



MEDOR® technology and applications



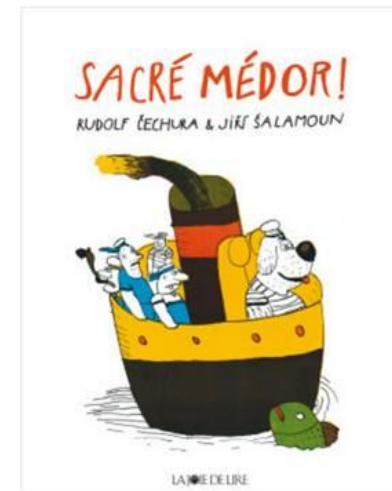
Origin of the name MEDOR®

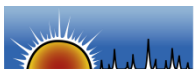
Based on:

- In English “**ME**asurement of o**DOR**”
- 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 !

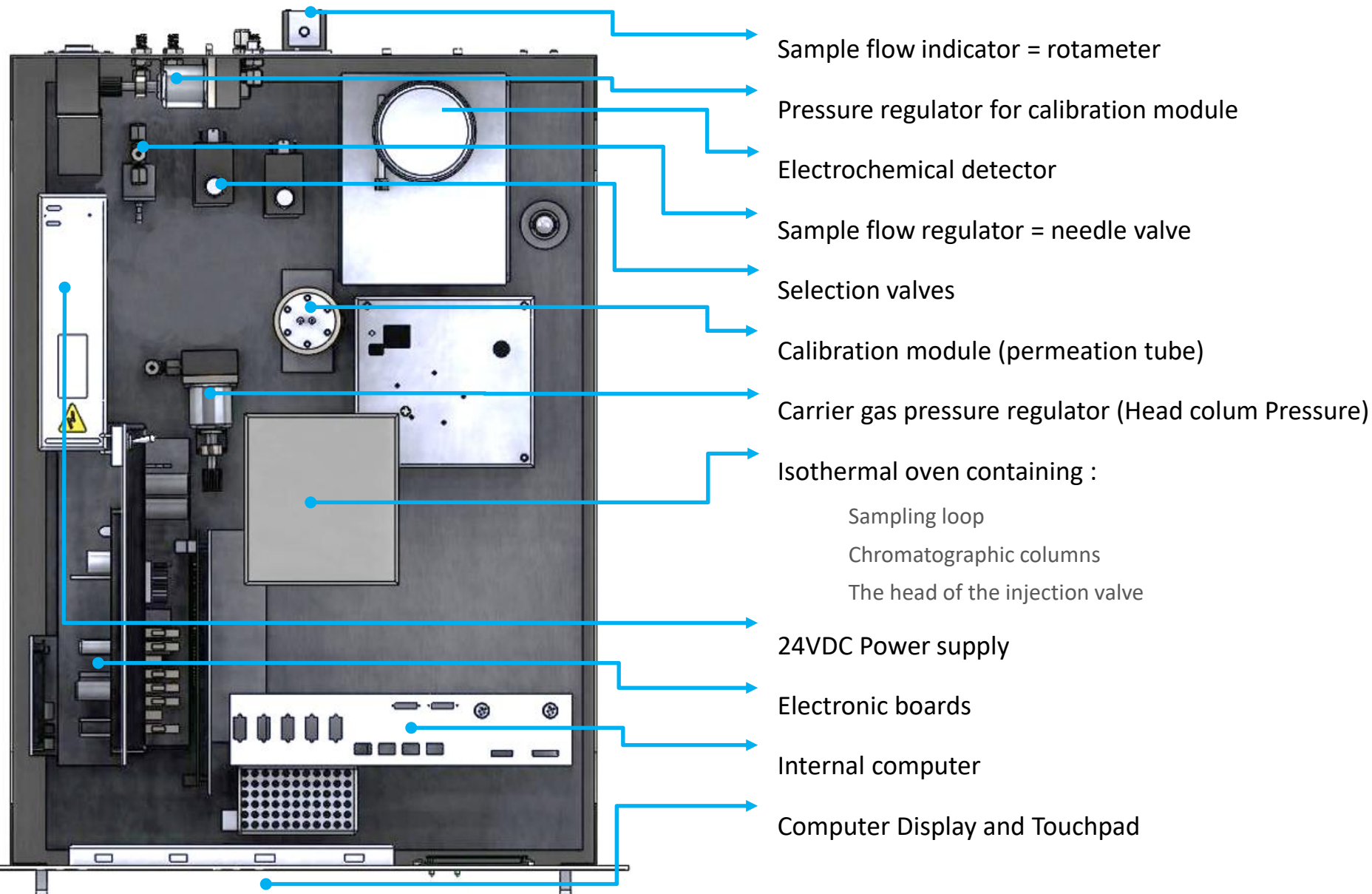




CHROMATOTEC[®] GROUP

Online Gas and Liquid Analyzer Experts

Top View



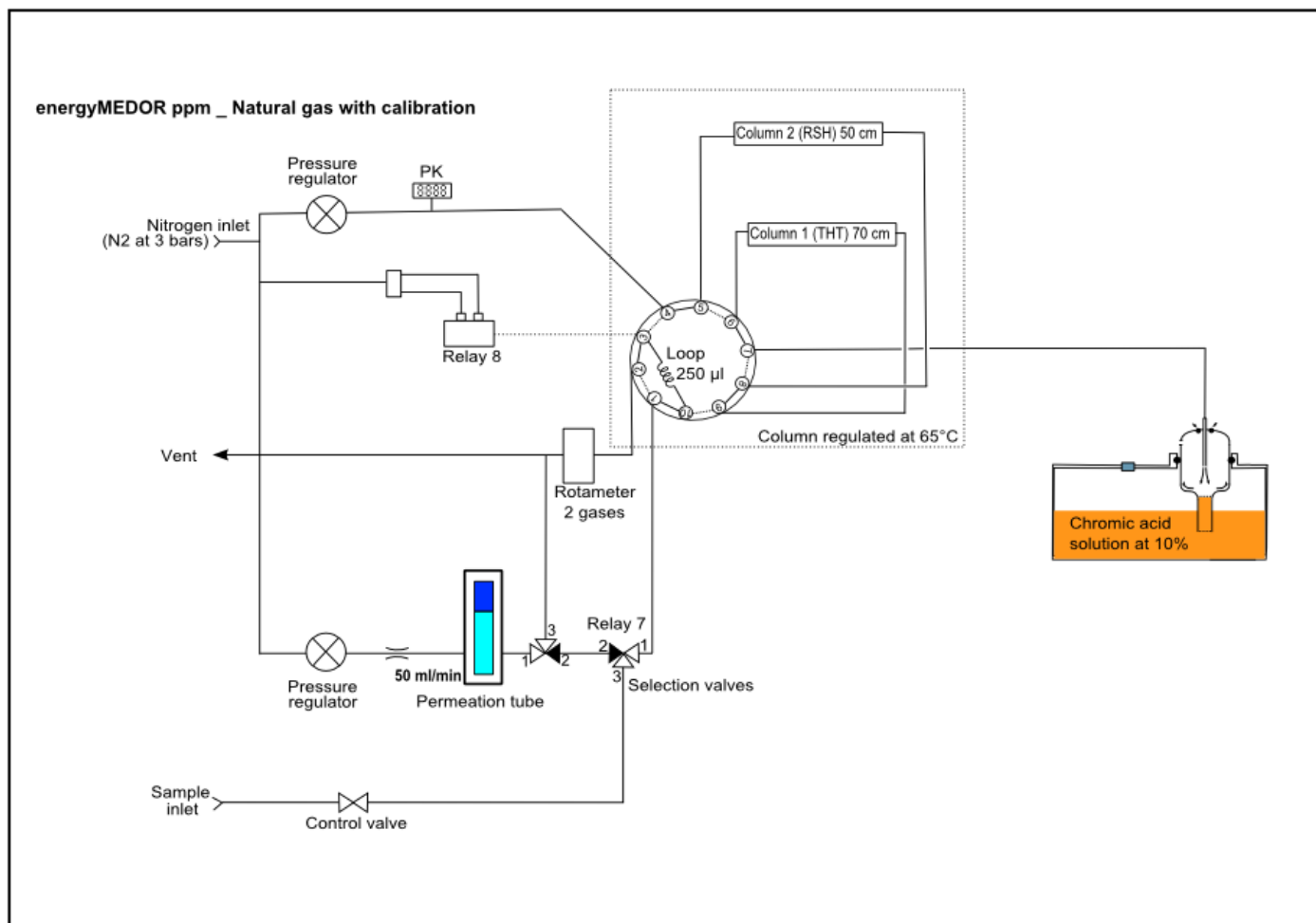
MEDOR Analyser

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.

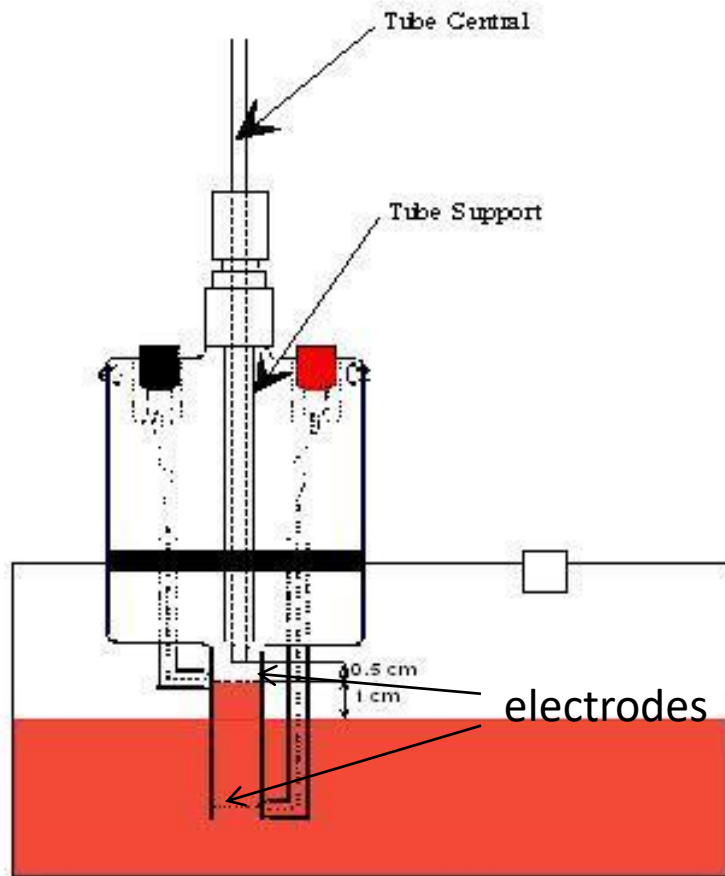
MEDOR Analyser

Principle of analysis



MEDOR Analyser

Wet cell detector



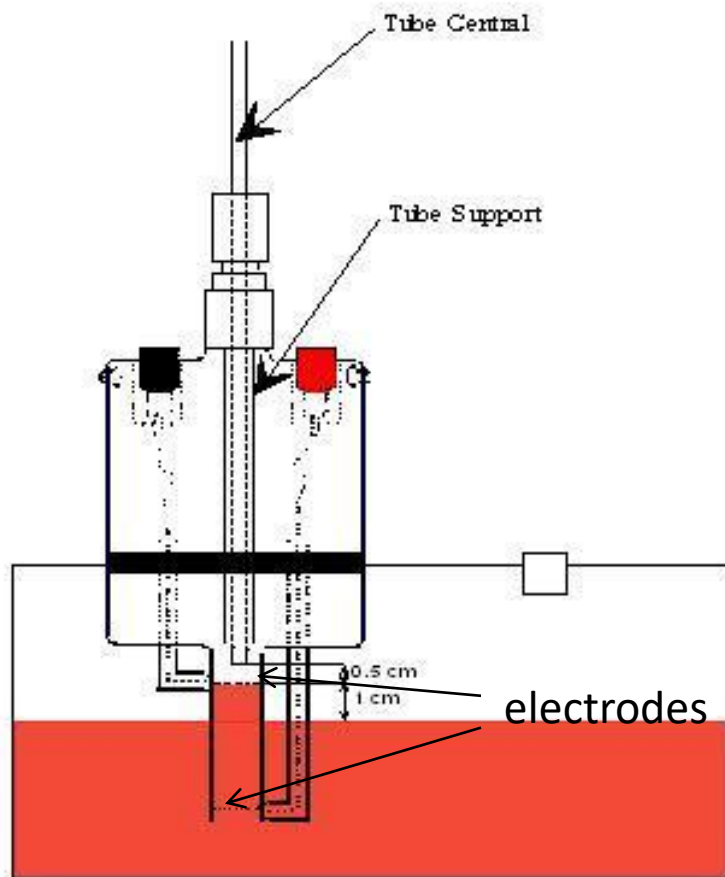
ASTM D7493-14

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:

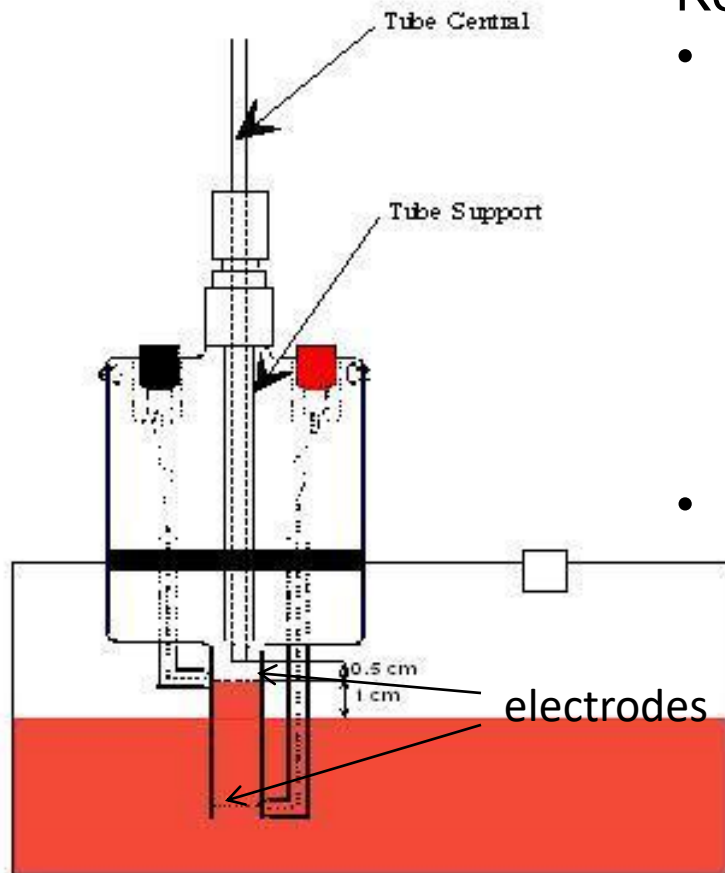
- The gas flow from the GC column is discharged through the narrow tube immediately above the upper grid center.
- Each sulfur sequentially elutes and react
- The redox reaction occurs at the electrode creating a potential difference between the two electrodes.
- Thus a current can be measured to quantify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

MEDOR Analyser

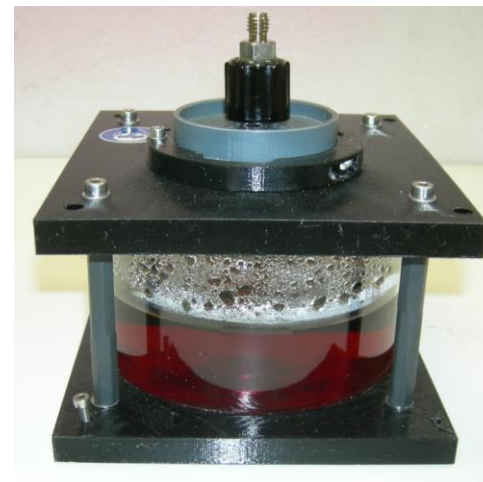
Wet cell detector

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**

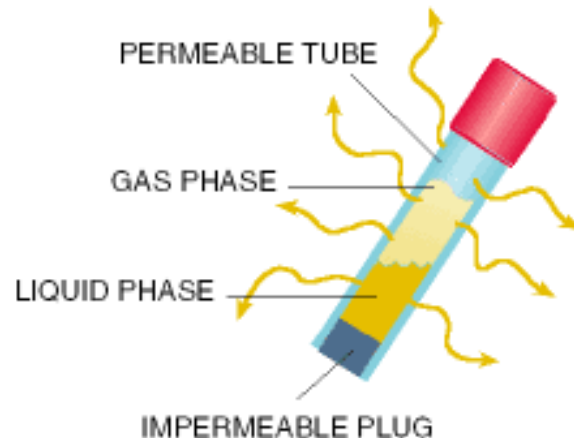
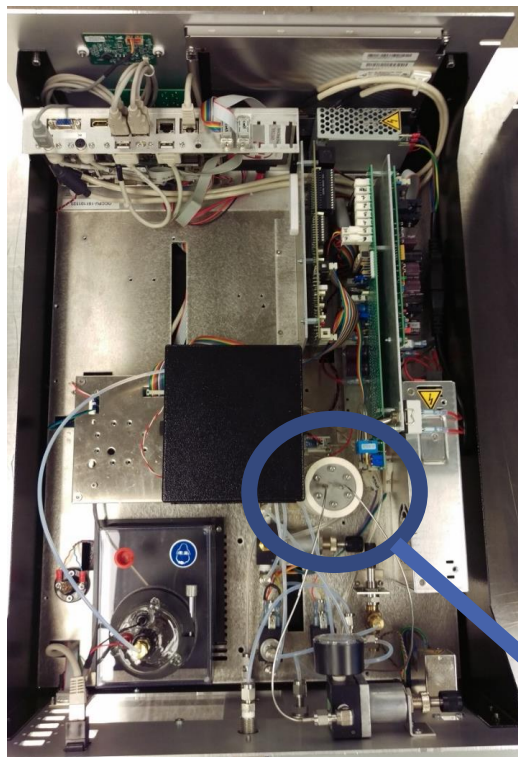


ASTM D7493-14



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

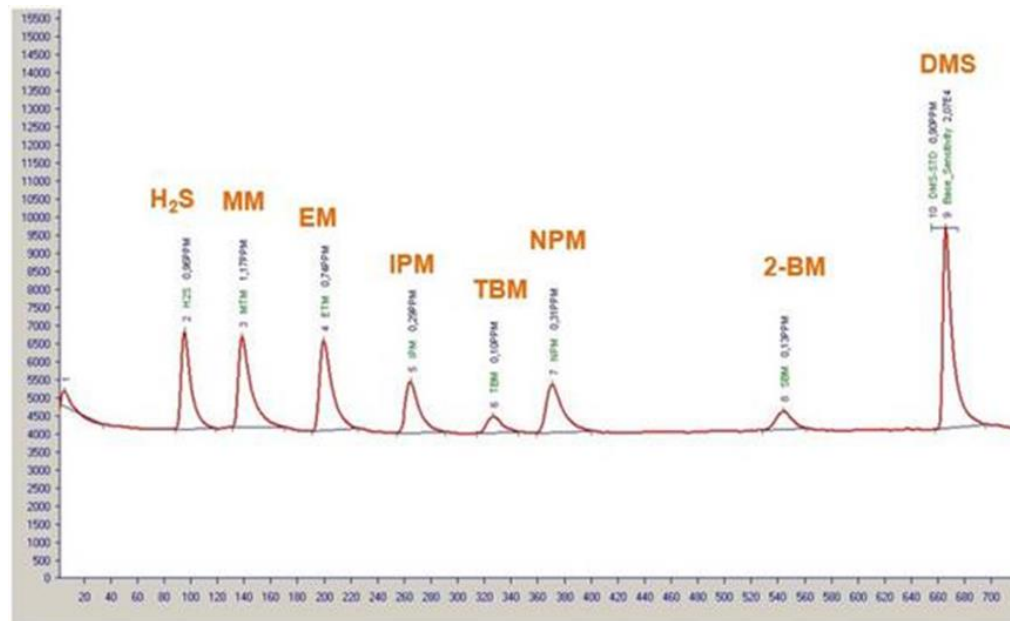
- Analysis of 8 compounds in standard using DMS permeation tube as calibration:
 - ✓ Stability tests
 - ✓ Linearity tests
- Analysis of up to 14 compounds available upon request



energyMEDOR
Ref: M42022

Performance tests

| | |
|--------------------------------|---|
| Hydrogen sulphide | H_2S |
| Methyl Mercaptan (MM or MTM) | $\text{CH}_3\text{-SH}$ |
| Ethyl Mercaptan (EM or ETM) | $\text{CH}_3\text{CH}_2\text{-SH}$ |
| Dimethyl Sulphide (DMS) | $\text{CH}_3\text{-S-CH}_3$ |
| (iso) 2-Propyl Mercaptan (IPM) | $(\text{CH}_3)_2\text{-CH-SH}$ |
| ter Butyl Mercaptan (TBM) | $(\text{CH}_3)_3\text{-C-SH}$ |
| (N) 1-Propyl Mercaptan (NPM) | $\text{CH}_3\text{CH}_2\text{CH}_2\text{-SH}$ |
| TetraHydroThiophene (THT) | $\text{C}_4\text{H}_8\text{S}$ |



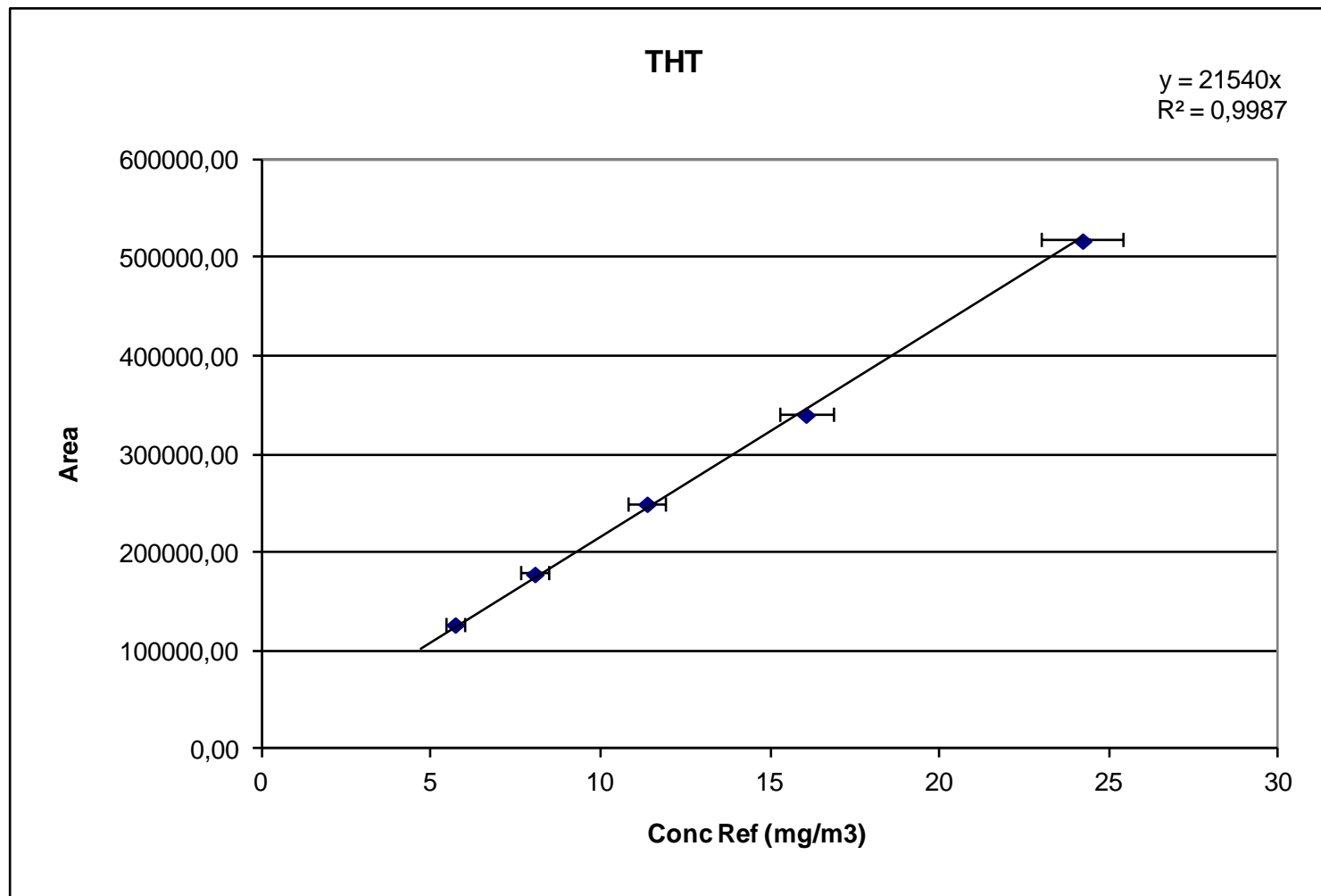
20 measurements are performed.

Stability tests

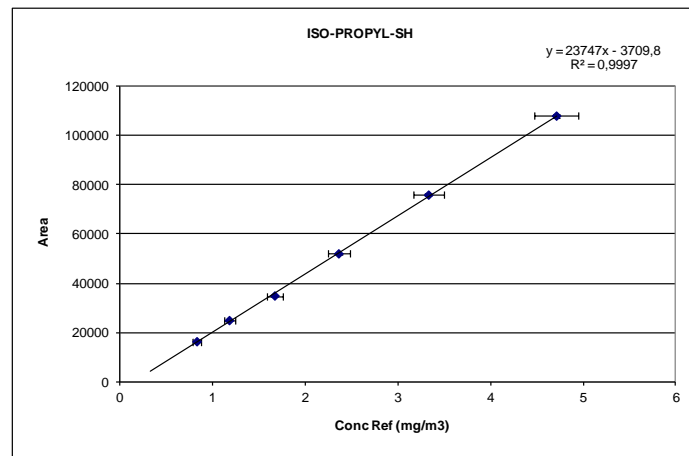
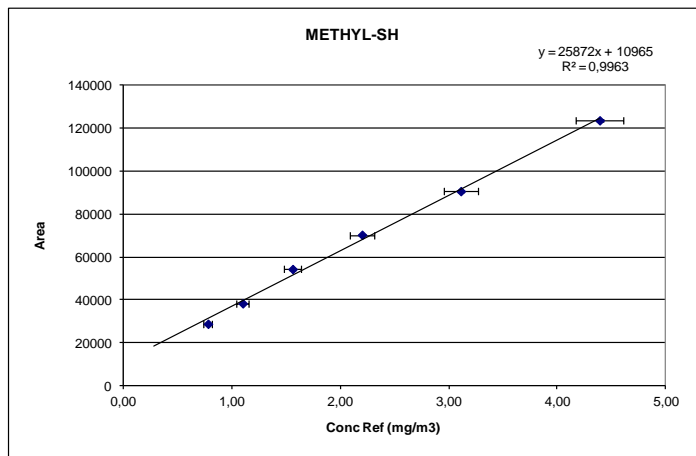
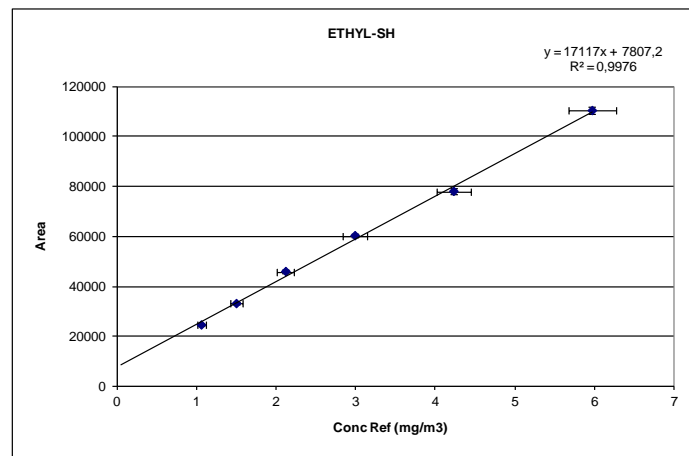
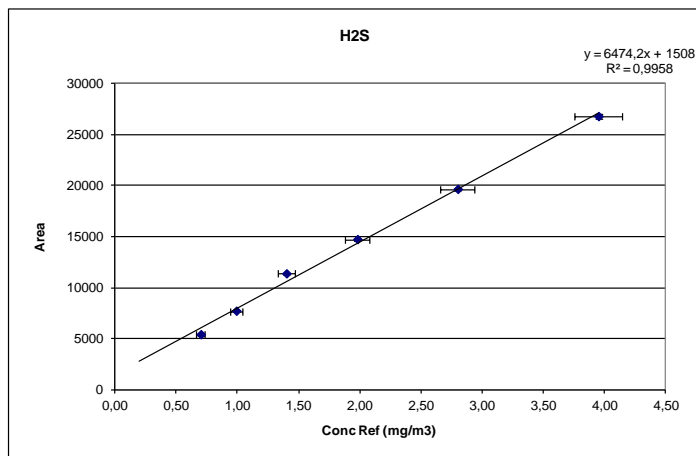
| | Concentration (mg/m ³) | | | | | | |
|-------------------------|------------------------------------|-----------------|-----------------|-----------------|-----------------|------------------|------------------|
| | H ₂ S | MM | EM | IPM | TBM | THT | DMS STD |
| Mean | 3,16 | 9,06 | 6,02 | 8,05 | 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%) |

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 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 |

Metrology conclusions

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

Sensitivity

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

- DMS LOQ < 1 ppb H₂S 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:

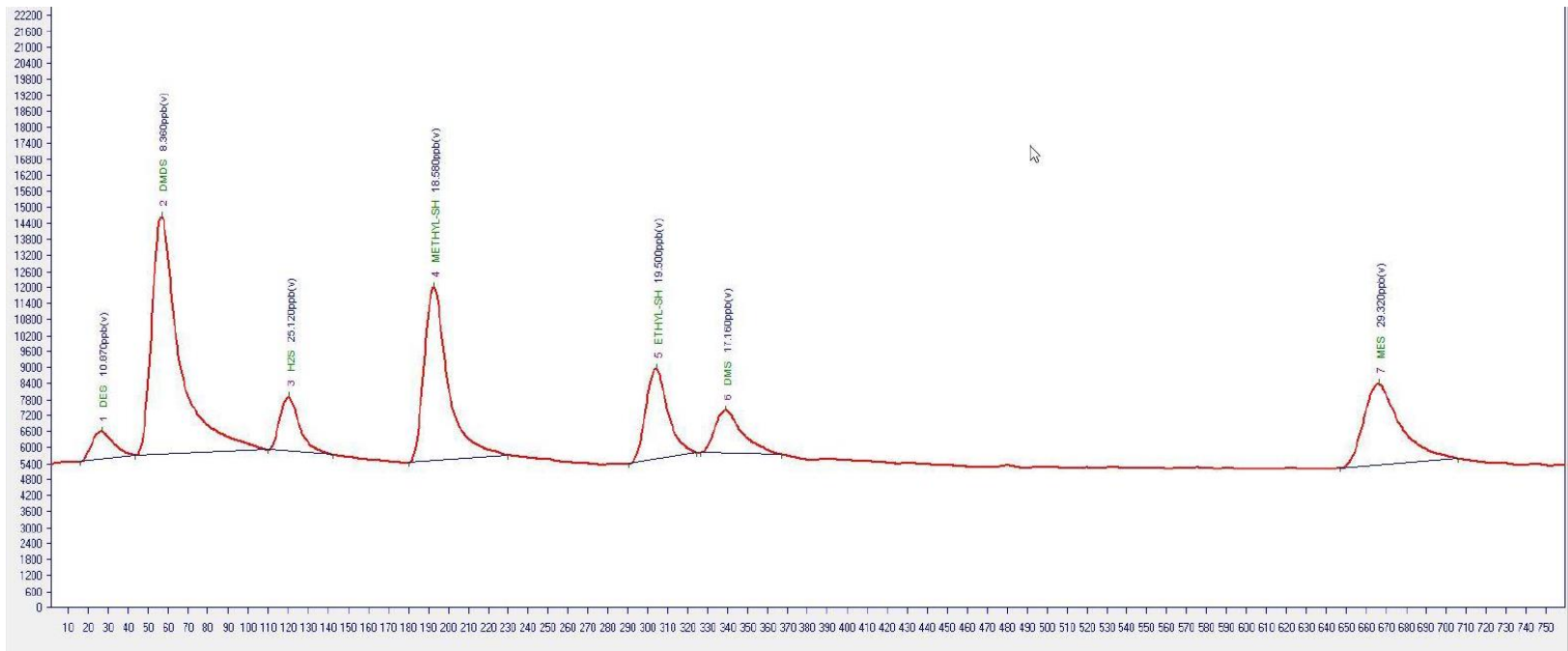
- 0 – 1 ppm / 0 – 10 ppm / 0 – 100 ppm
 - 0 to 5% with 0.1µl loop

Selectivity:

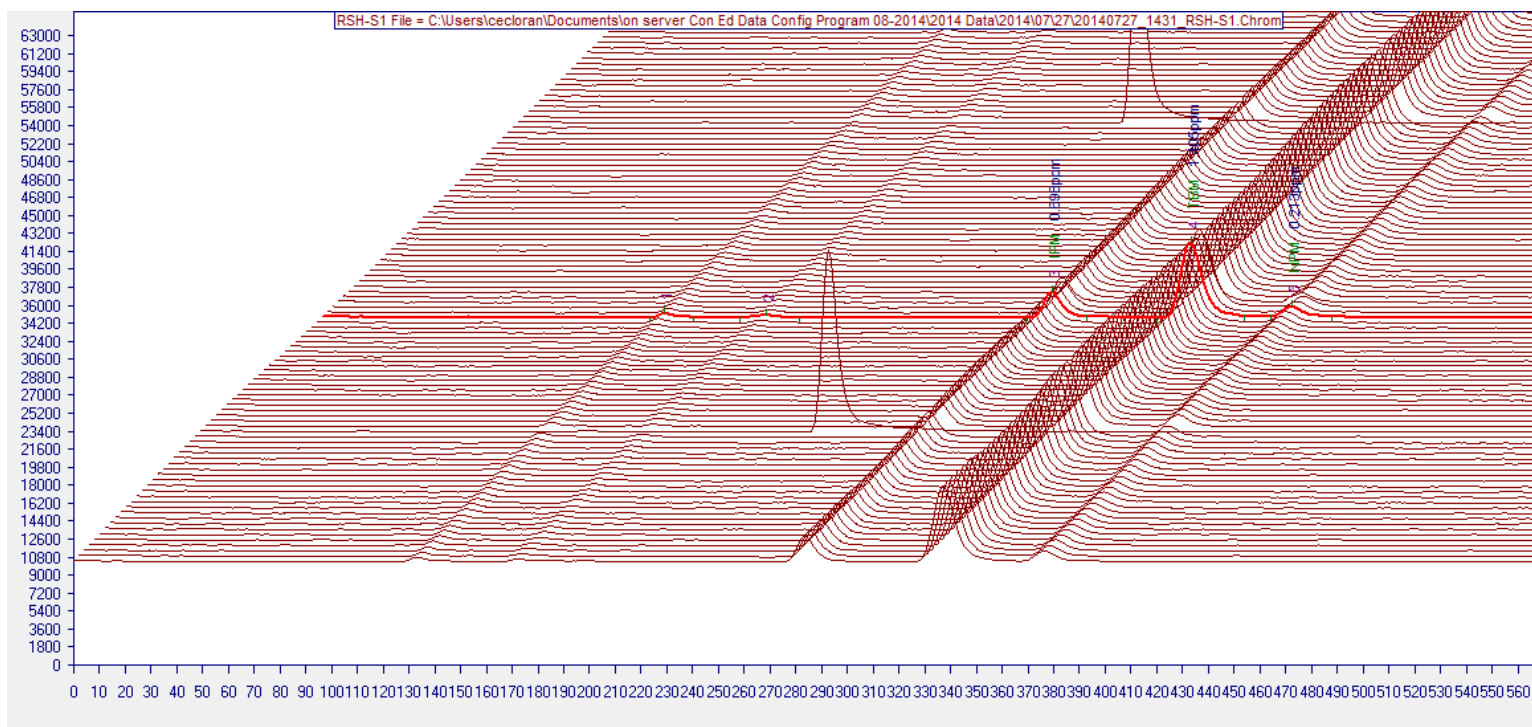
- No interference from hydrocarbons
 - Speciation of H₂ from H₂S in case of > 5% H₂ in the sample by specific GC columns

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**



KGS Exp Type certification for Zone 2 and **Zone 1 GROUP IIC T4**

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

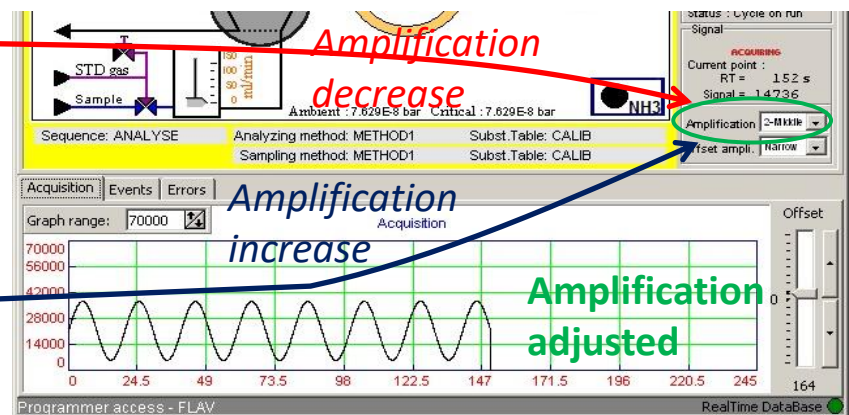
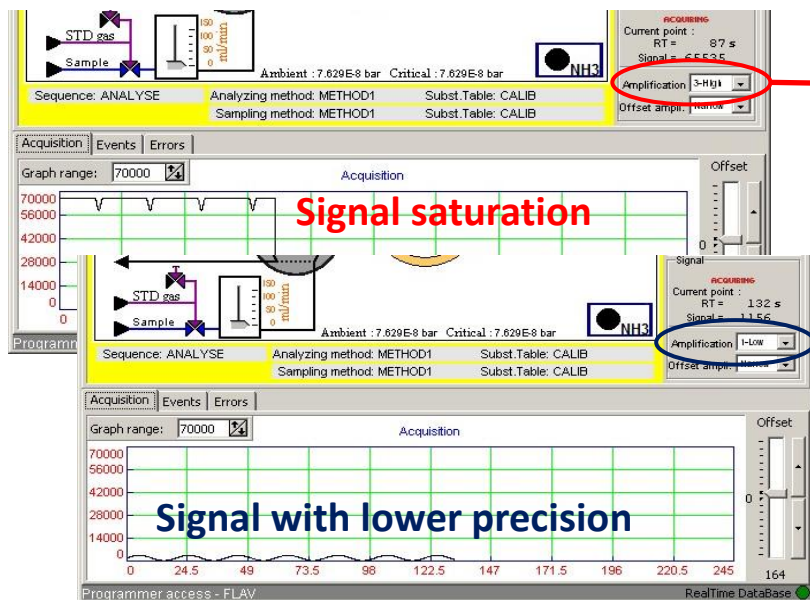
Exd (Flameproof) for MEDOR® and chromaTCD on request

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°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

Trace to % concentration H₂S analysis

Trace and ultra trace level of H₂S monitoring

- H₂S 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 H₂S in complexe mixture

- H₂S MEDOR used to analyse trace concentration of H₂S in complexe mixture:
 - Petrochemical mixture with more than 50 % H₂
 - 0 to 1 ppm H₂S



Reactor effluent driers outlet H₂S outlet

- Exhaust gas with high level of COS 5 000 ppm and 0 to 50 ppm H₂S



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

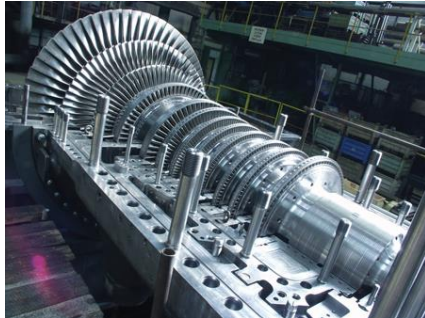
H₂S TOS TS

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 H₂S and total sulfurs is required to be monitored



Société Tunisienne
de l'Électricité et du Gaz



الشركة التونسية
لل كهرباء والغاز



Sales metering station

- Natural gas Sales metering station in Egypt

H₂S TS MEDOR 0 - 10 ppm



Pipeline Integrity Monitoring

Applications of the energyMEDOR H2S/TS MEDOR: (Integrity Monitoring)

- During the extraction of raw NG and following processing, Midstream companies are required to track the level of H₂S 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 H₂S from the gathering lines

- Every two minutes
- Can close quickly when the H₂S limit that is present over the limit

- Customer reference:

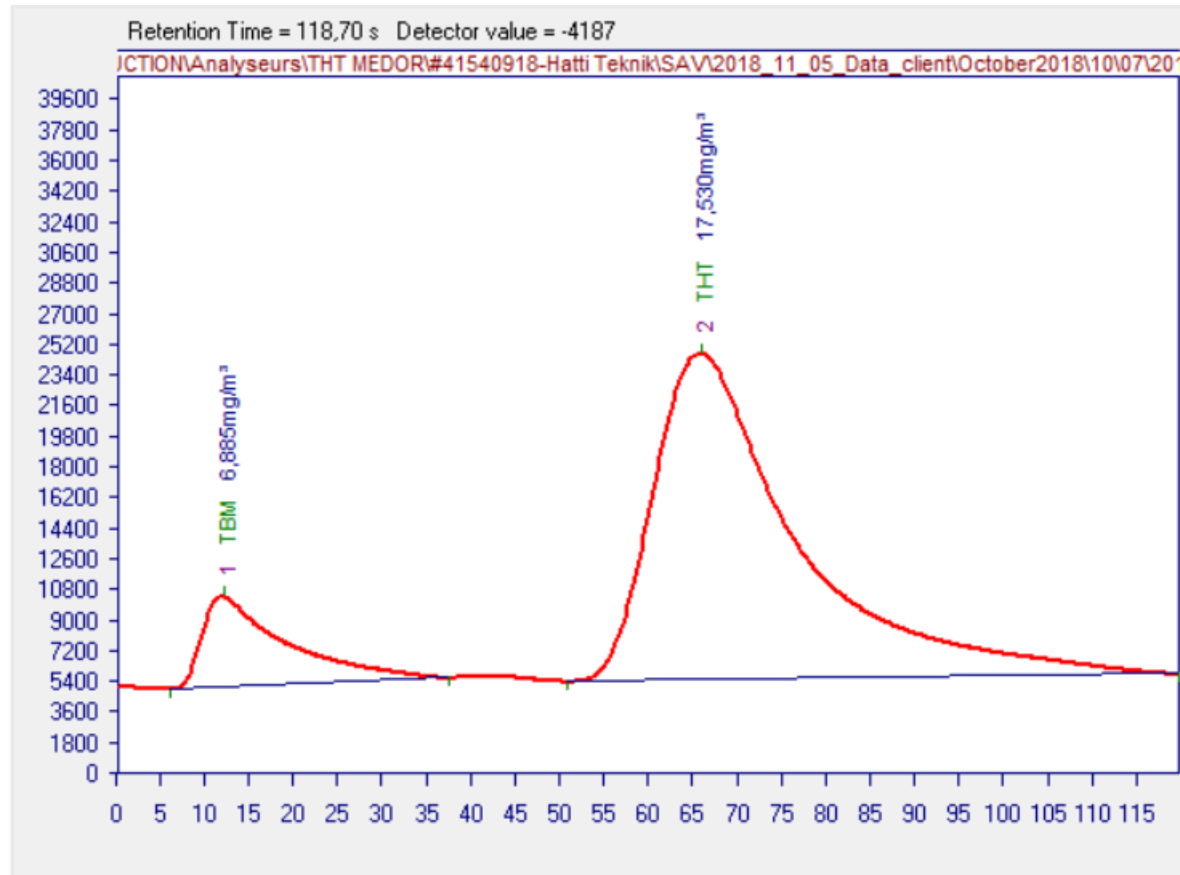


THT MEDOR®

- 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



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_2S 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



The B line that crosses Virginia 26 just north of the town of Appomattox failed at 7:44 a.m. on Sept. 14, a Sunday. The natural gas it released ignited a fireball that burned an area 345 meter in diameter. 100 homes were damaged in the blast

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

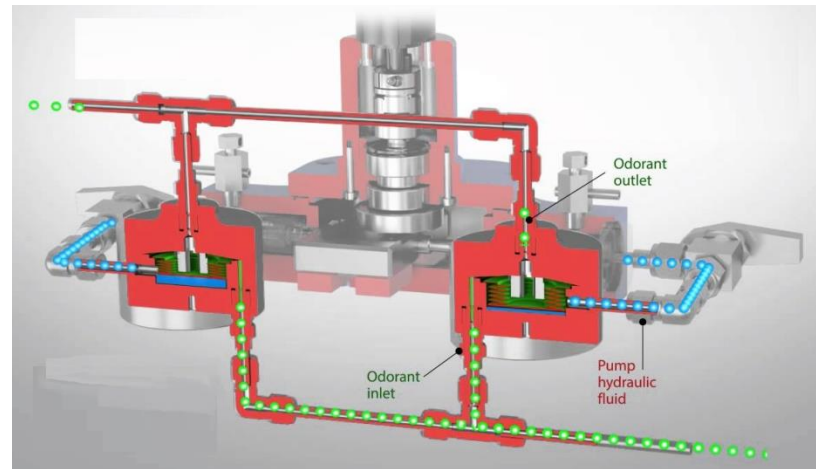
- The operator fills a box with a known sample volume:
 - Smell the gas
 - Decides if the amount of odorant is sufficient



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

**Natural Gas
ODORIZATION**
AUGUST 27-28, 2019

- 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, H₂S, 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

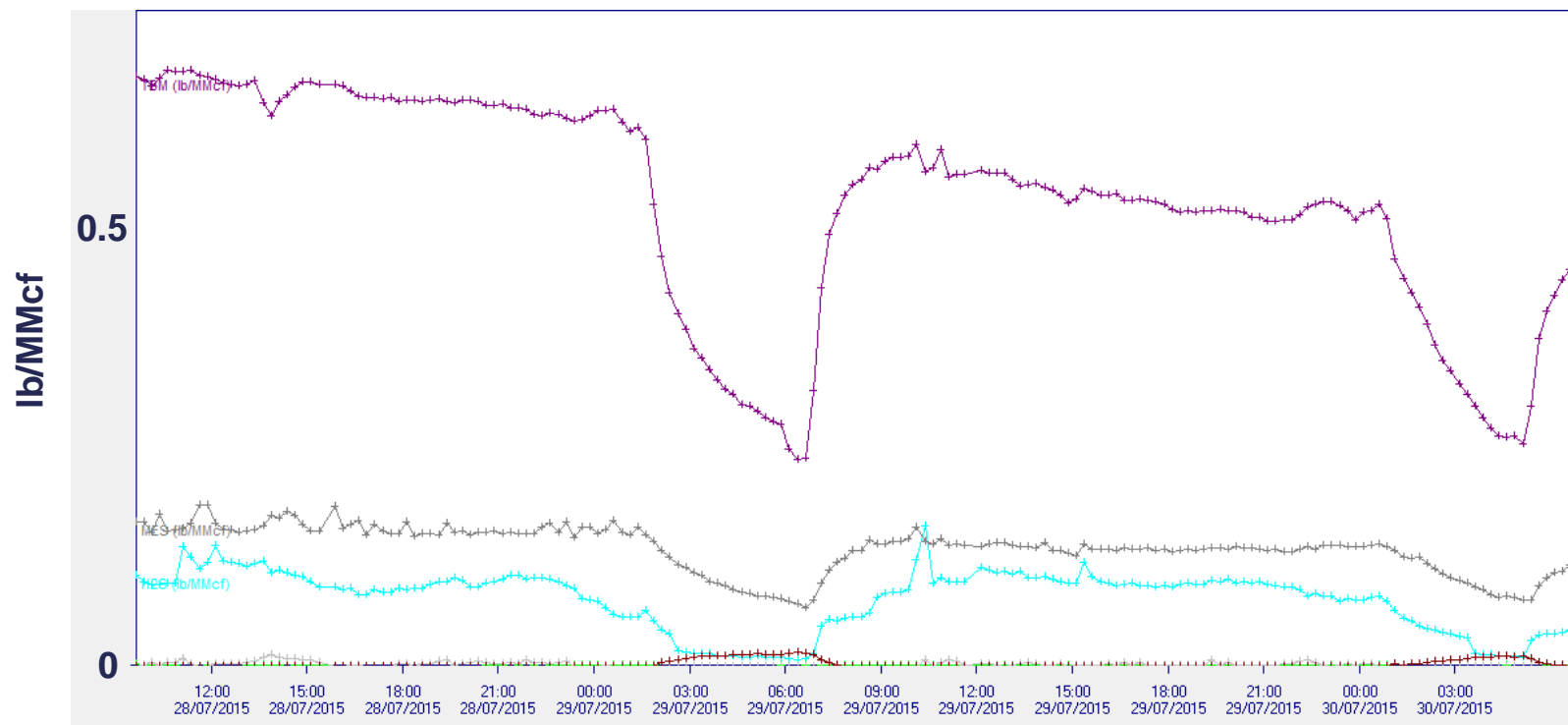
- We have had zero Low Odorant instances
- We have had no over odorization instances
- We have reduced maintenance by using analyzers as compared to doing manual testing
- We have reduced odorant usage by approximately 4000 gallons per year equivalent to 15 141,65 liters

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

Joe Marx

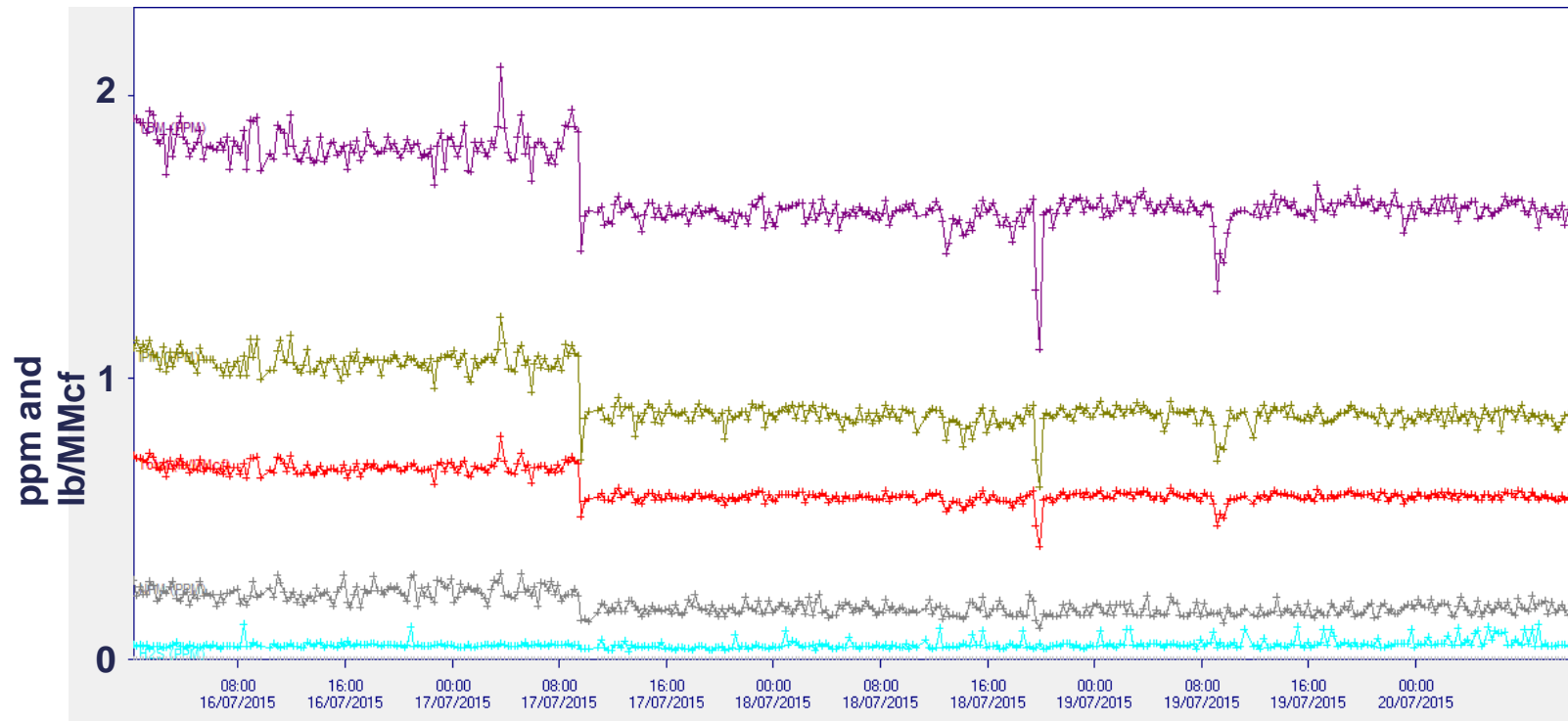
How Washington Gas Monitors and Maintains
Proper Odorant Levels in Gas From Multiple
Suppliers

Trend



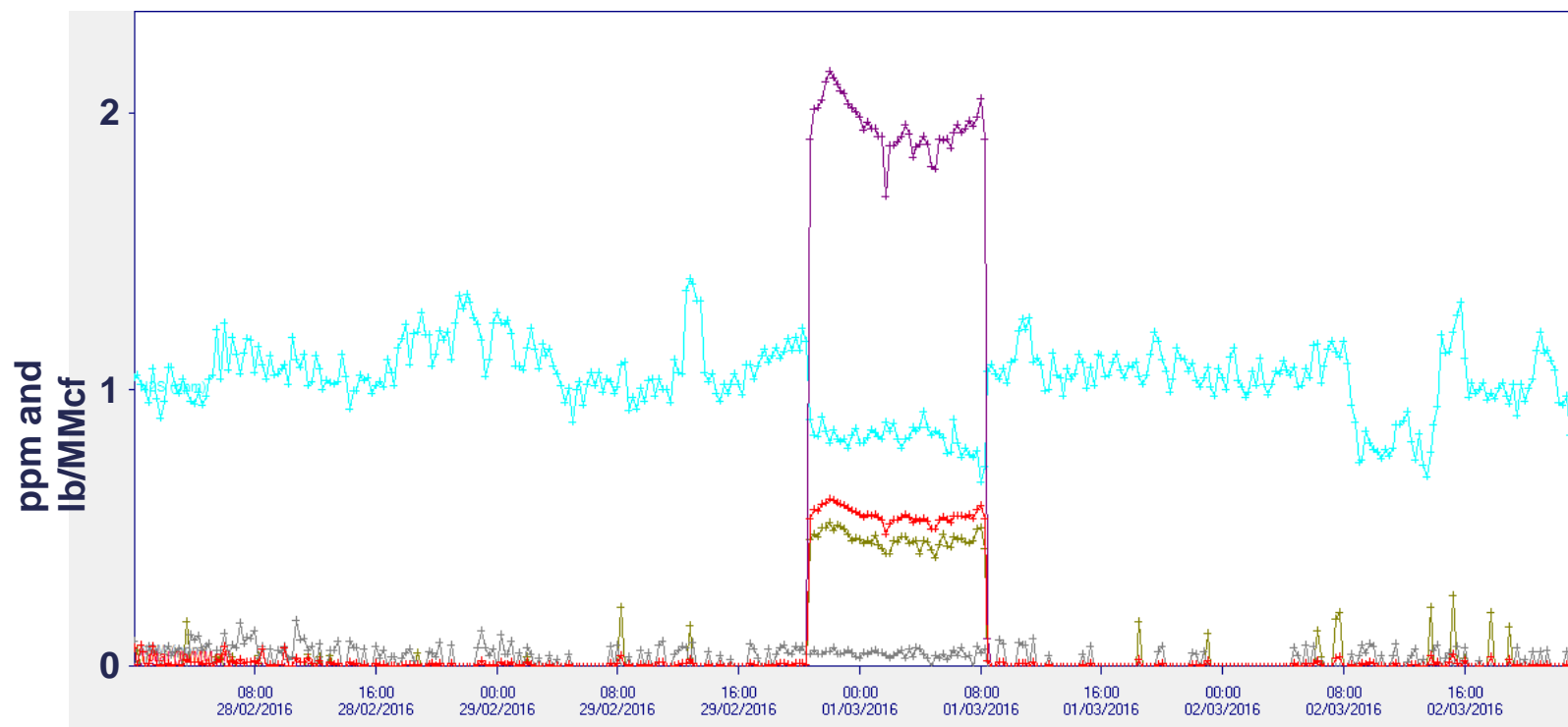
ODORANT MEASUREMENT AND INJECTION CONTROL

Trend



ODORANT MEASUREMENT AND INJECTION CONTROL

Trend



Some customer reference in odorization market

Americas:



Manzanillo LNG terminal

Middle East and Africa:

Asia:



Europe:



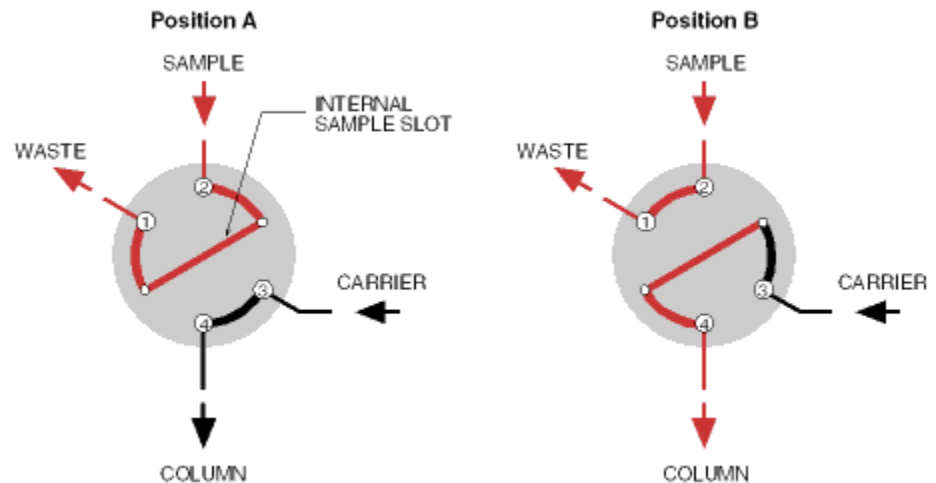
LPG application

- 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 μ l
 - Advantages:
 - very low consumption of liquefied gas
 - representative sample analysed



LPG Odorization

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_2S ... 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, H₂S... 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, H₂S... in natural gases :

By monitoring sulfur compounds levels during desulfurization :

- Industrials can avoid catalyst deactivation in steam-reforming units ; with high-level alarm threshold 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: H₂S, 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

Technology comparison

| Specification | Lead Acetate tape | UV like AAI OMA 300 | Chromatotec MEDOR® GC-ED |
|---------------------|---|---|---|
| Detection principle | Lead acetate tape for H ₂ 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 $R^2 > 0.995$ 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 ₂ S only and Total sulfur using convertor | H ₂ S with interference Individual mercaptans not analyzed | H ₂ 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 |

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 Lead tape waste disposal | | No Flame |

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 Exd version : 0l/min |
| Cycle time for H ₂ S 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 H ₂ S and Total sulfur using convertor. | 2 min for H ₂ S/TS 5 min for H ₂ S/MM/EM 12 min for H ₂ S/MM/EM/IPM/TBM/NPM/MES/THT More compounds on request |
| Carrier gas | Zero air or H ₂ 60 to 300 ml/min | N/A | N ₂ 3 ml/min from internal N ₂ gen. |
| Operating gas | H ₂ for flame (GC grade) 40 ml/min and 300 ml/min air | N/A | Nitrogen 50ml/min for CALIB in option (from N ₂ 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 H₂S 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?