

HyDetek

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PROCESS SENSING
TECHNOLOGIES

LDetek
A PST BRAND

HYDROGEN QUALITY CONTROL & MONITORING



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ATEX/IECEX AND USA
EX PROOF CERTIFIED
SOLUTION

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STANDARD RACKMOUNT
SOLUTION

**Turnkey gas analysis solution
that meets the requirements
of the hydrogen production
standards**



HYDROGEN PRODUCTION

Although abundant on earth as an element, hydrogen is almost always found as part of another compound, such as water (H₂O) or methane (CH₄) and must be separated into pure hydrogen (H₂) 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 (CH₄) 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
 $\text{CH}_4 + \text{H}_2\text{O} (+ \text{heat}) \rightarrow \text{CO} + 3\text{H}_2$

Water-gas shift reaction
 $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 (+ \text{small amount of heat})$

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
 $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 (+ \text{heat})$

Water-gas shift reaction
 $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 (+ \text{small amount of heat})$

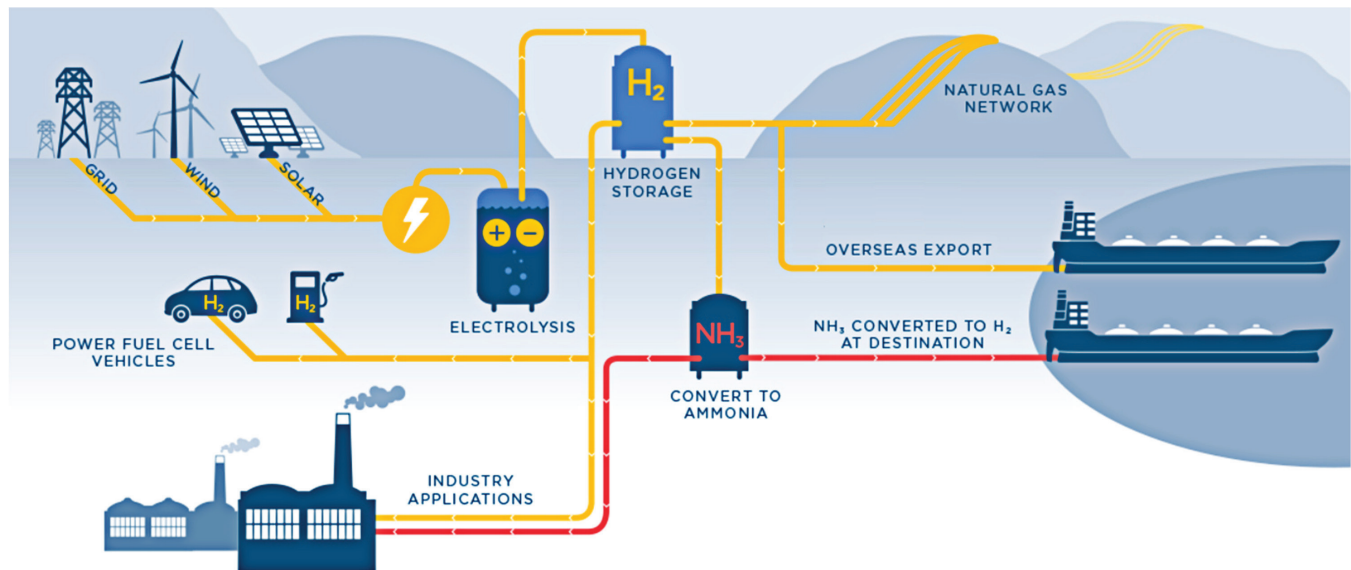
Why Is This Pathway Being Considered?

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, electrolyzers consist of an anode and a cathode separated by an electrolyte. Different electrolyzers 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: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ Cathode Reaction: $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$

Alkaline electrolyzers

Alkaline electrolyzers 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 electrolyzers, 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 electrolyzers must operate at temperatures high enough for the solid oxide membranes to function properly (about 700°–800°C, compared to PEM electrolyzers, which operate at 70°–90°C, and commercial alkaline electrolyzers, which operate at 100°–150°C). The solid oxide electrolyzers 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.

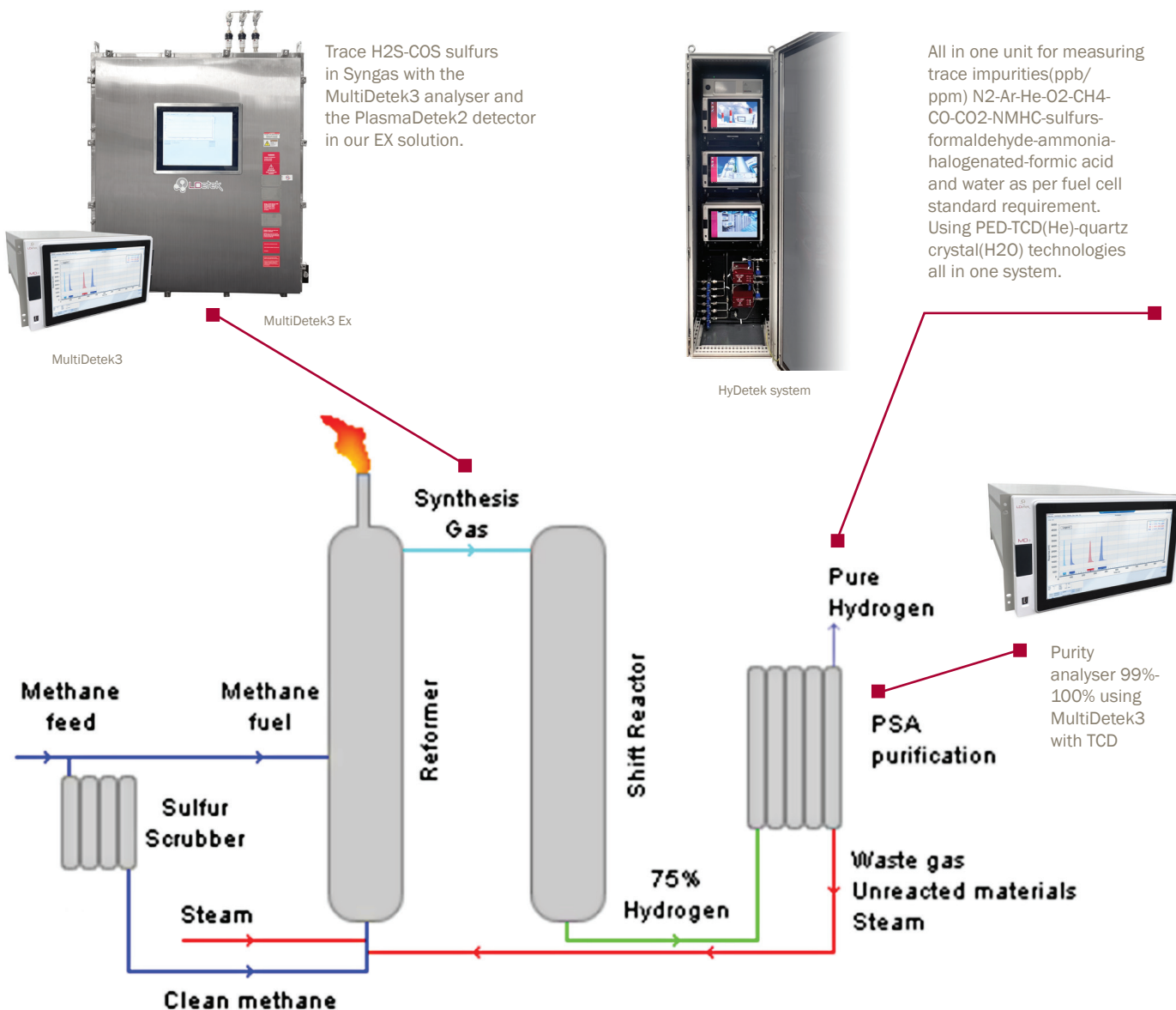
Why Is This Pathway Being Considered?

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



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 H₂, CO₂, CO as well as unreacted CH₄ and H₂O. 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 H₂S-COS in syngas to monitor the quality of synthesis gas used to produce 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 measure low ppm/ppb H₂S and COS in a gas mixture of H₂, CO₂ 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 performance 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 H₂ 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 O₂-Ar-N₂-CH₄-CO-CO₂-NMHC-He-H₂O.

ANALYSIS SOLUTION FOR WATER ELECTROLYSIS PRODUCTION



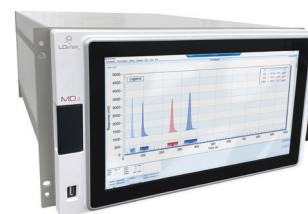
HyDetek system

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.



MultiDetek3 Ex

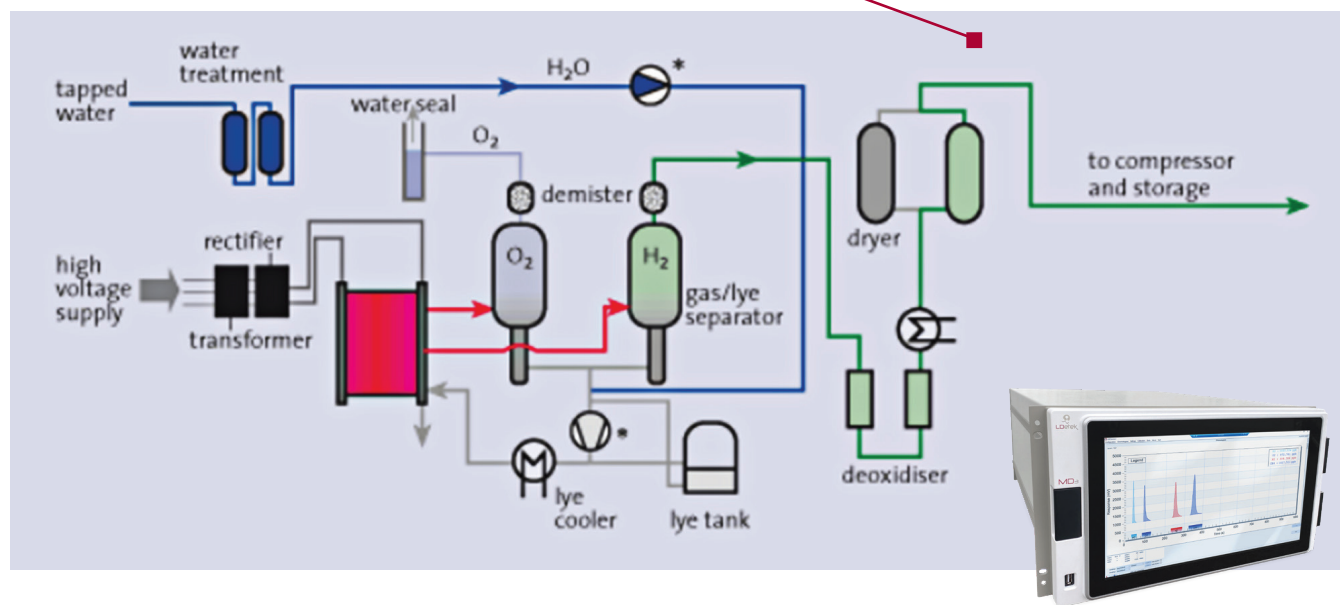
All in one unit for measuring trace impurities (ppb/ppm) N₂-Ar-O₂-CO-CO₂ and water as per fuel cell standard requirement. Using PED & quartz crystal(H₂O) technologies all in one system.



MultiDetek3

or

or

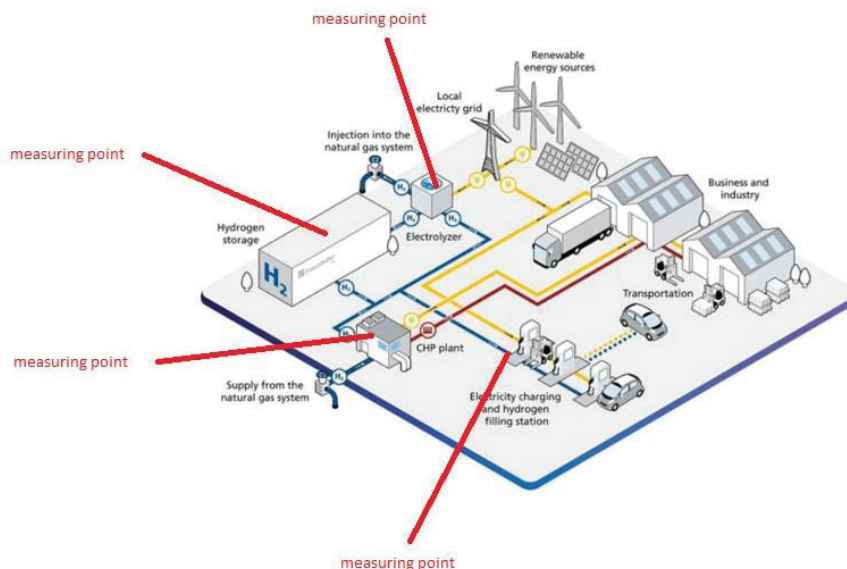


Purity analyser 99%-100% using MultiDetek3 with TCD

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
H ₂ S (hydrogen sulfide)	0-500	0.4	0.8	PED
COS (carbonyl sulfide)	0-500	0.5	0.6	PED
NH ₃ (ammonia)	0-1000	2.5	0.3	PED
CH ₂ O (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
CH ₄ S (methyl mercaptan)	0-500	0.5	1.5	PED
CS ₂ (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
H ₂ O	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

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
N ₂	0-10	1.5	0.1	PED
CH ₄	0-10	3.5	0.1	PED
CO	0-10	1.5	0.1	PED
CO ₂	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
O ₂	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
H ₂ O	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)
H ₂	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.



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