

APPLICATION NOTE

LD19-04



Measurement of sulfurs & mercaptans combined with THT-TBM in natural gas using the MultiDetek2 and PlasmaDetek2



▲ MultiDetek2

▲ PlasmaDetek2
patent US 9,310,308 B2

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

- ▶ **Adjust the amount of sulphur molecules in the gas**
- ▶ **Control of odorant passivation**
- ▶ **Aids in detection of leaks**

This application note is the continuity of the previous app. note LD15-09 and LD19-01 where the description of the method for the detection of THT and TBM is demonstrated.

LDETEK SOLUTION:

The use of a highly sensitive detection system (PlasmaDetek2) combined with a compact GC system (MultiDetek2) is able to analyse sulfurs, mercaptans, Diethyl sulfide (DES), Dimethyl sulfide (DMS), Dimethyl disulfide (DMDS), THT and total sulphur directly without convertor. With its built in industrial PC, the MultiDetek2 offers all the conventional communication protocols (analog output, Modbus, Profibus, RS232/RS485), data storage capability and alarm contacts required for a process GC. Complete remote control of the system can be performed from the Ethernet connection available on every unit.

Our solution can be used in safe zone with our 6U standard 19" rackmount enclosure or in hazardous area with our IP66 rated 316SS wall mount purged enclosure 30"(762mm)deep x 57"(1447mm) height x 38"(965mm) width. An X-purge controller is installed to create a constant positive flow of air inside the enclosure, thus making a positive pressure inside enclosure. The purge is set to prevent toxic fumes from going inside the instrument in case of hazardous leakage.

The X-purge controller located on the top of the purged SS enclosure is configured to control the purging time requires prior to apply power to the instrument and hardware inside the box. It is also used for monitoring the purge pressure and flow rate inside the purged enclosure. In case of low purge pressure and/or flow rate, the power is shutoff instantly.

An extra safety pneumatic Swagelok VCR shut-off valve is mounted externally to the purged box on the sample inlet line to ensure the sample flow will but shut off in case of air supply pressure drops.

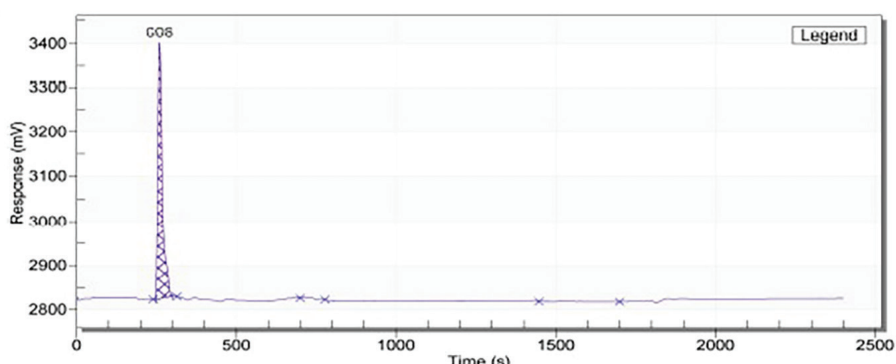
Internal temperature is monitored and controlled with a Vortex cooling system in case the unit isn't mounted in an air conditioned shelter. Our ATEX and IECEx solutions are certified by CSA following the standard II 2G Ex e mb ib pxb IIC T* Gb.

In this application note, the results of the performance are demonstrated for the analysis of sub ppb/ppm detection of COS-SO2-DES-DMDS-CS2-EM-DMS in natural gas. The representation of calibration chromatograms, the repeatability and the limit of detection well demonstrated the capability of our system for such type of application. One detector PlasmaDetek2 has been used. The multi channels of the MultiDetek2 GC are configured with coated diaphragm valves and coated metalized capillary columns to optimize the sensitivity and the carrier flow consumption. All channels merge together in the same PED for an optimal selectivity. More than one PED detector can be installed to allow parallel analysis and then reducing the analysis time when required. By this configuration, there is no interference coming from the other impurities present in the natural gas.

RESULTS:

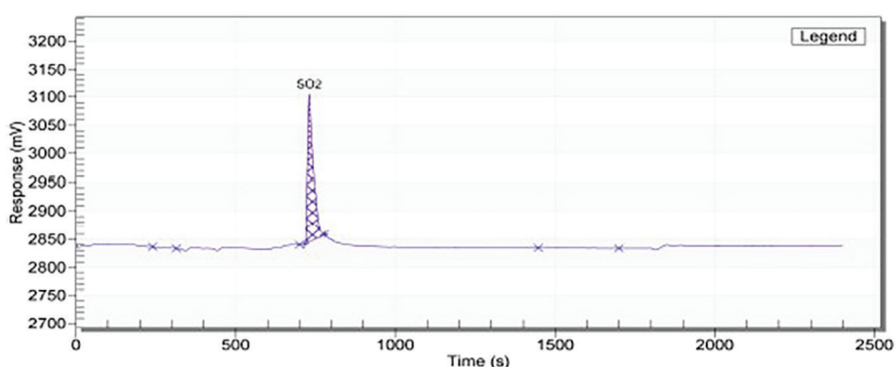
Chromatogram for 10.28ppm COS in natural gas

Peak	Unit	Calibration Value	Area Counts
COS	ppm	10.28	9607



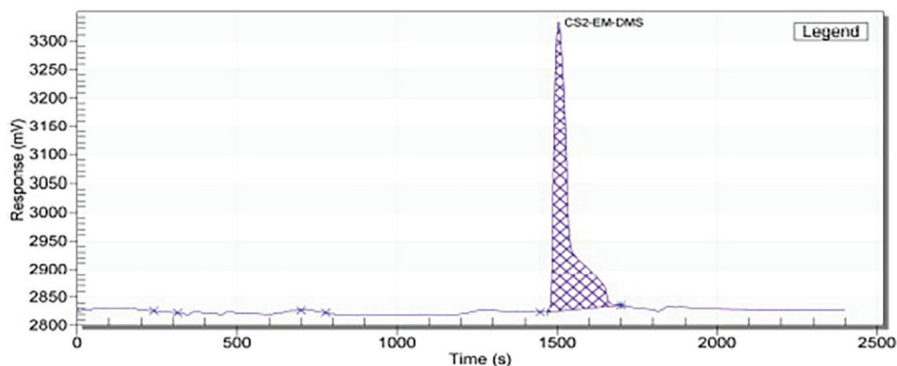
Chromatogram for 9.91ppm SO2 in natural gas

Peak	Unit	Calibration Value	Area Counts
SO2	ppm	9.91	5388



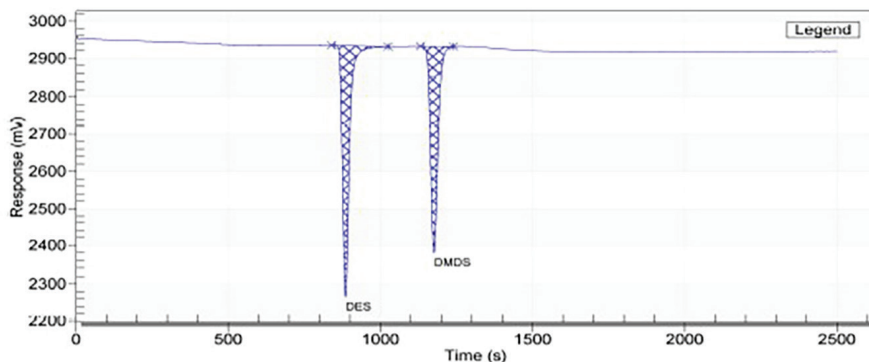
Chromatogram for 10.23ppm CS2-EM-DMS in natural gas

Peak	Unit	Calibration Value	Area Counts
CS2-EM-DMS	ppm	10.23	28361



Chromatogram for 10.09ppm DES and 9.79ppm DMDS in natural gas

Peak	Unit	Calibration Value	Area Counts
DES	ppm	10.09	16864
DMDS	ppm	9.79	14983



Repeatability to be at a value of $CV\% \times 3 < 5\%$ for a series of consecutive analysis at a fix concentration in a balance gas of natural gas.

COMPONENTS

Repeatability (CV% x 3)

DES	3.99%
DMDS	1.69%
COS	4.66%
SO2	3.83%
CS2	2.45%
EM	2.45%
DMS	2.45%

Results for THT and TBM are documented in our application note LD19-01.

Results (screenshot) of consecutive analysis at a fix concentration of 2.25ppm for DES and 2.10ppm for DMDS impurities in balance natural gas

Historic	
istoric	
Thu, Aug-17-2017	
13:56:24	COS[<LDL] SO2[<LDL] DES[2.284] DMDS[2.119]
13:34:32	COS[<LDL] SO2[<LDL] DES[2.253] DMDS[2.126]
13:12:39	COS[<LDL] SO2[<LDL] DES[2.207] DMDS[2.113]
12:50:47	COS[<LDL] SO2[<LDL] DES[2.274] DMDS[2.099]
12:28:52	COS[<LDL] SO2[<LDL] DES[2.290] DMDS[2.096]
12:07:00	COS[<LDL] SO2[<LDL] DES[2.257] DMDS[2.103]
11:45:08	COS[<LDL] SO2[<LDL] DES[2.243] DMDS[2.091]
11:23:14	COS[<LDL] SO2[<LDL] DES[2.260] DMDS[2.091]
11:01:21	COS[<LDL] SO2[<LDL] DES[2.231] DMDS[2.090]
10:30:23	COS[<LDL] SO2[<LDL] DES[2.224] DMDS[2.088] CS2-EM-DMS[<...

Results (screenshot) of consecutive analysis at a fix concentration of 2.10ppm for COS impurity in balance natural gas

Historic	
Historic	
Mon, Aug-21-2017	
08:01:30	COS[2.157] SO2[<LDL]
07:44:38	COS[2.166] SO2[<LDL]
07:25:37	COS[2.137]
06:45:19	COS[2.117] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<...
06:05:00	COS[2.100] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<...
05:24:42	COS[2.081] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<...
04:44:24	COS[2.049] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<...
04:04:05	COS[2.021] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<...
03:23:46	COS[2.016] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<...
02:43:26	COS[1.986] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<...

Results (screenshot) of consecutive analysis at a fix concentration of 1.50ppm for SO2 impurity in balance natural gas

Historic	
Sun, Aug-20-2017	
07:19:58	COS[<LDL] SO2[1.476] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<LDL]
06:39:39	COS[<LDL] SO2[1.519] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<LDL]
05:59:19	COS[<LDL] SO2[1.507] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<LDL]
05:18:59	COS[<LDL] SO2[1.471] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<LDL]
04:38:40	COS[<LDL] SO2[1.488] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<LDL]
03:58:19	COS[<LDL] SO2[1.479] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<LDL]
03:18:00	COS[<LDL] SO2[1.482] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<LDL]
02:37:40	COS[<LDL] SO2[1.499] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<LDL]
01:57:20	COS[<LDL] SO2[1.495] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<LDL]
01:17:00	COS[<LDL] SO2[1.471] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[<LDL]

Results (screenshot) of consecutive analysis at a fix concentration of 1.55ppm for CS2-EM-DMS impurities in balance natural gas

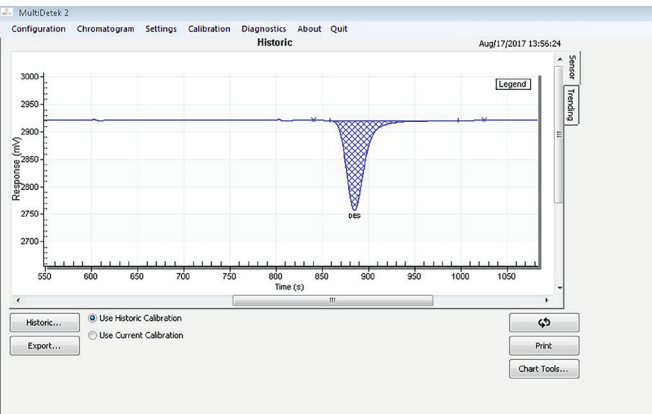
Historic	
Fri, Aug-18-2017	
16:23:39	COS[<LDL] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[1.571]
14:20:59	COS[<LDL] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[1.580]
13:40:39	COS[<LDL] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[1.563]
13:00:20	COS[<LDL] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[1.554]
12:20:00	COS[<LDL] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[1.588]
11:39:40	COS[<LDL] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[1.560]
10:53:10	COS[<LDL] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[1.605]
10:12:50	COS[<LDL] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[1.604]
09:32:30	COS[<LDL] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[1.597]
08:52:08	COS[<LDL] SO2[<LDL] DES[<LDL] DMDS[<LDL] CS2-EM-DMS[1.596]

Based on noise to ratio, LDL is calculated as follow :

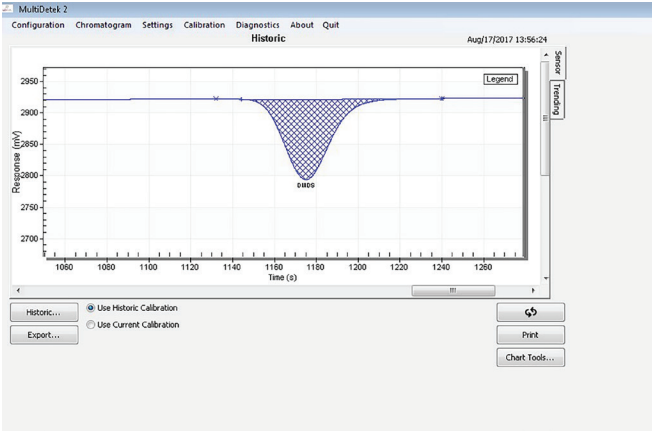
COMPONENTS	CONCENTRATION	PEAK HEIGHT	NOISE	LDL (3X NOISE)
DES	2.28 ppm	164 mV	0.4 mV	16.7 ppb
DMDS	2.11 ppm	128 mV	0.2 mV	9.9 ppb
COS	2.15 ppm	252 mV	0.3 mV	7.7 ppb
SO2	1.47 ppm	47 mV	0.2 mV	18.8 ppb
CS2	1.57 ppm	198 mV	0.4 mV	9.5 ppb
EM	1.57 ppm	198 mV	0.4 mV	9.5 ppb
DMS	1.57 ppm	198 mV	0.4 mV	9.5 ppb

Note: other LDL could be obtained with different injection volume and chromatographic condition

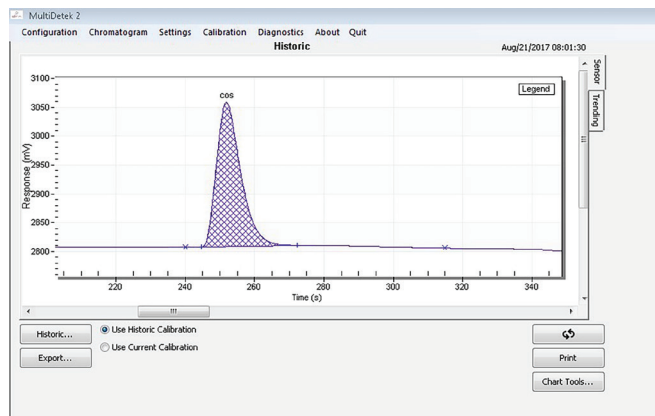
DES : 2.25 ppm



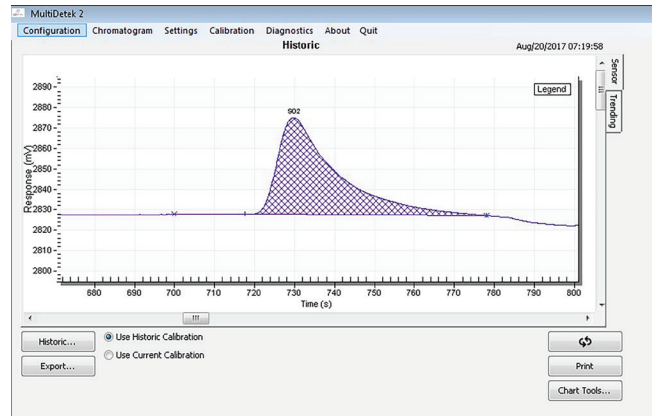
DMDS : 2.11 ppm



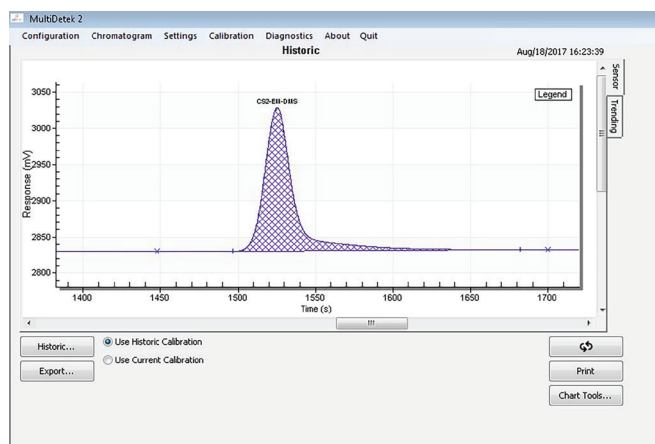
COS : 2.15 ppm



S02 : 1.47 ppm



CS2-EM-DMS : 1.57 ppm



CONCLUSION:

Our MultiDetek2 GC coupled with our PlasmaDetek2 selective detector can together in one rackmount instrument measured sulfurs, mercaptans and THT-TBM in natural gas. It allows measuring all these impurities in LNG without the use of multiple detectors and accessories. The GC only requires a constant source of helium carrier gas being configured for minimum flow consumption using coated metalized capillary columns. The same instrument configuration can be used in the industry for pipeline and storage quality control. As well as process monitoring for natural gas extraction, landfill or biogas and also for delivery station for non-odorized gas as aerosol application. As describes, our instrument can be used in safe zone with its standard rackmount enclosure or in hazardous area using our wall mount IP66 rated 316 SS ATEX/IECEx certified X-purged solution.



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