

Application Note 165

Optimised hydrogen fuel impurity analysis: identification, measurement and characterisation of volatile organic compounds by TD-GC-MS/SCD

Summary

Hydrogen fuel is emerging as a key player in the rapidly growing clean energy market. However, hydrogen can contain impurities (introduced during production, purification and along the hydrogen supply chain) that limit the efficiency of fuel cells and lead to concerns over pollution. Markes International's Multi-Gas thermal desorption systems offer on-line and off-line identification and quantitation of a wide range of these compounds of concern. This application note shows the robust, reproducible analysis of trace volatile organic compounds (VOCs), including aldehydes (i.e., formaldehyde), hydrocarbons, and halogenated and sulfur-containing compounds (i.e., hydrogen sulfide), by thermal desorption-gas chromatography-mass spectrometry/sulfur chemiluminescence detection (TD-GC-MS/SCD). Detection limits down to low ppt levels were achieved in accordance with standard methods (ISO 14687, EN 17124, ISO 21087, GB/T 37244 and ASTM D7892¹⁻⁵ and SAE J2719).



Introduction

Transportation is responsible for one-third of carbon dioxide emissions into the atmosphere, which can contribute to a variety of health effects.⁶ Hydrogen is an emerging renewable energy source that could enable a move away from fossil fuels and carbon-based energy. It is anticipated that widespread adoption of hydrogen fuel will limit dependency on fossil fuels, reducing air pollution and greenhouse gas emissions.⁷ Cars and other hydrogen-fuel-cell-powered vehicles could offer clean, carbon-neutral transportation.

However, hydrogen fuel cells require high hydrogen purity to prevent poisoning the catalysts that speed up the energy conversion process, and hydrogen quality is critical for increasing the reliability, stability and durability of the fuel cells. Any impurities may result in substantial degradation of the fuel cell, even at very low concentrations (parts per billion). Several methods are used to produce hydrogen for use at fuelling stations, including electrolysis of water, steam methane reforming (of natural gas or biogas) and the chlor-alkali process.

There is the potential for impurities to be introduced at various stages of hydrogen fuel production, purification and supply⁸ and, depending on the production method, there are a range of potential impurities that can have negative, often irreversible, effects on fuel cell performance.

Hydrogen impurities include VOCs that interfere with performance, accelerate degradation and sometimes cause permanent damage to fuel cell components:⁸⁻¹⁰

- **Hydrocarbons** contaminate proton-exchange membrane (PEM) fuel cells either by direct adsorption or by decomposing into carbon monoxide, which adsorbs on the catalyst's surface to reduce its active surface area.
- **Sulfur compounds** (mainly hydrogen sulfide) can cause permanent deactivation of the catalyst due to the formation of strong metal-S bonds.
- **Halogenated compounds** – traces of halogens such as hydrogen chloride and halogenated compounds can cause irreversible performance degradation of hydrogen fuel cell systems.
- **Formaldehyde** and other aldehyde species such as acetaldehyde are very reactive and can readily decompose with release of hydrogen and carbon monoxide, which can degrade platinum catalysts.

International hydrogen fuel quality standards specify maximum concentrations of contaminants for commercial PEM fuel cells. Both hydrogen producers and suppliers must safeguard hydrogen quality in accordance with these standards by analysing samples for all, or a subset, of the contaminants. Four key standards and their contaminant limit levels are listed in Table 1.

Maximum concentration of individual contaminants (µmol/mol)	ISO 14687 (2012) GB/T 37244	ISO 14687 (2019) EN 17124
Water	5	5
Total hydrocarbons	2	2
Methane	—	100
Oxygen	5	5
Helium	300	300
Nitrogen	100	300
Argon	100	300
Carbon dioxide	2	2
Carbon monoxide	0.2	0.2
Total sulfur compounds	0.004	0.004
Formaldehyde	0.01	0.2
Formic acid	0.2	0.2
Ammonia	0.1	0.1
Halogenated compounds	0.05	0.05
Particle concentration	1 mg/kg	1 mg/kg

Table 1: Relevant hydrogen purity standards and associated limit levels.

ISO 14687 specifies quality characteristics of hydrogen fuel for transport applications, including the list of contaminants and maximum concentrations of interest. In 2019, a new version was released with updates to these levels, namely an increase in the limits for formaldehyde, argon and nitrogen and the inclusion of methane.¹ EN 17124,⁴ a European-specific product specification and quality assurance document, is harmonised with the updated limits from ISO 14687, while the Chinese specification GB/T 37244³ follows the 2012 version. These standards are regularly updated so that the specifications and requirements for hydrogen fuel quality can be harmonised globally to protect the fuel cells from irreversible damage.

Sampling strategies and analytical options

The optimum sampling strategy for hydrogen fuels will depend on the sample location, stage of the supply chain and priority impurities for measurement. To reach the detection limits required for VOC impurities in hydrogen fuels, preconcentration using thermal desorption (TD) is required. TD sampling approaches for hydrogen fuels can be split into two categories:

On-line monitoring of gas streams

Automated, scheduled sampling and analysis from a hydrogen gas stream provides a regular measure of hydrogen supply purity at source and along the supply chain. The hydrogen gas stream is directed into the TD instrument and volatile impurities are concentrated on the sorbents in a focusing trap before injection to the GC. This process is completely unattended and can run continuously or at scheduled time points.

Off-line sampling

Where it is not practical or cost-effective to install a full analytical setup for every sampling point, it is necessary to

deploy a sampler to collect a sample and return it to a central laboratory for analysis. There are two key strategies for off-line sampling of hydrogen fuel impurities.

1. Sorbent tube sampling

Hydrogen sample gas is passed through an inert-coated stainless-steel tube, which is a little smaller than a typical pen, at a controlled flow rate, typically 50–100 mL/min. The tube contains one or more sorbent materials which retain the volatile impurities within the hydrogen gas while the bulk gas passes through. In this way, the impurities are quantitatively sampled from the gas and concentrated onto the sorbent tube, which is then returned to the laboratory for analysis. The sorbent tube is placed into an automated thermal desorber where the retained analytes are desorbed using heat and a flow of carrier gas and injected into a GC-MS/SCD instrument for analysis. This process can achieve concentration factors over several orders of magnitude.

Sorbent tubes are small, lightweight and easy to transport, making them the ideal field sampler. As analytes are retained on a sorbent bed, storage stability of samples is also extended compared to collecting a cylinder or bag of gas for off-line analysis. Highly volatile impurities, such as hydrogen sulfide and formaldehyde, are not quantitatively retained by sorbent tubes so an on-line or grab sampling strategy is required (see below). Sorbent tubes also offer quantitative analysis of less volatile impurities, up to nC₄₄ in volatility vs. nC₁₂₋₁₄ for cylinders and gas sampling bags, which allows untargeted screening of a wide range of potential impurities alongside known targets.

2. Grab sampling with a cylinder or bag

Grab sampling involves collecting an aliquot of hydrogen in an inert container such as specially designed cylinders or gas sampling bags. The 'whole hydrogen sample' is transferred to the laboratory where it is connected to the TD system. The injection process then proceeds as described for on-line sampling: the hydrogen gas sample is drawn across the focusing trap where VOC impurities are concentrated before transfer to the GC for analysis.

Grab sampling is predominantly used when there is a need to measure highly volatile compounds, such as formaldehyde and hydrogen sulfide, which cannot be sampled using sorbent tubes.

Markes International's UNITY-CIA Advantage-xr™ offers automated sampling from on-line gas streams and off-line cylinders and bags with the option to add water management capabilities for humid samples with Kori-xr™. Automated analysis of off-line sorbent tube samples can be added to the same instrument via the ULTRA-xr™ autosampler, equipping the laboratory with a single system that can be adapted to suit any laboratory's needs. For laboratories running high volumes of off-line sorbent tube samples, a dedicated instrument – TD100-xr™ – is available. Preconcentration techniques are paired with gas chromatography coupled with either mass spectrometry for identification of a broad range of analytes including non-targeted compounds, or compound-specific detectors such as those for SCD or electron capture detection (ECD), for targeted, routine analysis.

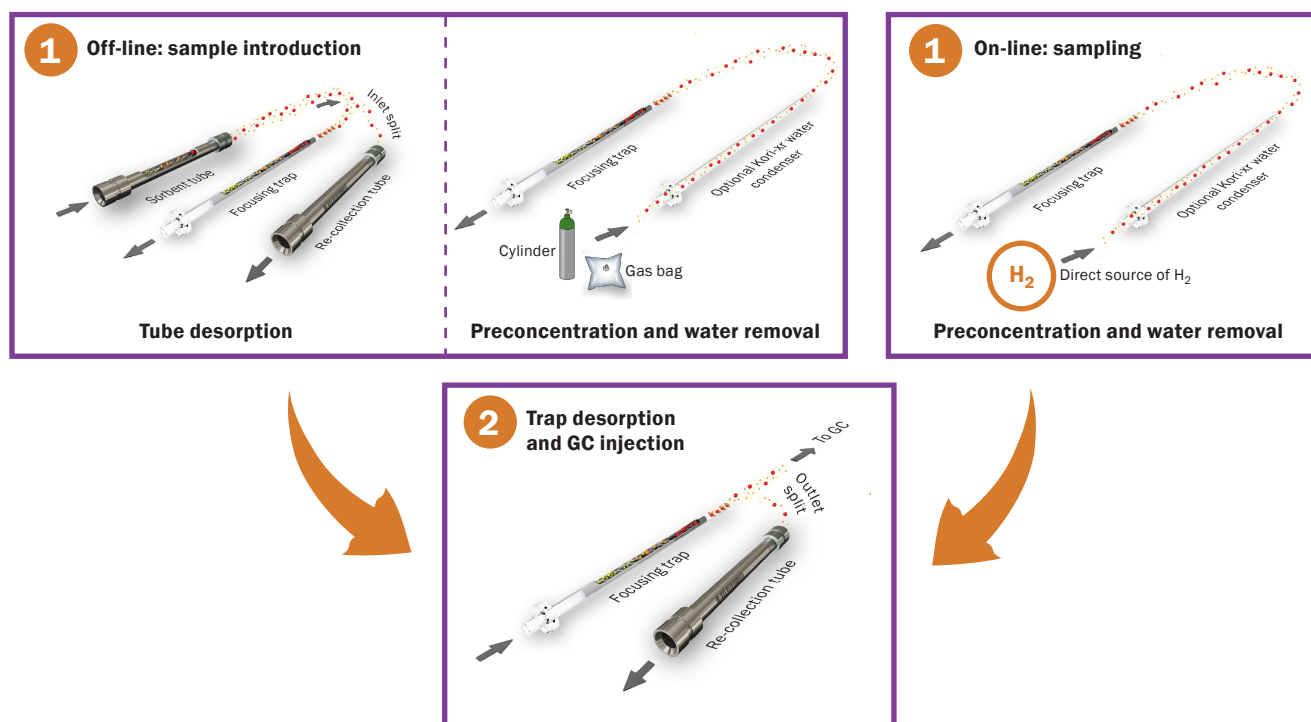


Figure 1: Sampling and preconcentration stages for TD-GC analysis of hydrogen fuels.

Sampling and analytical options

Profiling or targeted analysis

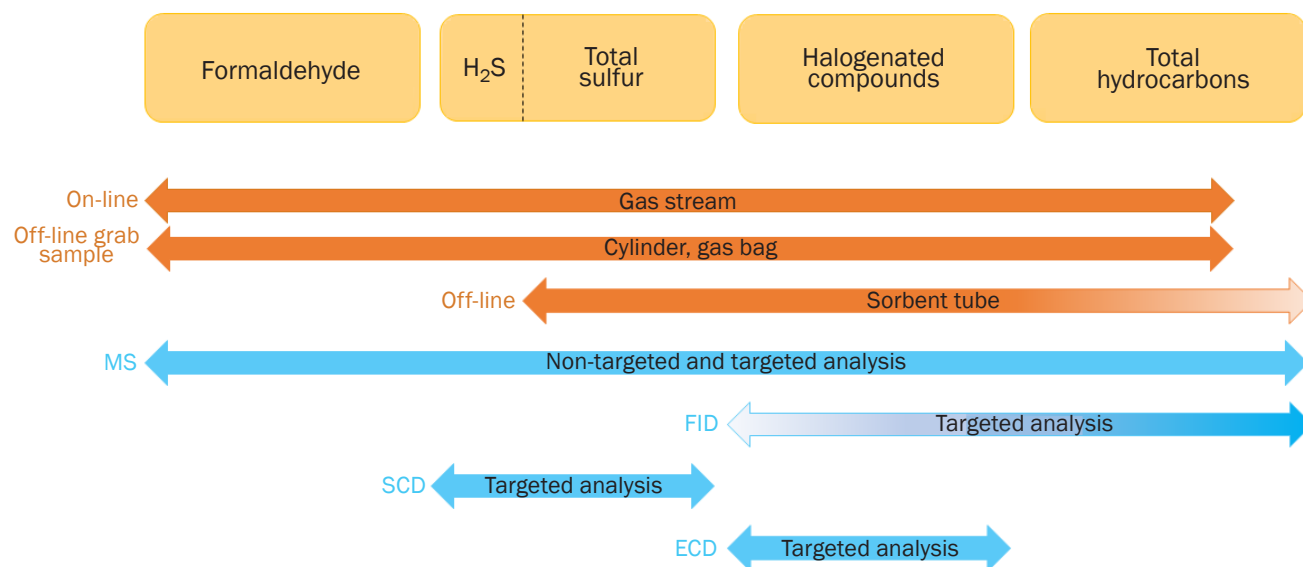


Figure 2: Sampling and analysis strategies for hydrogen fuel impurities, highlighting the complementary nature of the different sampling methods.

Optimisation of analytical systems for characterisation of hydrogen fuel impurities

Standard methods for hydrogen fuel impurities require the measurement of suites of compounds such as total sulfurs or total hydrocarbons. Simultaneously identifying and measuring individual impurities alongside reporting total species content provides an extra dimension of information, which will be invaluable as research progresses and the impact of individual impurities on fuel cell performance is better understood. TD coupled with GC-MS provides simultaneous total species measurement and speciation within each compound class with the additional benefit of untargeted screening across a wide range of potential impurities with no additional sample preparation or analysis.

The validation study outlined below demonstrates the versatility of the TD-GC-MS/SCD approach for targeted measurement and full impurity characterisation of hydrogen fuel samples.

Experimental

Preparation of standards

A gaseous mixture of the compounds listed in the Appendix was prepared from five commercially available gas standards (part numbers: Linde – 574146, Restek – 34436-PI and 34561-PI, Aldrich – 109207 and Merck – 8.21095.0250). The mixture was diluted with carrier-gas-grade hydrogen inside inert-coated Tedlar® bags (Sigma Aldrich, part number 30229-U), to give the stated concentration. A relative humidity of 50 ppm was obtained by adding calculated volumes of HPLC-grade water.

Analytical equipment

The analytical system used for this study was a CIA Advantage-xr autosampler and UNITY-xr thermal desorber with a Kori-xr water-removal device (Figure 3) coupled to a GC-MS system. The system harnesses Dry-Focus3™ technology, a unique, three-stage preconcentration and water-management mechanism that operates entirely without liquid cryogen.



Figure 3: UNITY-Kori-CIA Advantage-xr system for on-line and grab samples with an ULTRA-xr autosampler for sorbent tube analysis.

CIA Advantage-xr is an autosampler for the analysis of VOCs from up to 27 on-line gas streams or sample vessels. The sample stream passes through Kori-xr where water is selectively removed before reaching the focusing trap in the UNITY-xr where VOCs are preconcentrated before injection to the GC. This three-stage approach provides preconcentration over several orders of magnitude whilst operating completely without liquid cryogen, overcoming the limitations of legacy cryogen-based preconcentrators, which carry the burden of high running costs and frequent downtime due to ice blockages and delayed cryogen deliveries. CIA Advantage-xr also offers internal standard addition for continuous monitoring of instrument performance and quality control. Gas-phase internal standard is added to the focusing trap immediately prior to sampling via a 1-mL loop, which allows the use of less expensive high-concentration internal standard gases (typically 100 ppb–1 ppm). Alternatively, a larger volume of low-concentration internal standard can be used with mass-flow-controlled internal standard addition.

An optional sorbent tube autosampler, ULTRA-xr, can be added to UNITY-CIA Advantage-xr-Kori-xr to provide automated sorbent tube analysis and re-collection for up to 100 tubes. With the addition of ULTRA-xr, sampling of up to 27 on-line gas streams or grab samples and 100 sorbent tubes can be conducted on a single automated platform with no reconfiguration. ULTRA-xr also provides re-collection capability for sorbent tube samples as well as on-line gas streams and grab samples. During trap desorption and injection to the GC, the split flow can be directed onto a sorbent-packed tube in the ULTRA-xr where the hydrogen fuel impurities are retained for future analysis. This means that samples can be archived for re-analysis without needing to store bulky cylinders or sampling bags while storage is stable because the VOCs are entrained on the sorbent's surface.

Since 2021, a range of Markes' TD instruments has been multi-gas-enabled. 'Multi-Gas' is award-winning technology that enables the user to choose one of three carrier gases – helium, nitrogen or hydrogen – to achieve optimum analytical performance and safeguard against rising helium prices and unstable supply chains. Each Multi-Gas instrument has been independently tested and certified for hydrogen carrier and sample gas so that the full TD-GC-MS workflow can be confidently configured with hydrogen.

Sampling and analytical conditions

The instrument conditions used in the investigation were as follows:

On-line and grab samples

Gas sampling

Instrument:	CIA Advantage-xr Multi-Gas
Sample purge:	50 mL/min (4 min)
Sample flow:	50 mL/min
Sample volumes:	10 mL to 800 mL
Post-sample purge:	50 mL/min (5 min)

Water management

Instrument:	Kori-xr Multi-Gas
Temperature range:	-30 to 300°C

Tube sampling

Tubes:	'Odour/sulfur' inert-coated (part no. C2-CAXX-5314)
Tube pre-purge:	50 mL/min (1 min)
Tube desorption:	270°C (10 min)

TD parameters

Instrument:	UNITY-xr Multi-Gas
Flow path:	120°C
Sample flow:	50 mL/min
Trap purge:	50 mL/min (1 min)
Focusing trap:	'Hydrogen sulfide' (part no. U-T14H2S-2S)
Focusing trap low:	-30°C
Focusing trap high:	270°C (3 min)
Split ratio:	5:1

GC-MS parameters

Column:	Rxi-1ms®, 60 m × 0.25 mm i.d. × 1.00 µm film thickness
Column flow:	1 mL/min
Carrier gas:	Helium
Oven ramp:	35°C (10 min), 12°C/min to 200°C (5 min)
MS transfer line:	230°C
MS source:	230°C
Scan range:	30–350 m/z
SIM ions:	30, 34, 44, 46, 47, 57, 60, 62

GC-SCD parameters

Column:	DB-1™, 60 m × 0.32 mm × 1 µm
Column flow:	3.5 mL/min
GC oven:	35°C (10 min), 20°C/min to 115°C (1 min), 25°C/min to 245°C (5 min)
Carrier gas:	Helium

SCD

Furnace temp.:	850°C
Interface temp.:	200°C
H ₂ flow:	80 mL/min
O ₂ flow:	10 mL/min
O ₃ flow:	25 mL/min
N ₂ flow:	40 mL/min

For on-line gas streams or grab samples containing hydrogen sulfide or formaldehyde, a dedicated trap is required (U-T14H2S-2S). As shown later in this application note, this focusing trap provides excellent analytical performance for the full range of VOC hydrogen fuel impurities listed in the methods. For sorbent tube samples, or on-line/grab samples where hydrogen sulfide and formaldehyde measurements are not required, a more general-purpose sulfur-optimised focusing trap (U-T6SUL-2S) offers increased lifetime, provides high performance for the remaining target impurities and extends the applicable analyte range to lower volatility VOCs and SVOCs.

Results and discussion**On-line gas streams and grab samples by TD-GC-MS****Compound identification and peak shape**

A high-volume sample of a 10-ppb standard with 50 ppm of water was analysed and all compounds of interest (see Appendix) were readily identifiable with good peak shapes.

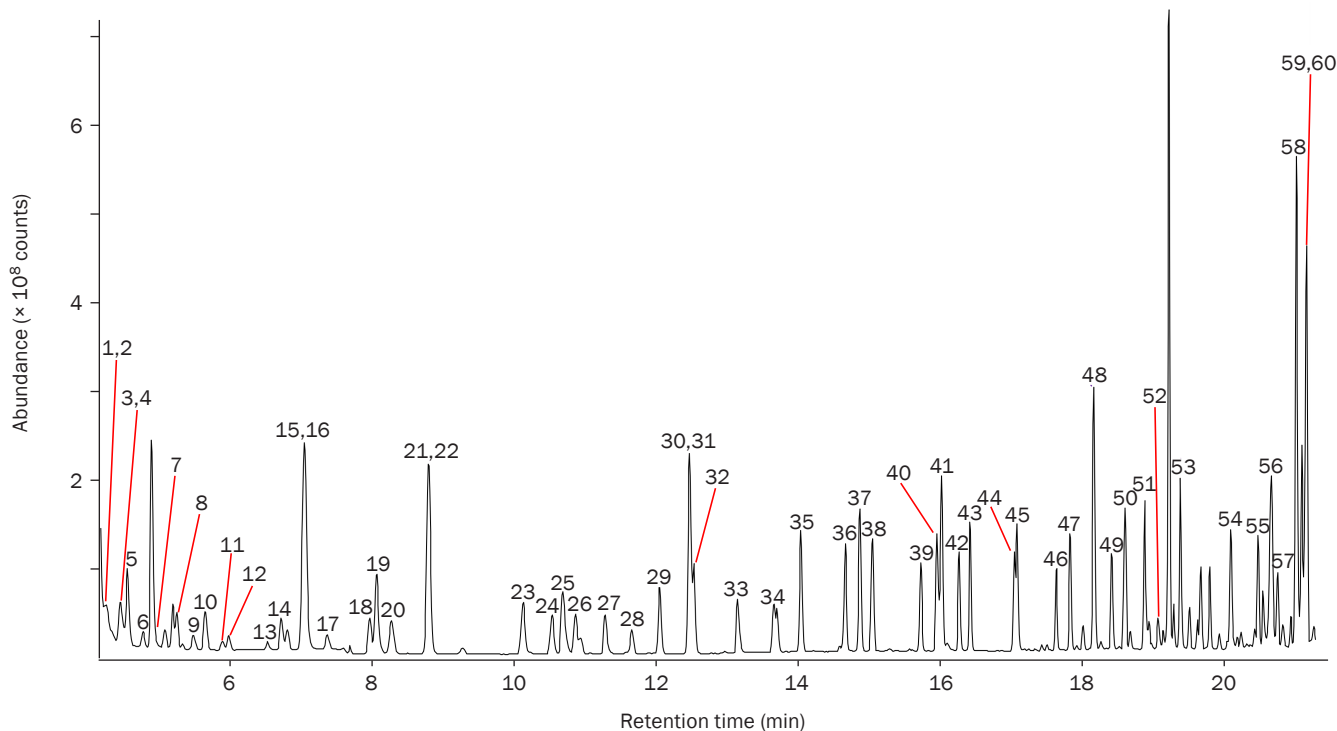
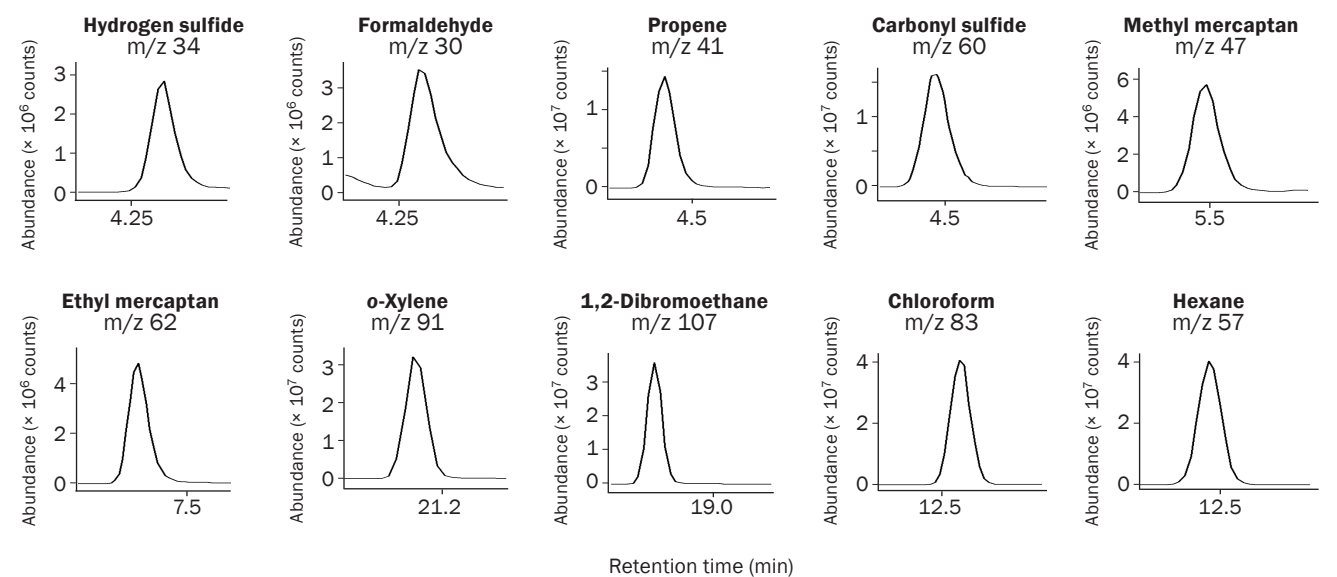
A typical total ion chromatogram (TIC) is shown in Figure 4. Extracted ion chromatograms (EICs) for priority hydrogen fuel impurities demonstrate the power of Dry Focus3 water removal and the desorption efficiency of UNITY-xr to generate high-quality data for these challenging compounds that encompass a range of volatilities and polarities as well as thermally labile species. Sharp peaks demonstrate great focusing and fast transfer to the GC for very volatile compounds such as formaldehyde and propene. Gaussian peaks with minimal tailing for hydrogen sulfide and ethyl- and methyl-mercaptan confirm a lack of reactivity in the flow path.

Linearity and reproducibility

Figure 5 shows excellent linearity for a subset of 12 analytes selected to represent the wide range of compound classes and volatilities that make up the VOC proportion of hydrogen fuel impurities. Across the calibration range of 0.25 to 10 ppb, R² values for all 60 compounds tested were >0.99, with 97% greater than 0.995. The high-quality linearity not only affords accurate quantitation, it also illustrates the applicability of the full analytical workflow across two orders of magnitude in concentration even for notoriously challenging compounds such as formaldehyde and hydrogen sulfide.

Reproducibility of the full analytical system was assessed in terms of response and retention time by analysing 10 × 400-mL replicates at a concentration of 10 ppb and 50 ppm water. These replicates were assessed for their relative standard deviation, and an average value of 2.32% was recorded across all compounds listed. Particular notice should be given to compounds such as hydrogen sulfide and formaldehyde, which, despite their labile nature, showed RSD values of 2.73% and 3.30%, respectively. Retention time stability is a key marker of data quality; excellent retention time stability allows for automated quantitation routines and saves significant time in data review. Retention times were highly stable across all compounds in this study with an average RSD of just 0.02%.

The high-quality data shown in this application note comfortably satisfies the criteria for standard methods in hydrogen fuel impurity measurement without the need for internal standard correction. It is good practice when running high-throughput, routine analysis by GC-MS to use an internal standard for continuous quality control checks of instrument performance and to correct drifting responses. Internal standard response reproducibility in this study was 3.67% RSD over a 24-desorption sequence including both calibration and reproducibility series with appropriate blanks to ensure system cleanliness, demonstrating the inherent stability of the overall system and utility of the internal standard in monitoring system performance over long sequences.



- | | | | |
|---------------------------|--|--------------------------------------|------------------------------|
| 1 Formaldehyde | 17 Ethyl mercaptan | 32 Chloroform | 48 Toluene |
| 2 Hydrogen sulfide | 18 Dimethyl sulfide | 33 Tetrahydrofuran | 49 Methyl-n-butyl ketone |
| 3 Propene | 19 1,1-Dichloroethene | 34 1,2-Dichloroethane | 50 Chlorodibromomethane |
| 4 Carbonyl sulfide | 20 Dichloromethane | 35 1,1,1-Trichloroethane | 51 1,2-Dibromoethane |
| 5 Dichlorodifluoromethane | 21 1,1,2-Trichloro-1,2,2-trifluoroethane | 36 Benzene | 52 Tetrahydrothiophene |
| 6 Chloromethane | 22 Carbon disulfide | 37 Tetrachloromethane | 53 Tetrachloroethene |
| 7 Acetaldehyde | 23 1,2-Dichloroethene | 38 Cyclohexane | 54 Chlorobenzene |
| 8 Butadiene | 24 1,1-Dichloroethane | 39 1,2-Dichloropropane | 55 Ethylbenzene |
| 9 Methyl mercaptan | 25 <i>tert</i> -Butyl methyl ether | 40 Bromodichloromethane | 56 <i>m/p</i> -Xylene |
| 10 Bromomethane | 26 Vinyl acetate | 41 Trichloroethene | 57 Tribromomethane |
| 11 Chloroethane | 27 Methyl ethyl ketone | 42 Methyl methacrylate | 58 Styrene |
| 12 Ethanol | 28 <i>tert</i> -Butyl mercaptan | 43 Heptane | 59 1,1,2,2-Tetrachloroethane |
| 13 Acrolein | 29 <i>trans</i> -1,2-Dichloroethene | 44 <i>cis</i> -1,3-Dichloropropene | 60 <i>o</i> -Xylene |
| 14 Acetone | 30 Ethyl acetate | 45 4-Methylpentan-2-one | |
| 15 Trichlorofluoromethane | 31 Hexane | 46 <i>trans</i> -1,3-Dichloropropene | |
| 16 Isopropanol | | 47 1,1,2-Trichloroethane | |

Figure 4: (Top) Extracted ion chromatograms for a selection of impurities covering the range of targets. (Bottom) Total ion chromatogram showing the peaks of interest for the 60 listed compounds, produced from a high-volume sample of 10-ppb standard in humid hydrogen gas.

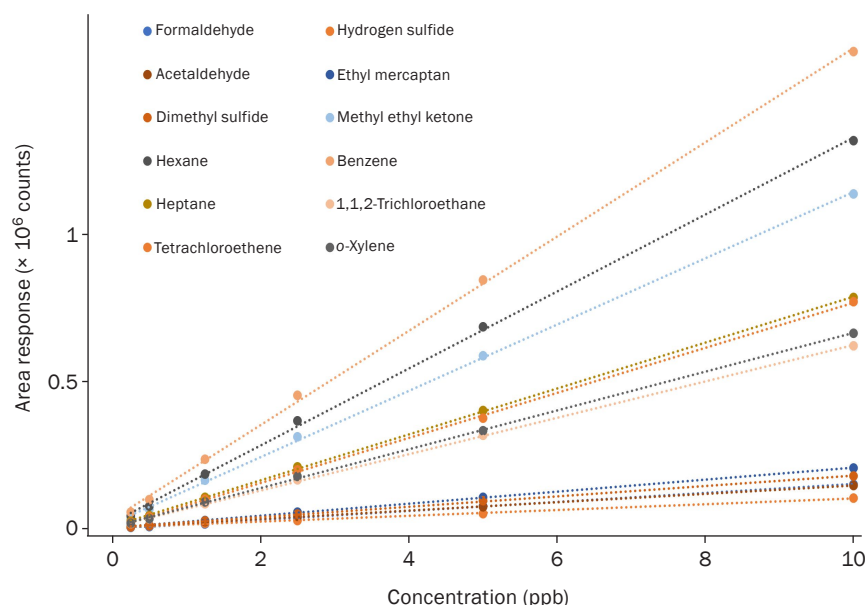


Figure 5: Linearity plots for a selection of compounds of interest in hydrogen at 50 ppm water, shown over a concentration range of 0.25–10 ppb.

Limits of detection

Limits of detection (LOD) and quantification (LOQ) were calculated according to the guidance in ISO 21087.² Twelve 5-mL replicates of a 10-ppb standard (giving an equivalent concentration of 0.125 ppb for a 400-mL sample) were analysed and their corresponding concentrations calculated via linear regression. The standard deviation of the 12 values was calculated and multiplied by three to obtain values for the LOD and by 10 to obtain values for the LOQ.

Excellent LOD values were achieved with an average of 16 ppt across all 60 compounds, with the highest being 88 ppt for isopropanol and the lowest being 4 ppt for chlorodibromomethane. Sulfur-containing impurities are of particular concern in hydrogen fuel analysis and represent some of the most analytically challenging target compounds. An average LOD of 13 ppt for these compounds allows for measurement well within the expected concentration range whilst providing the security of mass spectral matching for confident identification. Formaldehyde and acetaldehyde are also key impurity compounds that present analytical challenges. Detection limits of 14 and 41 ppt, respectively, for these compounds demonstrates the utility of the TD–GC–MS workflow for even the most volatile and highly reactive of hydrogen fuel impurities. LOD values for all compounds are significantly lower than required by standard methods, for example ISO 14687, which outlines a maximum allowable concentration of 2000 ppb for total hydrocarbons, 4 ppb for total sulfur compounds and 50 ppb for total halocarbons.

Equally impressive LOQ values were achieved with an average of 54 ppt across all 60 compounds, with the highest being 292 ppt for isopropanol and the lowest being 15 ppt for chlorodibromomethane and tetrachloroethene. Sulfur compounds had an average LOQ value of 42 ppt, while formaldehyde and acetaldehyde represented quantification limits of 46 and 136 ppt, respectively.

The complete data is in the Appendix.

Selective sulfur detection: TD–GC–SCD analysis of on-line gas streams and off-line grab samples

The data presented so far has resulted from the use of mass spectrometric detection, which enables confident identification and measurement of wide-ranging compound classes including untargeted screening. However, where targeted analysis is required, it can be advantageous to employ a selective detector. Measuring total sulfur content is a priority in hydrogen fuel impurity analysis so a sulfur chemiluminescence detector was employed in conjunction with the same TD and GC setup as described earlier. The detector is designed to detect sulfur compounds, removing analytical interference from impurities such as carbon dioxide, allowing for larger sample volumes and enhancing sensitivity for sulfur-containing compounds. Where sample volumes of 400 mL with mass spectrometers are typical to mitigate the impact from potential interferences, volumes of up to 800 mL can be used with an SCD to achieve maximum sensitivity and detect exceptionally low levels of sulfur compounds.

Figure 6 shows sensitive and highly reproducible measurement of sulfur compounds. These six replicates at 50 ppt, far below the required detection limits, give reproducibility for hydrogen sulfide at 0.89% RSD and signal-to-noise values far in excess of 3, indicating detection limits even lower than this 50-ppt standard. Of specific note are the cleanliness of the baseline, lack of any analytical interference and the sharp resolution of the peaks combining to deliver exceptional data quality and low detection limits.

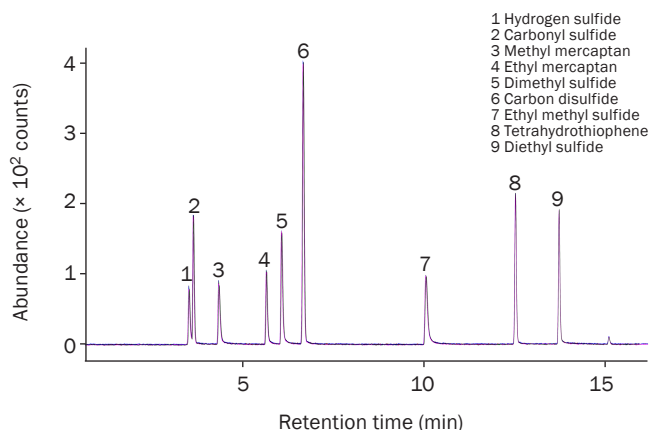


Figure 6: TD-GC-SCD data showing six replicate analyses of priority sulfur-containing compounds at 50 ppt.

Sorbent tubes for off-line analysis of hydrogen fuel impurities by TD-GC-MS

Sorbent-packed tubes can be used for sampling hydrogen fuels for easy sampling and transport as an alternative to cylinders or bags.

400 mL of a 10-ppb standard in hydrogen was purged onto a sorbent tube at a controlled flow rate of 100 mL/min. The sorbent tube was analysed using TD-GC-MS and the resulting TIC is shown in Figure 7. While many key hydrogen fuel impurities previously seen in grab samples can be identified, there are some important differences to highlight. Higher boiling VOCs can adsorb to the walls of sampling vessels such as bags or cylinders and are difficult to recover; with sorbent tubes, quantitative results are easily obtained for lower volatility compounds such as trichlorobenzene and hexachlorobutadiene. As discussed earlier, sorbent tubes are not suited to quantitative measurement of very volatile impurities such as formaldehyde and hydrogen sulfide and these peaks are notably more abundant in the grab sample

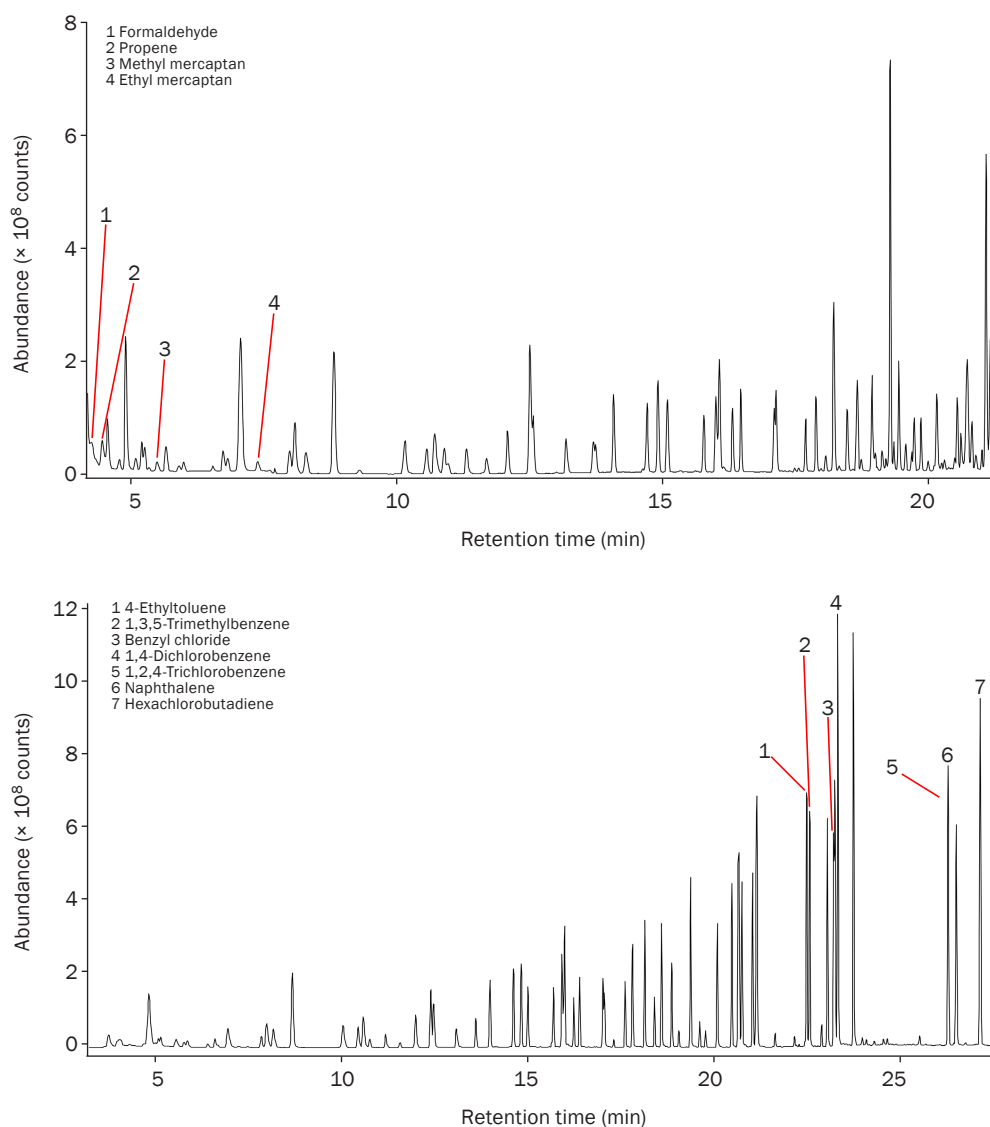


Figure 7: Total ion chromatograms of a simulated hydrogen fuel sample from a sampling bag, highlighting optimum recovery for very volatile compounds (top) and a simulated hydrogen fuel sample, collected on a sorbent tube, showing fewer volatile compounds (bottom).

TIC. Sorbent tubes and grab samples can be considered as complementary for full characterisation and untargeted screening of samples; when analysing a known target list, the optimum sampling method should be selected based on the compounds of interest.

In addition to extending the compound range and the transport and storage benefits mentioned earlier, sorbent tube autosamplers enable automated re-collection of split flows during GC injection. Split flows can be re-collected onto sorbent tubes whether the original sample was in a sorbent tube, sampling bag, cylinder or even an on-line gas stream; however, it is worth noting that highly volatile compounds, such as formaldehyde and hydrogen sulfide, will not be retained by a sorbent tube. A schematic of the re-collection process is shown in Figure 1. The key benefits of this process are: (1) samples can be archived for future re-analysis, which is particularly useful for on-line samples where the exact sample cannot be replicated, (2) it creates duplicate samples that can be analysed on a different instrument, perhaps with a selective detector and (3) better storage of thermally labile and reactive compounds, which are often more stable on sorbent tubes than in sampling bags or cylinders. Sorbent

tubes are also much easier to store than bags or cylinders of hydrogen sample.

Hydrogen carrier gas

Many laboratories were already looking to reduce their carbon footprints with fewer gas cylinder deliveries or a switch to renewable gas supplies, but the current helium shortage and associated increase in its cost has meant that future-proofing against further shortages has become a priority.

In support of green initiatives and to enable laboratories to keep operating at capacity despite challenges with helium supplies, Markes International has introduced Multi-Gas technology in its range of TD instruments. The instruments have been independently certified to be run with three gases – hydrogen, helium and nitrogen.

A significant additional benefit of hydrogen carrier gas is the associated productivity boost. GC-MS run times can be significantly reduced, without sacrificing data quality or peak resolution. Figure 8 shows a comparison of a hydrogen fuel impurity standard analysed with both helium and hydrogen carrier gases (the method parameters listed in the

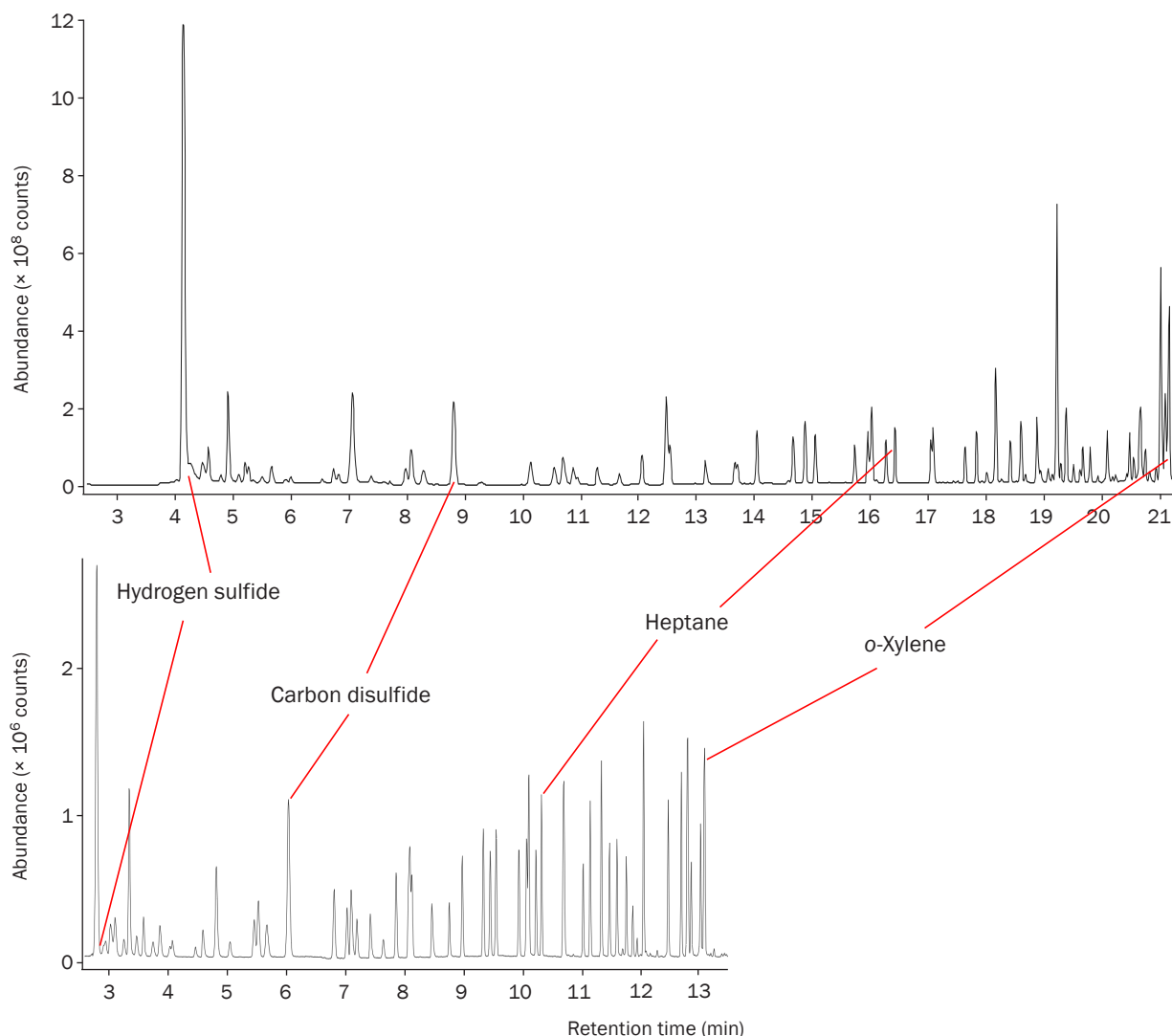


Figure 8: Total ion chromatograms for 800-mL, 10-ppb hydrogen fuel samples run using helium (top) and hydrogen (bottom) as carrier gases.

experimental section were translated for use with hydrogen carrier gas using a GC method translator). More information on the benefits of using fully-certified Multi-Gas instruments with hydrogen carrier gas can be found in Application Note 160: [Identification of impurities in hydrogen fuel supplies using Multi-Gas on-line TD-GC-MS systems](#)¹¹ and Instant Insight 007: [Using hydrogen carrier gas with a thermal desorption \(TD\) system](#).¹²

In Figure 8, the same profile is observed for both helium and hydrogen as carrier gases, but the 32-minute run time with helium is reduced to 21 minutes with hydrogen. This 34% reduction in analytical cycle time means a single system can provide 23 more results in 24 hours. When monitoring hydrogen quality within a supply chain, fast results could be vital in reducing downtime and ensuring low-quality hydrogen does not reach the end consumer – a clear advantage of the significant gains in cycle time achieved with hydrogen carrier gas.

Conclusion

In this application note, we have demonstrated the power of preconcentration using TD in exceeding the requirements for the analysis of VOCs as hydrogen fuel impurities. On-line and off-line sampling strategies have been shown to offer advantages for different types of impurities and sampling scenarios. Full characterisation of fuel impurities, in response to a complaint for example, could employ a complementary set of off-line sampling tools, such as sorbent tubes and grab samples in cylinders, which can be analysed on a single flexible instrument at a central laboratory.

Coupling TD with GC-MS has enabled reporting of total species content to well within the required detection limits whilst also providing confident impurity identification and speciation in a single analysis. Alternatively, coupling TD with a selective detector, such as with ECD or SCD (as shown here), allows for highly sensitive monitoring of a subset of target compounds with no interference from other impurity types. It is important to note that each detection technique – mass spectrometry and sulfur chemiluminescence detection – combined with preconcentration by TD has sufficient sensitivity that both detectors could be employed on the same system by splitting the column effluent. In this way, the advantages of both detectors could be employed whilst exceeding the sensitivity requirements of published hydrogen fuel impurity measurement methods.

Excellent data quality was shown for 60 compounds comprising hydrocarbons, halogenated compounds, sulfur-containing compounds and oxygenated VOCs including formaldehyde and acetaldehyde. High-quality data for reactive compounds such as formaldehyde and hydrogen sulfide confirms the inertness of the full analytical system and allows for confident routine analysis of these priority impurities. Managing water is critical for generating reliable data and for the longevity of analytical instrumentation. The validation shown in this application note uses Markes' Dry-Focus3 technology to manage humidity in on-line gas streams and grab samples. Data is shown for 50-ppm water content, which is ten times the maximum water content listed in ISO 14687.¹ This water management capability allows scientists to

confidently analyse hydrogen fuel samples in the knowledge that humidity levels far in excess of those typically present will not impact their results or instrumentation.

The application was evaluated with both helium and hydrogen carrier gases. Multi-Gas-certified TD instruments enable laboratories to future-proof against increasingly unstable helium supply chains and rapidly rising costs, with the added benefit of reduced run time, meaning more samples can be processed every day. When monitoring on-line streams of hydrogen fuel gas, in a production environment for example, the short analytical cycle time achieved with hydrogen carrier gas means an earlier warning if impurities reach an unacceptable level.

With both carrier gases, along with the introduction of humidity, excellent data was obtained. An average linearity of 0.9987 and average area reproducibility of 2.32% were achieved, allowing confident compliance with required quality standards such as ISO 14687, EN 17124, SAE J2719 and ASTM D7892.

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Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

Appendix

Peak no.	Compound name	CAS number	Quant. ion	RT	Linearity	RSD% (area)	RSD% (RT)	LOD (ppt)	LOQ (ppt)
1	Formaldehyde	50-00-0	30	4.30	0.9995	3.30	0.10	14	46
2	Hydrogen sulfide	7783-06-4	34	4.31	0.9973	2.73	0.00	21	68
3	Propene	115-07-1	41	4.48	0.9978	2.44	0.10	18	60
4	Carbonyl sulfide	463-58-1	60	4.50	0.9960	1.93	0.00	10	35
5	Dichlorodifluoromethane	75-71-8	85	4.50	0.9991	2.16	0.00	11	36
6	Chloromethane	74-87-3	50	4.75	0.9955	2.01	0.09	12	40
7	Acetaldehyde	75-07-0	44	4.97	0.9991	1.10	0.00	41	136
8	Butadiene	106-99-0	54	5.27	0.9925	4.62	0.06	12	40
9	Methyl mercaptan	74-93-1	47	5.45	0.9964	1.82	0.10	7	24
10	Bromomethane	74-83-9	94	5.67	0.9959	2.11	0.09	6	20
11	Chloroethane	75-00-3	64	5.95	0.9930	1.88	0.08	21	71
12	Ethanol	64-17-5	45	6.05	0.9962	1.55	0.09	62	206
13	Acrolein	107-02-8	56	6.50	0.9972	2.06	0.00	35	118
14	Acetone	67-64-1	43	6.70	0.9979	1.56	0.00	14	47
15	Trichlorofluoromethane	75-69-4	101	7.00	0.9994	2.08	0.00	12	41
16	Isopropanol	67-63-0	45	7.02	0.9961	4.51	0.05	88	292
17	Ethyl mercaptan	75-08-1	62	7.30	0.9997	1.68	0.00	8	26
18	Dimethyl sulfide	75-18-3	46	7.85	0.9995	2.00	0.06	17	56
19	1,1-Dichloroethene	75-35-4	61	8.10	0.9989	1.97	0.00	13	42
20	Dichloromethane	75-09-2	49	8.25	0.9978	1.99	0.00	16	52
21	1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	101	8.72	0.9995	1.74	0.00	8	25
22	Carbon disulfide	75-15-0	76	8.75	0.9990	1.69	0.04	13	43
23	1,2-Dichloroethene	540-59-0	61	10.10	0.9986	3.45	0.00	16	53
24	1,1-Dichloroethane	75-34-3	63	10.50	0.9992	1.91	0.00	20	66
25	tert-Butyl methyl ether	1634-04-4	73	10.70	0.9984	2.01	0.03	21	71
26	Vinyl acetate	108-05-4	43	10.90	1.0000	2.12	0.04	9	29
27	Methyl ethyl ketone	78-93-3	43	11.20	0.9994	2.51	0.04	18	58
28	tert-Butyl mercaptan	75-66-1	57	11.70	1.0000	1.44	0.03	23	75
29	trans-1,2-Dichloroethene	156-60-5	61	12.00	0.9992	2.01	0.04	11	38
30	Ethyl acetate	141-78-6	43	12.45	0.9997	1.79	0.00	16	55
31	Hexane	110-54-3	57	12.50	0.9993	1.87	0.00	22	72
32	Chloroform	67-66-3	83	12.50	0.9997	1.83	0.04	12	41
33	Tetrahydrofuran	109-99-9	42	13.20	0.9997	1.54	0.00	20	68
34	1,2-Dichloroethane	107-06-2	62	13.60	0.9995	3.66	0.00	13	43
35	1,1,1-Trichloroethane	1299-89-4	97	13.95	1.0000	1.75	0.00	7	22
36	Benzene	71-43-2	78	14.70	0.9993	2.01	0.00	31	103
37	Tetrachloromethane	56-23-5	117	14.90	1.0000	1.50	0.00	5	17
38	Cyclohexane	110-82-7	56	15.10	0.9994	2.05	0.00	13	44
39	1,2-Dichloropropane	78-87-5	63	15.70	0.9990	2.14	0.00	8	27
40	Bromodichloromethane	75-27-4	83	15.85	0.9998	1.69	0.00	7	25
41	Trichloroethene	79-01-6	88	16.02	0.9999	1.88	0.00	7	25
42	Methyl methacrylate	80-62-6	41	16.20	1.0000	3.04	0.00	19	64
43	Heptane	142-82-5	43	16.40	0.9998	2.70	0.00	12	40
44	cis-1,3-Dichloropropene	10061-01-5	75	17.00	0.9998	1.95	0.00	7	22
45	4-Methylpentan-2-one	108-10-1	43	17.10	0.9971	3.60	0.00	46	154
46	trans-1,3-Dichloropropene	10061-02-6	75	17.60	0.9999	2.06	0.00	7	25

Table A1: Complete data for compounds 1–60. (Continued on next page.)

Peak no.	Compound name	CAS number	Quant. ion	RT	Linearity	RSD% (area)	RSD% (RT)	LOD (ppt)	LOQ (ppt)
47	1,1,2-Trichloroethane	79-00-5	97	17.80	0.9997	2.07	0.00	8	27
48	Toluene	108-88-3	91	18.13	0.9996	2.65	0.03	8	26
49	Methyl-n-butyl ketone	591-78-6	43	18.40	0.9978	2.46	0.00	6	21
50	Chlorodibromomethane	124-48-1	129	18.57	0.9996	1.94	0.00	4	15
51	1,2-Dibromoethane	106-93-4	107	18.90	0.9999	2.47	0.00	8	27
52	Tetrahydrothiophene	110-01-0	60	19.10	0.9999	2.75	0.00	12	42
53	Tetrachloroethene	127-18-4	166	19.30	0.9996	2.54	0.00	5	15
54	Chlorobenzene	108-90-7	112	20.10	0.9999	2.62	0.00	10	33
55	Ethylbenzene	100-41-4	91	20.50	0.9996	2.99	0.00	11	37
56	m/p-Xylene	108-38-3/ 106-42-3	91	20.65	0.9996	2.99	0.00	24	81
57	Tribromomethane	75-25-2	173	20.71	0.9986	2.81	0.00	5	16
58	Styrene	100-42-5	104	21.00	0.9990	3.11	0.00	8	25
59	1,1,2,2-Tetrachloroethane	79-34-5	83	21.10	0.9995	2.52	0.00	15	51
60	o-Xylene	95-47-6	91	21.15	0.9997	2.96	0.02	13	42
Average					0.9987	2.32	0.02	16	53

Table A1: Complete data for compounds 1–60. (Continued from previous page.)