

AN-09

Trace-Level measurement of Sulfur-Based Compounds in Hydrogen with the Epd Technology



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ABSTRACT

A sample containing sulfur-based compounds in hydrogen was analysed using gas chromatography coupled with the Enhanced plasma discharge (Epd) technology. The results show that all the sulfur-based compounds could be detected, with a LOD down to 1ppb. The sensitivity of the method was further increased with pre-concentration of the sample using the μ nProve valve and the unique peak remodeling algorithm developed by ASDevices ^{Patent pending}. Linearity of the response as a function of concentration was also confirmed for all the compounds. To show the versatility of the Epd technology, a mix of sulfur-based compounds and light hydrocarbons was also analysed using a single chromatographic and optical channel. The results obtained show that the Epd technology is a revolutionary alternative to sulfur chemiluminescence detectors (SCD) and flame photometric detectors (FPD) for the measurement of sulfur-based impurities in fuel-grade hydrogen.

INTRODUCTION

Table 1 – Maximum allowable limits of contaminants in fuel-grade hydrogen from ISO FDIS 14687-2

Water (H ₂ O)	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 (NH ₃)	0.1 ppm
Total Halogenated compounds	0.05 ppm
Total Non-Hydrogen Gases	300 ppm

Hydrogen fuel cells are among the most promising devices for powering vehicles and are expected to soon become a major technology that will help us reduce greenhouse gas emission. In such device, a current is generated from a redox reaction between hydrogen and oxygen or another oxidizing agent. Many different designs have been developed over the past decades, but they all contain a cathode, an

anode and an electrolyte (often a proton-exchange polymer membrane) that separate the two sides of the cell [1]. In 2016, the United States Department of Energy identified key contaminants in hydrogen that can affect these components and significantly reduce the efficiency and durability of the fuel cells: carbon monoxide (CO), ammonia (NH₃), methane (CH₄), inert gases (N₂, noble gases, etc.) and sulfur (S) species [2]. Although the Epd technology can be used to detect all these contaminants, the present document will mostly focus on the detection of sulfur-based compounds [3].

The measurement of ultra-trace level sulfur-based compounds in hydrogen is of outmost importance, as very low amounts of these molecules can be irreversibly adsorbed on the surface of the electrodes and cause permanent degradation of the fuel cells performances [2]. These compounds include hydrogen sulfide (H₂S), carbon disulfide (CS₂) and mercaptans (R-SH, R-S-R). As presented in Table 1, the current ISO standard for hydrogen fuel quality (ISO FDIS 14687-2) limits the total sulfur compounds concentration to 4 ppb. However, even with such a low concentration, the sulfur compounds still affect the performances of fuel cells. Therefore, it was recommended to reduce the maximum limit of

total sulfur to 2 ppb [2]. Indeed, measuring such low concentrations requires highly sensitive instrumentation and passivated components.

In 2011, the National Physical Laboratory (United Kingdom) developed a method for measuring total sulfur compounds in hydrogen using gas chromatography (GC) coupled with a sulfur chemiluminescence detector (SCD), leading to a detection limit (LOD) of 1 ppb [4]. Despite being highly sensitive, SCDs suffer from many drawbacks. Before being measured, every sulfur-based compound must first be converted into sulfur monoxide (SO) by combustion in a reaction furnace or a reducing hydrogen/air flame. Light emission is then measured from the reaction between SO and ozone (O₃) in a separated chemiluminescence chamber [5]. Since this chemiluminescence mechanism is highly sensitive to the presence of water (which is generated during the conversion of sulfur-based compounds into SO), multiple moisture traps must always be used in such system. The ozone excess must also be trapped, as it is highly toxic. Therefore, SCDs are bulky, complex, require multiple high-purity gases to operate and can easily cost more than 40 000\$ (without the GC section and pre-concentration system). Furthermore, for SCDs using a hydrogen/air flame, the response strongly depends on the conditions and position of a ceramic probe used to sample post-flame gases. This ceramic probe must often be cleaned and conditioned to remove impurities and the results are often unsatisfactory, preventing this type of detector to be used in process instruments, as it can only be operated by skilled analysts [6].

The flame photometric detector (FPD) is a simpler and more affordable alternative to the SCD. This detector is similar to the flame ionization detector (FID), but measures light emission from the sulfur-based molecules in the flame with a photomultiplier tube equipped with an optical filter centered at

394 nm. Since the FPD measures light emission from S₂ radicals that are formed in the flame, the detector output is theoretically proportional to the square of the sulfur mass flow rate [7]. The FPD is also much less sensitive than SCD, with a LOD in the order of 50 ppb for most compounds. It also requires high purity hydrogen and air to fuel the detector. Better LOD can be achieved with a pulsed FPD (PFPD), but this detector is much more complicated to operate, as it requires two different combustible gas flows and a gated amplifier to record specific components of each pulse.



Figure 1 – The ASDevices SePdd™

Detectors based on the Enhanced plasma discharge (Epd) technology from Analytical Sensing Devices can be used for the measurement of sulfur-based compounds, as well as many other contaminants, with multiple advantages compared to other technologies. The following document intends to present how the Epd technology can be used for ultra-trace level measurement of sulfur-based compounds in fuel-grade hydrogen.

EXPERIMENTAL INFORMATION

Enhanced Plasma Discharge (Epd)

All the measurements were done with the SePdd™ from Analytical Sensing Devices (See Figure 1). It is a fully scalable development kit for OEM and system integrators based on our Epd technology. Due to its high sensitivity, versatility, ease of use and low maintenance cost, Epd is an interesting alternative to DID, PDID, HID, FID, FPD, SCD and TCD on most GC systems.

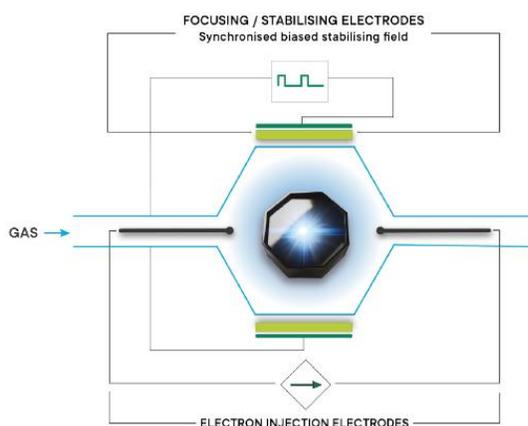


Figure 2- Schematic representation of the SePdd™ stabilising and electron-injection electrodes

With its highly energetic stabilised and focused plasma discharge, most molecules can be ionised and consequently measurable. It can be operated with argon, helium, nitrogen, oxygen, hydrogen and CO₂ carrier gas. Since the carrier gas used for the chromatography is also the plasma discharge gas, there is no need for additional UHP gases to operate the detector. Multiple measurement modes are available (emission, tracer, power balance), allowing detection and quantification of various analytes from the ppb to the percent range. The sensitivity of the Epd is further increased thanks to the presence of electron injection and stabilising electrodes, which

significantly decrease the background noise (See Figure 2) ^{Patent Pending}. The digital signal processing (DSP) platform is equipped with 4 (8 optional) independent and simultaneous measurement channels, allowing measurements of 4 or 8 different optical wavelengths. With our plug and play philosophy in mind, the platform can be easily integrated to any GC platform. The platform is also equipped with Ethernet communication ports and is Industrial Internet of Things (IIoT) Ready. More information concerning the Epd technology is available in the document *Introduction to the Enhanced Plasma Discharge Detector* [3].

Experimental Parameters

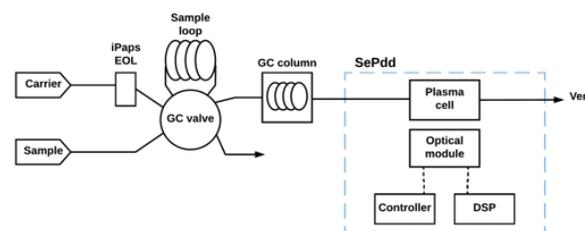


Figure 3 - Configuration of the GC system

Here, the SePdd™ was configured in tracer mode using water as a dopant. A selective narrow optical filter (± 3 nm) was also added to the optical module. The selected wavelength corresponds to a reaction product that is formed when the sulfur-based compounds react with OH radicals from water in the plasma chamber. A configuration with a GC valve, a GC column, and the Epd detector was used, as presented in Figure 3. This setup was incorporated in the iMOV GC platform developed by ASDevices. Thanks to the unique stabilisation electrodes used in the Epd technology, the plasma is not extinguished by the hydrogen matrix, allowing measurement of

the sulfur-based compounds without heartcut valve or hydrogen trap. Therefore, this results in a cost-efficient and simple chromatographic setup.

The samples were certified mixtures of H₂S, methylmercaptan, dimethyl sulfide, CS₂ and dimethyl disulfide in argon or in helium from Linde. The sulfur-based compounds were diluted in 5.0N hydrogen or a light hydrocarbon mix prior to the analysis. A μ InProve chromatographic valve for sulfur equipped with a 490 μ L *sulfinert*-treated sample loop was used for sample injection. Argon (5.0N) or helium (5.0N) was used as the carrier gas, with a flow rate of 10 mL/min. The carrier gas was further purified with the ASDevices iPaps^{EO} series purifier, based on a double heated vessel design which provides carrier gas with less than 1 ppb total impurity. In addition, all of our purifiers use ASDevices LipLOKTM fittings to guarantee the leak integrity and

compatibility with existing instrumentation fittings in the field. Purified carrier gas was also flowing through a permeation tube containing a water-based solution with additives, with a flow rate of 5 mL/min for doping the plasma. All the components in contact with the sulfur-based compounds were treated with *sulfinert*, as these compounds tend to stick to stainless steel. A 1m x 1mm RT-XLSulfur micropacked GC column from Restek was ramped from 30°C to 230°C at a rate of 15°C/min during the experiment to separate the sulfur-based compounds from the hydrogen matrix. The column was regenerated and flushed with high-purity argon for at least 24h before the analysis.

RESULTS AND DISCUSSION

Sulfur-based compounds in hydrogen with helium carrier

The sulfur-based compounds were measured using the tracer mode, by monitoring an emission line from a reaction product that is formed when the analytes react with OH radicals from the water used as a dopant in the plasma chamber. Since all the sulfur-based compounds in the mixture react with the OH radicals, this mode can be used for the detection of these molecules. The mixture was first analysed using helium as the carrier gas. Figure 4 presents the chromatogram acquired with the method described in the previous section. It is also to be noted that all chromatograms are provided in raw format as well as in “peak remodeled” format. The “peak remodeled” format is the resulting chromatogram following the post-processing of our proprietary peak remodeling algorithm^{Patent pending}. The peak remodeling algorithm enhance the signal to noise

ratio and consequently improve results by doing advanced signal processing in the time and frequency domain and the use of pattern recognition. The results show that the SePdd is highly sensitive to all the sulfur-based compounds in the mixture. All the compounds are also well separated from the hydrogen matrix with the Rt-XLSulfur column, with CS₂ and dimethyl sulfide co-eluting. The LOD was calculated for each compound as 3 times the signal to noise ratio. For the raw data, a LOD of 5 ppb was calculated for H₂S and for methylmercaptan, 3 ppb for dimethyl disulfide and 4 ppb for CS₂ + dimethyl sulfide. With peak remodeling, the LOD can be decreased by 3 times. Considering that a small sample loop of 490 μ L was used, a much better LOD would also be expected with a bigger one. Furthermore, the sample can be pre-concentrated, either with a commercially available pre-concentrator, or by pressurising the sample loop.

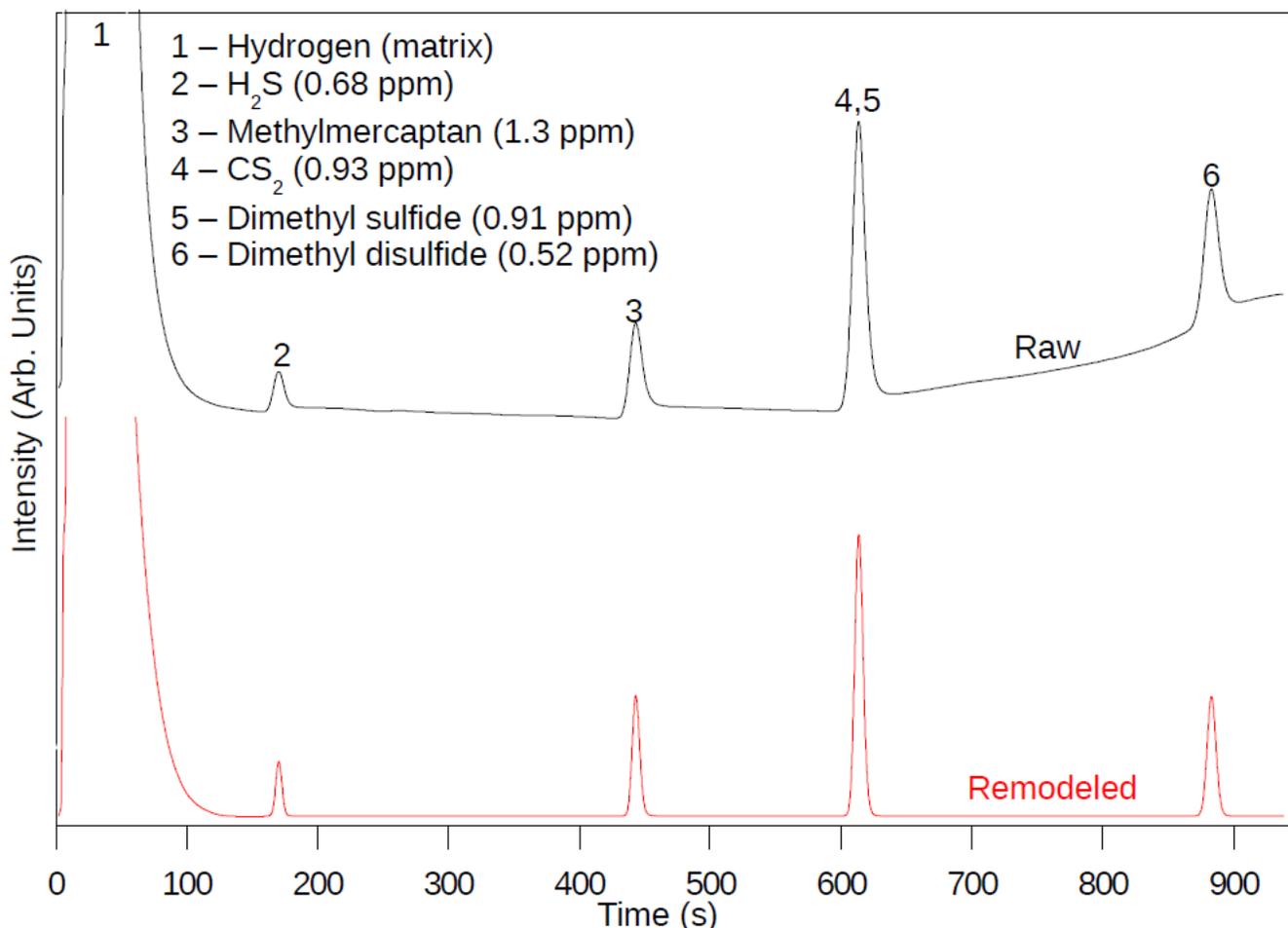


Figure 4 – Chromatogram for a mix of sulfur-based compounds in hydrogen with helium carrier. Raw format (black line) peak remodeled format (red line) are presented.

Sample pre-concentration with the μ InProve

It is well known that increasing the pressure of the sample is a simple strategy to increase the number of molecules injected. However, due to the poor leak integrity of traditional GC valves, this strategy is usually not used. This is especially true for molecules like hydrogen and helium, as they tend to leak due to their small size. Indeed, cross-port leaks, which occurs on most types of valves at high pressure

would have a negative impact on the chromatography.

Here, a μ InProve valve for sulfur was used, as it offers the best leak integrity, even after 1 000 000 actuations. Its design contains no dead volume and thanks to its unique purging grooves, cross-port contamination is virtually impossible [8]. This is the only GC valve on the market that possesses all the required characteristics for pre-concentration in the sample loop without negatively affecting the chromatography.

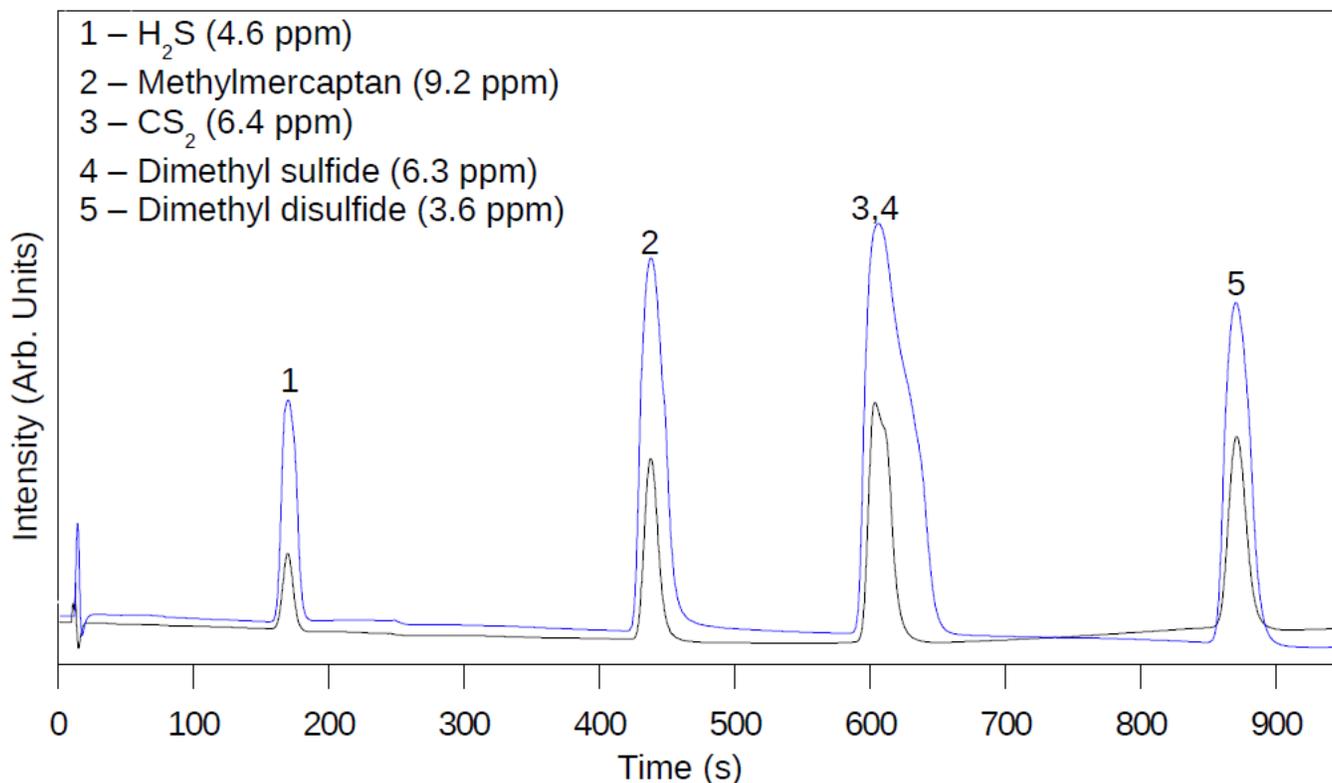


Figure 5 – Chromatogram for a mix of sulfur-based compounds in helium with the sample loop at ambient pressure (black line) and 60 psi (blue line).

The ideal gas law is often used to approximate the behaviour of most gases under different conditions :

$$PV = nRT$$

Where P is the pressure, V is the volume, n is the number of molecules, R is the ideal gas constant and T is the temperature. From this equation, considering a sample loop of a given volume and constant temperature, the number of molecules can be increased by increasing its pressure. Since processes involving high-purity hydrogen often take place under high pressure, the the sample loop should be easily pressurised with the addition of a restrictor, if the valve used is leak-tight.

The sample containing sulfur-based compounds in helium was analysed with the method previously described, with different sample loop pressures. The raw chromatograms presented in Figure 5 were

acquired with the sample loop at ambient pressure and with the sample loop pressurised at 60 psi. The results show that the signal to noise ratio can be increased up to 3 times simply by pressurising the sample loop, with no significant effect on the chromatographic separation. For the raw signal at 60 psi, a LOD of 2 ppb was measured for H_2S and methylmercaptan, 3 ppb for CS_2 + dimethyl sulfide and 1 ppb for dimethyl disulfide.

Furthermore, there are multiple materials available on the market for sulfur pre-concentration. Such material can be used to pre-concentrate the sample up to 200 times, leading to LOD below 0.1 ppb. Therefore, with the use of an adequate pre-concentration technique, the Epd technology is sensitive enough for the measurement of ultra-trace level sulfur-based compounds in fuel-grade hydrogen.

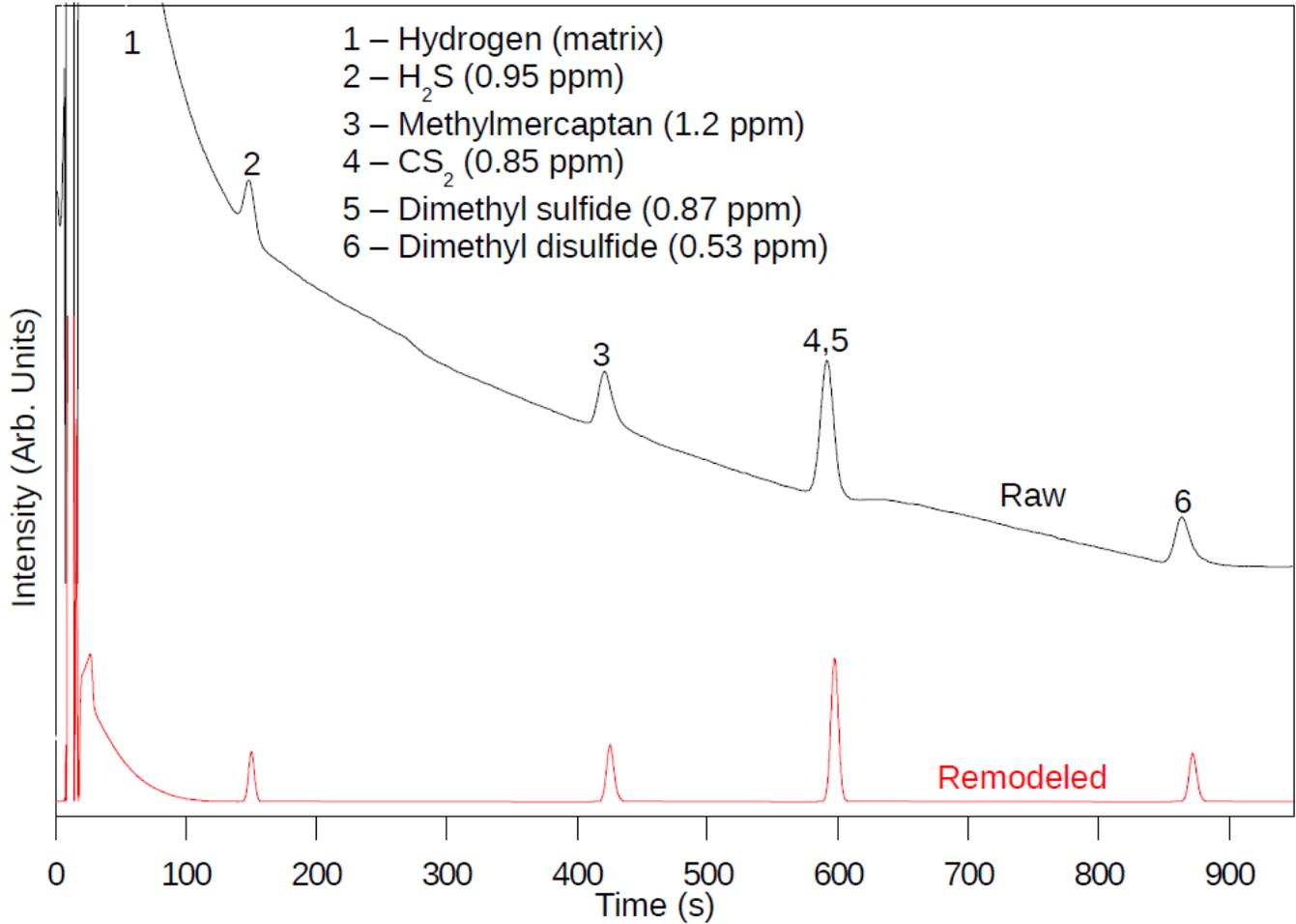


Figure 6 – Chromatogram for a mix of sulfur-based compounds in hydrogen with argon carrier. Raw format (black line) peak remodeled format (red line) are presented.

Sulfur-based compounds in hydrogen with argon carrier

Argon can also be used as the carrier gas for the Epd. When it is possible, the use of argon should be considered, as it is much less expensive than helium. With argon, the tracer mode was also used for the measurement of sulfur-based compounds. The chromatogram acquired for the mix of sulfur-based compounds in hydrogen using argon as the carrier gas is presented in Figure 6.

The results show that the hydrogen matrix takes more time to elute with argon as the carrier compared to helium, due to the different velocity through the column. Despite this, the intense peaks from the sulfur-based compounds can still be used for quantification. Furthermore, with the use of the peak remodeling algorithm, the resulting baseline is much more flat. A LOD of 35 ppb was calculated for H₂S, 42 ppb for methylmercaptan, 29 ppb for CS₂ + dimethyl sulfide and 20 ppb for dimethyl disulfide. Despite being less sensitive than with helium as the carrier, such LOD is satisfactory for

many applications. Furthermore, with pre-concentration of the sample, fuel-grade hydrogen could be analysed with argon as the carrier.

Signal linearity

For precise quantification, it is important to know the relation between the analyte concentration and the signal. Indeed, in the case of FPD, the response is proportional to the square of the sulfur mass flow rate, as it measures the emission of S₂ radicals, which requires the reaction between two molecules of analytes. Here, in the case of the tracer mode of the Epd, we measure the direct interaction between the sulfur-based compounds and OH radicals from water doping. By-products are formed proportionally to the sulfur-based compounds concentration, which can be monitored at a specific wavelength. To show the linearity of this measurement mode, the sample was diluted in various volumes of hydrogen to reach concentrations of sulfur species between 1 ppm and 15 ppm and was measured with the method described previously. The signal intensity as a function of methylmercaptan concentration with argon as the carrier is presented in Figure 7. The results show a linear response with an excellent R² of 0.9999. A linear response was also measured for all the other compounds in the sample using both argon and helium as the carrier gas.

Measurement of other impurities

Light hydrocarbons (C1-C4) are common impurities often found in hydrogen along with the sulfur-based compounds. To show the versatility of the Epd technology, a mix containing sulfur-based compounds and light hydrocarbons in argon was injected and analysed using the method previously described, but with a temperature ramp from 60°C to 230°C and a sample loop of 250 µL. The chromatogram acquired is presented in Figure 8. This result was obtained with a single optical and

chromatographic channel, as the light hydrocarbons also react with the OH radicals. Since the Rt-XLSulfur column from Restek was specifically designed to separate the sulfur-based compounds from hydrocarbons, there is no interference from these compounds, allowing their accurate quantification [9]. The permanent gases from air (O₂, N₂, CO, CO₂) will also eluate before the H₂S peak.

Results obtained in previous studies have shown that the Epd technology can be used for precise measurement of light hydrocarbons, with a LOD of 5 ppb using argon as the carrier gas and 1 ppb with helium, without the use of a pre-concentrator [10]. In these conditions, methane could not be measured in hydrogen, as it would co-elute with the matrix, but using a heartcut method with a molecular sieve 5A, such analysis would be easy. Other common contaminants such as the permanent gases, NH₃, noble gases, etc. can also be measured with different wavelengths using the Epd technology [3].

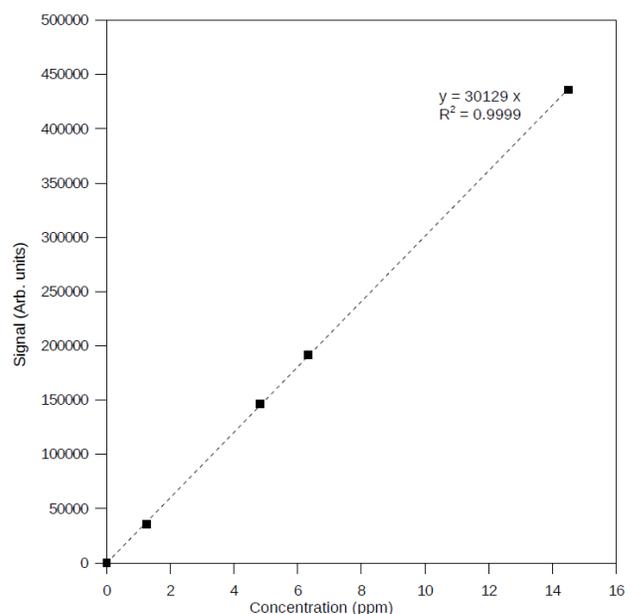


Figure 7 – Signal as a function of methylmercaptan concentration using argon as the carrier.

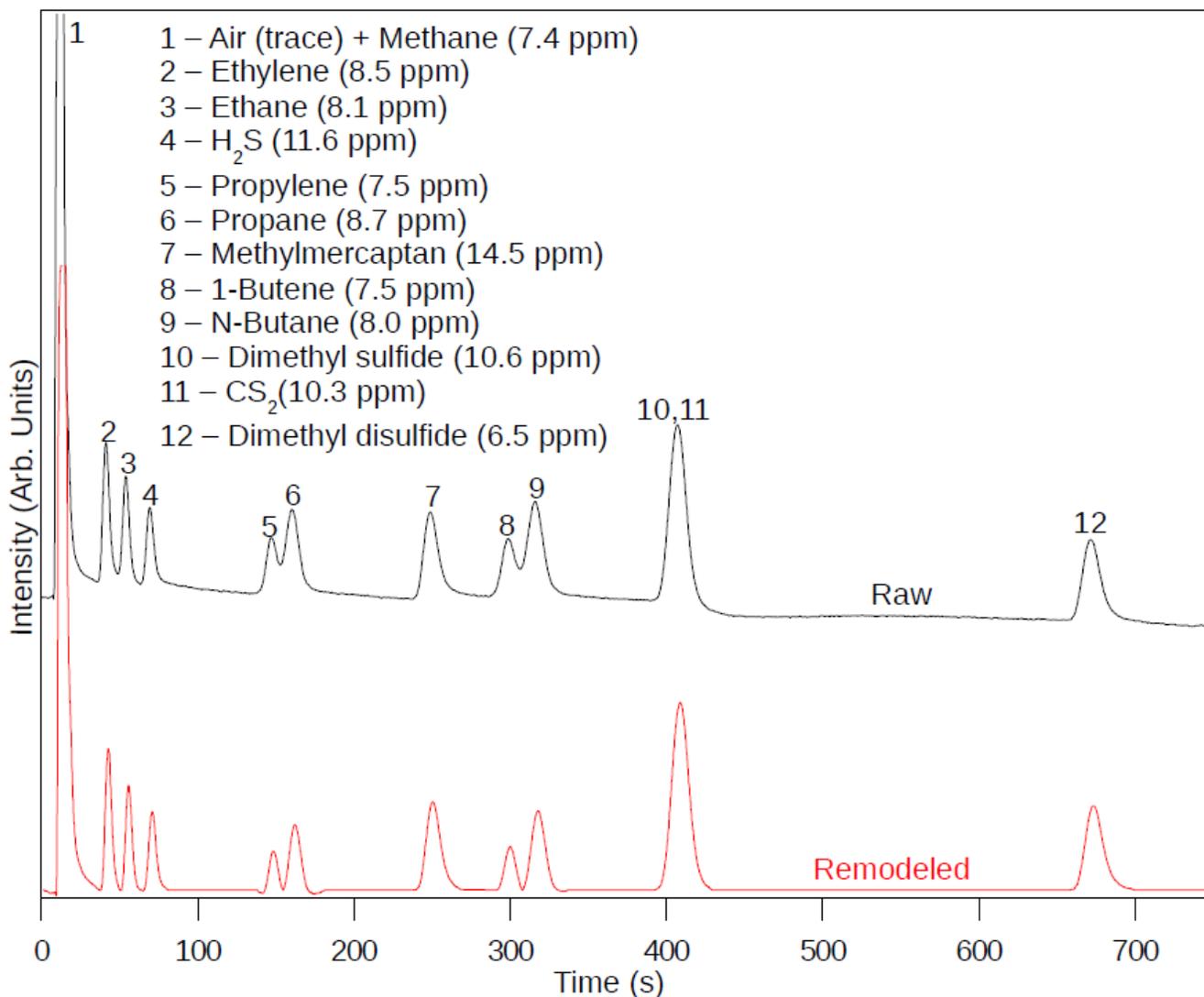


Figure 8 – Chromatogram obtained for a mix of light-hydrocarbons and sulfur-based compounds with a 1m x 1mm Rt-XLSulfur column. Raw format (black line) peak remodeled format (red line) are presented.

CONCLUSIONS

In conclusion, the Epd is a very versatile and sensitive technology that can be used for the measurement of trace-level sulfur species, as well as many other contaminants such as light hydrocarbons and

permanent gases. Thanks to the stabilisation and electron-injection electrodes of the Epd detector, the measurement of impurities in hydrogen can be done without heartcut or hydrogen trap, as the

plasma is not extinguished by the matrix. A sample containing H₂S, methylmercaptan, dimethyl sulfide, CS₂ and dimethyl disulfide dispersed in hydrogen was analysed by GC combined with Epd. Using helium as the carrier gas, a LOD between 1 and 3 ppb was calculated for all these compounds. Using argon as the carrier also resulted in highly sensitive detection of sulfur species. The signal to noise ratio can be further increased with our unique peak processing algorithm. Thanks to the excellent leak integrity of the μ InProve valve, the sample loop can be

pressurised, further increasing the signal to noise ratio up to 3 times. The linearity of the response as a function of the sulfur-based compounds concentration was also demonstrated. In combination with an adequate pre-concentration system and GC, the Epd technology can therefore be used for the analysis of fuel-grade hydrogen that respects the ISO FDIS 14687-2 standard.

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