

# **PURGED LIP SEALING VALVE TECHNOLOGY FOR IMPROVED PERFORMANCES IN GAS CHROMATOGRAPHY**

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## **KEYWORDS**

GAS CHROMATOGRAPHY, VALVE, PURGE, LEAK INTEGRITY, DURABLE, LOW FRICTION, SURFACE TREATMENT

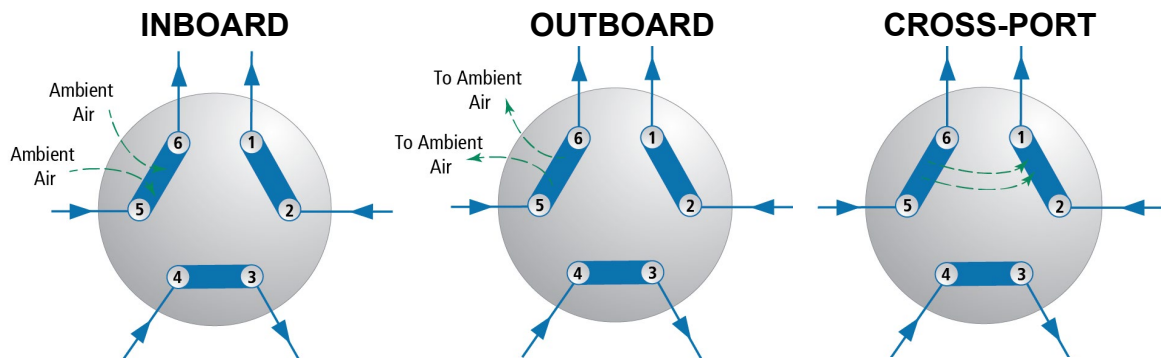
## **ABSTRACT**

Since the 1960s, conical rotary valves have been commonly used in gas chromatography (GC), because of their cost-effectiveness. However, this type of valve is prone to leaks and is not recommended for ultra high purity (UHP) gases analysis. Furthermore, due to the high force required for sealing, it cannot be used for more than a few thousand actuations. This is because of valve wearing caused by high friction. Therefore, most surface treatments for inerting the valves are not durable, making the analysis of reactive species such as sulfur compounds more challenging. For UHP gases analysis, diaphragm valves are more commonly used. While they are less prone to leaks and can be inerted for reactive compounds analysis, the diaphragm loses flexibility over time, leading to pressure drops and peak shifting. Therefore, process GCs using this type of valve require frequent maintenance and fine-tuning. Furthermore, diaphragm valves are known to contain dead volumes, which can trap the sample and create “ghost peaks” due to reinjection. More recently, CVProducts, a division of ASDevices, released the purged leap sealing valve (PLSV) technology, which possesses the advantages of both valve types without any of their drawbacks. This technology offers advantages, not only for UHP applications, but for all GC applications. Since it uses a rigid rotor, there is no pressure drop over time. Moreover, the rotor is flat and the sealing is achieved only with a small lip that has a minimal surface area, which requires minimal sealing force, leading to much less wearing compared to conical rotary valves. Therefore, PLSV can be used for over 3,000,000 actuations without performance loss and valve head can be inerted with surface treatment, thanks to low friction. Furthermore, it was designed with an internal

purge that prevents inboard, outboard and cross-ports leaks without a bulky external purge box. This presentation intends to show how the PLSV technology can be used in high-sensitivity process GCs with minimal maintenance. First, the importance of using valves with a good leak-integrity and negative impacts of leaks in GC will be discussed. Then, results from an independent study that compared the performance of PLSV with diaphragm valves will be presented. Results obtained with PLSV integrated in process GCs that uses the Enhanced Plasma Discharge (EPD) technology for the measurement reactive species such as sulfur compounds and water, and ppt-levels permanent gases will also be presented, as well as results obtained after long-term intensive use to demonstrate the robustness of the PLSV technology.

## INTRODUCTION

In gas chromatography, the ideal valve would have constant pressure/flow drop between the different positions and ports over its lifetime, no dead/unswept volume, no leaks and last over 1,000,000 actuations. Neither of the two most common commercially available valve types, conical rotary and diaphragm valves, offer all the characteristics mentioned above. Choosing either valve type always requires a compromise in features. Three types of leaks can be encountered in GC valves: inboard, outboard and cross-port. They are illustrated in Figure 1.



**FIGURE 1. LEAK TYPES ENCOUNTERED IN GC VALVES**

Leak integrity is especially important for the measurement of trace-level permanent gases ( $H_2$ ,  $O_2$ ,  $N_2$ ,  $CH_4$ ,  $CO$ ,  $CO_2$ ), as they are present at high concentrations in air. Inboard leaks could cause interference when analyzing UHP gases. However, this is not the only application where leak integrity is important. Indeed, many GC columns are susceptible to contamination by water, oxygen and/or carbon dioxide from ambient air. Over time, inboard leaks can cause accumulation of these impurities on the columns, leading to peak shifting and degradation of the chromatographic performances. The same can occur from cross-ports leaks, especially with small molecules such as hydrogen. Furthermore, this could cause baseline variations that impact the performance of the analyzer. It is also important to consider that gases can leak outside the valve. This is especially problematic

when working with flammable or toxic gases, as it can cause hazardous situations. In these cases, an internal purge is especially important to capture and safely eliminate the leaking gases.

## CONICAL ROTARY VALVES

The conical rotary valve is the most widely used valve concept in chromatography. Despite not being a perfect valve, it is used for many applications where leaks would not cause major issues on the chromatography. Unfortunately, they lack performance for UHP type applications, especially when trace  $N_2$  needs to be measured. Still, their advantage is the constant pressure/flow drop. Having a constant pressure/flow drop means the valve restriction to flow is the same in all ports and all positions. This is important for many applications in order to have a very good baseline stability when valves are actuated, thus reducing maintenance or fine-tuning over time. Baseline fluctuations can interfere with chromatographic peaks and provide inaccurate measurements. Unfortunately, all commercially available conical rotary valves are known to wear rapidly due to the friction and high level of force required to seal them properly. This is an inherent problem to all conical rotary valves. Properly machining and matching two conical parts, the rotor and the stator, is difficult hence a high sealing force and high friction are inherent. The result is a valve that begins to leak after only a few thousand actuations [1]. In order to overcome this problem, design improvements were introduced, as shown in Figure 2. Such design resolves the inboard/outboard leak issue, as it purges the volume around the rotor. However, it does not address cross-port leaks. The most common cross-port leak in chromatography is the sample gas that leaks in the carrier gas. This causes carrier gas contamination and hence detector baseline noise, which is especially problematic when analyzing hydrogen or helium, as these gases are prone to leak, due to their small molecular size. More recently, a technology named CLP (Cross-port Leak Protection) was introduced. While this design resolved the cross-port leak issue, it still suffers from fast wearing due to the required sealing force that is inherent to the conical rotary valves. Furthermore, this new design also suffers from depressurization issues that can affect the baseline.

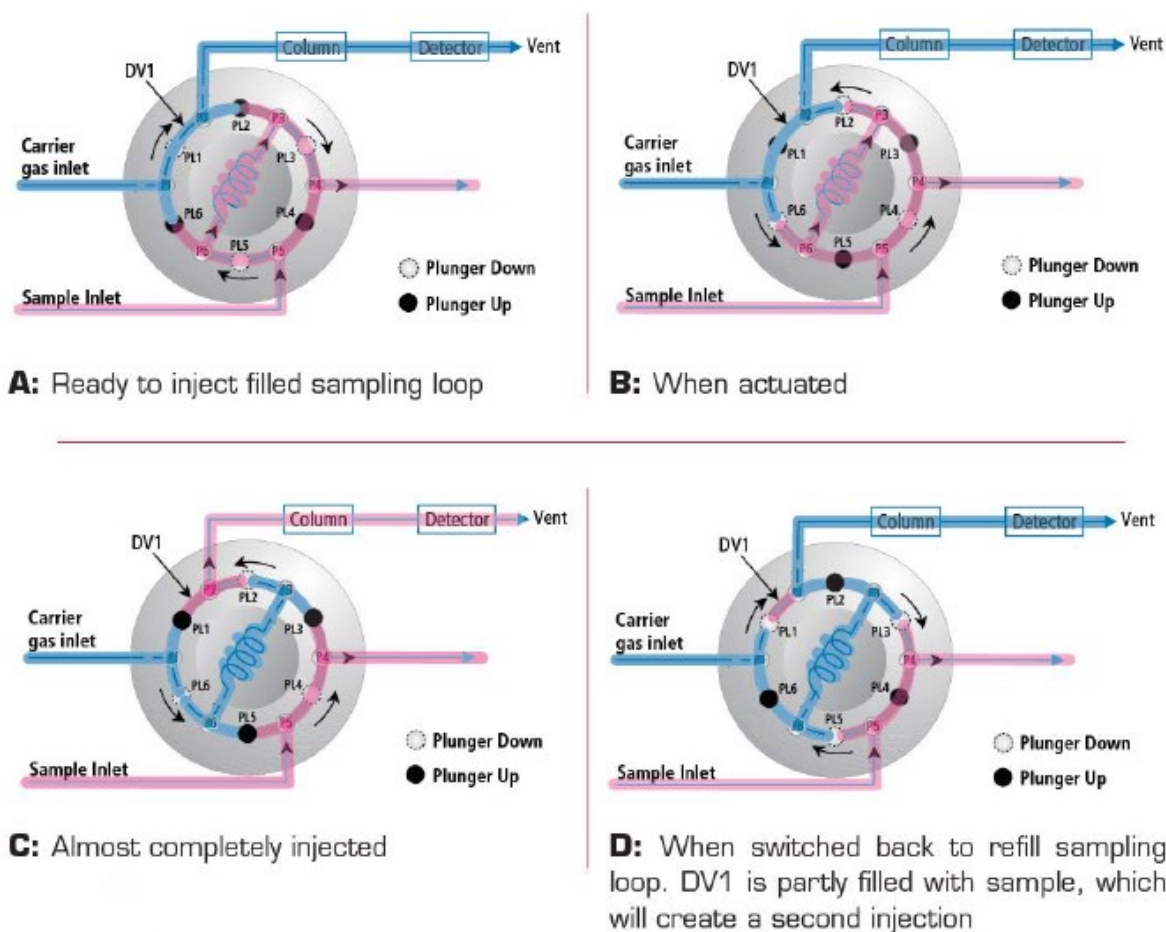


**FIGURE 2. TYPICAL PURGED ROTARY VALVE**

Another issue caused by high friction is that surface treatment on conical rotary valves peels away very quickly. Inert surface treatment of the whole flow path is essential for accurate measurement of reactive compounds like sulfur compounds in common applications such as food-grade CO<sub>2</sub> and fuel-grade hydrogen analysis [2, 3]. Therefore, conical rotary valves are not optimal for the analysis of reactive compounds.

## DIAPHRAGM VALVES

Diaphragm valves were introduced to resolve many issues associated with the short lifetime of conical rotary valves. However, their design came with new issues: pressure/flow drop, dead/unswept volume and air/sample permeation through the diaphragm membrane [4]. Diaphragm valves can also suffer from inboard/outboard leaks. The most recent designs successfully introduced an internal purge or a purge ring to address the leak issues, making them suitable for UHP applications. However, no manufacturer has addressed the fundamental problem of pressure/flow drop, which impacts the chromatographic performance and cross-port leaks.



**FIGURE 3. DIAPHRAGM VALVE DEAD VOLUME ISSUE**

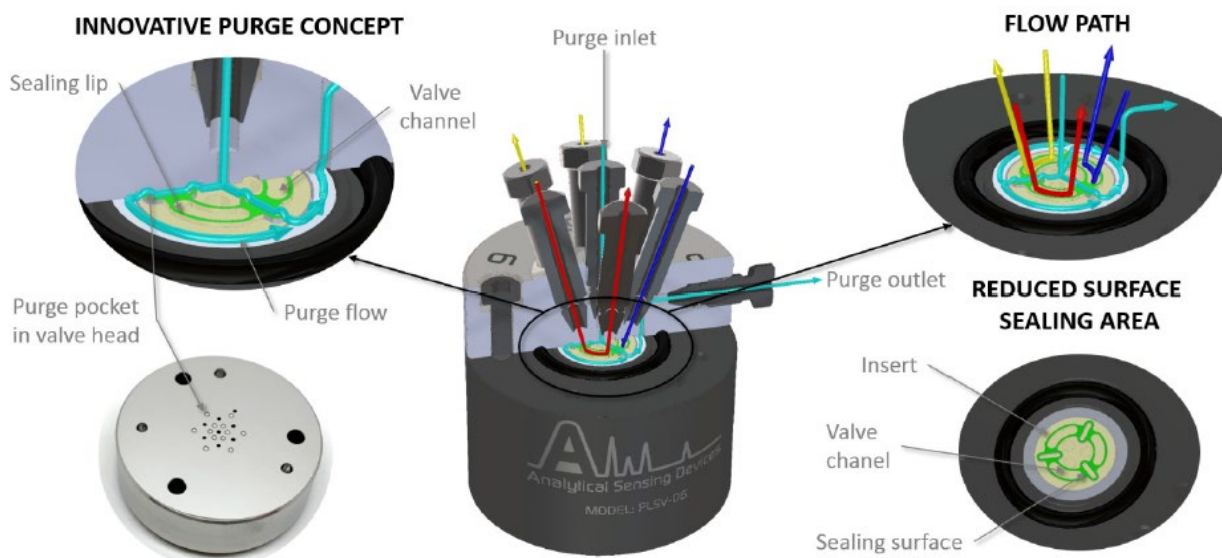
The dead volumes of diaphragm valve are represented in Figure 3. These dead volumes are located between the plungers and the valve ports, which can result in double injection of a few microliters of the sample. In regard to pressure drop, this is due to the elastic nature of the diaphragm. When working with capillary columns, the column head pressure is very low, but the gas velocity is high. In that case, any slight variation in the port pressure drop upon actuation affects the carrier gas flow velocity in the column, which causes variations in peak elution time and baseline. Examples of chromatograms acquired with a diaphragm valve showing double injection and pressure drop effects are presented in the Results section.

Furthermore, the diaphragm material can lose flexibility over time, leading to carrier gas and sample flow variations and peak shifting. This is especially problematic for process and continuous GCs, as this leads to frequent need for maintenance and fine-tuning.

### **PURGED LIP SEALING VALVES (US PATENT 11,885,774 B2)**

The PLSV technology combines the advantages of conical rotary and diaphragm valves, without any of their drawbacks. This can be achieved thanks to its unique insert design that offers a reduced surface sealing area and a purging groove associated with the valve's head pockets, as presented in Figure 4. Soft cushioning is used to make a perfect alignment between the valve's head and the insert. The wearing and friction have been reduced by optimising the sealing surface area. The sealing lip size and shape design have been optimised using finite element modeling (FEM) and real-life testing. The result is a sealing surface area that is equal to 14% of a standard conical rotary valve. Furthermore, the insert material is treated by a proprietary process to improve the surface finish, hardness and creeping. The result is a valve that is easy to seal and that requires very little force for actuation compared to a traditional conical rotary valve. This design allows the PLSV technology to be actuated over 3,000,000 times in UHP applications without losing performance. Furthermore, the valve's head can be inerted with surface treatment for continuous analysis of reactive compounds without peeling.

The leak integrity is achieved by an internal purge, illustrated in Figure 4. It involves purging grooves, which are located between two adjacent valve channels and purging pockets that are machined in the valve head. The purging pockets are used to connect the purging inlet and outlet together through the purging grooves and allow purge gas to flow freely from the purge inlet to outlet. With this concept, it is impossible to have inboard/outboard and cross-port leaks as the volume around the insert and between ports is continuously purged. The purge gas is typically the same as the carrier gas but may vary depending on the application. This technology, unlike diaphragm valves, does not suffer from pressure/flow drop issue, which has been made possible by the use of a rigid material similar to a conical rotary valve. However, the PLSV surface is flat, which is easier to mechanically match than the conical rotary valve surface.



**FIGURE 4. PLSV TECHNOLOGY CONCEPT**

This document intends to present how the PLSV technology can be used to improved the performance of GCs in various applications. First, the results from an independent study that compared chromatograms obtained with a GC-MS equipped with a purged diaphragm valve and a PLSV will be presented. Then, results acquired by GC-EPD for reactive compounds and ultra-trace level permanent gases, including chromatograms that were obtained with a valve that was previously used for more than 1,000,000 actuations will also be presented.

## EXPERIMENTAL

The comparison test between diaphragm valve and PLSV was conducted independently by Focused Photonics Inc (FPI) on their EXPEC-5310 GC-MS platform configured for the measurement of volatile organic compounds (VOCs). This platform traditionally used a 10-port ELDV-2 diaphragm valve from Analytical Flow Products in a backflush configuration. A first series of results was acquired with this configuration. Then, another series of results was acquired with a 10-ports PLSV from CVProducts replacing the diaphragm valve. The gas connections and actuation pressure were kept unchanged. All the GC and detector parameters remained the same to do a direct comparison. The actuation pressure was set to 60 PSIG. To confirm the fast actuation of the PLSV technology, the GC-MS software impulse time was set to 100 ms. The duration of the pulse, which drives the actuation solenoid, was used to determine the actuation time. The proper actuation was confirmed by assessing the valve position after the impulse. The test demonstrated that 100 ms is sufficient to drive the valve. It was not possible to verify shorter actuation time due to the software limitation. The effects of pressure drop and

dead volume were studied by injecting a blank air sample and actuating the valve (ON and OFF) every 2 minutes.

All the other results presented following this comparison test were acquired using ASDevelopments' KA8000 process-GC equipped with a 6-port PLSV and a detector based on the Enhanced Plasma Discharge (EPD) technology (US Patent 10,379,054 B2). For each analyte, the optimal optical filter was selected for measurement with the EPD-based detector. For the analysis of trace water and H<sub>2</sub>S, the valve's head and gas flowpath in contact with the sample were sulfonert-treated and argon was used as the carrier/discharge gas. For the measurement of water, the GC was equipped with a 30m x 0.25mm x 0.2µm film Watercol 1910 column from Supelco. For the measurement H<sub>2</sub>S, a 1m x 1mm Rt-XLSulfur column from Restek was used. For measuring the permanent gases, the GC was equipped with a 6' x 1/8" molecular sieve 5A column from ASDevelopments and helium was used as the carrier/discharge gas. All the samples were generated using certified span gas bottles from Messer, diluted using ASDevelopments' iGCS gas dilution system, based on sonic orifices. In all cases, the carrier gas was further purified using ASDevelopments' ASDPure dual-getter purifier, which can generate argon or helium with less than 1 ppb total impurities from a 5.0N bottle.

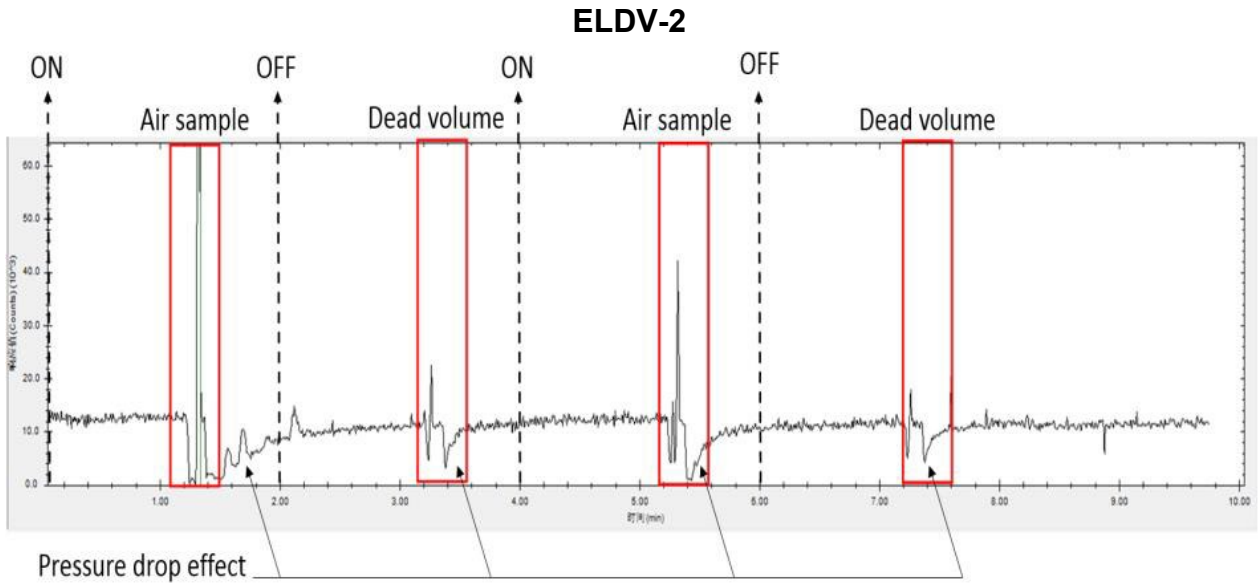
## **RESULTS**

### **COMPARISON BETWEEN DIAPHRAGM VALVE AND PLSV WITH GC-MS**

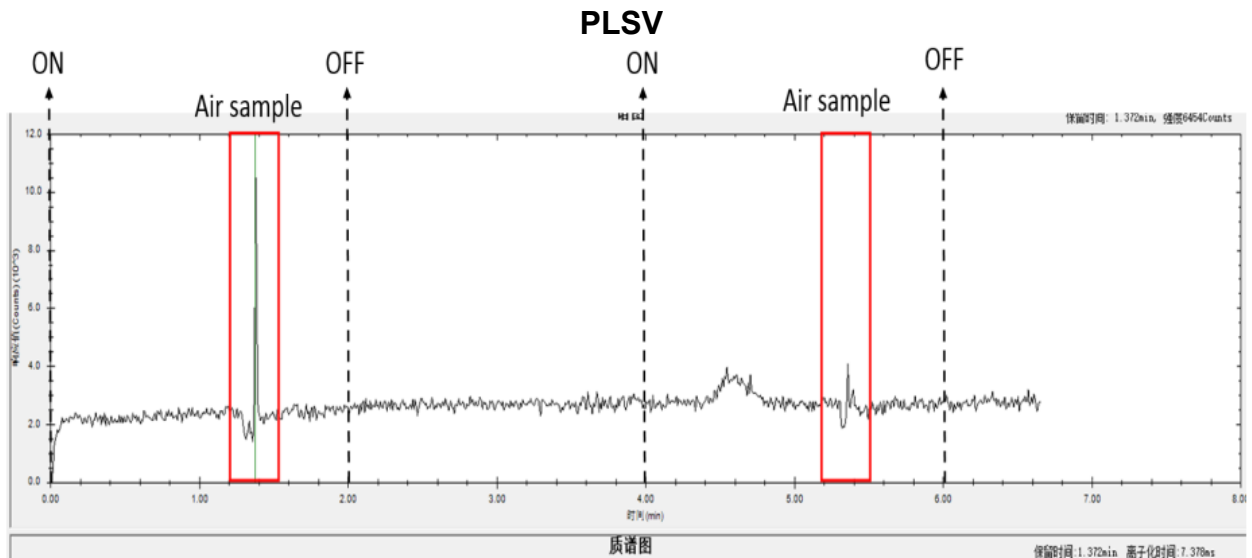
The effects of the pressure drop and dead volume of the diaphragm valve and the PLSV were tested on FPI's GC-MS platform with a blank air sample. The valve was switched ON and maintained in this position for 2 minutes, before being switched OFF. This sequence was then repeated two minutes later. With these GC conditions, it was determined that the air peak requires 1.1 minute to elute from the chromatographic column after injection (ON). In the chromatogram, the peaks at around 1.1 minutes and 5.1 minutes are from the air sample injection, as the sample is injected at 0 minute and 4 minutes. In Figure 5, it can be seen that ELDV-2 dead volume effect appears at 3.1 minutes and 7.1 minutes, as the valve is switched OFF at 2 minutes and 6 minutes. This behaviour is not present with the PLSV technology, thanks to its design, as can be seen on Figure 6. As mentioned previously, all diaphragm valves have, by design, a dead volume which is a major limiting factor, which is well represented in this test.

Due to the elastic nature of the diaphragm, the pressure drop across the diaphragm valve is not the same in both positions (ON vs OFF). As a consequence, the pressure drop has an impact on the carrier flow into the column and eventually appears as a baseline fluctuation as the flow perturbation travels across the chromatographic system. This is seen in Figure 7 with the baseline suddenly decreasing, followed by a re-stabilisation. Using the PLSV technology, it can be seen that this effect does not occur, as the insert is

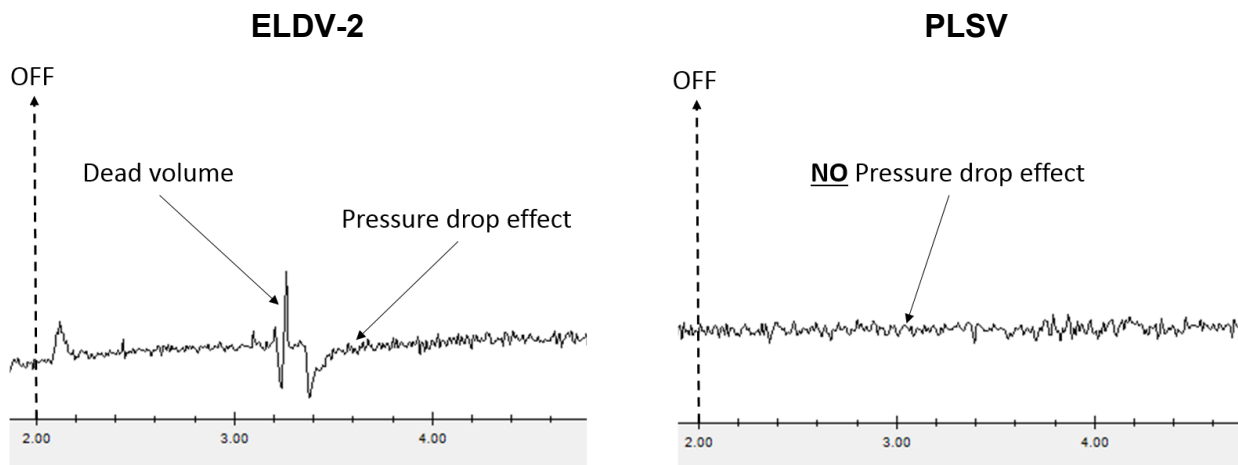
made of solid material, compared to ELDV-2 soft polymer diaphragm. This type of baseline fluctuations is problematic in chromatography as it may interfere and make peak measurement and detection more difficult. It is to be noted in Figures 5 and 6 that the average baseline signal is lower with the PLSV technology due to better leak integrity of the valve [5].



**FIGURE 5. ELDV-2 DEAD VOLUME AND PRESSURE DROP PERFORMANCE**



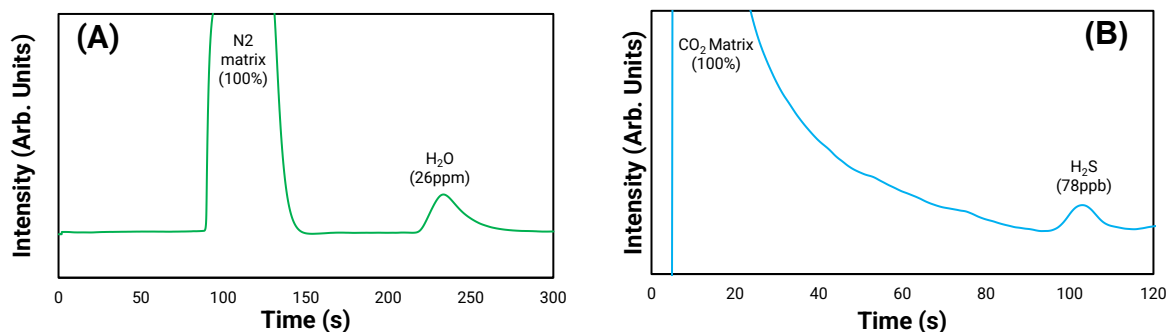
**FIGURE 6. PLSV DEAD VOLUME AND PRESSURE DROP PERFORMANCE**



**FIGURE 7. COMPARISON BETWEEN DIAPHRAGM VALVE AND PLSV**

## REACTIVE COMPOUNDS ANALYSIS

Figure 8 presents chromatograms acquired for 26 ppm moisture in nitrogen (A) and 75 ppb H<sub>2</sub>S in food-grade CO<sub>2</sub> (B). It was acquired with ASDeices' KA8000 process-GC equipped with Sulfinert-treated tubing and PLSVs, due to the high reactivity of these compounds. Without this treatment, these analytes would stick to the stainless-steel, making these measurements unreliable. Such analysis is typically done using diaphragm valves, since surface treatment is not durable on conical rotary valves. Thanks to the low friction of the PLSV, this is not an issue with this technology, even after thousands of actuations.

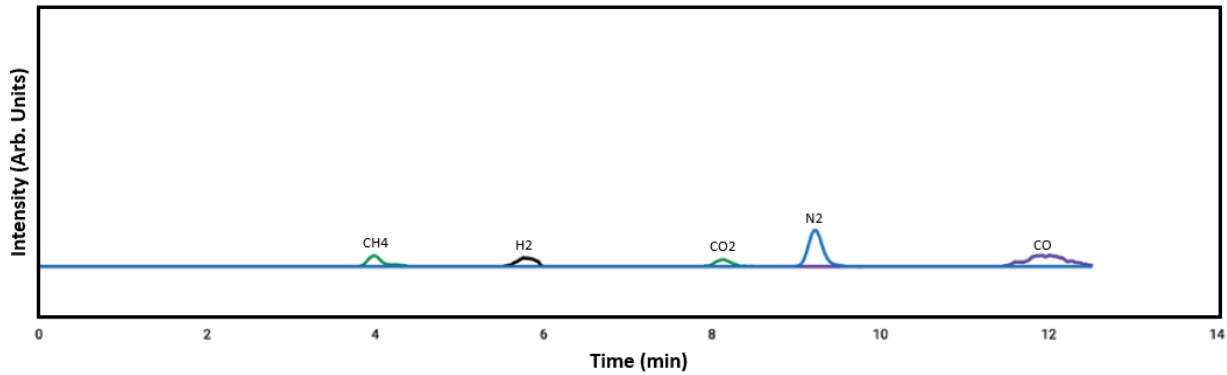


**FIGURE 8. CHROMATOGRAMS ACQUIRED FOR (A) 26 PPM H<sub>2</sub>O IN N<sub>2</sub> AND (B) 78 PPB H<sub>2</sub>S IN FOOD-GRADE CO<sub>2</sub>.**

## ULTRA-TRACE LEVEL PERMANENT GASES

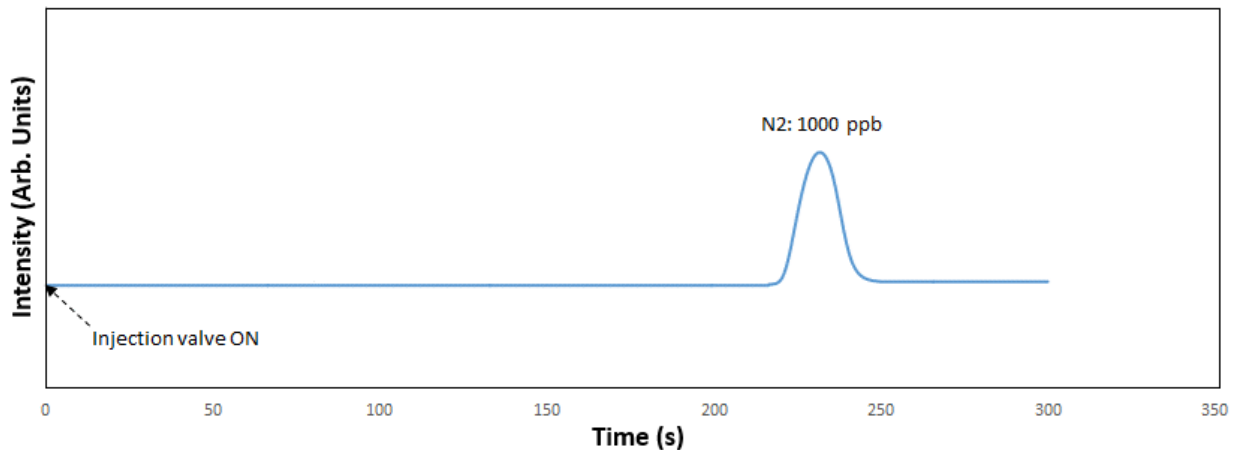
The measurement of permanent gases by GC requires components that are leak-tight, especially at the sub-ppm level. Figure 9 presents a chromatogram acquired for 700 ppt

of permanent gases in helium and illustrates the excellent leak integrity of the PLSV technology. As a comparison, the average base leak rate of a brand-new conical rotary valve is around 0.3 ppm and quickly reaches the ppm level after a few thousand actuations, which would make the measurement of nitrogen and oxygen impossible at such low concentration [1].



**FIGURE 9. CHROMATOGRAM ACQUIRED FOR 700 PPT OF PERMANENT GASES IN HELIUM.**

To demonstrate the robustness of the PLSV technology, a KA8000 GC equipped with a brand-new valve was calibrated by peak integration from the software with a sample containing 1000 ppb N<sub>2</sub> in helium. The valve was then replaced with a PLSV that had been previously actuated every 5 seconds over an extended period to reach more than 1,000,000 actuations. A typical chromatogram acquired with the used valve is presented in Figure 10. This sample was analysed 5 consecutive times, with consistent results. Then, 5.0N helium that was further purified with an ASDPure purifier was injected 5 times to demonstrate that air was not leaking in the sample stream from the valve. The calculated N<sub>2</sub> concentrations are presented in Table I.



**FIGURE 10. CHROMATOGRAM ACQUIRED FOR 1000 PPB N<sub>2</sub> IN HELIUM WITH A PLSV PREVIOUSLY ACTUATED MORE THAN 1,000,000 TIMES.**

**TABLE I. MEASURED N<sub>2</sub> CONCENTRATIONS**

INJECTION #	MEASURED N <sub>2</sub> CONCENTRATION (PPB)				
	1	2	3	4	5
1000 PPB N <sub>2</sub> IN HELIUM (NEW VALVE)	1000.0	*Calibration*			
1000 PPB N <sub>2</sub> IN HELIUM (USED VALVE)	998.1	999.2	997.4	998.3	998.7
UHP HELIUM (USED VALVE)	0.2	0.1	0.2	0.3	0.2

## DISCUSSION AND CONCLUSION

In this document, results showing the multiple advantages of the PLSV compared to the diaphragm and conical rotary valves were presented. The results acquired using a GC-MS platform show that the dead volume of diaphragm valves can cause sample reinjection. This can be especially problematic when measuring multiple compounds at a low concentration, as this reinjection peak could cause interference with other peaks. Furthermore, due to the flexibility of the diaphragm, pressure-drop effects caused a baseline variation that could also interfere with other peaks and impact the analytical performances. Thanks to the design of the PLSV that has no dead volume and its rigid insert, none of these phenomena were observed with this valve technology. Interestingly, as seen in Figure 6, the baseline was higher when the ELDV-2 was installed, compared to the PLSV, which confirms that the leak integrity of the PLSV is better than purged diaphragm valves. Also, it is known that diaphragms lose flexibility over time, which can cause flow and pressure variations, leading to peak shifting, although this particular effect was not within the scope of the testing results presented above. Therefore, process and continuous GCs that are equipped with diaphragm valves typically require more maintenance compared to those equipped with PLSV.

The PLSV technology also has multiple advantages compared to conical rotary valves. Figure 8 presents chromatograms acquired for trace-level water and H<sub>2</sub>S, which are highly reactive compounds. They are known for sticking to stainless-steel and the use of inert components is essential for their accurate measurement. Surface treatment such as Sulfinert cannot be applied on conical rotary valves, because of the high sealing force that causes treatment peeling after only a few actuations. Here, the PLSV head was Sulfinert-treated and allowed the measurement of these reactive compounds. Thanks to its reduced sealing area and sealing force, surface treatment peeling was not observed, even after thousands of actuations.

The PLSV also showed much better leak integrity compared to the conical rotary valve. This type of valve is typically not used for the analysis of trace and ultra-trace level

permanent gases, as brand-new conical rotary valves have a leak rate in the hundreds of ppb and eventually reach the ppm level after only a few thousand actuations. The results presented in Figure 9 for 700 ppt permanent gases can only be achieved using a valve with excellent leak integrity. Since the unique purge design of the PLSV fully protects against inboard, outboard and cross-ports leaks, nitrogen, oxygen and other impurities from air cannot reach the sample or carrier gas stream, preventing from interference and allowing measurement at such low concentrations. Furthermore, the robustness of the PLSV was also demonstrated by using a valve that was previously actuated more than 1,000,000 times to analyze a sample containing 1000 ppb N<sub>2</sub> in helium and purified helium. The instrument was calibrated using a brand-new PLSV and the results obtained afterwards with the used PLSV were consistent with a leak-tight system. Indeed, as presented in Table I, an average N<sub>2</sub> concentration of 998.3 ppb was measured for the span gas and 0.2 ppb for the purified helium, even after 1,000,000 actuations. Best available information indicates that no other valve technology has been able to demonstrate this level of leak integrity after so many actuations. Furthermore, multiple instruments have been equipped with PLSV on customer sites where the valves have been actuated more than 3,000,000 times and are still providing very accurate results, even for trace-level nitrogen. Table II summarises the key characteristics of the conical rotary, diaphragm, and PLSV valve technologies.

**TABLE II. SUMMARY OF VALVE TECHNOLOGY CHARACTERISTICS**

	<b>CONICAL ROTARY</b>	<b>DIAPHRAGM</b>	<b>PLSV</b>
<b>LIFETIME IN UHP APPLICATIONS</b>	<50,000 Actuations	500,000 – 1,000,000 Actuations	3,000,000+
<b>PRESSURE/FLOW DROP</b>	GOOD	POOR	GOOD
<b>INBOARD/OUTBOARD LEAK INTEGRITY</b>	POOR	GOOD	IMPOSSIBLE
<b>CROSS-PORT LEAK</b>	POOR	GOOD	IMPOSSIBLE
<b>DEAD VOLUME</b>	GOOD (no dead volume)	POOR	GOOD (no dead volume)
<b>INERT TREATMENT</b>	NOT POSSIBLE	POSSIBLE	POSSIBLE
<b>PEAK SHIFTING OVER TIME</b>	NO	YES	NO

In conclusion, the key characteristics of a good chromatographic valve are the long lifetime, constant pressure drop, inboard, outboard and cross-port leak integrity and the absence of dead volume. When measuring reactive species, it is also important that the valve is inerted with a surface treatment for accurate measurements. Finally, stability of the chromatography over time is another important parameter to consider, especially in continuous and process-GCs, which need to operate with minimal maintenance. While conical rotary valves have a constant pressure drop, have no dead volume, and offer

stable chromatography over time, they are limited to less than 50,000 actuations, they offer poor leak integrity and cannot be inerted with surface treatment due to the high sealing force. Diaphragm valves can be used for 500,000 to 1,000,000 actuations with good leak integrity and they can be inerted for measuring reactive species, but the pressure drop is not constant because of the diaphragm flexibility and dead volumes that can cause sample re-injection, and peaks that can shift over time, especially if the valve has not been actuated for a long time. Therefore, there is always a trade-off when choosing between these two types of valves. Thanks to its unique design, the PLSV technology has all the advantages of diaphragm and conical rotary technologies, without any of the drawbacks. Furthermore, considering the negative impacts that leaks can have on the instrumental performance, there are only advantages in using the PLSV for all GC applications, not only for the measurement of trace nitrogen and oxygen UHP gases.

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