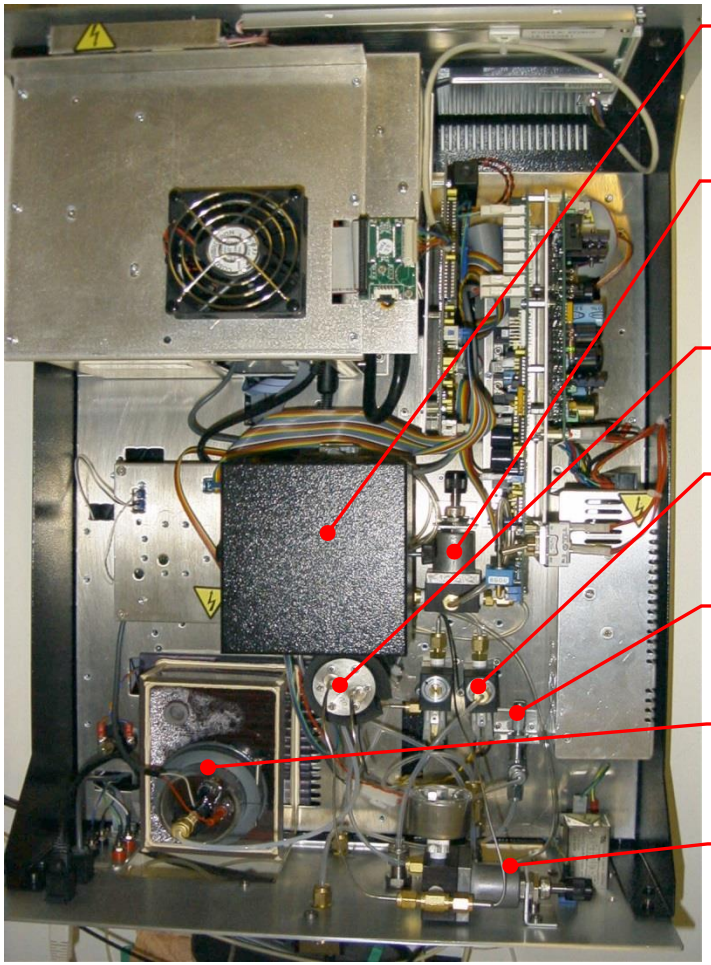
Natural gas and sulfur compounds analysis

Chromatotec®

Outline

- MEDOR technology
  - **Introduction**
  - energyMEDOR
  - H2S TS MEDOR
  - MEDOR COS
  - TRS MEDOR
  - airmoMEDOR
- chroma technology
  - Introduction
  - chromaS
  - chromaS COS
  - chroma FID
  - chromENERGY

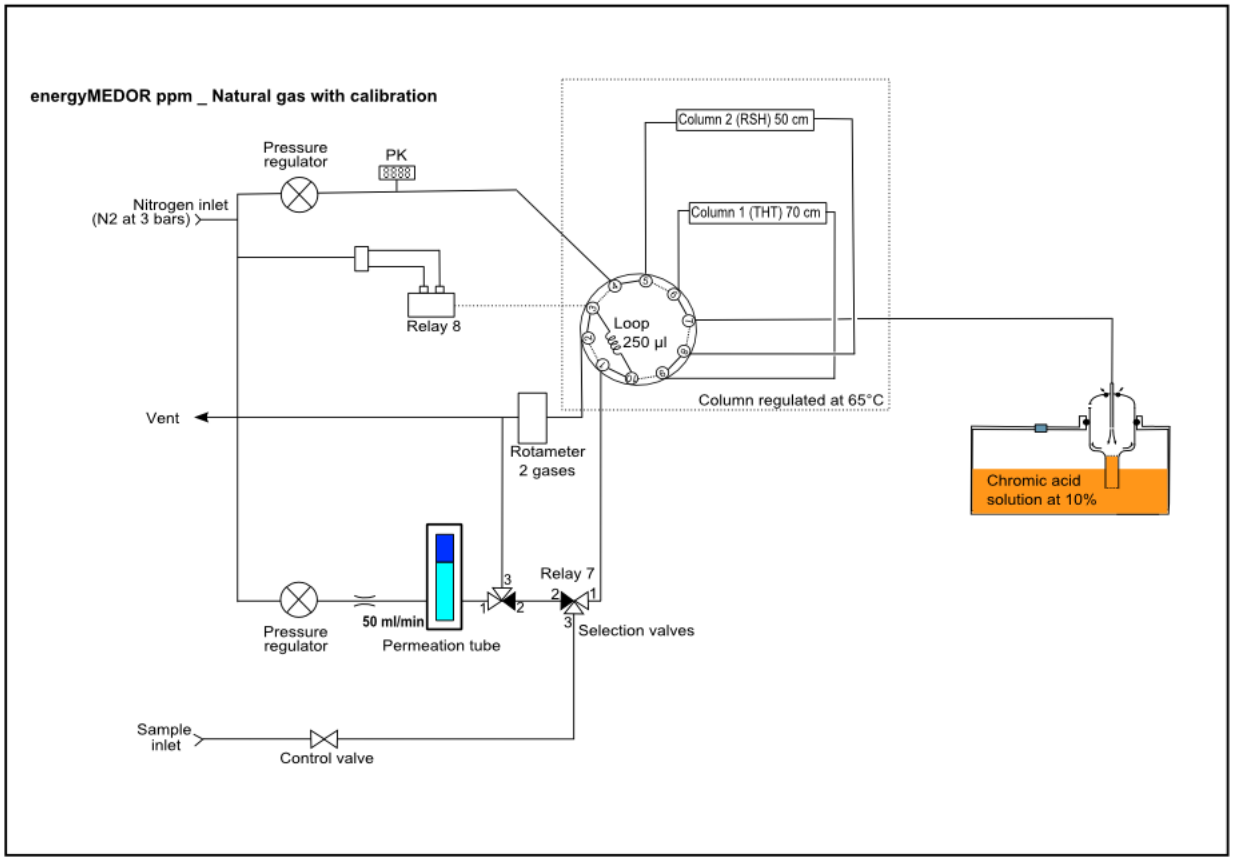
MEDOR



- Oven (inside) : injection valve, sampling loop and chromatographic column
- Pressure regulator to adjust carrier gas flow
- Calibration system (permeation tube inside the oven)
- Selection valve (solenoid valve)
- Adjustment valve to set the sampling flow
- Electrochemical detector
- Pressure regulator to adjust the flow of the calibration system

MEDOR analysis principle

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


energyMEDOR ppm _ Natural gas with calibration
Pressure regulator
PK
Nitrogen inlet (N2 at 3 bars)
Relay 8
Column 2 (RSH) 50 cm
Column 1 (THT) 70 cm
Loop 250 µl
Column regulated at 65°C
Vent
Rotameter 2 gases
Chromic acid solution at 10%
Relay 7
Pressure regulator
50 ml/min
Permeation tube
Selection valves
Sample inlet
Control valve

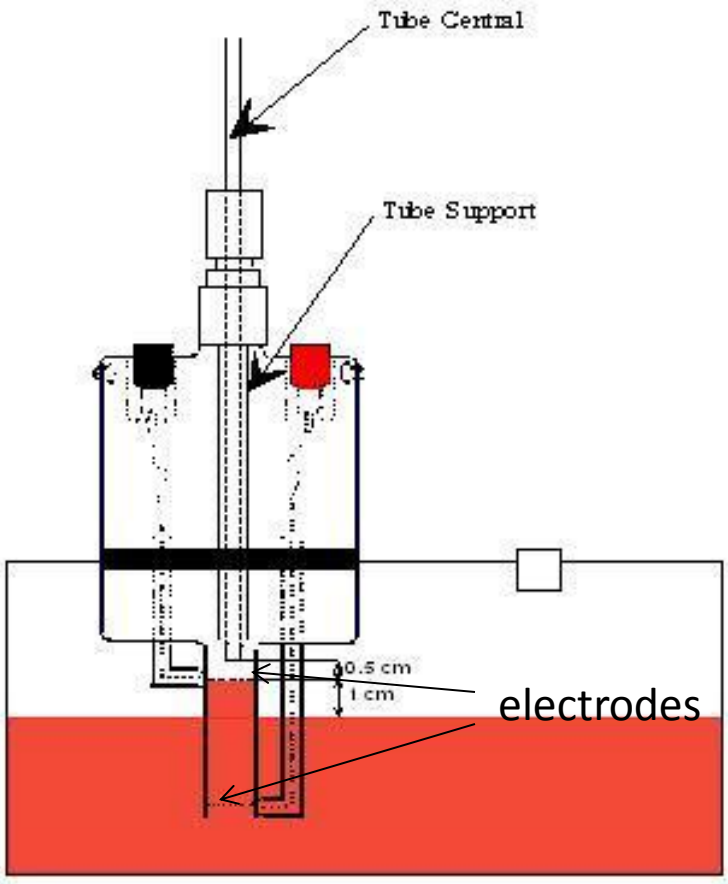
MEDOR analysis principle

- 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.

Wet Cell

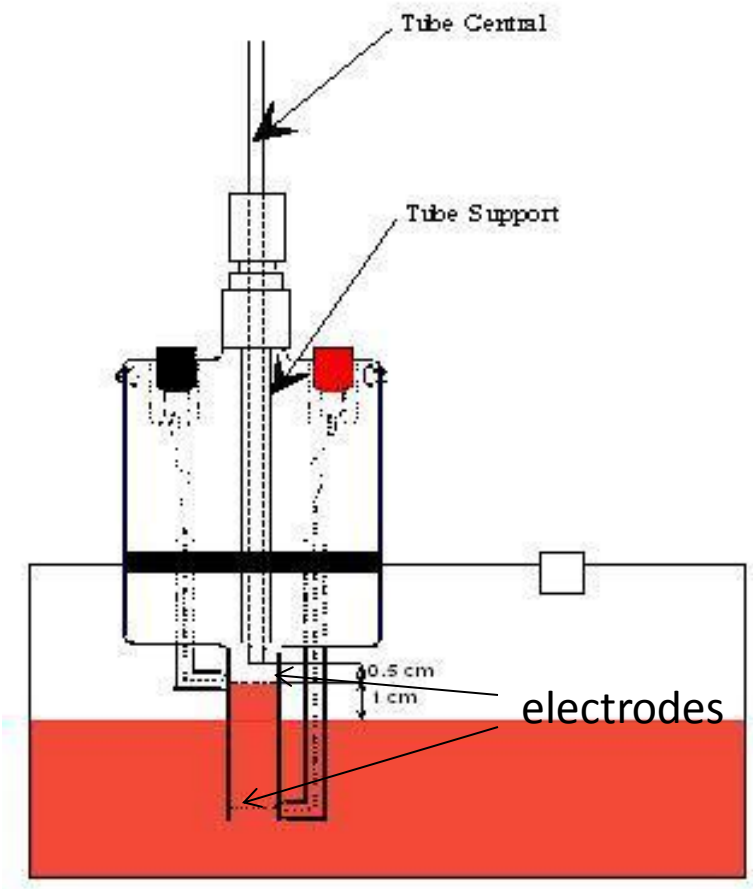


ASTM D7493-08

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.

Wet Cell

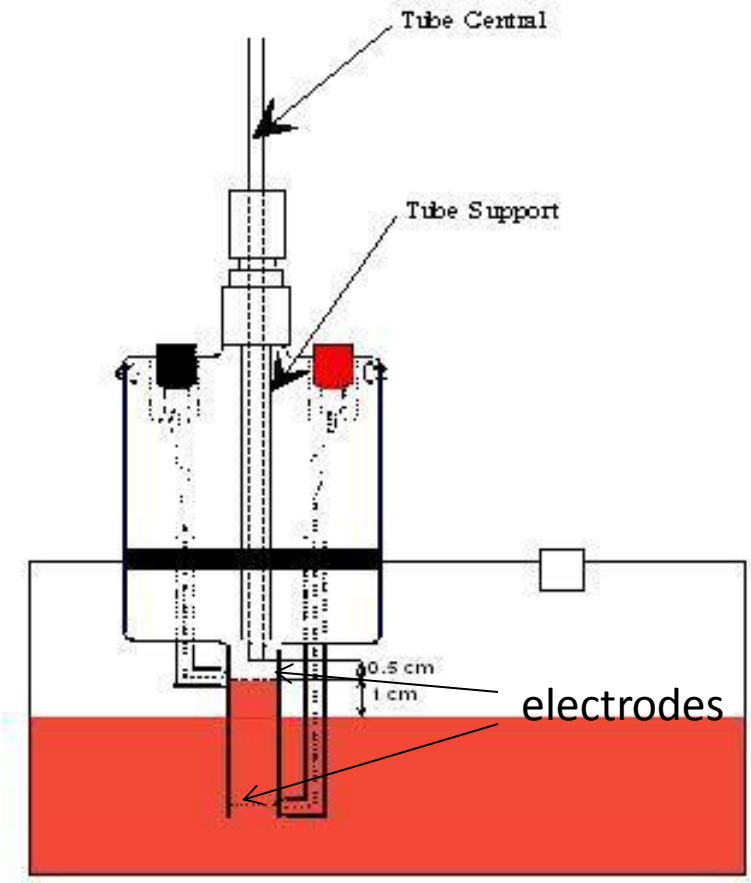


ASTM D7493-08

Technical characteristics:

- The gas flow from the GC column is discharged through the narrow tube immediately above the upper grid center.
- Each sulfure 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

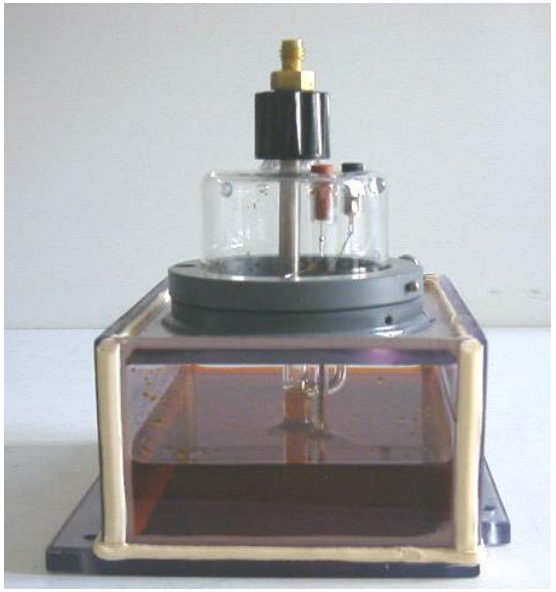
Wet Cell



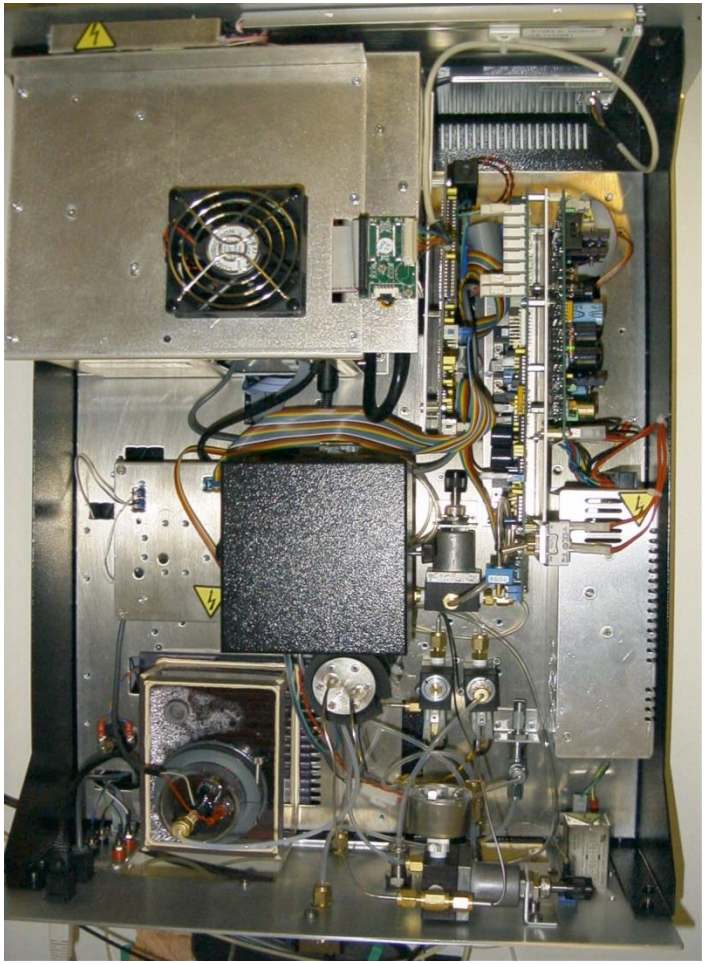
ASTM D7493-08

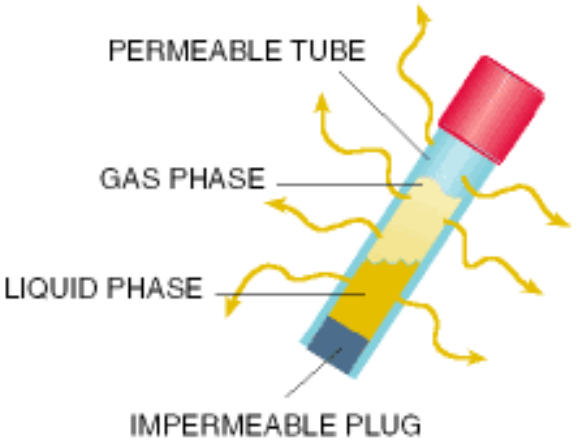
Key points:

- 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)



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!

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- ChromaS technology
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  - chromaS COS
  - chroma FID
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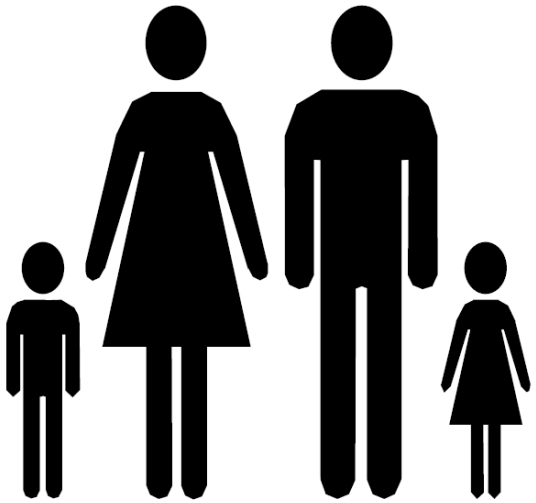
Natural gas and Biogas

- Sulfur compounds:
  - Very strong smell
  - Used to odorize gas
- Odorization process and control
  - General company for natural gas
  - Natural gas transportation
  - Natural gas storage
  - LPG company

Odorization Requirements

Why Odorize ??

To protect human life in industry and in housing!



How much odorant do we need ?

Is it possible to use the same sulfur mixture for all gases?

Causes of odor fade

Gas Quality

- Wet Gas
  - Odorant can dissolve in condensed hydrocarbons resulting in “odor fade”

Pipeline condition

- Reaction of mercaptans with oxygen in presence of rust (iron oxide) to form non-odorous disulfides
  - ✓ One solution is to use very high amount of odorant species
    - ➢ Expensive solution!
    - ➢ Sulfur compounds are corrosive to equipment and can inhibit or destroy catalysts employed in gas processing and other end uses

Sulfur compounds can be found naturally in gas

- No need for other injection

Some sulfur odorants are reactive and may be oxidized to form more stable compounds having lower odorant thresholds which adversely impact the potential safety of the gas delivery and gas users

Odorization 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

Save a lot of money!

Sulfur analysis

On-line instruments to continuously identify and quantify individual target sulfur species in gaseous fuel with automatic calibration and validation

energyMEDOR
Ref: M42022

– **energyMEDOR**
  - Electrochemical detection
  - Carrier gas: Air
  - Sampling: Loop
  - Speciation of sulfur compounds in gas

Instruments for Sulfur analysis

energyMEDOR – *GAS application*

Instrument used as **reference** in the ASTM D7493 08

energyMEDOR
Ref: M42022

ASTM D7493 08 *: Standard Test Method for Online Measurement of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatograph and Electrochemical Detection*

Designation: D 7493 – 08

Explosive atmosphere

Instruments can be placed in hazardous environment:

CSA international for explosive atmosphere:

Ex Class 1, Div 2, Group B,C&D

(Class 1 = Flammable gases, vapors or liquids; Division 2 = where ignitable concentrations of flammable gases, vapors or liquids are not likely to exist under normal operating conditions; Group C&D = Ethylene, propane gas group).

Performance tests

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

- Analysis of 14 compounds

energyMEDOR
Ref: M42022

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.

Calculation

Measurements are carried out to evaluate the repeatability and reproducibility of the results (according to EN ISO 19739)

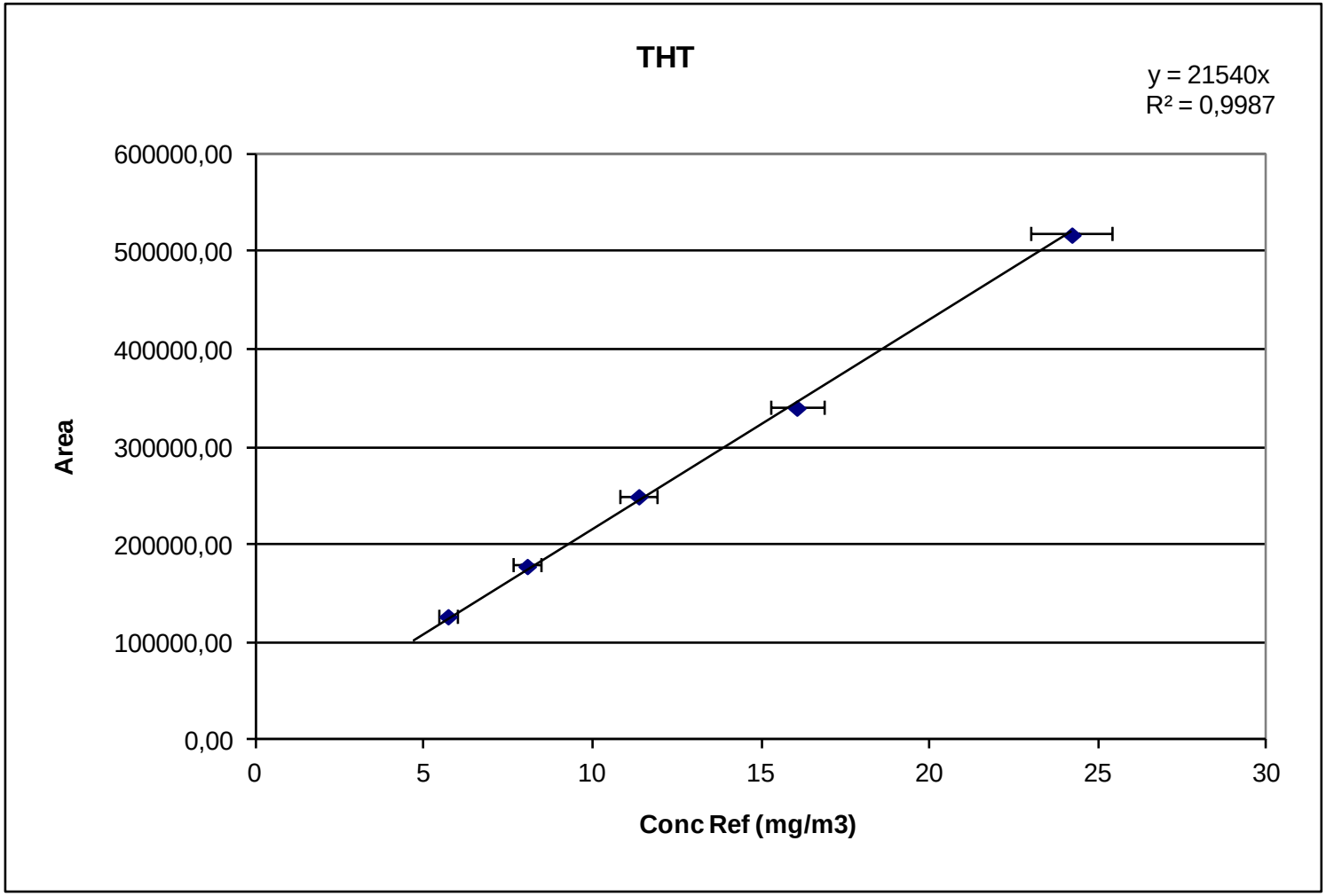
$$\text{Relative error in \%} = \frac{(\text{Mean} - \text{Reference concentration}) * 100}{\text{Reference concentration Relative}}$$

$$\text{Repeatability (\%)} = \frac{2 * \text{ Standard deviation}}{\text{Mean} * 100}$$

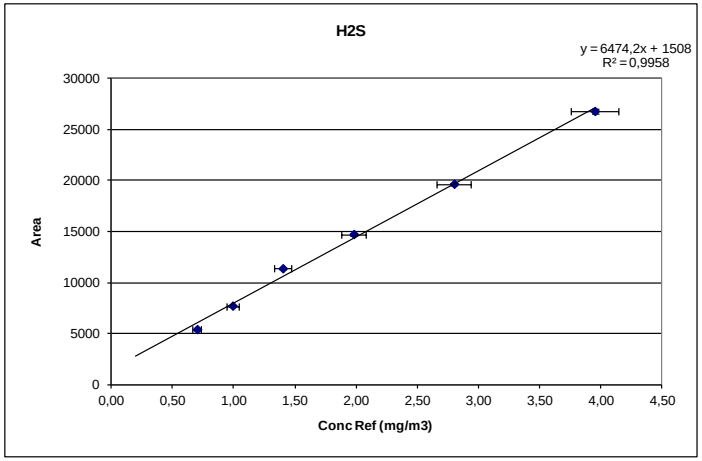
Stability tests

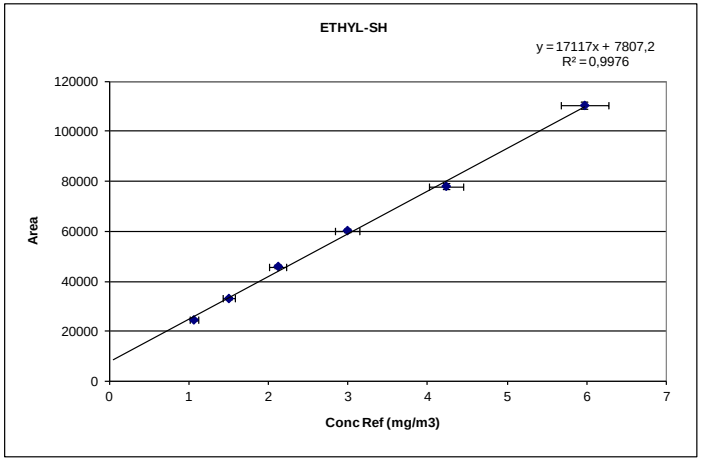
	Concentration (mg/m3)						
	H_2S	MM	EM	IPM	TBM	THT	DMS STD
Mean	3,16	9,06	6,02	8,05	5,18	27,20	6,04
Standard deviation	0,011	0,031	0,072	0,048	0,031	0,146	0,021
Relative Error (%)	1,50	0,84	0,21	2,06	0,96	0,51	0,19
Repeatability (%)	0,72	0,68	2,38	1,20	1,21	1,07	0,71
Reference concentration	3,11 (+/-4%)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

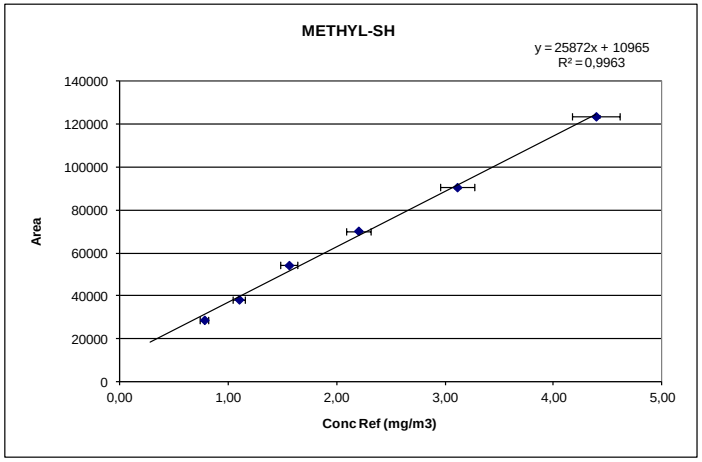
Linearity tests

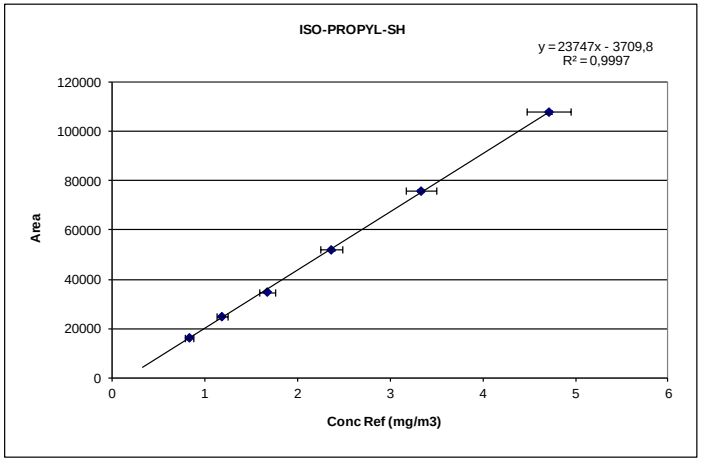


Linearity tests









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:

- Very accurate
  - Good repeatability
  - Linearity
- ppm and ppb range
- Online continuous sampling
- Very specific (no interference)
- Low maintenance
- Automatic validation

energyMEDOR
Ref: M42022

Profitability

- According to the law in the US:
  - Gas has to be odorized by gas company
  - Gas must be checked every 24 hours

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

Comparison

Disadvantage of using sniff tests:

- Needs operators to measure
- One person can smell one gas every 4 hours
- Not reliable
- No data recorded

Advantage of using energyMEDOR:

- One measurement every 30 minutes
- Reliable measurements
- Data recorded

energyMEDOR

- Prices

M31022	5U	* THT MEDOR - inbuilt computer **no sampling pump included**	25 800 EUR
M41022	5U	* energyMEDOR ppm - inbuilt computer **no sampling pump included**	32 600 EUR
M42022	5U	* energyMEDOR ppb - inbuilt computer **CALIBRATION** included **no sampling pump included**	36 400 EUR
M43000		*** energyMEDOR Ex certified (complete system)**	48 990 EUR

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  - chromaS
  - chromaS COS
  - chroma FID
  - chromENERGY

Sulfur analysis

- **H2S TOS TS MEDOR**
  - Electrochemical detection
  - Carrier gas: Air
  - Sampling: Loop
  - New Backflush system
  - H2S and TS* in two minutes
  - Standard analysis range: 0 – 3 ppm

H2S TOS TS
Ref: M51022-TS

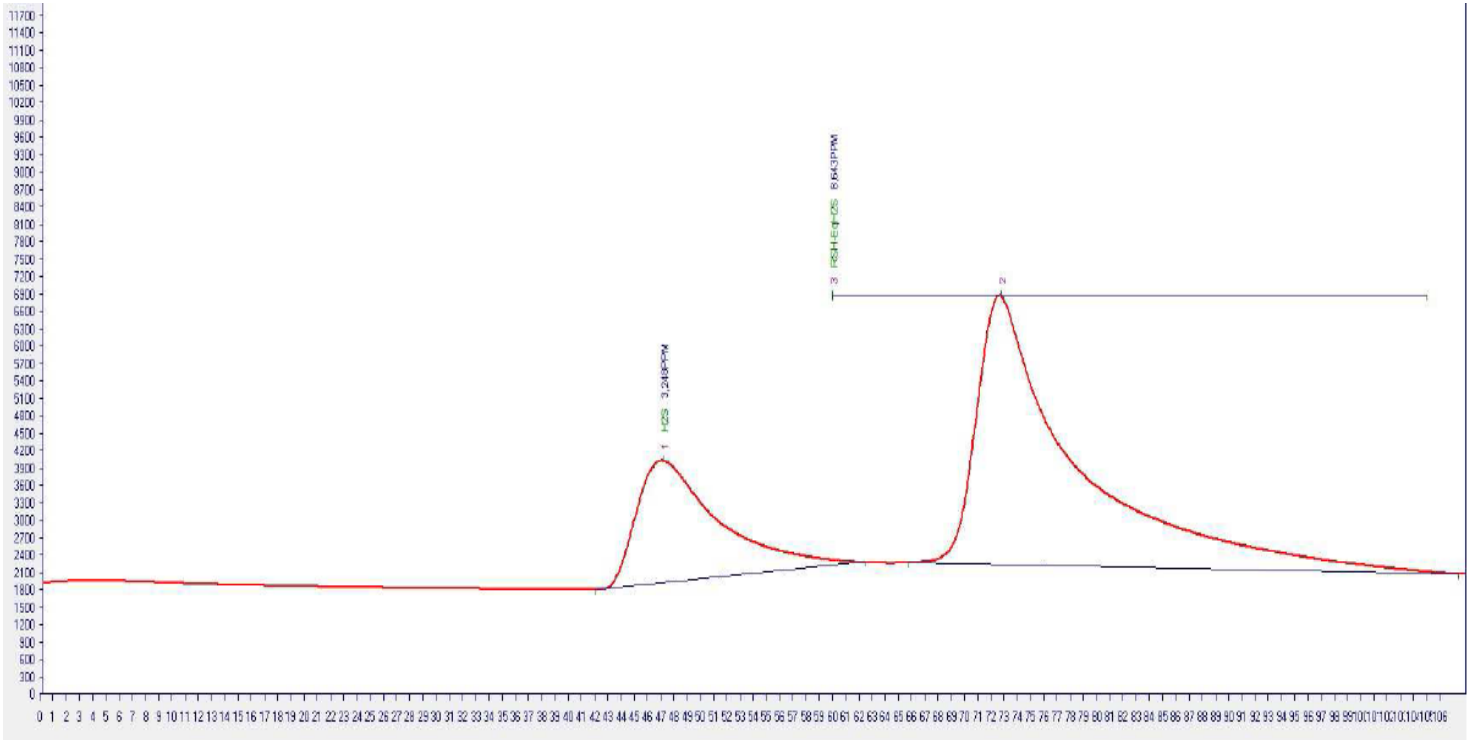
*TS: Total sulfur without COS and CS2 (not required in natural gas)

Applications

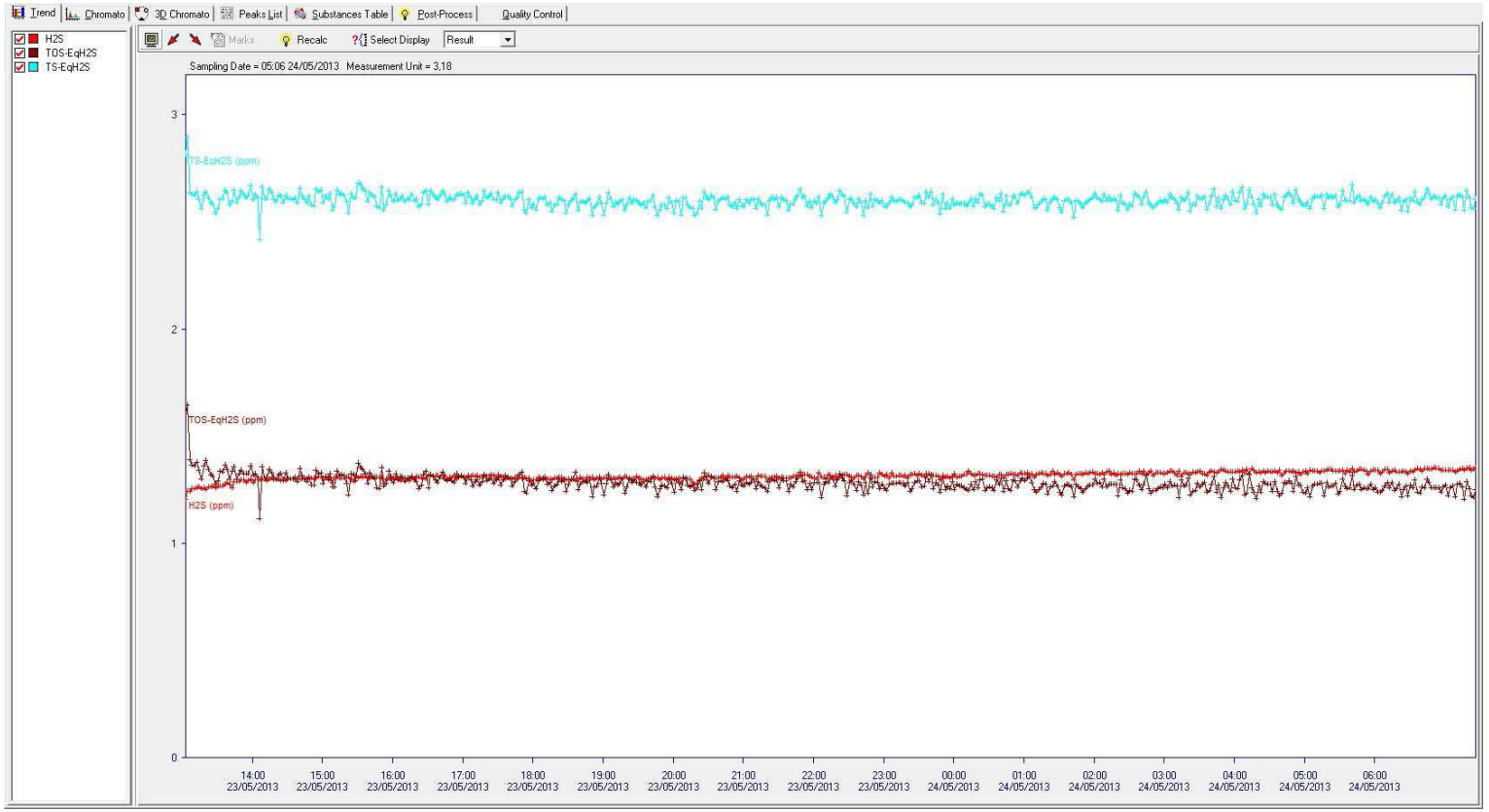
- H2S is very corrosive
  - Can damage pipelines
  - Can be present in big quantities in natural gas

Preventing natural gas containing H2S to enter pipelines can save a lot of money

Measurement of Total sulfur content in 2 minutes



Measurement of Total sulfur content in 2 minutes



Measurement of Total sulfur content in 2 minutes

Measurement of Total sulfur content in 2 minutes

H2S TOS MEDOR is designed for process control application:

- Online continuous sampling
- Very specific (no interference)
- Low maintenance
- Automatic validation
- GC instrument which Allows quantification and identification of H2S and TOS
- Fast measurement

H2S TOS TS
Ref: M51022-TS

Profitability

Gas transportation company can check the amount of H2S coming into pipelines

- Every two minutes
- Can react rapidly when H2S loaded gas gets into pipeline
- Can save a lot of money

H2S TOS MEDOR

- Prices

M51022	5U	* H2S MEDOR - inbuilt computer **no sampling pump included**	17 200 EUR
M51022-TS	5U	*** MEDOR TS (H2S-TOS) : H2S/TS/TOS**	**19 200 EUR**

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MEDOR COS

- **MEDOR COS**

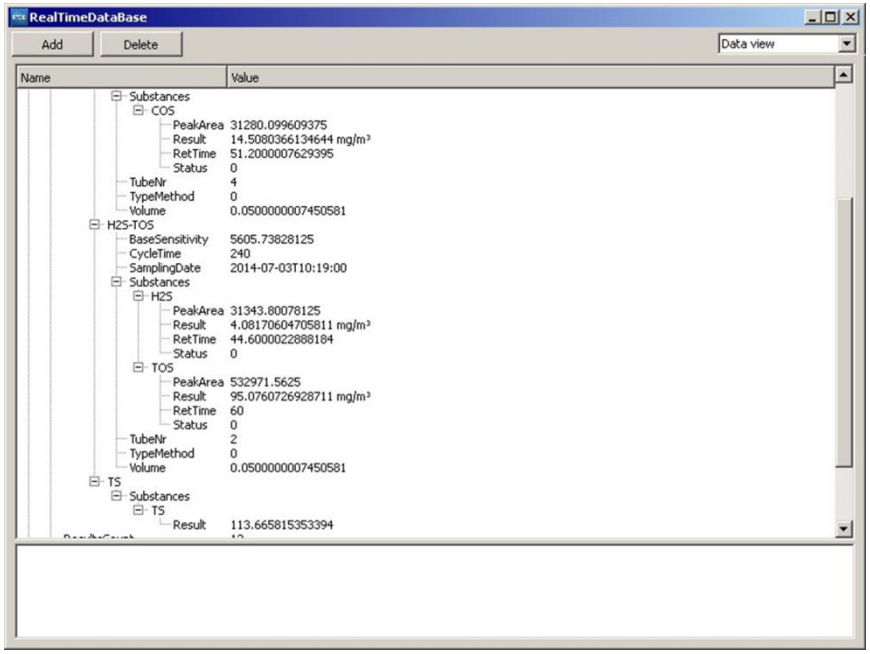
  - Electrochemical detection (using different chemical solution)
  - Carrier gas: Air
  - Sampling: Loop
  - Specific filter to removed other sulfur compounds

MEDOR COS
Ref: MXX000

MEDOR COS

– **MEDOR COS**

- Possible to have double detection system
- Complementary to H2S / TOS / TS MEDOR
- Calculation of total sulfur* concentration including COS on two methods with our new Real Time Data Base and software



*Total Sulfur excluding CS2

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TRS MEDOR

Applications :

- As a result of the confinement of the waste water stations, toxic components such as H2S increased.
- Safety of employees is major problem
- Filtering systems are used to clean pollutions
  - Constant air quality control
  - Filter replacement can be optimized

TRS MEDOR

- The TRS MEDOR, placed in this hostile and difficult environment, answered this need measuring **every 10 minutes** DES, DMDS, H2S, SO2, methyl-SH, DMS+DMDS on site.

- Coupled with a stream selector the TRS MEDOR gives the necessary data to **anticipate the time at which filters of H2S needs to be changed (one at every purification systems).**

- RESULTS :
  - increased efficiency and time gain for the laboratory assistants
  - increased safety for the technical personnel
  - better management of the filter changes with cost savings.

TRS MEDOR

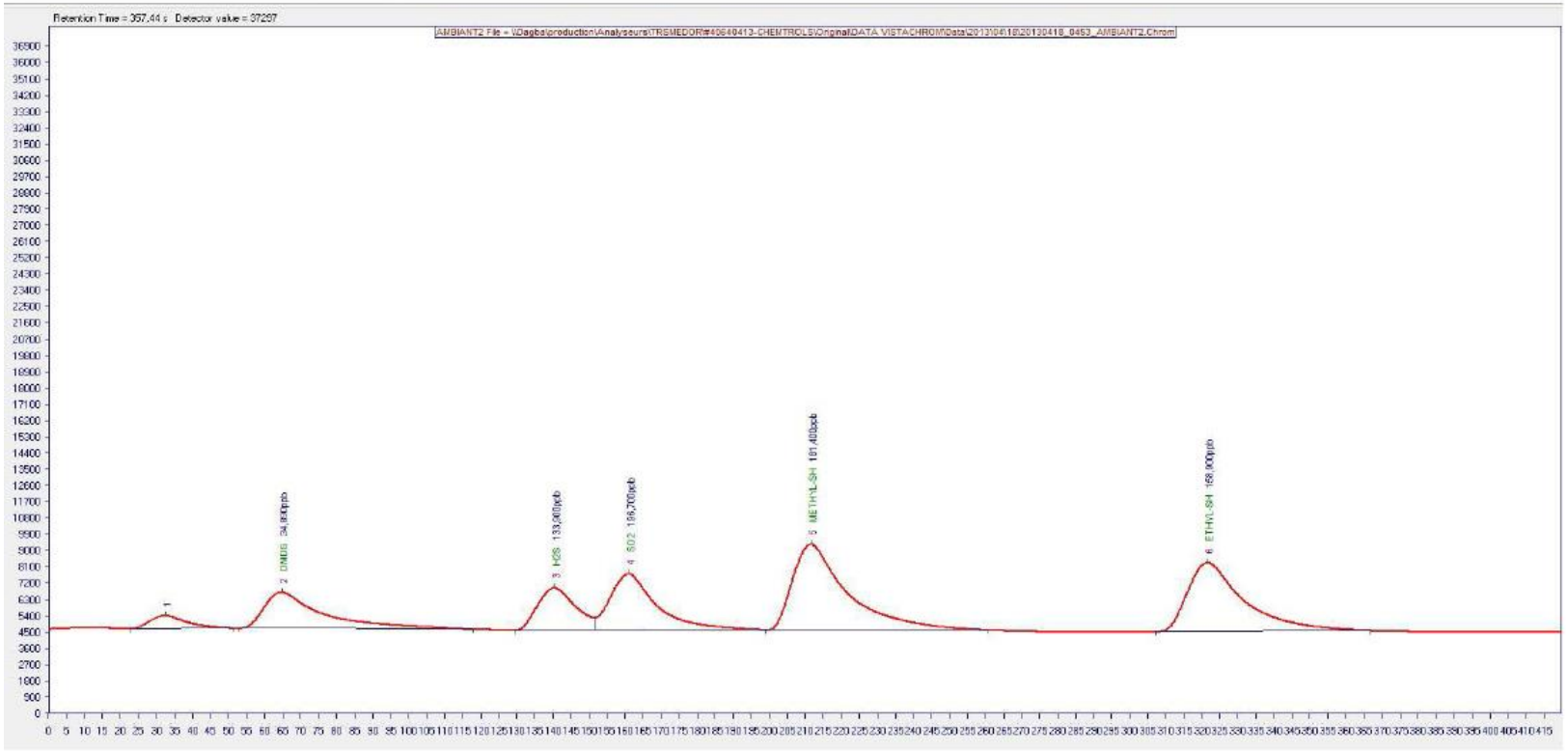
- At the point of arrival of the wastewater at the stripping area of the plant, the polluted air is captured and thereafter passed in a circuit that neutralizes it. These odors are caused by bacteriological fermentation. Successive chemical cleanings in the deodorization towers neutralize these odors.

- The bad odors are largely due to the transformation of sulfides into H2S by the bacteria in the fermentation process.

- Placed at the outlet of the stripping process, the TRS MEDOR measures the H2S concentrations and pilots the adjunction of calcium nitrate. This process allows to the bacteria to have an oxygen reserve and therefore to stop sulfate transformation into sulfides and then in H2S.

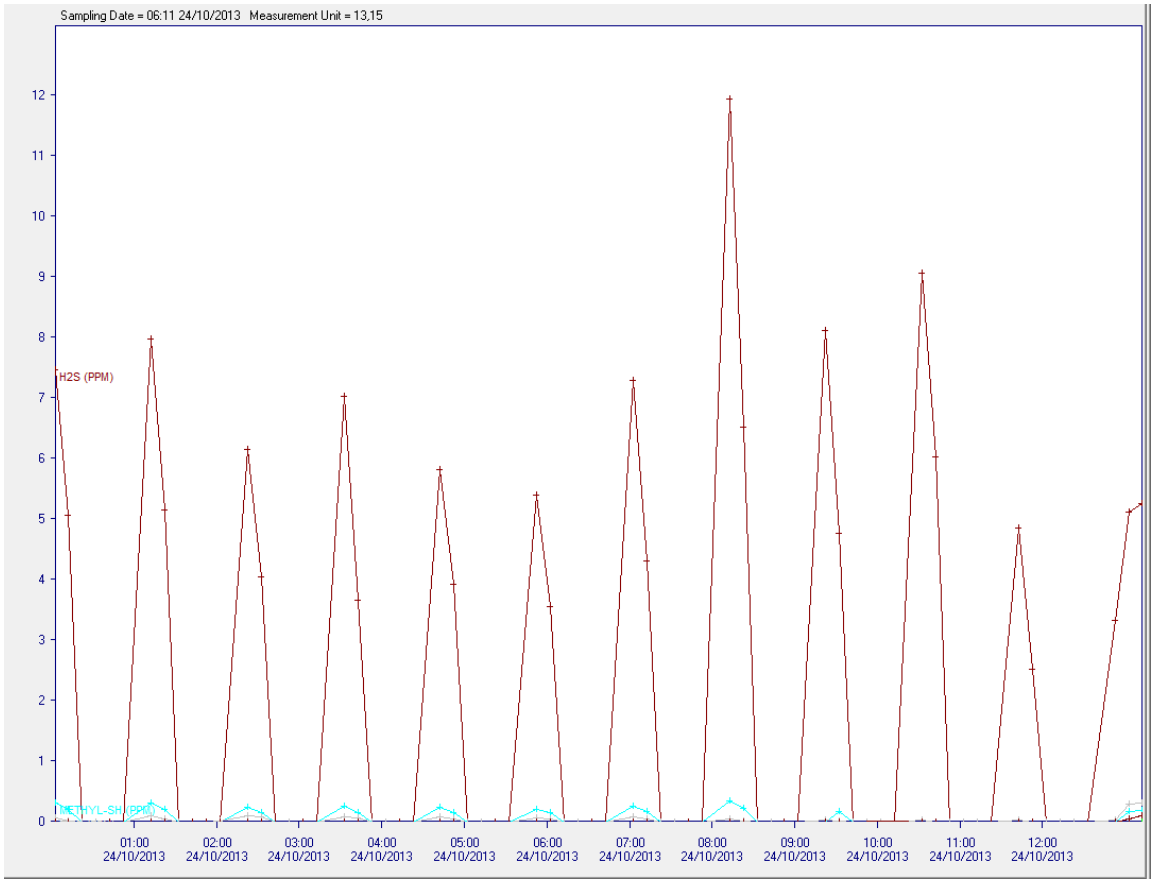
TRS MEDOR

10 minutes cycle
420 s acquisition time



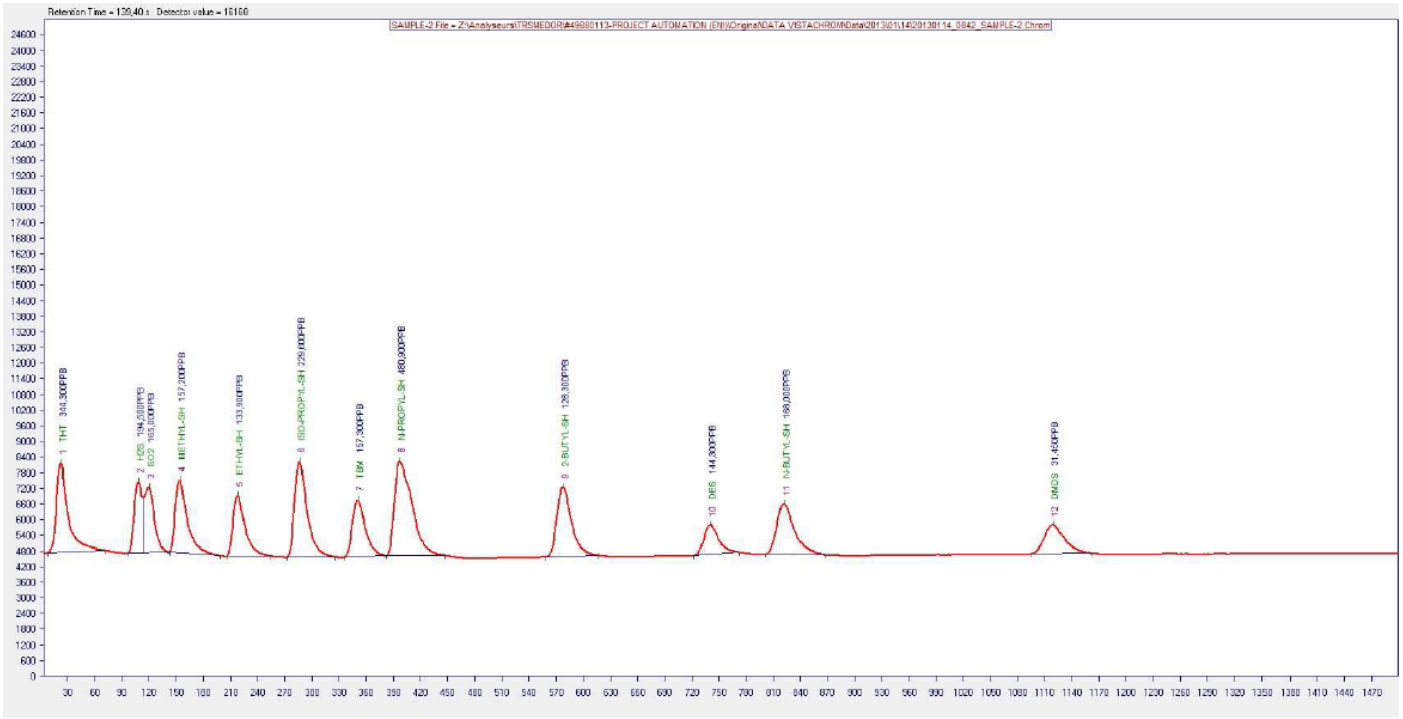
TRS MEDOR

Tests before and after air purificator system



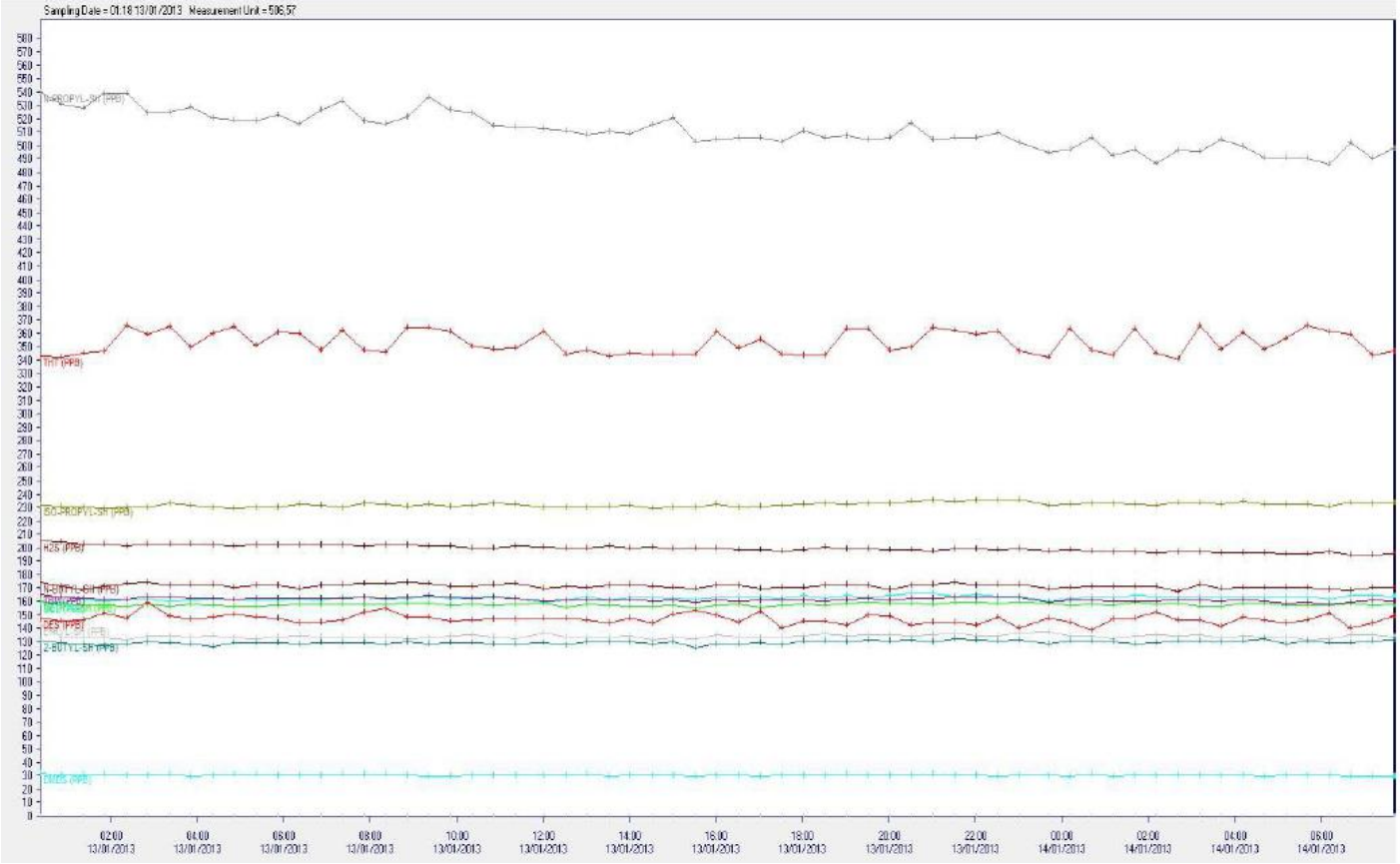
TRS MEDOR

30 minutes cycle
1500 Seconds acquisition time



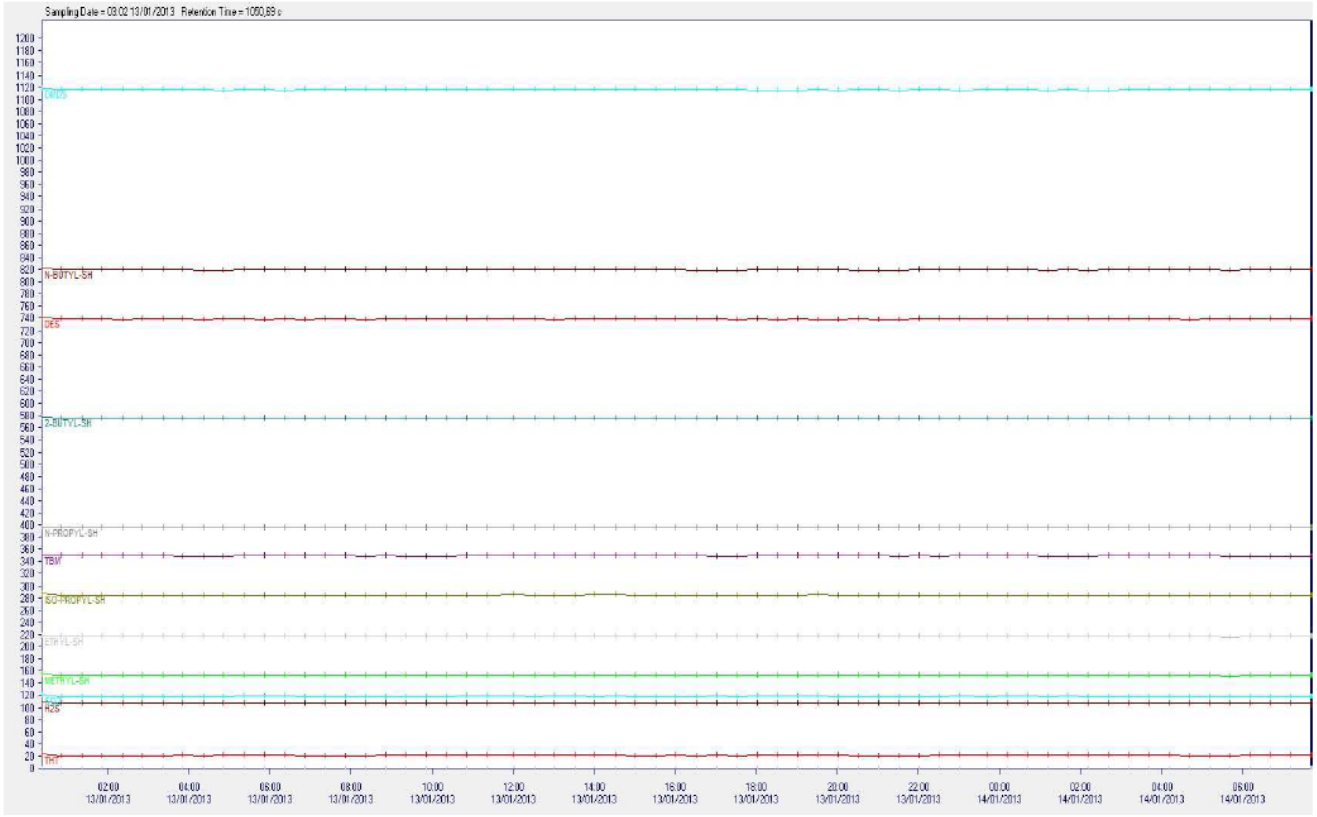
TRS MEDOR

30 minutes cycle
1500 Seconds acquisition time



TRS MEDOR

30 minutes cycle
1500 Seconds acquisition time



TRS MEDOR

Results :

- Automatic regulation of odour neutralisation.
- Time needed to technically pilot the process greatly diminished.
- Cost savings with much less calcium nitrate used.

The main qualities of the unique TRS MEDOR system are :

- Robust (utilisation in industrial environments)
- Sensitivity as of 1 ppb for methyl mercaptan.
- The rapidity of the measures (less than3 minutes for safety needs in a site exposed to H2S)
- A very stable linearity
- Easy handling
- On line monitoring
- Ease of use (manually in a laboratory with a syringe)

TRS MEDOR

- Prices

M52022	5U	* TRS MEDOR ppb- inbuilt computer **CALIBRATION** included **no sampling pump included**	26 000 EUR
M54022	5U	* TRS MEDOR ppm - inbuilt computer **CALIBRATION** included **no sampling pump included**	24 500 EUR

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MEDOR

- airmoMEDOR
  - Trap
  - Detection limit
    - < 10 ppt

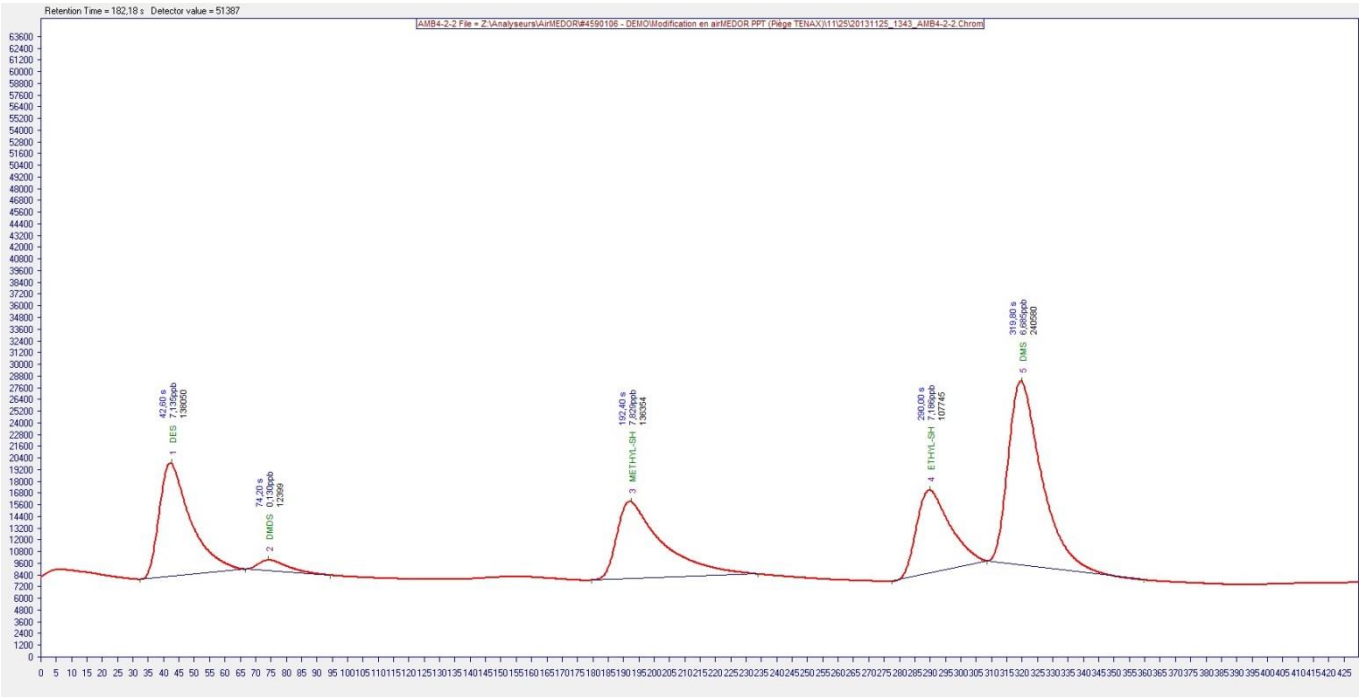
- Sulfur compounds:
  - MS
  - ES
  - DES
  - DMDS
  - DMS

- TRS MEDOR
  - Loop
  - Detection limits
    - ppm
    - ppb

- Light and heavy sulfur compounds

If minimum area is 2 000, LOQ in middle amplification (2) is

	DES	METHYL-SH	ETHYL-SH	DMS DMDS	DMDS
LOQ in ppt	100	110	130	55 0.04	20



airmoMEDOR

- Prices

M53000	4U	* airmoMEDOR ppt - **CALIBRATION** included - **(trap) See airmo range with trap ,for DMS / DMDS only**	28 200 EUR

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chromaS

Sulfur compounds analysis:

- chromaS

Detection range: 4 ppb to 100 ppm

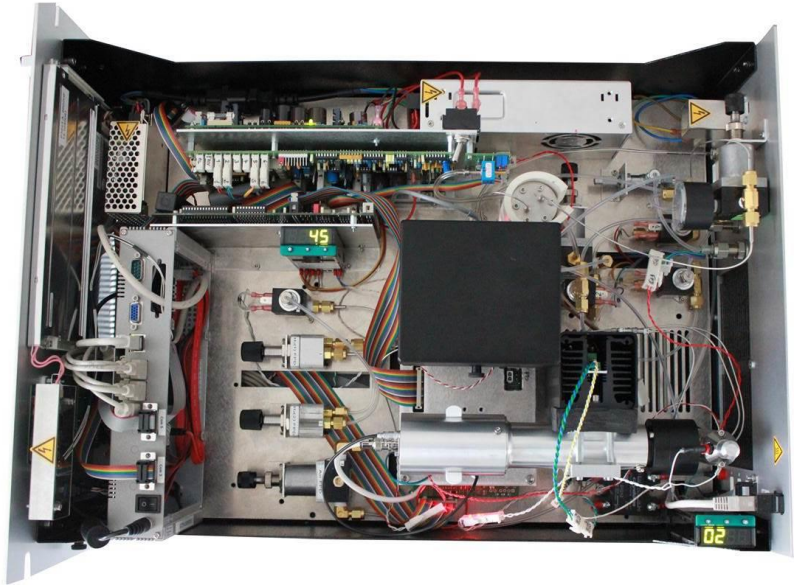
The instrument has:

- FPD detector
- Loop
- Column for separation

chromaS

Sulfur compounds analysis:

- chromaS



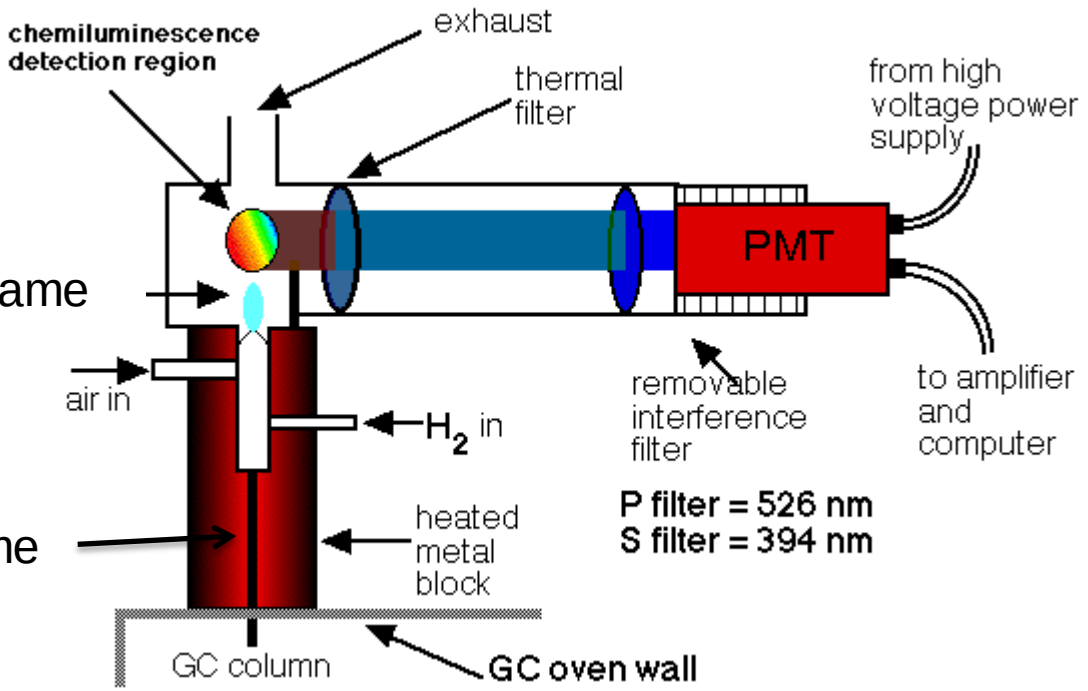
FPD detector

PMT

chromaS

Second flame: analitycal flame

First flame: Working flame



chromaS

- First flame:
  - Optimized to oxidize hydrocarbons toward carbon dioxide formation
- Second flame
  - Optimized to produce analyte chemiluminescence for measurement S_2*

➢ Reduced quenching
➢ Improved response uniformity
➢ Improved reproducibility

Anal. Chem. **2009** vol. 81, 8858-8867

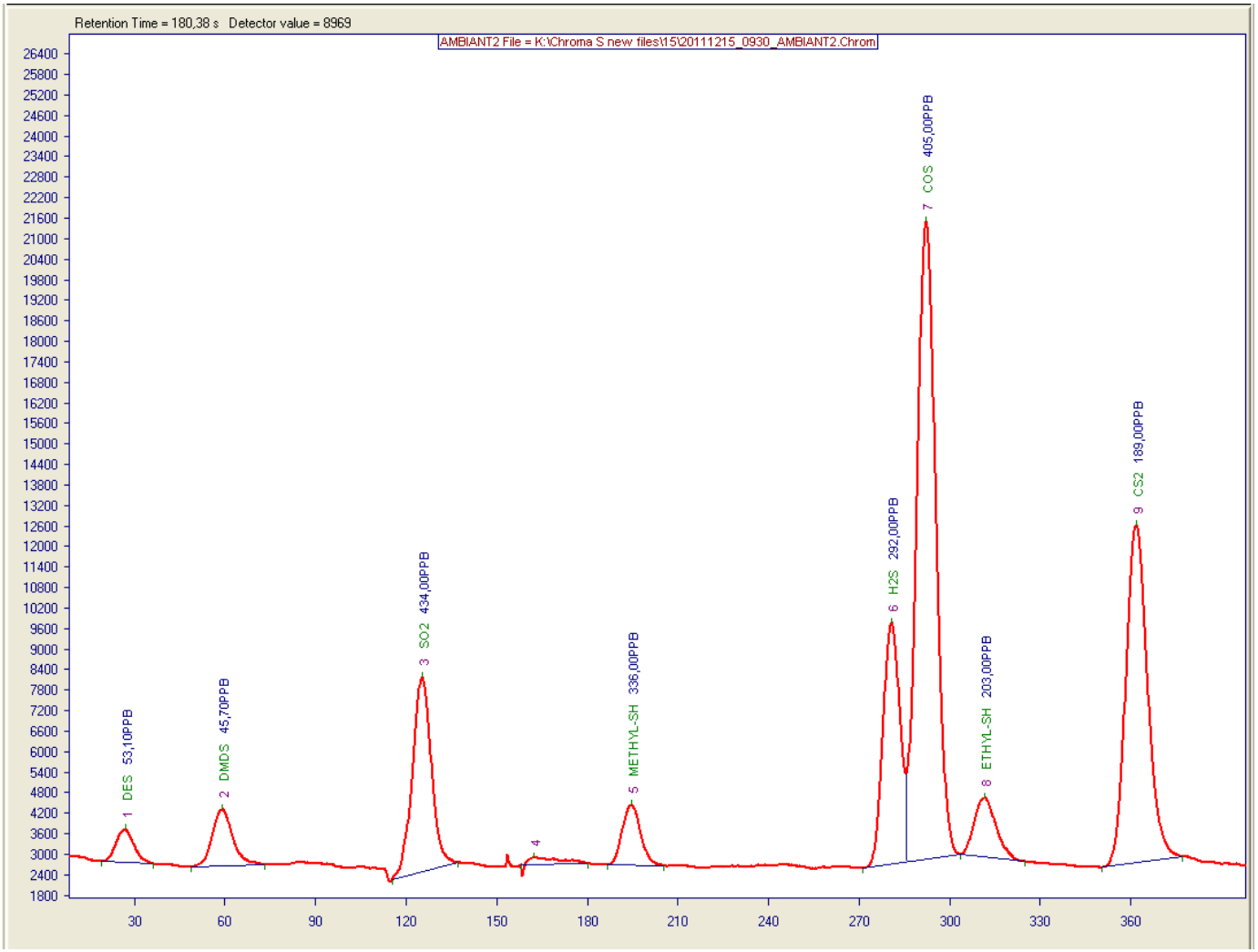
	MEDOR	chroma S
detection	electrochemical cell, chromic acid solution at 10%	flame photometer detector, interferenting filter (λ(S)=390 nm)
gas supply		
> carrier gas	dry air or N2 4 to 15 ml/min depending on columns 3 bars	dry air or N2 4 to 20 ml/min depending on columns 3 bars
> flame	-	H2 70 ml/min 2 bars air 80 ml/min 3 bars
CALIB	dry air 50 to 400 ml/min 3 bars	dry air 50 to 400 ml/min 3 bars
Amplification	3 ranges available	3 ranges availables
cycle time (mn)	5 to 10 in standard - free access	10 in standard - free access
sampling	loop 50 to 500 µL	loop 50 to 250 µL
Analysed compounds	H2S, R-SH, DMS, DMDS, sulfurs, SO2	H2S, R-SH, DMS, DMDS, sulfurs SO2, CS2, COS
low detection limit	1 ppb (H2S)	15 ppb (H2S)
specifications	[concentration]: RSD< 3% Retention time : RSD 1% 48H	[concentration]: RSD< 5% Retention time: RSD 1% 24H
CALIB permeation tube	DMS	DMS
norms	ISO 6326/2 or DIN51855/7 ASTM D7493-08 natural gas or air	-
in-built computer	yes	yes

chromaS

The analyses were performed using a certified cylinder containing 9 Compounds:

➢**DES / DMDS / SO2 / Methyl Mercaptan / H2S / COS / Ethyl Mercaptan / DMS / CS2**

- **Analytical Column: Carbopack filled capillary**
- **Pre – Analytical column: Carbopack filled capillary**
- **Cycle duration: 600 seconds**
- **Isothermal Column Temp: 38°C**


Retention Time = 180,38 s Detector value = 8969
AMBIANT2 File = K:\Chroma S new files\15\20111215_0930_AMBIANT2.Chrom
1 DES 53,10PPB
2 DMDS 45,70PPB
3 SO2 434,00PPB
4
5 METHYL-SH 336,00PPB
6 H2S 292,00PPB
7 COS 405,00PPB
8 ETHYL-SH 203,00PPB
9 CS2 189,00PPB
26400
25800
25200
24600
24000
23400
22800
22200
21600
21000
20400
19800
19200
18600
18000
17400
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12000
11400
10800
10200
9600
9000
8400
7800
7200
6600
6000
5400
4800
4200
3600
3000
2400
1800
30
60
90
120
150
180
210
240
270
300
330
360

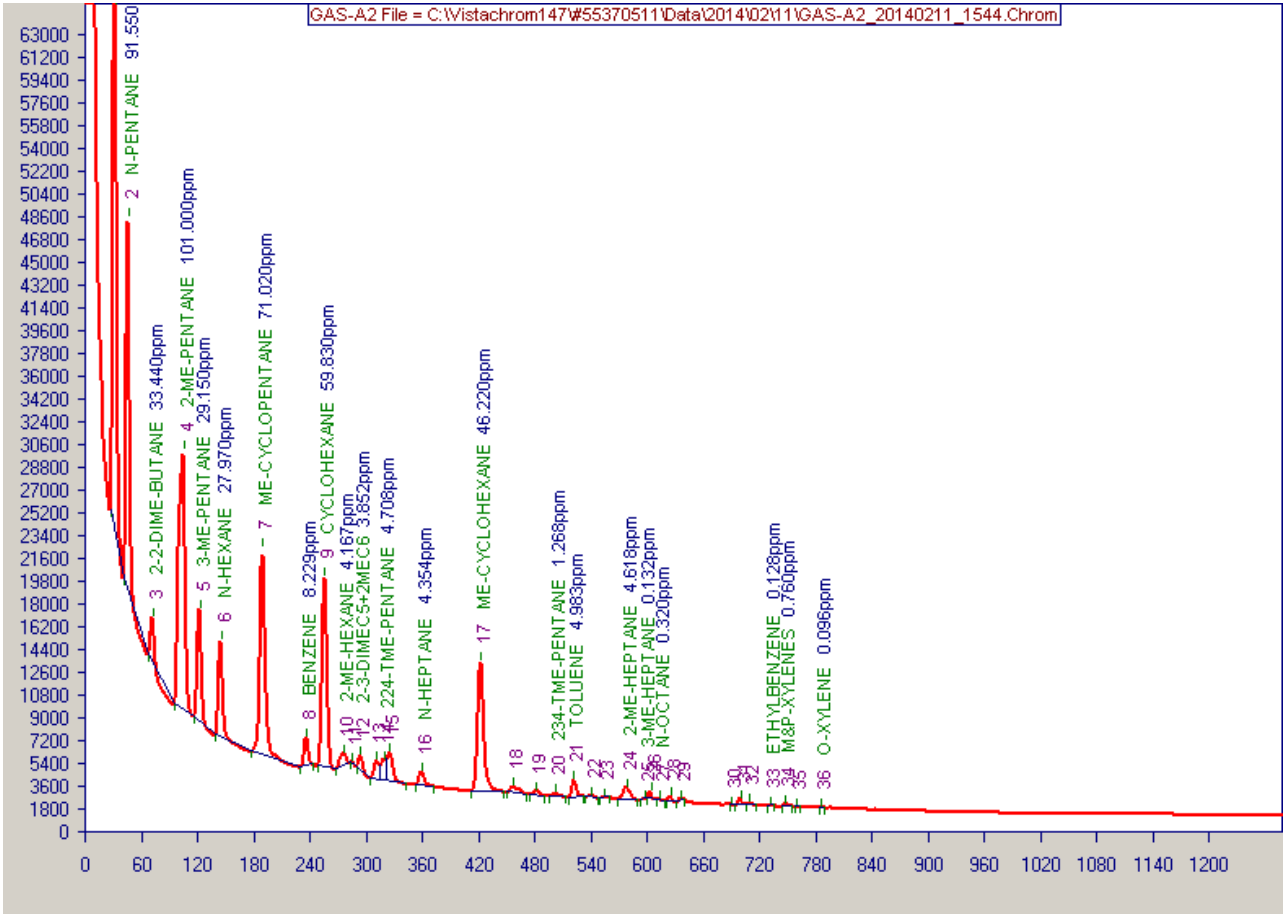
Outline

- MEDOR technology
  - Introduction
  - energyMEDOR
  - H2S TS MEDOR
  - MEDOR COS
  - TRS MEDOR
  - airmoMEDOR
- chroma technology
  - Introduction
  - chromaS
  - chromaS COS
  - **chroma FID**
  - chromENERGY

chroma FID

- chroma FID:
  - Used to analyze hydrocarbons in natural gas:
    - Carrier gas: Hydrogen
    - Cycles time: 30 minutes
    - Natural gas without dilution
    - Sampling flow : 5 mL/min
    - Loop volume : 100µl

chroma FID



Substance	Result	Unit
I-BUTANE	198.000	ppm
N-PENTANE	91.546	ppm
2-2-DIME-BUTA	33.435	ppm
2-ME-PENTANE	100.994	ppm
3-ME-PENTANE	29.152	ppm
N-HEXANE	27.967	ppm
ME-CYCLOPEN	71.021	ppm
BENZENE	8.229	ppm
CYCLOHEXANE	59.831	ppm
2-ME-HEXANE	4.167	ppm
2-3-DIMEC5+2M	3.852	ppm
224-TME-PENT	4.708	ppm
N-HEPTANE	4.354	ppm
ME-CYCLOHEX	46.217	ppm
234-TME-PENT	1.268	ppm
TOLUENE	4.983	ppm
2-ME-HEPTANE	4.618	ppm
3-ME-HEPTANE	0.132	ppm
N-OCTANE	0.320	ppm
ETHYLBENZEN	0.128	ppm
M&P-XYLENES	0.760	ppm
O-XYLENE	0.096	ppm

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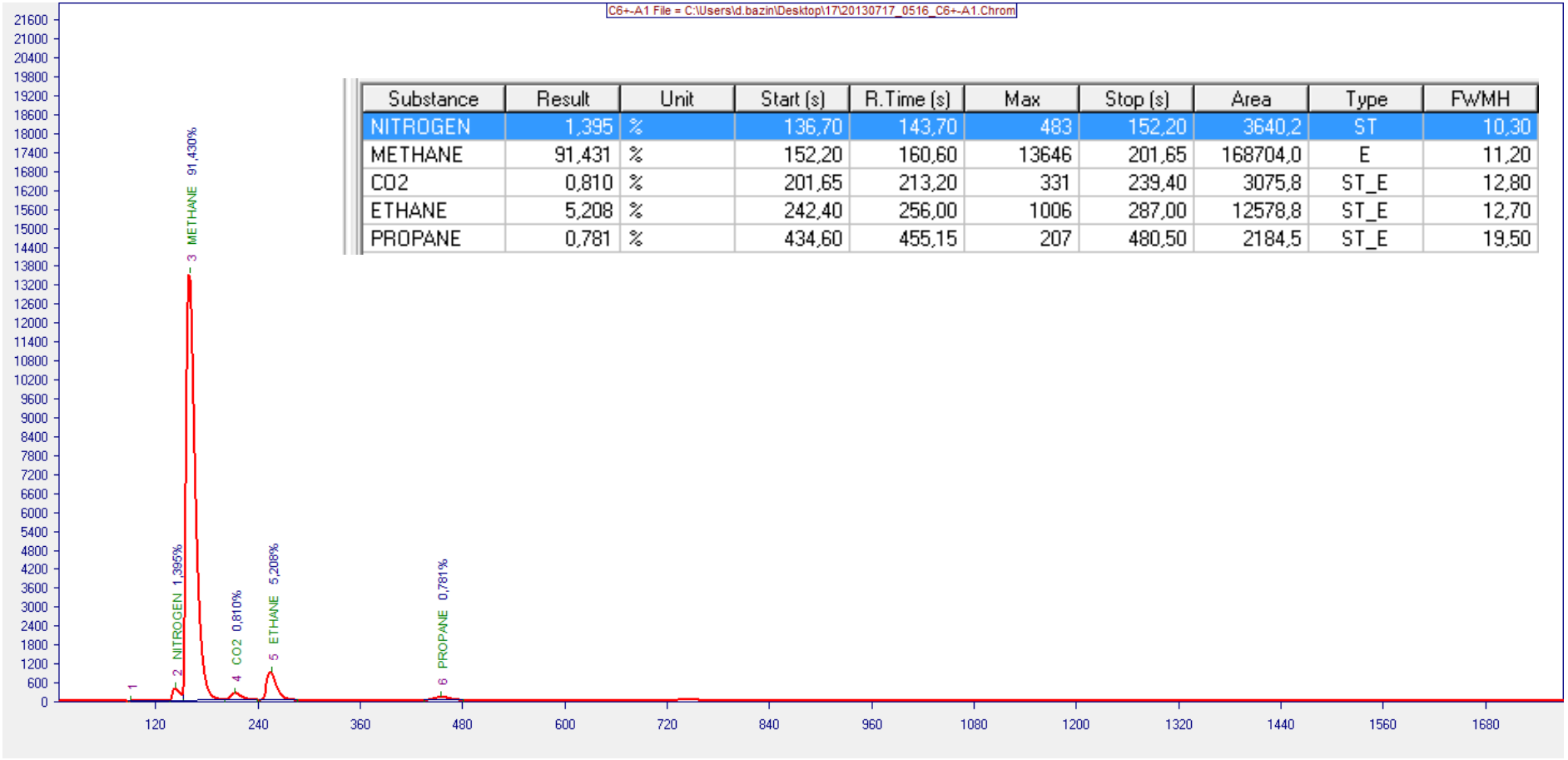
  - chromaS COS
  - chroma FID
  - **chromENERGY**

chromENERGY

- chromENERGY:
  - Used to analyze C1 to $C6^{+}$:
    - Carrier gas: Helium
    - Natural gas without dilution
    - Sampling flow : 5 mL/min
    - Detector: Thermal Conductivity Detector
  - Wobbe Index and Calorific value computation

chromENERGY



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

Conclusion

Key points:

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

H2S TOS TS
Ref: M51022-TS

energyMEDOR
Ref: M42022

ChromaS
Ref: C51052

Thank you for your attention !