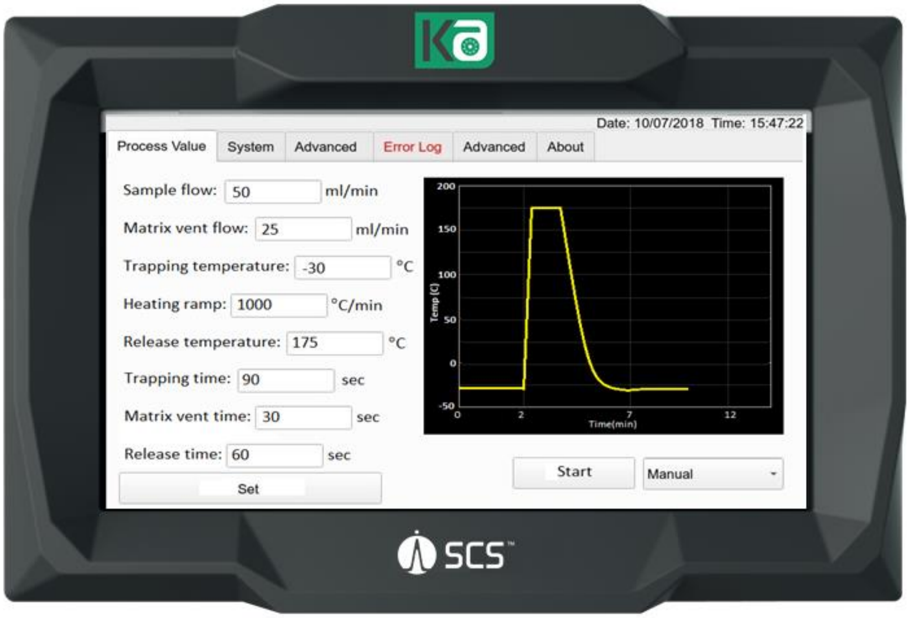
Analytical Sensing Devices

AN-11

New Method Using Argon as an Alternative to Helium for Sub-ppb Level Measurement of Permanent Gases With the T&R PLSV and the Epd Technology



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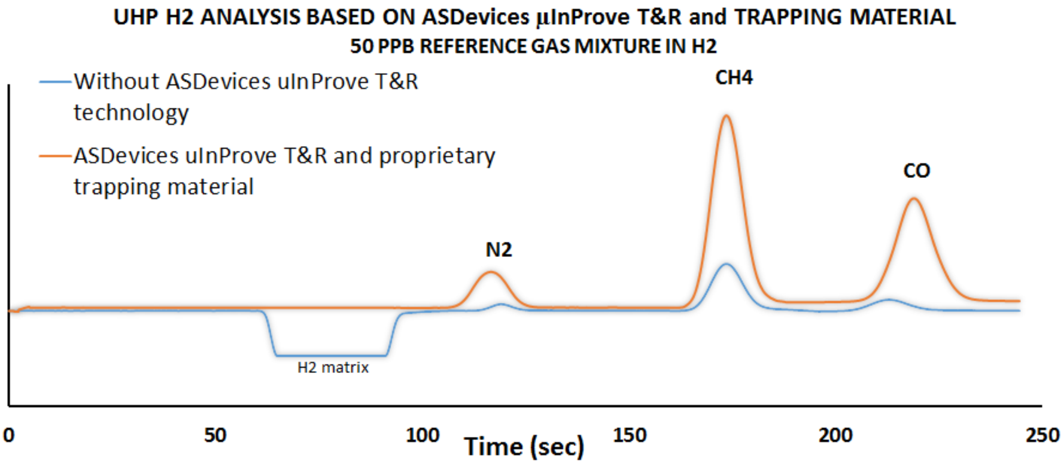
Sample flow: 50 ml/min
Matrix vent flow: 25 ml/min
Trapping temperature: -30 °C
Heating ramp: 1000 °C/min
Release temperature: 175 °C
Trapping time: 90 sec
Matrix vent time: 30 sec
Release time: 60 sec

μInProve™
Trap and Release


UHP H2 ANALYSIS BASED ON ASDevices μInProve T&R and TRAPPING MATERIAL
50 PPB REFERENCE GAS MIXTURE IN H2

January **2020**

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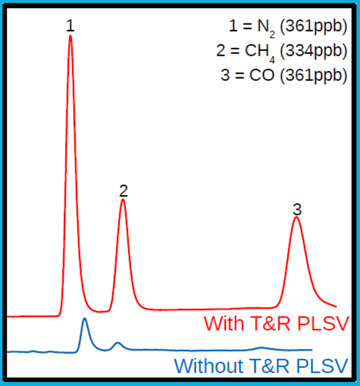
ABSTRACT

This application note will present a new measurement method using the ASDevices' pre-concentration system based on the Trap & Release Purge Lip Sealing Valve. Such method can be used to simplify the chromatography and improve the limit of detection for permanent gases in various matrix. Thanks to our unique proprietary nanostructured trapping materials and the valve matrix venting feature, most of the matrix can be easily eliminated without using a heartcut or backflush, allowing improved reliability, significant analysis time and hardware cost savings. Using argon as the carrier and discharge gas, limits of detection below 1 ppb were reached. The use of helium can now be limited to highly specific applications that call for limit of detection in the low-ppt range.



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* = Patent Pending ** = Patented

INTRODUCTION

Constant monitoring of the ultra-high purity (UHP) gases used in the fabrication of semiconductors and other electronic materials is of utmost importance, as even low ppb-level of impurities can cause irreversible damages to the materials [1]. Permanent gases (H_2, O_2, N_2, CH_4, CO and CO_2) are among the most common impurities found in UHP gases, as they are the most abundant molecules in air and common reaction by-products, but they can be difficult to measure due to their high ionization or excitation energy.

Over the past decades, highly sensitive detectors relying on helium, such as the Discharge Ionization Detector (DID), the Pulsed DID (PDID), the Helium Ionization Detector (HID) and the Plasma Emission Detector (PED) have been developed. Helium is typically used in these detectors because of its high ionization energy, which allows the measurement of almost any molecule [2]. However, due to the increasing demand and low supplies, the price of helium skyrocketed in the last years and its access is becoming more and more limited [3]. The PED can also be operated with argon, which is significantly less expensive than helium, but due to its lower ionization energy, the limit of detection (LOD) achieved for most permanent gases is above 25 ppb. More recently, ASDevices developed the Enhanced Plasma Discharge (Epd) technology, which is an improvement over the more traditional PED, also invented by Yves Gamache in the 1990s. With its unique plasma stabilisation and electron-injection compound electrodes* the signal to noise ratio is significantly increased, leading to much better LOD.

Using helium as the carrier and discharge gas, a LOD of 0.1 ppb can be achieved for N_2 and 0.5 ppb for the other permanent gases. Still, due to its lower ionization energy, the LOD achieved with argon is approximatively 5 times higher.

In order to decrease the LOD even further, ASDevices is now introducing a new pre-concentration system and methodology that use the Trap & Release Purge Lip Sealing Valve (Figure 1). Thanks to the unique design of the PLSV, cross-ports leak is virtually impossible, which is essential for the pre-concentration of ultra-trace level permanent gases.

Figure 1 – The Trap & Release Purge Lip Sealing Valve

This pre-concentration system also uses unique mixtures of synthetic materials optimised for trapping the analytes while eliminating a significant amount of matrix, thus improving the LOD. Thanks to the amount of matrix eliminated with this system, the chromatography can even be simplified.

This application note intends to show how our new measurement method using the T&R PSLV-based pre-concentration system combined with the Epd technology, can be used to measure sub-ppb level of permanent gases in various matrix using argon as the carrier/discharge gas and to simplify chromatography.

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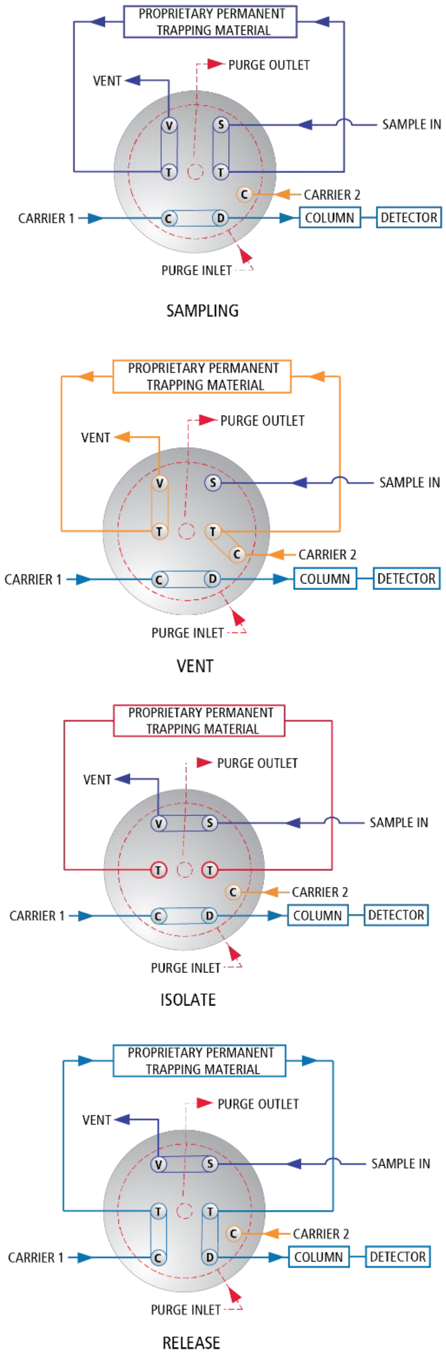
EXPERIMENTAL INFORMATION

Trap and Release Purge Lip Sealing Valve Pre-Concentration System

The ASDevices' Purged Lip Sealing Valve (PLSV)* combines the advantages of the rotary and the diaphragm valves, without any of their drawbacks. The superior performance of the PLSV is achieved by its unique insert technology. It offers a reduced surface sealing area, a unique purging groove associated with valve's head pocket and soft cushioning to make a perfect alignment between the head and the insert. Thanks to the reduced sealing surface area of the PLSV and a proprietary treatment of the materials, the force required for actuation is minimal compared to a conical rotary valve. Therefore, such valve can be used for over 1 000 000 actuations without any impact on the performance, even in UHP applications. This technology is now implemented in 6, 8 and 14 ports valves, stream selection valves and the Trap & Release (T&R) valve. More information about this technology is available in the document AN-08 PLSV Technology – A Quantum Leap for Chromatographic Valve [5].

Schematics representing the four positions of the T&R PLSV are presented in Figure 2. The first step is sampling, where the sample is pre-concentrated on a trap containing one of our proprietary nanostructured materials. During this step, it is important to pay attention to the sample flow rate, as it will impact the amount of analytes retained on the trap. The duration of this step may vary according to the expected concentration range of the analytes. The second step is optional trap venting. It allows complete or partial removal of the matrix, thus simplifying the analysis of permanent gases by GC. Results presented in this application note will show the advantages of this venting step. The third step is trap isolation. It allows heating of



SAMPLING

VENT

ISOLATE

RELEASE

Figure 2- Schematic representation of the T&R PLSV with its 4 positions. From top to bottom: Sampling, Vent, Isolate and Release

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the trap without losing the analytes. The final step is release, which allows injection of the analytes once the trap reaches its optimal desorption temperature. Note that it is important to reach thermal equilibrium before sample release. The T&R PLSV is the only GC valve on the market designed especially for the method presented in this document.

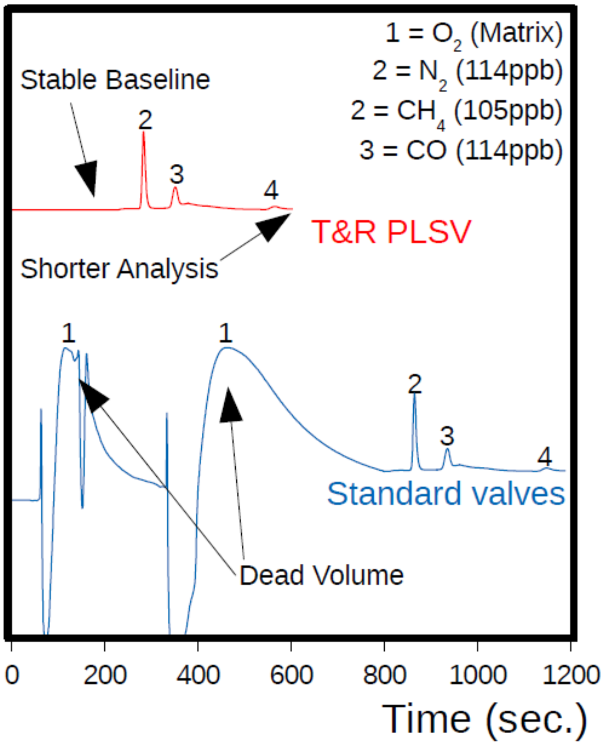

Figure 3 – Oxygen containing 114 ppb N_2, 105 ppb CH_4 and 114 ppb CO analysed with the T&R PLSV pre-concentration system (Red line) and with a pre-concentration system made with two regular GC valves (Blue line)

A similar T&R system can technically be made with two standard GC valves, but this option is not convenient due to the important dead volume from the tubes that connect the valves together (See Figure 6). In this method, the dead volume is filled with sample and this content is injected through the column when the valves are actuated, as seen in Figure 3. Since it is necessary to wait for complete elution of this content before injecting the pre-concentrated sample, analysis with such setup can take additional time. In this example, oxygen containing trace-level N_2, CH_4 and CO was analysed with the T&R PLSV and with a pre-concentration system made of two standard GC valves. With the standard valves, the dead volume is injected twice and a significant amount of time is lost waiting for complete elution of the oxygen matrix before the pre-concentrated sample can be released. Note that the scale in Figure 3 was selected because of the peaks from the oxygen matrix. A better chromatogram for impurities in O_2 is presented in Annex I. Furthermore, the setup with two valves is more expensive, less reliable and takes more space. With the T&R PLSV, only one valve is required and all the connections between the ports are grooved in the valve insert with a total volume of less than 4 µL, as seen in Figure 4. Therefore, no significant amount of sample is injected during valve actuation before the ‘’release’’ step, which allows valuable time saving.

Figure 4 – The T&R PLSV insert

As seen in Figure 2, the unique design of the T&R PLSV also includes a configuration for venting, which allows easy elimination of the matrix without heartcut. This results not only in lower costs in term of equipment (less columns and valves), but also in fine-tuning time, since setting all the heartcut times for each matrix can be a long and tideous task, especially at low concentrations. The T&R PLSV is also designed in a way that sampling can be done at the same time as the chromatogram acquisition once the sample is released, allowing even more time saving. Indeed, thanks to the two carrier gas inlets, there is always gas flowing trough the GC system, even during the sampling step. Therefore, all the

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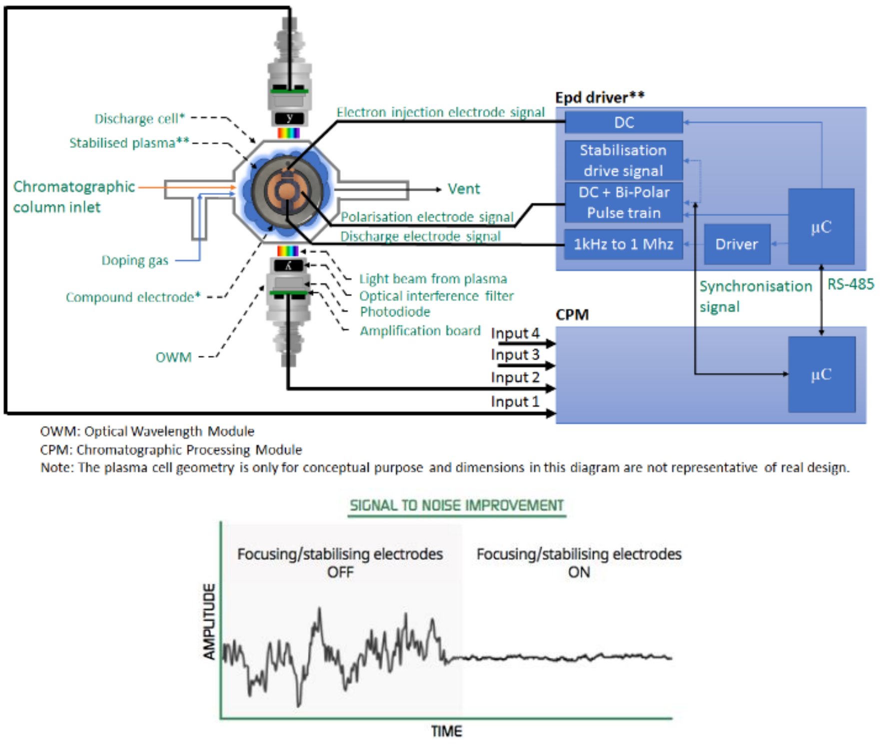
permanent gases can easily be measured in 5 to 15 minutes, depending on the sample matrix and concentrations.

Enhanced Plasma Discharge (Epd)**

The SePdd™ from Analytical Sensing Devices was used for all the measurements presented in this document. 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.

With its highly energetic stabilised and focused plasma discharge, all molecules can be ionised and consequently measurable. It can be operated with argon, helium, nitrogen, oxygen, hydrogen and CO_2 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 sub-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 5)*. The chromatographic processing module (CPM) 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 system. 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* [4].



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 5- Conceptual overview of the SePdd™ stabilising/electron-injection electrodes and effect of noise cancelling by the electrode

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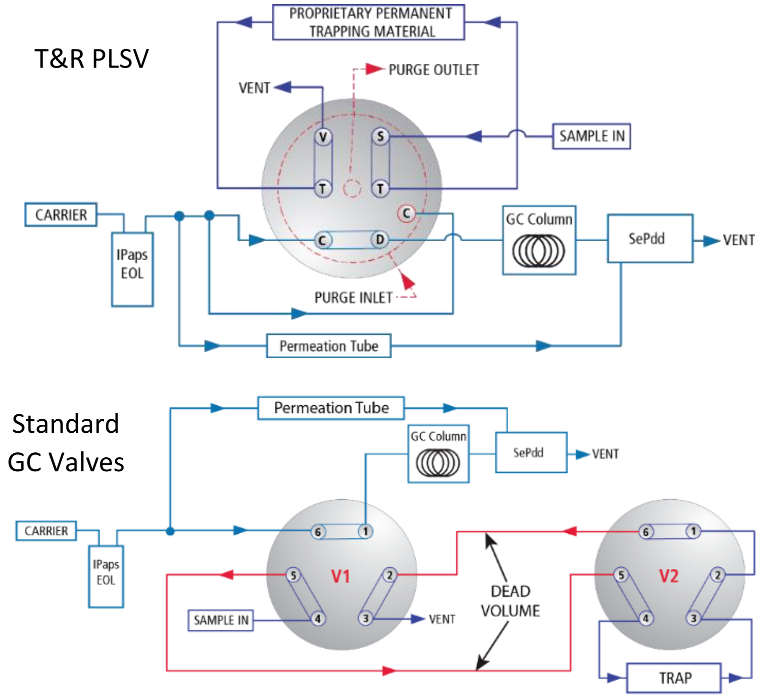

Figure 6 - Schematic representation of the GC system with the T&R PLSV (above) and with two standard GC valves (below)

Experimental Parameters

This application note will focus on the analysis of nitrogen, methane and carbon monoxide in different matrix. The sample was a certified 12ppm permanent gas mix in argon from Messer. This sample was diluted in various UHP gases with the GCS from ASDevices to obtain a permanent gas concentration of a few hundreds ppb. The absence of the analytes from the dilution gases was confirmed prior to the analysis. The measurements were done with a simple injection setup that includes the pre-concentration system, a GC column and a detector, as presented in Figure 6. Here, these components were incorporated in the iMov GC platform developed by ASDevices. For ultra-low level analysis (below 100ppb), a heartcut valve and an additional GC column can be added to the setup to remove the remaining traces of matrix that could still affect the baseline at such low concentrations.

Argon (5.0N) was used as the carrier and discharge gas, with a flow rate of 25 mL/min. Argon was further purified with the ASDevices iPaps^{EOL} series purifier, based on a double heated vessel design which provides carrier gas with less than 1 ppb total impurity. The use of a gas purifier is of utmost important here, as the pre-concentration system will also concentrate the impurities of the carrier gas, which could affect the analysis results. In addition, all of our purifiers use ASDevices LipLOK^{TM} fittings to guarantee the leak integrity and compatibility with existing instrumentation fittings in the field. The GC column used was a molecular sieve 5A maintained at constant temperature. The length and temperature of the column were selected according to the application. Purified argon 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. The optical modules of the SePdd^{TM} were equipped with narrow bandwidth

(±3 nm) optical filters for the measurement of N_2, CH_4 and CO.

A T&R PLSV chromatographic valve equipped with a trap containing one of our proprietary chemically-treated nanostructured material optimised for the analysis of N_2, CH_4 and CO was used as the pre-concentration system. The sampling step was done at room temperature for two minutes, with a sample flow rate of 100 mL/min. Sampling was followed by the venting step. This was done at room temperature for 10 to 60 seconds, depending on the sample matrix. The trap was then isolated and heated to 250°C at a rate of 100°C/min. This temperature was selected, as it is optimal for the desorption of these analytes on this trapping material. Once this temperature was reached, the sample was released.

Alternative Configuration with Standalone Module

In the configuration used in this application note, the trap is directly inline with the rest of the GC column and detector, as seen in Figure 6 (above). This is the simplest and less expensive configuration, which is ideal for repetitive applications such as long-term process monitoring, as it only requires a T&R valve. All the restrictors and operating pressures of the iMov platform were adjusted for this specific trap. Still, the pre-concentration system offers the possibility to easily change the pre-concentration trap depending on analytes to detect. For example, longer traps can be used to increase the maximum pre-concentration factor, but are also more restrictive. The trapping material used also affects the gas pressure and flow rate trough the trap. Therefore, the restrictors and operating pressures must be readjusted for each trap. The ASDevices' T&R standalone module is the ideal tool to overcome all these issues, as it allows easy control on the gas flow and pressure for applications where different traps are often used. This module can be connected to any standard GC system as seen in Figure 7. In such configuration, the pre-concentrated sample is injected in a sample loop and therefore, the chromatography is not affected by pressure drops and variations that may occurs from the various traps.

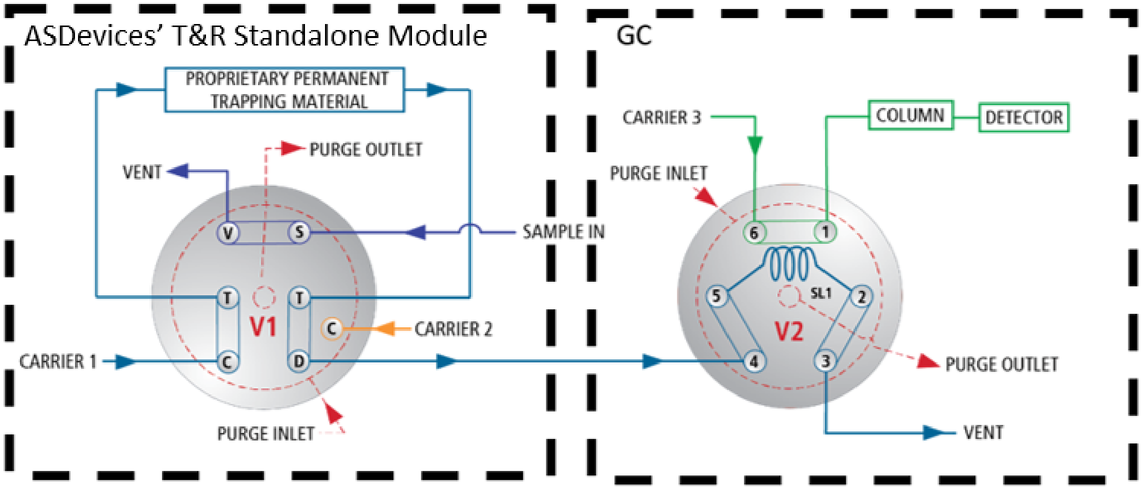

Figure 7 - Schematic representation of the standalone T&R module connected to a GC system, with the pre-concentrated sample injected in a sample loop

RESULTS AND DISCUSSION

Improving the Limit of Detection

Indeed, the main role the T&R PLSV system is to pre-concentrate the sample to improve the LOD of the analytes. To show the efficiency of this system, a sample containing trace amounts of N_2, CH_4 and CO in argon was analysed with the method described in the previous section. The results acquired with the pre-concentration system were compared with results acquired with a 2.1mL sample loop (stainless steel tube containing no trapping material). With the sample loop, the results are representative of an injection with a typical GC setup, as the sample is not pre-concentrated. The volume of the sample loop was selected as it corresponds to the internal volume of the trap used in the T&R system. The comparative results are presented in Figure 8. Here, ''time zero'' for the sample analysed with the T&R PLSV system corresponds to the ''release'' step in order to facilitate the comparison between the results. For the analysis with the T&R system, the sample was pre-concentrated during 2 minutes. Since the sample matrix is the same as the carrier gas, venting was not used for this analysis.

As seen in Figure 8, the signal for N_2 is 8 times higher, CH_4 15 times higher and CO 35 times higher with the T&R PLSV system compared to the results obtained only with the sample loop. Here, the LOD was calculated as 3 times the signal to noise ratio. The iMov platform has an advanced signal treatment algorithm that uses artificial intelligence to cancel the noise and improve the LOD by 3 times. When this Enhanced LOD algorithm was activated, a LOD of 0.1 ppb was achieved for N_2, 0.5 ppb for CH_4 and 1.0 ppb for CO. Note that these results were acquired with a 6ft MS5A column at 70°C. Such LOD for CO is usually only achievable using helium as the carrier/discharge gas and with a much shorter column at higher temperature. Such ultra low-level measurement of permanent gases in argon can only be achieved thanks to the PLSV technology. Indeed, due to the important pre-concentration factor, even small cross-ports leaks that would be negligible in normal circumstances can be problematic for such analysis. Thanks to the unique design of the PLSV that includes purges, such a leak is virtually impossible (See Figure 4).

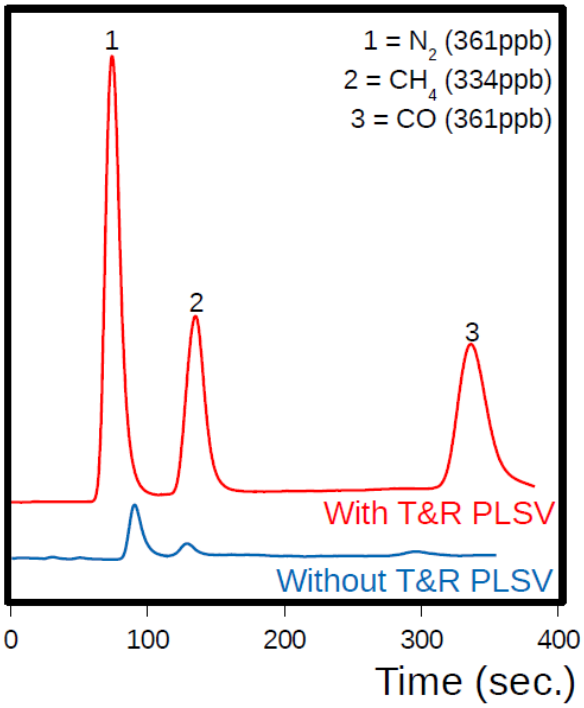

Figure 8 – Chromatogram acquired for 361 ppb N_2, 334 ppb CH_4 and 361 ppb CO in Argon analysed with the T&R PLSV system after 2 minutes sampling (Red line) and with a 2.1mL sample loop (Blue line)

Simplification of the chromatography with the T&R PLSV

To show the benefits of the T&R PLSV technology in the simplification of chromatography, a sample containing N_2 (105 ppb), CH_4 (95 ppb) and CO (105 ppb) in H_2 was analysed with three different methods. Here, no heartcut was used, only injection with one GC valve and column. The resulting

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chromatograms are presented in Figure 9. First, the sample was injected from a 2.1 mL sample loop containing no trapping material (Red line). Then, the same sample was pre-concentrated for two minutes with the T&R PLSV system, but was not vented (Blue line). Finally, the sample was injected after two minutes of sampling and 10 seconds of venting (Black line).

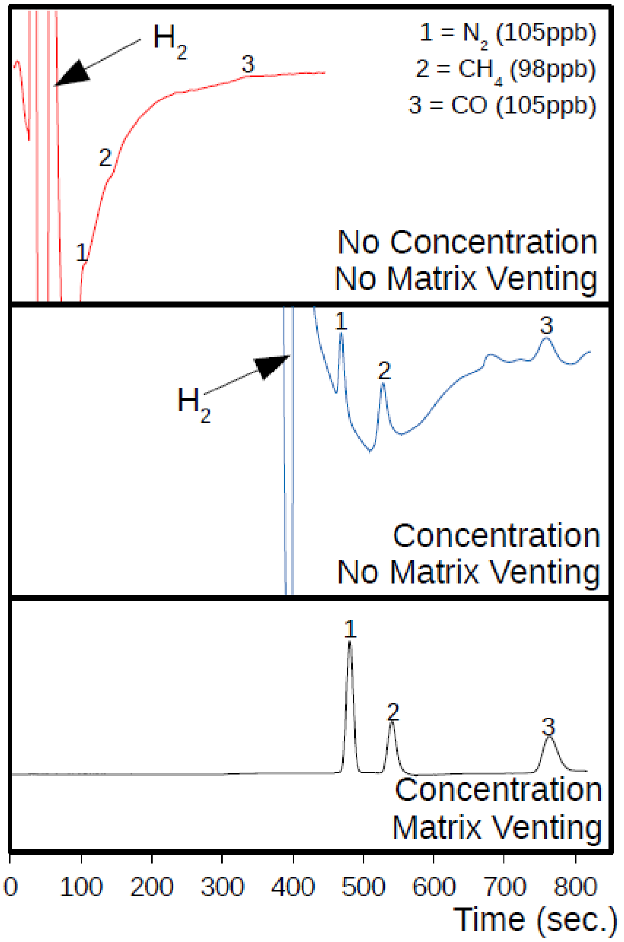

Figure 9 – Chromatogram acquired for 105 ppb N_2, 98 ppb CH_4 and 105 ppb CO in hydrogen using a 2.1mL sample loop (Red line), two minutes pre-concentration without venting (Blue line) and two minutes pre-concentration with 10 seconds venting (Black line)

In the case of direct injection with the sample loop, there is no clear peak from the analytes due to the important ammount of hydrogen matrix interfering with the baseline and the low concentration of the analytes. This is the reason why a heartcut method is typically used for such analysis when the T&R PLSV system is not implemented. This is even the case for hydrogen as the matrix, which is know for its fast elution on most GC columns.

With the pre-concentrated sample, peaks from the analytes can clearly be seen, but, they cannot be used for good quantification due to the important amount of hydrogen still affecting the baseline. However, thanks to the propriatary nanostructued material used in the trap, most hydrogen is easily eliminated after only 10 seconds venting. The resulting peaks can then be used for quantification, as seen in Figure 9 (Black line). This result shows how useful this venting step is, especially when the matrix is not the same as the carrier/discharge gas. Indeed, heartcut fine-tuning can be a long and tideous task that can often be avoided with this method. This venting step is only possible thanks the unique design of the T&R PLSV. Furthermore, as previously discussed, with the small dead volume in the insert, there is no interference from the matrix on the chromatogram before the release of the pre-concentrated sample, allowing significant time savings. More results acquired for different matrix are presented in Annex I.

Linearity and Repeatability

The linearity of the response for N_2, CH_4 and CO was confirmed by measuring pre-concentrated samples at 5 different concentrations ranging from 25 ppb to 400 ppb in argon after 1 minute sampling and no matrix venting. A good R^2 of 0.99 or above was measured for all the analytes, as presented in Figure 10. The small deviations observed did not only come from the pre-concentration system, but also variations from all the components of the GC system, including the sample dilution system, the flow controllers, the detector, etc.

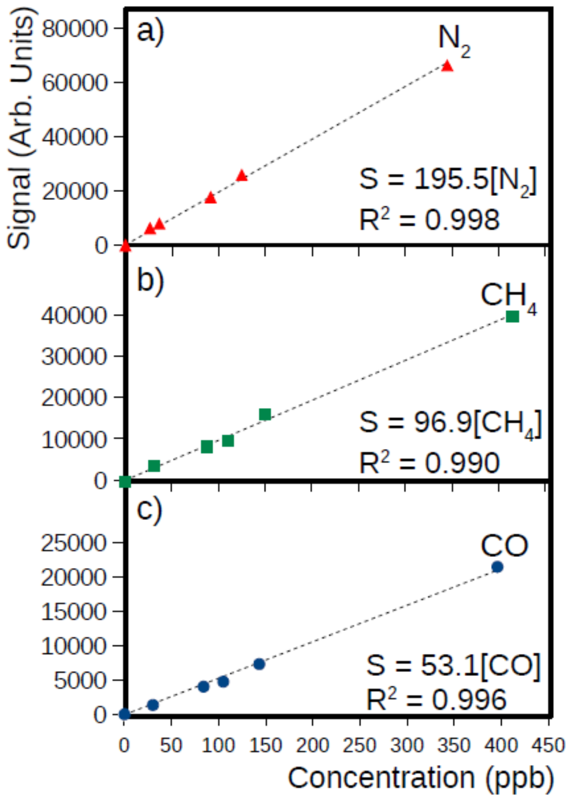

Figure 10 – Signal as a function of concentration for N$_2$, CH$_4$ and CO in argon measured with the T&R PLSV system after 1 minute sampling and no matrix venting

The repeatability of the results was also tested on a 24h period. The standard deviation of the concentration of each analyte was calculated after every 10 acquisitions. As presented in Table 1, average standard deviation of 1.1% was calculated for N$_2$, 1.7% for CH$_4$ and 2.0% for CO. Therefore, the results acquired confirm that the iMOV GC platform equipped with the T&R PLSV pre-concentration system is highly stable and can be used in long-term process monitoring of UHP gases.

Table 1 – Standard deviation (%) on 10 consecutive analysis over a 24h period for a sample containing ~150 ppb N$_2$, CH$_4$ and CO in Ar

Acquisition	N$_2$	CH$_4$	CO
1-10	1.37%	1.88%	2.36%
11-20	0.94%	1.34%	1.81%
21-30	0.98%	1.76%	1.76%
31-40	1.11%	1.81%	2.31%
41-50	1.05%	1.78%	2.22%
51-60	0.96%	1.55%	1.93%
61-70	1.02%	1.43%	1.85%

CONCLUSIONS

In conclusion, the pre-concentration system based on the ASDevices' T&R PLSV is a very versatile tool that can be used to improve the LOD of permanent gases and simplify their chromatography in various matrix. Thanks to its unique design and proprietary trapping materials, the analytes can be pre-concentrated, while most of the matrix can be eliminated, thus simplifying the chromatography. Its unique purged lips design makes cross-ports leaks virtually impossible, which is essential for sample pre-concentration, especially in ultra-trace level analysis.

In the past, sub-ppb level measurements of permanent gases could only be achieved with technologies that rely helium or more expensive detectors. With the new method introduced in this document, sub-ppb level measurement of permanent gases can now be easily achieved using low-cost argon as the carrier/discharge gas combined with the Epd technology. Thanks to the good repeatability of the results and short analysis times, this method can be automated and used in long-term process monitoring. Such results would be impossible without the T&R PLSV technology and our nanostructured trapping materials. While this document focussed on the measurement of N_2, CH_4 and CO, other propriatary trapping materials were also developed for the measurement of H_2, CO_2 and light hydrocarbons. The results acquired for these analytes will be presented in future documents.

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ANNEX I – Chromatogram Examples for Permanent Gas Concentration

N_2, CH_4 and CO in Ar

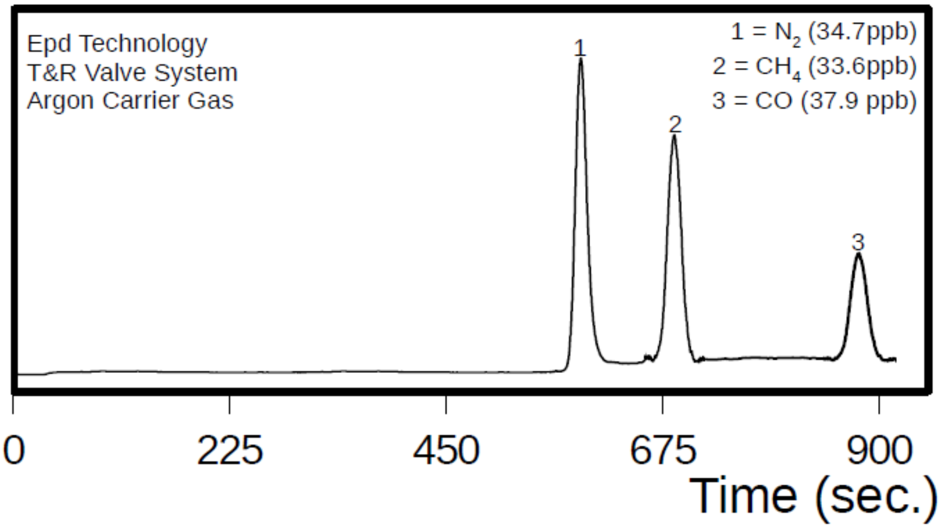

Figure A1 – Chromatogram acquired for 34.7 ppb N_2, 33.6 ppb CH_4 and 37.9 ppb CO in Ar after 2min. sampling without venting

N_2, CH_4, CO in He

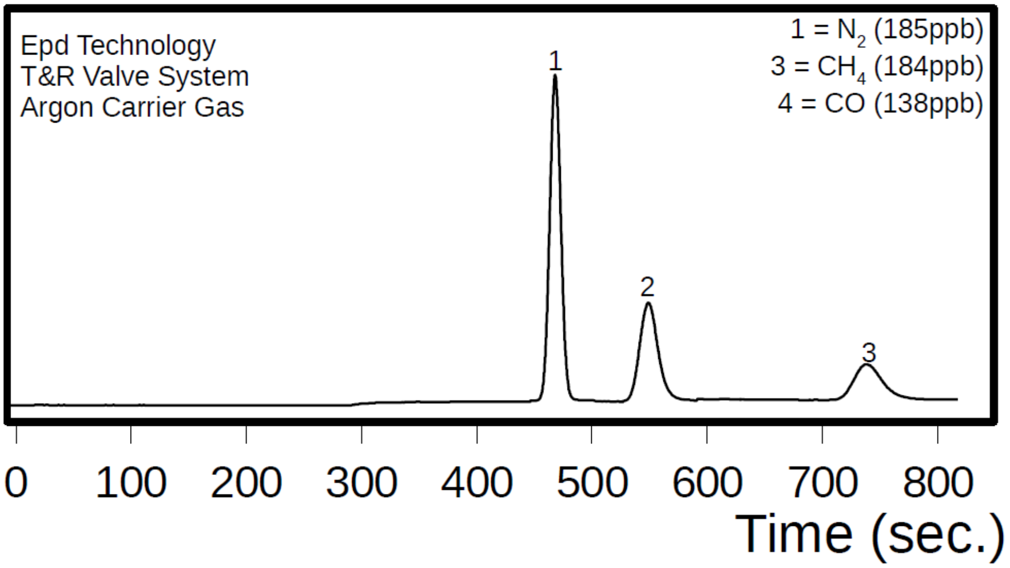

Figure A2 – Chromatogram acquired for 185 ppb N_2, 184 ppb CH_4 and 138 ppb CO in Ar after 2min. sampling and 10 sec. venting

N_2, CH_4 and CO in H_2

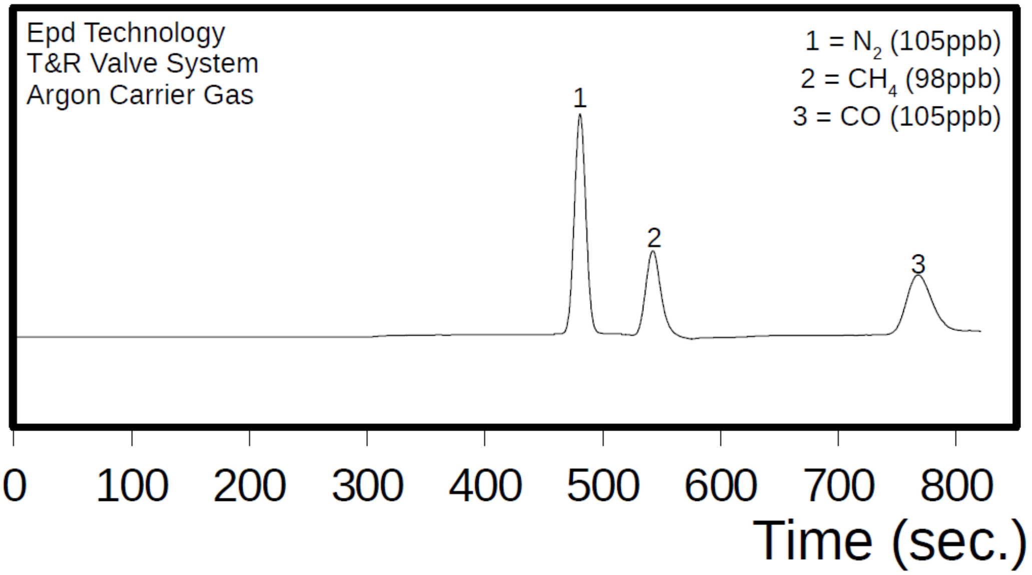

Figure A3 – Chromatogram acquired for 105ppb N_2, 98ppb CH_4 and 105ppb CO in TOC Air after 2min. sampling and 10 sec. venting

N_2, CH_4 and CO in O_2

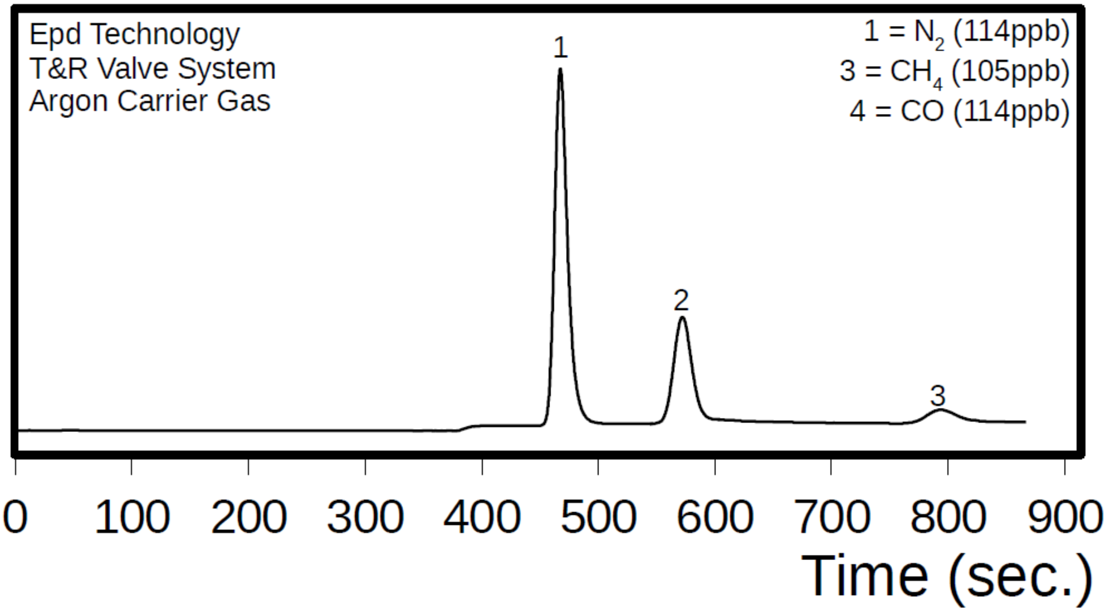

Figure A4 – Chromatogram acquired for 114ppb N_2, 105ppb CH_4 and 114ppb CO in O_2 after 2min. sampling and 30 sec. venting

ANNEX II – Other Applications

CO_2, Ethane and Propane in Ar

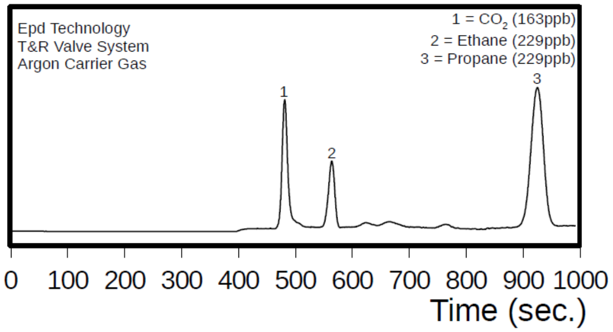

Figure A5 – Chromatogram acquired for 163ppb CO_2, 229ppb Ethane and 229ppb Propane in argon after 1min. sampling and no venting

VOCs in air

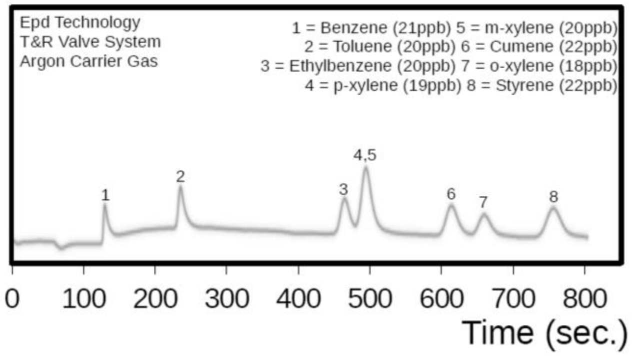

Figure A6 – Chromatogram acquired for 20ppb VOCs in air after 1min. sampling and 30 sec. venting

Sulfur-Based Compounds in air

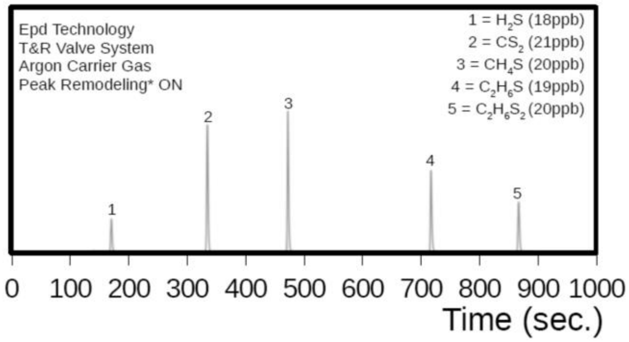

Figure A7 – Chromatogram acquired for 20ppb sulfur-based compounds in air after 1min. sampling and 30 sec. venting

Trace-Level Water Measurement

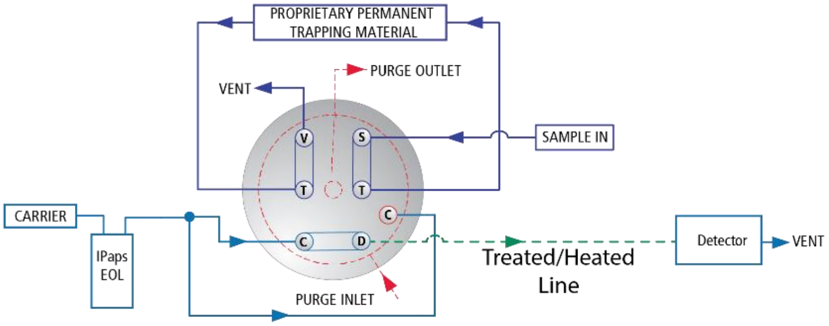

Figure A8 – Setup with the T&R PLSV for trace-level water analysis

The measurement of trace-level water can be extremely challenging, since this molecule sticks to stainless steel and is trapped or highly delayed on most GC columns. Therefore we developed the configuration presented in Figure A8. In this configuration, the GC is replaced with a heated stainless steel line. This line and the valve's head are both passivated with our propriatary surface treatment to avoid water losses, allowing easy trace-level water measurement.

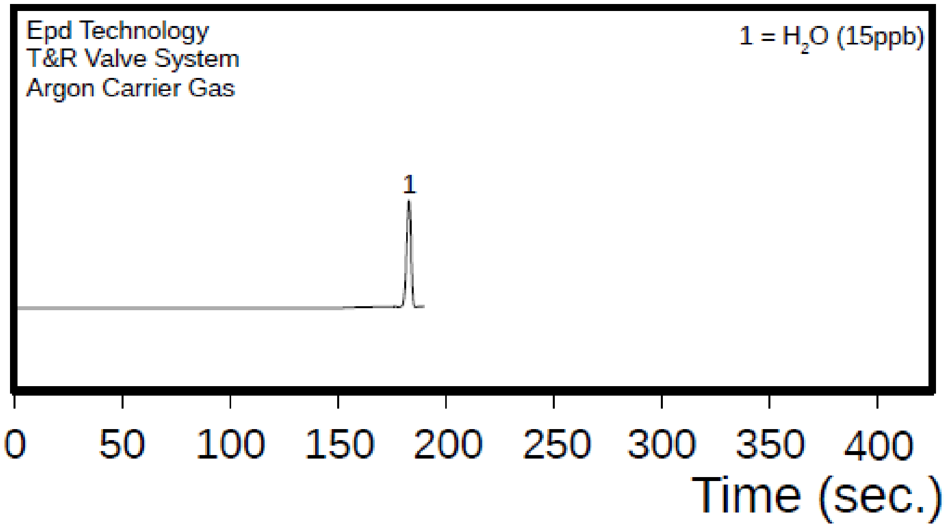

Figure A9 – Chromatogram acquired for 15ppb water in argon after 2min. sampling and no venting

* = Patent Pending ** = Patented