APPLICATION NOTE
LD22-02

Measurement of trace impurities in UHP hydrogen for fuel cells with the HyDetek system solution

▲ MultiDetek3 Ex

▲ HyDetek system

SHIFT POWER TO ZERO EMISSION

Hydrogen fuel cells offer reliability and a smaller carbon footprint compared to diesel and battery systems.

An hydrogen fuel cell is an electrochemical cell that converts the chemical energy of a fuel (hydrogen) and an oxidizing agent (often oxygen) into electricity through a pair of redox reactions.

Fuel cells come in many varieties; however, they all work in the same general manner. They are made up of three adjacent segments: the anode the electrolyte, and the cathode. Two chemical reactions occur at the interfaces of the three different segments. The net result of the two reactions is that fuel is consumed, water is created, and an electric current is created, which can be used to power electrical devices, normally referred to as the load.

To keep the durability and the performances of the fuel cells, the hydrogen used must conform to the ISO 14687 Part 2 to know and measure the acceptable limits of contaminants as listed in the table.

Constituent	Chemical Formula	Limits	Laboratory Test Methods to Consider and Under Development[e]	Minimum Analytical Detection Limit
Hydrogen fuel index	H_2	> 99.97%		
Total allowable non-hydrogen, non-helium, non-particulate constituents listed below		100		
Acceptable limit of each individual constituent				
Water[a]	H_20	5	**ASTM D7653-10, ASTM D7649-10**	0.12
Total hydrocarbons[b] (C_1 basis)		2	**ASTM D7675-11**	0.1
Oxygen	O_2	5	**ASTM D7649-10**	1
Helium		300	**ASTM D1945-03**	100
Nitrogen, Argon	N_2, Ar	100	**ASTM D7649-10**	5
Carbon dioxide	CO_2	2	**ASTM D7649-10, ASTM D7653-10**	0.1
Carbon monoxide	CO	0.2	**ASTM D7653-10**	0.01
Total sulfur[c]		0.004	**ASTM D7652-11**	0.00002
Formaldehyde	HCHO	0.01	**ASTM D7653-10**	0.01
Formic acid	HCOOH	0.2	**ASTM D7550-09 , ASTM D7653-10**	0.02
Ammonia	NH_3	0.1	**ASTM D7653-10**	0.02
Total halogenates[d]		0.05	(Work Item 23815)	0.01
Particulate Concentration		1 mg/kg	**ASTM D7650-10 , ASTM D7651-10**	0.005 mg/kg

The purpose of this hydrogen fuel quality standard is to specify hydrogen fuel quality requirements for all commercial hydrogen fueling stations for proton exchange membrane (PEM) fuel cell vehicles (FCVs).

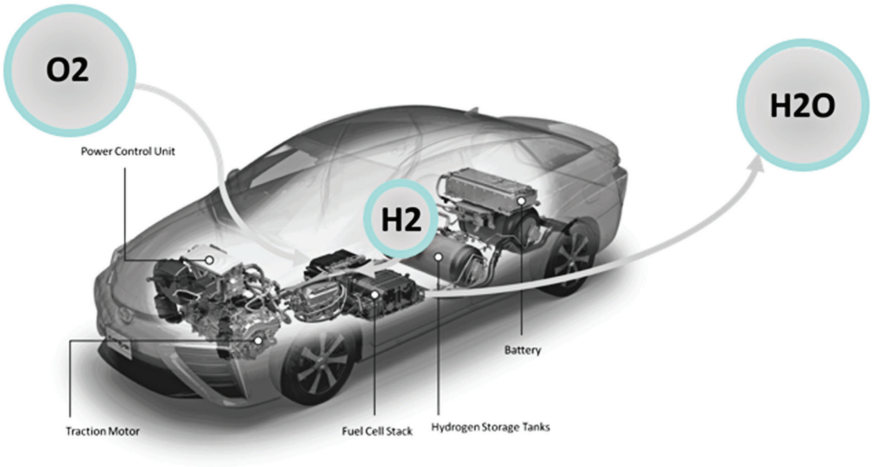
APPLICATIONS

Power

Stationary fuel cells are used for commercial, industrial and residential primary and backup power generation. Fuel cells are very useful as power sources in remote locations, such as spacecraft, remote weather stations, large parks, communications centers, rural locations including research stations, and in certain military applications. A fuel cell system running on hydrogen can be compact and lightweight and have no major moving parts.

Transports

A hydrogen vehicle is a vehicle that uses hydrogen fuel for motive power. Hydrogen vehicles include automobiles, buses, forklifts, trains, boats, airplanes, submarines, rockets and others. The power plants of such vehicles convert the chemical energy of hydrogen to mechanical energy either by burning hydrogen in an internal combustion engine or, more commonly, by reacting hydrogen with oxygen in a fuel cell to run electric motors which generate water as green contaminant.



HYDROGEN PRODUCTION

Although abundant on earth as an element, hydrogen is almost always found as part of another compound, such as water (H_2O) or methane (CH_4) and must be separated into pure hydrogen (H_2) for use in fuel cell electric vehicles.

Hydrogen can be produced from diverse, domestic resources including fossil fuels, biomass, and water electrolysis with electricity. The environmental impact and energy efficiency of hydrogen depends on how it is produced.

Although today most hydrogen is produced from natural gas, the Fuel Cell Technologies Office is exploring a variety of ways to produce hydrogen from renewable resources. We will explain here the most common techniques used to produce hydrogen for fuel cell which are NG reforming and water electrolysis.

PRODUCTION BY NATURAL GAS REFORMING

Natural gas reforming is an advanced and mature production process that builds upon the existing natural gas pipeline delivery infrastructure. Today, most of the hydrogen produced in the world is made by natural gas reforming in large central plants. This is an important technology pathway for near-term hydrogen production.

How does it work?

Natural gas contains methane (CH_4) that can be used to produce hydrogen with thermal processes, such as steam-methane reformation and partial oxidation.

Steam-methane reforming

Most hydrogen produced today is made via steam-methane reforming, a mature production process in which high-temperature steam (700°C–1,000°C) is used to produce hydrogen from a methane source, such as natural gas. In steam-methane reforming, methane reacts with steam under 3–25 bar pressure (1 bar = 14.5 psi) in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. Steam reforming is endothermic—that is, heat must be supplied to the process for the reaction to proceed. Subsequently, in what is called the «water-gas shift reaction,» the carbon monoxide and steam are reacted using a catalyst to produce carbon dioxide and more hydrogen. In a final process step called «pressure-swing adsorption,» carbon dioxide and other impurities are removed from the gas stream, leaving essentially pure hydrogen. Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane, or even gasoline.

Steam-methane reforming reaction
$CH_4 + H_2O$ (+ heat) $\rightarrow CO + 3H_2$

Water-gas shift reaction
$CO + H_2O \rightarrow CO_2 + H_2$ (+ small amount of heat)

Partial oxidation

In partial oxidation, the methane and other hydrocarbons in natural gas react with a limited amount of oxygen (typically from air) that is not enough to completely oxidize the hydrocarbons to carbon dioxide and water. With less than the stoichiometric amount of oxygen available, the reaction products contain primarily hydrogen and carbon monoxide (and nitrogen, if the reaction is carried out with air rather than pure oxygen), and a relatively small amount of carbon dioxide and other compounds. Subsequently, in a water-gas shift reaction, the carbon monoxide reacts with water to form carbon dioxide and more hydrogen.

Partial oxidation is an exothermic process—it gives off heat. The process is, typically, much faster than steam reforming and

requires a smaller reactor vessel. As can be seen in chemical reactions of partial oxidation, this process initially produces less hydrogen per unit of the input fuel than is obtained by steam reforming of the same fuel.

Partial oxidation of methane reaction
$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ (+ heat)

Water-gas shift reaction
$CO + H_2O \rightarrow CO_2 + H_2$ (+ small amount of heat)

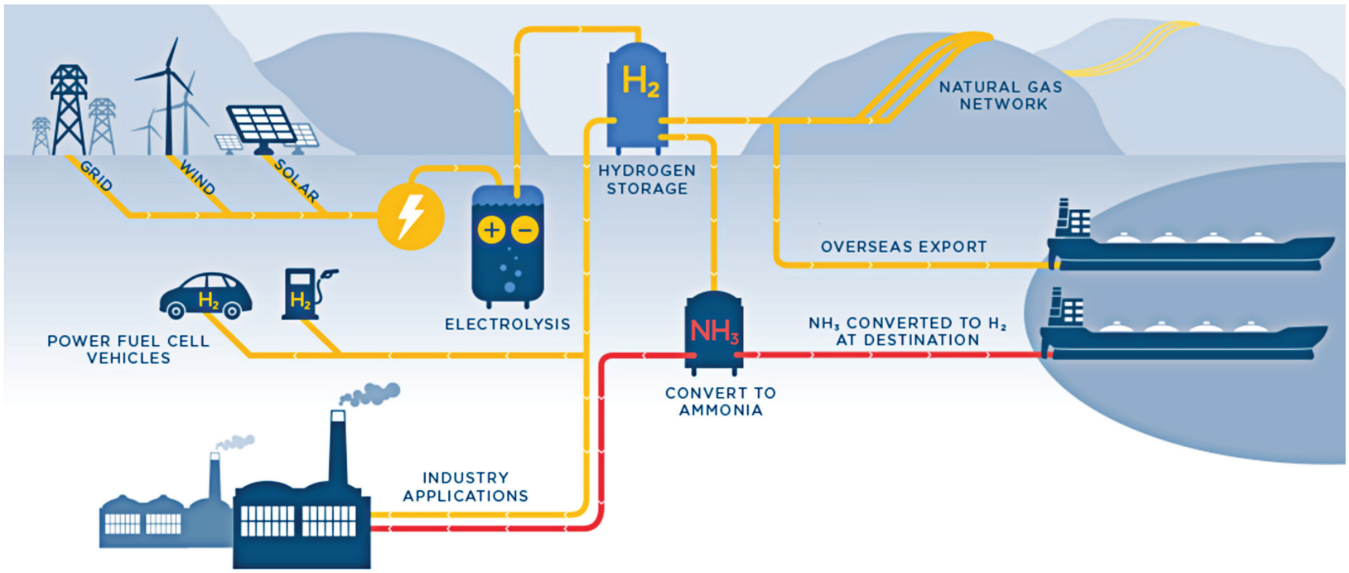
Why Is This Pathway Being Considered?

Reforming low-cost natural gas can provide hydrogen today for fuel cell electric vehicles (FCEVs) as well as other applications. Over the long term, DOE expects that hydrogen production from natural gas will be augmented with production from renewable, nuclear, coal (with carbon capture and storage), and other low-carbon, domestic energy resources.

Petroleum use and emissions are lower than for gasoline-powered internal combustion engine vehicles. The only product from an FCEV tailpipe is water vapor but even with the upstream process of producing hydrogen from natural gas as well as delivering and storing it for use in FCEVs, the total greenhouse gas emissions are cut in half and petroleum is reduced over 90% compared to today's gasoline vehicles.

PRODUCTION BY WATER ELECTROLYSIS

Electrolysis is a promising option for hydrogen production from renewable resources. Electrolysis is the process of using electricity to split water into hydrogen and oxygen. This reaction takes place in a unit called an electrolyser. Electrolysers can range in size from small, appliance-size equipment that is well-suited for small-scale distributed hydrogen production to large-scale, central production facilities that could be tied directly to renewable or other non-greenhouse-gas-emitting forms of electricity production. The hydrogen produced is used by the industries, transports and for the production of ammonia and methanol.



How does it work?

Like fuel cells, electrolysers consist of an anode and a cathode separated by an electrolyte. Different electrolysers function in slightly different ways, mainly due to the different type of electrolyte material involved.

Polymer electrolyte membrane electrolyzers

In a polymer electrolyte membrane (PEM) electrolyser, the electrolyte is a solid specialty plastic material.

- Water reacts at the anode to form oxygen and positively charged hydrogen ions (protons).
- The electrons flow through an external circuit and the hydrogen ions selectively move across the PEM to the cathode.
- At the cathode, hydrogen ions combine with electrons from the external circuit to form hydrogen gas.
  Anode Reaction: 2H2O → O2 + 4H+ + 4e- Cathode Reaction: 4H+ + 4e- → 2H2

Alkaline electrolyzers

Alkaline electrolysers operate via transport of hydroxide ions (OH-) through the electrolyte from the cathode to the anode with hydrogen being generated on the cathode side. Electrolysers using a liquid alkaline solution of sodium or potassium hydroxide as the electrolyte have been commercially available for many years. Newer approaches using solid alkaline exchange membranes as the electrolyte are showing promise on the lab scale.

Solid oxide electrolyzers

Solid oxide electrolysers, which use a solid ceramic material as the electrolyte that selectively conducts negatively charged oxygen ions (O2-) at elevated temperatures, generate hydrogen in a slightly different way.

- Water at the cathode combines with electrons from the external circuit to form hydrogen gas and negatively charged oxygen ions.
- The oxygen ions pass through the solid ceramic membrane and react at the anode to form oxygen gas and generate electrons for the external circuit.

Solid oxide electrolysers must operate at temperatures high enough for the solid oxide membranes to function properly (about 700°–800°C, compared to PEM electrolysers, which operate at 70°–90°C, and commercial alkaline electrolysers, which operate at 100°–150°C). The solid oxide electrolysers can effectively use heat available at these elevated temperatures (from various sources, including nuclear energy) to decrease the amount of electrical energy needed to produce hydrogen from water.

Why Is This Pathway Being Considered?

Hydrogen produced via electrolysis can result in zero greenhouse gas emissions, depending on the source of the electricity used. The source of the required electricity—including its cost and efficiency, as well as emissions resulting from electricity generation—must be considered when evaluating the benefits and economic viability of hydrogen production via electrolysis. In many regions of the country, today's power grid is not ideal for providing the electricity required for electrolysis because of the greenhouse gases released and the amount of fuel required due to the low efficiency of the electricity generation process. Hydrogen production via electrolysis is being pursued for renewable (wind) and nuclear energy options. These pathways result in virtually zero greenhouse gas and criteria pollutant emissions.

Potential for synergy with renewable energy power generation

Hydrogen production via electrolysis may offer opportunities for synergy with variable power generation, which is characteristic of some renewable energy technologies. For example, though the cost of wind power has continued to drop, the inherent variability of wind is an impediment to the effective use of wind power. Hydrogen fuel and electric power generation could be integrated at a wind farm, allowing flexibility to shift production to best match resource availability with system operational needs and market factors. Also, in times of excess electricity production from wind farms, instead of curtailing the electricity as is commonly done, it is possible to use this excess electricity to produce hydrogen through electrolysis.

ANALYSIS SOLUTION FOR NATURAL GAS REFORMING PRODUCTION

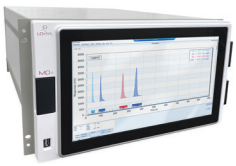
Trace H2S-COS sulfurs in Syngas with the MultiDetek3 analyser and the PlasmaDetek2 detector in our EX solution.

MultiDetek3 Ex

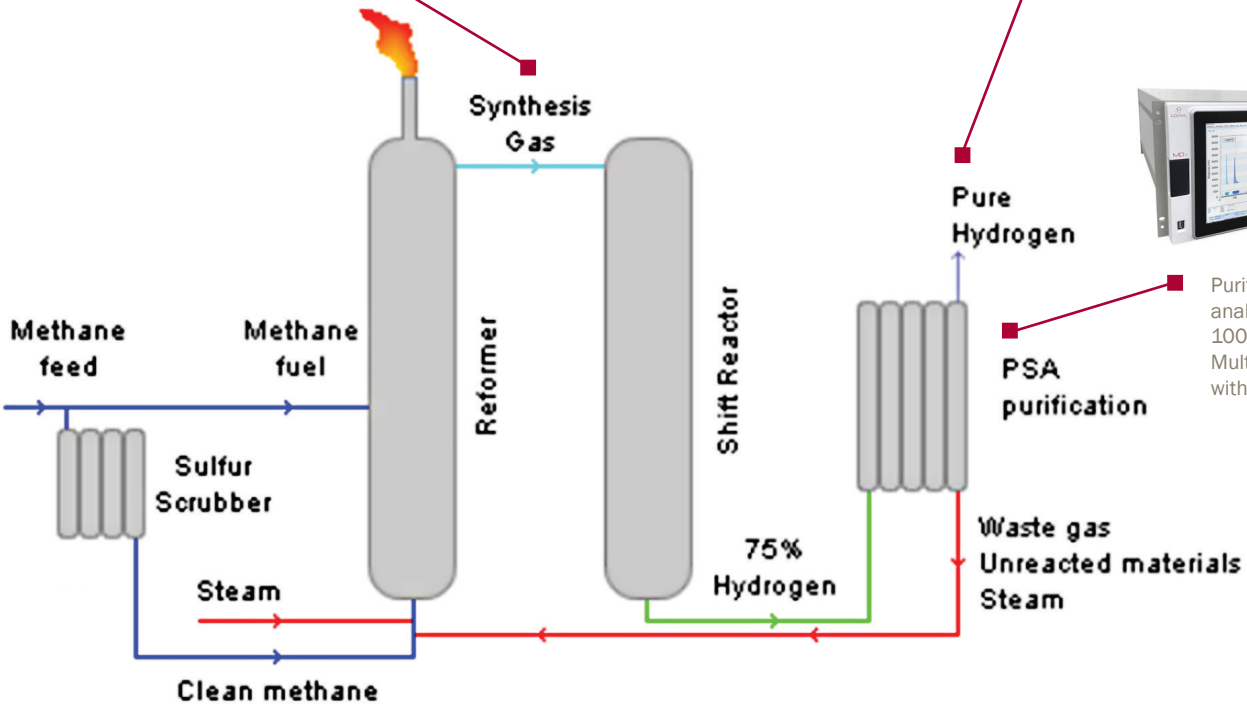
MultiDetek3

HyDetek system

All in one unit for measuring trace impurities(ppb/ ppm) N2-Ar-He-O2-CH4-CO-CO2-NMHC-sulfurs-formaldehyde-ammonia-halogenated-formic acid and water as per fuel cell standard requirement. Using PED-TCD(He)-quartz crystal(H2O) technologies all in one system.



Purity analyser 99%-100% using MultiDetek3 with TCD



About one-quarter of the incoming natural gas is burned to provide the necessary energy for the reaction, while the rest is stripped of its sulfur content. High pressure steam is added, which reacts with the methane over a nickel-alumina catalyst. The synthesis gas contains a mixture of H_2, CO_2, CO as well as unreacted CH_4 and H_2O. This gas is passed into the cooler shift reactor. The output of the shift reactor is about three quarters hydrogen. In the pressure surge adsorption unit, the impurities are removed, and recycled back through the burner, giving more than 99.9% pure hydrogen.

Synthesis gas (Syngas) measuring point

LDetek gas process analyser (GC) is used for measuring trace H_2S-COS in syngas to monitor the quality of synthesis gas used to produced carbon neutral synthetic fuels for transports and industries. The syngas produced is also used in the production of ammonia and methanol. The unit used is the MultiDetek3 GC with one PlasmaDetek2 detector configured with the right optical configuration to selectively measured low ppm/ppb H_2S and COS in a gas mixture of H_2, CO_2 and CO. The GC is configured with a MXT capillary column coated with sulfinert to avoid surface absorption for sticky impurities as sulfurs. The whole analyser flow path is coated with sulfinert to ensure the performances of the unit for measuring low ppm/ppb sulfurs. The unit can be configured for safe area with our standard compact rackmount instrument or for an Ex-Proof area with our purged/pressurized enclosure.

Pressure swing adsorption (PSA) hydrogen measuring point

The MultiDetek3 is also installed for measuring the purity of H_2 in percent right after the PSA stage. The unit is configured for measuring 99%-100% hydrogen purity with a TCD. The unit can be configured for safe area with our standard compact rackmount instrument or for an Ex-Proof area with our purged/pressurized enclosure.

Pure hydrogen measuring point

Most importantly the MultiDetek3 is used to measure the final high purity hydrogen produced. The instrument is configured with a combination of detectors like PED for sub ppb impurities measurement and our TCD for ppm He analysis and the quartz crystal module for trace moisture. With all the modules being mounted in the same analysis solution, LDetek can provide the complete spectrum of analysis required for the fuel cell hydrogen as per SAE standards. The unit can be configured for safe area with our standard compact rackmount instrument or for an Ex-Proof area with our purged/pressurized enclosure. As described in the results section, two instruments model MultiDetek3 GCs are required to cover the complete application. One GC for the analysis of ppb sulfurs, formic acid, formaldehyde, ammonia and halogenated. Another GC for measuring the trace O_2-Ar-N_2-CH_4-CO-CO_2-NMHC-He-H_2O.

ANALYSIS SOLUTION FOR WATER ELECTROLYSIS PRODUCTION

HyDetek system

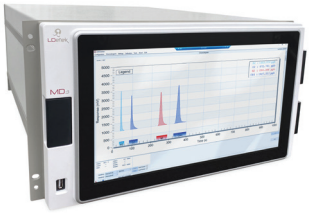
All in one unit for measuring trace impurities(ppb/ ppm) N2-Ar-He-O2-CH4-CO-CO2-NMHC-sulfurs-formaldehyde-ammonia-halogenated-formic acid and water as per fuel cell standard requirement. Using PED-TCD(He)-quartz crystal(H2O) technologies all in one system.

or

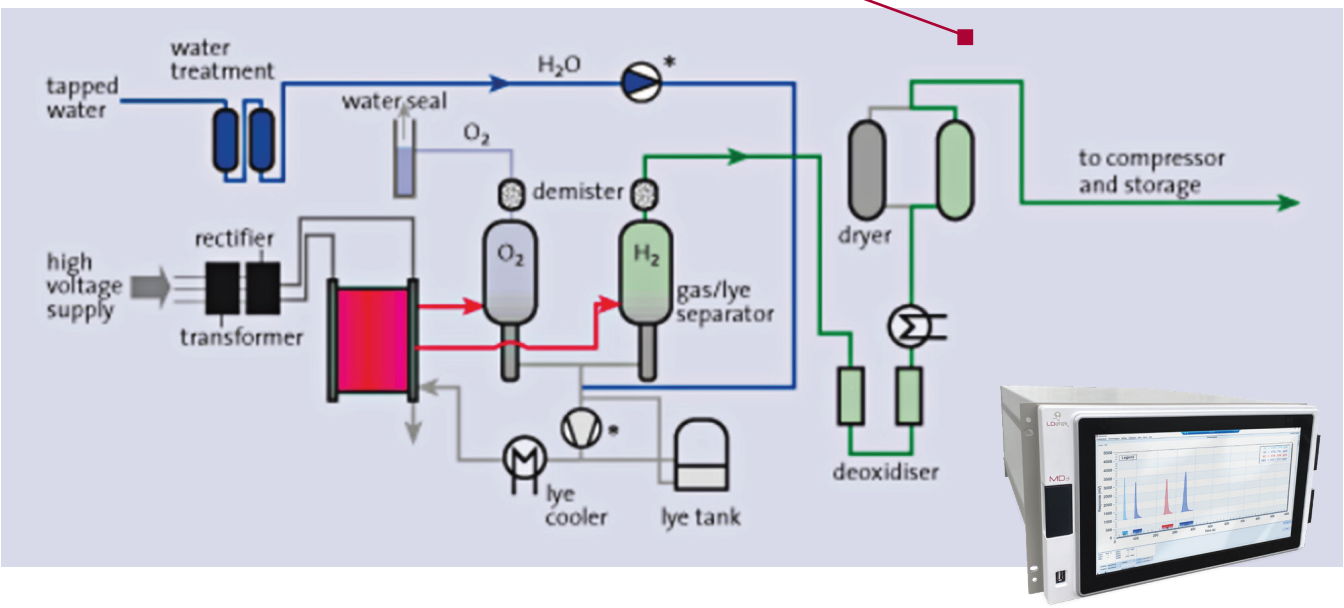
MultiDetek3 Ex

All in one unit for measuring trace impurities(ppb/ ppm) N2-Ar-O2-CO-CO2 and water as per fuel cell standard requirement. Using PED & quartz crystal(H2O) technologies all in one system.

or



MultiDetek3

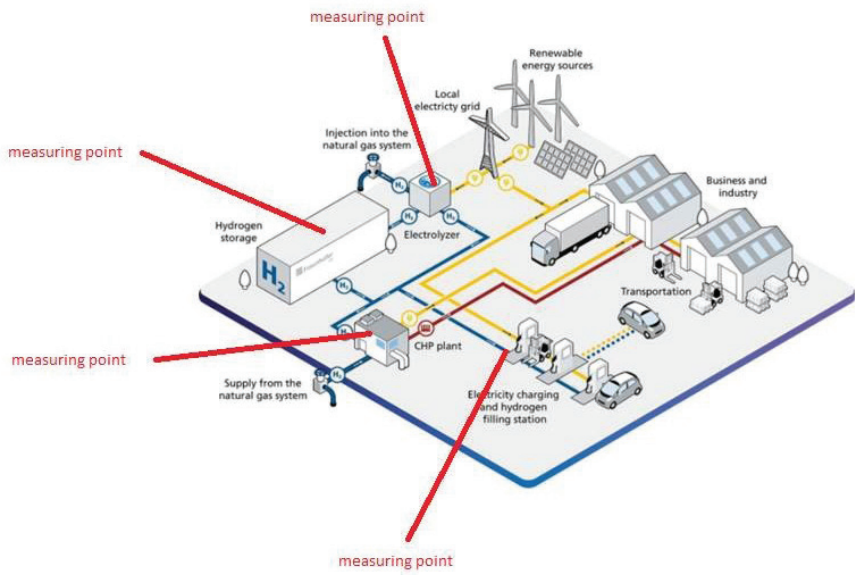


Purity analyser 99%-100% using MultiDetek3 with TCD

Pure hydrogen measuring point

For the hydrogen production by water electrolysis the MultiDetek3 is used for measuring the purity of hydrogen with its percent solution mode using our TCD detector with a range of 99%-100%. For the trace impurities in sub ppb, the unit is configured with its PED for all impurities required by SAE standards and its quartz crystal module for trace moisture. By this production method, it generally becomes not necessary to measure sulfurs, halogenated, formaldehyde, hydrocarbons and formic acid since the production process doesn't produce/contains these contaminants. It makes an analysis solution being simpler and focus on the analysis of the trace O2-Ar-N2-CO-CO2-H2O. Other configuration variances of the MultiDetek3 with more or less impurities to measure can be modified with the modularity of the MultiDetek3 platform.

MEASURING POINTS FOR HYDROGEN PRODUCTION



HOW ARE THE MULTIDETEK3 INSTRUMENTS CONFIGURED

Using its PlasmaDetek2 detector (patented) combined with a TCD (He) and the quartz crystal (H2O), LDetek can provide a solution for the complete analysis of all the contaminants that must be measured in hydrogen fuel cell. Combined with its GC modular platform MultiDetek3, this document will demonstrate how the units are configured to achieve sub ppb detection required for this application.

The most complete configuration for the complete fuel cell hydrogen production requires up to three instruments model MultiDetek3. The modularity of the unit makes it possible to apply some variances depending of application requirements. Each GC is configured with different channels that will be described.

MULTIDETEK3 GC#1

CHANNEL 1: H2S-COS-NH3-CH2O-CH2CL2

IMPURITIES	RANGE (PPB)	LDL (PPB)	REPEATABILITY (%)	DETECTOR
H2S (hydrogen sulfide)	0-500	0.4	0.8	PED
COS (carbonyl sulfide)	0-500	0.5	0.6	PED
NH3 (ammonia)	0-1000	2.5	0.3	PED
CH2O (formaldehyde)	0-500	2.0	0.4	PED
Halogenated as HCL	0-1000	10.0	1.0	PED

CHANNEL 2: CH4S-CS2-DMS-DMDS-HCOOH

IMPURITIES	RANGE (PPB)	LDL (PPB)	REPEATABILITY (%)	DETECTOR
CH4S (methyl mercaptan)	0-500	0.5	1.5	PED
CS2 (carbon disulfide)	0-500	0.2	0.7	PED
DMS (dimethyl sulfide)	0-500	0.2	0.9	PED
DMDS (dimethyl disulfide)	0-500	0.45	1.6	PED
HCOOH (formic acid)	0-1000	2.0	0.4	PED

CHANNEL 3: *CHOICE BETWEEN HE OR H2O

IMPURITIES	RANGE (PPM)	LDL (PPB)	REPEATABILITY (%)	DETECTOR
He	0-1000	1 (ppm)	0.5	TCD
H2O	0-10	10.0	0.5	Quartx crystal

*This channel can be split or interchanged in GC#1 or GC#2 depending of the requirements

Both channels 1-2 used the PlasmaDetek2 detector configured with a selective optical filter for sulfurs and one for formaldehyde/ammonia/formic acid. Each optic has a narrow wavelength limiting the interference from hydrogen background and offering a sensitivity to sub ppb. Both channels are configured with proper sulfinert coated diaphragm valves, fittings and tubing to avoid any risk of surface absorption for the impurities to measure at ppb level. The columns used are capillaries/sulfinert/metalized MXT series offering no resistance to sticky and absorptive gases. Outstanding sensitivity can be obtained by combining the right GC components together with our sensitive/selective PlasmaDetek2 sensor.

The third channel can be configured with a TCD for measuring ppm Helium or with a quartz crystal detector for measuring trace H2O. If both are required, then the second detector can be mounted in the channel 3 of the GC#2. For the trace He with a TCD, an Argon carrier gas is required to the unit. In case of measuring trace H2O, then the quartz crystal detector module is mounted with its internal calibration device. Refer to our design report on the trace moisture module integrated in our MultiDetek3 for more details. (document link is available in the reference section).

MULTIDETEK3 GC#2

CHANNEL 1: N2-CH4-CO-CO2

IMPURITIES	RANGE (PPM)	LDL (PPB)	REPEATABILITY (%)	DETECTOR
N2	0-10	1.5	0.1	PED
CH4	0-10	3.5	0.1	PED
CO	0-10	1.5	0.1	PED
CO2	0-10	1.5	0.1	PED

CHANNEL 2: AR-O2-NMHC

IMPURITIES	RANGE (PPM)	LDL (PPB)	REPEATABILITY (%)	DETECTOR
Ar	0-10	0.5	0.2	PED
O2	0-10	10.0	0.2	PED
NMHC	0-10	4.0	0.6	PED

CHANNEL 3: *CHOICE BETWEEN HE OR H2O

IMPURITIES	RANGE (PPM)	LDL (PPB)	REPEATABILITY (%)	DETECTOR
He	0-1000	1 (ppm)	0.5	TCD
H2O	0-10	10.0	0.5	Quartz crystal

*this channel can be split or interchanged in GC#1 or GC#2 depending of the requirements

This unit can be configured differently depending of the requirements. The modularity of the MultiDetek3 brings the advantages of selecting the appropriate module for your need. Here, the system has been configured with a first channel with a PED for measuring trace N2-CH4-CO-CO2. This block is configured with a PlasmaDetek2 with a selective optical filter for N2, for CH4 and one for CO/CO2.

The second channel also used a PED for measuring Ar-O2-NMHC. Here the PlasmaDetek2 is configured with 3 selective optical filters. One is used for Ar, a second one is used for O2 and a third one is used for NMHC. The analysis of trace O2 here required a doping gas system to allow a stable and repetitive ppb detection of O2.

The third channel is configured as described in the GC#1 description.

MULTIDETEK3 GC#3

CHANNEL 1: PURITY HYDROGEN

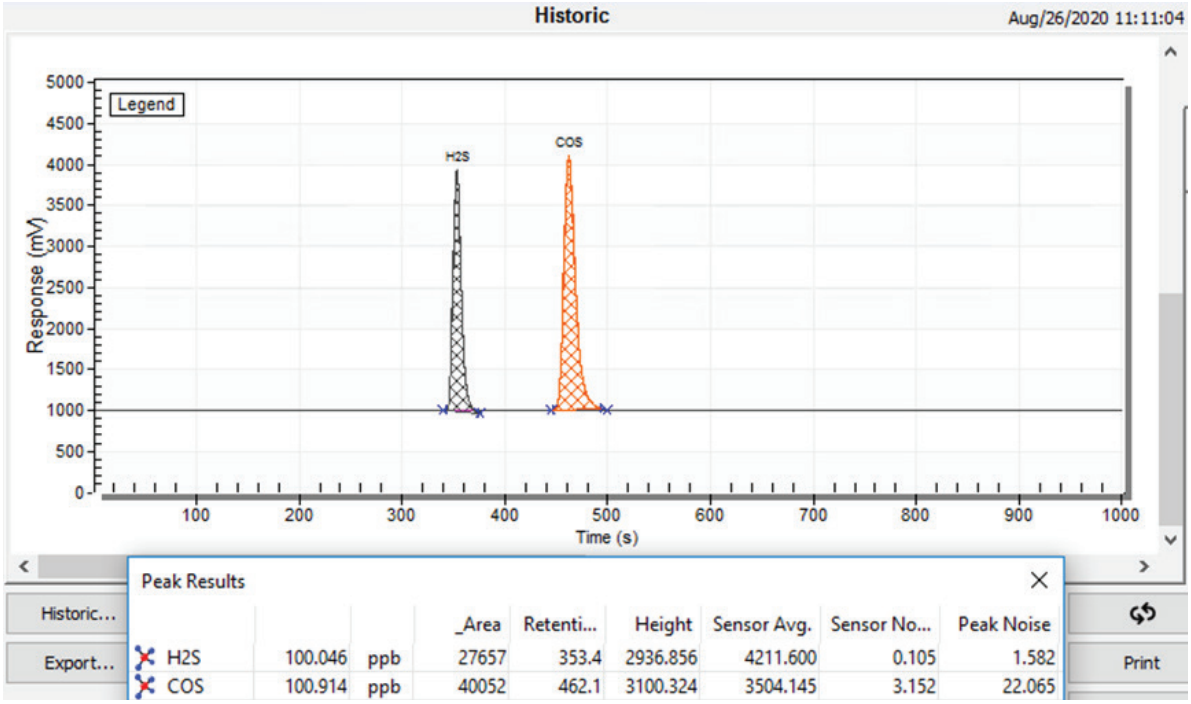
Impurities	Range (%)	Accuracy (%)	Detector	Analysis time (sec)
H2	99-100	0.001	TCD	60

This instrument is required for monitoring the total purity of hydrogen from 99%-100% generally installed in combination with the trace impurities analysers. This purity instrument offers a quick analysis time of 1 minute to monitor quickly the purity of hydrogen produced. In case of a process alarm from this instrument, the trace impurities instruments will give the details of the problematic impurities. The use of both instruments is the best practice to ensure rapidity and accuracy for the hydrogen production. This Multidetek3 GC is configured with a TCD detector and a straight injection. All impurities come as one peak which is measured by the TCD. The reference and the carrier gases use are hydrogen.

RESULTS

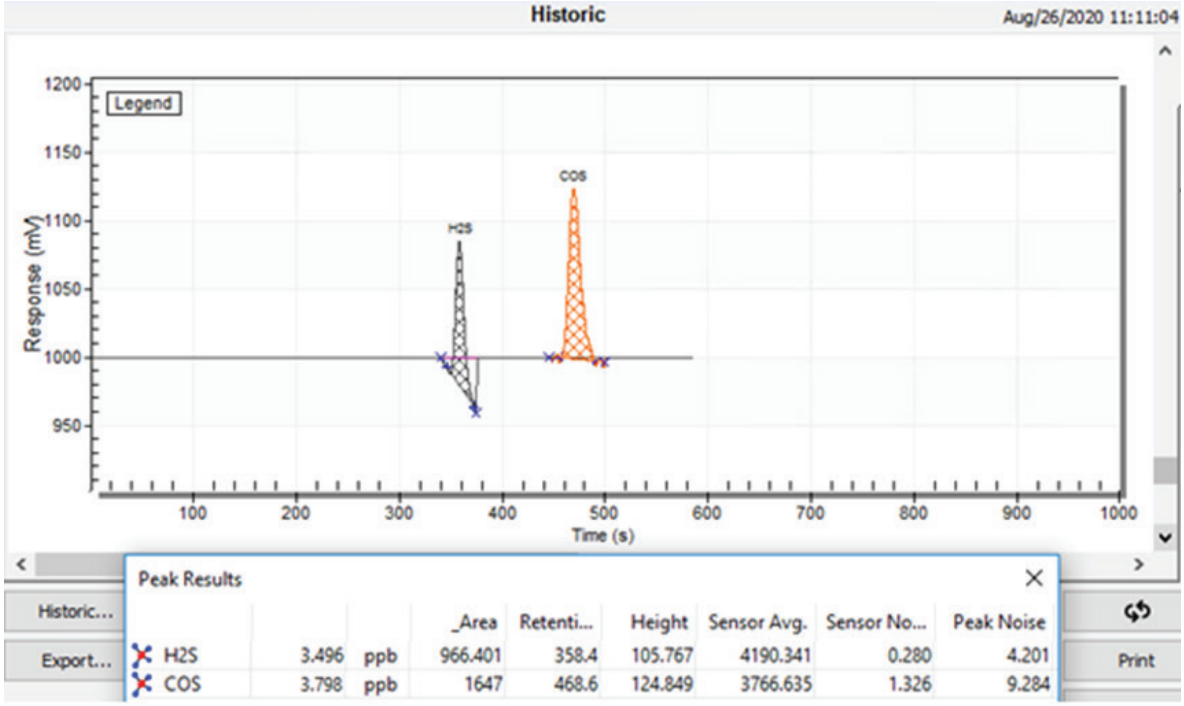
Chromatograms : GC#1/Channel 1

Sample : 100ppb H2S, COS Balance H2



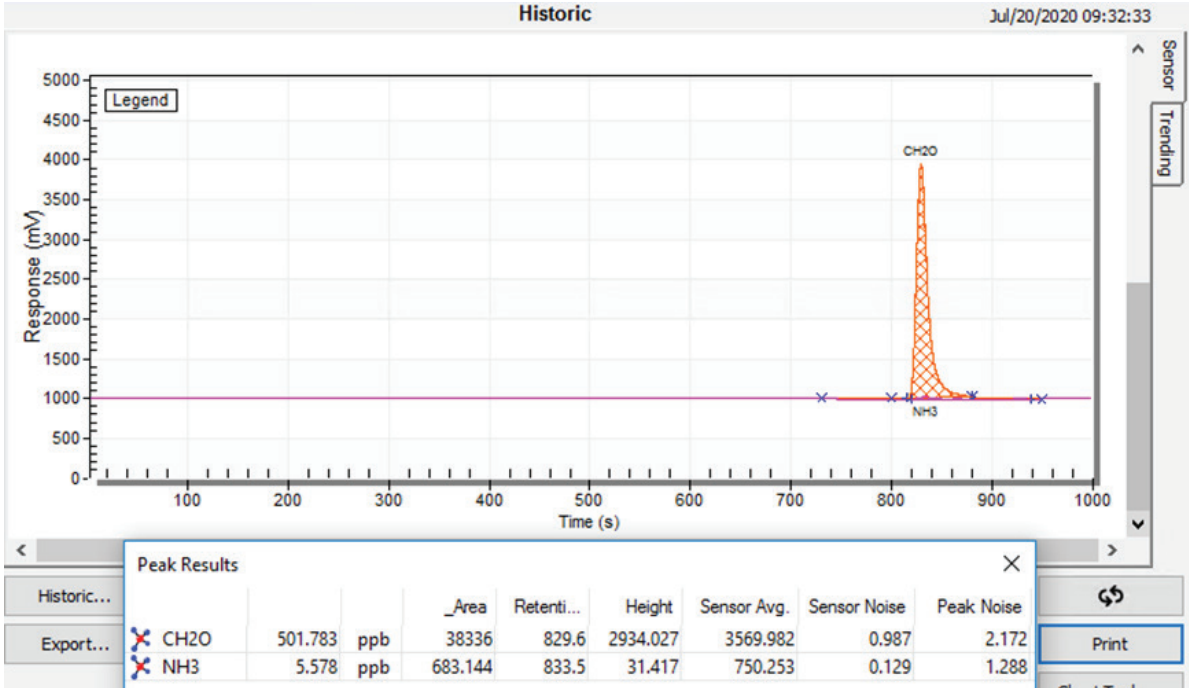
			_Area	Retenti...	Height	Sensor Avg.	Sensor No...	Peak Noise
H2S	100.046	ppb	27657	353.4	2936.856	4211.600	0.105	1.582
COS	100.914	ppb	40052	462.1	3100.324	3504.145	3.152	22.065

Sample : 3ppb H2S, COS Balance H2

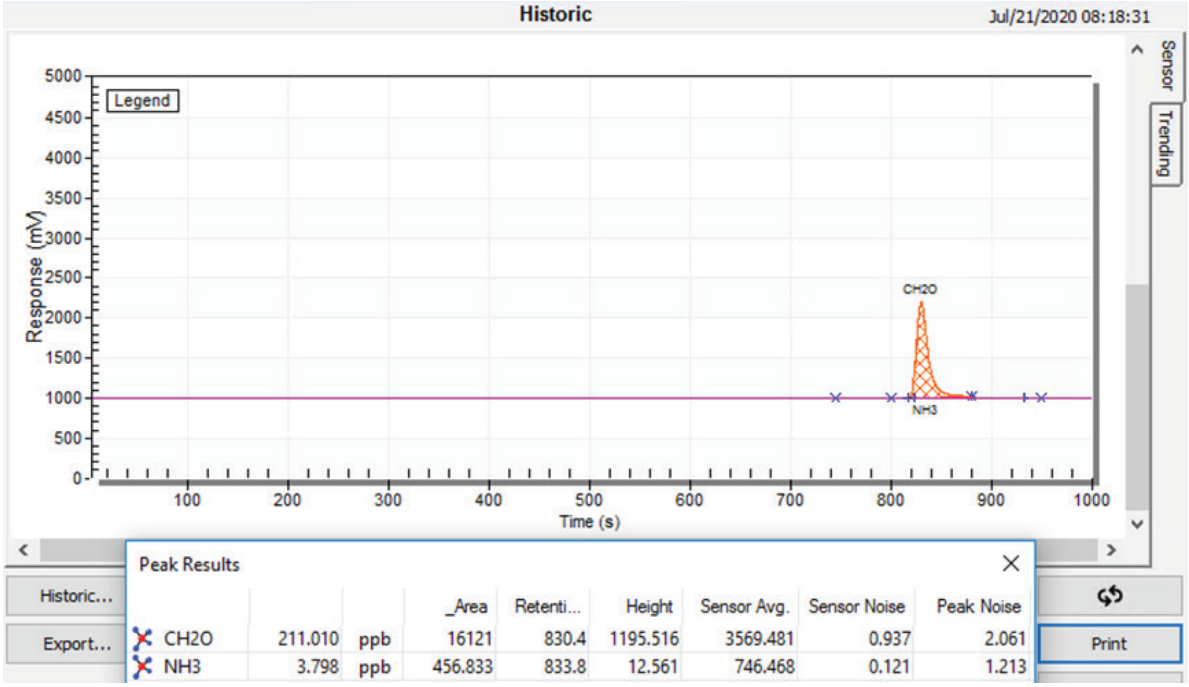


			_Area	Retenti...	Height	Sensor Avg.	Sensor No...	Peak Noise
H2S	3.496	ppb	966.401	358.4	105.767	4190.341	0.280	4.201
COS	3.798	ppb	1647	468.6	124.849	3766.635	1.326	9.284

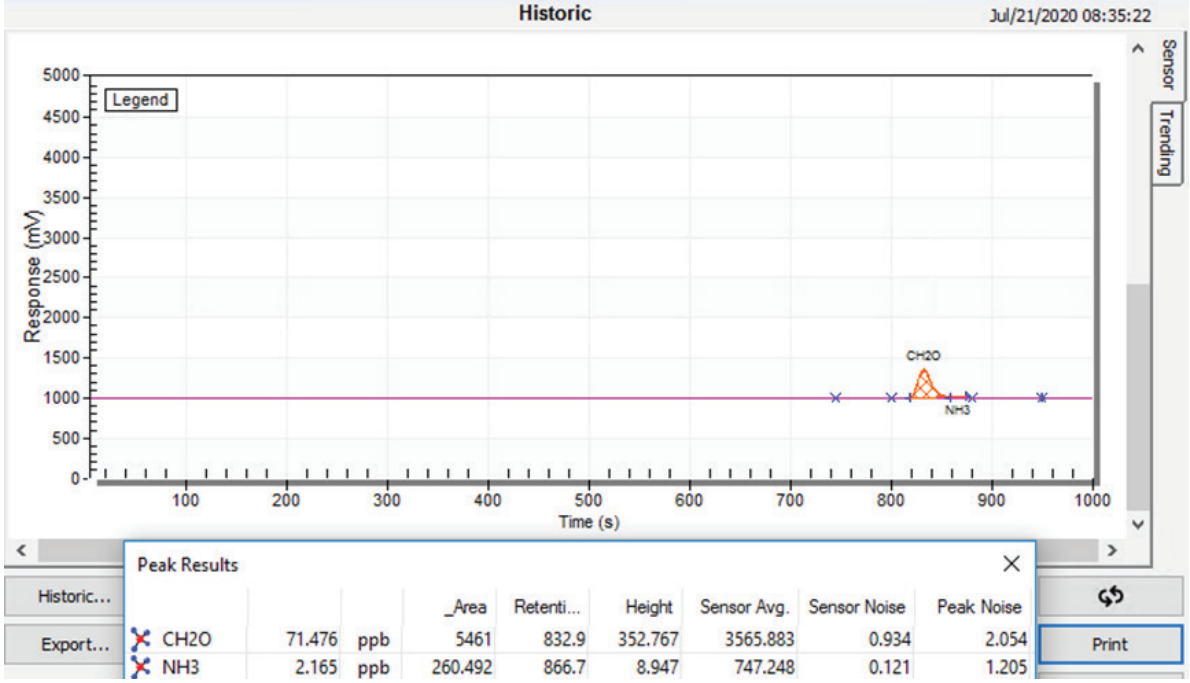
Sample: 500ppb CH2O Balance H2



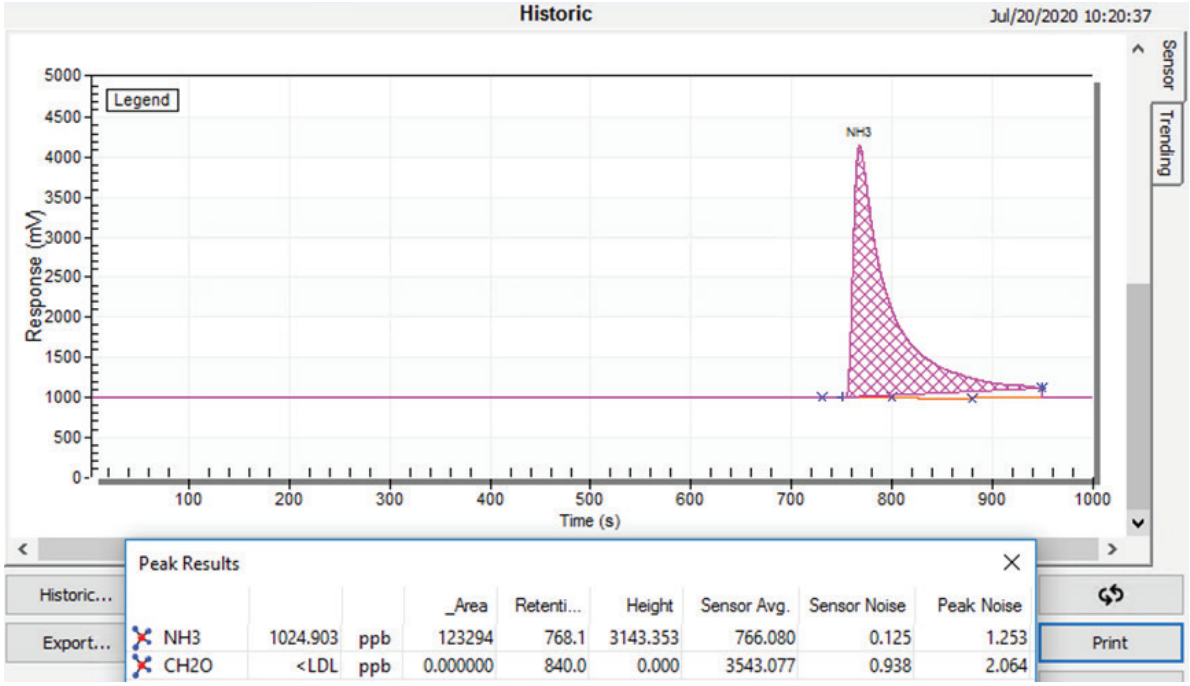
Sample: 210ppb CH2O Balance H2



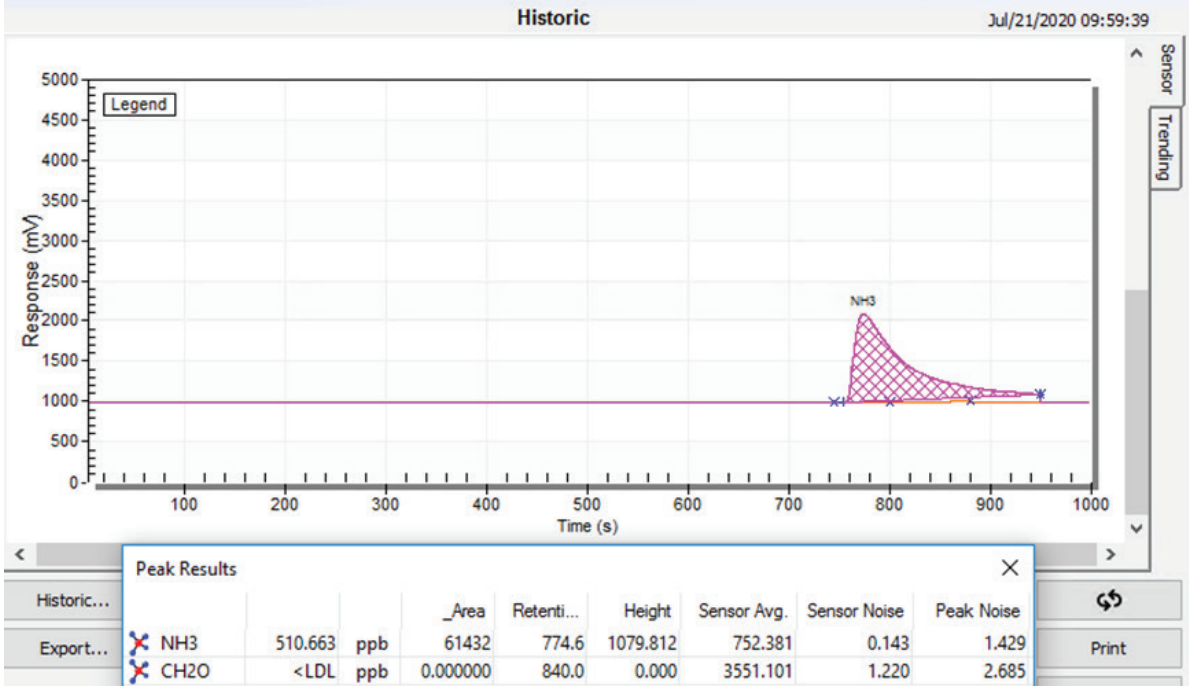
Sample: 70ppb CH2O Balance H2



Sample: 1025ppb NH3 Balance H2

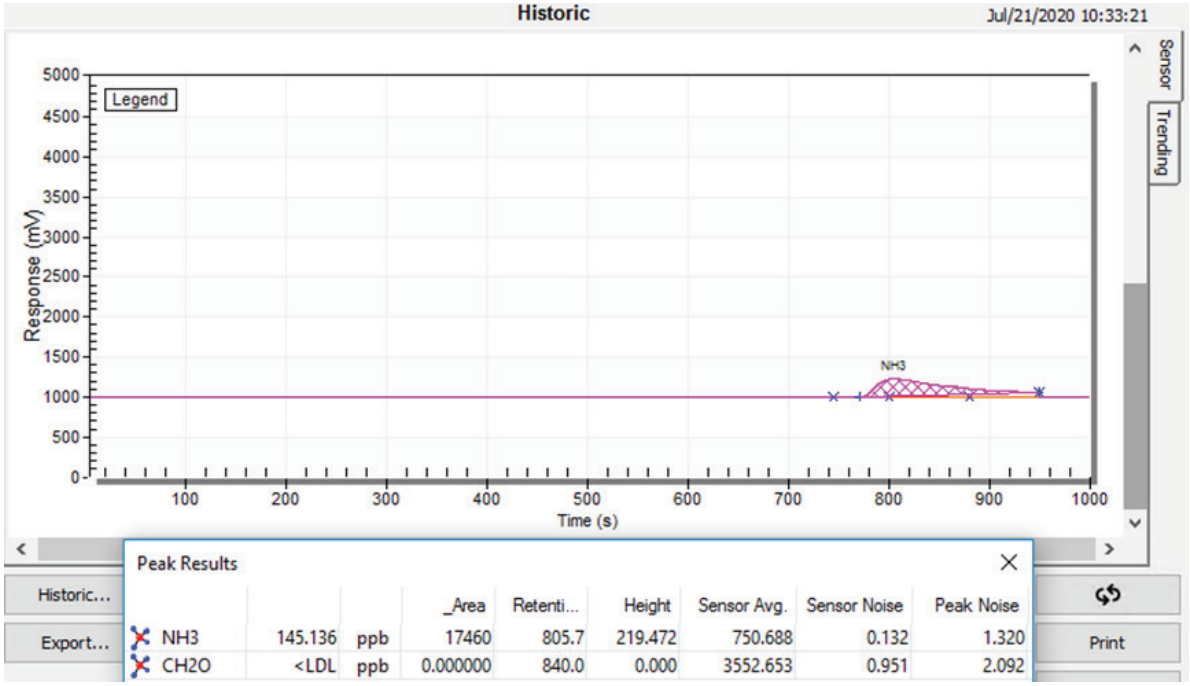


Sample: 510ppb NH3 Balance H2



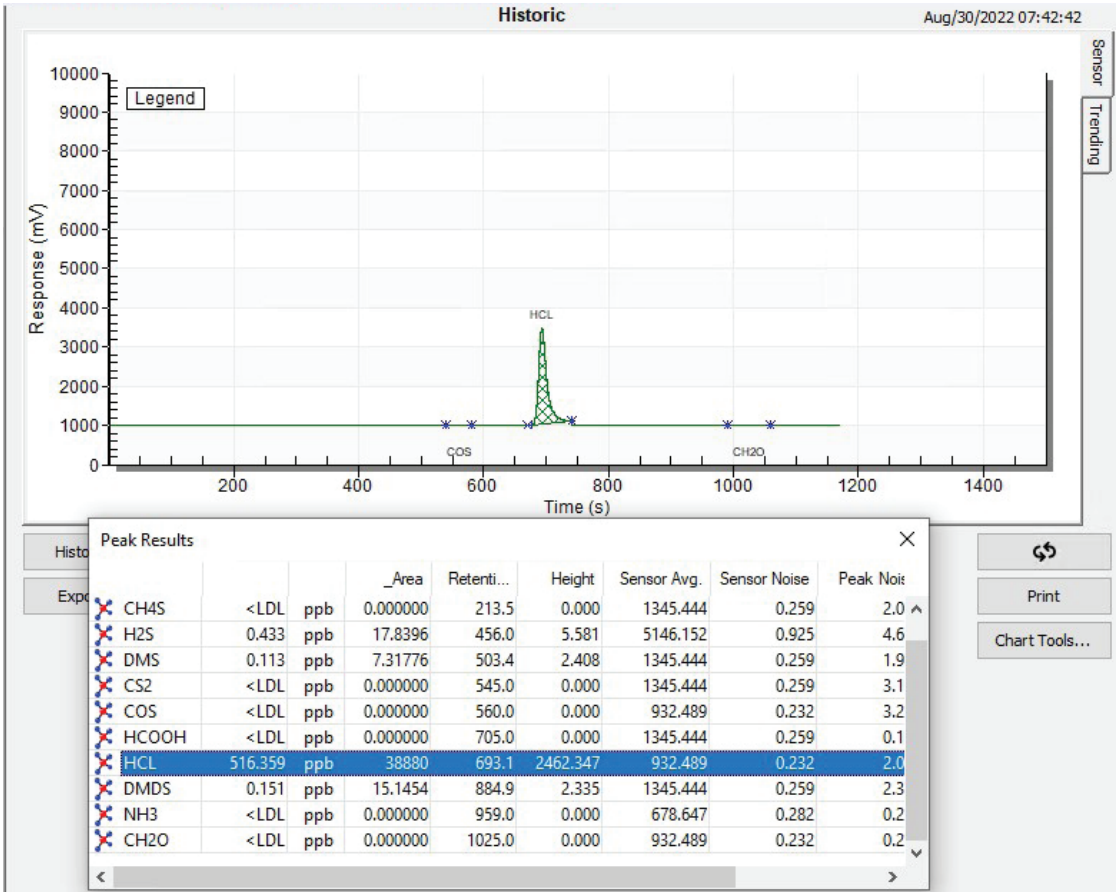
			_Area	Retenti...	Height	Sensor Avg.	Sensor Noise	Peak Noise
NH3	510.663	ppb	61432	774.6	1079.812	752.381	0.143	1.429
CH2O	<LDL	ppb	0.000000	840.0	0.000	3551.101	1.220	2.685

Sample: 150ppb NH3 Balance H2



			_Area	Retenti...	Height	Sensor Avg.	Sensor Noise	Peak Noise
NH3	145.136	ppb	17460	805.7	219.472	750.688	0.132	1.320
CH2O	<LDL	ppb	0.000000	840.0	0.000	3552.653	0.951	2.092

Sample: 516ppb ppb HCL (hydrogen chloride) in balance gas hydrogen



			_Area	Retenti...	Height	Sensor Avg.	Sensor Noise	Peak Nois
CH4S	<LDL	ppb	0.000000	213.5	0.000	1345.444	0.259	2.0
H2S	0.433	ppb	17.8396	456.0	5.581	5146.152	0.925	4.6
DMS	0.113	ppb	7.31776	503.4	2.408	1345.444	0.259	1.9
CS2	<LDL	ppb	0.000000	545.0	0.000	1345.444	0.259	3.1
COS	<LDL	ppb	0.000000	560.0	0.000	932.489	0.232	3.2
HCOOH	<LDL	ppb	0.000000	705.0	0.000	1345.444	0.259	0.1
HCL	516.359	ppb	38880	693.1	2462.347	932.489	0.232	2.0
DMDS	0.151	ppb	15.1454	884.9	2.335	1345.444	0.259	2.3
NH3	<LDL	ppb	0.000000	959.0	0.000	678.647	0.282	0.2
CH2O	<LDL	ppb	0.000000	1025.0	0.000	932.489	0.232	0.2

LDL :

Component	Concentration (ppb)	Peak height (mV)	Noise (mV)	LDL (3x Noise) (ppb)
H2S (hydrogen sulfide)	3.5	105.8	4.2	0.41
COS (carbonyl sulfide)	3.79	124.9	9.2	0.80
CH2O (formaldehyde)	71.4	352.7	2.05	1.24
NH3 (ammonia)	145	219.4	1.32	2.61
HCL (hydrogen chloride)	516	2462	2.0	1.25

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

Repeatability :

Sample : 3ppb H2S, COS Balance H2

	Description	H2S	COS
Wed, Aug-26-2020			
17:39:32		3.564	4.102
17:29:23		3.565	4.145
17:19:13		3.533	4.151
17:09:03		3.543	4.185
16:58:53		3.506	4.121
16:48:42		3.530	4.145

Sample : 135ppb NH3 & 75ppb CH2O Balance H2

	Description	NH3	CH2O
Historic			
Tue, Jul-21-2020			
13:55:43		136.162	75.984
13:38:50		136.759	76.416
13:22:00		136.398	76.441
13:05:08		136.709	76.621
12:48:16		136.848	76.707
12:31:24		137.460	76.683

IMPURITIES	H2S	COS	NH3	CH2O
Average (ppb)	3.534	4.142	136,7	76,48
Sigma σ (ppb)	0.028	0.028	0.44	0.27
CV (%)	0.80	0.68	0.32	0.35
CV x 3 (%)	2.40	2.05	0.97	1.06
Status	pass	pass	pass	pass
Repeatability (%)	0.8	0.6	0.3	0.4

Using a series of 6 consecutive analysis, the repeatability conformity test must be below 5% considering a value of 3 times the coeficient of variation (CV) to be accepted.

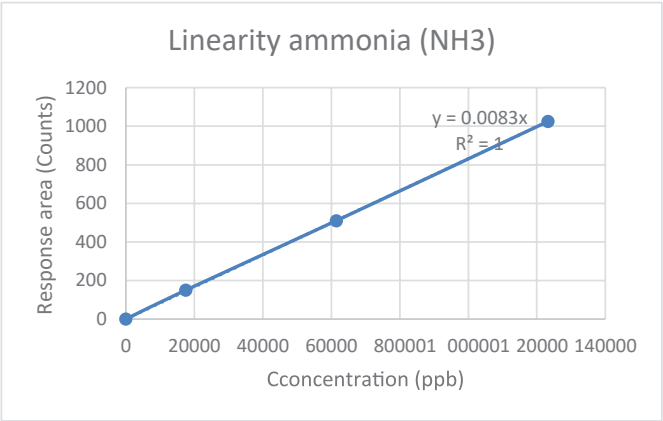
The repeatability % is obtained by applying the sigma of the 6 consecutive analysis on the average of these 6 same analysis.

The test has been performed at the bottom of the scale which is the most rigourous concentration to get a good repeatability. Running such repeatability test at higher concentration is just easier to get a better repeatability. It demonstrates the performance of the system in terms of repeatability at very low concentration.

Linearity :

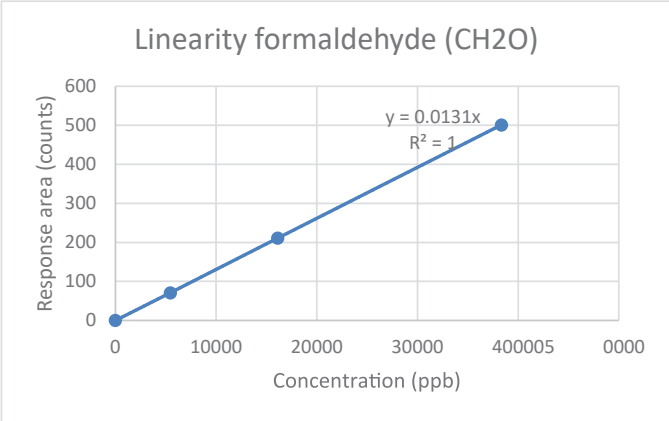
Impurity : Ammonia (NH3)

Response area (counts)	Concentration (ppb)
0	0
17460	150
61432	510
123294	1025



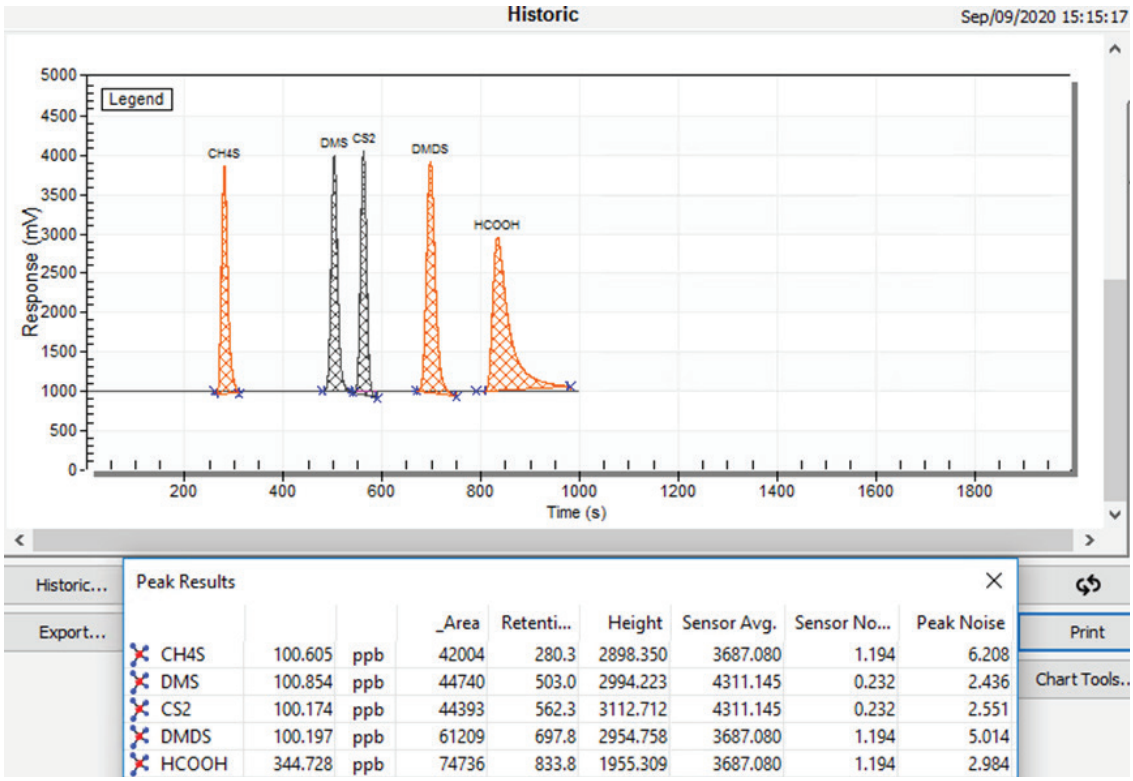
Impurity : Formaldehyde (CH2O)

Response area (counts)	Concentration (ppb)
0	0
5461	71
16121	211
38336	501



Chromatograms : GC#1/Channel 2

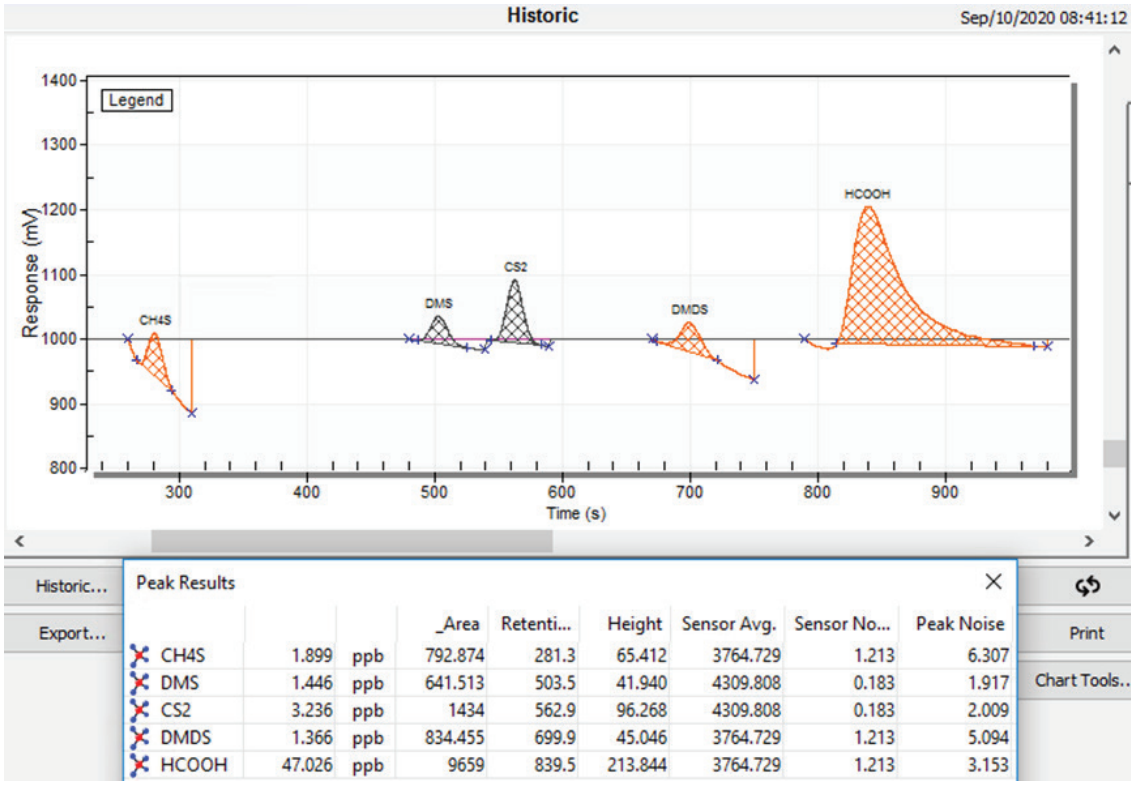
Sample: 100ppb CH4S-CS2-DMS-DMDS / 330ppb HCOOH Balance H2



Peak Results

			_Area	Retenti...	Height	Sensor Avg.	Sensor No...	Peak Noise
CH4S	100.605	ppb	42004	280.3	2898.350	3687.080	1.194	6.208
DMS	100.854	ppb	44740	503.0	2994.223	4311.145	0.232	2.436
CS2	100.174	ppb	44393	562.3	3112.712	4311.145	0.232	2.551
DMDS	100.197	ppb	61209	697.8	2954.758	3687.080	1.194	5.014
HCOOH	344.728	ppb	74736	833.8	1955.309	3687.080	1.194	2.984

Sample : 2ppb CH4S-CS2-DMS-DMDS / 50ppb HCOOH Balance H2



Peak Results

			_Area	Retenti...	Height	Sensor Avg.	Sensor No...	Peak Noise
CH4S	1.899	ppb	792.874	281.3	65.412	3764.729	1.213	6.307
DMS	1.446	ppb	641.513	503.5	41.940	4309.808	0.183	1.917
CS2	3.236	ppb	1434	562.9	96.268	4309.808	0.183	2.009
DMDS	1.366	ppb	834.455	699.9	45.046	3764.729	1.213	5.094
HCOOH	47.026	ppb	9659	839.5	213.844	3764.729	1.213	3.153

LDL :

Component	Concentration (ppb)	Peak height (mV)	Noise (mV)	LDL (3x Noise) (ppb)
CH4S (methyl mercaptan)	1.89	65.4	6.3	0.50
DMS (dimethyl sulfide)	1.44	41.9	2.0	0.20
CS2 (carbon disulfide)	3.23	96.3	1.91	0.19
DMDS (dimethyl disulfide)	1.36	45.0	5.0	0.45
HCOOH (formic acid)	47.0	213.9	3.15	2.00

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

Stability :

Sample : 2ppb CH4S-CS2-DMS-DMDS / 50ppb HCOOH Balance H2

	Description	CH4S	DMS	CS2	DMDS	HCOOH
Historic						
⊟ Thu, Sep-10-2020						
07:49:10		1.879	1.334	3.344	1.265	47.865
07:32:18		1.873	1.316	3.338	1.230	48.020
07:15:26		1.904	1.343	3.359	1.226	47.958
06:58:35		1.924	1.317	3.384	1.272	48.074
06:41:43		1.951	1.343	3.397	1.265	48.279
06:24:51		1.940	1.326	3.389	1.259	48.295

IMPURITIES	CH4S	DMS	CS2	DMDS	HCOOH
Average (ppb)	1.91	1.33	3.37	1.25	48,08
Sigma σ (ppb)	0.03	0.012	0.024	0.02	0.17
CV (%)	1.66	0.91	0.74	1.57	0.36
CV x 3 (%)	4.98	2.73	2.22	4.72	1.08
Status	pass	pass	pass	pass	pass
Repeatability (%)	1.5	0.9	0.7	1.6	0.4

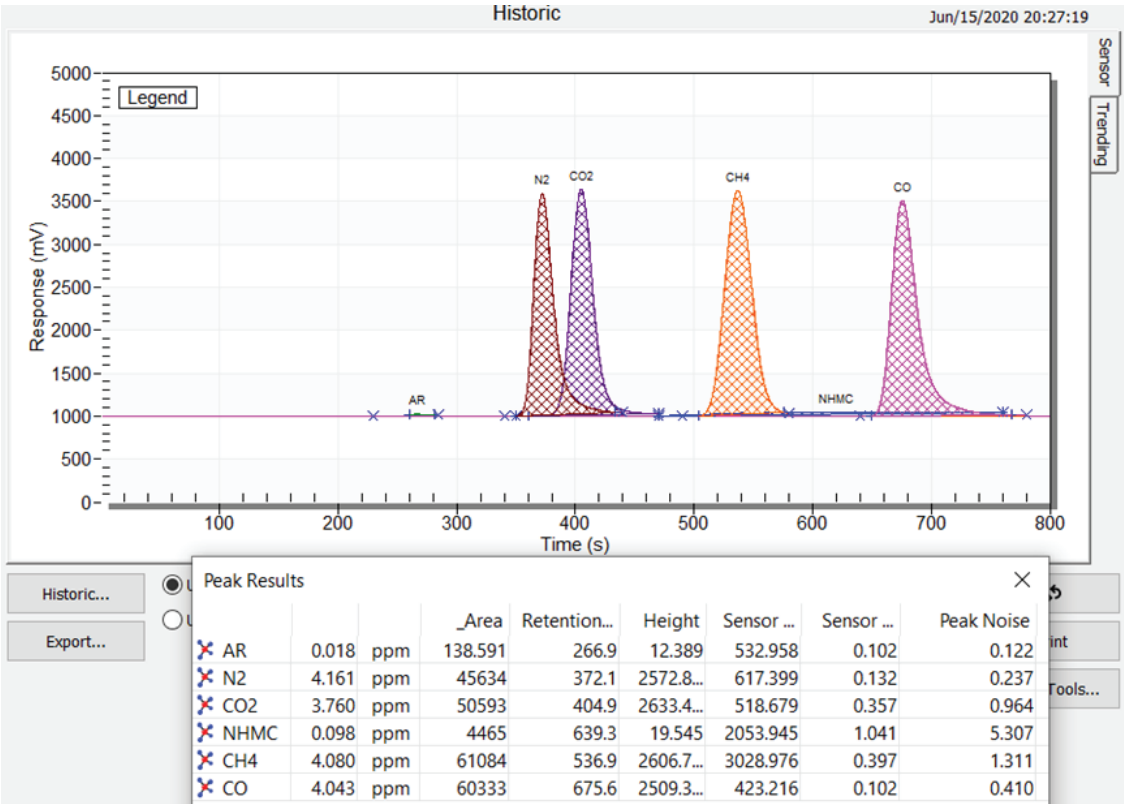
Using a series of 6 consecutive analysis, the repeatability conformity test must be below 5% considering a value of 3 times the coeficient of variation (CV) to be accepted.

The repeatability % is obtained by applying the sigma of the 6 consecutive analysis on the average of these 6 same analysis.

The test has been performed at the bottom of the scale which is the most rigourous concentration to get a good repeatability. Running such repeatability test at higher concentration is just easier to get a better repeatability. It demonstrates the performance of the system in terms of repeatability at very low concentration.

Chromatograms : GC#2/Channel 1

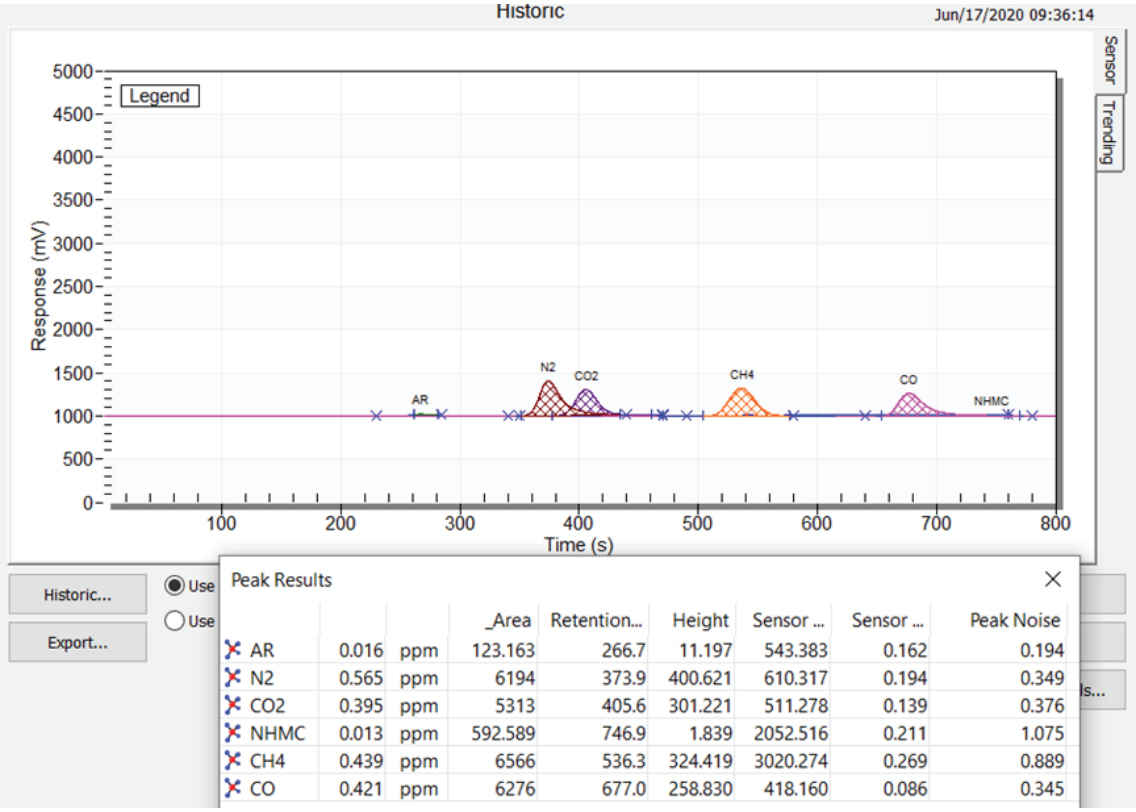
Sample : 4ppm N2-CO2-CH4-CO Balance H2



Peak Results

			_Area	Retention...	Height	Sensor ...	Sensor ...	Peak Noise
AR	0.018	ppm	138.591	266.9	12.389	532.958	0.102	0.122
N2	4.161	ppm	45634	372.1	2572.8...	617.399	0.132	0.237
CO2	3.760	ppm	50593	404.9	2633.4...	518.679	0.357	0.964
NHMC	0.098	ppm	4465	639.3	19.545	2053.945	1.041	5.307
CH4	4.080	ppm	61084	536.9	2606.7...	3028.976	0.397	1.311
CO	4.043	ppm	60333	675.6	2509.3...	423.216	0.102	0.410

Sample : 500ppb N2-CO2-CH4-CO Balance H2

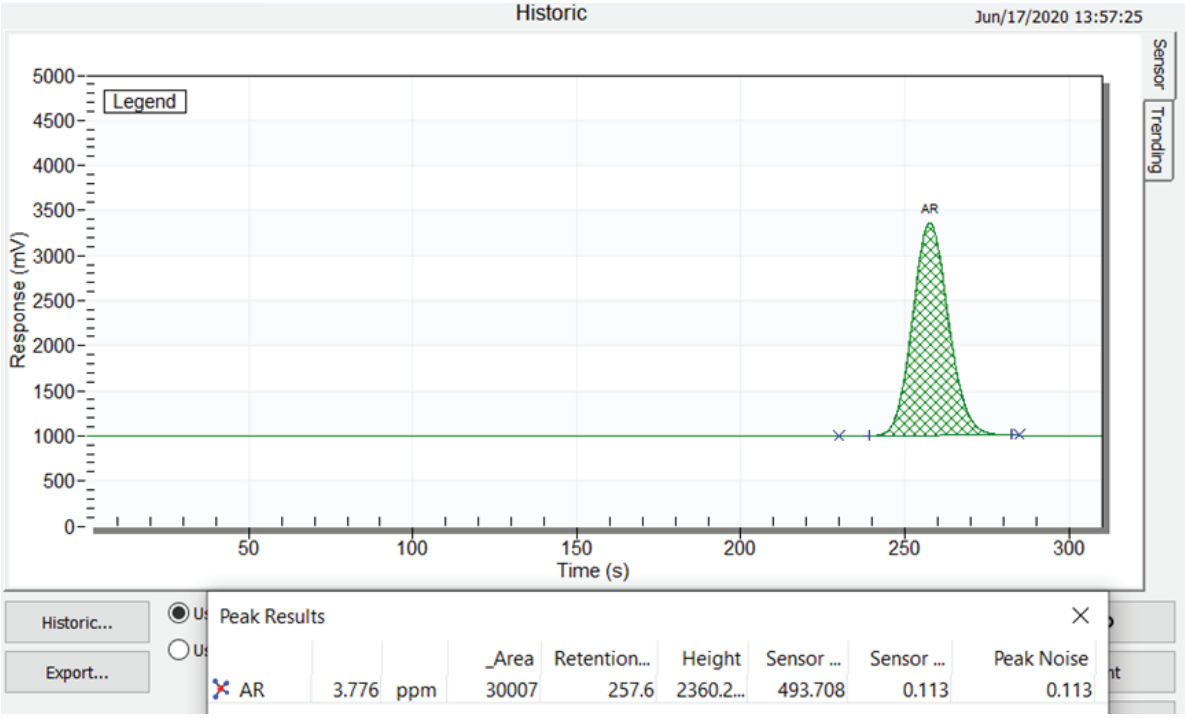


Peak Results

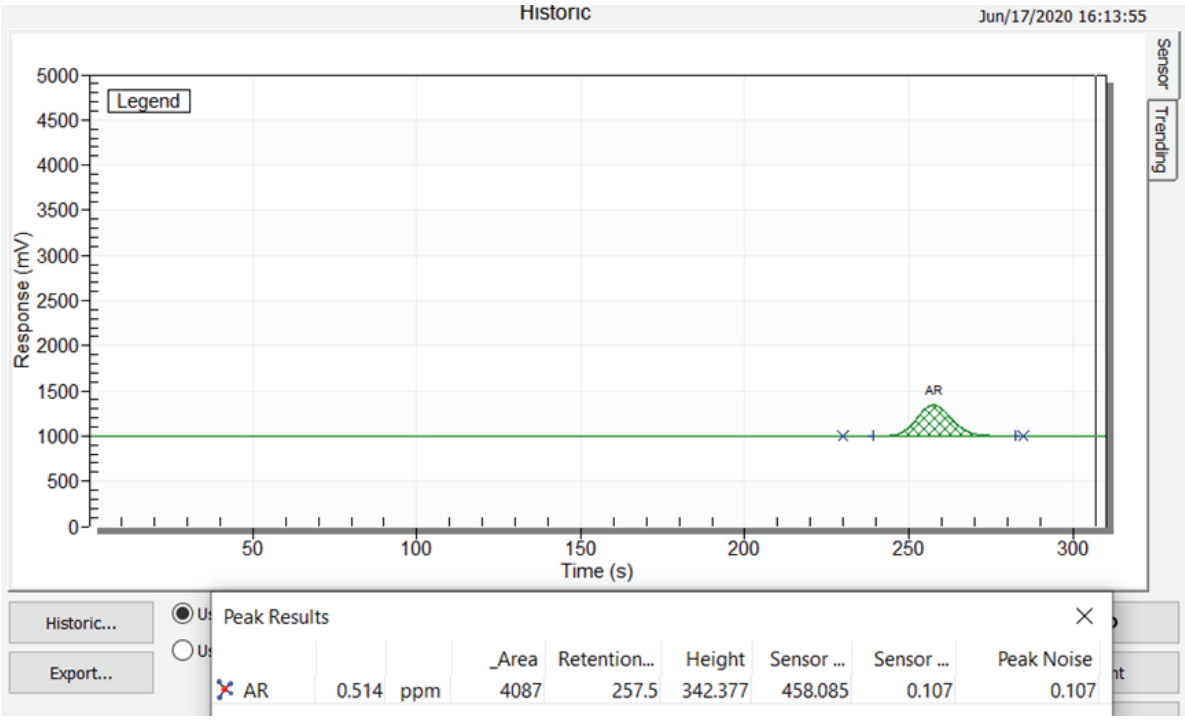
			_Area	Retention...	Height	Sensor ...	Sensor ...	Peak Noise
AR	0.016	ppm	123.163	266.7	11.197	543.383	0.162	0.194
N2	0.565	ppm	6194	373.9	400.621	610.317	0.194	0.349
CO2	0.395	ppm	5313	405.6	301.221	511.278	0.139	0.376
NHMC	0.013	ppm	592.589	746.9	1.839	2052.516	0.211	1.075
CH4	0.439	ppm	6566	536.3	324.419	3020.274	0.269	0.889
CO	0.421	ppm	6276	677.0	258.830	418.160	0.086	0.345

Chromatograms : GC#2/Channel 2

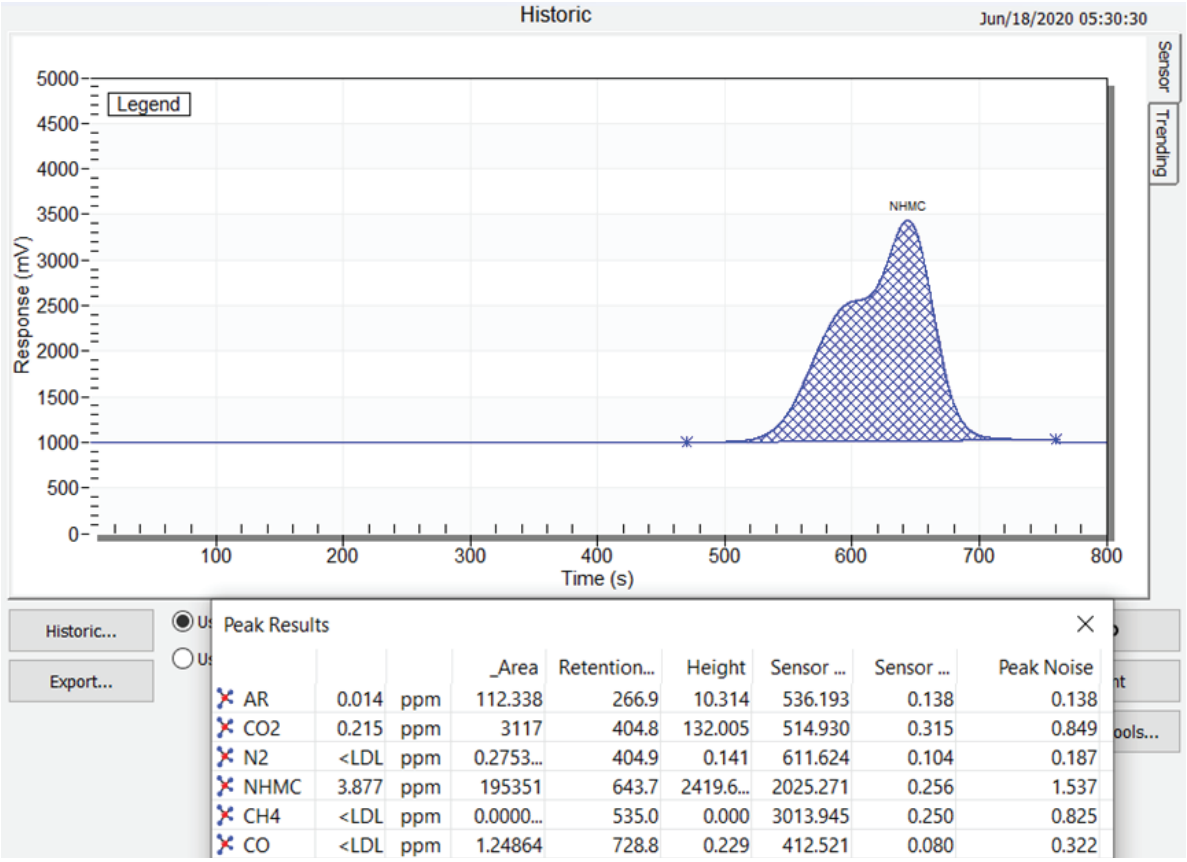
Sample : 4ppm Ar Balance H2



Sample : 500ppb Ar Balance H2

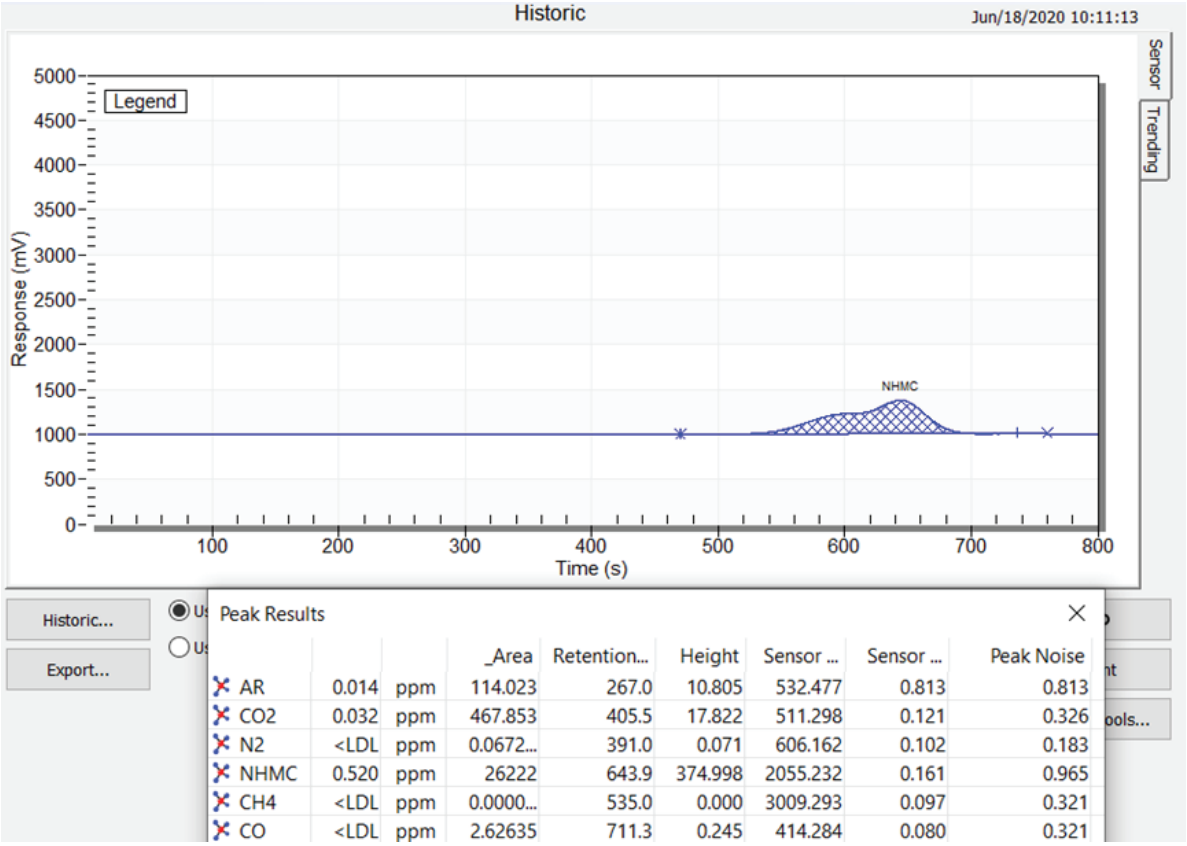


Sample : 4ppm NMHC(C3H8) Balance H2



			_Area	Retention...	Height	Sensor ...	Sensor ...	Peak Noise
AR	0.014	ppm	112.338	266.9	10.314	536.193	0.138	0.138
CO2	0.215	ppm	3117	404.8	132.005	514.930	0.315	0.849
N2	<LDL	ppm	0.2753...	404.9	0.141	611.624	0.104	0.187
NHMC	3.877	ppm	195351	643.7	2419.6...	2025.271	0.256	1.537
CH4	<LDL	ppm	0.0000...	535.0	0.000	3013.945	0.250	0.825
CO	<LDL	ppm	1.24864	728.8	0.229	412.521	0.080	0.322

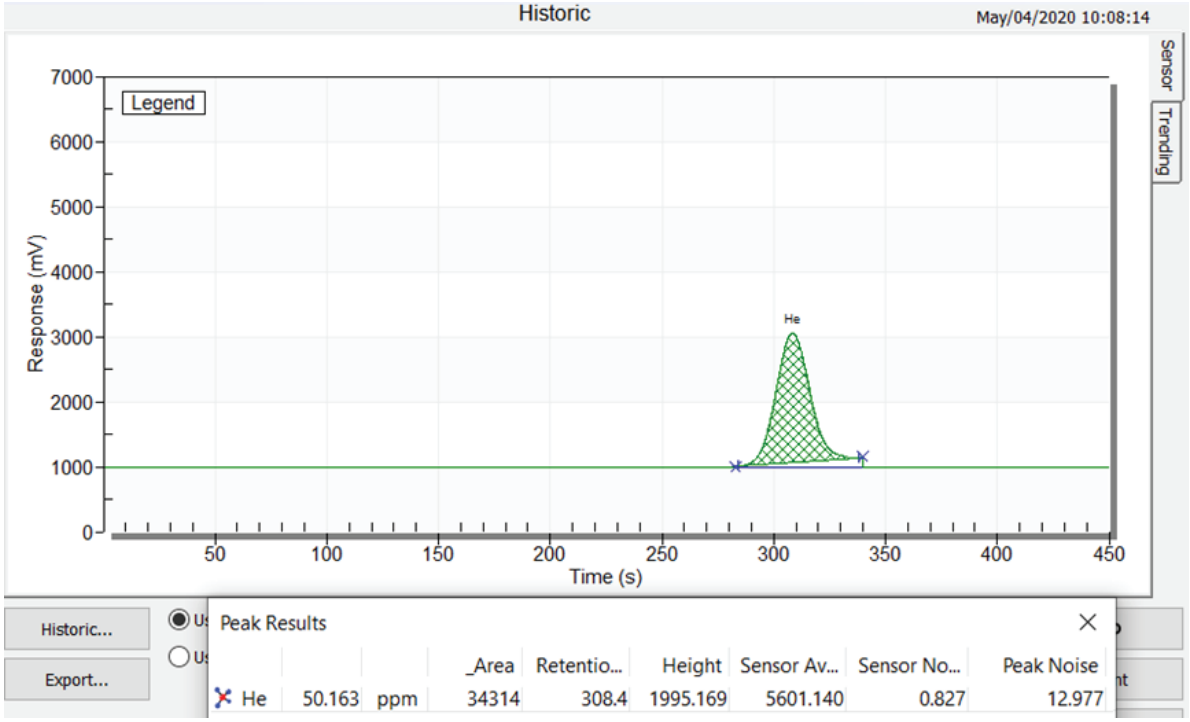
Sample : 500ppb NMHC(C3H8) Balance H2



			_Area	Retention...	Height	Sensor ...	Sensor ...	Peak Noise
AR	0.014	ppm	114.023	267.0	10.805	532.477	0.813	0.813
CO2	0.032	ppm	467.853	405.5	17.822	511.298	0.121	0.326
N2	<LDL	ppm	0.0672...	391.0	0.071	606.162	0.102	0.183
NHMC	0.520	ppm	26222	643.9	374.998	2055.232	0.161	0.965
CH4	<LDL	ppm	0.0000...	535.0	0.000	3009.293	0.097	0.321
CO	<LDL	ppm	2.62635	711.3	0.245	414.284	0.080	0.321

Chromatograms : GC#2/Channel 3

Sample : 50ppm He Balance H2



LDL :

Component	Concentration (ppb)	Peak height (mV)	Noise (mV)	LDL (3x Noise) (ppb)
N2	565	401	0.349	1.48
CO2	395	301	0.376	1.48
CH4	439	324	0.889	3.61
CO	421	259	0.345	1.68
Ar	514	342	0.107	0.48
NMHC	520	375	0.965	4.01
He	50(ppm)	1995	12.97	1.00(ppm)

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

Stability :

Sample : 1ppm Ar-N2-NMHC-CO2-CH4-CO Balance H2

Start	AR	N2	NHMC	CO2	CH4	CO
2020-05-21 20:16	0.889 ppm	1.171 ppm	0.564 ppm	1.045 ppm	1.161 ppm	1.042 ppm
2020-05-21 20:02	0.889 ppm	1.174 ppm	0.567 ppm	1.045 ppm	1.161 ppm	1.042 ppm
2020-05-21 19:49	0.886 ppm	1.174 ppm	0.568 ppm	1.044 ppm	1.161 ppm	1.042 ppm
2020-05-21 19:35	0.886 ppm	1.174 ppm	0.571 ppm	1.046 ppm	1.159 ppm	1.041 ppm
2020-05-21 19:21	0.886 ppm	1.174 ppm	0.573 ppm	1.044 ppm	1.160 ppm	1.042 ppm
2020-05-21 19:08	0.887 ppm	1.176 ppm	0.573 ppm	1.042 ppm	1.163 ppm	1.043 ppm

IMPURITIES	Ar	N2	NMHC	CO2	CH4	CO
Average (ppb)	887.2	1173.8	569.3	1044.3	1160.8	1042
Sigma σ (ppb)	1.47	1.60	3.61	1.37	1.33	0.63
CV (%)	0.17	0.14	0.63	0.13	0.12	0.06
CV x 3 (%)	0.5	0.41	1.90	0.39	0.35	0.18
Status	pass	pass	pass	pass	pass	pass
Repeatability (%)	0.2	0.1	0.6	0.1	0.1	0.1

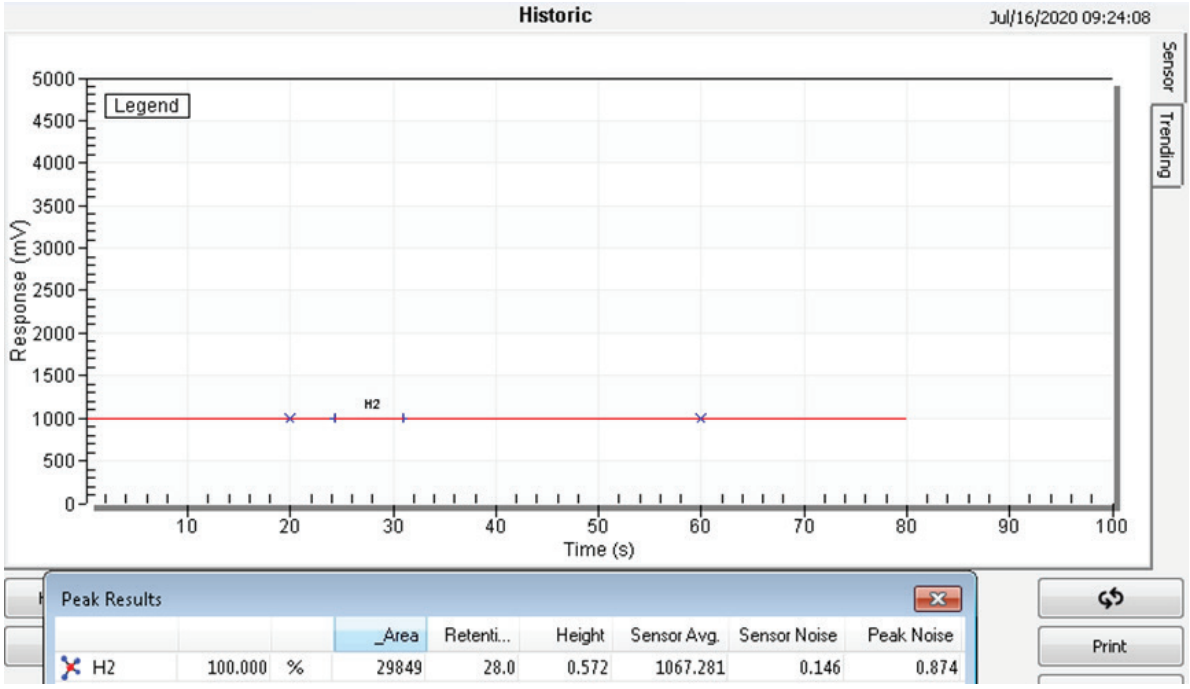
Using a series of 6 consecutive analysis, the repeatability conformity test must be below 5% considering a value of 3 times the coeficient of variation (CV) to be accepted.

The repeatability % is obtained by applying the sigma of the 6 consecutive analysis on the average of these 6 same analysis.

The test has been performed at the bottom of the scale which is the most rigourous concentration to get a good repeatability. Running such repeatability test at higher concentration is just easier to get a better repeatability. It demonstrates the performance of the system in terms of repeatability at very low concentration.

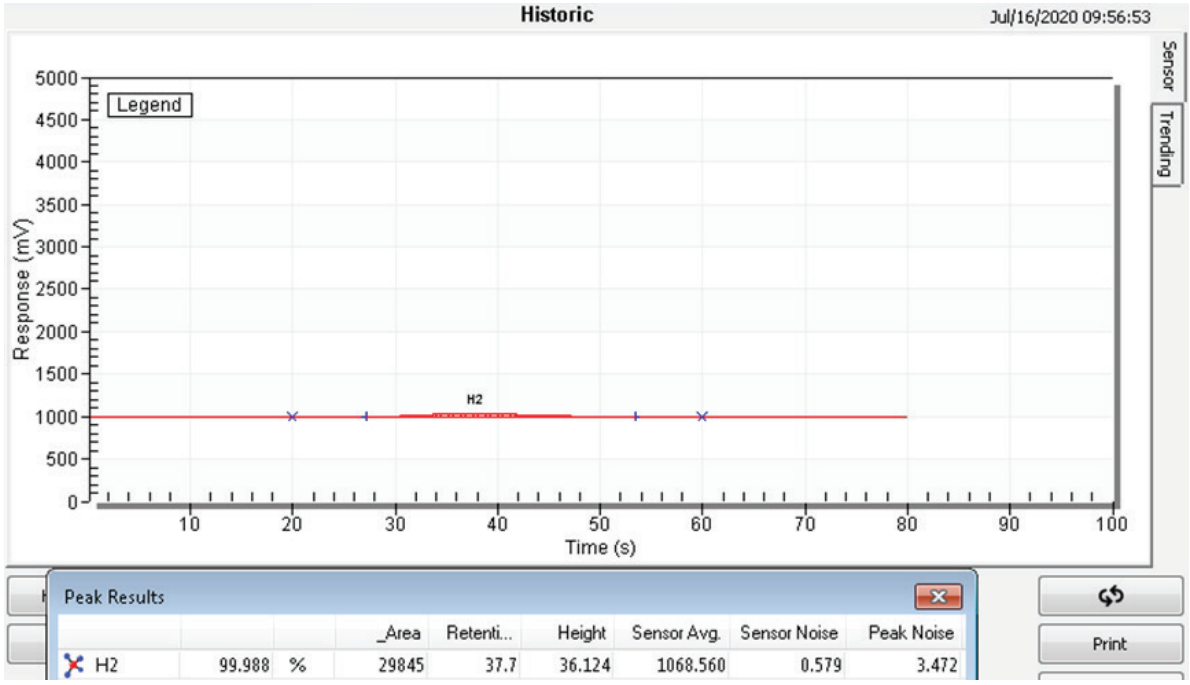
Chromatograms : GC#3/Channel 1

Sample: 100.000% H2

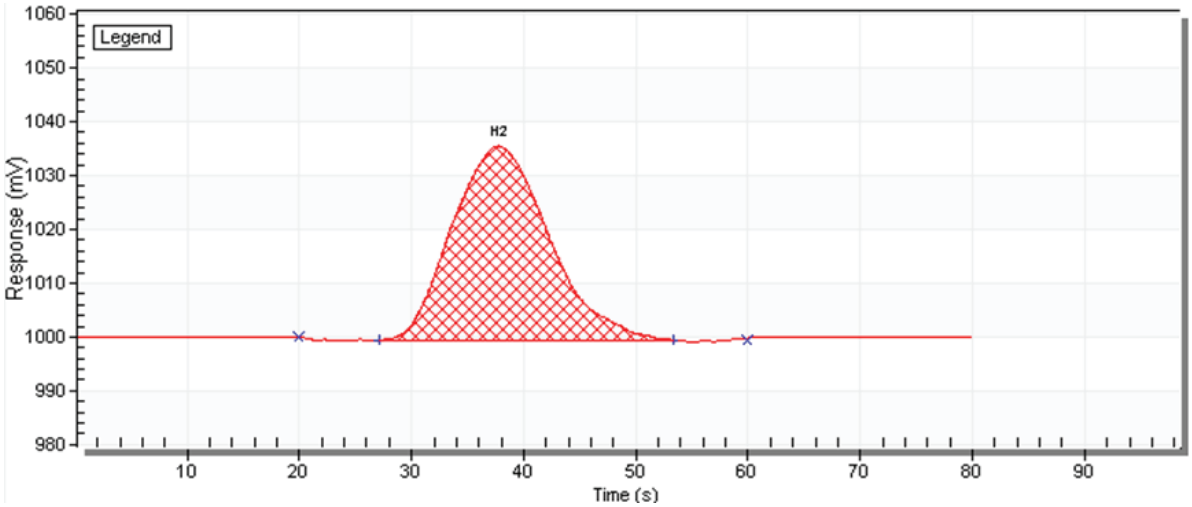


			_Area	Retenti...	Height	Sensor Avg.	Sensor Noise	Peak Noise
H2	100.000	%	29849	28.0	0.572	1067.281	0.146	0.874

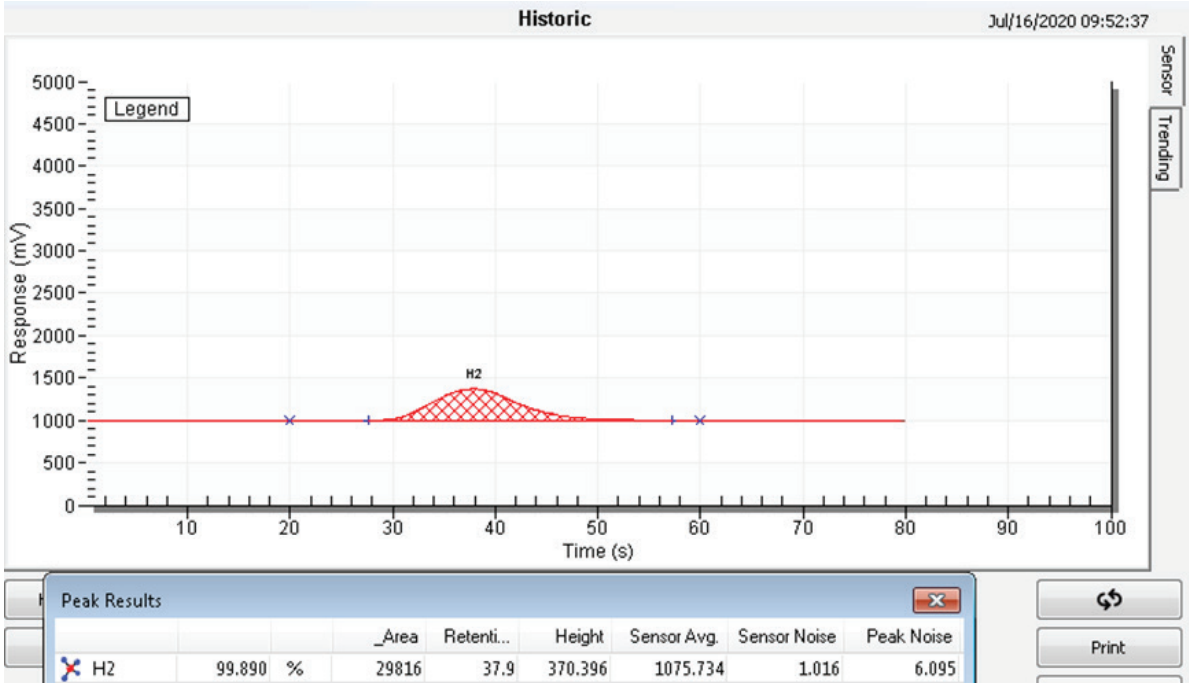
Sample: 99.989% H2



			_Area	Retenti...	Height	Sensor Avg.	Sensor Noise	Peak Noise
H2	99.988	%	29845	37.7	36.124	1068.560	0.579	3.472

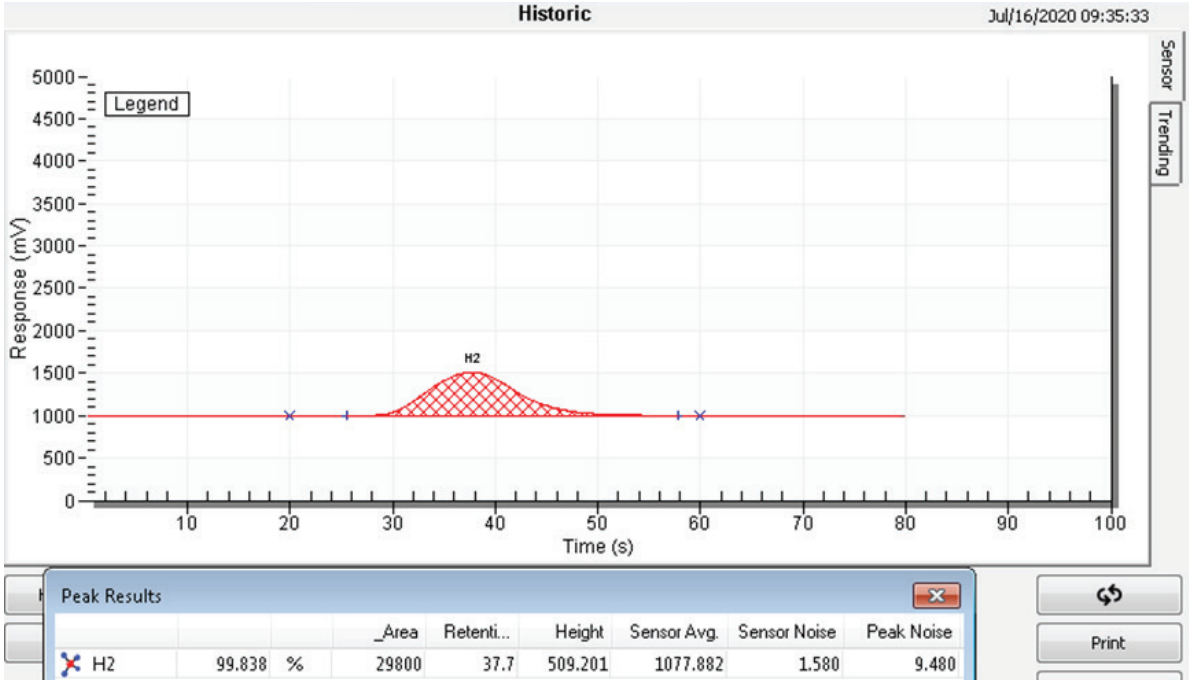


Sample: 99.890% H2



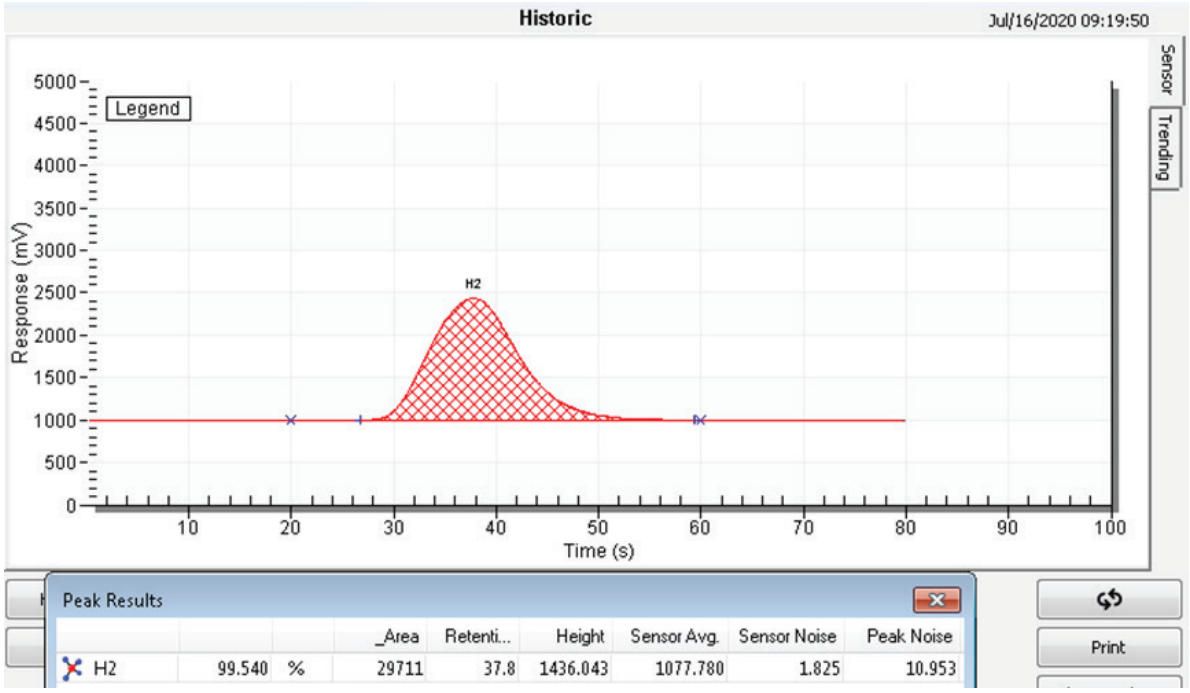
			_Area	Retenti...	Height	Sensor Avg.	Sensor Noise	Peak Noise
H2	99.890	%	29816	37.9	370.396	1075.734	1.016	6.095

Sample: 99.837% H2



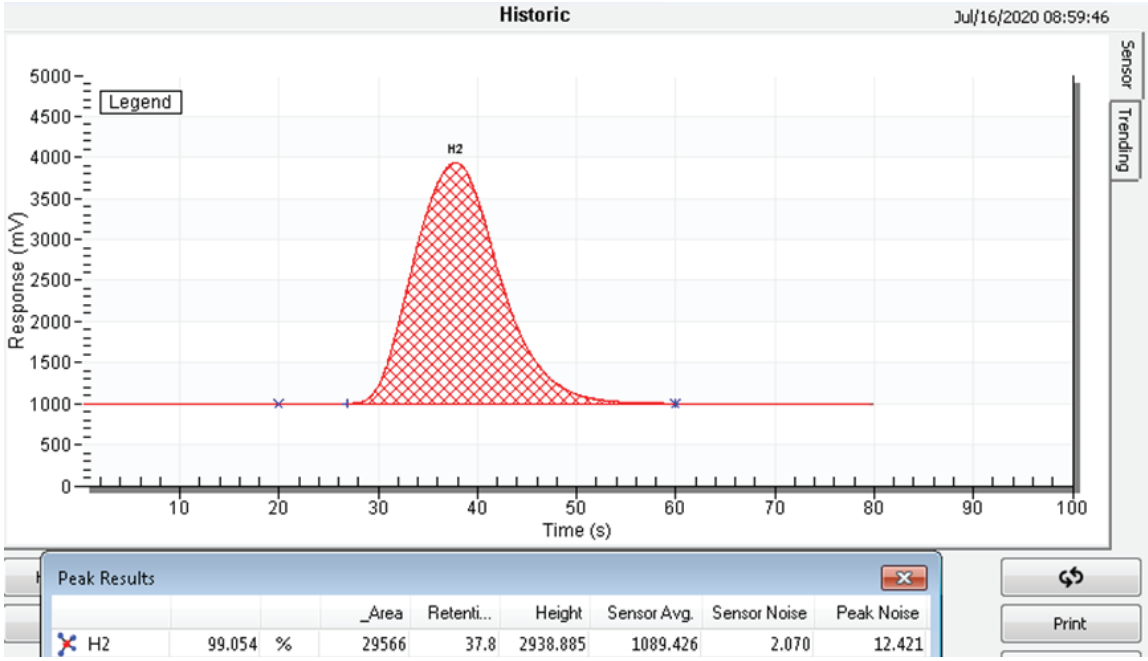
			_Area	Retenti...	Height	Sensor Avg.	Sensor Noise	Peak Noise
H2	99.838	%	29800	37.7	509.201	1077.882	1.580	9.480

Sample: 99.541% H2



			_Area	Retenti...	Height	Sensor Avg.	Sensor Noise	Peak Noise
H2	99.540	%	29711	37.8	1436.043	1077.780	1.825	10.953

Sample: 99.055% H2



LDL /Accuracy :

The concentration in % is obtained by dilution H2/N2. The difference between 100% H2 and the diluted H2 concentration is applied.

Component	**Concentration** (%)	**Peak height** (mV)	**Noise** (mV)	**LDL** (3x Noise) (%)	**Accuracy** (3x Noise) (%)
H2	0.012	36.124	3.472	0.003	+/-0.0015

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

Stability :

Sample : 99.750% H2

Start	H2
2020-07-16 10:28	99.756 %
2020-07-16 10:26	99.756 %
2020-07-16 10:25	99.756 %
2020-07-16 10:24	99.756 %
2020-07-16 10:22	99.756 %
2020-07-16 10:21	99.756 %
2020-07-16 10:19	99.756 %
2020-07-16 10:18	99.755 %
2020-07-16 10:16	99.755 %
2020-07-16 10:15	99.755 %
2020-07-16 10:14	99.755 %

ATEX

IECEx TEST REPORT of NATIONAL DIFFERENCES

ExTR Reference Number.....:	CA/QPS/ExTR19.0028/00
ExTR Free Reference Number.....:	X35775-1
Compiled by + signature (ExTL)....:	Alenko Vranes
	Kerry Nice, A.Sc.T.
Reviewed by + signature (ExTL)....:	Rob Kohuch, P. Eng.
Date of issue.....:	January 24, 2020
Ex Testing Laboratory (ExTL).....:	QPS Evaluation Services Inc.
Address.....:	81 Kelfield St, Unit 8, Toronto, ON M9W 5A3
Applicant's name.....:	LDetek Inc.
Address.....:	990 Rue Monfette E Thetford Mines, QC G6G 7K6, Canada
Country/Region.....:	Europe: Switzerland (CH), Czech Republic (CZ), Germany (DE), Denmark (DK), Finland (FI), France (FR), United Kingdom (GB), Hungary (HU), Italy (IT), the Netherlands (NL), Norway (NO), Romania (RO), Sweden (SE) and Slovenia (SI)
Standards.....:	EN 60079-0:2012/A11:2013; EN 60079-2:2007; EN 60079-7:2007; EN 60079-11:2012; EN 60079-18:2009.
Test Report Form Number.....:	ExTR National Differences_3 (released 2018-02)

No national differences between below European standards and International standards		**Verdict**
European Standards:	**International Standards:**	
EN 60079-2:2007	IEC 60079-2:2007 Edition 5.0	**Pass**
EN 60079-7:2007	IEC 60079-7:2006 Edition 4.0	**Pass**
EN 60079-11:2012	IEC 60079-11:2011 Edition 6.0	**Pass**
EN 60079-18:2009	IEC 60079-18:2009 Edition 3.0	**Pass**

IECEx TEST REPORT COVER

ExTR Reference Number.....:	CA/QPS/ExTR 19.0028/00
ExTR Free Reference Number .....:	X35775-1
Compiled by + signature (ExTL) ....:	Alenko Vranes
	Kerry Nice, A.Sc.T.
Reviewed by + signature (ExTL)....:	Rob Kohuch, P. Eng.
Approved by + signature (ExCB) ...:	Dave Adams, P. Eng.
Date of issue .....:	February 21, 2020
Ex Testing Laboratory (ExTL).....:	QPS Evaluation Services Inc.
Address .....:	81 Kelfield St. Unit 7-9, Toronto. Ont. M9L 1S1. Canada
Ex Certification Body (ExCB).....:	QPS Evaluation Services Inc.
Address .....:	81 Kelfield St. Unit 7-9, Toronto. Ont. M9L 1S1. Canada
Applicant's name.....:	LDetek Inc.
Address .....:	990 Rue Monfette E Thetford Mines, QC G6G 7K6, Canada
Standards associated with this ExTR package .....:	IEC 60079-0:2011, Edition 6.0
	IEC 60079-2:2007, Edition 5.0
	IEC 60079-7:2006, Edition 4.0
	IEC 60079-11:2011, Edition 6.0
	IEC 60079-18:2009, Edition 3.0
Clauses considered .....:	All clauses considered
Related Amendments, Corrigenda or ISHs .....:	All items are considered
Test item description.....:	Gas Chromatograph MultiDetek 2 EX
Model/type reference .....:	MultiDetek Ex
Code (e.g. Ex __ II__ T__).....:	Ex eb ib mb pxb IIB+H2 T4 Gb
Rating.....:	MultiDetek 2 EX
	Purge Controller Power: 230 V AC, 47 – 63 Hz, 660 Watts
	Maximum sample gas pressure: 689 mbar (10 psi)
	Minimum purge flow: 120 l/min
	Minimum purge time: 78 minutes
	Maximum overpressure: 6.7 mbar
	Minimum overpressure: 1.24 mbar
	Maximum supply air pressure: 6.9 bar
	Minimum supply air pressure: 1.4 bar
	Door clamps tightening torque: 3.4 – 3.9 Nm

IECEx Test Report Summary

INTERNATIONAL ELECTROTECHNICAL COMMISSION
IEC Certification System for Explosive Atmospheres

for rules and details of the IECEx Scheme visit www.iecex.com

ExTR Ref. No.:	**CA/QPS/ExTR19.0028/00**	**Page 1 of 1**
ExTR Free Ref. No.:	**X35775-1**	**Status: Issued**
List of Standards Covered:	**IEC 60079-0:2011 Edition:6.0, IEC 60079-11:2011 Edition:6.0, IEC 60079-18:2009 Edition:3, IEC 60079-2:2007-02 Edition:5, IEC 60079-7:2006-07 Edition: 4**	**Date of issue: 2020-02-21**
Issuing ExTL:	**QPS - QPS**	
Endorsing ExCB:	**QPS - QPS**	
Manufacturer:	**LDetek Inc.** 990 Rue Monfette E Thetford Mines G6G 7K6 QC	
Location of Manufacturer:	**Canada**	
Ex Protection:	**Ex eb ib mb pxb IIC T4 Gb**	
Ratings:	**115 V AC, 25 A, 50/60 Hz** **IP55**	
Equipment:	**Gas Chromatograph**	
Model Reference:	**MultiDetek 2 EX**	

Related IECEx Certificates:

IECEx QPS 19.0032X Issue 0

Comments:

CE

In compliance with EMC directive 2004/10EC, EN 61000-6-2-2005 for immunity & EN 61000-6-4:2007 for emissions.

File No. 53220 / EMC Test Report

Test name Standard	Limit Test level	EUT	Results
Measurement of conducted emissions CISPR 22: 2008	Class A	E35421 E35422 E35423	Pass
Measurement of radiated emissions CISPR 22: 2008, up to 6 GHz	Class A	E35421 E35422	Pass
Measurement of conducted emissions FCC Part 15: 2015, Subpart B	Class A	E35421 E35422 E35423	Pass
Measurement of radiated emissions FCC Part 15: 2015, Subpart B, up to 8 GHz	Class A	E35421 E35422	Pass
Radiated electromagnetic field immunity – radio frequencies IEC 61000-4-3: 2006 A1: 2007 A2: 2010	10 V/m 80-1000 MHz 3 V/m 1.4-2.7 GHz	E35421 E35422	Pass
Conducted immunity IEC 61000-4-6: 2008	10 V power	E35421 E35422	Pass
Electrostatic discharge immunity IEC 61000-4-2: 2008	±4 kV contact ±8 kV air	E35421 E35422	Pass
Electrical fast transient immunity IEC 61000-4-4: 2012	±2 kV power	E35421 E35422	Pass
Surge immunity IEC 61000-4-5: 2005	±1 kV L - L ±2 kV L - Ground	E35421 E35422	Pass
Magnetic field immunity IEC 61000-4-8: 2009	30 A/m / 50 Hz	E35421 E35422	Pass
Voltage dips, short interruptions and voltage variation immunity IEC 61000-4-11: 2004	0% - 1 cycle 40% - 10 cycles 70%, 25 cycles 0% - 250 cycles	E35421 E35422	Pass

CONCLUSION

The MultiDetek3 analyzer can measure all the contaminants at the required limit of detection, with the appropriated repeatability and linearity by combining its PlasmaDetek2 (patented) with TCD and quartz crystal sensors all in one system. The modularity of the instrument gives the ability to adapt the analyzer as per your requirements. The system is compact and rackmount. It can be configured for any safe area using the LDRack integration solution. When an Ex-proof area installation is required, then our certified pressurized enclosure for Ex-proof area is used. With our temperature-controlled solution configured for outdoor temperature going from -30C to 40C, our system can be used for any indoor or outdoor installations. A one source manufacturer to provide a certified solution for measuring fuel cell hydrogen as per the industry standard.

REFERENCES

Hydrogen Fuel Quality for Fuel Cell Vehicles
SAE J2719 SEP2011
http://www.sae.org

Design report for quartz crystal sensor integrated in the MultiDetek3 GC for trace moisture analysis :
http://www.ldetek.com/uploads/cgblog/id53/Trace_moisture_analysis.pdf

EMC test report for MultiDetek3 GC and LDP1000 gas purifier
CRIQ file 670-53220

ATEX & IECEx test reports and certifications

QPS : ExTR Reference No. CA/QPS/ExTR19.0028/00