

APPLICATION NOTE

LD19-01



Measurement of THT-TBM odorants in natural gas using the MultiDetek 2 and PlasmaDetek 2



▲ MultiDetek2

▲ PlasmaDetek2
patent US 9,310,308 B2

The quick analysis of trace tetrahydrothiophene (THT) in LNG is required for controlling the amount of this odorant added in the natural gas. The THT is used for his smell to detect any presence of gas leakage in natural gas distribution network. The THT is generally used in mixture containing tert-Butylthiol (TBM) which is an organosulfur compound. In presence of TBM in natural gas, it is required to measure its concentration at low ppb/ppm because of its strong odor that causes nausea. The permissive expose limit (PEL) is in the range of 500ppb and it is the reason why highly sensitive detection system is required for both measuring THT and TBM in natural gas. This application note is the continuity of the previous app. Note LD15-09.

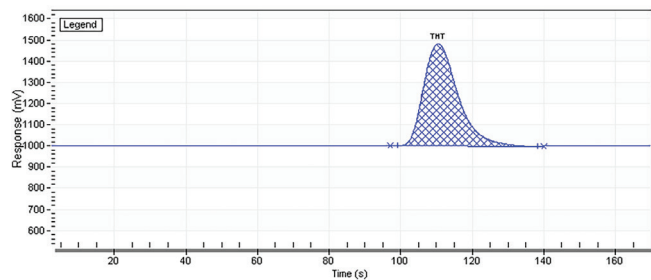
LDETEK SOLUTION:

The use of a highly sensitive detection system (PlasmaDetek2) combined with a compact GC system (MultiDetek2) are required for such type of analysis where sensitivity, robustness and speed are necessary. 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.

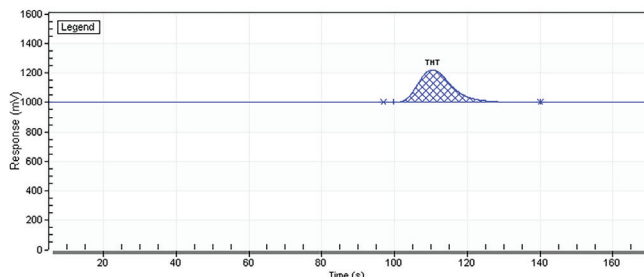
In this application note, the results of the performance are demonstrated for the quick analysis of sub ppb/ppm detection of THT and TBM in LNG. The representation of few chromatograms, the linearity, the repeatability and the limit of detection well demonstrated the capability for such type of application. One detector PlasmaDetek2 has been used. The two channels are configured with coated diaphragm valves and coated MXT capillary columns to optimize the sensitivity and the analysis time. Both channels merge together in the same PED for an optimal selectivity. By this configuration, there is no interference from any hydrocarbons presence in the sample gas.

RESULTS:

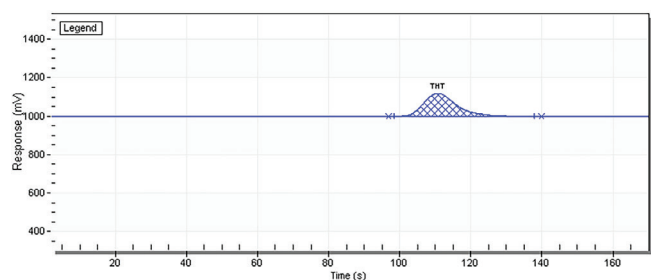
Chromatogram for 11.9ppm THT



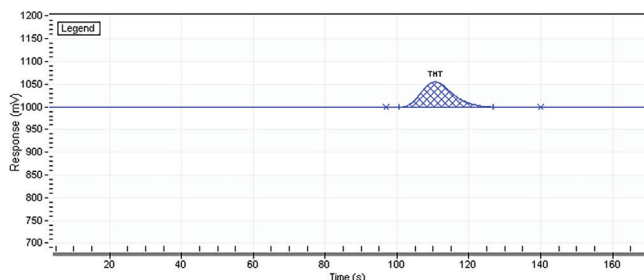
Chromatogram for 5.3ppm THT



Chromatogram for 2.9ppm THT

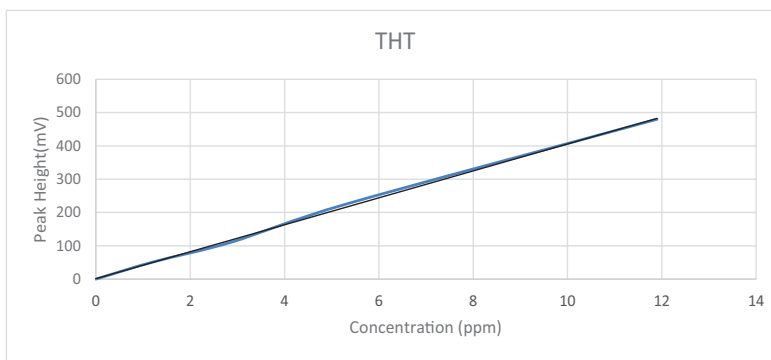


Chromatogram for 1.2ppm THT



Based on the 4 chromatograms for THT, the linearity is as follow :

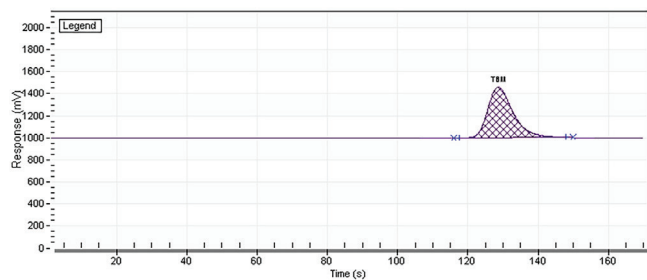
Impurity : THT	
Concentration	
ppm from dilution	Peak height(mV) from MD2
11.9	480
5.3	225
2.9	112
1.2	51
0	0



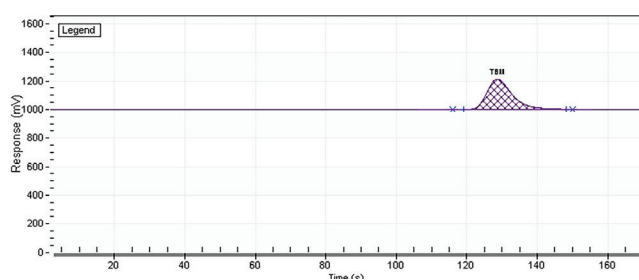
Coefficient correlation (R^2)	0.9990	Accepted
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R^2 for 5 points within the range must be between 0.998-1.00 to be accepted

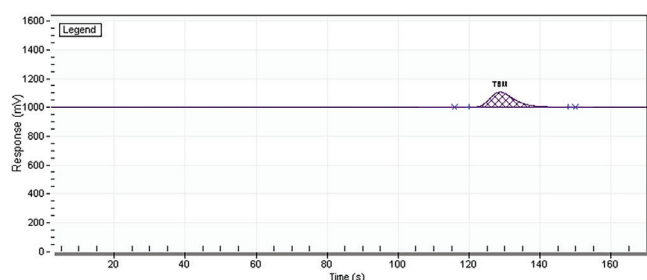
Chromatogram for 11.3ppm TBM



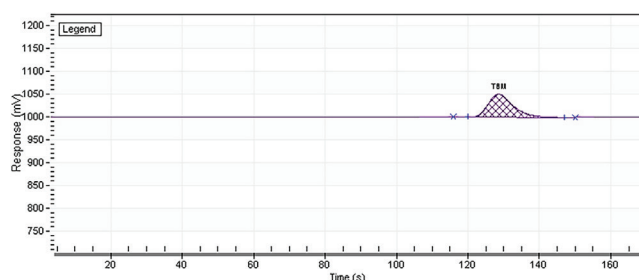
Chromatogram for 5.4ppm TBM



Chromatogram for 2.8ppm TBM

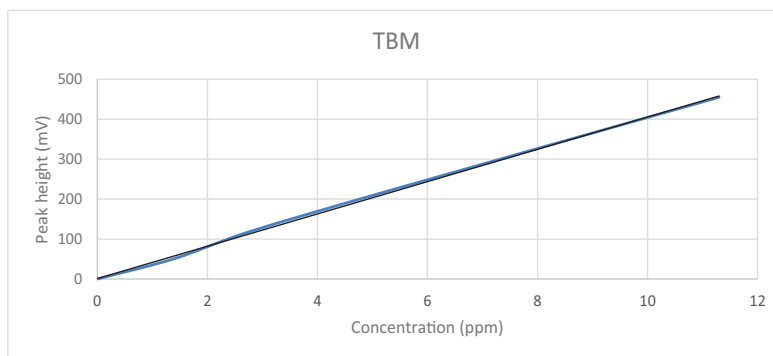


Chromatogram for 1.4ppm TBM



Based on the 4 chromatograms for TBM, the linearity is as follow :

Impurity : TBM	
Concentration	
ppm from dilution	Peak height(mV) from MD2
11.3	455
5.4	225
2.8	120
1.4	51
0	0



Coefficient correlation (R^2)	0.9991	Accepted
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R^2 for 5 points within the range must be between 0.998-1.00 to be accepted

Repeatability for THT at a known concentration of 4.0 ppm in LNG.

Start	stream	THT	THTbis	TBM1701	TBM	TBMbis
2019-03-12 04:00		4.021 ppm			<LDL	
2019-03-12 03:57		3.942 ppm			<LDL	
2019-03-12 03:54		3.999 ppm			<LDL	
2019-03-12 03:51		4.117 ppm			<LDL	
2019-03-12 03:48		4.060 ppm			<LDL	
2019-03-12 03:45		3.980 ppm			<LDL	
2019-03-12 03:42		3.939 ppm			<LDL	
2019-03-12 03:39		4.005 ppm			<LDL	
2019-03-12 03:36		4.038 ppm			<LDL	
2019-03-12 03:33		4.077 ppm			<LDL	
2019-03-12 03:30		3.990 ppm			<LDL	
2019-03-12 03:27		4.090 ppm			<LDL	
2019-03-12 03:24		4.001 ppm			<LDL	
2019-03-12 03:21		3.988 ppm			<LDL	
2019-03-12 03:19		3.954 ppm			<LDL	
2019-03-12 03:16		4.027 ppm			<LDL	
2019-03-12 03:13		4.069 ppm			<LDL	

For an 8 hours period, the repeatability is accepted at 2.16% for CV% x 3.

Repeatability for TBM at a known concentration of 5.2 ppm in LNG.

Start	stream	THT	THTbis	TBM1701	TBM	TBMbis
2019-03-11 05:46		<LDL			5.163 ppm	
2019-03-11 05:43		<LDL			5.176 ppm	
2019-03-11 05:40		<LDL			5.201 ppm	
2019-03-11 05:37		<LDL			5.137 ppm	
2019-03-11 05:34		<LDL			5.151 ppm	
2019-03-11 05:31		<LDL			5.188 ppm	
2019-03-11 05:28		<LDL			5.198 ppm	
2019-03-11 05:25		<LDL			5.173 ppm	
2019-03-11 05:22		<LDL			5.190 ppm	
2019-03-11 05:19		<LDL			5.204 ppm	
2019-03-11 05:16		<LDL			5.205 ppm	
2019-03-11 05:14		<LDL			5.199 ppm	
2019-03-11 05:11		<LDL			5.190 ppm	
2019-03-11 05:08		<LDL			5.145 ppm	
2019-03-11 05:05		<LDL			5.175 ppm	
2019-03-11 05:02		<LDL			5.199 ppm	
2019-03-11 04:59		<LDL			5.177 ppm	

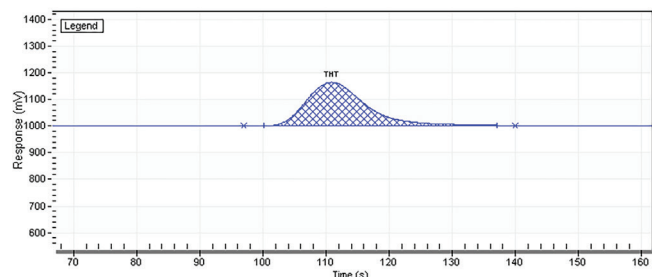
For an 8 hours period, the repeatability is accepted at 1.05% for CV% x 3.

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

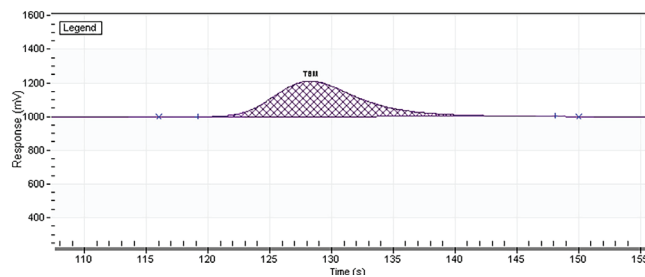
COMPONENT	CONCENTRATION	PEAK HEIGHT	NOISE	LDL (3X NOISE)
THT	3.91ppm	164mV	0.4mV	28.7ppb
TBM	5.17ppm	208mV	0.3mV	22.3ppb

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

3.91 ppm of THT measured in **channel 1**



5.17ppm of TBM measured in **channel 2**



CONCLUSION:

Using a solution combining the PlasmaDetek 2 and MultiDetek 2 is the best way to achieve sensitivity, selectivity, simplicity, robustness and speed in an industrial compact system. Our solution can be used in safe zone or hazardous area. A purged version of the MultiDetek2 gas analyser is available to meet the ATEX and IECEx requirements if an ex proof solution is required.



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