Application note

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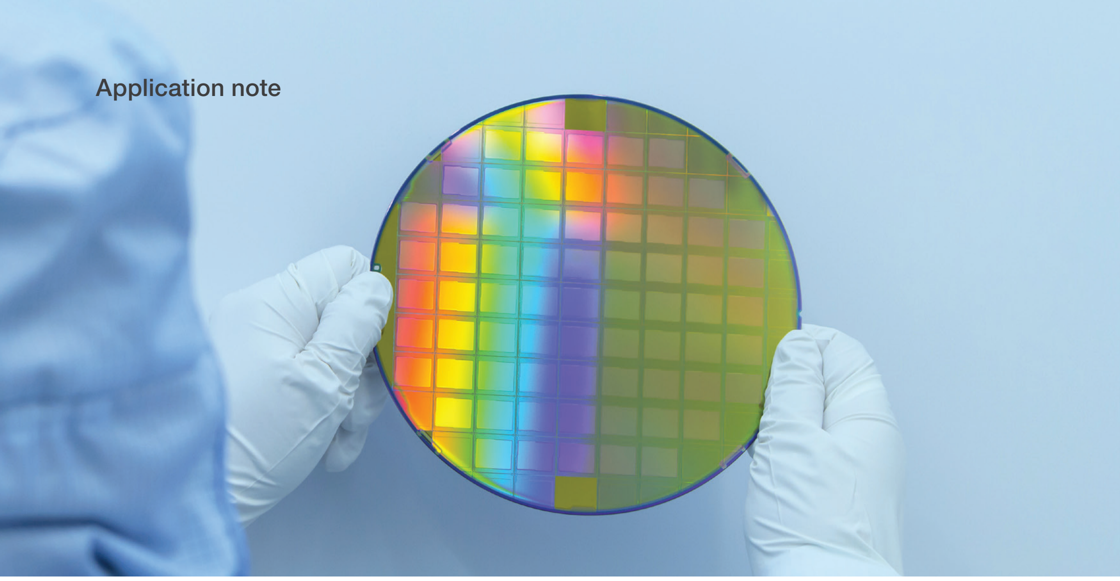

Hydrogen purity analysis

Hydrogen is used in many industrial chemical processes. For example, in the semiconductor industry, hydrogen is used as a carrier gas for thin-film deposition and to protect semiconductor devices from damage by neutralizing residual oxygen. These semiconductor processes require ultra-high purity hydrogen, certified to >99.999%

Hydrogen has recently gained momentum as a fuel source for fuel cell electric vehicles (FCEV) which reduce greenhouse gas emissions, air pollution, and dependency on fossil fuels compared to standard combustion engines. Even at low part-per-billion (ppb) levels, impurities such as ammonia, hydrogen fluoride, hydrogen chloride, formic acid and formaldehyde reduce performance of the fuel cell. This application requires hydrogen at a purity of 99.97% or greater.

Purity challenge

To meet the challenging purity requirements of hydrogen applications such as those in semiconductor and automotive described above, instrumentation must have detection limits in the low ppb range. It also should be capable of simultaneously measuring many gases to provide a fast and cost-effective solution.

Traditionally, analyzing the numerous impurities outlined by the International Standard for Organization in ISO 14687 for fuel cell hydrogen requires multiple analyzers, typically using a combination of spectroscopic and gas chromatography (GC) techniques. GC techniques can meet the sensitivity requirements, but maintenance costs are high and analysis times are often long due to required separation of the sample. FTIR spectroscopy provides real-time accurate analysis for a lower cost of ownership, however most FTIR instruments on the market require a detector cooled with liquid nitrogen and cannot achieve the required detection limits for these challenging applications.

Solution

The Thermo Scientific™ MAX-iR™ FTIR Gas Analyzer with a deuterated triglycine sulfate (DTGS) detector can monitor the entire IR spectral range (500-5000 cm^{-1}) without the need for liquid nitrogen. The MAX-iR analyzer allows for fast and accurate quantification of most required impurities with detection limits equal to or better than cumbersome liquid nitrogen cooled mercury-cadmium-telluride (MCT) detectors. This makes the MAX-iR analyzer ideal for use in the field at fueling stations.

An optional sensitivity enhancement called Thermo Scientific™ StarBoost™ Technology allows the MAX-iR analyzer to detect impurities at levels never achieved before with compact FTIR gas analysis, down to 1 ppb or less.

Experimental

To assess the detection limits of the MAX-iR FTIR Gas Analyzer, a series of 12 consecutive blank samples were analyzed. The blank sample used was either research grade (99.9999%) hydrogen or nitrogen with no detectable impurities. The instrument detection limit (DL) was defined as three times the standard deviation of the 12 replicates. The MAX-iR analyzer configuration used in the assessment had a DTGS detector which could be run 24/7 since it requires no maintenance and no liquid nitrogen.

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Compounds	Max allowable limit in ISO 14687 (ppm)	MAX-iR DTGS DL (ppm)
Ammonia	0.1	0.020
Carbon dioxide	2	0.010
Carbon monoxide	0.2	0.020
Formaldehyde	0.2	0.030
Formic acid	0.2	0.010
Hydrogen chloride	50*	0.020
Hydrogen fluoride	50*	0.010
Water	5	0.100
Total hydrocarbon (C1-C5)	2	0.200
Non-methane hydrocarbon (C2-C5)	2	0.200
Methane	100	0.010
Ethane	--	0.020
Ethylene	--	0.050
Propane	--	0.040
Butane	--	0.080
Pentane	--	0.050

* Limit for total halogenated compounds is 50ppm

Table 1. Detection limit assessment.

In addition to the gases listed in Table 1, the DTGS configuration could be used to analyze other halogenated species, including but not limited to dichlorodifluoromethane, chloromethane, vinyl chloride, and dichloromethane.

The StarBoost technology configuration for the MAX-iR analyzer has a narrower spectral range than the DTGS, but provides enhanced sensitivity for impurities such as CO, CO_2, and CH_4. To validate the performance of the StarBoost configuration for the analysis of trace impurities in hydrogen, NIST traceable calibration standards were obtained with 5 ppm of CO, CO_2, and CH_4 in a balance of hydrogen. This standard was diluted to concentrations as low as 10 ppb using a gas blending system. Research grade hydrogen was used for both blank samples and dilution of the 5 ppm calibration blend. Four concentration levels (10 ppb to 5 ppm), each with at least 4 replicates, were analyzed in random order by the MAX-iR analyzer with StarBoost configuration every day for 3 days to determine linearity, accuracy, and method detection limit (MDL). A repeatability study was also conducted to assess precision, in which a concentration of 10x the detection limit was analyzed 30 times (shown in Figure 1).

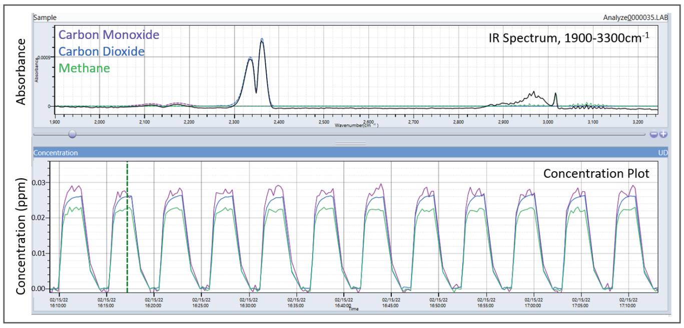

Figure 1. Concentration plot for 25 ppb repeatability study on StarBoost configured MAX-iR instrument.

	Accuracy	Linearity	Precision	EPA 821-R-16-006
	% of Expected	R^2	RSD	MDL_S (ppb)
Carbon dioxide	1.25%	0.9999	0.70%	0.7
Carbon monoxide	2.91%	0.9999	2.43%	0.6
Methane	2.15%	0.9998	0.88%	1.1

Table 2. Summary results of validation study on StarBoost configured MAX-iR system.

Conclusion

The MAX-iR analyzer is a flexible, sensitive analytical tool for the simultaneous measurement of many trace level impurities in bulk hydrogen. For quality monitoring of fuel cell grade hydrogen (99.97% purity), the analyzer's DTGS detector provides the most efficient solution for fast, accurate analysis of the many impurities outlined in ISO 14687.

For monitoring of ultra-high purity hydrogen for industries with stringent requirements such as semiconductor, the StarBoost configuration provides dramatically enhanced sensitivity for a narrower subset of impurities. The validation study demonstrates that the StarBoost configured MAX-iR analyzer is a highly precise, accurate, and reliable instrument that achieves detection limits down to 1 ppb. Both the MAX-iR system alone and the MAX-iR with StarBoost configuration are suitable for field use and can be run 24/7 as no maintenance nor liquid nitrogen are needed.

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