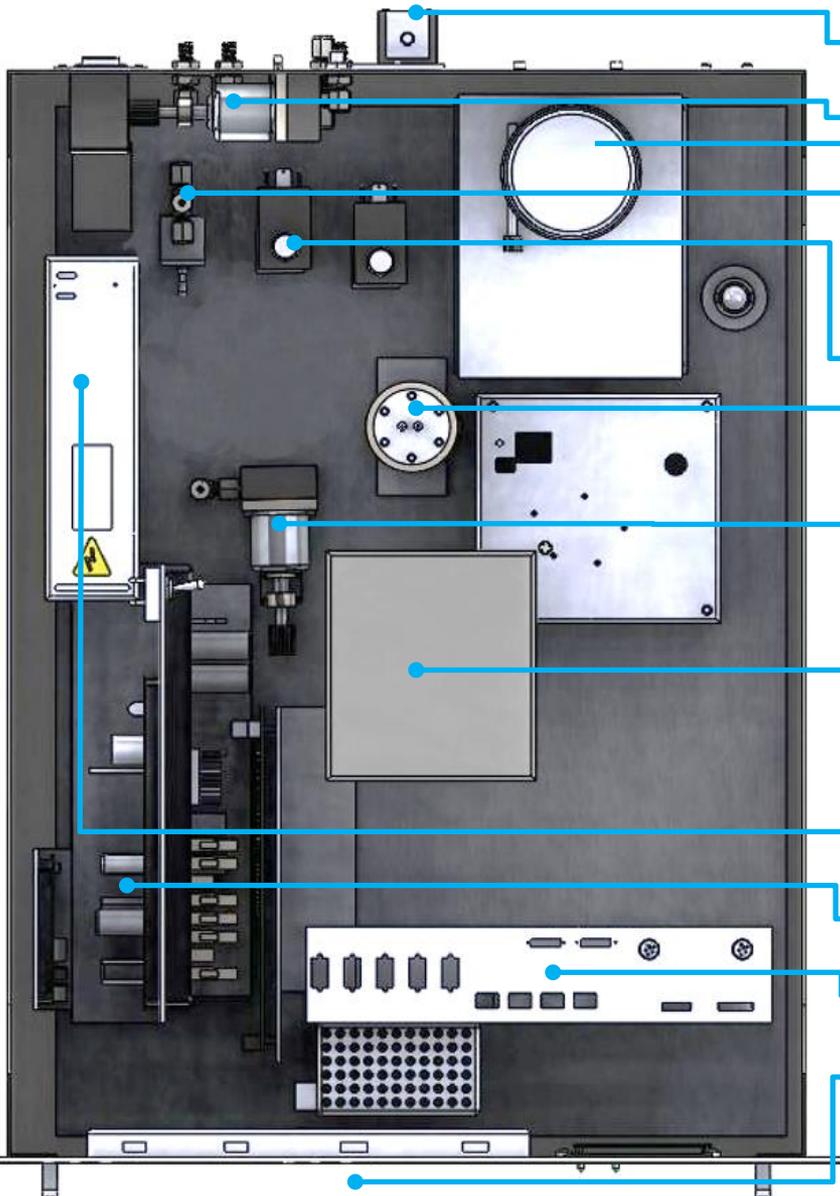
- In English “**ME**asurement of **oDOR**”
- In French “**ME**sure **D’OdeuR**”
- In Europe in the years 1970s it is a famous name for a Dog.



Dogs are very sensitive to odor !



# Top View



- Sample flow indicator = rotameter
- Pressure regulator for calibration module
- Electrochemical detector
- Sample flow regulator = needle valve
- Selection valves
- Calibration module (permeation tube)
- Carrier gas pressure regulator (Head column Pressure)
- Isothermal oven containing :
  - Sampling loop
  - Chromatographic columns
  - The head of the injection valve
- 24VDC Power supply
- Electronic boards
- Internal computer
- Computer Display and Touchpad

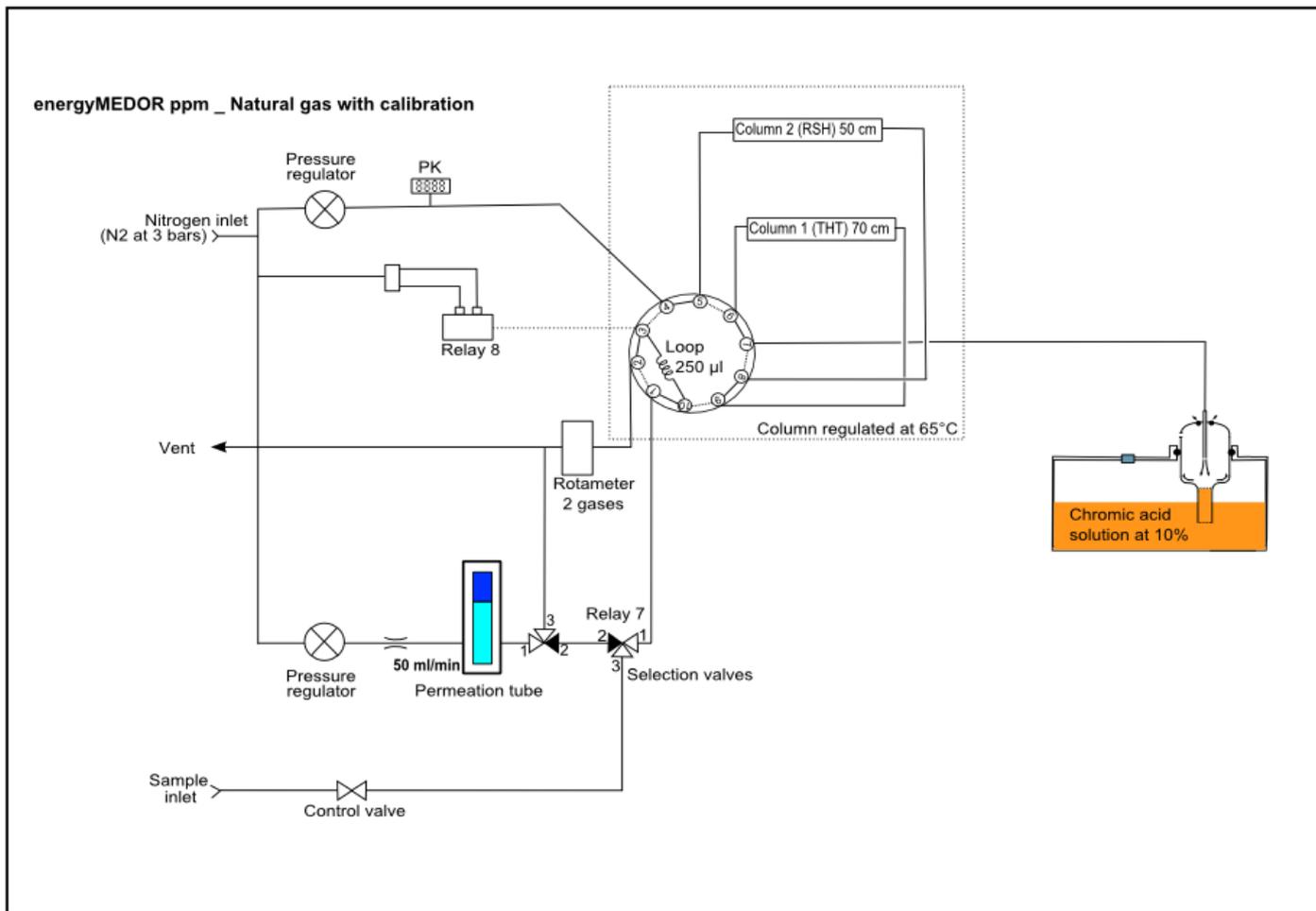
# MEDOR Analyser

## Principle of analysis

- Normal operation
  - Carrier gas travels through the columns and into detector (5ml/min)
  - Sample gas travels through the loop.
- Injection step
  - Sample volume is injected into the columns.
- The sulfur compounds are more or less retained by the column's support and exit the column with different retention times according to their affinity for the absorbent material.
- They are then detected by the wet cell where a gas-liquid reaction happens. The identification of the compounds is based on their retention time of elution from the column.

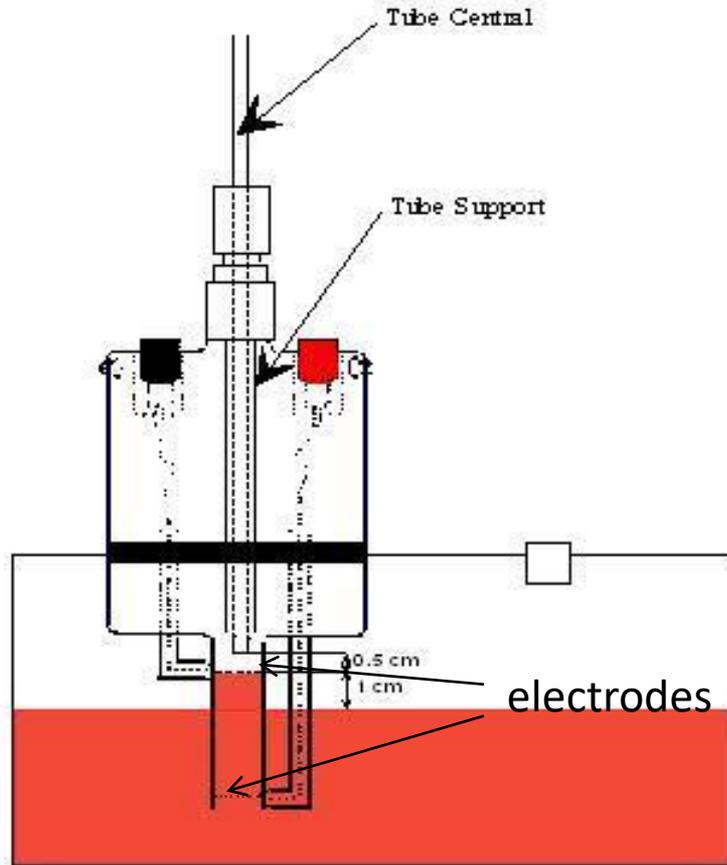
# MEDOR Analyser

## Principle of analysis



# MEDOR Analyser

## Wet cell detector



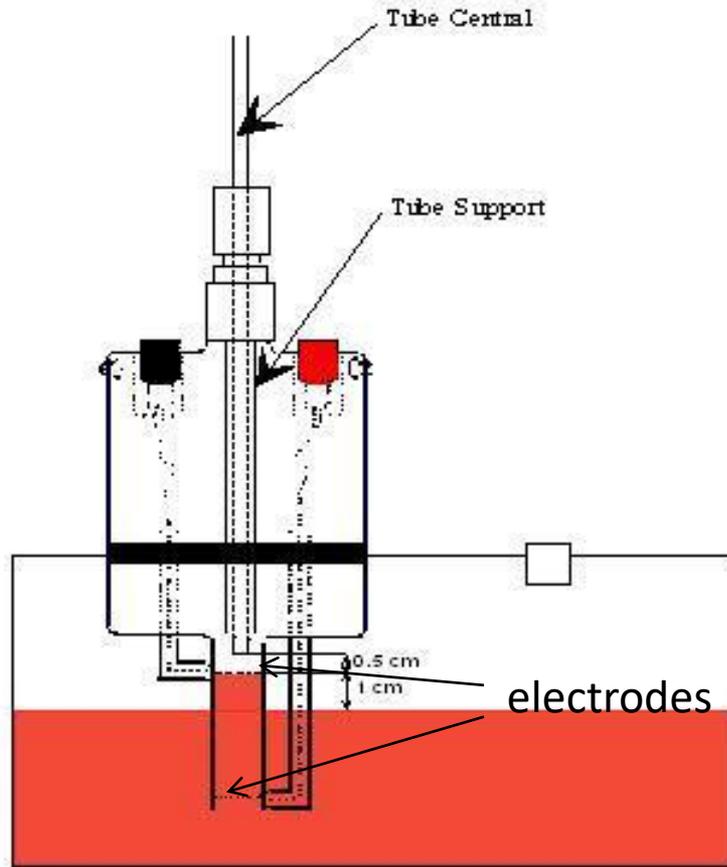
ASTM D7493-14

### Technical characteristics:

- Glass container.
- A solution of Chromium (VI) oxide in distilled water .
- Two platinum electrodes are arranged vertically in parallel and are connected to an amplifier for data acquisition.
- A tube fitted with the electrode is dipped into the solution such that the liquid is retained by capillary action within the tube.

# MEDOR Analyser

## Wet cell detector



ASTM D7493-14

### Technical characteristics:

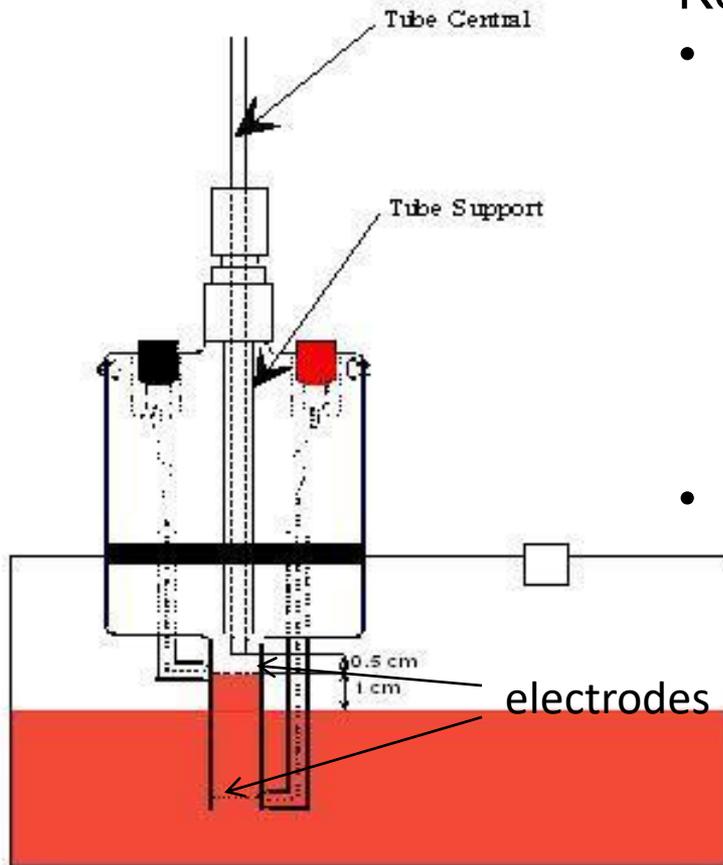
- The gas flow from the GC column is discharged through the narrow tube immediately above the upper grid center.
- Each sulfur sequentially elutes and react
- The redox reaction occurs at the electrode creating a potential difference between the two electrodes.
- Thus a current can be measured to quantify the amount of sulfur species in the gas

# MEDOR Analyser

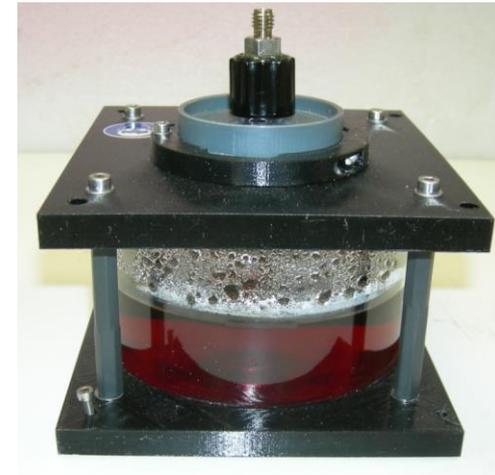
## Wet cell detector

### Key points:

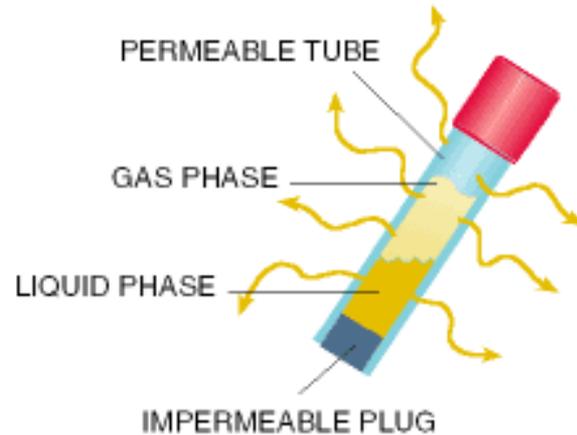
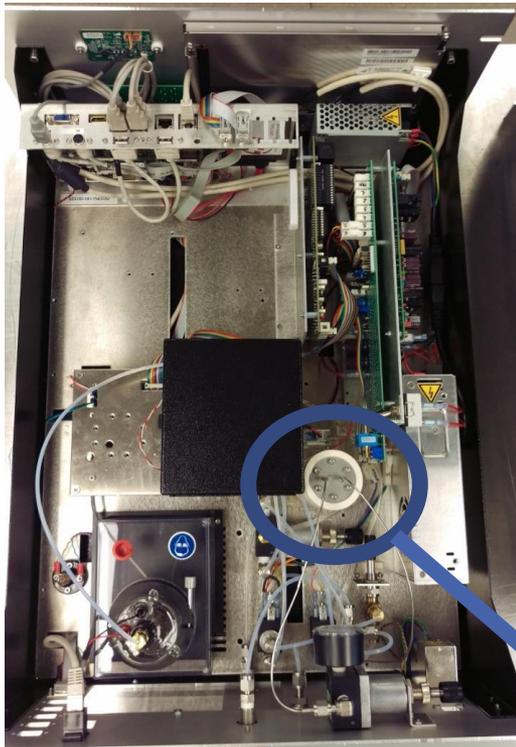
- Very low maintenance is necessary - addition of around 5ml of water in the reservoir every 3 months.
  - Low evaporation rate
    - Small diameter
    - Small carrier gas flow (5ml/min)
- **Lifetime of electrolyte > 10 years**



ASTM D7493-14



# MEDOR Analyser Calibration – Permeation tube



Gas phase goes through the permeable membrane:

- Constant temperature ( $\pm 0.1^\circ \text{C}$ )
- Constant flow rate

**Automatic calibration** of the instrument and validation of the results

**Compact calibration system** integrated inside analyzer  
**Programmable** once a day or each analysis

No need of cylinder!

# Performance tests

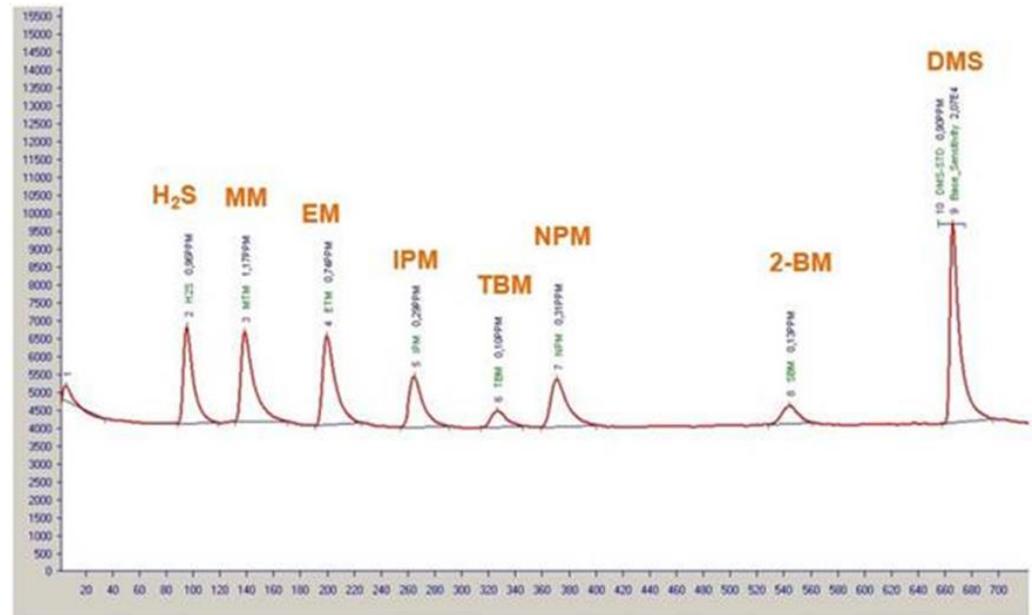
- Analysis of 8 compounds in standard using DMS permeation tube as calibration:
  - ✓ Stability tests
  - ✓ Linearity tests
  
- Analysis of up to 14 compounds available upon request



*energyMEDOR*  
*Ref: M42022*

# Performance tests

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



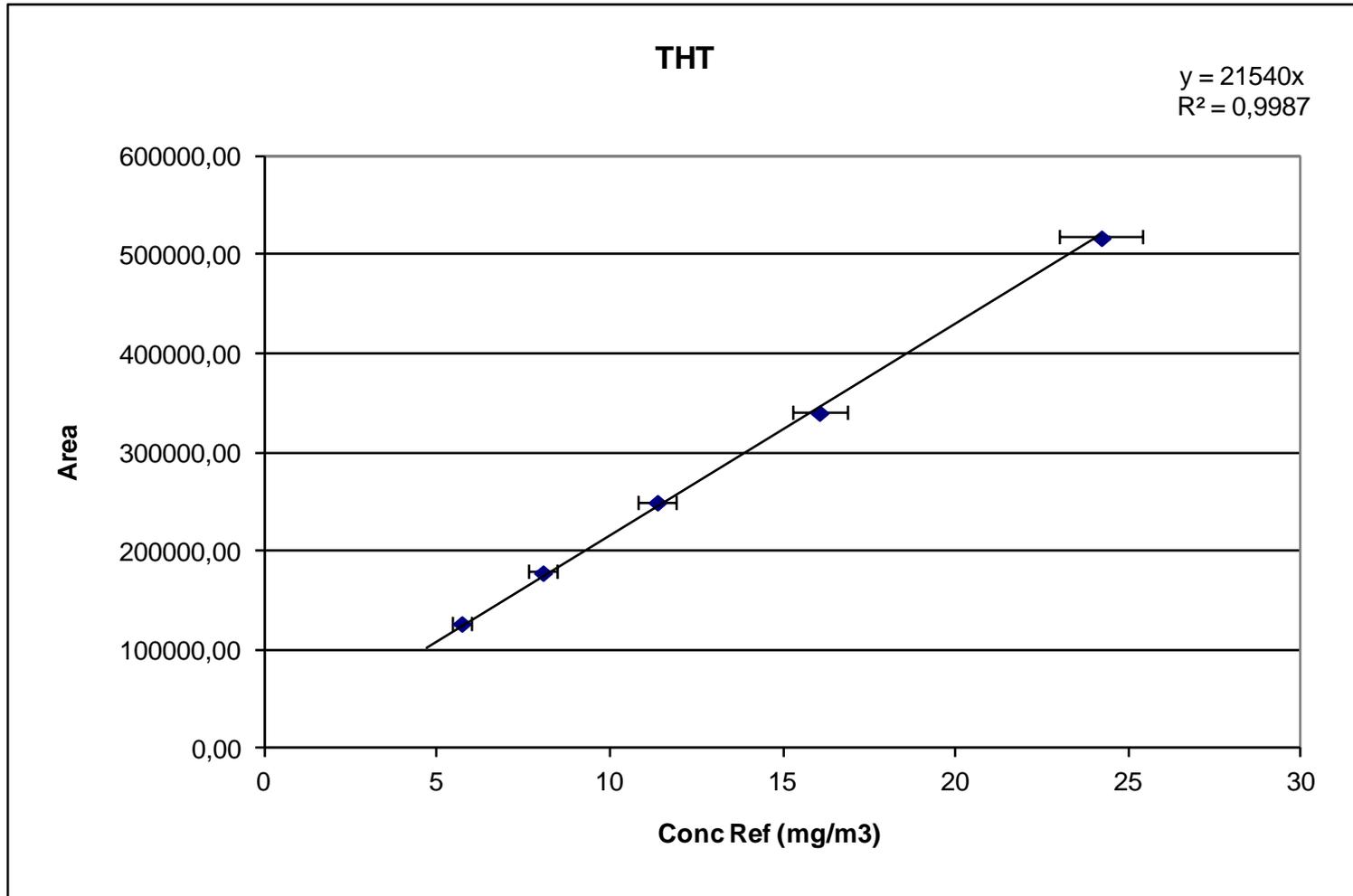
20 measurements are performed.

# Stability tests

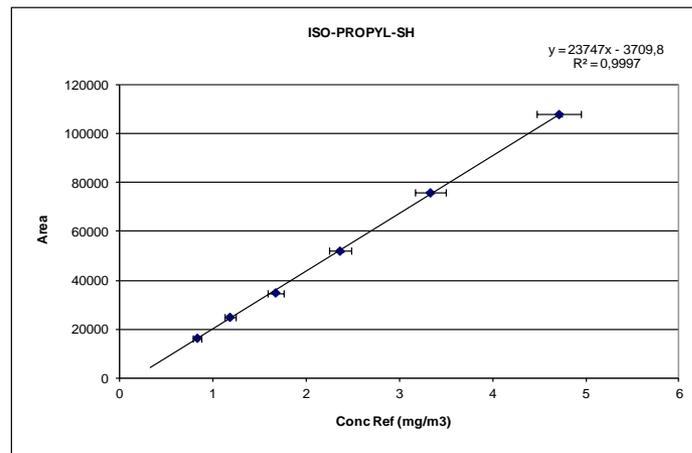
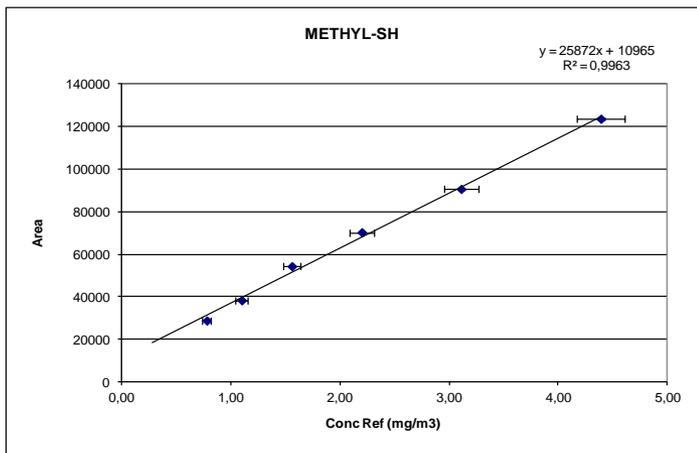
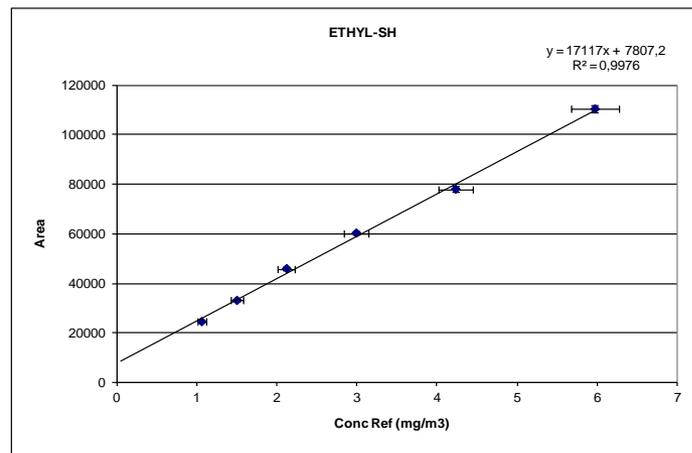
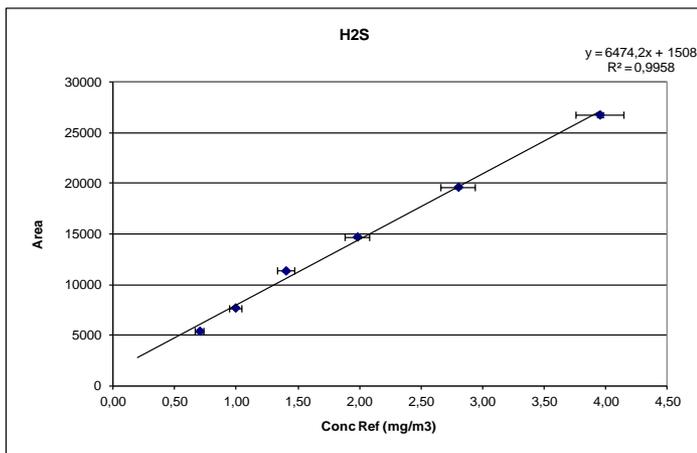
	Concentration (mg/m3)						
	H <sub>2</sub> S	MM	EM	IPM	TBM	THT	DMS STD
Mean	3,16	9,06	6,02	8,05	5,18	27,20	6,04
SD	0,011	0,031	0,072	0,048	0,031	0,146	0,021
Relative Error (%)	1,50	0,84	0,21	2,06	0,96	0,51	0,19
Repeatability (%)	0,72	0,68	2,38	1,20	1,21	1,07	0,71
Reference concentration	3,11 (+/-4%)	9,14 (+/-4%)	6,01 (+/-4%)	8,22 (+/-4%)	5,13 (+/-4%)	27,06 (+/-4%)	6,03 (+/-10%)

Repeatability < 3%  
Relative error < 2%

# Linearity tests



# Linearity tests



$R^2 > 0,995$  for all compounds

# Linearity tests

	Repeatability (%)		Relative reproducibility (%)	
	Min Performance Criteria from ISO 19739	Obtained value	Min Performance Criteria from ISO 19739	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

## Metrology conclusions

- energyMEDOR performance complies with EN ISO 19739
- Values are much better than the standard requirement

- **energyMEDOR ppb LDL in Amplification 3:**

- DMS LOQ < 1 ppb H<sub>2</sub>S LOQ < 1,2 ppb

Concentration range 0 – 100 ppb in Amplification 3

Concentration range 0 – 500 ppb in Amplification 2

Higher concentration range with smaller loop or dual loop system:

- 0 – 1 ppm / 0 – 10 ppm / 0 – 100 ppm

- 0 to 5% with 0.1µl loop

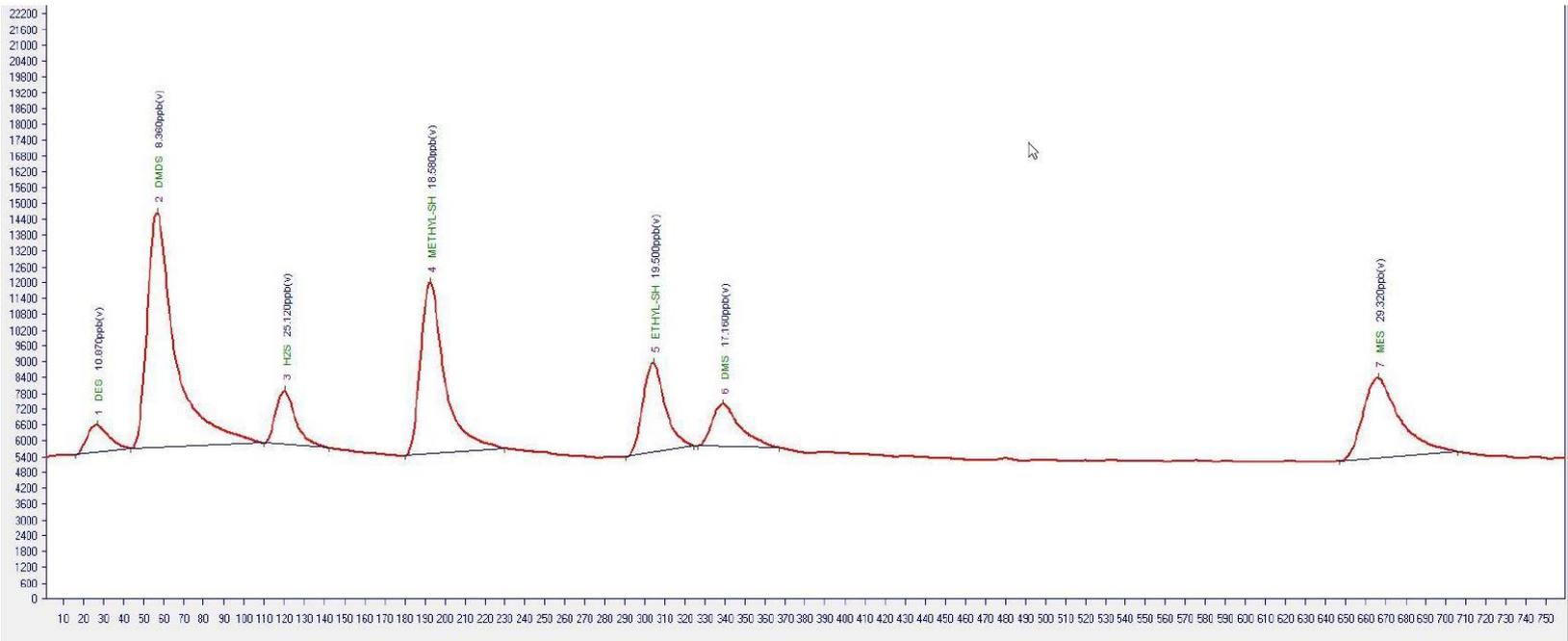
Selectivity:

- No interference from hydrocarbons

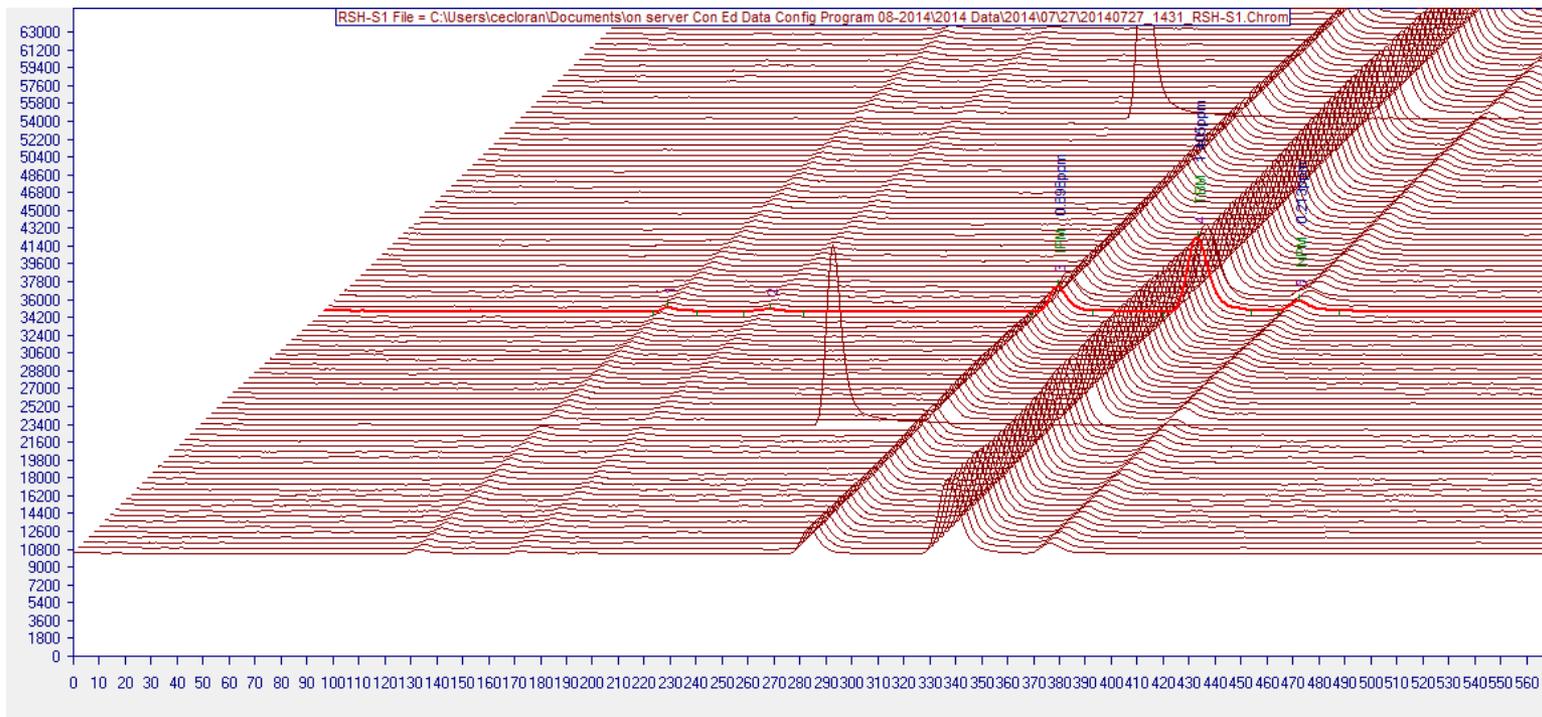
- Speciation of H<sub>2</sub> from H<sub>2</sub>S in case of > 5% H<sub>2</sub> in the sample by specific GC columns

# energyMEDOR sensitivity

- Measure all sulfur compounds individually with good separation at very low ppb level
- Total sulfur by sum



# HIGH RETENTION TIME STABILITY



3D CHROMATOGRAMS TO VALIDATE RETENTION TIME STABILITY OVER TIME

# MEDOR® certifications and standards



D7493-14 : Standard Test Method for Online Measurement of Sulfurs Compounds In Natural Gas and Gaseous Fuels by Gas Chromatograph and Electrochemical Detection



Russian GOST certification for MEDOR®



In compliance with ISO 19739:2004  
Determination of sulfur compounds using gas chromatography annex D



# MEDOR® certifications and standards



ATEX Exp and Exd type certification for Zone 2 and **Zone 1 GROUP IIC T4**



IECEX Exp and Exd type certification for Zone 2 and **Zone 1 GROUP IIC T4**



CSA Exp and Exd Field certification for **Class 1 Division 2 Group B, C & D T4**



**Exp** (Pressurised) version for MEDOR®, chromaTCD, chromaPID and airTOXIC

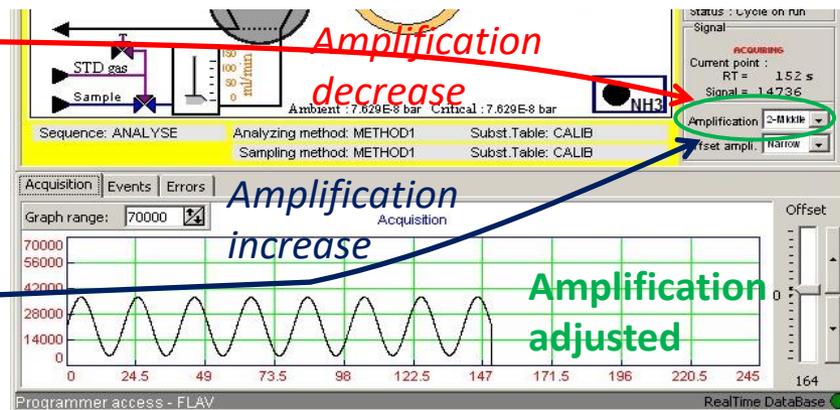
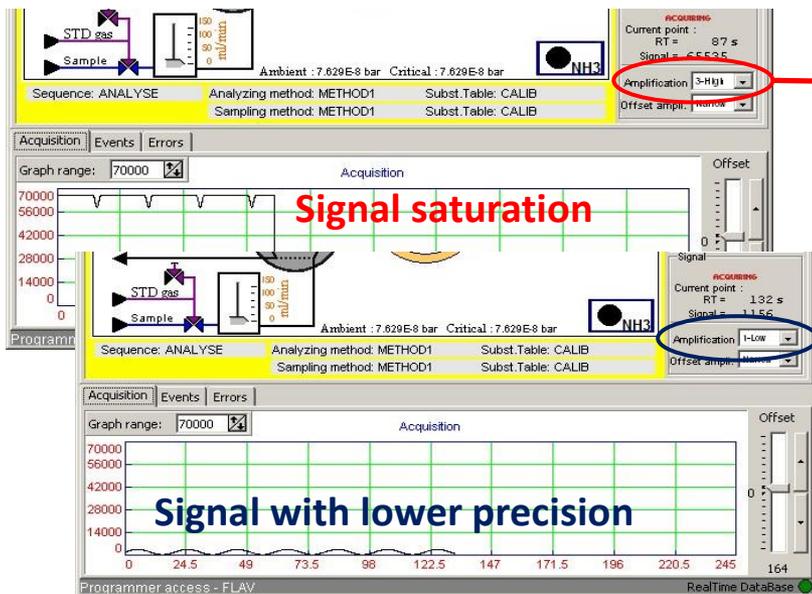
**Exd** (Flameproof) for MEDOR® and chromaTCD on request

# MEDOR® latest development

- Auto offset
  - Adaptation of offset without user's intervention to have the baseline at the requested value
  - Avoid any loss of signal and increase availability of results
  - No temperature influence on baseline level

# MEDOR® latest development

- Auto range:
  - During an analysis, Vistachrom could detect:
    - Signal saturation (value at 65535)
    - Signal with lower precision
  - Amplification adjustment for the next method



**Extended analytical concentration range on multiple amplification**

# MEDOR® latest development

- Different configuration with explosion proof certifications
- Internal temperature regulation to be installed in area from  $-20^{\circ}\text{C}$  to  $+40^{\circ}\text{C}$ 
  - VORTEX cooler option for up to  $+55^{\circ}\text{C}$



Pressurised type



Flameproof type

# MEDOR® latest development

- Integrated carrier gas generator
  - Instrument is cylinder free thanks to its internal nitrogen generator used for carrier gas

# MEDOR® applications

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# Trace to % concentration H<sub>2</sub>S analysis

## Trace and ultra trace level of H<sub>2</sub>S monitoring

- H<sub>2</sub>S down to **2 minutes**
- **LDL down to 1 ppb** for low range
- Standard analysis range:
  - 0-1 / 0-10 / 0-100 ppm
  - Low % range in option (up to 5%) with sampling valve



# Trace H<sub>2</sub>S in complexe mixture

- H<sub>2</sub>S MEDOR used to analyse trace concentration of H<sub>2</sub>S in complexe mixture:
  - Petrochemical mixture with more than 50 % H<sub>2</sub>
  - 0 to 1 ppm H<sub>2</sub>S



Reactor effluent driers outlet H<sub>2</sub>S outlet

- Exhaust gas with high level of COS 5 000 ppm and 0 to 50 ppm H<sub>2</sub>S



# H2S and Total Sulfur analysis

## H2S TOS TS MEDOR®

- Electrochemical detection
- Carrier gas: Air or nitrogen
- Sampling: Loop
- New Backflush system
- H2S and TS\* in **2 minutes**
- Standard analysis range:
  - 0-1 / 0-10 / 0-100 ppm
  - Low % range in option

\*TS: Total sulfur by sum H2S + TOS



H2S TOS TS  
Ref: M51022-TS-ATEX-Z1



H2S TOS TS  
Ref: M51022-TS

# Thermal power plant turbine integrity

Turbine integrity for natural gas thermal power plant:

- Turbine can accept a level of sulfurs and in order to prevent the damage of the turbine H<sub>2</sub>S and total sulfurs is required to be monitored



Société Tunisienne  
de l'Électricité et du Gaz



الشركة التونسية  
للكهرباء والغاز



# Sales metering station

- Natural gas Sales metering station in Egypt

H<sub>2</sub>S TS MEDOR 0 - 10 ppm



# Pipeline Integrity Monitoring

## Applications of the energyMEDOR H<sub>2</sub>S/TS MEDOR: (Integrity Monitoring)

- During the extraction of raw NG and following processing, Midstream companies are required to track the level of H<sub>2</sub>S and TS (*total sulfur*).
- If the concentration of either exceed the required levels the Midstream provider will shut down the gathering line until the required levels are met.

# Pipeline Integrity Monitoring

Gas transportation company can check the amount of H<sub>2</sub>S from the gathering lines

- Every two minutes
- Can close quickly when the H<sub>2</sub>S limit that is present over the limit

- Customer reference:



# THT MEDOR®

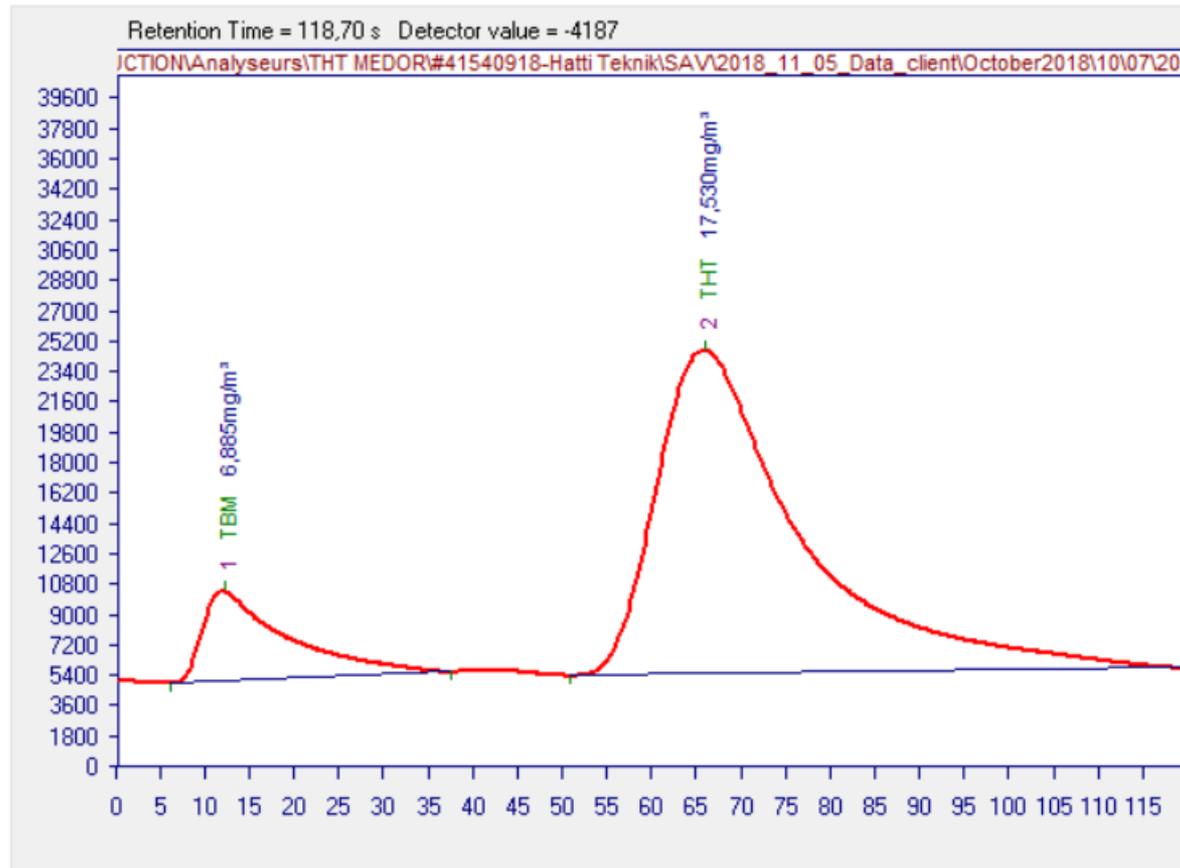
- MEDOR® specific version for automatic monitoring of THT in natural gas with TBM in option
  - Automatic calibration using permeation tube : THT
  - Very low maintenance
  - Online instrument
  - Cycle time 3 to 5 minutes





Online Gas and Liquid Analyzer Experts

# THT MEDOR® for Odorization market



# Odorization control

## Why monitor odor in Natural Gas ?

- Public Safety: Natural gas is colorless and odorless in its most pure form
- Natural Gas when extracted can contain sulfurs such as H<sub>2</sub>S that when in the presence of moisture can produce sulfuric acid that can degrade the pipeline

Note: MEDORs monitor up to 21 Bcf/d NG (6000 Million Cubic Meters). Total Gas consumption per day is estimated at 76.7Bcf/d.

# Odorization control

Non odorized gas may be dangerous!

Natural gas is odorless and must be odorized with sulfurized compounds



## Requirements

There is a need to measure and control precisely the level of odorant species in natural gas:

- Adjust the amount of sulfur in the gas
- Control of odorant passivation
- Aids in detection of leaks



# Odorization control

## What are transport companies concerns?

- Under odorization – if we trust that gas is odorized we could potentially not odorize or under odorize causing public safety hazard
- Over odorization – if we over odorize we could see increased leak calls, putting strain on company resources, emergency responders, cry wolf
- Increased maintenance – How will we find out if gas is odorized? If we adjust our injection rates how will we do this?

# Odorization control

## Currently in the USA

- According to the law in the US:
  - Gas has to be odorized by local distribution company
  - Gas must be checked periodically

The sniff test is commonly used to check odorization levels

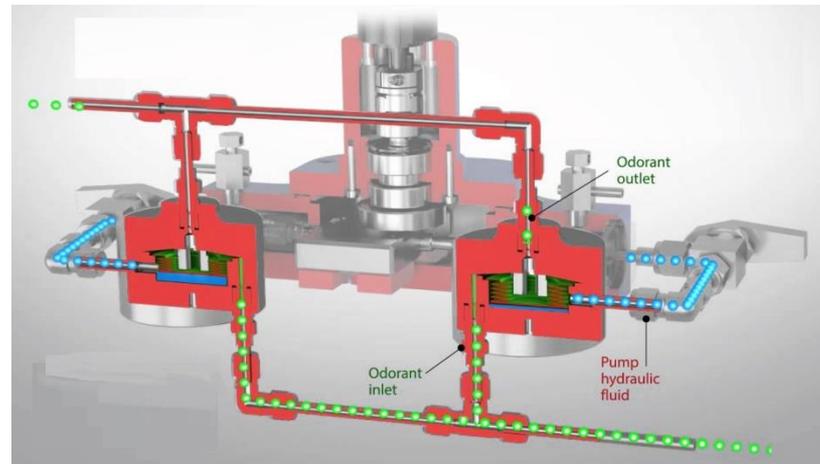
- The operator fills a box with a known sample volume:
  - Smell the gas
  - Decides if the amount of odorant is sufficient



## Applications

The energyMedor is used for 2 applications:

- Odorant verification
- Odorant injection control



## APP1 :Odorant verification

The energyMEDOR monitors downstream (with the option of upstream, “2 stream”) of the injector.

The data is the actual concentration of odor present. \*OR\* End of line monitoring, the energyMEDOR provides the concentration of odorant that is present (this accounts for **odor fade** in the pipeline)

## APP2 : Odorant Injection control

The energyMEDOR monitors downstream (*with the option of upstream, "2 stream"*) of the injector.

The output of the energyMEDOR is monitored by a PLC or directly input to the Odorizer via a feed back loop.

The Odorizer monitors the output concentration of the energyMEDOR and adjusts the injection rate of odorant accordingly.

**Avoid over odorization under odorization**

**Allow to save odorant injected in natural gas**

**= save money with high level safety !**

# Final customer testimony

- We quickly determined that we needed some type of hard installed instrument that could do this work for us.
- We explored or tested 8 different analyzers.
  - Accuracy
  - Sample Time
  - What can it detect
  - Ease of Maintenance
  - Initial Cost
  - Maintenance Cost
- We determined that we should install two different types of analyzers
  - Major Gates – high accuracy, fast sample time
  - Minor Gates – lower accuracy, slower sample time

**Joe Marx**

How Washington Gas Monitors and Maintains  
Proper Odorant Levels in Gas From Multiple  
Suppliers

# Final customer testimony

- Energy Medor Chromatotec GC866
- 15 min Sample time includes calibration
- Automatic internal calibration is done using a DMS permeation tube
- Uses an electrochemical cell that allows it to detect specific sulfurs
- Detection is achieved by a gas-liquid reaction
- Able to detect THT, H<sub>2</sub>S, MTM, ETM, DMS, IPM, TBM, NPM, SBM
- Preventative maintenance and support provided by CAS
- Currently installed at 11 Major Gates



## Joe Marx

How Washington Gas Monitors and Maintains Proper Odorant Levels in Gas From Multiple Suppliers

# Final customer testimony

## Results

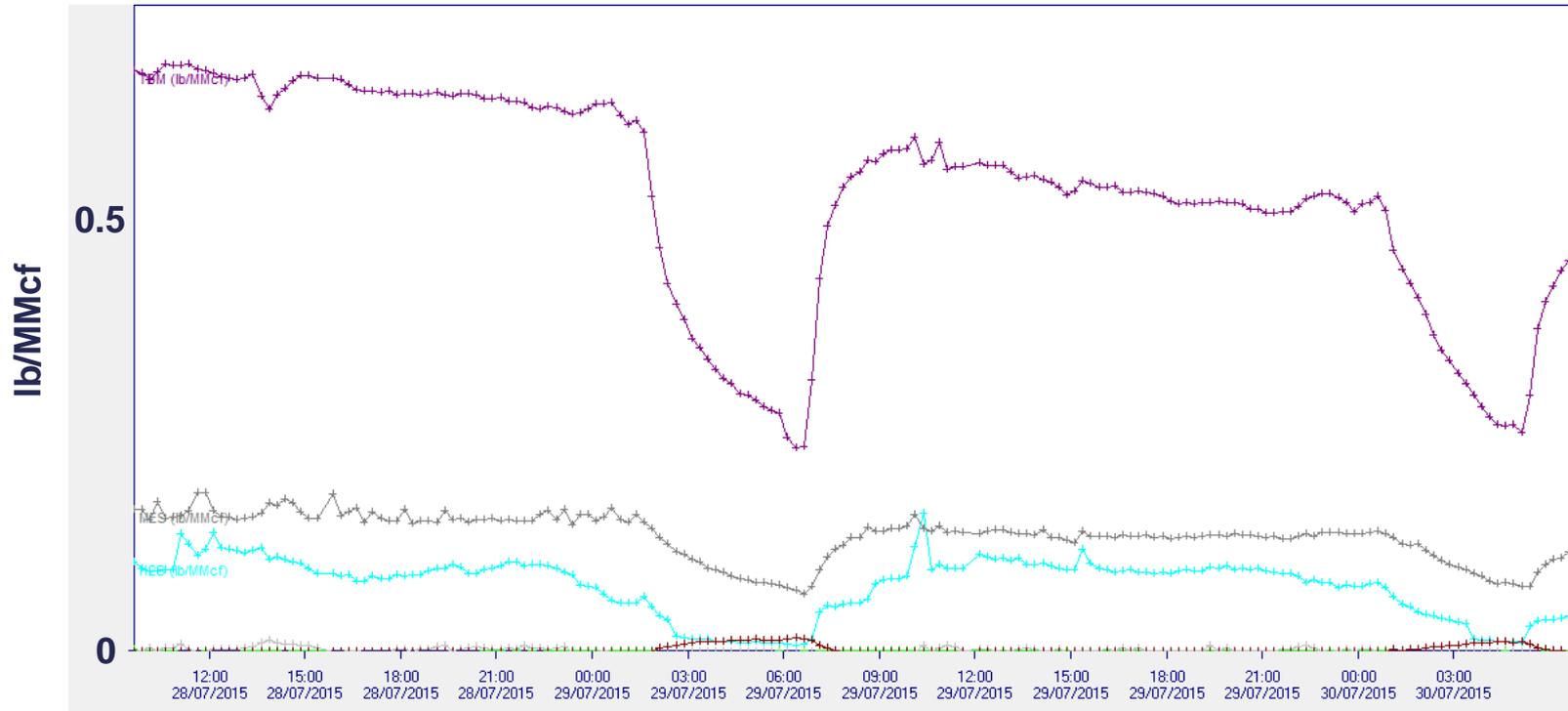
- We have had zero Low Odorant instances
- We have had no over odorization instances
- We have reduced maintenance by using analyzers as compared to doing manual testing
- We have reduced odorant usage by approximately 4000 gallons per year equivalent to 15 141,65 liters

CHROMATOTEC comments: Approximate cost of odorant 25 à 40 \$/gallon

**Joe Marx**

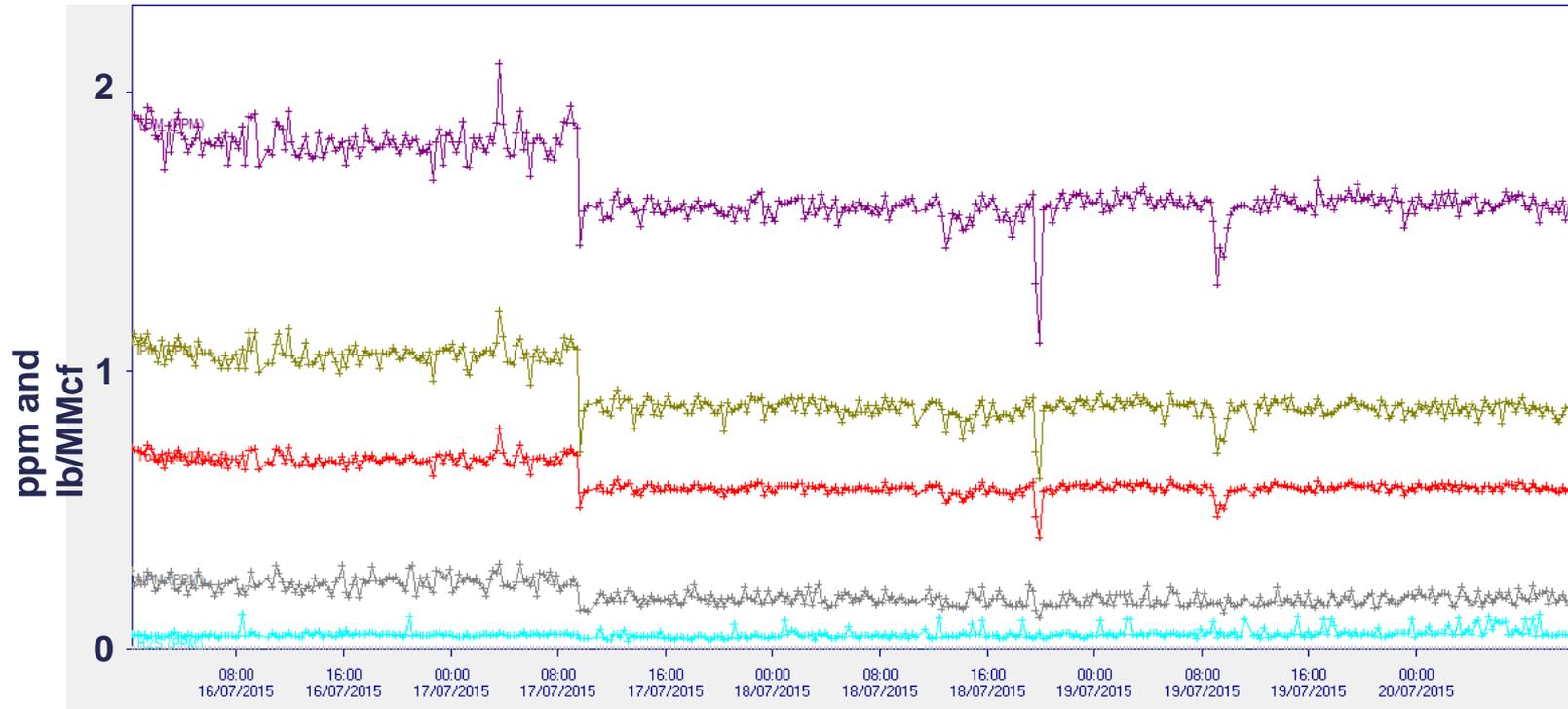
How Washington Gas Monitors and Maintains  
Proper Odorant Levels in Gas From Multiple  
Suppliers

# Trend



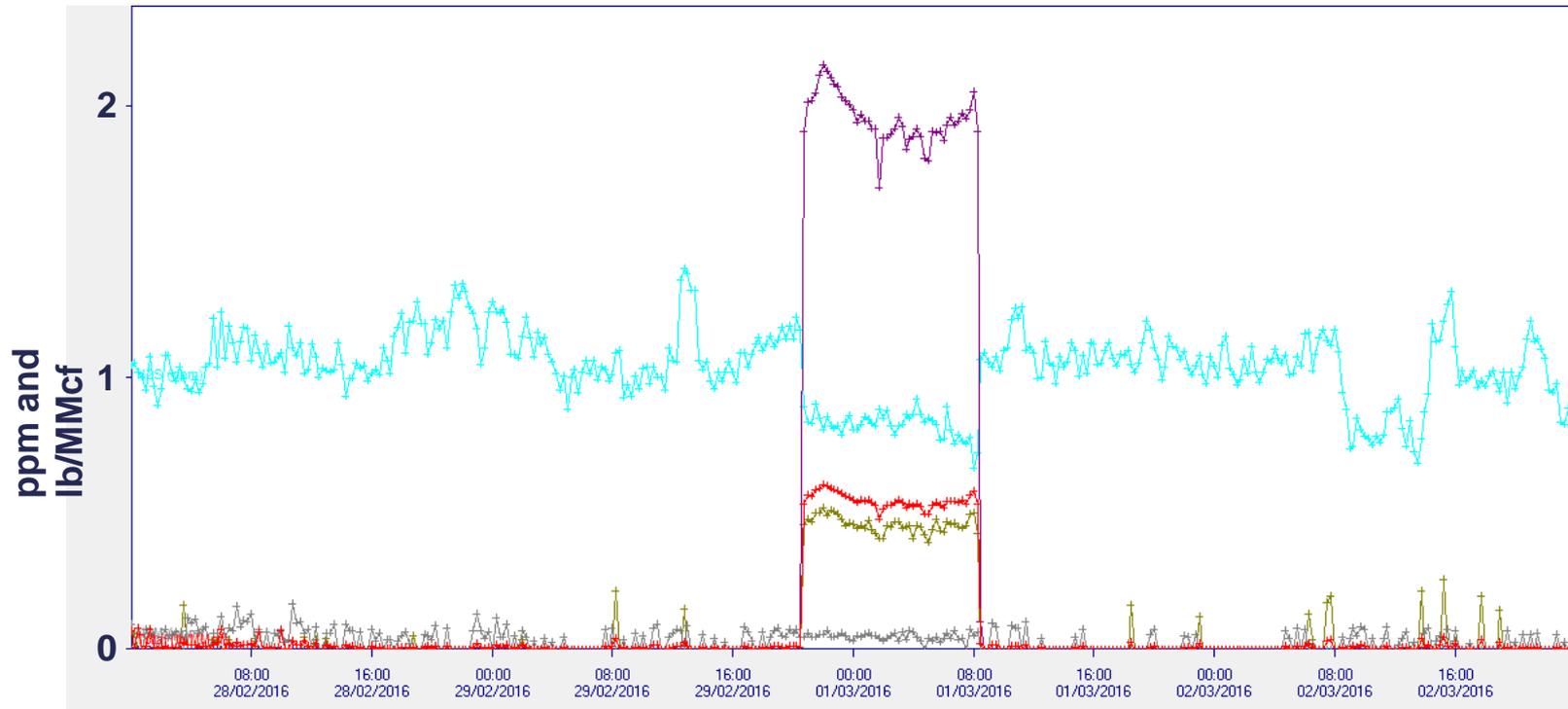
ODORANT MEASUREMENT AND INJECTION CONTROL

# Trend



ODORANT MEASUREMENT AND INJECTION CONTROL

# Trend





Online Gas and Liquid Analyzer Experts

# Some customer reference in odorization market

## Americas:



Manzanillo LNG terminal

## Middle East and Africa:

## Asia:



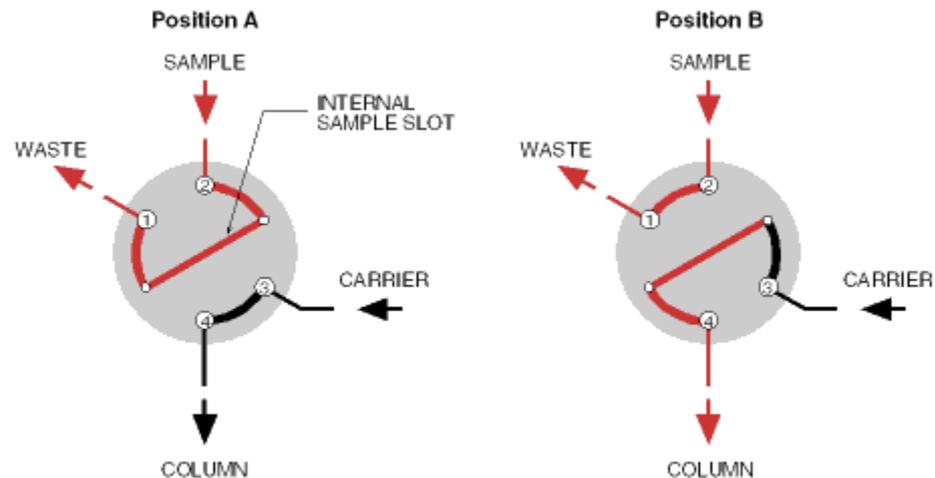
## Europe:



- Specification & Purpose
    - “Odorized” ppm of sulfurs energy, cooking
    - “Non Odorized” **ppb of sulfurs** chemicals, blowing agent
    - “Deodorized” low ppb of sulfurs
- Propellant, Blowing agent, Refrigerant**

# LPG sampling valve

- 2 position Valve regulated in temperature and controlled by Vistachrom allow :
  - vaporisation of LPG using very low volume :
    - equal or less than 1  $\mu$ l
    - Advantages:
      - very low consumption of liquefied gas
      - representative sample analysed



## LPG Odorization control for human safety:

- Ethyl-Mercaptan or DMS with Ter Buthyl Mercaptan are used to odorized LPG in ppm range
  - energyMEDOR ppm analyze automatically with validation EM, DMS and TBM
- Some reference



# LPG DeOdorization

storage → tower → storage (products)



Molecular  
Sieves



**TAIYO NIPPON SAN SO**  
The Gas Professionals



Deodorized=De-sulfurized (low ppb level)

# Quality control of deodorized LPG

- Sulfur at low ppb level
  - Gas Chromatography
    - energyMEDOR ppb with LPG sampling valve
      - LDL down to 1 ppb in automatic



Model: M41022

# Deodorized LPG applications

AEROSOL  
Propellant gas  
Health care



# Hydrodesulfurization of natural gas

- Energy MEDOR used to analyse trace concentration of sulfur compounds such as THT, mercaptans, H<sub>2</sub>S... in natural gases :
  - Matrix composed of methane and light alkanes
  - Monitoring of desulfurization process to obtain high purity methane used to produce hydrogen by steam-reforming
  - Comparative sulfur monitoring before and after the catalytic unit



# Hydrodesulfurization of natural gas

- Energy MEDOR used to analyse trace concentration of sulfur compounds such as THT, mercaptans, H<sub>2</sub>S... in natural gases :
  - Limit of detection of 5 ppb or 0,1 ppm depending of the application
  - Cycle time from 5 min to 20 min including and internal calibration



# Hydrodesulfurization of natural gas

- Energy MEDOR used to analyse trace concentration of sulfur compounds such as THT, mercaptans, H<sub>2</sub>S... in natural gases :

By monitoring sulfur compounds levels during desulfurization :

- Industrials can avoid catalyst deactivation in steam-reforming units ; with high-level alarm treshold and dry contacts, processes can be stopped at any moment automatically
- Processes are adapted, to reduce the amount of reagents and catalysts ; lowering their environmental and economic impact

# NG fiscal metering station

Quality control of natural gas at fiscal metering station or custody transfer:

- Sulfur compounds at low ppm
  - energyMEDOR® for sulfurs contents: H<sub>2</sub>S, Mercaptans (RSH):MM/EM/IPM/TBM/NPM and MES
  - Total mercaptans and total sulfurs by sum

Customer reference:



# MEDOR® Keypoint

H2S TS MEDOR® is :

- Designed for process control application
- Online continuous sampling
- Very specific to sulfur compounds (no interference)
- Very Low maintenance
- No conversion for total sulfur measurement
- Automatic data validation
- GC instrument which Allows quantification and identification of H2S and TOS
- Fast measurement: Total measurement is 2 minutes



*H2S TOS TS*  
*Ref: M51022-TS*



Online Gas and Liquid Analyzer Experts

# Technology comparison

Specification	Lead Acetate tape	UV like AAI OMA 300	Chromatotec MEDOR® GC-ED
Detection principle	Lead acetate tape for H <sub>2</sub> S and convertor for TS	UV-Vis / SW-NIR absorbance spectrum	GC with Electrochemical wet cell Detector SSD
LDL	Few ppb with several minutes cycle time	Around 10 ppm	Down to 1 ppb in automatic
Linearity	Delayed answered due to humidifier which create important dead volume		Linear on peak area R <sup>2</sup> > 0.995 for each compound at ppb or ppm
Long term stability		Variation with matrix change	RSD on 48 hours < 3% at 1 ppm for all compounds
Interferences	Not identified	Very sensitive to humidity, temperature variation, mercaptans and other compounds not SSD	Not sensitive to humidity and hydrocarbons. Temperature controlled Sulfur Specific Detector
Compounds measured	H <sub>2</sub> S only and Total sulfur using convertor	H <sub>2</sub> S with interference Individual mercaptans not analyzed	H <sub>2</sub> S/Methyl Mercaptan /EM/IPM /TBM/NPM/MES/THT More compounds on request: 2BM/IBM/NBM/DMS/DMDS/DTBM
Instrument air			Exp : 30 l/min      Exd : 0l/min



Online Gas and Liquid Analyzer Experts

# Technology comparison

Specification	Lead Acetate tape	UV like AAI OMA 300	Chromatotec MEDOR® GC-ED
Cycle time for H2S and mercaptans	3-4 minutes for high sensitivity or to reduce lead tape consumption	< 20 sec but memory effect due to big volume of optical cell. Only H2S and Total sulfur using convertor.	2 min for H2S/TS 5 min for H2S/MM/EM 12 min for H2S/MM/EM/IPM/TBM/NPM/MES/THT More compounds on request
Carrier gas	N/A	N/A	N2 3 ml/min from internal N2 gen.
Operating gas	He + H2 + air (cylinder are required)	N/A	Nitrogen 50ml/min for CALIB in option (from N2 generator)
Maintenance	High cost because of lead tape replacement every 2 to 5 weeks. Recycling of lead tape generate environmental issue		The lowest on the GC market. Less than 1 day/year for maintenance
Calibration	External cylinder		1 or 2 points thanks to linear response. With internal CALIB
Data availability	Low data capture because of lead tape replacement and lead tape failure		>95%
Problems	Onsite intervention needed when lead tape is broken <b>Lead tape waste disposal</b>		No Flame



Online Gas and Liquid Analyzer Experts

# Technology comparison

Specification	GC-FPD	UV like AAI OMA 300	Chromatotec MEDOR® GC-ED
Detection principle	GC with single Flame Photometric Detector (FPD) = quenching effect*	UV-Vis / SW-NIR absorbance spectrum	GC with Electrochemical wet cell Detector SSD
LDL	1 ppm	Around 10 ppm	1 ppb
Linearity	FPD have a quadratic sulfur response = not linear = require linearization curve for all compounds = more service		Linear on peak area $R^2 > 0.995$ for each compound at ppb or ppm range
Long term stability	Drift due to detector H2 and air flow variation affect the flame	Variation with matrix change	RSD on 48 hours < 3% at 1 ppm for all compounds
Interferences	Sensitive to humidity and quenching effect	Very sensitive to humidity, temperature variation, mercaptans and other compounds not SSD	Not sensitive to humidity and hydrocarbons. Temperature controlled Sulfur Specific Detector
Compounds measured	H2S, individual mercaptans, sulfides and total sulfur	H2S with interference Individual mercaptans not analyzed	H2S/Methyl Mercaptan /EM/IPM /TBM/NPM/MES/THT More compounds on request: 2BM/IBM/NBM/DMS/DMDS/DTBM

# Technology comparison

Specification	GC-FPD	UV like AAI OMA 300	Chromatotec MEDOR® GC-ED
Instrument air	100 to 150 l/min for the oven		Exp version : 30 l/min version : 0l/min
Cycle time for H2S and mercaptans	20 minutes with speciation and around 10 minutes for total sulfur using convertor no direct measurement	< 20 sec but memory effect due to big volume of optical cell. Only H2S and Total sulfur using convertor.	2 min for H2S/TS 5 min for H2S/MM/EM 12 min for H2S/MM/EM/IPM/TBM/NPM/MES/THT More compounds on request
Carrier gas	Zero air or H2 60 to 300 ml/min	N/A	N2 3 ml/min from internal N2 gen.
Operating gas	H2 for flame (GC grade) 40 ml/min and 300 ml/min air	N/A	Nitrogen 50ml/min for CALIB in option (from N2 generator)
Maintenance	High because of complexity of the system		The lowest on the GC market. Less than 1 day/year for maintenance
Calibration	For linearization curve at least 5 points = long service time		1 or 2 points thanks to linear response. With internal CALIB
Data availability	Low		>95%
Problems	Flame off and high-level service		No Flame

# MEDOR®easy

- A more attractive solution all in one for 1 or 2 compounds:
  - Stand alone solution
  - 5 minutes cycle time
  - MEDOR performance
  - THT or H<sub>2</sub>S or TBM or other compounds



MEDOR is designed to continuously identify and quantify individual target sulfur species in gaseous fuel with automatic calibration and validation:

- Accurate
- Repeatable
- Linear
- ppb to %
- Online continuous sampling
- Sulfur specific (no interference) 9 compounds in standard
- Odor unit calculation
- Low maintenance (less than 1 day per year)
- Automatic validation and calibration



*MEDOR*



**THANK YOU FOR YOUR  
ATTENTION!**

Questions?