AN-15 : TRACE SULFUR IN H_2 ANALYSIS WITHOUT SCD, FPD AND THERMAL DESORBER

A PROCESS GC SOLUTION—KA8000Plus SULFURS IN FUEL-GRADE H_2 TEST REPORT

The fuel-grade hydrogen market is currently booming. Standards containing the maximum allowable concentration of impurities in hydrogen were recently defined as well as laboratory oriented analytical methods. Currently, for ultra-trace sulfur analysis, a gas chromatograph based on a SCD detector is suggested by some standards for laboratory tests. However, the SCD detector is less than ideal for process use due to its size, required maintenance and potential hazard due to the use of ozone and heated furnace. Another contender is the PFPD, but this detector is also difficult to use on the field and involves the use of a hazardous flame which is again not ideal with the presence of flammable hydrogen.

The **KA8000Plus** from **KA Solutions**, powered by **ASDevices,** has been selected as the preferred process-oriented solution by **Impact Scientific Instrument**. All the components are high quality and the sensor, the **SePdd**, is very simple to use. It only involves the use of inert carrier gas and is solid state. Also, there is no need for a thermal desorber to concentrate the sulfur impurities contained in the sample to achieve the 4 ppb LOD (Limit Of Detection) target defined as the current standard.

ISO FDIS 14687-2 for fuel-grade hydrogen	
Water (H_2O)	5 ppm
Total hydrocarbons	2 ppm
Oxygen (O_2)	5 ppm
Helium (He)	300 ppm
Total Nitrogen (N_2) and Argon (Ar)	100 ppm
Carbon Dioxide (CO_2)	2 ppm
Carbon Monoxide (CO)	0.2 ppm
Total Sulfur Compounds	0.004 ppm
Formaldehyde (HCHO)	0.01 ppm
Formic Acid (HCOOH)	0.2 ppm
Ammonia (NH3)	0.1 ppm
Total Halogenated compounds	0.05 ppm
Total Non-Hydrogen Gases	300 ppm

Table 1—ISO FDIS 14687-2 standard

* Patent pending ** Patented

This report contains the results obtained by a third-party company, **Impact Scientific Instrument**, for the analysis of ultra trace sulfur components in hydrogen based on a **KA8000Plus** from **KA Solutions**. The **KA8000Plus** was configured based on the method published by **ASDevices** in the application note AN-09 [3]. The method used is specific to **ASDevices** and only possible with **ASDevices** components. The use of other components will not allow to achieve the same performance. The overall performance is not due to one single component, but to the combination of all of them.

The results obtained are exceeding the requirements of the ISO FDIS 14687-2 for fuel-grade hydrogen. LODs between 0.13 and 0.79 ppb were obtained for all sulfur components in hydrogen. If lower LODs are required, it is also possible to integrate **ASDevices** sample concentrator module based on the **µInProve Trap and Release** valve into the **KA8000Plus**. Low ppt LODs are achievable with that option.

REVIEW OF KA8000Plus DESIGN AND CONFIGURATION

µInProve chromatographic valve

The chromatographic valve is another very important part of this system. The PLSV technology (figure 1) offers many advantages over the other existing chromatographic valve technologies (see AN-10) [4][2][5]. For ultra trace sulfur analysis, it is necessary to treat the valve head with an inerting treatment. Due to its reduced surface sealing area and reduced sealing force, the treated valve has a long life time.

> "Due to its reduced surface sealing area and reduced sealing force, the treated valve has a long life time. "

Moreover, H_2 is a very small molecule that leaks easily between ports, causing cross port leaks. This carrier gas contamination from the sample due to a cross port leak is a known source of instrument failure. The **PLSV***, which is the only have technology to prevent cross-leaks, is another major advantage that makes this measurement possible. Without this valve it would not be possible.

SePdd** Sensor

For ultra trace sulfur analysis, it is necessary to have a very sensitive detector designed for process use. The **ASDevices SePdd** based on the **Epd**** technology (figure 2) offers many advantages compared to the traditional FPD, PFPD and SCD. The **SePdd** is a better option as it is solid-state, sensitive and only inert carrier gas is required for operation. No safety hazard caused by a flame or a heated furnace. It is also very compact with no maintenance required.

> "The SePdd is a better option as it is solid -state, sensitive and only inert carrier gas is required for operation."

The performance of the **SePdd** is achieved by its innovative patented design. The **Epd**** (Enhanced Plasma Discharge) is a gas detector technology based on a stabilised dielectric barrier discharge (DBD) plasma. The breakthrough is down to the focusing and stabilising compound electrodes[patent pending] which generates a more stable plasma discharge across a broad range of operating conditions. It uses the highly energetic plasma behaviours to perform measurements. Its versatility and sensitivity make it a technology of choice to measure molecules with high ionisation potential such as the permanent gases as well as molecules with lower ionisation potentials such as VOCs, Hydrocarbons and sulfurs from ppt to % range.

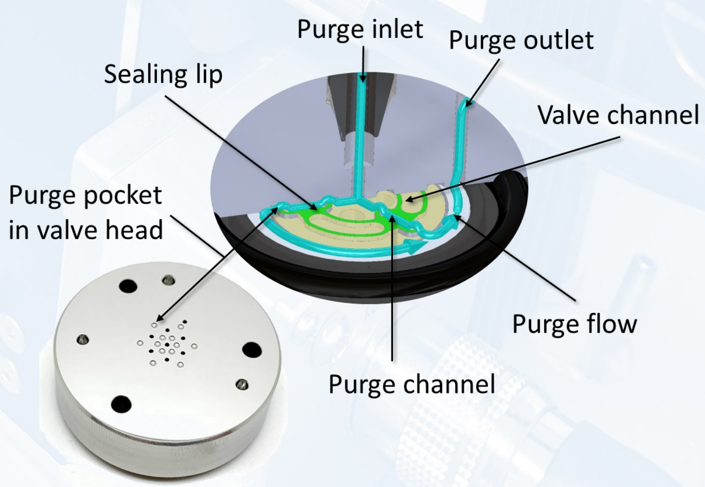

Figure 1—PLSV* Technology principle

* Patent pending
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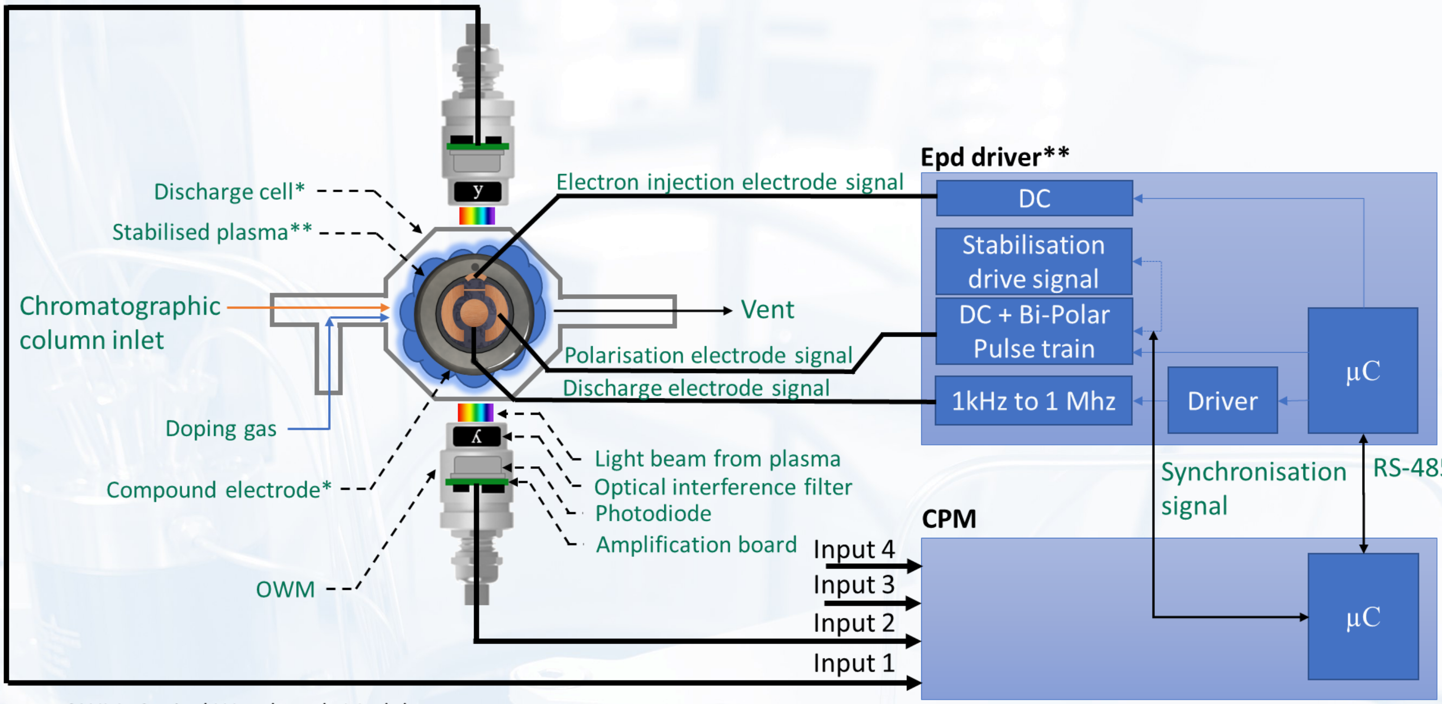

OWM: Optical Wavelength Module
CPM: Chromatographic Processing Module
Note: The plasma cell geometry is only for conceptual purpose and dimensions in this diagram are not representative of real design.

Figure 2—Epd** principle

iMOv* Chromatographic platform

The chromatographic platform also plays an important role in the overall performance. From a mechanical standpoint, the **iMOv** platform offers many advantages. Its unique modular oven design allows easy and robust integration of all the key analytical components.

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The **iMOv** also integrates a Low Thermal Mass (LTM) ramping oven module. This module has been selected for this application as it is very robust. The column used for the application is a micro-packed type column wrapped with a low thermal mass heater. This allows precise temperature control and fast cooling time which is important for repeatability and fast analysis.

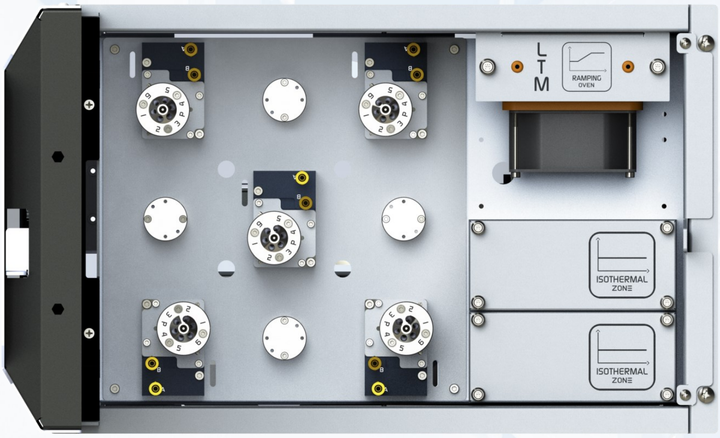

Figure 3—iMOv* Thermal zone configuration

* Patent pending
** Patented

CPM Signal processing

The unique **iMOv*** platform embedded GC Software and CPM platform integrate very advanced signal processing methods which are unique to **ASDevices**.

Spectral compensation*

The spectral compensation (see TN-05) [6] function was used in this method to supress interferences caused by sample matrix. To achieve this, two optical wavelength modules (OWM) are used on the **SePdd**** sensor. The signals from the OWM are connected to a DSP block. DSP blocks are signal processing algorithms that are used inside the CPM embedded firmware to process signals. The output of the spectral compensation DSP block is used as the chromatographic signal

Enhanced LOD and Peak Remodeling

The **iMOv** embedded GC software also offers two unique proprietary advanced signal processing algorithms. The Enhanced LOD (ELOD) and Peak remodeling (Figure 4). The ELOD algorithm analyses and learn the detector baseline noise and peak shape overtime based on a number of consecutive chromatograms defined in the software. The learning process allows to better understand the power distribution of the signal and differentiate between noise and a meaningful signal from an impurity. This advanced principle based on artificial intelligence allows to recover the peak shape in a noisy signal. SNR improvement between 3 to 10 times can be achieved. The final processing step is the peak remodeling which, based on raw peak shape, remodeled the peak into a gaussian shape for while keeping the area constant. This improves peak integration. The overall result is an improved LOD[7].

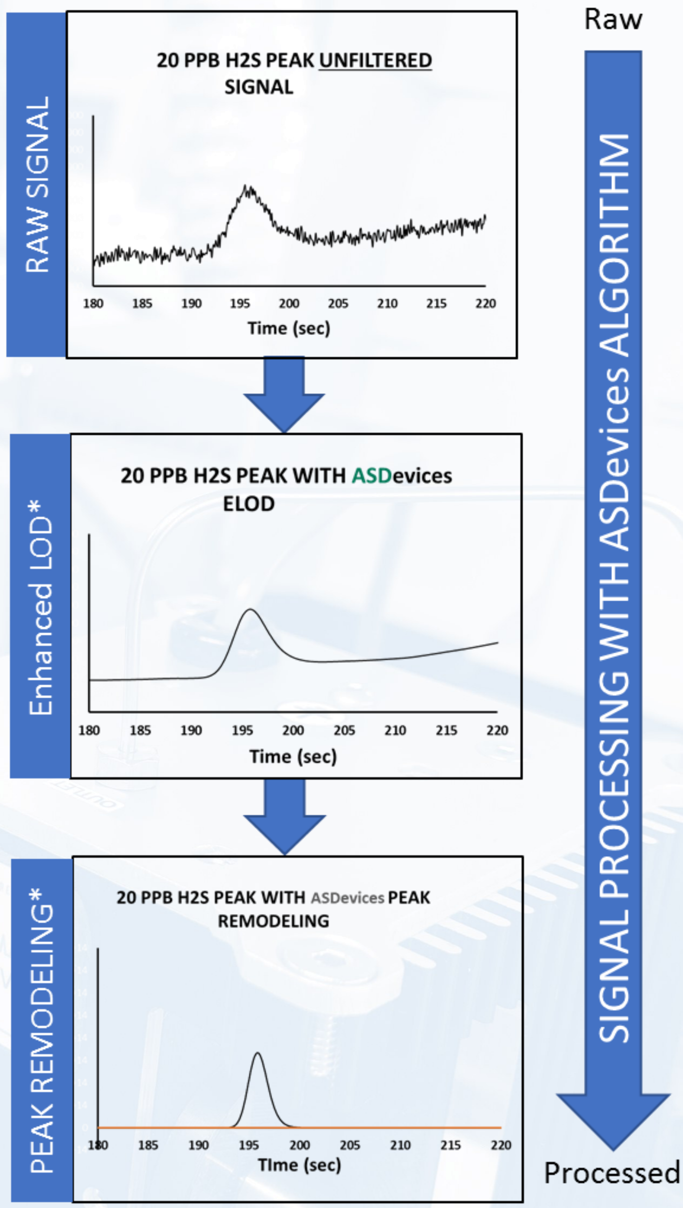

Figure 4—**ASDevices** peak processing step by step

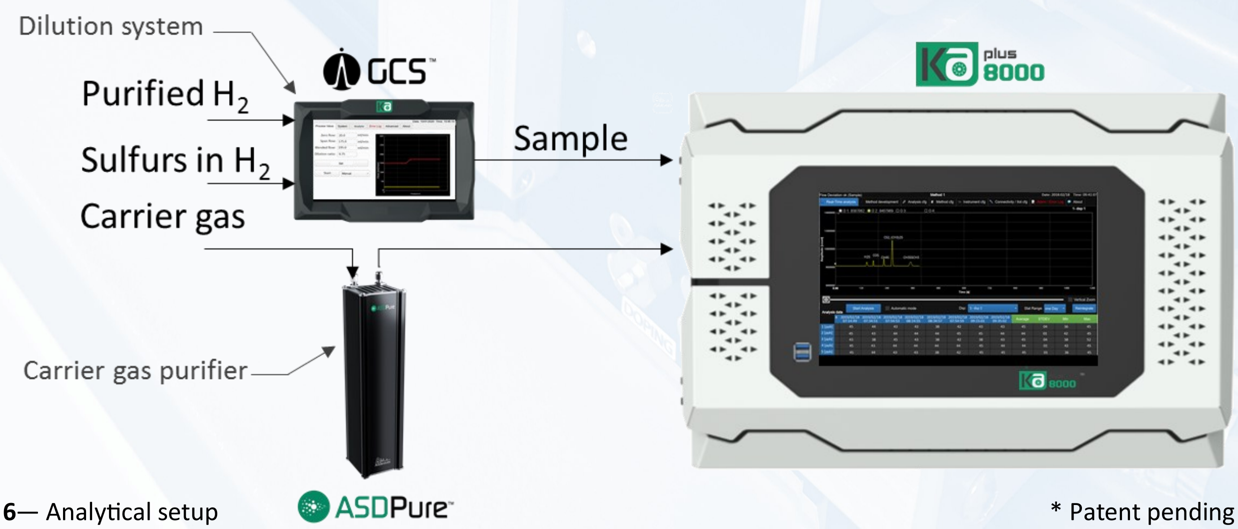

Figure 6— Analytical setup

* Patent pending ** Patented

Flow path design

It is very important that the entire flow path is inert and without any dead volume. To achieve this requirement, specially treated tubes and fittings from **ASDevices** were used to preserve the sample integrity during the analysis and make an accurate measurement. **ASDevices LipLOK*** fittings were used for carrier and sample gas inlet.

Figure 7—Purged EPC

The flow path does also contains active components such as the Electronics Pressure Controller (EPC). For this measurement, two models of Electronics Flow Controller (EPC) were used. For the carrier gas control, a **ASDevices** purged inline electronics pressure flow controller was used. The benefits of this flow controller is its leak integrity and low dead volume. It is well known that ambient air leaks can impact the baseline noise. With its purged design, it is impossible for ambient air to leak into the carrier gas through the EPC. Without its purged design, it would not have been possible to use an inline type EPC. The advantage of the inline control mode over the bypass mode is the reduced carrier gas consumption as no carrier gas is wasted in the bypass vent. This is especially important when helium carrier gas is used.

For the sample flow control, a bypass flow controller is used. On the sample side, it makes sense to use bypass control. The bypass makes sure there is a high flow into the sample line and no mechanical parts can be in contact with the sample gas. Mechanical components can contaminate or alter the sample gas composition.

GC METHOD

To achieve the required performance, it is not only the hardware components used that are important, but also the chromatographic method. For process use, simplicity is very important. Minimising the number of components that can fail is of outmost importance. The chromatographic method used for the application is very simple and only possible using **ASDevices** high quality and unique components. It has been possible to use a simple injection method with only one chromatographic valve, one column and one detector. There is no need for a sample concentrator (thermal desorber) to concentrate the sample and achieve the required sensitivity.

To achieve the sensitivity without sample concentrator, the sample loop has been pressurised to 30 PSIG. This pressure is enough to achieve LODs of less than 1 ppb for all components. Without the use of the **PLSV*** technology, it would not have been possible to pressurise the sample. Other valve technologies would have hydrogen cross port leak at such pressure. The pressurisation of the loop has been done to increase the sample volume (number of molecule) contained in a smallest possible loop in order to have high sensitivity and sharp peaks.

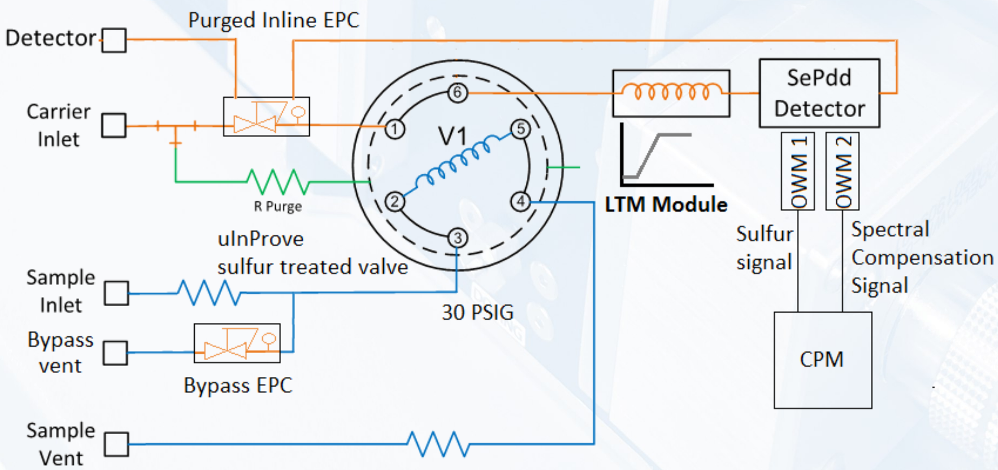

Figure 8—Chromatographic method

RESULTS

The results obtained with the KA8000Plus configured for ultra-trace sulfur analysis are presented in this section. For optimum performance, the carrier gas was purified using a **ASDevices ASDPure** gas purifier. The sample concentration were generated using a **ASDevices iSCS** gas dilution system with internal treated wetted parts for sulfur analysis. The tests were performed by a third-party company, **Impact Scientific Instrument**. The tests were focusing on the validation of the repeatability and limit of detection. Other data such as linearity and cross interference are contained in AN-09 [3].

	Results (ppb)				
Analysis #	**H2S**	**COS**	**CH4S**	**C2H6S**	**C2H6S2**
1	19.5	19.8	21.3	20.1	20.2
2	19.8	19.8	21.4	20.1	20.2
3	19.8	20.1	21.4	20.1	20.6
4	19.5	20.2	21.3	20.1	20.4
5	19.9	20.3	21.4	20.1	20.2
6	19.7	20.3	21.4	20.1	19.7
7	19.8	20.4	21.4	20.1	19.8
8	19.7	20.4	21.4	20.2	20.0
9	19.7	20.5	21.4	20.2	20.2
10	19.5	20.6	21.3	20.2	20.4
11	19.7	20.5	21.3	20.1	20.1
12	19.6	20.3	21.3	20.1	20.1
13	19.4	20.3	21.1	20.1	20.5
14	19.4	20.4	21.0	20.2	21.0
15	19.3	20.5	21.0	20.2	21.1
16	19.6	20.5	21.1	20.1	20.6
17	19.7	20.5	21.1	20.2	20.7
18	19.9	20.6	21.2	20.1	20.3
19	19.7	20.6	21.4	20.1	20.4
20	19.8	20.8	21.4	20.2	21.0
21	20.0	21.0	21.4	20.1	20.9
22	20.1	21.1	21.7	20.1	20.9
23	19.9	21.2	21.5	20.1	20.5
24	19.8	21.4	21.4	20.1	20.5
25	19.6	21.3	21.3	20.0	20.2
26	19.7	21.4	21.2	20.0	20.5
27	19.5	21.3	21.1	20.0	20.5
28	19.5	21.3	21.0	20.0	20.3
29	19.7	21.1	20.9	20.0	20.1
30	19.3	21.1	20.8	20.0	19.8
Average (ppb)	**19.67**	**20.65**	**21.26**	**20.11**	**20.39**
σ (ppb)	**0.18**	**0.46**	**0.20**	**0.06**	**0.35**
LOD (ppb)	**0.43**	**0.79**	**0.13**	**0.15**	**0.77**
Repeatability (%)	**0.9%**	**2.2%**	**0.9%**	**0.3%**	**1.7%**

Table 2—Repeatability at 20 ppb and LOD

	Results (ppb)				
Analysis #	**H2S**	**COS**	**CH4S**	**C2H6S**	**C2H6S2**
1	103.2	106.8	102.9	99.0	111.8
2	103.3	108.1	103.1	99.1	112.4
3	103.4	109.2	103.1	98.8	111.0
4	102.8	108.2	102.5	98.6	112.1
5	102.8	109.4	102.3	98.9	111.7
6	102.8	107.7	102.0	99.3	113.6
7	102.7	106.1	101.7	99.2	113.5
8	102.8	106.7	101.9	99.0	112.4
9	102.8	105.8	101.7	99.0	113.6
10	102.2	106.1	101.6	98.7	113.0
Average (ppb)	**102.88**	**107.40**	**102.29**	**98.96**	**112.52**
σ (ppb)	**0.36**	**1.29**	**0.60**	**0.22**	**0.89**
Repeatability (%)	**0.3%**	**1.2%**	**0.6%**	**0.2%**	**0.8%**

Table 3—Repeatability at 100 ppb

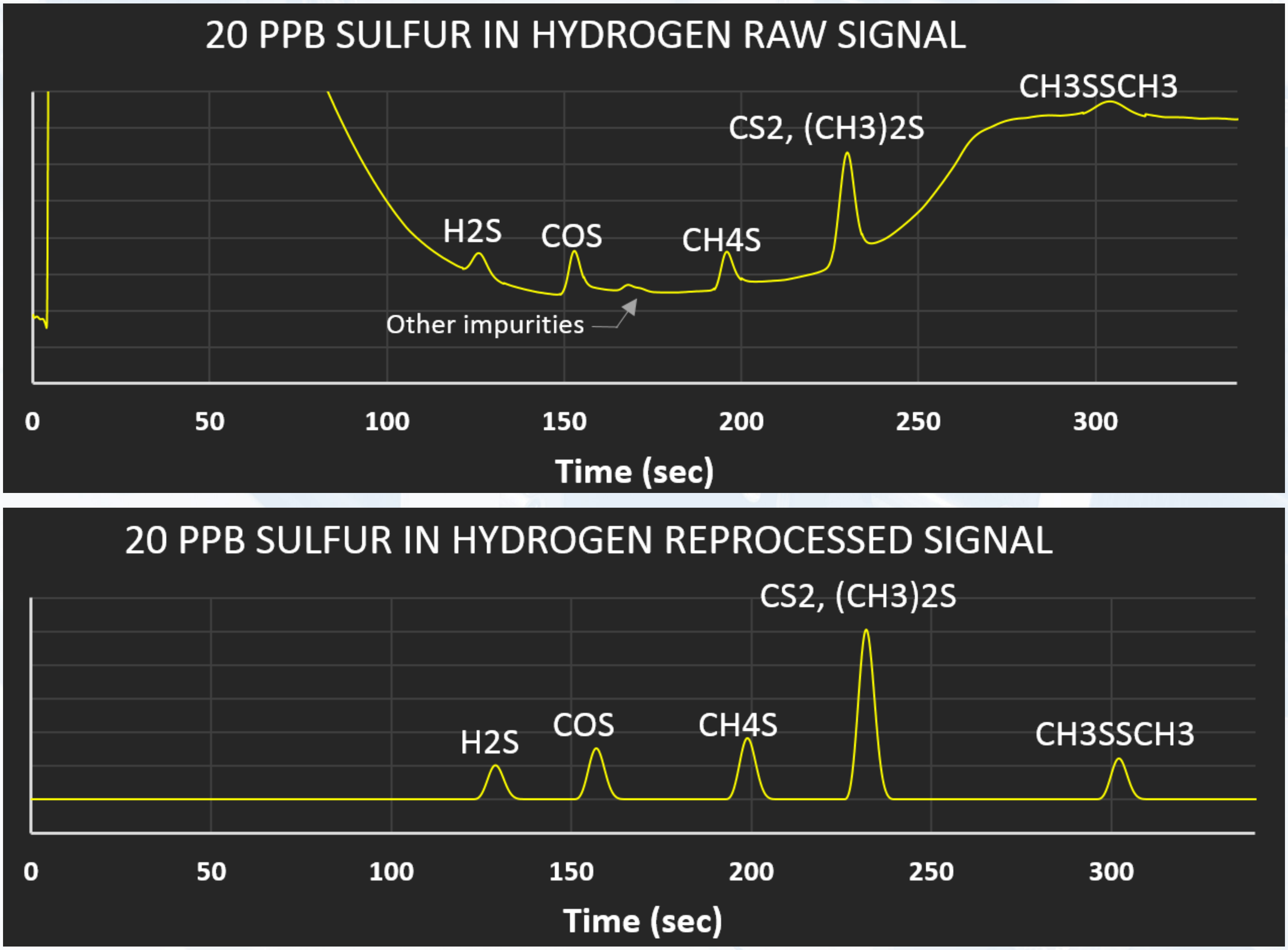

Figure 9—Sulfurs in H_2 chromatogram at 20 ppb

CONCLUSION

In conclusion, the tests performed by **Impact Scientific Instrument** shows that the **KA8000Plus** is suitable for ultra-trace sulfur analysis in fuel-grade hydrogen. It allows to achieve LODs below 1 ppb. LODs between 0.13 and 0.79 ppb were obtained for all sulfur components in hydrogen. The **SePdd** sensor based on **ASDevices** patented **Epd**** technology is simple to use and robust compared to alternative such as SCD and PFPD. The **µInProve** valve design for sulfur analysis based on the **PLSV*** technology in combination with the **iMOv*** GC platform makes it a very robust instrument for process and field use.

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PHOTO GALLERY