CHROMATOTEC® GROUP
Expert in gas analysis

ISO 9001
ENTREPRISE CERTIFIÉE

Natural gas and gaseous fuels applications

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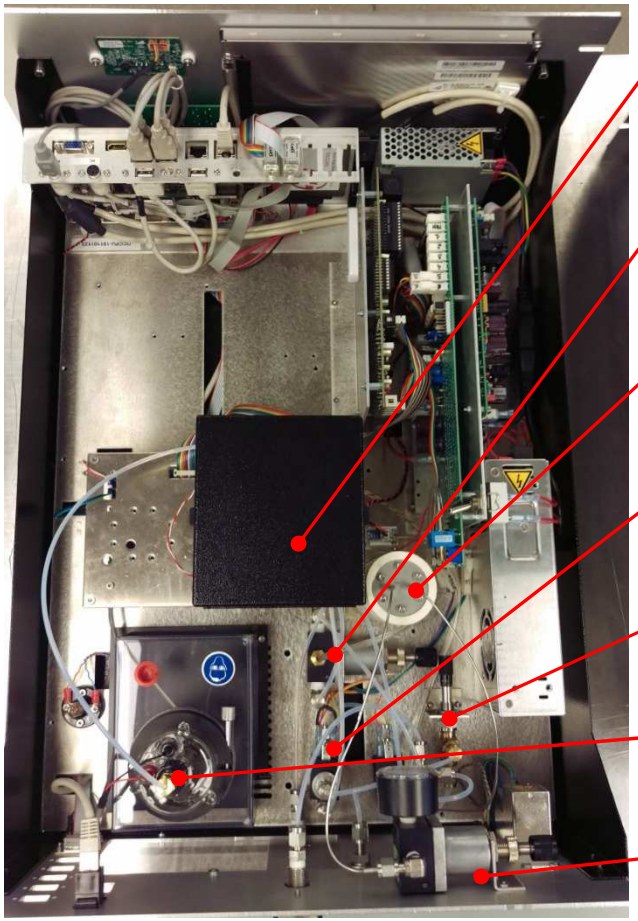
Outline

- MEDOR® technology
- Different versions
- Performance test
- Applications for natural gas and gaseous fuels
- chromENERGY / chromaTCD
- Peripherals
- Customer reference

MEDOR® Analyser Technology



Oven (inside) : injection valve, sampling loop and metallic capillary chromatographic column

Pressure regulator to adjust carrier gas flow (piezzo valve for energyMEDOr version)

Calibration system (permeation tube inside the oven)

Selection valve (solenoid valve)

Adjustment valve to set the sampling flow

MEDOR® Electrochemical Wet cell Detector

Pressure regulator to adjust the flow of the calibration system

MEDOR® Analyser
Principle of analysis

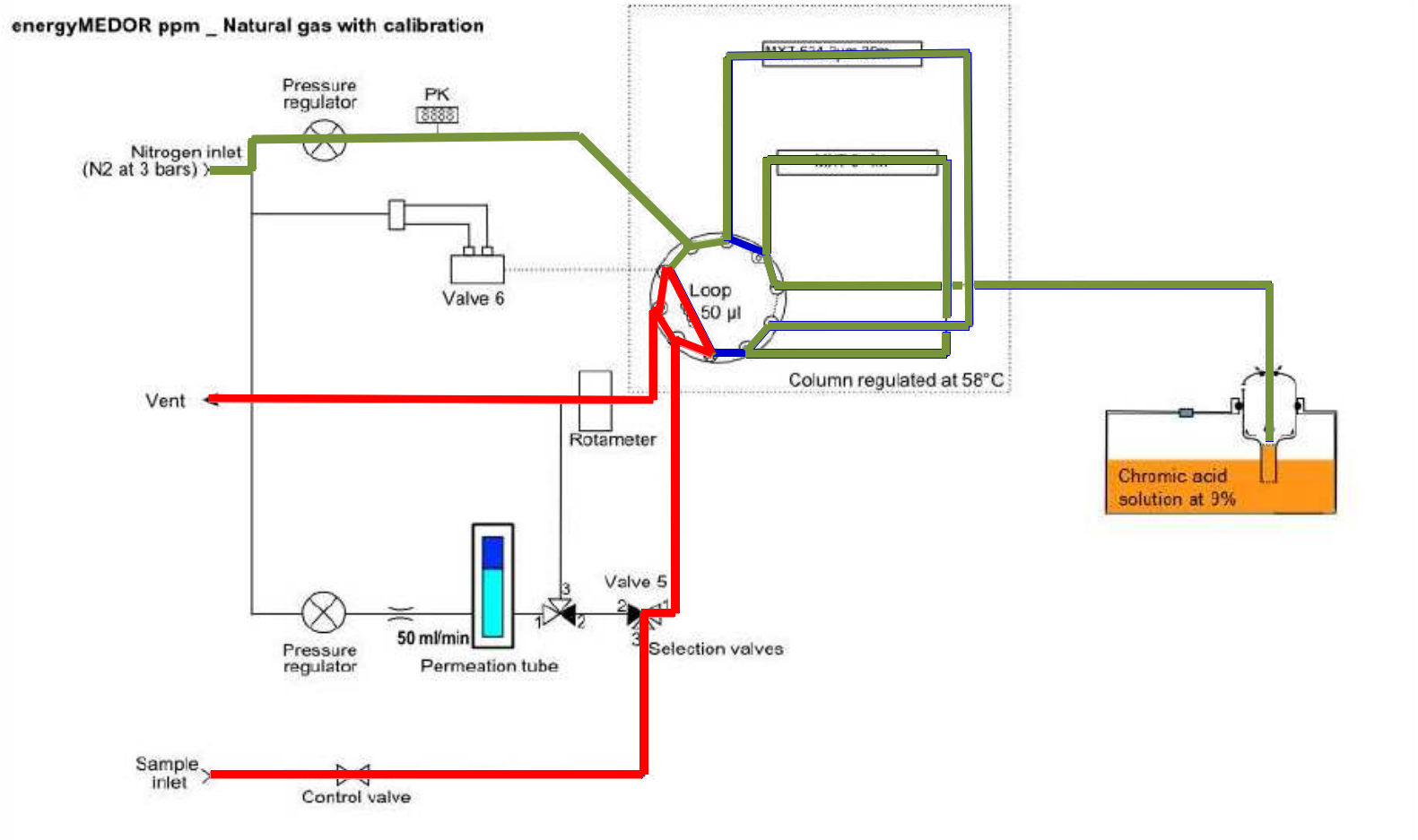
- Normal operation
  - Carrier gas travels through the columns and into detector (5ml/min)
  - Sample gas travels through the loop.

- Injection step
  - Sample volume is injected into the columns.

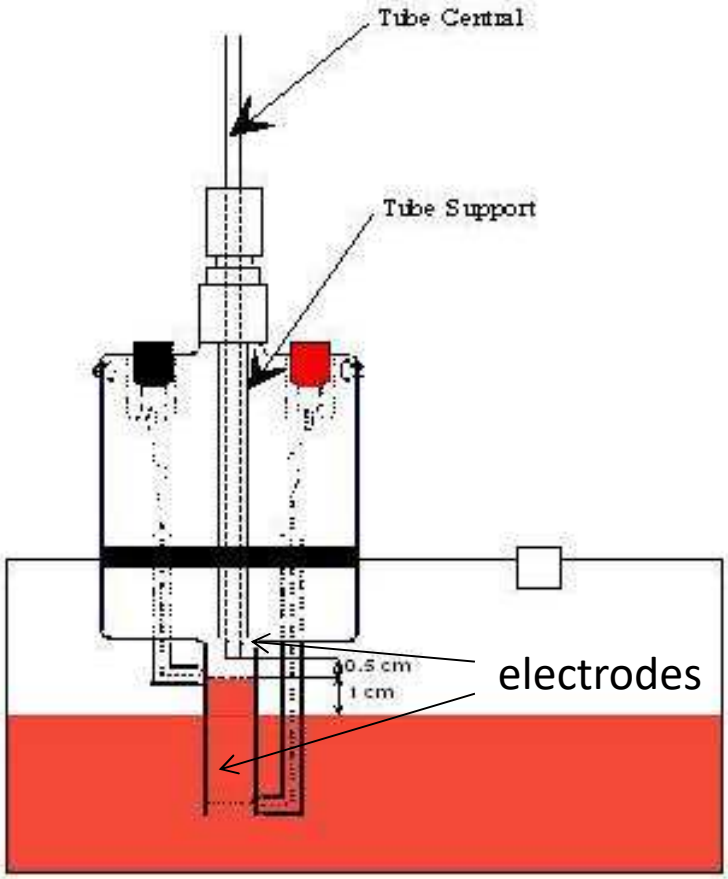
- The sulfur compounds are more or less retained by the column's support and exit the column with different retention times according to their affinity for the absorbent material.

- 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

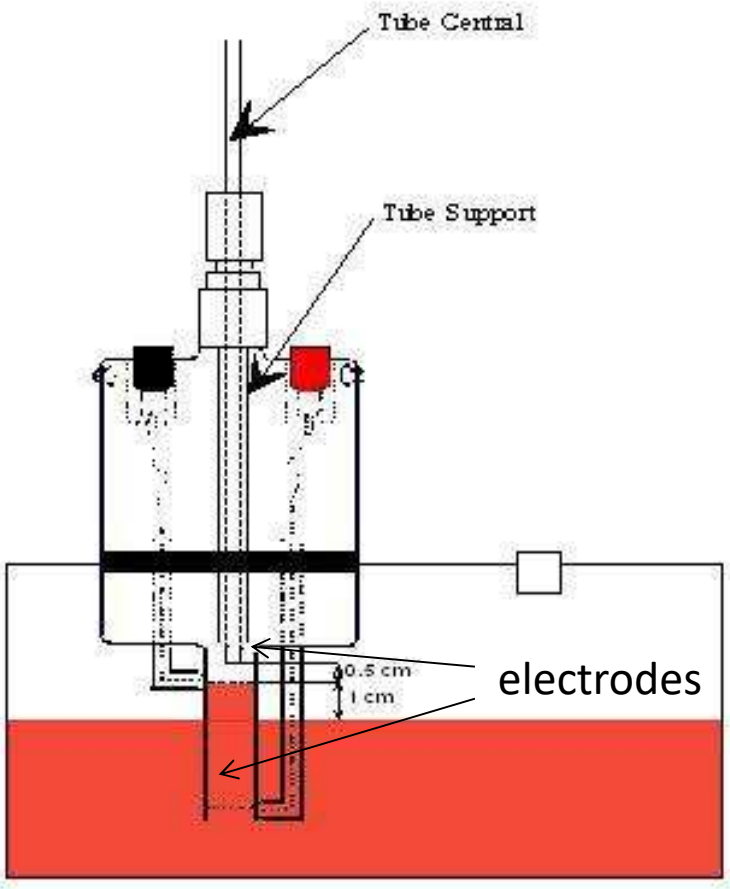


ASTM D7493-14

Technical characteristics:

- Glass container.
- A solution of Chromium (VI) oxide in distilled water .
- Two platinum electrodes are arrange 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

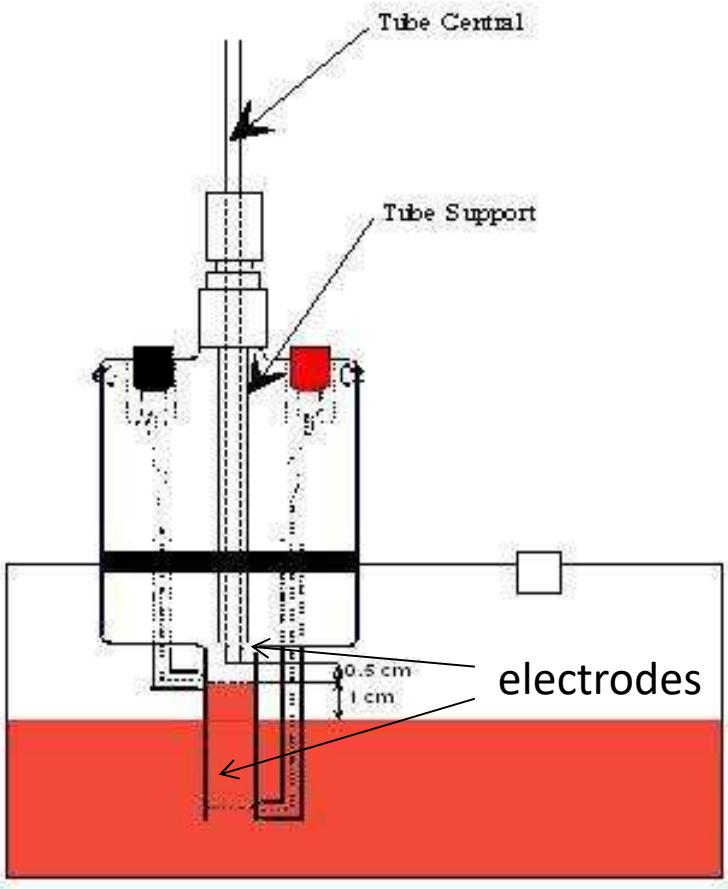


ASTM D7493-14

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 courant can be measured to quantify the amount of sulfur species in the gas

MEDOR® Analyser
Wet cell detector

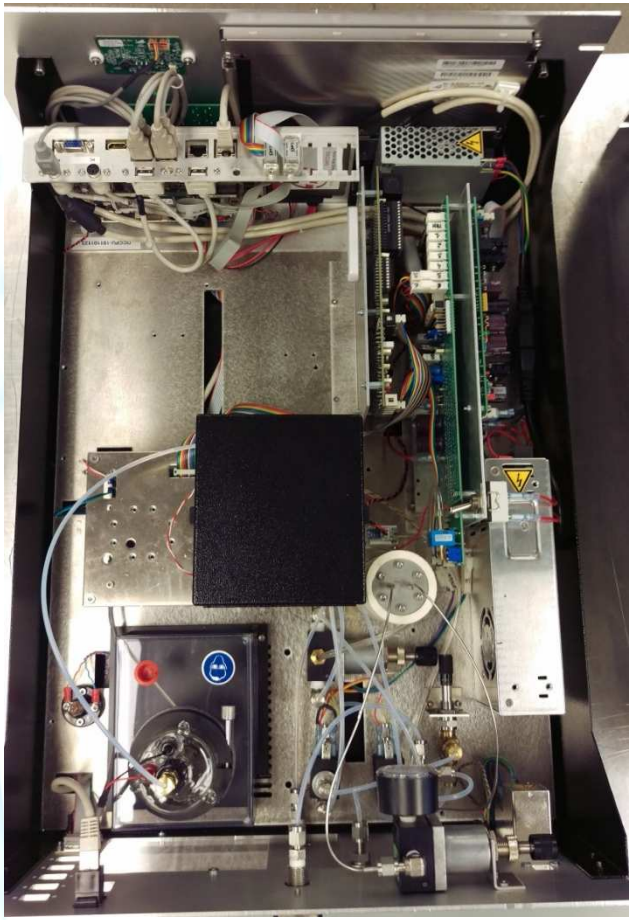


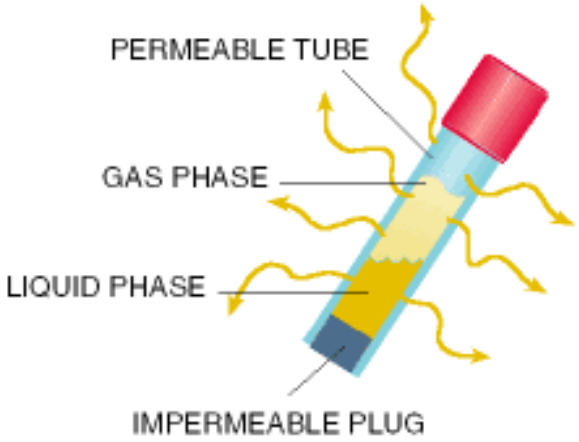
ASTM D7493-08

Key points:

- Only very low maintenance is necessary - addition of water to the detector every 3 months.
  - Low evaporation rate
    - Small diameter
    - Small carrier gas flow (5ml/min)

MEDOR® Analyser
Calibration – Permeation tube





Gas phase goes through the permeable membrane:

- Constant temperature (±0.1° C)
- Constant flow rate

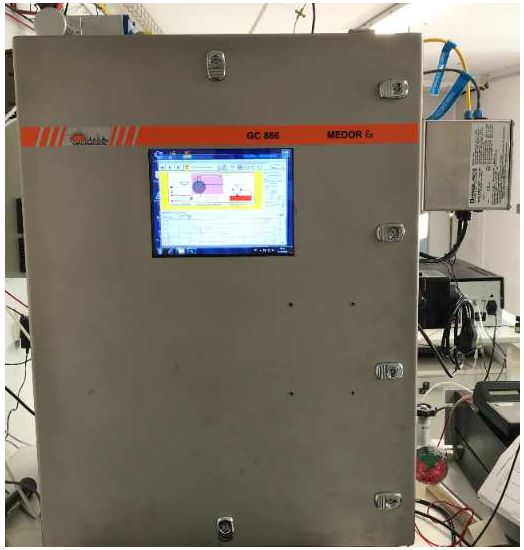
Allows automatic calibration of the instrument and validation of the results

No need of cylinder!

MEDOR® certifications and standards

D7493 : 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

- Different version of MEDOR®:
  - *H2S/TS MEDOR*
  - *THT MEDOR*
  - *energyMEDOR*

Outline

- MEDOR® technical introduction
- Different versions
  - H2S MEDOR
  - H2S/TS MEDOR
  - THT MEDOR
  - energyMEDOR
- Performance test
- Applications for natural gas and gaseous fuels
- chromENERGY / chromaTCD
- Peripherals
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H2S analysis

H2S MEDOR®

- Electrochemical detection
- Carrier gas: Air or nitrogen
- Sampling: Loop
- H2S in two minutes
- LDL down to 1 ppb for low range
- Standard analysis range:
  - 0-1 / 0-10 / 0-100 ppm
  - Low % range in option

H2S MEDOR
Ref: M51022-ATEX-Z1

H2S MEDOR
Ref: M51022

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 two 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

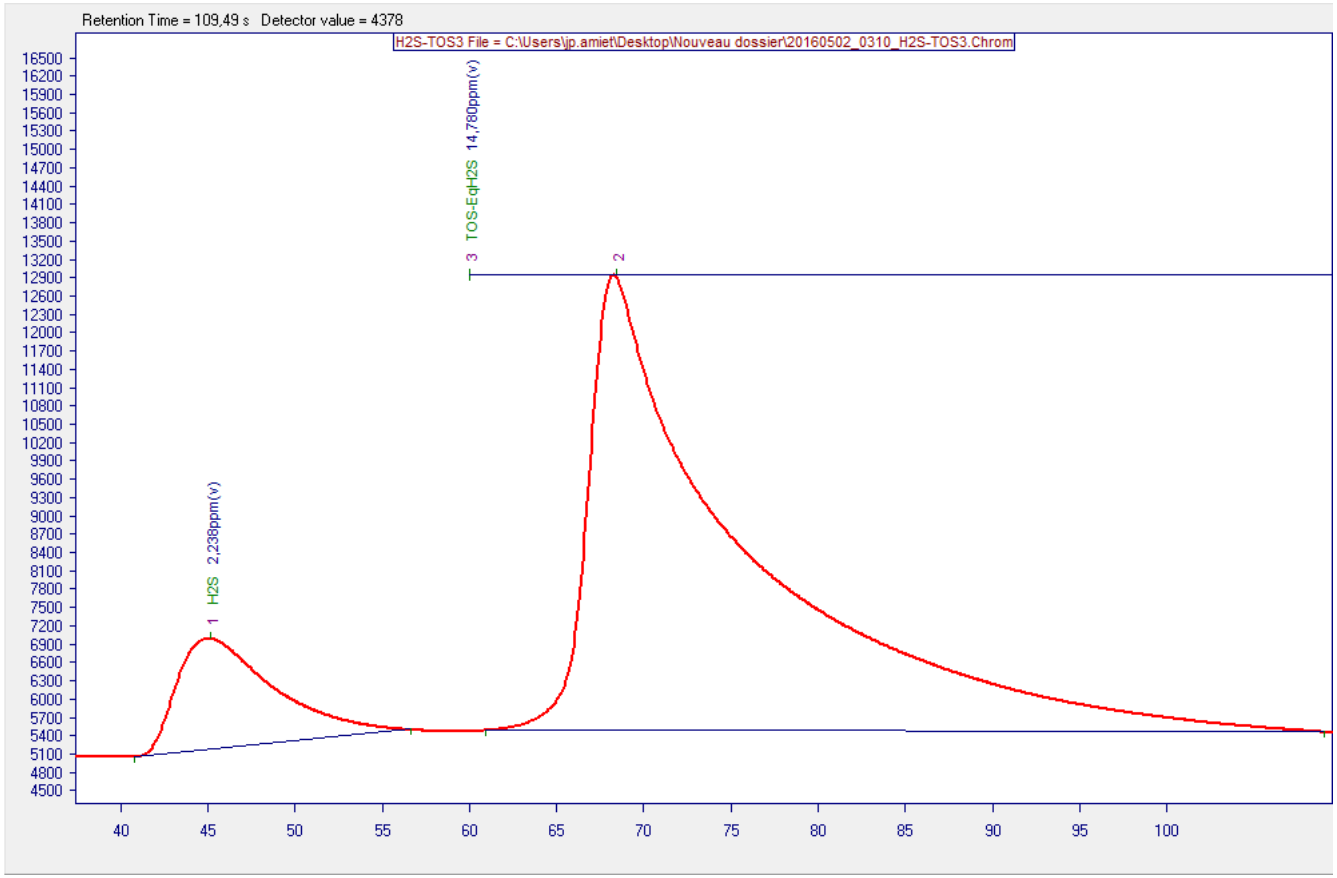
Measurement of H2S and Total sulfur content in2 minutes

H2S TS MEDOR® is :

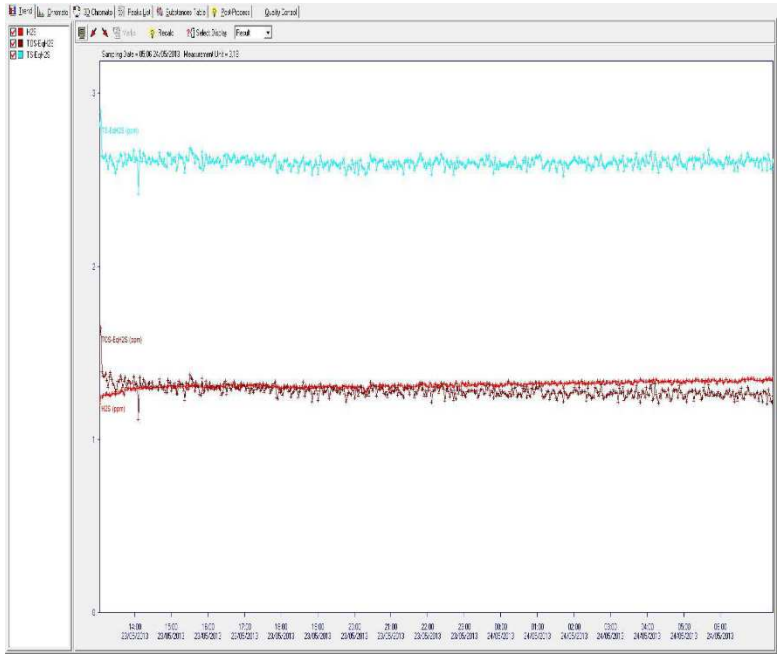
- Designed for process control application
- Online continuous sampling
- Very specific to sulfur compounds (no interference)
- Very Low maintenance
- No conversion for total sulfur measurement
- Automatic validation
- GC instrument which Allows quantification and identification of H2S and TOS
- Fast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

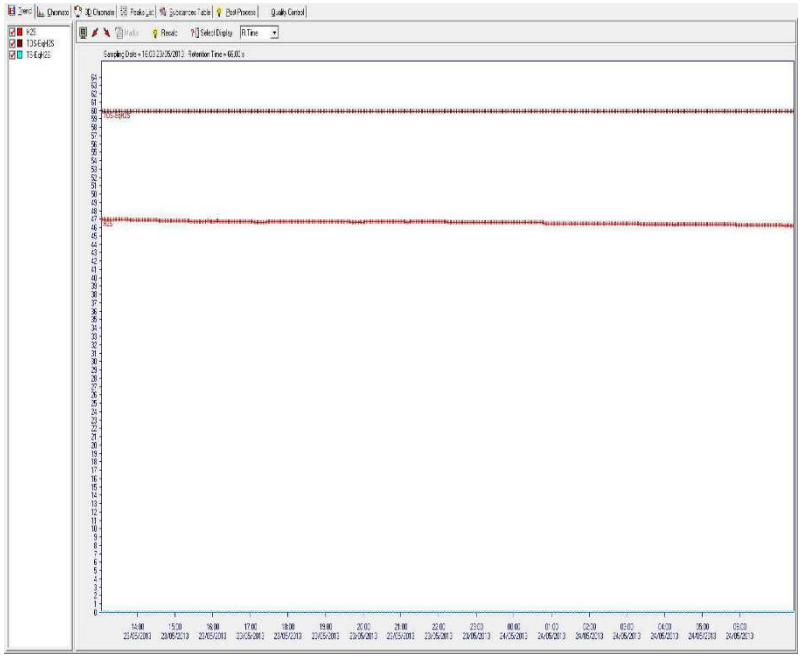
H2S TOS TS
Ref: M51022-TS

Measurement of H2S and Total sulfur content in2 minutes



Measurement of H2S and Total sulfur content in2 minutes



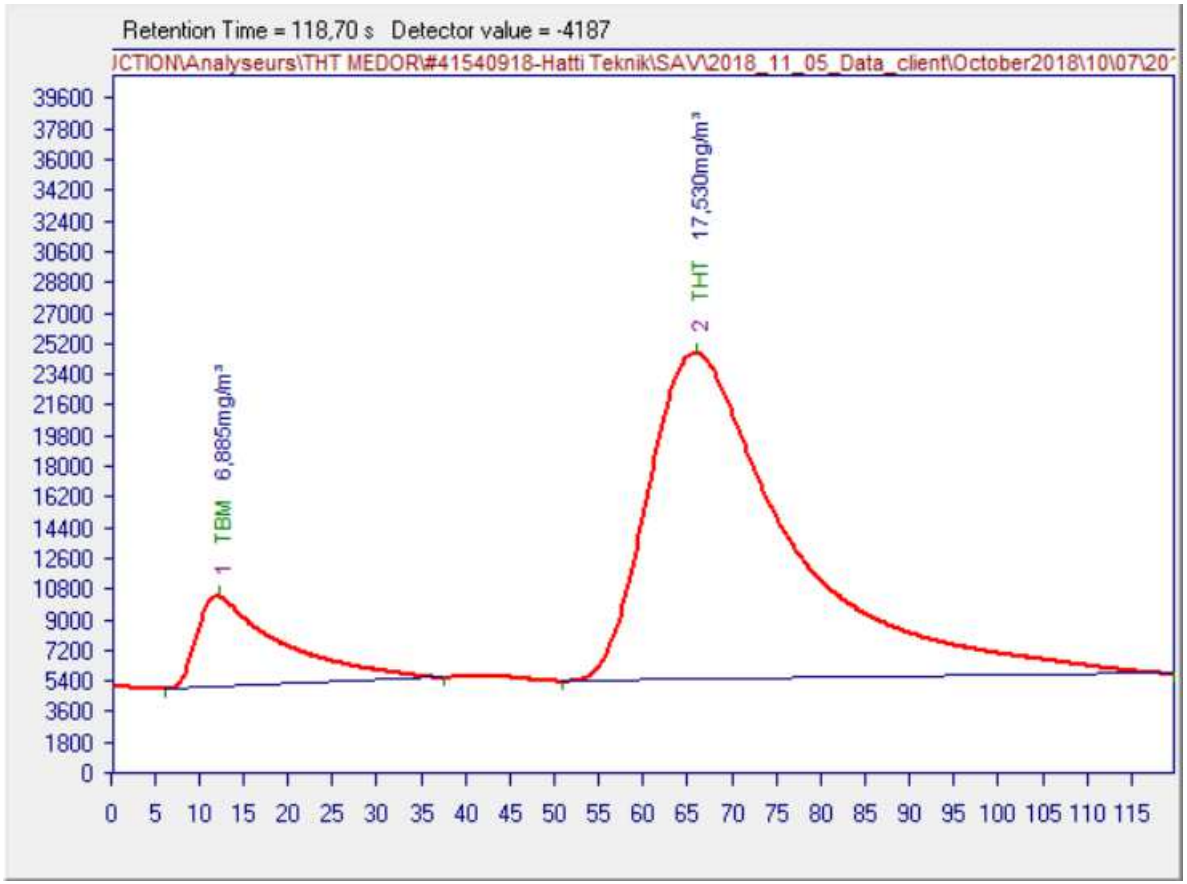


THT MEDOR®

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

Model: M31022

THT MEDOR®

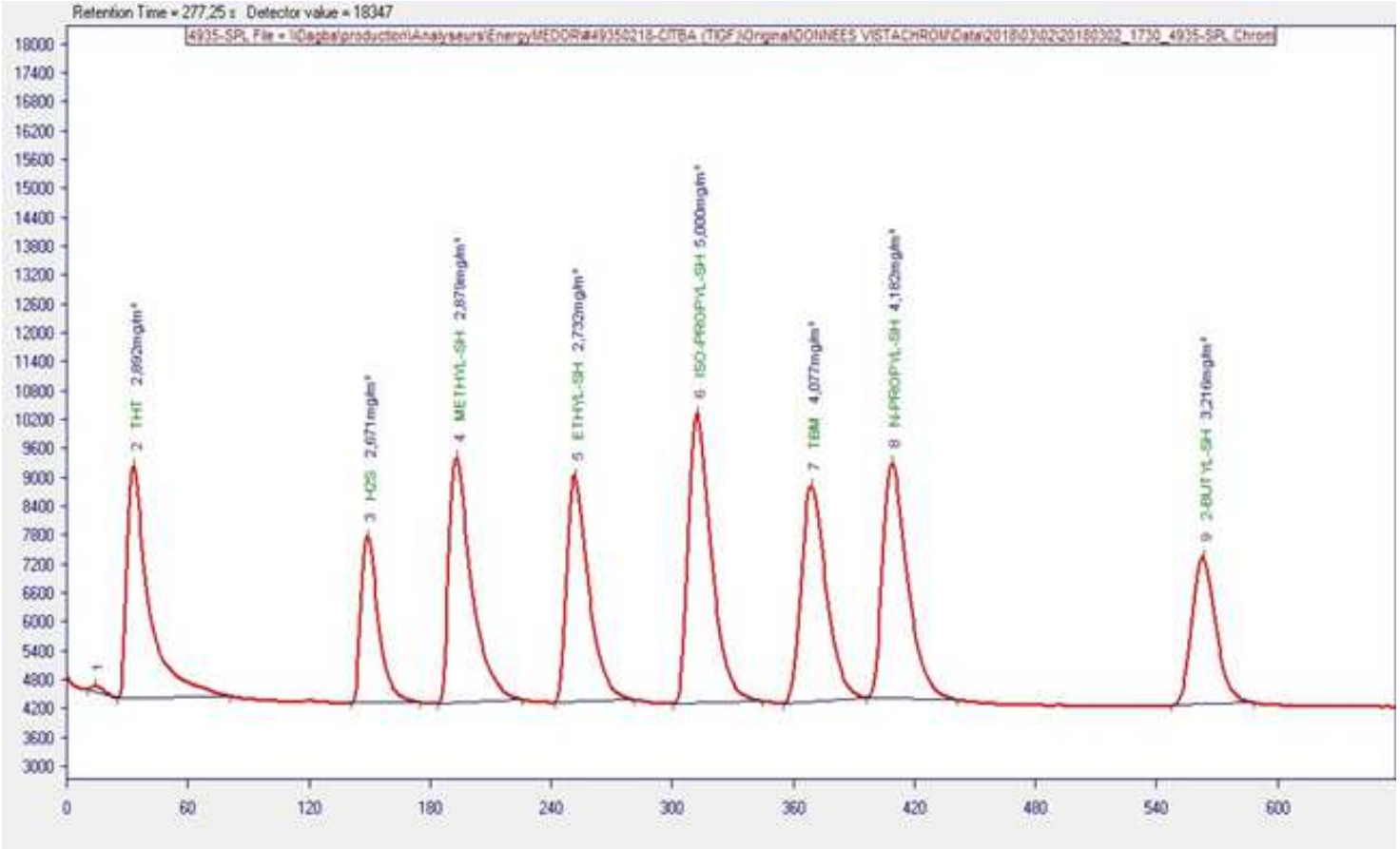

Retention Time = 118,70 s Detector value = -4187
JCTION\Analyseurs\THT MEDOR\#41540918-Hatti Teknik\SAV\2018_11_05_Data_client\October2018\10\07\20
1 TBM 6,885mg/m³
2 THT 17,530mg/m³
39600
37800
36000
34200
32400
30600
28800
27000
25200
23400
21600
19800
18000
16200
14400
12600
10800
9000
7200
5400
3600
1800
0
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115

energy MEDOR®

- energyMEDOR® version for automatic monitoring of all sulfur compounds
  - H2S, Mercaptans (RSH): MM/EM/IPM/TBM/NPM and MES
  - Total mercaptans and total sulfurs by sum
  - In option: 2 BM, IBM, NBM
  - MEDOR® Electrochemical wet cell Detector : SSD
  - Carrier gas: nitrogen
  - Cycle time from 12 minutes to 20 minutes

energyMEDOR
Ref: M42022

energy MEDOR®



Different enclosure

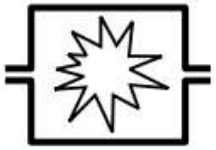
- Rack for non hazardous area

- Hazardous area zone 2 or zone 1
  - Exp

  - Exd

MAIN IEC PROTECTION TECHNIQUES

FLAMEPROOF "d"



- ZONE 1
- Contain internal explosion
- Control external temperature of enclosure
- Similar to NEC® explosion proof

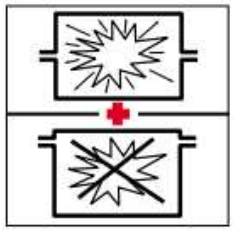
INCREASED SAFETY "e"

- ZONE 1
- High impact resistant enclosures—FRP, GRP, sheet steel/aluminum
- Will not hold static charge
- Use approved components
- Control internal and external temperature
- Maintain minimum of IP 54 ingress protection
- No arcs, no sparks

FLAMEPROOF PLUS INCREASED SAFETY "de"

"d"

"e"



- ZONE 1
- Location of arcing has "d" protection (flameproof)
- Connection terminals have "e" protection (increased safety)
- Typical use in switches, lighting, power outlets—where arcs can normally occur
- Control internal and external temperature

MAIN IEC PROTECTION TECHNIQUES

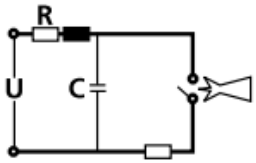
NON-SPARKING "n"

- ZONE 2
- Equipment has no normally arcing parts
- Thermal effects incapable of ignition
- nA=non sparking
- nR=restricted breathing
- nC=hermetically sealed non incendive

PRESSURIZED APPARATUS "p"

- ZONE 1
- Expels ignitable vapor/gas
- Maintains positive enclosure pressure

INTRINSIC SAFETY "ia"-"ib"



- ia ZONE 0 & 1
- ib ZONE 1
- Incapable of releasing enough energy to cause an explosion

Outline

- MEDOR® technical introduction
- Different versions
- **Performance test**
- Applications for natural gas and gaseous fuels
- chromENERGY / chromaTCD
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Performance tests

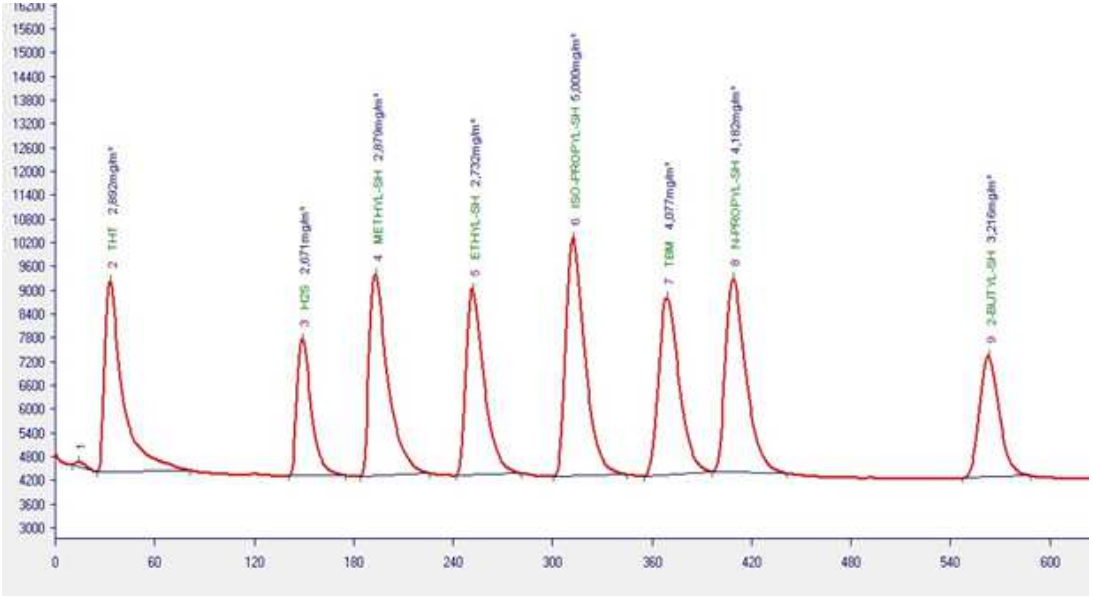
- Analysis of 8 compounds in standard using DMS permeation tube as calibration:
  - ✓ Stability tests
  - ✓ Linearity tests

energyMEDOR
Ref: M42022

- Analysis of 14 compounds available upon request

Performance tests

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

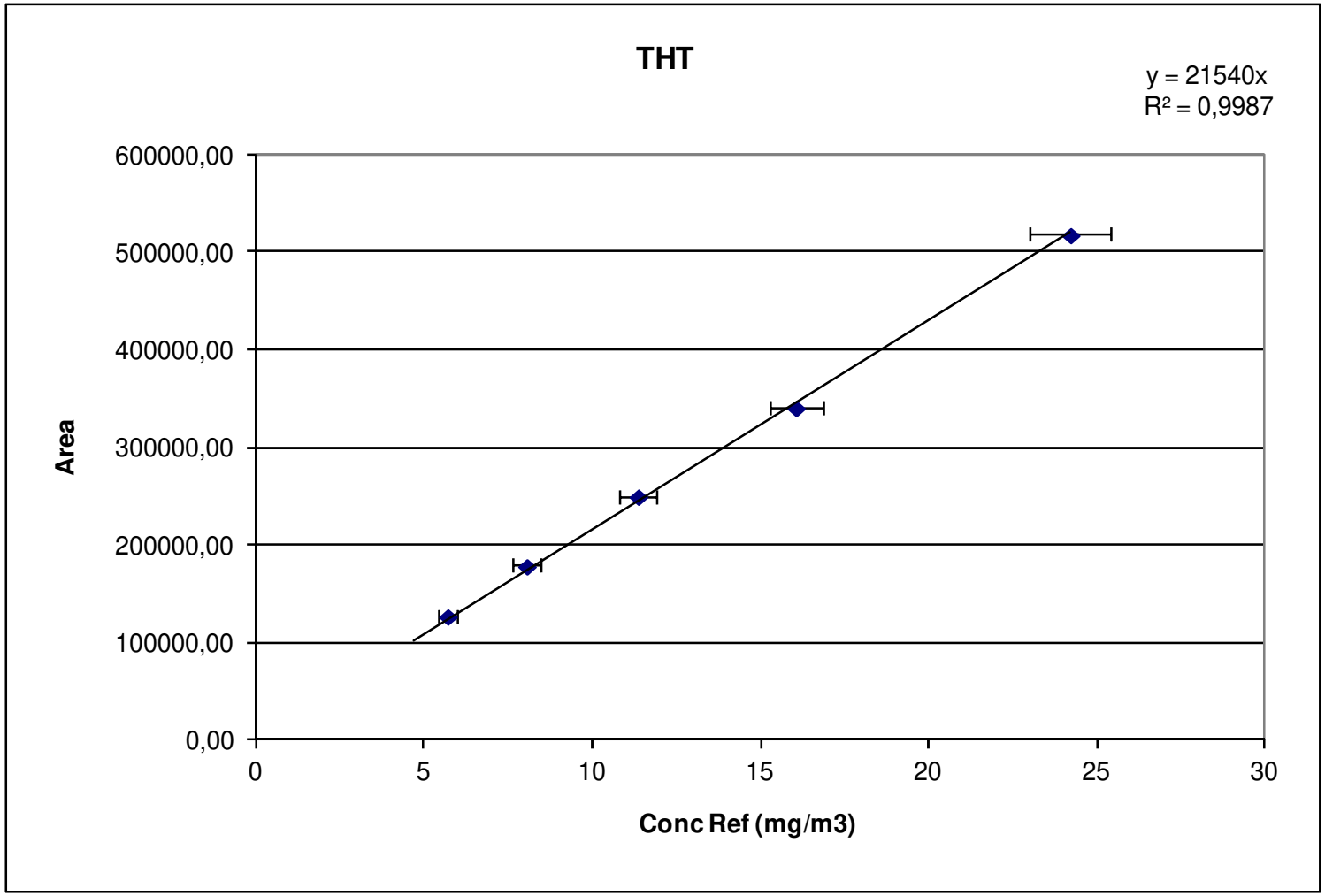


20 measurements are performed.

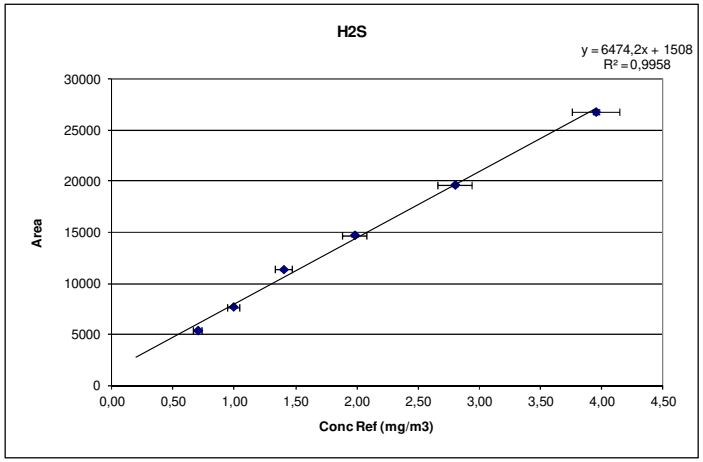
Stability tests

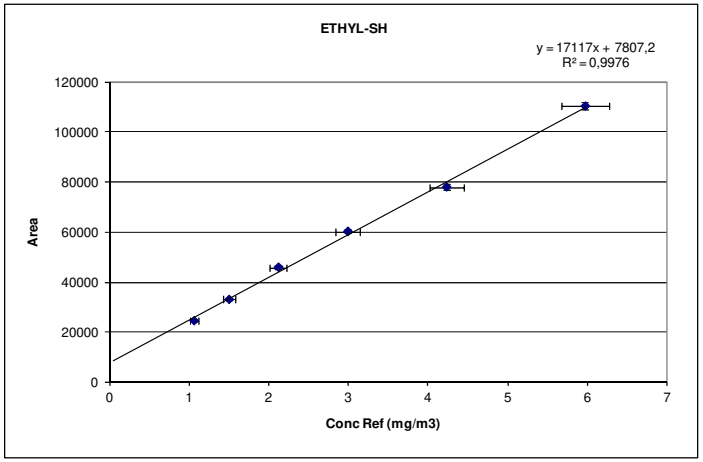
	Concentration (mg/m3)						
	H_2S	MM	EM	IPM	TBM	THT	DMS STD
Mean	3,16	9,06	6,02	8,05	5,18	27,20	6,04
SD	0,011	0,031	0,072	0,048	0,031	0,146	0,021
Relative Error (%)	1,50	0,84	0,21	2,06	0,96	0,51	0,19
Repeatability (%)	0,72	0,68	2,38	1,20	1,21	1,07	0,71
Reference concentration	3,11 (+/-4%)	9,14 (+/-4%)	6,01 (+/-4%)	8,22 (+/-4%)	5,13 (+/-4%)	27,06 (+/-4%)	6,03 (+/-10%)

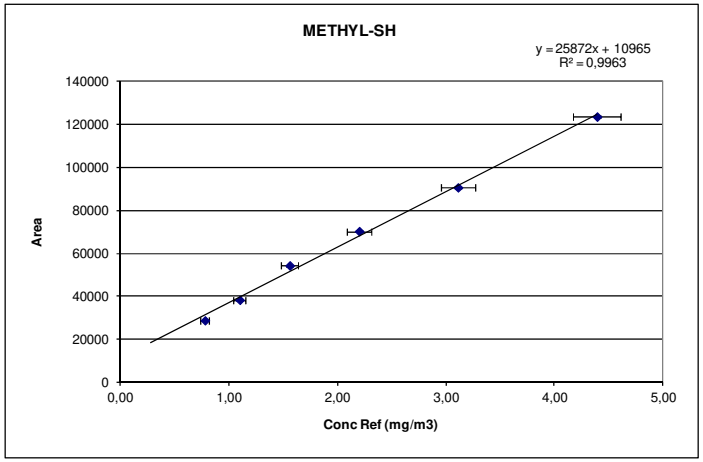
Linearity tests

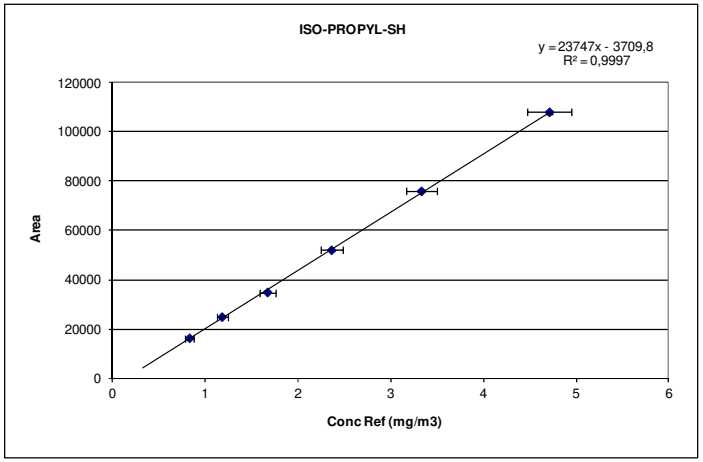


Linearity tests









Linearity tests

	Repeatability (%)		Relative reproducibility (%)	
	Performance criteria	Obtained value	Performance criteria	Obtained value
H_2S	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®

energyMEDOR® 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

energyMEDOR®
Ref: M42022

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CHROMATOTEC APPLICATIONS FOR NATURAL GAS AND GASEOUS FUELS MARKET

- NG Sales metering station/ Custody transfer
- Pipeline integrity monitoring
- Natural gas odorisation control
  - Odorant verification
  - Odorant injection control
- LPG odorisation control
- NG/LNG/LPG deodorization control
- Thermal power plant turbine integrity
- Liquid hydrocarbons: diesel / crude oil / condensates quality control

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

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

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

ODORISATION 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 H2S 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.

ODORISATION 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

ODORISATION CONTROL 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

ODORISATION 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

ODORISATION CONTROL REQUIREMENTS

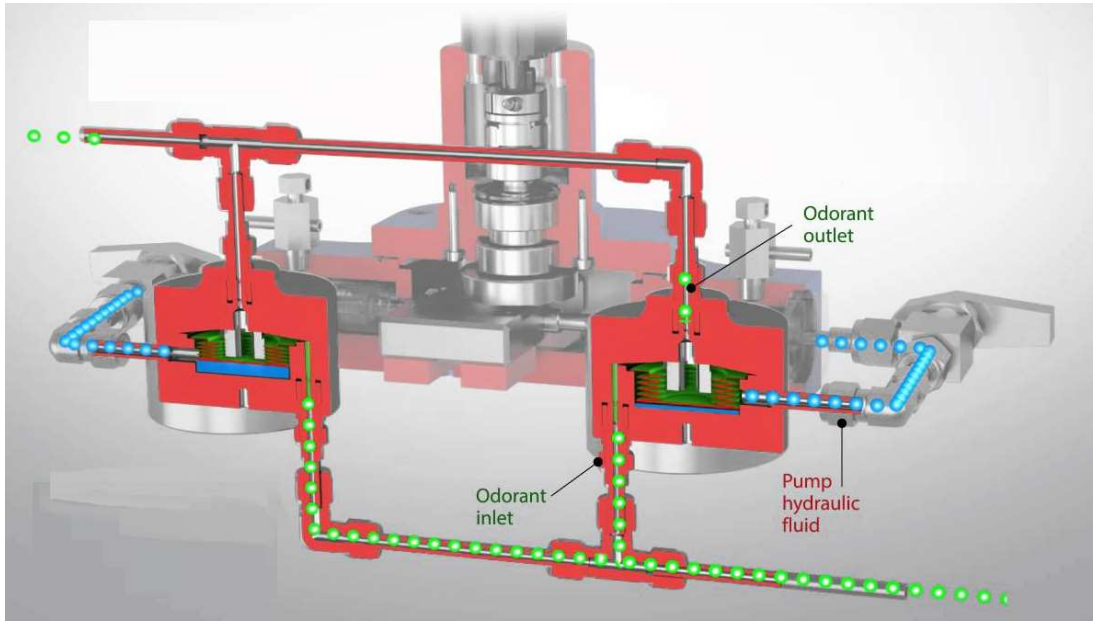
NG is required to be readily detected by a person with a normal sense of smell. To achieve this, Odorant is injected into the natural gas in a mass ratio between 0.5-1.0#/MMCF of gas (8 to 16 mg/m3).

- There are 2 suppliers of odorant in the NA market
  - Arkema (spotleak) 7 grades
  - Chevron Phillips (Scentinel) 21 mixtures

ODORISATION CONTROL APPLICATIONS

The energyMedor is used for 2 applications:

- Odorant verification
- Odorant injection control



ODORISATION CONTROL APPLICATIONS

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)

ODORISATION CONTROL APPLICATIONS

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.

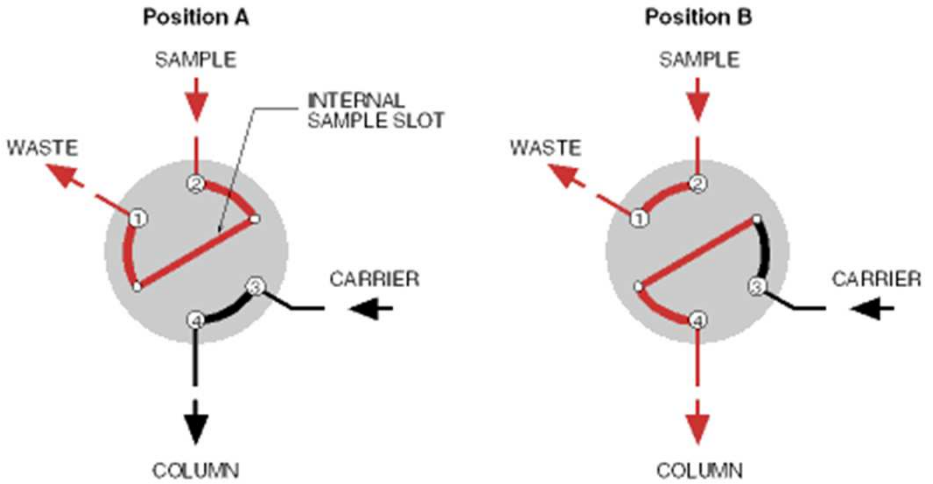
LPG APPLICATION

- 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

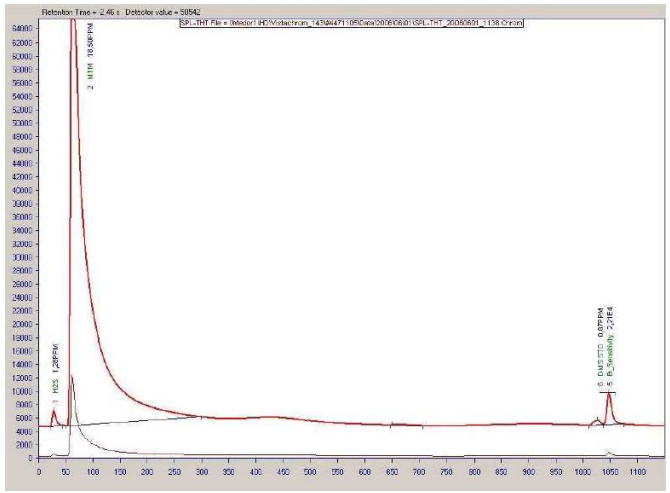
- 2 position Valve regulated in temperature and conctroled by Vistachrom allow :
  - vaporisation of LPG using very low volume :
    - egual or less than 1 µl
    - Advantages:
      - very low consumption of liquefied gas
      - representative sample analysed



LPG ODORISATION

LPG odorisation control for human safety:

- **Ethyl-Mercaptan is used to odorized LPG in ppm range**
  - **energyMEDOR ppm analyze automatically with validation Ethyl-Mercaptan**



LPG DEODORISATION

storage → tower → storage (products)

Molecular Sieves

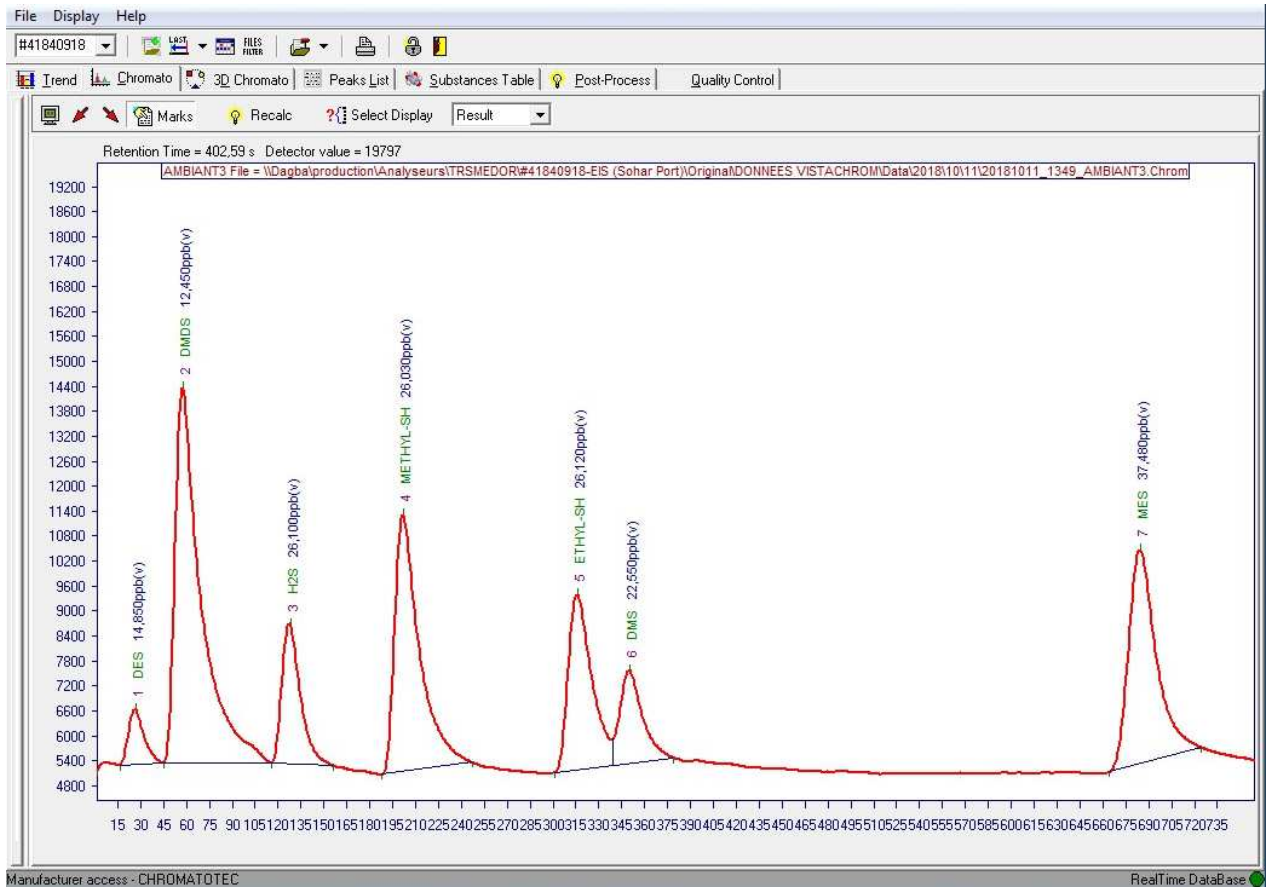
Deodorized=De-sulfurized (low ppb level)

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

PPB ANALYSIS OF SULFURS



DEODORIZED LPG APPLICATIONS

AEROSOL

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**

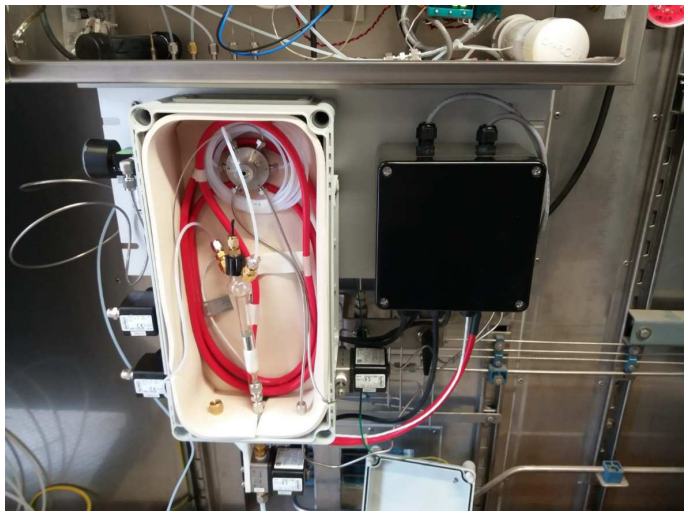
SULFURS IN LIQUID HYDROCARBONS: DIESEL / CRUDE OIL / CONDENSATES

Quality control of liquid hydrocarbons:

diesel

crude oil

condensates



- With liquid sampling system to extract dissolved sulfur and H2S/TS MEDOR

Outline

- MEDOR® technical introduction
- Different versions
- Performance test
- Applications for natural gas and gaseous fuels
- chromENERGY / chromaTCD
- Peripherals
- Customer reference

chromENERGY

Specific instrument dedicated to hydrocarbons measurement in natural gas

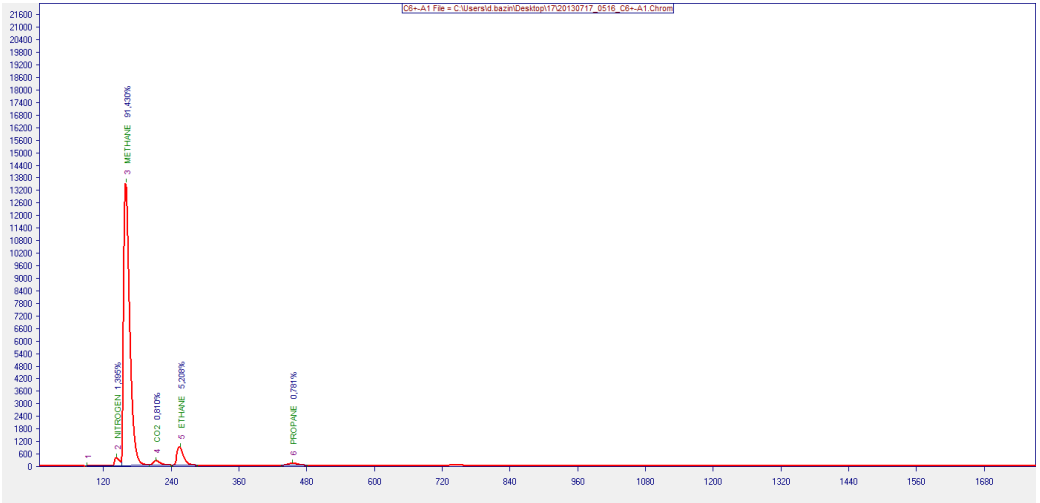
The instrument is composed by:

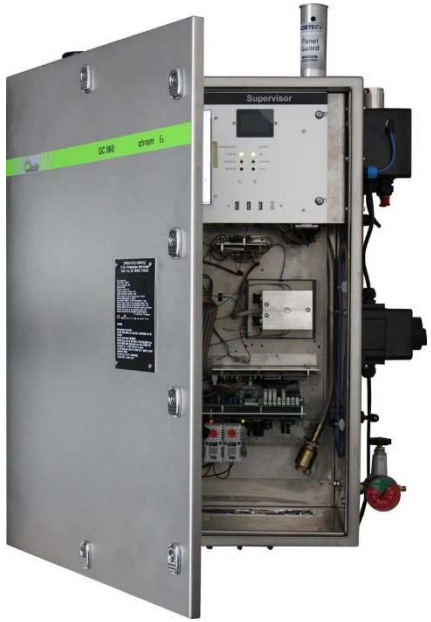
- GC-TCD detector
- Loop
- Columns for separation
- Embedded supervisor with Windows 7 based computer
  - Specific software module for:
    - Calorific values
    - WOBBE index
  - Possibility to receive data from other analyzer: flowmeter, T° , P° etc.
  - Total energy calculation
  - Communication of the data by Modbus
- Possibility to adjust result units

chromENERGY

Measure of the 11 main components of natural gas: C1 to C6+
Calculation of calorific value following ISO 6976

Substance	Result	Unit	Start (s)	R.Time (s)	Max	Stop (s)	Area	Type	FWMH
NITROGEN	1,395	%	136,70	143,70	483	152,20	3640,2	ST	10,30
METHANE	91,431	%	152,20	160,60	13646	201,65	168704,0	E	11,20
CO2	0,810	%	201,65	213,20	331	239,40	3075,8	ST_E	12,80
ETHANE	5,208	%	242,40	256,00	1006	287,00	12578,8	ST_E	12,70
PROPANE	0,781	%	434,60	455,15	207	480,50	2184,5	ST_E	19,50





Outline

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CHROMATOTEC complete solution for hazardous area

- Gas generator
- Sampling
- Temperature control for analyzers
- Exemple of integration

Gas Generators

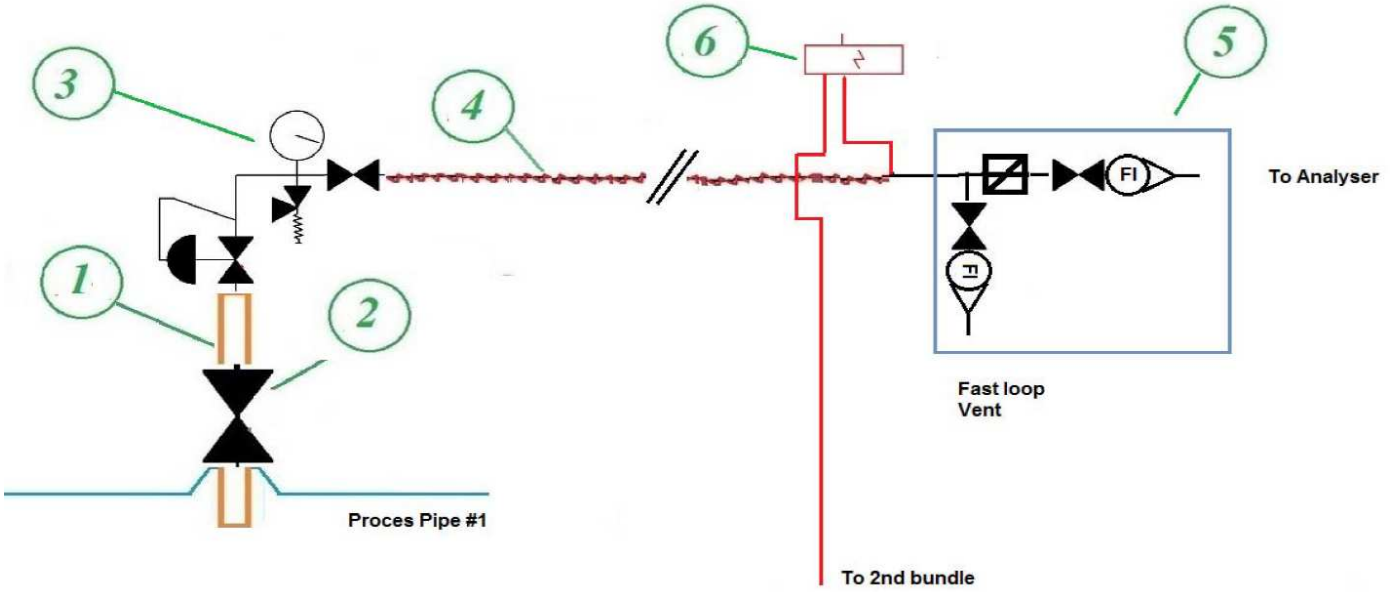
- MEDOR® is a fully autonomous autoGC-ED with
  - embedded nitrogen generator wall mounted
  - internal calibration
  - No cylinder are required for operation
  - Very simple installation

- MEDOR® Exp required only power supply and instrument air for purge and for nitrogen generator inlet

- MEDOR® Exd required only power sypply
  - Nitrogen generator can have ATEX compressor or instrument air can be used

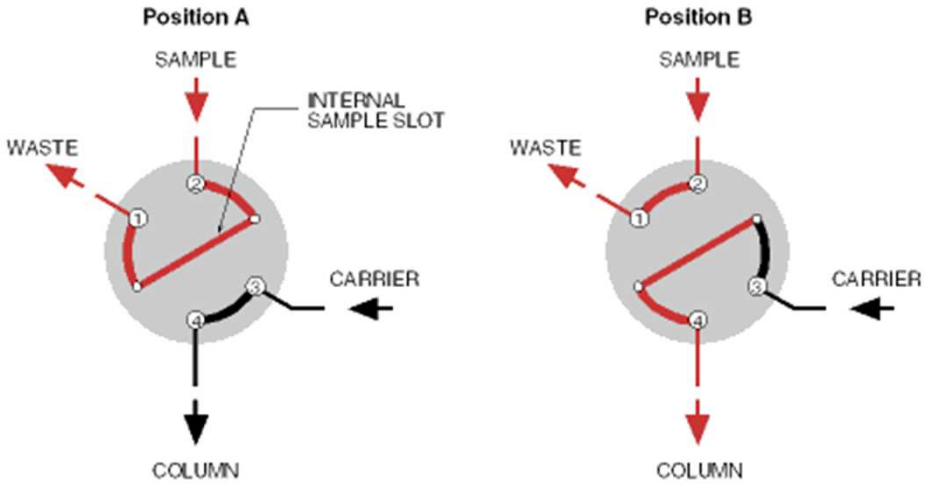
Sampling

- Sampling system from the probe to the analyzer designed with a french partner
  - For natural gas



Sampling for LPG and/or high concentration

- 2 position Valve regulated in temperature and conctroled by Vistachrom allow :
  - vaporisation of LPG or liquifed gas using very low volume :
    - egual or less than 1 µl
    - Advantages:
      - very low consumption of liquefied gas
      - representative sample analysed
  - Injection of very low volume for high concentration of sulfurs :
    - very high ppm or % range
    - Advantages: no need of dillution gas



Temperature control for analyzers

- **ATEX Air conditioned cabinet for analyzers integration**

Advantages:

- stability of temperature
- need only electricity
- High level of protection for analyzer, cylinder and sampling

Disadvantage:

- Need a cabinet
- price

Temperature control for analyzers

- **VORTEX cooler system**

Advantages:

- price
- no need of external cabinet

Disadvantages:

- Air consumption (several hundreds liter/min)

Operation with ambient temperature up to + 55° C

- **Internal heater**

Operation with ambient temperature down to – 20° C

- **Purge controller**

Additional purge flow when high temperature is reached

Operation with ambient temperature up to + 40° C

Autonomous solution

- MEDOR Ex and chrom Ex range work on 24 V DC
- Internal nitrogen generator controlled by MEDOR and certified for hazardous area:
  - Using instrument air or with ATEX compressor

- Work with solar panel

Key benefits & conclusions

Embedded Supervisor Windows® based

- All technical data stored in Real Time Data Base
- Remote control access for easier maintenance
- Intelligent system with tunable and interactive alarms levels
- Full traceability with on board archiving of results and chromatograms
- QC Set up and control of threshold alarms
- Data export by MODBUS / 4-20 mA / 0-10 V
- Time stamp results

CHROMATOTEC historical sales for hazardous areas

Protection mode EX p

•CSA us Field certification* Class 1 division 2 in June **2009**

Instrument installed in California USA for odorisation control

•CSA international Field certification* Class 1 division 2 in January **2012**

Field Certification
Certificate of Compliance

Certificate: 2497230 Master Contract: 255145

Project: 2497230 Date Issued: March 7, 2012

Issued to: Chromatotec
15 route d'artigalongue
32240 ln ANTOINE
FRANCE
Attention: Mr Dupuy Pierre

The products listed below are eligible to bear CSA Field Certification Labels, bearing the CSA Mark shown with adjacent indicator 'US'.

US

Issued by: E Gnerb
T. Gnerb

PRODUCTS

Class No: 2258 82 PROCESS CONTROL for hazardous locations – to US requirements

Class I Division 2 Groups: C, D Temperature Code T3

Natural Gas Analyzer, Model MEDOR2X, with a type 2 purge. Electrical ratings: 230 Vac, 50/60 Hz, 1 ph, 3.15 A; Internal Volume 83.4 liters.
Minimum purge rate 50 l/hour. Minimum purge time 14 minutes, maximum release under abnormal conditions: 240 ml/minute.
Ambient temperature range: +5°C<Ta<+40°C

1 CSA Field Certification Label LI104725 issued for serial number 46980112
Location: Singapore LNG Tank Terminal

Instrument installed in Singapore LNG terminal for odorisation control

** Field certification : Certification by unit after production. Need to perform a certification for each unit.*

CHROMATOTEC historical sales for hazardous areas

Protection mode EX p

- CSA international Class 1 division 2 in January **2013**

Instrument installed in United Emirates at metering station after refinery

- ATEX zone 1 Field certification in **2014** with VORTEX cooler of **6 MEDOR Ex**

Instruments for LPG process control

CHROMATOTEC historical sales for hazardous areas

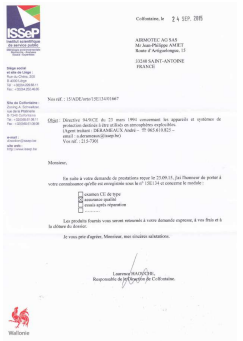
Protection mode EX p

- CSA us energyMEDOR Exp in 2014
- ATEX zone 1 Type certification* in **2015**
  - Type certification number 15E135
  - ATEX quality assurance certification number 15E134

Instrument for South California Gaz USA, odorisation control

- CSA us Field certification Class 1 Division 2 December **2015**

Instrument for odorisation control at metering station,



Instrument for South California Gaz USA,
odorisation control

**Type certification : the production (Chromato-Sud) is certified to produce ATEX zone 1 and 2 certified instruments. No need to certify each instrument after production they are already certified.*

Some customer reference

Singapore LNG terminal:

- **Unloading metering of LNG terminal**

  - **THT MEDOR in hazardous area**

Some customer reference

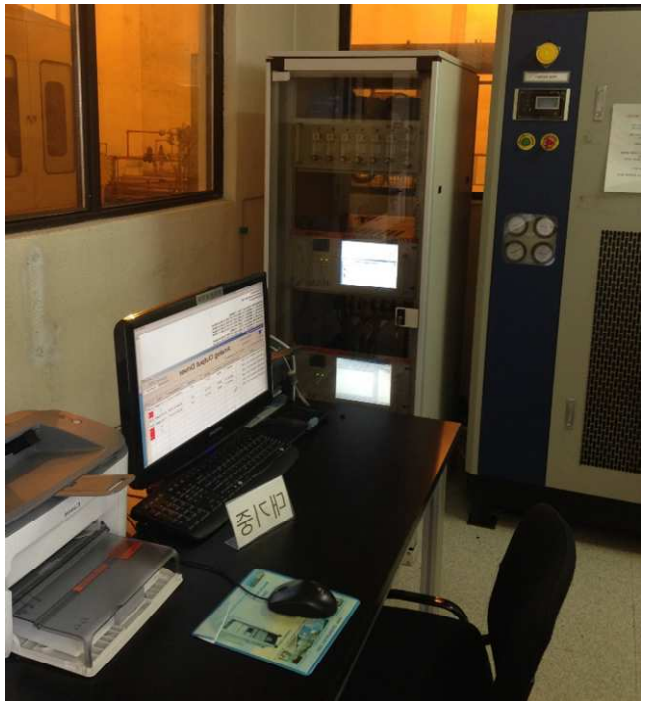
Odor in ambient air in Chile at LPG odorization station: GASMAR

TRS MEDOR Exd for odor in ambiant air at ppb level

Some customer reference

Odorisation control in South Korea at Kogas

2 MEDOR with 6 streams multiplexor



Some customer reference

- Thermal power plant in Tunisia

H2S TS MEDOR high ppm for turbine integrity protection

Société Tunisienne de l'Électricité et du Gaz

الشركة التونسية للكهرباء والغاز

Some customer reference

- Natural gas Sales metering station in Egypt

H2S TS MEDOR 0 - 10 ppm

Some customer reference

- Condensates Sales metering station in Egypt

H2S TS MEDOR 0 - 10 ppm
with liquid sampling system

Some customer reference

energyMEDOR Exd ATEX

- **H2S, mercaptans, Total Sulfur in sales metering station**
- **Flameproof certified version**

Amber Grid

CHROMATOTEC® GROUP
Expert in gas analysis

Some customer reference

Conclusions

- Chromatotec is the provider of autoGC analyzers with calibration, sampling device, shelters and generators
- Chromatotec will provide full support to his partners for on-site installation and application
- Chromatotec develop in continue his product for oil and gas application

Conclusions nat. Gaz

- Detectors are highly sensitive to sulfur compounds at ppm or ppb level
- Very clear separation of the compounds
- Instruments are fully automatic rugged industrial analyzers that need very low maintenance.
- All in one solution for Gas Monitoring with pack energyMEDOR & ChromEnergy
- Complete solution for natural gas analysis
- Good stability of the results and a validation of the results with standard permeation tube.

energyMEDOR
Ref: M41022

ChromENERGY
Ref: C42022

CHROMATOTEC® GROUP

Expert in gas analysis

Thank you for your attention !