ORNL/TM-2023/2940

Commercially available Hydrogen Detection Systems for Corrosive, Oxygen-free Gas Streams: A Technical Summary

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July 2023

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Nuclear Energy and Fuel Cycle Division

COMMERCIALLY AVAILABLE HYDROGEN DETECTION SYSTEMS FOR CORROSIVE, OXYGEN-FREE GAS STREAMS: A TECHNICAL SUMMARY

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July 2023

Prepared by
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managed by
UT-BATTELLE LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

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ABSTRACT

The growing use of hydrogen gas across energy, transportation, and chemical applications necessitates better hydrogen sensors and detectors. Few sensors exist for quantifying hydrogen gas in a corrosive, oxygen-free gas stream due to the challenging nature of the sampling environment and current technological status. Handheld, economic options include palladium-based, metal oxide, catalytic bead, and electrochemical sensors. More permanent and costly options include electrochemical sensors, thermal gas analyzers, mass spectrometers, gas chromatographs, and Raman spectrometers. In this technical report, a short review of current technology, along with the associated commercially available products, is provided. Raman spectroscopy is recommended as an ideal technology for on-line detection of hydrogen at low concentrations in a corrosive, oxygen-free gas stream.

1. INTRODUCTION

Hydrogen gas can be found in a variety of chemical and industrial processes, but though it is advantageous in some applications, it poses challenges to others. Hydrogen has many uses in petrochemical processing, chemical synthesis, as a coolant, or even as an energy carrier. However, it may also be produced as an unwanted byproduct in industrial processes [3]. It is explosive at concentrations greater than 4% (lower explosive limit, LEL) and tends to leak because of its small molecular size [4]. Therefore, hydrogen detection is critical in both leak detection and for quantification in process gas streams to ensure safety in industrial processes.

Detection of hydrogen gas is challenging because of its specific chemical properties and the low detection limits required to ensure safety. At low hydrogen gas concentrations, the chemical properties of hydrogen limit the choices for detection techniques. Hydrogen is a diatomic molecular with no dipole moment, preventing traditional on-line gas detection using infrared (IR) spectroscopy. Therefore, specialized sensing options must be explored while maintaining as low of a detection limit as possible. In addition to concerns related to detection limits and techniques that can detect hydrogen, hydrogen gas requires specialized handling. At hydrogen gas concentrations above the LEL, specialized explosion-proof devices must be used for detection. Hydrogen detection is further complicated if detection is required in industrial process gas streams, which may be corrosive or oxygen-free. Specifically, corrosive gas streams may be incompatible with common construction materials, such as stainless steel, thus limiting the options for detectors or requiring customized detectors with compatible construction materials.

The combination of hydrogen's chemical properties with the handling and compatibility concerns in industrial process gases creates a unique difficulty for on-line hydrogen gas monitoring. Therefore, viable sensing options for this niche system must be explored and identified. The objective of this technical report is to identify and compare commercially available hydrogen sensors, reporting product highlights and product limitations. Product specifications and comparisons are utilized to suggest an optimal sensor for on-line hydrogen detection in an oxygen-free, corrosive gas stream.

2. COMMON TYPES OF HYDROGEN SENSORS

Numerous criteria must be met by on-line hydrogen monitoring in process gas streams to meet the chemical compatibility, detection limit, and time-response needs. An on-line technique must be able to measure hydrogen as it is produced, returning the analyzed gas to the original gas stream. If corrosive chemicals are present in the gas stream, then the materials of the hydrogen sensor or detector must be inert to the gas stream, which can contain corrosive chemicals such as HCl(g). Many stainless steels are susceptible to corrosion under acidic conditions. Hastelloy, Inconel, or other nickel-based materials as well as lined materials may be appropriate for acid-bearing gas streams. High temperatures and pressures may be likely in process gas streams. Finally, for some industrial processes, a sensor must be able to measure hydrogen in an oxygen-free environment.

Several techniques may be used for hydrogen sensing. The analytical instruments include gas chromatography, mass spectrometry, and Raman spectroscopy, all of which may be used without oxygen in the sample stream. However, because of their high costs and frequent calibration or maintenance requirements, these techniques are often impractical for industrial applications. Thermal conductivity, solid-state detectors such as catalytic bead and metal oxide detectors as well as electrochemical techniques are other possibilities for hydrogen detection. These techniques are often cheaper than the analytical techniques, but they all rely on the presence of oxygen for operation. Finally, new palladium-based sensors are promising solutions in oxygen-free environments and are more cost-effective than the analytical techniques for hydrogen detection [1]. Table 1 provides a summary of these sensor technologies and their properties.

Table 1: Common types of hydrogen sensors and notable properties

Type of sensor	Price	Oxygen required?	Estimated limit of detection	Estimated lifetime/ maintenance	Response Time
Gas chromatography	$$$	No	50–100 ppm	Frequent maintenance (months)	Long (minutes)
Mass spectrometry	$$$	No	100 ppb	Frequent maintenance (months)	Long (minutes)
Raman spectroscopy	$$$	No	500 ppm	Long (>5 years)	Medium (seconds – minutes)
Thermal conductivity	$$	No	50 ppm	Unknown	Medium (seconds – minutes)
Catalytic bead	$	Yes	Varies	Short	Short (seconds)
Metal oxide	$	Yes	Varies	Short	Short (seconds)
Electrochemical	$	Yes	10 ppm	Approx. 5 years	Short (seconds)
Palladium	$$	No	1–50 ppm	Est. 6 months – 3 years	Medium (seconds – minutes)

2.1 GAS CHROMATOGRAPHY

When coupled with an optimum detector, gas chromatography (GC) can be used to separate and detect the hydrogen in a sample gas stream [5]. Here, a carrier gas moves a sample through a column containing a stationary phase, and molecules in the sample interact with the stationary phase at various rates. Detection of the separated components is often done by either a thermal conductivity detector or mass spectrometer [6]. Quantification of the other components in the gas sample is possible but at the cost of additional time and cost to the analysis and is often minimized in process streams. Long response times, consumption of the carrier gas, and maintenance of the instrument—such as replacement of the column and frequent instrument calibration—are characteristic of GC. All challenges are amplified if the sample stream contains a corrosive material [7]. Therefore, it is not recommended for hazardous or corrosive gas streams.

2.2 MASS SPECTROMETRY

A mass spectrometer can be used to detect hydrogen in an on-line process gas stream by ionizing the gaseous sample and measuring the mass-to-charge ratio of the ions. The ratio or fragmentation pattern of the ions can be used to identify and quantify the hydrogen concentration of the sample [8]. Residual gas analyzers (RGAs) are robust mass spectrometers often used to measure gaseous impurities, such as hydrogen, in vacuum systems [9]. In general, however, mass spectrometers, including the more robust RGAs, require a significant amount of maintenance and upkeep. Corrosion of the stainless-steel components may also shorten the life of the mass spectrometer [10]. Using mass spectrometry may be useful for laboratory-scale operations but more challenging in industrial application. RGAs have also shown issues with residual hydrogen in the analyzer, particularly when exposed to HCl that fragments to hydrogen and chlorine atoms.

2.3 THERMAL CONDUCTIVITY DETECTORS

Known for high precision and low limits of detection, thermal conductivity detectors (TCDs) are commonly used in industrial settings for hydrogen measurement. A reference, pure carrier gas is used as a comparison to the thermal conductivity of the sample gas. The difference in thermal conductivity is detected by the change in temperature inside the gas measurement cell when the analyte is introduced. A Wheatstone bridge detects the temperature, and a signal is converted to voltage, proportional to the concentration of the gas analyte in a sample [11]. Hydrogen has a relatively high thermal conductivity at 186 mW m^{-1} K^{-1} at 300 K, whereas other gases under the same conditions have a thermal conductivity of 14 (HCl), 17 (argon), 26 (nitrogen), 26 (oxygen), and 26 (air) mW m^{-1} K^{-1} at 300 K, for example [12].

Despite being one of the most common detectors for measuring hydrogen, TCDs' response and measurement quality can be influenced by several factors. The temperature of the sample cell, the flow rates of the reference gas and sample gas, and the type of thermistors used must be consistent for a precise measurement. Any variance must be closely monitored. Furthermore, any reactive chemicals in the sample gas will sacrifice the integrity of the wire thermistors, rendering them useless [13, 14]. For this reason, a TCD may not be an optimal detection device for measuring hydrogen in a variable, corrosive process gas stream.

2.4 RAMAN SPECTROSCOPY

Hydrogen can be detected via Raman spectroscopy by measuring the light scattered by the bond vibration in the molecule. There are three types of light scattering: Rayleigh, Stokes, and anti-Stokes. Most of the scattered light is equivalent in frequency to that of the incident light, resulting in Rayleigh scattering, or elastic scattering. Raman scattering is inelastic scattering, made of Stokes and anti-Stokes scattering. This type of scattering occurs less frequently than Rayleigh. The two types of scattering must be effectively separated, allowing the Raman signals to proceed through the instrument to the detector [15]. Though Raman spectroscopy is inherently less sensitive than other detection techniques, Raman can be used where other techniques cannot. Flow cells can be designed with a variety of materials for online measurements, even in corrosive atmospheres without the presence of oxygen.

2.5 CATALYTIC BEAD SENSORS

Catalytic bead sensors are solid-state sensors that rely on the change of electrical resistance in a gaseous atmosphere due to the presence of hydrogen [16]. Two coils of platinum wire are embedded into a bead of alumina, connected in a Wheatstone bridge. One of the sensing elements is coated in a catalyst that promotes oxidation in the sample gas, while the other element inhibits oxidation. Oxidation in the sample gas may not be specific to hydrogen if other compounds are present in the gas stream. The coils are heated, oxidation on the catalyst occurs, and the resistance of the wires triggers a voltage change in the Wheatstone bridge. Any change in voltage directly relates to the concentration of a gas in the sample [1,17].

Metal oxide sensors are a specialized class of catalytic bead sensors, and there are various classifications of metal oxide sensors, such as resistance, work function, optical, and acoustic based sensors, that all rely on differences in thermal conductivity of gases for detection. Like all other catalytic bead sensors, metal oxide sensors require oxygen in the sample gas stream and must be operated at high temperatures (300–500°C) [18].

2.6 ELECTROCHEMICAL SENSORS

Amperometric, potentiometric, and conductometric devices are the three major types of electrochemical sensors used commercially for measuring hydrogen that rely on electrochemical reactions between hydrogen and the sensing electrode. These devices have an anode and cathode submerged in an electrolyte [19]. Based on the temperature of the sensor operation, the type of electrolyte used can be altered. Liquid and polymer electrolytes are used for low to room temperature applications, while solid-state electrolytes are applicable for high temperatures. An electrochemical reaction between the anode and cathode occurs in the presence of hydrogen, changing either the voltage or current in the electrical circuit [1]. In general, the reaction at the anode is seen in (1) and the reaction at the cathode is seen in (2) for the most commonly used amperometric sensor [19]. Oxygen in the sample gas stream is required for use.

$$H_2\,(g) \rightarrow 2\,H^+ + 2\,e^- \tag{1}$$

$$1/_2\,O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O \tag{2}$$

2.7 PALLADIUM-BASED SOLID-STATE SENSORS

Palladium is widely used for hydrogen sensing due to its unique response and high sensitivity to hydrogen gas. As seen in Figure 1, molecular hydrogen dissociates on the surface of the palladium, chemisorbing hydrogen atoms onto the surface. The atoms diffuse into the palladium lattice network [1]. The change to the lattice results in a conductive phase change, resulting in a change of electrical conductivity across the bulk palladium. The geometry varies greatly across the many types of palladium-based sensors due to the surface-mediated reaction with the hydrogen molecules. The most common type of geometries seen for sensors are thin films, nanowires, nanoparticle networks, nanoclusters, and nanotubes, all designed to

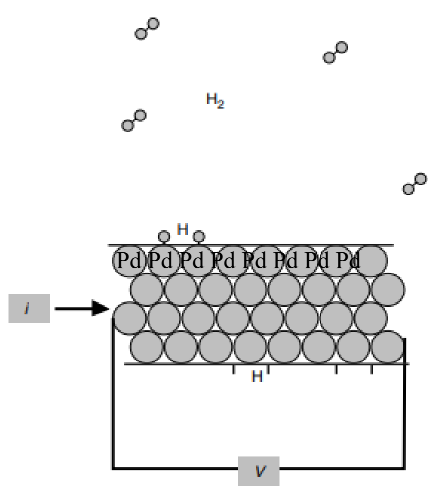

Figure 1. Interaction of hydrogen with a palladium surface; adapted from Soundarrajan and Schweihardt [1].

increase the surface-to-volume ratio [20]. An increased surface-to-volume ratio will result in a better sensor response.

The specifications of the palladium-based sensors vary. Some require heating (resistors), some are expensive (fiber optic detectors), and others experience interference with ambient conditions such as humidity (nanoparticle network). For all sensors, however, the basis of the catalytic interaction between palladium and hydrogen could be disrupted by poisoning of the palladium. Carbon monoxide, nitrogen oxides, sulfuric compounds, or other gaseous species present in high concentrations may poison or deactivate the sensors [21–23].

3. COMMERCIALLY AVAILABLE PRODUCTS

Commercially available products were researched to identify a viable sensor for on-line hydrogen measurements in an oxygen-free, corrosive gas stream. First, laboratory-scale, portable detectors were investigated. The specifications of these sensors were suitable for use in a laboratory setting, and products represent an economical option for quick results. Second, semi-permanent sensors were investigated as they may be more robust for industrial on-line sensing. Though more expensive, these options are more suited for the corrosive, oxygen-free on-line hydrogen measurements.

3.1 HANDHELD, ECONOMICAL HYDROGEN SENSING DEVICES

Handheld hydrogen sensors may be useful in laboratory applications for on-line gas sensing for hydrogen. Many of these sensors are portable, with simple software for ease of use. All options are less than $15,000 with variable need for sensor replacement and maintenance.

3.1.1 H2scan palladium – based suite

H2scan specializes in hydrogen detection using the palladium-based technology. Each product costs around $10,000, and specifications are given in Table 2 [24–26]. The sensors can measure either in a low range of detection (ppm – 0.5% v/v) using a capacitor or a high range of detection (up to 100%) using a resistor. Both the high- and low-range sensors utilize palladium to catalyze hydrogen into atomic hydrogen, which is absorbed into the palladium nickel alloy lattice. These sensors are both specific to hydrogen and may operate in oxygen-free environments. The three models available use the same sensors but vary in form factors, power requirements, and electrical/safety certifications [27]. However, none of the palladium nickel alloy sensors are designed to withstand high concentrations of corrosive gases and may be corroded upon exposure to a sample gas stream.

Table 2. Summary of H2scan handheld hydrogen sensor products [24–26].

	HY-OPTIMA 710B*	HY-OPTIMA 1720*	HY-OPTIMA 2710
Cost	$10,440	~$10,000	~$10,000
Lowest estimated range	700 -10,000 ppm	4000-50,000 ppm	1000-100,000 ppm
Gas temperature range	−20 – 40°C	−20 – 40°C	−20 – 55°C
Calibration	In lab – 90 days	90 days	90 days
Flow rate	0.1 − 10 SLPM	0.1 – 10 SLPM	0.1 – 10 SLPM
Operating pressure	13 – 15.1 PSIG	13 – 15.1 PSIG	13 – 15.1 PSIG
Compatible with corrosives	No	No	No
Response time	<90 seconds	<60 seconds	<90 seconds
Power	12V DC power	24V DC power supply	120V AC
Compatible with oxygen-free atmosphere	Yes	Yes	Yes

*uses a probe tip purchased separately and tied inline to the gas stream.

3.1.2 MLT thermal conductivity detector

Two viable options for hydrogen detection in an oxygen-free gas stream are portable TCDs from the MLT line of gas sensors [28, 29]. The comparison between the two models, the K522 and K1550, can be seen in Table 3 below. The primary difference between the two products is the electronic interface on the instrument. Whereas the K522 is controlled via connection to a PC, the K1550 model has a digital display to control the instrument.

Table 3. Summary of MLTGas hydrogen sensor products

	K522	**K1550**
Cost	$6,126	$9,230
Lowest estimated range	0 – 10% in N_2 or Ar	0 – 5%
Gas temperature range	−40 – 40°C	0 – 40°C
Calibration	3 – 6 months	3 – 6 months
Flow rate	Unknown	100 – 300 liter/minute
Operating pressure	14.6 +/- 1.4 PSIG	Up to 87 PSIG
Compatible with corrosives	No	No
Response time	~20 seconds	20 seconds
Power	24V DC	110V
Compatible with oxygen-free atmosphere	Yes	Yes

The products can be customized based on the application. The K1550 model can be purchased with an intrinsically safe barrier, K1550FX. This barrier is a flameproof encloser to be used in hazardous areas when the concentration of hydrogen is greater than 4%. Additionally, a PTFE sensor for the K1550 is available and is recommended for a corrosive gas stream. However, the PTFE sensor is physically not compatible when the K1550FX is in use [29]. Therefore, either the sensor can be used in hazardous areas with a hydrogen concentration greater than 4% *or* it can be used with a corrosive gas stream.

3.1.3 Gas Sensing electrochemical sensors

Handheld electrochemical detectors are among the cheapest options for hydrogen detection. Gas Sensing sells two options [30–33]. The specifications for the Aeroqual series 500 (S-500HA) hydrogen sensor and Model H10-18 are detailed in Table 4. Both devices use interchangeable sensors for a variety of gases. The hydrogen sensors are inexpensive (~$400) but may require frequent replacement depending on usage frequency and conditions. Furthermore, because both are electrochemical-based sensors, they require oxygen and may not be compatible with corrosive gas streams.

Table 4. Summary of Gas Sensing and Aeroqual handheld sensors

	Gas sensing – Model H10-18	**Aeroqual series 500 (ATI S-500HA)**
Cost	$1,600 replacement sensors: $425	$1,440 Replacement sensors: $435
Estimated range	10–2000 ppm	5–500 ppm
Lifetime	~24 months (clean conditions)	~ 24 months (clean conditions)
Gas temperature range	−30 – 55°C	0 – 40°C
Calibration	Initial for $50 custom – for 6 months	Every 6 months w/calibration kit
Flow rate		1 SLPM
Operating pressure	−3 – 3 PSIG	
Compatible with corrosives	No	Unknown

Response time	75 seconds	30 seconds
Power	Rechargeable battery	12V DC power with Li battery
Compatible with oxygen-free atmosphere	No	No

3.2 PERMANENT OR SEMI-PERMANENT HYDROGEN SENSING DEVICES

Permanent or semi-permanent hydrogen sensors may be more applicable for industrial applications, particularly for corrosive gas streams. Some of the commercially available mounted sensors use the same technology as those of the handheld devices. Because the sensor serves only one purpose, they are often offer more customizable to an application.

3.2.1 RKI Instruments catalytic bead and metal oxide sensors

Solid-state sensors, like catalytic bead and metal oxide sensors, are commonly used for hydrogen detection. RKI Instruments carries both types of devices utilizing a single-channel wall-mounted gas detector. Both sensors require oxygen for operation [34, 35]. Corrosive gases at low concentrations may be trapped using a charcoal scrubber upstream from the sensor. However, at higher concentrations of corrosive gases (estimated >5%), the scrubber may quickly become saturated, resulting in poisoning of the sensor [36]. For these reasons, RKI Instruments sensors are not recommended for hydrogen detection in a corrosive gas stream.

3.2.2 RC systems electrochemical sensors

Though often utilized as handheld devices, fixed electrochemical sensors may also be utilized for hydrogen detection. RC Systems sells an electrochemical sensor used for measuring hydrogen in a gas stream, with instrument specifications provided in Table 5 [37, 38]. Like other electrochemical sensors, it requires oxygen. However, personal communications with the technicians from RC systems confirmed that a secondary sample line may be set up to pull in either air or oxygen from a designated line to flush the sensor after gas sampling. This allows for continual hydrogen detection.

Table 5. RC systems hydrogen sensor specifications

	Electrochemical hydrogen sensor with sample smart XP
Cost	Est. $15,000
Lowest estimated range	100 ppm – 4%
Gas temperature range	−20 – 40°C
Lifetime	2 years
Calibration	Every 6 months
Flow rate	1.5 SLPM
Operating pressure	Variable
Compatible with corrosives	Yes
Response time	<40 seconds
Power	24V DC
Compatible with oxygen-free atmosphere	No, but can add a secondary line

Prior to purchase, RC Systems has also offered to perform preliminary tests replicating the actual environment of gas sampling to ensure corrosives in the gas stream will not interfere with hydrogen detection [39].

3.2.3 Hiden Analytical RGAs

Analyses from RGAs have shown some of the lowest limits of detection for hydrogen. Hiden Analytical carries a mass spectrometer gas analyzer with estimated limits of detection for hydrogen at 100 ppm using the HPR-200 R&D Gas Analysis System [40,41]. Although it is one of the more expensive options for hydrogen detection at ~$70,000, this technique has the potential to be the most sensitive among other detectors reported. There is a variety of flow and pressure options, sampling a gas stream between liters per minute and microliters per minute, and between 1 mbar and 30 bar.

For the HPR-200, a 3F (triple filter) series triple-stage mass filter mass spectrometer provides higher sensitivity and long-term stability of the instrument. In a corrosive environment, the bulk of the ions deposit during a pre-filter stage, as shown in Figure 2, minimizing corrosion or contamination on the primary filter. As with all instruments, the lifetime of the instrument could be reduced under continuous corrosive conditions. Corrosive-resistant upgrades can be purchased, yet there is no guarantee on the lifetime of the instrument.

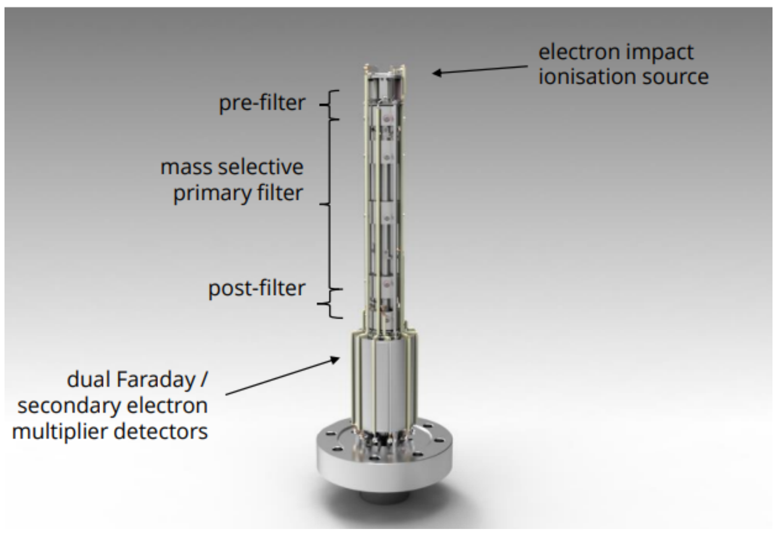

Figure 2. Hiden HPR-20 R&D analyzer, 3F series triple filter mass spectrometer.

3.3 RAMAN SPECTROMETERS

Although Raman spectroscopy inherently has a lower sensitivity than other analysis techniques, and therefore has not been widely utilized for hydrogen detection, it may still present a promising technology for some applications [42]. For applications that may not require extremely low limits of detection (LODs) (<100 ppm), such as those monitoring the flammability limit, a simple Raman spectrometer may be used. A variety of vendors carry Raman spectrometers capable of reaching limits of detection of 500 ppm and greater. Marqmetrix, W2 Innovations, and Endress + Hauser are among some of the manufacturers of the instrument.

3.3.1 Marqmetrix

Specialized Raman spectrometers sold by Marqmetrix have all-in-one continuous flow-through capabilities for hydrogen measurements. The Hastelloy flow cell coupled with a sapphire sphere connecting to the spectrometer allow for highly corrosive environments. Gold sealing material, instead of the standard perfluoroelastomer, allows for operations up to 2000 psi and 350°C [43]. Specifications for the instrument can be found in Table 6. Though at the lowest price of the three listed Raman spectrometers, one of the four signature Raman peaks for hydrogen is located at 4152 cm^{-1} [44]. With a spectral range of 100 – 3250 cm^{-1}, the Marqmetrix would not be a recommended product for hydrogen detection.

Table 6. Raman spectrometer specifications

	Marqmetrix 8023 All-In-One with 8021 Flowcell	W2 Innovations Graman-532 with SigE-FTCell	Rxn4 with HastelloyC 276 Flowcell
Cost	$74,950	$85,000 – $98,000	>$130,000
Incident wavelength	785 nm	488 nm	532 nm
Spectral range	100 – 3250 cm^{-1}	150 – 4400 cm^{-1}	150 – 4350 cm^{-1}
Excitation Power	10 – 450 mW	100 – 200 mW	120 mW
Lowest estimated LOD	Between 100-500 ppm	Est. below 500 ppm	Est. below 500 ppm
Gas temperature range	−20 – 350°C	20 – 200°C	20 – 300°C
Estimated lifetime	>200 weeks per calibration	Approx 10 years or 20,000 operation hours	Unknown
Highest operating pressure	2000 psi	2000 psi	Unknown
Compatible with corrosives	Yes, with Hastelloy flowcell	Yes	Yes, with AlloyC 276 flowcell
Power	12V DC, 2A	100 – 240V	100 – 240V
Compatible with oxygen-free atmosphere	Yes	Yes	Yes

3.3.2 W2 Innovations

W2 Innovations sells a gas phase Raman spectrometer capable of detecting gases down to the ppb level. Low levels of detection are possible when using the signal enhancing accessory (SigE-FTCell). Traditionally, this accessory is stainless steel. However, from personal communications, it was found that it may be made from a corrosion-resistant alloy [45]. The specifications for the spectrometer can be seen in Table 6 [45].

3.3.3 Endress + Hauser

The Rxn suite of Raman spectrometers, purchased from Endress + Hauser, have a wide variety of applications. Most suited for gas phase samples, the Rxn4 equipped with an AlloyC 276 gas flow cell is capable of low limits of detection under a corrosive atmosphere. Though the device has the highest costs among the other Raman spectrometers, the spectral range and capabilities of the Rxn4 are optimal for hydrogen detection.

3.3.4 Specialized Raman spectrometers

Due to the intrinsic low sensitivity of Raman spectroscopy, many have investigated methods to decrease the lower limits of detection (i.e., <500 ppm). Combinations of specialized sample cells, arrays of collection channels, and the shape of various cavities may be configured to improve sensitivity of the instrument.

The use of multi-reflection, cavity-enhanced Raman spectroscopy (CERS) has been reported to have the highest sensitivity toward hydrogen [42]. A cavity is generally a set of mirrors and material between those mirrors to increase the number of times a beam passes through a sample. Optimizing the geometry of the cavity increases the Raman signal, resulting in lower limits of detection [46].

In the context of hydrogen measurements, three studies have reported detection of hydrogen with lower limits of detection of 132, 75, and 140 ppm using various configurations [2, 47, 48]. Wen et al. used a Laser Quantum OPUS660, producing 1.5 W of radiation at 660 nm, with a custom-built four-mirror multiple pass gas flow cell (full set up seen in Figure 3). A fiber optic cable then feeds into a CCD Princeton Pixis 300BRX array [2]. Given that this is a custom configuration for experimental research, this technology is not commercially available at the time of this report.

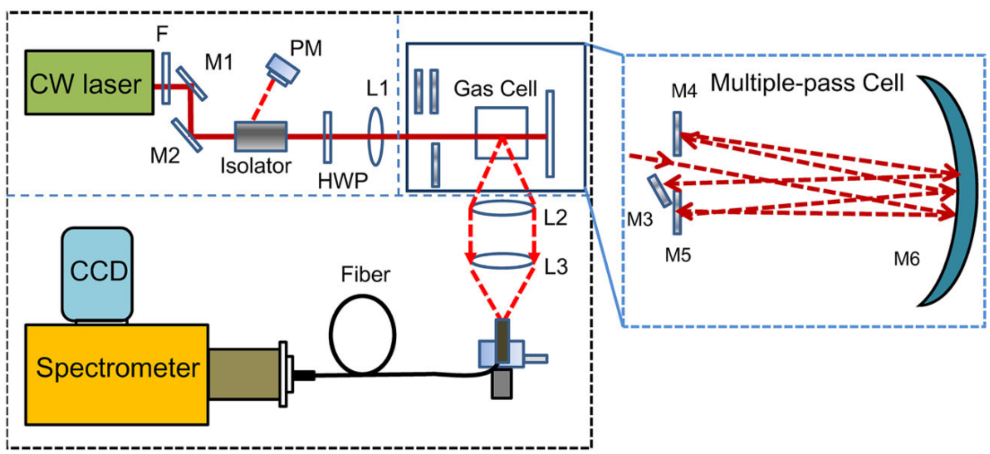

Figure 3. Scheme of full experimental set up by Wen et al. to achieve a LOD for hydrogen of 132 ppm [2].

Wang et al. built a confocal microprobe Raman spectrometer using a diode pumped solid-state laser to produce a 100 mW laser at 532 nm, with the schematic of the instrument seen in Figure 4. Following the laser, the objective lens focused the laser into the sample gas cell with two mirrors. A general CCD device is connected to the spectrometer to quantify the concentration of each gas in the sample [47].

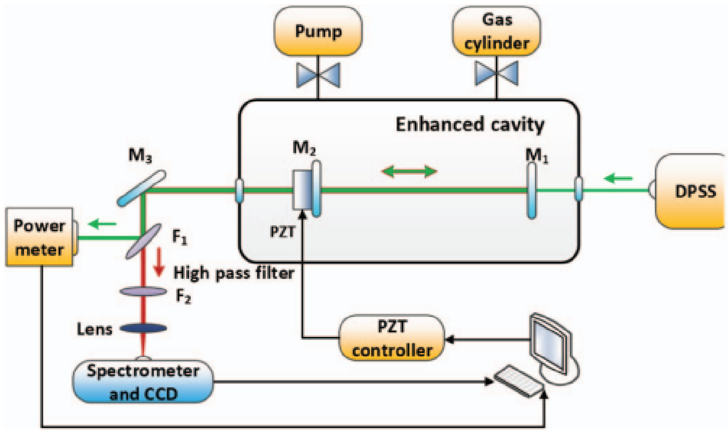

Figure 4. Schematic of equipment set up by Wang et al. to achieve a LOD for hydrogen of 75 ppm [47].

Finally, Hippler reports a Fabry–Perot continuous-wave diode LD laser (Hitachi HL6322G, 80 mA) set up with aspheric lenses, an anamorphic prism pair that makes the laser beam circular, and two Faraday isolators (OFR, 30–36 dB isolation each) to remove unwanted back reflections. The optical cavity has two concave high-reflectivity mirrors, and a variety of other optic parts to optimize the sensitivity of the instrument. The entire instrument set up can be seen in Figure 5 [48].

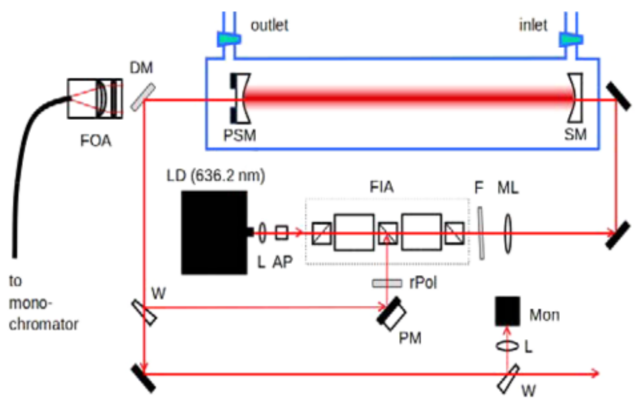

Figure 5. Schematic of equipment set up by Hippler to achieve a LOD for hydrogen of 140 ppm [48].

Though low limits of detection (<200 ppm) for hydrogen are possible, the high likelihood of corrosion of the specialized optical pieces in corrosive gas streams necessitate different specialized equipment suited for this environment. The Tritium Laboratory Karlsruhe (TLK) utilizes Raman spectroscopy for gas analysis in a corrosive environment. TLK has optimized their equipment to detect hydrogen on-line at low concentrations (<100 ppm). The TLK Raman set up, seen in Figure 6, is made of stainless steel-lined hollow glass fibers/capillaries as the Raman gas sample cell. The first implementation of these gas cells was in a high-pressure (44.8 bar, 650 psig) application by Buric et al. to monitor on-line gas composition [49, 50].

The robust nature of materials of construction, availability of flow cell technology, and discrete sensing for multiple gases make Raman spectrometry a potentially useful technique for on-line detection of hydrogen in an oxygen-free, corrosive gas stream. Though many of the commercially available instruments are expensive and may be time-intensive to set up, little maintenance is required once the instrument is operational. The most sensitive Raman measurements and lowest detection limits are seen in the custom-built Raman spectrometers and flow cells, which are not commercially available. However, the use of even commercially available options may provide the sensitivity required for some applications.

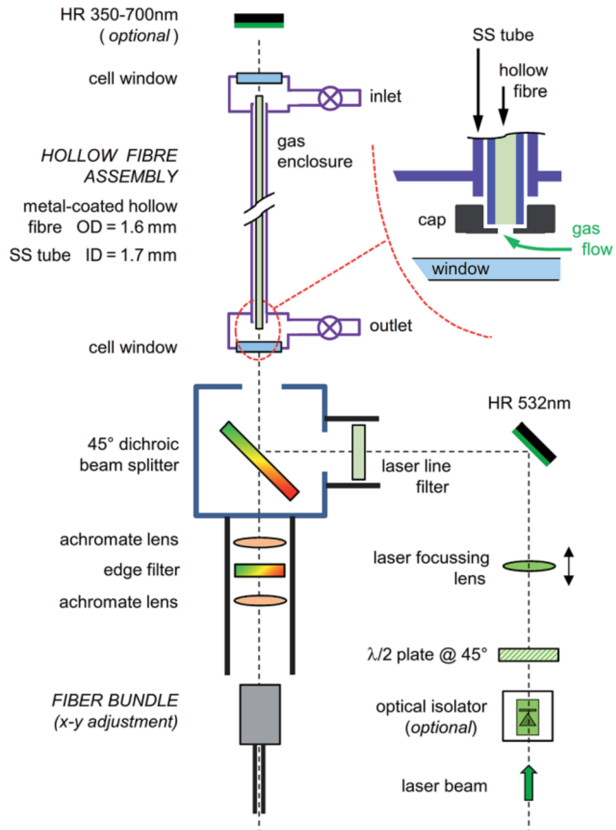

Figure 6. Schematic of TLK Raman spectrometer.

4. SUMMARY OF COMMERCIAL PRODUCTS

Though not all are viable for an oxygen-free corrosive gas stream, multiple portable and permanent/semi-permanent options are available for on-line hydrogen detection utilizing various technologies. Table 7 summarizes the products investigated in this report along with important details regarding their viability in an industrial, corrosive oxygen-free gas stream. The maintenance requirements, lowest limits of detection, and cost are also relevant when selecting a hydrogen detector and are also given in Table 7. The results of this investigation indicate that Raman spectroscopy shows promise for on-line hydrogen quantification at low limits of detection for corrosive, oxygen-free gas streams. Future work will include experiments testing the various conditions by which the lowest limits of detection may be possible with Raman spectroscopy.

Table 7. Overview of commercial products

Sensor	Compatible with corrosives	Compatible with oxygen-free sampling	Maintenance	Lower limit of detection/low range product	Cost
Portable sensors					
Hyoptima (710B, 1720, 2710) Platinum based sensor	No	Yes	Replace sensor every 2 yr. and calibration 6 mo.	700 – 10,000 ppm	Approx. $10,000
RKI Instrument Catalyic Bead	<5%	No	Replace sensor every 2 yr. and calibration 6 mo.	0 – 100% LEL	~$2000
RKI Instrument Metal oxide	<5%	No	Replace sensor every 2 yr. and calibration 6 mo.	200 – 4000 ppm	~$2000
MLTGas K522 TCD	No	Yes	Replace sensor every 2 yr. and calibration 3 mo.	0-10%	$6,126
MLTGas 1550 TCD	PTFE not compatible with hazardous environment, no	Yes	Replace sensor every 2 yr. and calibration 3 mo.	0–5%	$9,230
Gas sensing Model H10-18 Electrochemical	No	No	Replace sensor every 2 yr. and calibration 3 mo.	10 – 2000 ppm	$1,700
Aeuoqual Series 500 Electrochemical	No	No	Replace sensor every 2 yr. and calibration 3 mo.	5 – 500 ppm	$1,440
Semipermanent/permanent					
RC electrochemical system	Yes	No, but can add secondary line	Calibration every 6 mo.	100 – 40000 ppm	Est $15,000
Hiden HPR-200 Thermal gas analyzer mass spectrometer	Yes, with additional purchase	Yes	Unknown	100 ppm – 100%	$75,800
MarqMetrix Raman spectrometer	Yes	Yes	Dependent on baseline Infrequent replacement/calibration	100-500 ppm	$74,950
W2 Innovations Raman spectrometer	Yes	Yes	Dependent on baseline Infrequent replacement/calibration	Est. below 500 ppm	$85,000 – 98,000

Rxn4 Raman spectrometer	Yes	Yes	Dependent on baseline Infrequent replacement/calibration	Est. below 500 ppm	Est. >130,000

FUNDING ACKNOWLEDGEMENT

This work was supported by the US Department of Energy, Office of Nuclear Fuel Cycle and Supply Chain, Material Recovery and Waste Form Development Campaign (NE-43).

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