MARKES international

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Application Note 160

Identification of impurities in hydrogen fuel supplies using Multi-Gas on-line TD–GC–MS systems

Summary

A Multi-Gas thermal desorber from Markes International was used to analyse impurities in hydrogen fuel. Performance criteria and detection limits were exceeded for a range of target compounds, complying with ISO-14687-2, ISO-21087 and ASTM D7892 standard methods.

Introduction

Hydrogen fuel cells offer great potential for clean, carbon-neutral transportation; however, providing an unadulterated source of hydrogen can be a challenge. Contaminants introduced along the hydrogen supply chain could damage fuel cells, shorten component lifespan and increase pollution.

As hydrogen is an emerging sustainable energy source, the quality of hydrogen fuel is being closely regulated by several institutions around the world. For example, method ISO 14687-2[1] specifies the analysis of total sulfur compounds in hydrogen fuel, which have a maximum allowable concentration of 4 ppb, while ISO 21087[2] prescribes analytical methods for quality control of hydrogen fuel at distribution facilities. Method ASTM D7892[3] determines concentrations of total organic halides and total non-methane hydrocarbons by measurement of individual target halocarbons and hydrocarbons, including formaldehyde. SAE 2719[4] states that hydrogen fuel should contain less than 50 ppb total halogenates (including organic halides), 20 ppb total non-methane hydrocarbons and 10 ppb formaldehyde.

Analysis of hydrogen fuel impurities is carried out by a number of different analytical techniques. Thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) is an approach that improves efficiency compared to the other techniques by allowing simultaneous identification of many components and provides improvements in detection limits. The technique has been enhanced by the introduction of Markes' Multi-Gas on-line and canister TD systems. The Air Server-xr™ and CIA *Advantage*-xr™ instruments are now certified for use with helium, nitrogen or hydrogen as a carrier and/or sample gas. One driving factor for this advancement is that helium is a finite resource that is increasingly expensive and difficult to source as a GC carrier gas. Also, it must be extracted and stored before being shipped around the world, giving it a high carbon footprint. Hydrogen, on the other hand, is simple to generate on demand using water and electricity so seems to be the obvious environmentally friendly alternative. Securing against helium shortages in the long term and offering immediate cost and operational savings, hydrogen also promises shorter analytical cycle times and faster sample throughput. The Multi-Gas development enables the use of hydrogen as a sample gas on the same certified instrument, making it the ideal system for the analysis of hydrogen fuel.

This application note shows the robust, reproducible analysis of trace VOCs and sulfur-containing compounds with detection limits in the range of ppb to low ppt from hydrogen fuel.

Analytical equipment

The analytical system used for this study was the Air Server–Kori–UNITY-xr™ coupled to a GC–MS system (Figure 1). The entire system is cryogen-free and can be controlled remotely, making it ideal for unattended operation in remote locations. The individual components of the system are briefly described next.

With the Air Server-xr Multi-Gas instrument, the hydrogen sample gas is drawn at a controlled rate from a bag. An automatic interchange between three or eight sample channels allows remote system calibration or validation. Before entering the thermal desorber, samples pass through a Kori-xr™ device, which removes humidity from the sample stream (Figure 2). As well as eliminating the risk of poor chromatography caused by water interference, this allows lower temperatures to be used in the focusing trap without risk of water retention, so that VOCs, VVOCs (such as H_2S), oxygenates and monoterpenes in humid samples can be quantitatively retained. Note that as well as bag sampling, Air Server–Kori–UNITY-xr can also be applied to canister and on-line samples.

When excess water is removed, samples pass into the UNITY-xr™ Multi-Gas thermal desorber. This instrument contains a narrow focusing trap, electrically cooled down to -30°C, filled with porous polymer and an additional strong adsorbent. Once analytes are trapped, the flow of gas is reversed and the trap is heated rapidly (up to 100°C/s), to 'backflush' the analytes onto the GC column.

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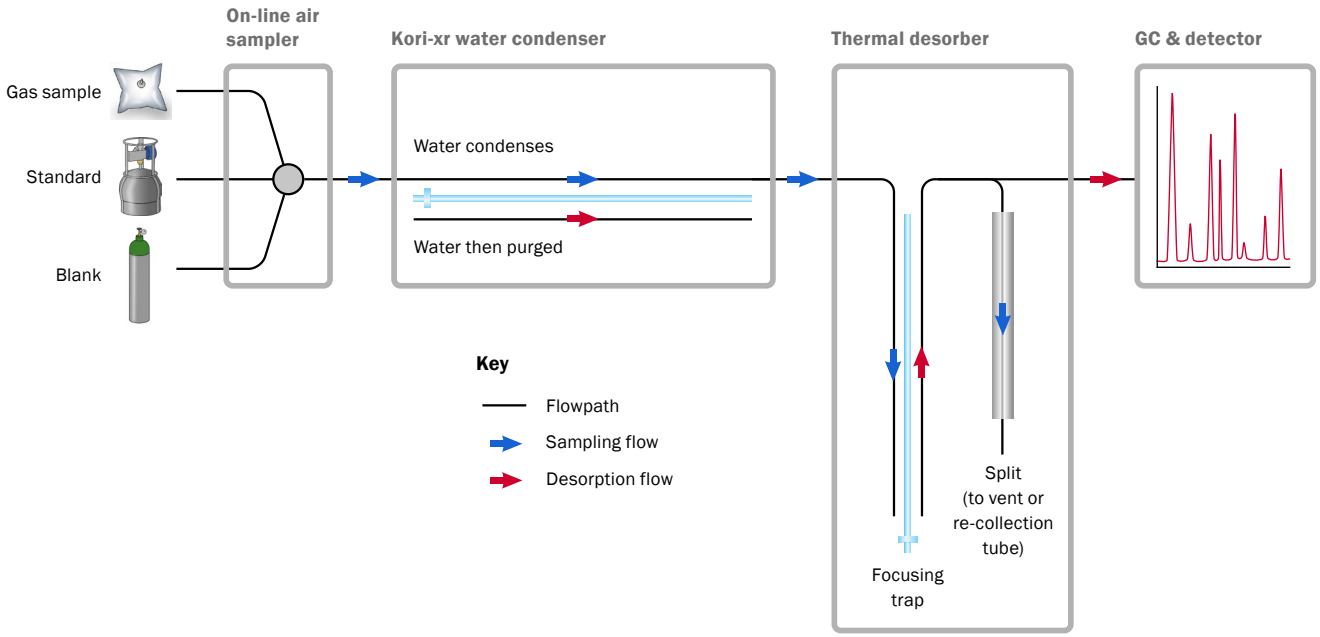
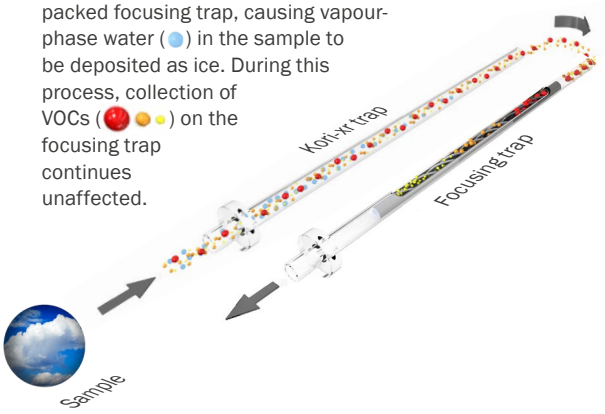


Figure 1: Equipment configuration for the Air Server–Kori–UNITY-xr.

1 Gas sampling and water removal:

The empty Kori-xr trap, held below 0°C, sits in-between the sample inlet and the sorbent-packed focusing trap, causing vapour-phase water ( ) in the sample to be deposited as ice. During this process, collection of VOCs ( ) on the focusing trap continues unaffected.



2 Trap desorption and water purging:

When sampling is complete, the analytes are transferred from the focusing trap to the GC, and ice is purged from the Kori-xr trap, to prepare it for the next sample.

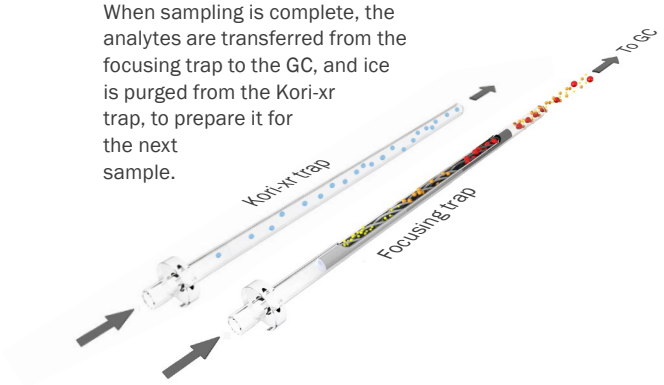


Figure 2: Operation of the Kori-xr device for removing water from humid sample streams.

Sampling through the entire Air Server–Kori–UNITY-xr system is performed using an electronic mass flow controller and pump, located downstream of the focusing trap to avoid contamination. Once the trap has desorbed, the system re-equilibrates and begins collecting the next sample, while analysis of the previous sample continues, saving time.

At the point of trap desorption, the sample can be split, either to vent or onto a clean sorbent tube for storage and/or re-analysis at a later time (it should be noted that sorbent tubes are not able to retain very volatile compounds such as H_2S and acetylene). Sample splitting and re-collection can be fully automated by adding an ULTRA-xr™ 100-tube autosampler.

Sampling and analysis

Preparation of standards:

A range of chemical species were used to validate the methodology. A 1-ppm gaseous mix of 65 compounds, traditionally used for Ambient Air Monitoring methods (US EPA method TO-15), was chosen, as many impurities of interest were found in this commercial standard (* in Table 1). Five sulfur compounds were obtained in a separate gaseous mix at 1 ppm each († in Table 1) and additional gas standards of tetrahydrothiophene and *tert*-butyl mercaptan were made up from liquid standards to concentrations of 14 and 11 ppm, respectively. All standards were in nitrogen. Prior to analysis, all compounds were mixed in inert-coated Tedlar bags (Sigma Aldrich, part number 30228-U) under four sample gas conditions: dry nitrogen, 50% RH (relative humidity) nitrogen, dry hydrogen and 50% RH hydrogen.

Simulated samples:

Since obtaining real hydrogen samples for analysis is currently not possible, simulated hydrogen fuel samples were prepared

for this study (see section on Simulated Real-World Samples). A representative range of analytes and concentrations was used. Samples consisted of analytes of interest at unknown concentrations, and different volumes of each standard were used for the most realistic representation. Further, different relative humidity levels were used. Simulated samples were run in triplicate at sample volumes of 400 mL.

Sampling and analytical conditions

The instrument conditions used in the investigation were as follows.

Gas sampling:

Instrument:	Air Server-xr
Sample purge:	4 min at 50 mL/min
Sample flow:	50 mL/min
Sample volume:	400 mL
Post-sample purge:	2 min at 50 mL/min

Water management:

Instrument:	Kori-xr
Trap range:	-30 to 300°C

TD:

Instrument:	UNITY-xr
Recollection:	ULTRA-xr
Flow path:	80°C
Sample flow:	50 mL/min
Re-collection tube:	'Odour/Sulfur' inert-coated (part no. C2-CAXX-5314)
Tube pre-purge:	1 min at 50 mL/min
Tube desorb:	280°C (10 min)
Trap purge:	1 min at 50 mL/min
Focusing trap:	'Hydrogen sulfide' (part no. U-T14H2S-2S)
Focusing trap low:	-30°C
Focusing trap high:	270°C (2.8 min)
Outlet split:	4 mL/min

GC:

Column:	DB-624™, 60 m x 0.25 mm x 1.4 µm
Carrier gas:	Helium, constant flow
Column flow:	2 mL/min
Oven:	35°C (5 min), 10°C/min to 180°C, 25°C/min to 230°C (0.5 min)

MS:

Source:	230°C
Transfer line:	230°C
Scan range:	m/z 30–350
SIM windows:	0–4 min: m/z 29, 34, 50, 60 4–6 min: m/z 47, 94 6–8 min: m/z 31, 43, 45, 62, 76 8–10 min: m/z 57, 63, 73 10–13 min: 43, 78, 83, 117 13–20 min: 60, 91, 104

Results and discussion

Compound identification and peak shape

A 400-mL sample of a 4-ppb standard was analysed and all compounds of interest (Table 1) were readily identifiable with good peak shapes. Some compounds co-eluted but were easily distinguished spectrally by their different ions (Figure 3).

A comparison was made to evaluate compound response from both nitrogen and hydrogen sample gases at both 0% and 50% RH (Figure 4). Very similar chromatographic profiles were obtained regardless of sample gas type or humidity, demonstrating the effectiveness of the Multi-Gas-enabled TD systems and the ability of the Kori-xr water management system to obtain consistent high-quality data.

Linearity and reproducibility

Reproducibilities for retention time (RT) stability and analyte response were calculated using seven replicate measurements at 4 ppb in dry and humid nitrogen from the standard mix (Table A1 Appendix) and dry and humid hydrogen (Table A2 Appendix). Excellent results were achieved for all compounds across all conditions, with all linearities of $R^2 > 0.99$ (Figure 5), most response RSDs below 2% and most RT RSDs below 0.1% (Figure 6), complying with key quality criteria. The highest RSD values were 5.79% and 0.28% for response and RT, respectively, well below the ISO 21087 requirement of 10% RSD for reproducibility. In addition, the peaks produced by selected compounds over a range of the concentrations used for this linearity study are shown in Figure 6, showing excellent peak shape even at low concentration values.

Limits of detection (LODs) and quantitation (LOQs)

Given the very similar results obtained under all sample gas conditions, subsequent tests were performed with only humid hydrogen. Limits of detection (LODs) and limits of quantitation (LOQs) were calculated according to the guidance in ISO 21087. Twelve 5-mL replicates of a 4-ppb standard (equivalent to 0.05 ppb) were analysed and the standard deviation was multiplied by three or ten to obtain values for the LOD or LOQ, respectively. The concentrations corresponding to these values were then calculated from a calibration curve and taken as the LOD or LOQ. Note that a multiplication factor of ten to calculate LOQ is the most stringent factor proposed by ISO 21087.

Excellent LOD and LOQ values were achieved: the highest values were for hydrogen sulfide, with an LOD and LOQ of 28.37 and 94.58 ppt, respectively, while the mean values were 8.16 and 27.21. ISO 14687 gives a maximum allowable concentration of 2000 ppb for total hydrocarbons, 4 ppb for total sulfur compounds and 50 ppb for total halocarbons (Table A2 Appendix).

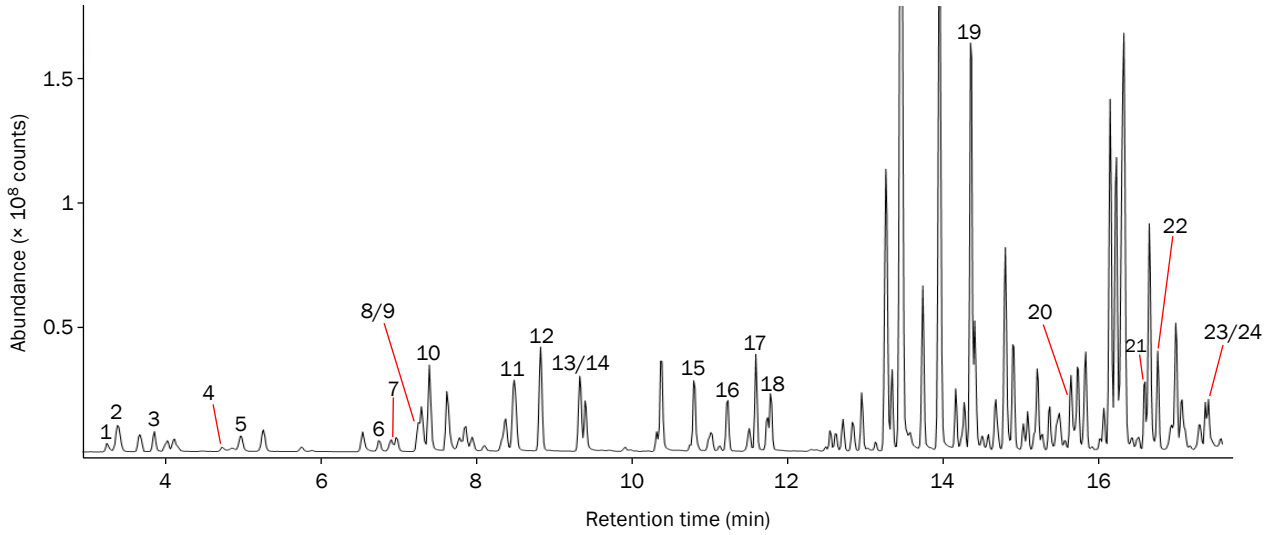


Figure 3: Extracted ion chromatogram showing the major ions of 24 compounds of interest, produced from a 400-mL sample of a 4-ppb standard in dry nitrogen. Peak identifications are given in Table 1. Additional peaks represent other compounds in the TO-15 gas standard mix.

No.	Compound	Quantitative ion	RT
1	Hydrogen sulfide†	34	3.25
2	Carbonyl sulfide†	60	3.36
3	Chloromethane*	50	3.83
4	Methyl mercaptan†	47	4.73
5	Bromomethane*	94	4.96
6	Ethyl mercaptan†	62	6.77
7	Ethanol*	31	6.88
8	Dimethyl sulfide†	62	7.24
9	Acetone*	43	7.3
10	Carbon disulfide*	76	7.4
11	*tert*-Butyl methyl ether*	73	8.46
12	Hexane*	57	8.84
13	1,1-Dichloroethane*	63	9.33
14	*tert*-Butyl mercaptan	57	9.33
15	Chloroform*	83	10.79
16	Carbon tetrachloride*	117	11.22
17	Benzene*	78	11.58
18	Heptane*	43	11.78
19	Toluene*	91	14.4
20	Tetrahydrothiophene	60	15.64
21	Ethylbenzene*	91	16.58
22	*m/p*-Xylene*	91	16.75
23	*o*-Xylene*	91	17.36
24	Styrene*	104	17.41

Table 1: Compounds of interest as contaminants of hydrogen fuel, along with ions used for quantitation and retention times under the instrumental conditions of this study.
*Relevant components in the mixed VOC TO-15 standard.
†Components of a mixed sulfurs standard.

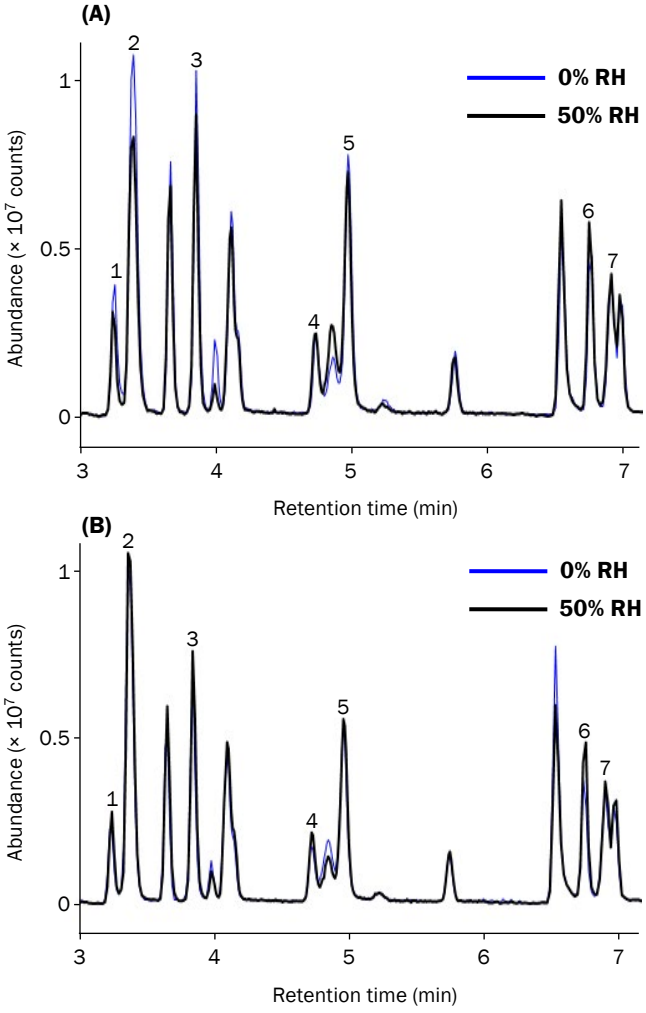


Figure 4: Extracted ion chromatogram showing early early-eluting compounds in nitrogen (A) and hydrogen (B) at 0% RH (blue) and 50% RH (black), giving displaying consistent responses and retention times regardless of sample gas type or humidity. Peak identifications are given in Table 1. Additional peaks represent other compounds in the TO-15 gas standard mix.

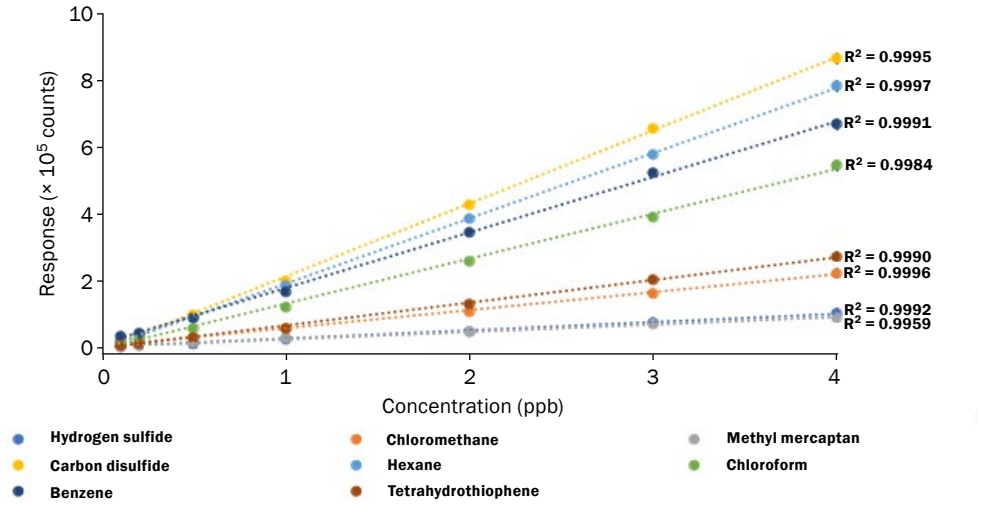


Figure 5: Linearity plots for a selection of compounds of interest in humid hydrogen over a concentration range of 0.1–4 ppb.

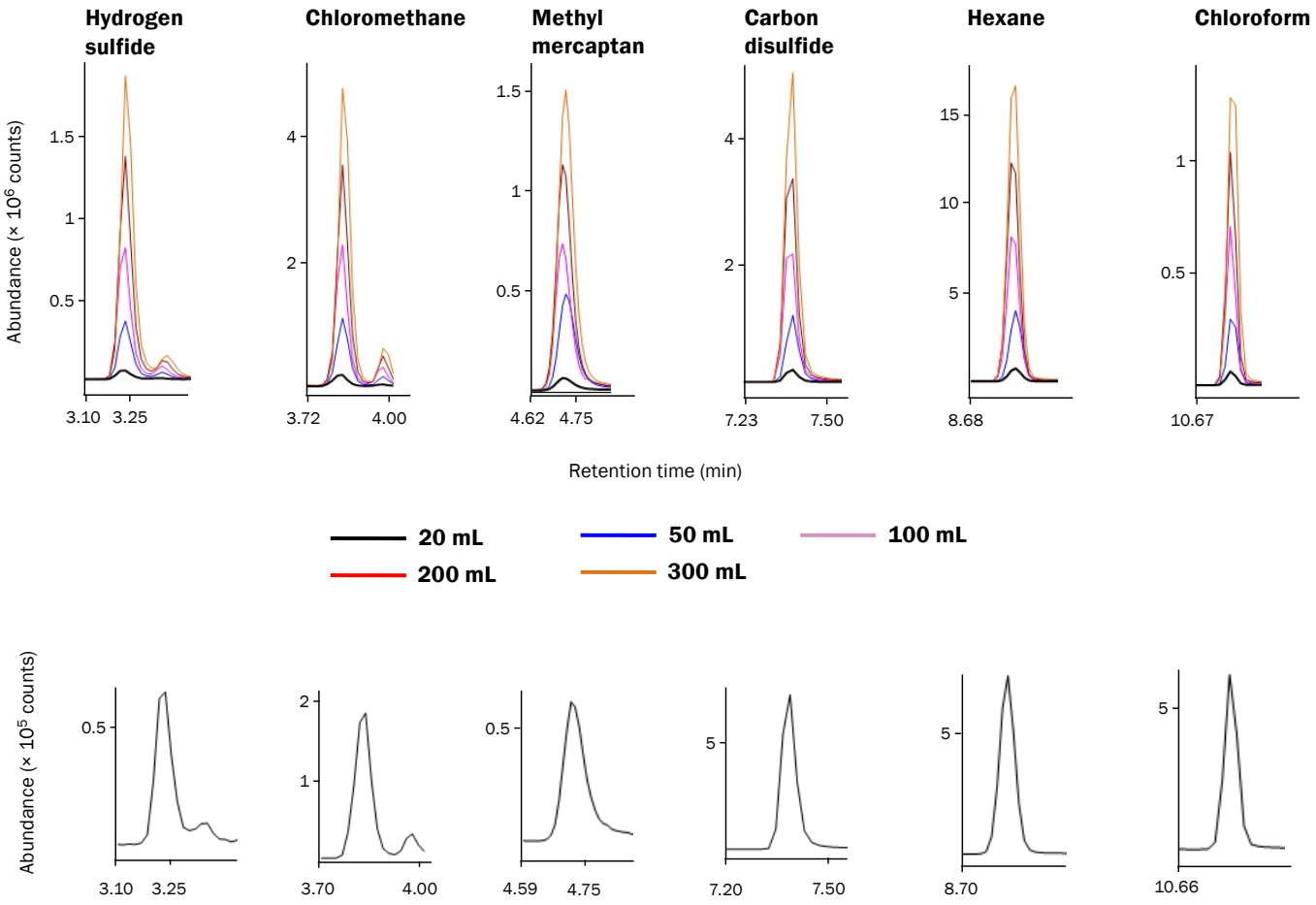


Figure 6: Extracted ion chromatograms showing selected compounds of interest at 4 ppb in humid hydrogen (50% RH).
Top: Overlay of peaks produced at various sample volumes. Bottom: Close-up of the same peaks produced at a 20-mL sample volume.

Re-collection

A key advantage of Markes' TD systems is the ability to split a sample and re-collect a portion of that sample onto a clean sorbent tube. With the addition of the modular tube automated ULTRA-xr, this re-collection can become fully automated. This is particularly useful for archiving and storing unique samples but also enables future re-analysis with different method parameters or even different analytical equipment such as alternative detectors. It should be noted that compounds that are too volatile to be sampled onto sorbent tubes, for example hydrogen sulfide, will not be quantitatively retained on the re-collection tube.

Re-collection is a simple and efficient way of validating analyte recovery through the entire TD–GC system and is mentioned in numerous standard methods.[5,6] It is therefore particularly beneficial to perform this analytical process when analysing reactive target compounds such as these to confirm that no analyte losses *via* thermal degradation, for example, do not occur.

Optimised results display a consistent profile across the chromatogram for the initial analysis and subsequent re-analysis (Figure 7). Responses for thermally labile sulfur compounds such as dimethyl sulfide, carbon disulfide and *tert*-butyl mercaptan (peaks 8, 10 and 14, respectively) match the same reduction in response displayed by other compounds confirming no degradation is observed and highlighting the benefits of an inert flow path. This can be confirmed further by plotting the theoretically calculated reduction using the method parameters and comparing the reduction of compound responses (Figure 8). A matching profile confirms quantitative re-collection, ensuring data quality and maintaining confidence in results.

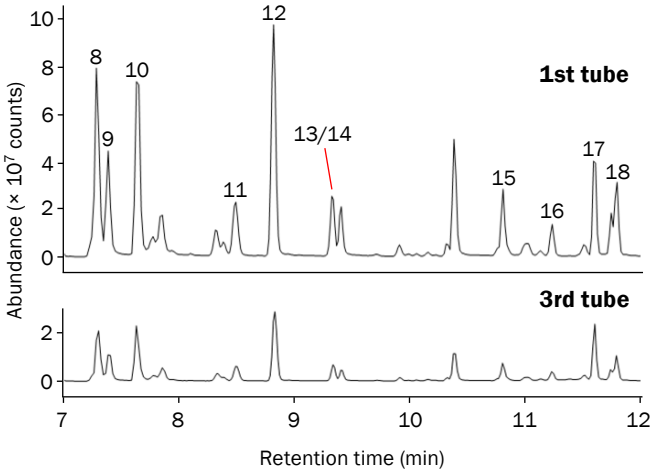


Figure 7: The merged extracted ion chromatogram displays initial tube analysis after re-collection of a standard, and subsequent third analysis of the same standard displaying a consistent sample profile across the chromatogram.

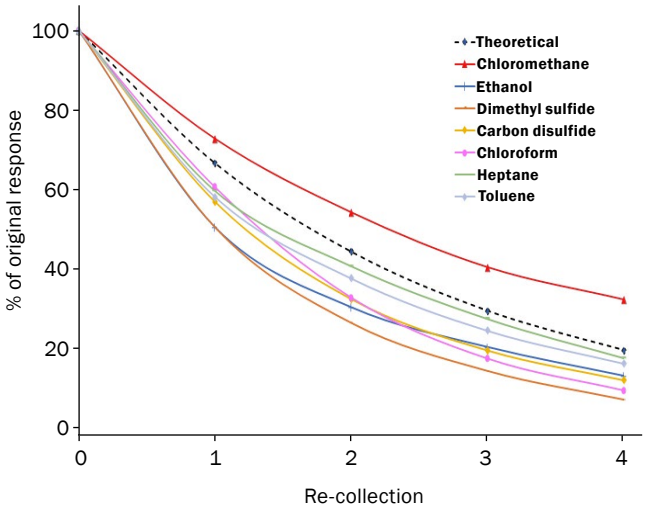


Figure 8: Re-collection series of target compounds displaying reduction of compounds matching the theoretically calculated profile, confirming a quantitative re-collection process and fully inert flow path.

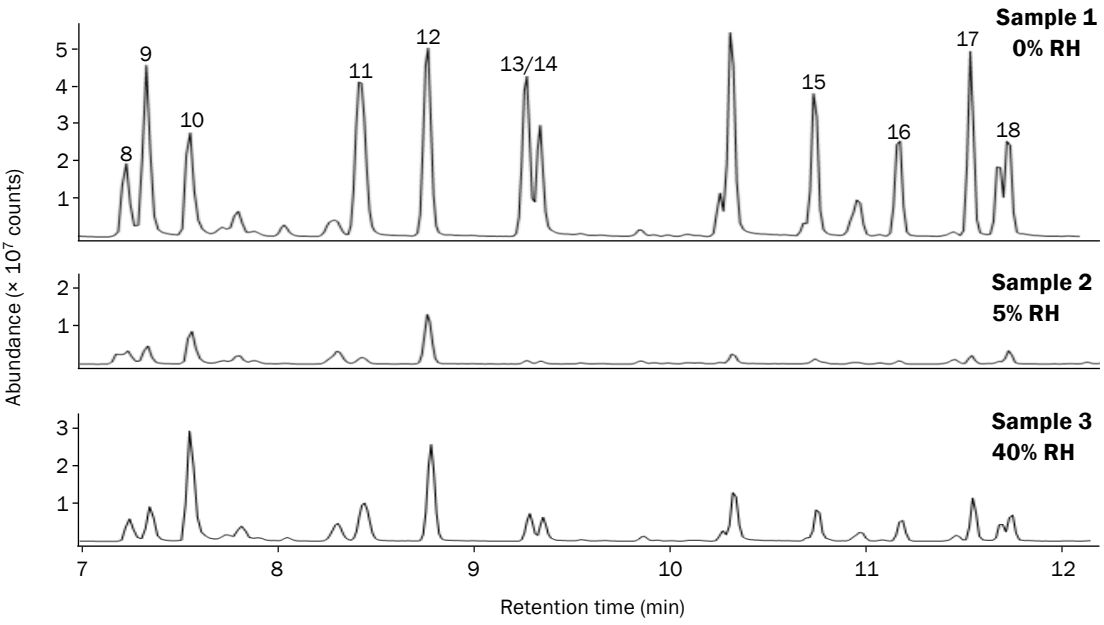


Figure 9: Extracted ion chromatograms comparing simulated hydrogen fuel samples displaying a range of target compounds at varying concentrations and no effects from varied sample humidities.

No.	Compound	Mean concentration (ppb, n = 3)		
		Sample 1	Sample 2	Sample 3
1	Hydrogen sulfide	0.44	1.61	0.00
2	Carbonyl sulfide	0.79	1.42	0.00
3	Chloromethane	7.27	0.34	0.00
4	Methyl mercaptan	0.06	1.38	0.00
5	Bromomethane	7.23	0.31	2.06
6	Ethyl mercaptan	0.10	1.60	0.00
7	Ethanol	7.38	0.47	0.78
8	Dimethyl sulfide	0.33	1.19	0.00
9	Acetone	6.48	1.16	2.16
10	Carbon disulfide	7.55	0.86	1.88
11	*tert*-Butyl methyl ether	7.46	0.34	2.06
12	Hexane	7.06	1.70	3.95
13	1,1-Dichloroethane	8.23	0.09	0.45
14	*tert*-Butyl mercaptan	7.50	0.00	2.08
15	Chloroform	8.00	0.33	2.22
16	Carbon tetrachloride	8.23	0.29	2.23
17	Benzene	7.86	0.37	2.12
18	Heptane	7.13	0.88	2.09
19	Toluene	8.63	3.45	3.94
20	Tetrahydrothiophene	2.35	0.42	0.12
21	Ethylbenzene	6.56	0.75	1.89
22	*m*/*p*-Xylene	6.31	1.49	2.22
23	*o*-Xylene	6.63	0.98	1.96
24	Styrene	7.17	1.93	2.52
	Relative humidity	**0%**	**5%**	**40%**

Table 2: Average concentrations of target compounds from triplicate analyses of simulated hydrogen fuel samples.

Simulated real-world samples

Three simulated real-world samples containing unknown concentrations of target impurities were analysed in triplicate and quantified from calibrations (Table 2).

Inspection of the extracted ion chromatograms showed good peak shape across the range with response varying according to the calculated concentration and unaffected by variations in humidity of the sample (Figure 9).

Conclusion

In summary, the Multi-Gas UNITY–Air Server-xr preconcentration system with water removal by Kori-xr allows confident on-line GC–MS analysis of an extended range of impurities in hydrogen fuel, including sulfur species, non-methane hydrocarbons, halo carbons and hydrocarbons, in accordance with the recommendations in various global standards.[1–4]

Using gas standards, we have demonstrated excellent system stability, with relative standard deviations for analyte response and retention time exceeding quality criteria. The quantitative nature of the analysis was demonstrated by all compounds displaying excellent linearity across the 0.1–4 ppb range. Finally, LOD and LOQ were all in the sub-ppb range, with most LOQ values well below 50 ppt and no deterioration of results was experienced when using humid sample gas, demonstrating the effectiveness of Kori-xr for water management. We show fully automated re-collection onto TD tubes with ULTRA-xr, highlighting the expected quantitative reduction of response with each re-collection. Finally, having validated our method using gas standards, we simulated real hydrogen fuel samples and analysed these, quantifying components at various concentrations and humidity levels.

Key features of Markes' TD systems for this application are:

- Cryogen-free analysis of the most volatile VVOCs, hydrocarbons, sulfur species and other VOCs in humid hydrogen gas with excellent linearities and reproducibilities for increased data quality and rapid, unattended reporting.
- Certification of Multi-Gas systems for the use of hydrogen as a sample and carrier gas, which ensures safe and cost-effective analysis.
- Electrical trap cooling (both in the UNITY-xr thermal desorber and the Kori-xr water condenser), which makes this system ideal for remote or field locations by eliminating the requirement for a liquid cryogen.

Additional features of all Markes' TD systems, including the UNITY–Air Server-xr system used in this study, are the ability to (a) run standard 3½″ thermal desorption sample tubes and (b) re-collect the split portions of samples onto clean sorbent tubes for easier method validation and sample storage.

References

1. ISO 14687:2019, Hydrogen fuel quality — Product specification, https://www.iso.org/standard/69539.html.
2. ISO 21087:2019, Gas analysis — Analytical methods for hydrogen fuel — Proton exchange membrane (PEM) fuel cell applications for road vehicles, https://www.iso.org/standard/69909.html.
3. ASTM D7892-15, Standard test method for determination of total organic halides, total non-methane hydrocarbons, and formaldehyde in hydrogen fuel by gas chromatography/mass spectrometry, https://www.astm.org/d7892-15.html.
4. SAE 2719, Hydrogen Fuel Quality for Fuel Cell Vehicles, 2011, https://www.sae.org/standards/content/j2719_201109/.
5. ISO 16000-6:2011, Indoor air — Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS–FID, https://www.iso.org/standard/52213.html.
6. ASTM D6196-15e1, Standard practice for choosing sorbents, sampling parameters and thermal desorption analytical conditions for monitoring volatile organic chemicals in air, 2018, https://www.astm.org/d6196-15e01.html.

Trademarks

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

Appendix

No.	Compound	0% RH			50% RH		
		R^2	Area RSD (%)	RT RSD (%)	R^2	Area RSD (%)	RT RSD (%)
1	Hydrogen sulfide	0.9991	1.54	0.16	0.9996	3.47	0.12
2	Carbonyl sulfide	0.9939	1.13	0.00	0.9937	2.44	0.22
3	Chloromethane	0.9998	1.33	0.25	0.9999	1.91	0.28
4	Methyl mercaptan	0.9989	0.83	0.15	0.9920	1.83	0.00
5	Bromomethane	0.9999	2.32	0.11	0.9981	2.18	0.10
6	Ethyl mercaptan	0.9988	1.15	0.00	0.9952	3.15	0.16
7	Ethanol	0.9995	2.41	0.00	0.9999	2.64	0.15
8	Dimethyl sulfide	0.9959	0.88	0.13	0.9998	1.63	0.00
9	Acetone	0.9979	0.70	0.00	0.9999	0.26	0.15
10	Carbon disulfide	0.9967	1.42	0.14	0.9996	1.87	0.00
11	*tert*-Butyl methyl ether	0.9992	0.87	0.12	0.9994	2.11	0.09
12	Hexane	0.9994	1.00	0.06	0.9998	1.38	0.06
13	1,1-Dichloroethane	0.9992	0.74	0.05	0.9991	1.69	0.10
14	*tert*-Butyl mercaptan	0.9991	0.54	0.11	0.9997	1.80	0.04
15	Chloroform	0.9996	1.54	0.03	0.9990	1.68	0.09
16	Carbon tetrachloride	0.9900	1.2	0.03	0.9982	1.92	0.09
17	Benzene	0.9978	1.17	0.05	0.9980	1.25	0.00
18	Heptane	0.9985	1.44	0.04	0.9993	0.86	0.05
19	Toluene	0.9977	1.94	0.03	0.998	0.83	0.04
20	Tetrahydrothiophene	0.9907	1.82	0.03	0.9989	0.79	0.03
21	Ethylbenzene	0.9971	2.75	0.03	0.9995	1.68	0.02
22	*m*/*p*-Xylene	0.9968	2.52	0.05	0.9985	1.61	0.03
23	*o*-Xylene	0.9956	2.80	0.05	0.9974	1.52	0.06
24	Styrene	0.9903	2.85	0.03	0.9986	1.81	0.02
	Mean	**0.9971**	**1.54**	**0.07**	**0.9984**	**1.76**	**0.08**

Table A1: Analytical performance for 24 compounds at 4 ppb in dry (0% RH) and humid (50% RH) nitrogen. Linearity (R^2) was measured over seven calibration levels from 10–400 mL of a 4-ppb standard. Relative standard deviation of response area (area RSD) and of retention time (RT RSD) was measured over seven replicates of 200 mL samples.

No.	Compound	0% RH			50% RH				
		R^2	Area RSD (%)	RT RSD (%)	R^2	RSD (n = 7)	RSD (RT)	LOD (ppt)	LOQ (ppt)
1	Hydrogen sulfide	0.9978	0.92	0.00	0.9992	4.74	0.23	28.37	94.58
2	Carbonyl sulfide	0.9996	0.88	0.22	1.0000	2.56	0.00	3.77	12.56
3	Chloromethane	0.9995	1.09	0.00	0.9996	2.91	0.00	4.05	13.50
4	Methyl mercaptan	0.9974	1.68	0.10	0.9959	1.10	0.00	13.57	45.23
5	Bromomethane	0.9998	0.75	0.08	0.9993	1.19	0.08	3.65	12.17
6	Ethyl mercaptan	0.9965	3.29	0.00	0.9992	1.48	0.00	7.26	24.20
7	Ethanol	0.9997	1.45	0.11	0.9996	2.59	0.00	15.33	51.09
8	Dimethyl sulfide	0.9993	0.60	0.15	0.9996	0.93	0.15	4.62	15.40
9	Acetone	0.9992	0.51	0.00	0.9995	1.06	0.10	12.78	42.61
10	Carbon disulfide	0.9983	1.02	0.00	0.9995	1.35	0.10	7.14	23.80
11	*tert*-Butyl methyl ether	0.9988	0.91	0.06	0.9993	1.02	0.09	6.40	21.35
12	Hexane	0.9993	0.98	0.04	0.9997	0.92	0.04	7.49	24.97
13	1,1-Dichloroethane	0.9993	0.59	0.08	0.9997	1.18	0.08	8.54	28.46
14	*tert*-Butyl mercaptan	0.9992	0.92	0.06	0.9995	0.90	0.06	9.90	32.99
15	Chloroform	0.9981	1.37	0.07	0.9984	1.84	0.07	7.13	23.78
16	Carbon tetrachloride	0.9966	1.00	0.09	0.9995	5.79	0.10	8.80	29.35
17	Benzene	0.9993	1.14	0.00	0.9991	2.60	0.07	13.67	45.58
18	Heptane	0.9985	0.69	0.00	0.9996	1.57	0.00	4.03	13.45
19	Toluene	0.9995	2.76	0.00	0.9988	1.57	0.05	6.13	20.43
20	Tetrahydrothiophene	0.9992	1.74	0.00	0.9990	1.10	0.02	2.78	9.26
21	Ethylbenzene	0.9992	1.24	0.06	0.9979	1.36	0.06	3.03	10.09
22	*m*/*p*-Xylene	0.9995	1.36	0.02	0.9967	1.09	0.00	7.64	25.48
23	*o*-Xylene	0.9993	1.34	0.04	0.9969	1.58	0.00	4.48	14.93
24	Styrene	0.9985	1.72	0.04	0.9949	1.00	0.06	5.34	17.82
	Mean	**0.9988**	**1.25**	**0.05**	**0.9988**	**1.81**	**0.06**	**8.16**	**27.21**

Table A2: Analytical performance for 24 compounds at 4 ppb in dry (0% RH) and humid (50% RH) hydrogen. Linearity (R^2) and relative standard deviations of response area (area RSD) and of retention time (RT RSD) were measured as described in Table A1. Limits of detection (LOD) and quantitation (LOQ) assume a 400 mL sample volume.