

AN-08

PLSV technology – A quantum leap for chromatographic valve



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ABSTRACT

This application note demonstrates the unique characteristics of the Purge Lip Sealing Valve (PLSV) technology for gas chromatography and sample stream selection. The performance is demonstrated from results obtained on a chromatograph designed to measure trace N₂ with a range of 1000 ppb and a limit of detection of 1 ppb.

INTRODUCTION

For almost three decades, we have been involved in the measurement of trace permanent gases for the air separation and electronics industry. We have made multiple technology breakthroughs and designed systems which are currently used by the most renowned companies. Our first innovation was a highly sensitive and selective plasma emission detector in the 90s under the company Contrôle Analytique (KA) followed by high quality chromatographic valves under the Analytical Flow Products (AFP) brand name in the years 2000s. Despite those major technology improvements, there are still many areas of improvements in term of performance and reliability. For that very reason, we have introduced a novel valve design which is a quantum leap in the field.

CHROMATOGRAPHIC VALVES – EXISTING TECHNOLOGIES REVIEW

In chromatography, the ideal valve would have constant pressure/flow drop between the different ports, over its lifetime and across a wide temperature range, no dead/unswept volume, no leak and last over 1,000,000 actuations. Commercial chromatographic valves, which are separated in two categories, do not offer all those characteristics unfortunately. There is always a compromise.

	Conical rotary	Diaphragm	PLSV ¹
Lifetime for UHP application	<50,000	500,000 to 1,000,000 ²	1,000,000+
Pressure/Flow drop	GOOD	POOR	GOOD
Inboard/Outboard integrity	POOR	GOOD	NOT POSSIBLE
Crossport leak	POOR	GOOD	NOT POSSIBLE
Dead volume	GOOD (No dead volume)	POOR	GOOD (No dead volume)
High temperature operation	GOOD	POOR	GOOD

Table 1 – Valve technology characteristics

¹ PLSV: Purged Lip Sealing Valve, ASDevices patent pending technology

² Application dependant

CONICAL ROTARY VALVE



The conical rotary valve is the most widely used valve concept in chromatography. Despite not being a perfect valve, it performs very well 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.

One of its benefits is the constant pressure/flow drop. What we mean by constant pressure/flow drop is that the valve restriction to flow is the same in all ports and all positions and across a wide temperature range. This is important for many applications in order to have a very good baseline stability when valves are actuated and reduces maintenance or fine tuning overtime. Baseline fluctuations can interfere with chromatographic peak and provide inaccurate measurements.

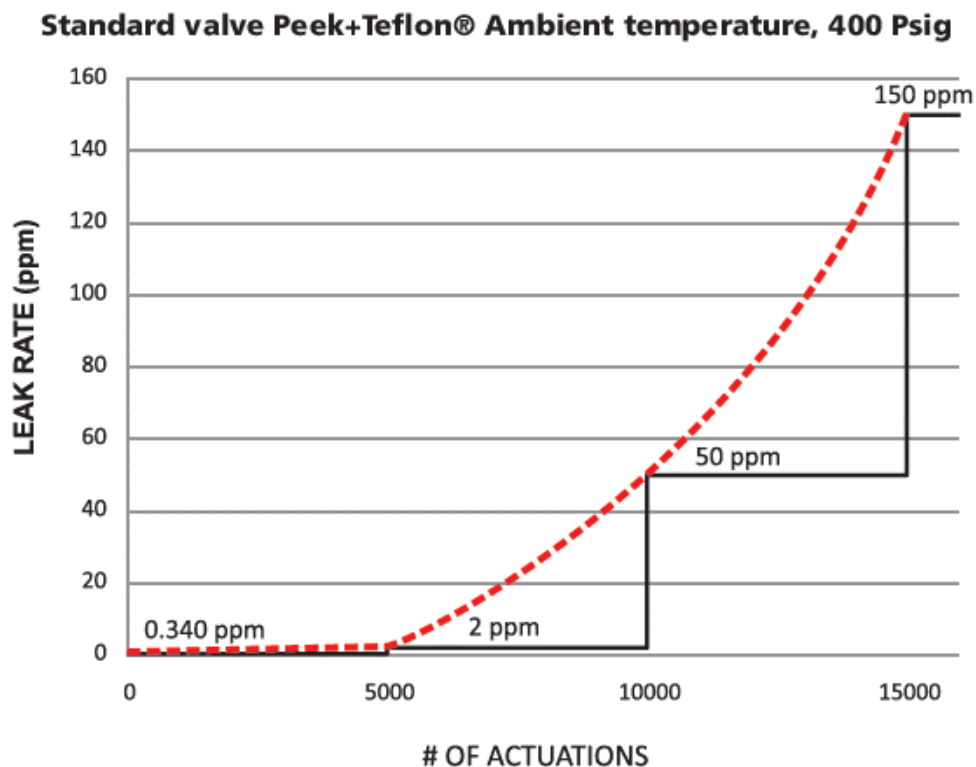


Figure 1 – Typical rotary valve performance

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. The result is a valve that begins to leak after only a few 1000 actuations³ as shown in figure 1.

In order to overcome this problem, design improvements were introduced as shown in Figure 2. This design, which is offered in two different implementations, indeed resolves the inboard/outboard leak issue as it purges the volume around the rotor. However, it does not address the more important issue, crossport leak. The most common crossport leak in chromatography is the sample gas that leaks in the carrier gas. This causes carrier gas contamination and hence detector baseline noise.



Figure 2 – Valco purged rotary valve

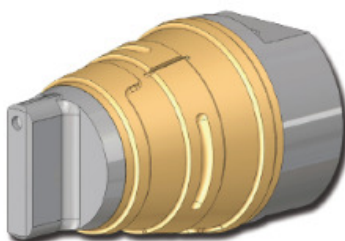


Figure 3 – AFP CLP purged rotor technology

Further improvements were introduced by Analytical Flow Products (AFP). The technology was named the CLP (Figure 3) technology. This design truly addressed the inboard/outboard contamination as well as the cross-port leak problem. The CLP design was a major breakthrough. However, it was still suffering from wearing due to the required sealing force which is inherent to conical rotary valves.

³ Y. Gamache, 2015, AFP Cookbook vol 1.4, p. 71, DR2 – Rotary valves, then and now

DIAPHRAGM VALVE



Diaphragm valves were introduced to resolve many issues associated to the rotary valve. However, the diaphragm valve concept introduced new issues: **pressure/flow drop**, **dead/unswept volume⁴** and **air/sample permeation** through the diaphragm membrane. Similar to rotary valves, diaphragm valves can suffer from inboard/outboard.

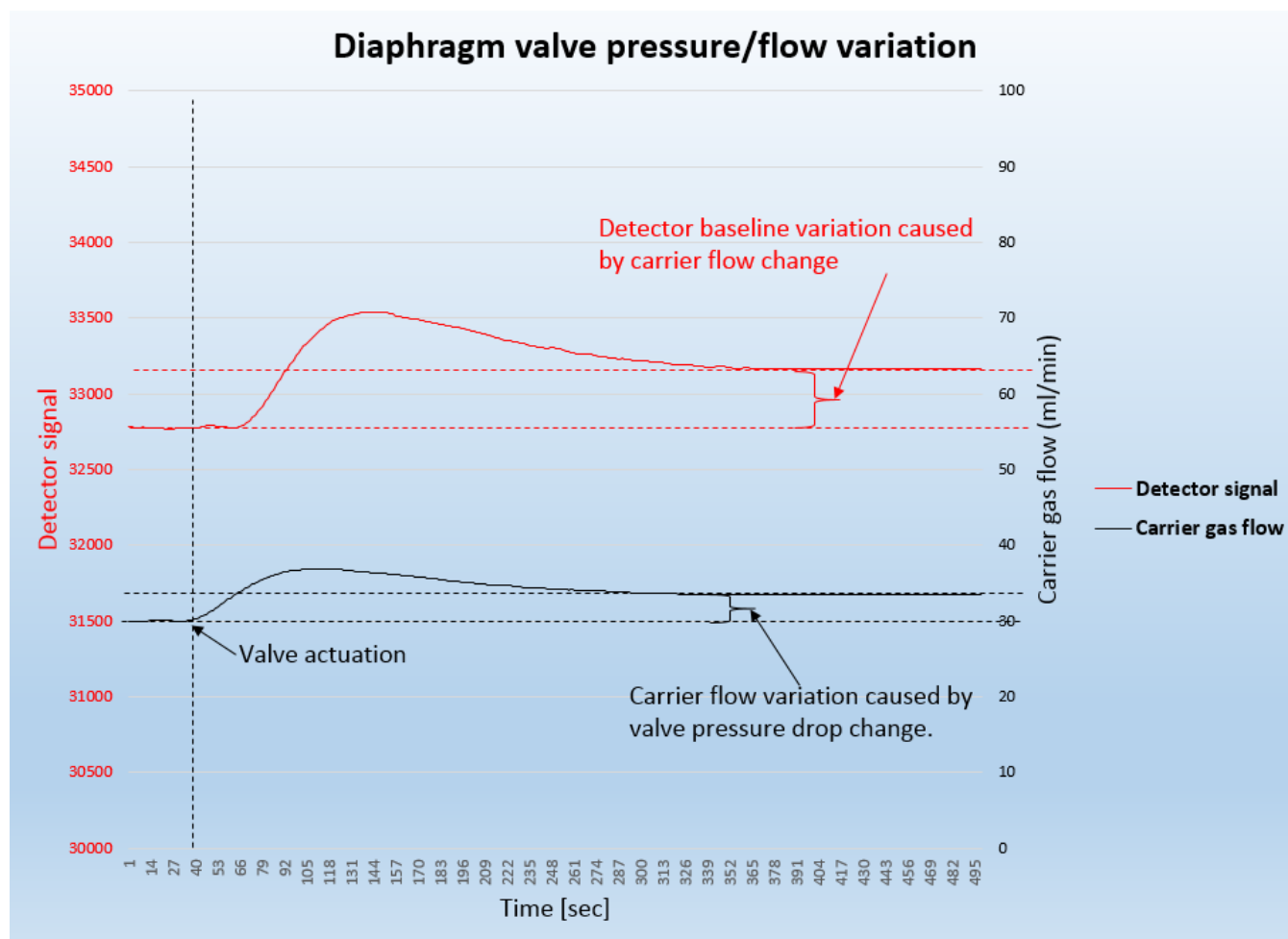


Figure 4 – Diaphragm valve pressure/flow variation

⁴ Y. Gamache, 2015, AFP Cookbook vol 1.4, p. 249, AB-04, Things you should know about GC diaphragm valve

Valve manufacturers have all tried to address the leak integrity and permeation issue. AFP, with its patented purged concept (Figure 5), has addressed the permeation by purging the back of the diaphragm and improved leak integrity by introducing purging grooves. In regards to Valco, it has introduced a purged ring (Figure 6) in order to address the inboard/outboard leak integrity.

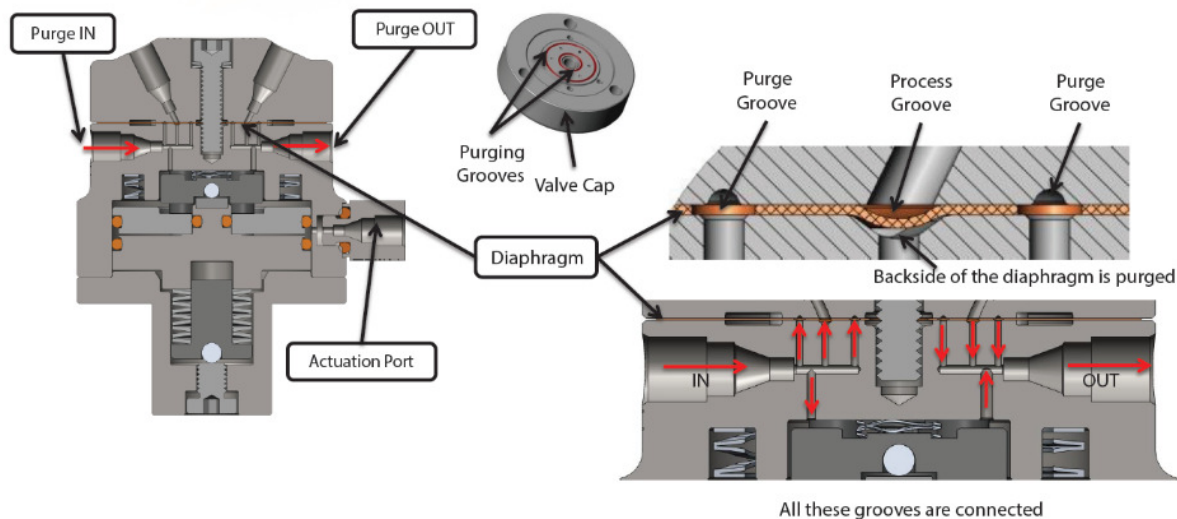


Figure 5 – AFP purge technology



Figure 6 – Valco purge ring

As for the dead/unswept volume, AFP offered its valve with a mixing feature³. Unfortunately, no manufacturer has addressed the fundamental problem of pressure/flow drop which limits the chromatographic performance, especially at trace level measurement and at high temperature. Figure 4 shows the impact of pressure/flow drop variation. In this example, the valve configured in heartcut configuration is activated. The result is a flow variation which results in a detector baseline variation. This variation, when overlapped with chromatographic peaks, impacts the chromatograph performance.

ASDEVICES PURGE LIP SEALING VALVE (PLSV) TECHNOLOGY



The PLSV^{patent pending} concept is the result of many years of experience, frustration and customer feedback in a quest to improve the diaphragm and conical rotary valve concept. This valve concept *combines the best of the rotary and diaphragm valve*. There is no compromise. There is no need to select between rotary or diaphragm. This technology does it all.

The superior performance of the PLSV technology is achieved by its unique insert technology^{patent pending} (figure 7). It offers a reduced surface sealing area, a unique purging groove associated with valve's head pocket (figure 9), soft cushioning concept to make a perfect alignment between the valve head and the insert and a proprietary material treatment process.

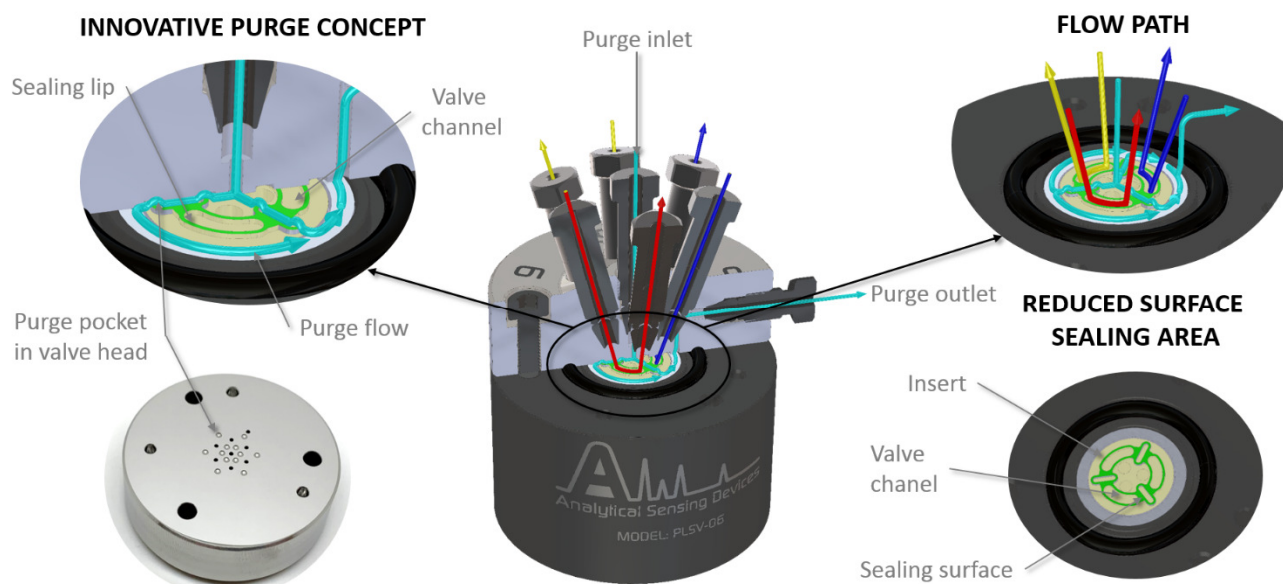


Figure 7 – PLSV valve concept

VALVE WEARING, LEAK INTEGRITY AND LIFETIME

The valve wearing and friction has been reduced by optimising the sealing surface area. The sealing leap size and shape design has been optimised using finite element modeling (FEM) and real life testing. The result is a sealing surface area which is equal to 14% of a standard conical rotary valve.

Furthermore, the insert material is specially treated by a proprietary process in order to improve the surface finish, hardness and creeping. All of those unique characteristics are what makes this performance possible. 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 this technology to be actuated over 1,000,000 times in UHP applications without losing performance.

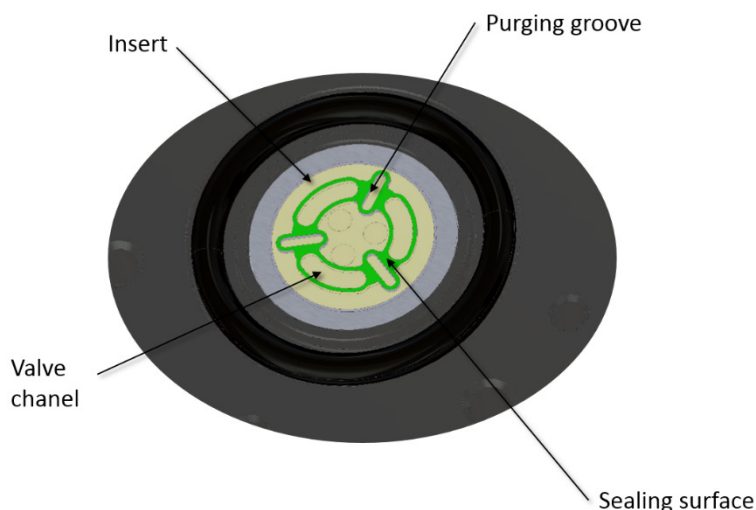


Figure 8 – Typical PEEK insert

The leak integrity performance is achieved by the unique purge concept^{patent pending}. The purging principle (figure 9) involves purging grooves which are located in between two adjacent valve channels and valve head purging pockets which are machined into 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 an inboard/outboard and crossport leaks as the volume around the insert and in between ports is continuously purged.

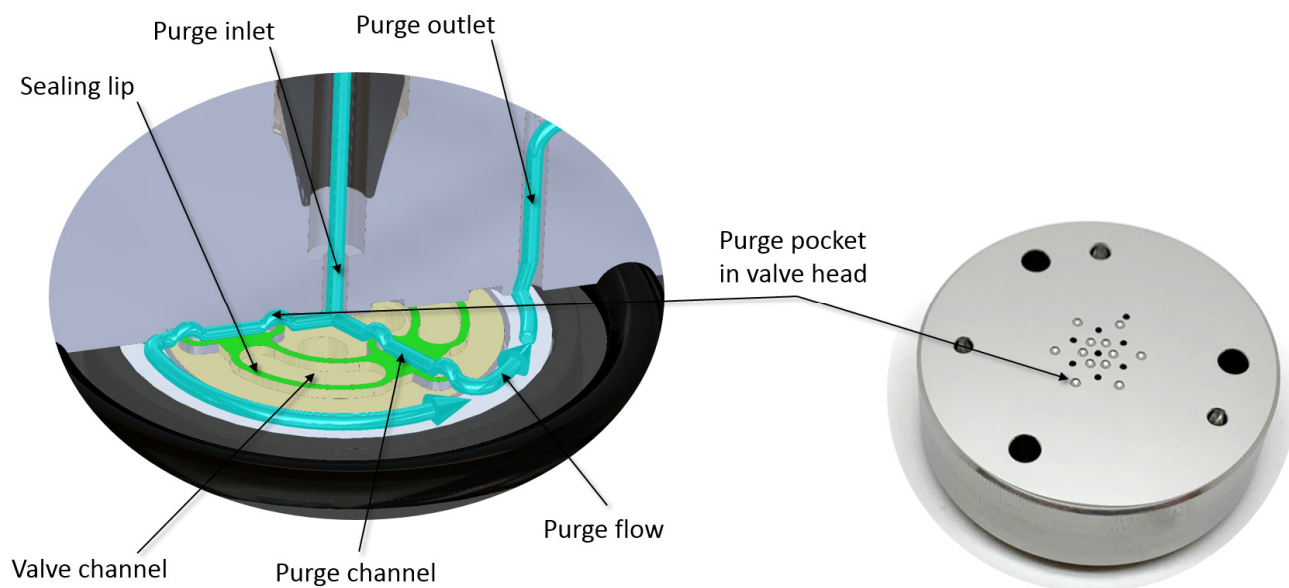
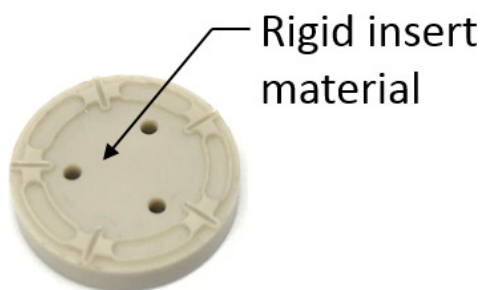


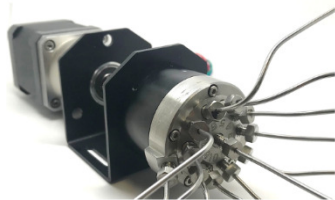
Figure 9 – Purging groove principle

CONSTANT PRESSURE/FLOW DROP



This valve, unlike diaphragm valves, does not suffer from pressure/flow drop issue. This has been made possible by the use of a rigid material similar to a conical rotary valve. Unlike a conical rotary valve, our design does not involve conical surfaces. Only flat surfaces and this is important as they are easier to mechanically match. The pressure/flow drop consequently remains constant.

PLSV TECHNOLOGY AS A SAMPLE STREAM SELECTION SYSTEM



The unique characteristics of this technology makes it perfect to design sample stream selection systems and this for any kind of samples (Figure 10). It could be used for VOC analysis where multiple sorbent traps need to be analysed, for instruments where multiple streams need to be measured such a CQC (Continuous Quality Control) systems in the electronics industry or calibration systems. The valve can be controlled by a pneumatic actuator or by a high precision stepper motor with embedded position encoder for enhanced reliability.

The characteristics, which are beneficial to chromatography such as lifetime, constant pressure/flow drop, ability to work across a wide temperature range and high leak integrity are all the requirements for the best sample stream selection system.

**For more information on using the PLSV technology for sampling system, read our AN-09.*

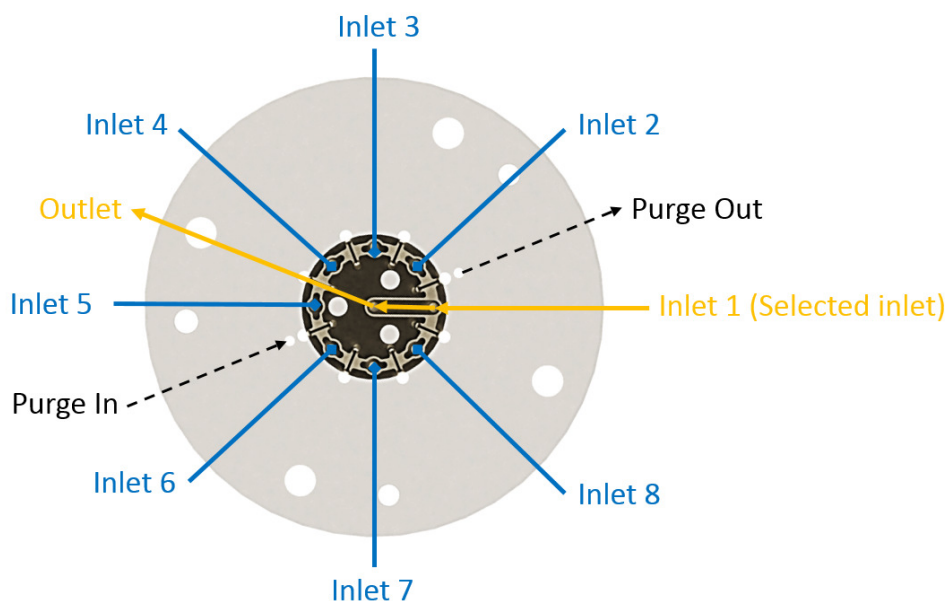


Figure 10 – PLSV technology for sample stream selection

PLSV TECHNOLOGY IN THE REAL WORLD



This section shows the result obtained with the PLSV technology for a UHP application which consists of measuring N_2 at ppb level in H_2 . The technology is not only used for the chromatography, but also as a sample stream selection system. This chromatographic application has been selected as any valve malfunction would drastically impact the measurement. Ambient air contains 80% N_2 , so any inboard leak would impact the trace N_2 measurement. H_2 is a very small molecule that leaks in any small scratches. Consequently, it would leak in any crossport leak and cause noise and baseline problem.

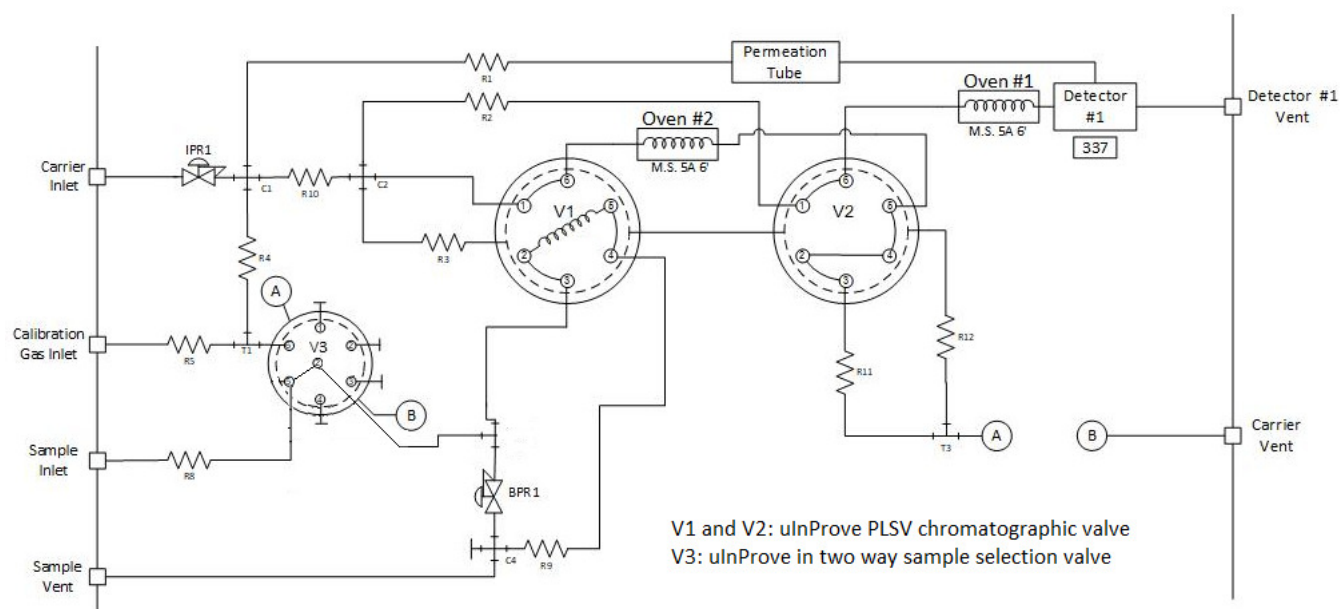


Figure 11 – Chromatograph piping schematic

In regards to calibration system, a uInProve selection valve has been used to switch between the process gas and calibration gas. As the measurement range is 1000 ppb, the leak integrity is extremely important. This valve technology is consequently perfect for the job.

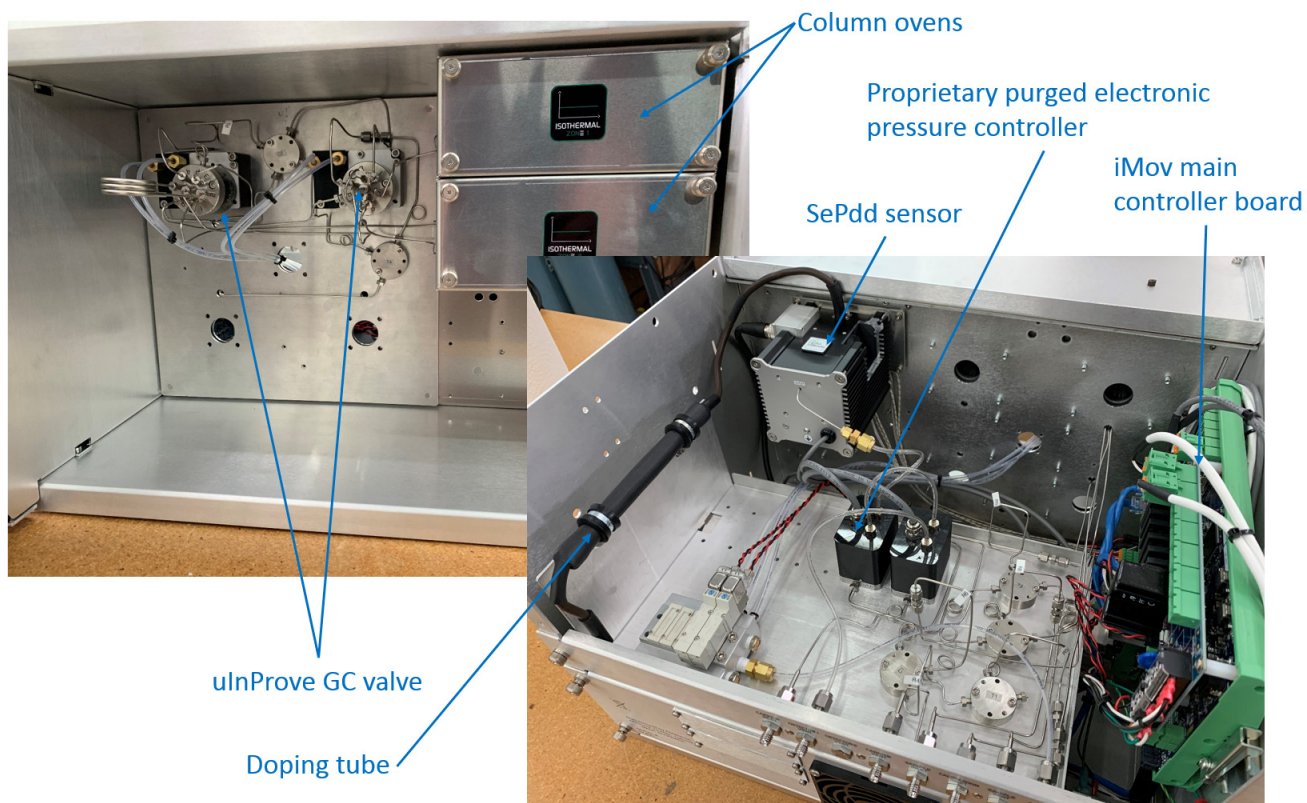


Figure 12 – Chromatograph configured for N₂ analysis

The chromatograph uses ASDevices iMov platform^{patent pending} and SePdd sensing technology^{patent pending} and of course, the PLSV valve technology (Figure 12). A heartcut technique has been implemented to separate the N₂ impurity from the sample matrix and to also prove that no baseline fluctuation occurs when the valve is actuated. It demonstrates the baseline stability. Figure 13 shows that no baseline fluctuation occurs during the analysis and table 2 shows the chromatographic performance as well as leak integrity performance of the sample stream selection valve. For that demonstration, the valve was submitted to accelerated life testing by actuating the valves every 5 seconds for a prolonged period of time in order to exceed 1,000,000 actuations.

TEST RESULTS AFTER 1,000,000 ACTUATIONS

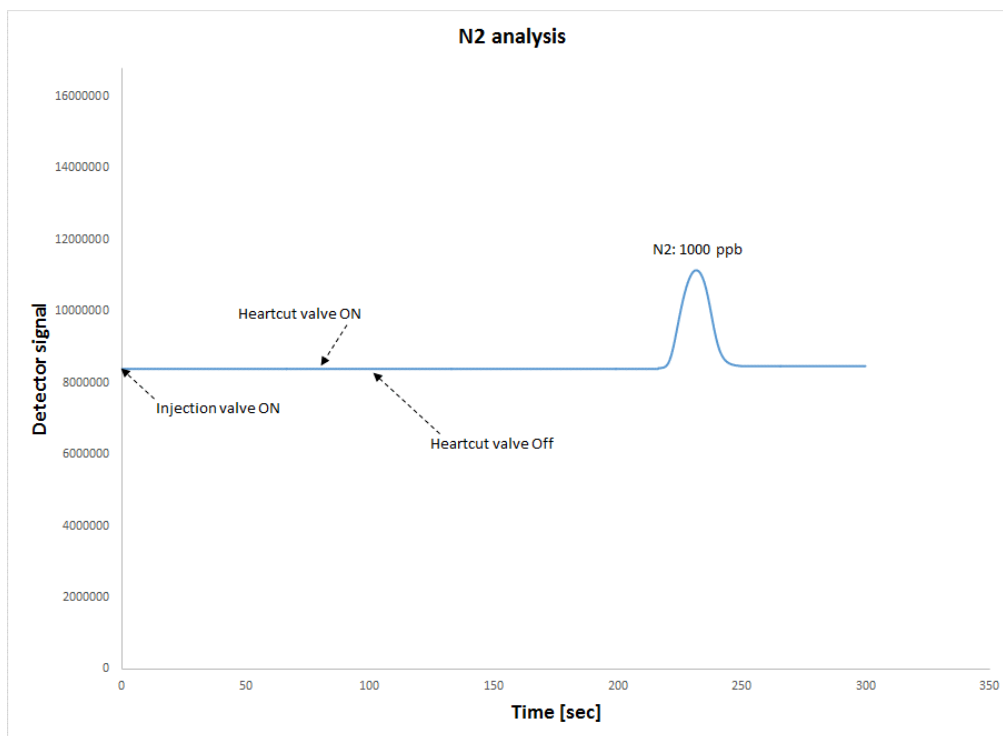


Figure 13 – N₂ analysis

Sample gas	N ₂ (ppb)	Comment
1000 ppb N ₂ in He	998.1	Sample stream selection valve on calibration gas position
1000 ppb N ₂ in He	999.2	
1000 ppb N ₂ in He	997.4	
1000 ppb N ₂ in He	998.3	
1000 ppb N ₂ in He	998.7	
9N ⁵ helium	0.2	Sample stream selection valve on process gas position
9N helium	0.1	
9N helium	0.2	
9N helium	0.3	
9N helium	0.2	

Table 2 – Validation chromatograph

This is just one example where this valve technology can be used. As described in this application note, this technology is a replacement for all existing valve technologies and can be used for a broad range of applications such as VOC analysis, hydrocarbon analysis, sulfur analysis, etc...

⁵ 9N helium is obtained by purifying a 5N grade helium with a ASDevelop ASDPure purifier

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