AN-10

PLSV – Improved valve technology for ultra-trace sulfur analysis

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ABSTRACT

Ultra-trace sulfur analysis is known to be a difficult measurement. Special consideration need to be taken in regards to the inertness of all inert parts. For that reason, special coating technologies were developed. A component that has suffer from poor performance with inert coating is the chromatographic valve. This document explains the benefits of the PLSV valve technology.

INTRODUCTION

The requirements for the limit of detection of sulfur compounds is getting lower and lower. For example, the standard for Hydrogen fuel quality for Polymer Electrolyte Fuel Cells in road vehicle is asking for a total sulfur measurement range of 4 ppb [1]. At such level, special care must be taken in order to make sure the sulfur compounds reaches the detector. All wetted components consequently need to be inerted with special coatings.

An area that has posed problem is the inert coating of chromatographic valves which are necessary in order to inject the sample volume. The inert coating deposited on conical rotary valve wears very rapidly leaving the diaphragm valve as the only solution. Unfortunately, the diaphragm valve technology has other issues such as dead volume and pressure drop especially with capillary columns which are very often necessary in order speciate all sulfur compounds.

This is now a story of the past with the uInProve PLSV technology for trace sulfur analysis.

LIMITATION OF EXISTING TECHNOLOGIES

The conical rotary valve is a well-known technology and has been around for many decades. Unfortunately, this valve technology suffers from wearing [2] and consequently cross port and inboard leaks which are problematic especially with ultra-sensitive detectors such as Epd, mass-spectrometer, PDHID, DID, PED, etc. The wearing is due to the friction between the stator and the rotor. The force involved to seal a conical rotary valve is high due to the surface area involved and the fact that two conical parts, rotor and stator, need to be properly matched in order to achieve sufficient sealing. This friction poses a technical problem for sulfur analysis. The inert coating, which is deposited on the valve stator surface, is too soft and peals from the rotor over time, generating particulates which damages the valve and other components such as the chromatographic columns.

Due to that problem, many chromatographers have migrated to the diaphragm valve technology. As there is no friction in this type of valve, the deposited inert material treatment works well. Unfortunately, the diaphragm valve is not a perfect technology either. It has dead volumes and inconsistent pressure drop between the two valve operating states[3].

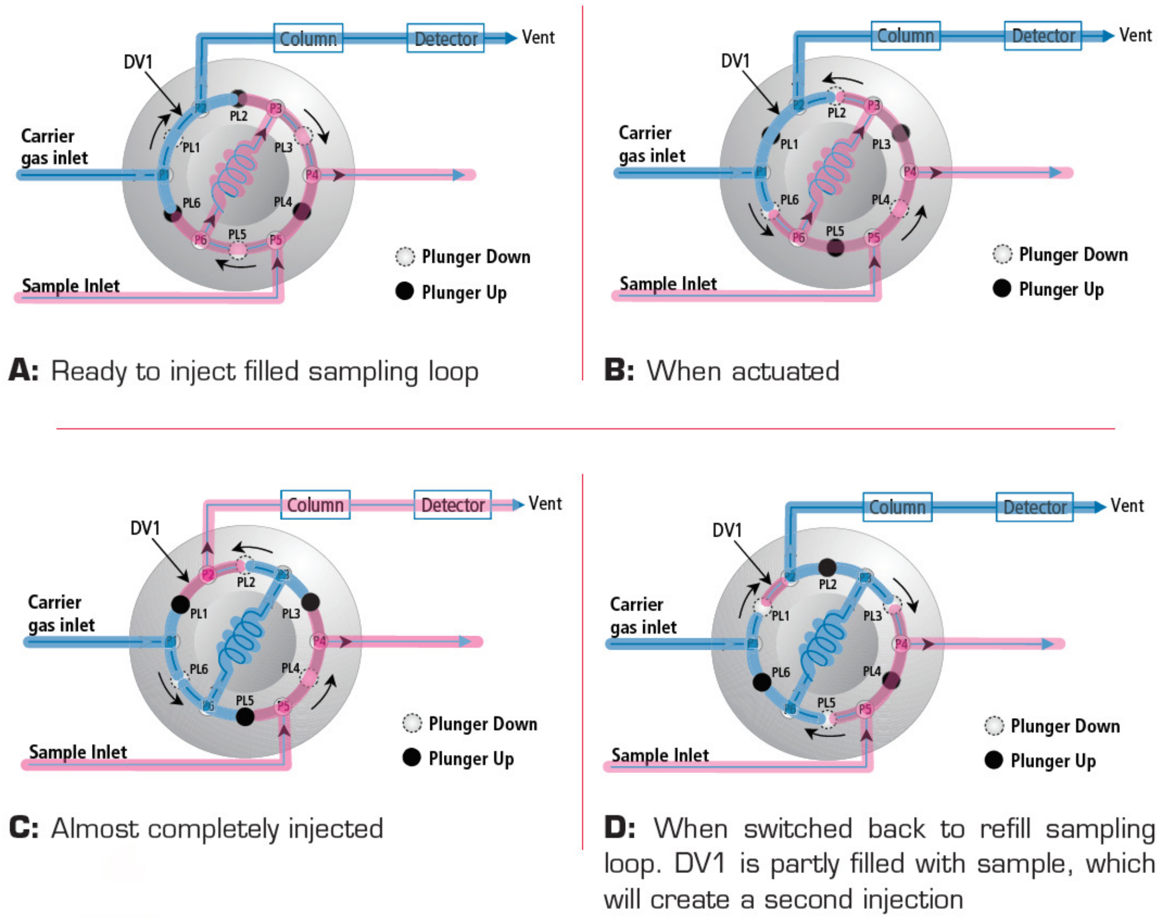


Figure 1 – Diaphragm valve dead volume issue [3]

The dead volume issue of the diaphragm valve is represented in figure 1. This dead volume is located between the plungers and the valve ports. The result is a double injection which is clearly shown in figure 2. The two small O_2 and N_2 peaks are caused by the reinjection of the dead volume which is not ideal, especially when dealing with small sample loops and ultra-trace level measurement [3]. In regards to port pressure drop, this is down to the elastic nature of the diaphragm valve. 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 and hence variations in peak elution time and baseline. So despite the fact that it is possible to coat a diaphragm valve for ultra-trace sulfur analysis, the performance is limited by design!

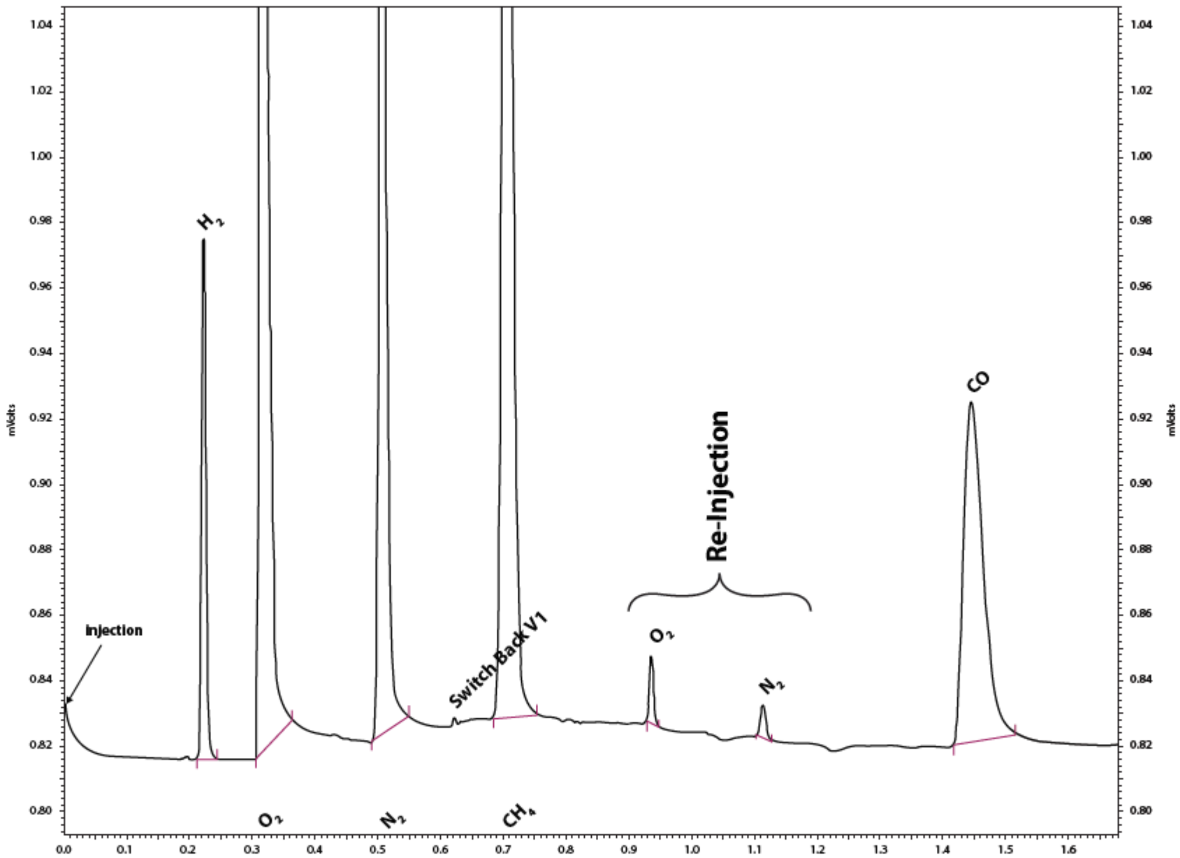
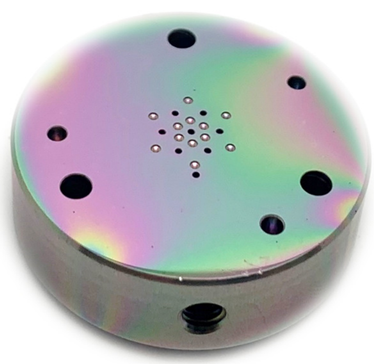


Figure 2 – Diaphragm valve dead volume re-injection issue

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.



Due to the reduced sealing force compared to a standard conical rotary valve (figure 3) which results in low friction, it is consequently possible to coat the valve with an inert layer and measure ultra-trace levels of sulfurs without reliability issues. The reduced sealing force is down to the reduced surface sealing area which is 14% of a standard conical rotary valve. This valve technology consequently allows GC system designers to have all wetted parts (tubes, fittings, valves, detectors) with an inert coating. Previously, many integrators were making a compromise on the valve due to the previously mentioned issues. With the PLSV, there is now no need to make that compromise.

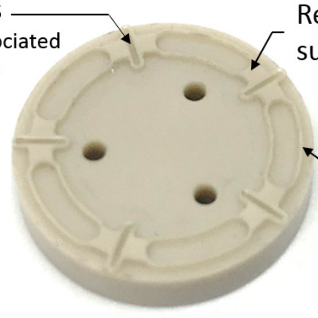


Figure 3 – PLSV insert

Also, this valve technology does not suffer from dead volume issue like the diaphragm valve. The valve insert is designed in rigid material (figure 3 and the machined groove, which is used to connect the ports, is always the same dimension regardless of the position.

For a complete technology review of the PLSV technology, read our AN-08 document.

MEASURING ULTRA-TRACE SULFUR WITH PLSV TECHNOLOGY

Measuring ultra-trace sulfur in air is an application that is known to be difficult. The purpose of this measurement is to monitor sulfur emissions in air emitted by industrial processes. This is what is called fence line monitoring. For such application, an air sample is collected on a sorbent tube and released into a gas chromatograph for quantification. With a 0.5 ppb limit of detection requirement, it is obvious that all wetted parts need to be inerted.

This application shows all the benefits of the PLSV[patent pending] valve technology for ultra-trace sulfur analysis. The method is based on an Agilent 30 meter GasPro column with an argon carrier gas flow of 3 ml/min. The sample loop used is 62 ul. ASDevices Epd[patent pending] sensing technology has been used as a replacement for the traditional FPD/PFPD detector and bulky an expensive SCD. The Epd is more compact and cost effective. It also only requires in this case argon as carrier gas. No other supporting gases such as hydrogen fuel or oxygen are required.

Capillary column, small sampling loop and ultra-trace level components are all parameters that make this measurement difficult. The chromatogram in figure 4 and figure 5 demonstrates the performance obtained with this chromatographic setup. It demonstrates the ultra-trace level analysis of sulfur and nice chromatographic peak shape of the H_2S peak.

Figure 4 represents the power of ASDevices Peak Remodeling Algorithm[patent pending]. This technology uses proprietary advanced processing algorithm based on neural network and frequency domain analysis to improve peak shape, reduce noise and improve performance.

Figure 5 is presented in order to demonstrate that even without processing, the peak symmetry for trace sulfur is good due to the inert coating.

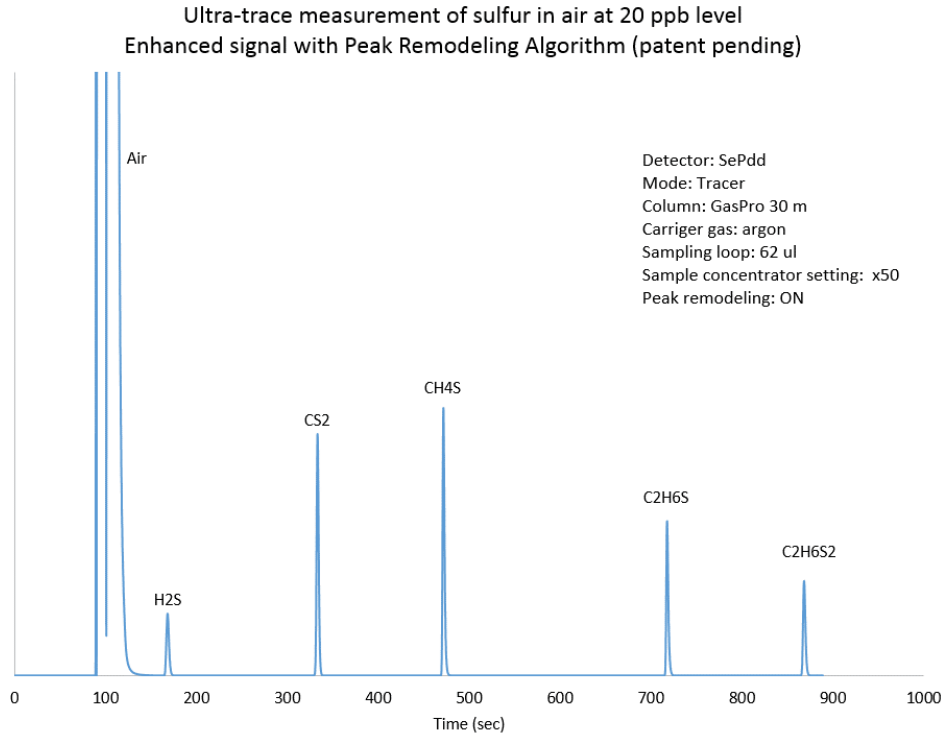


Figure 4 –Chromatogram Sulfur in air with Peak Remodeling Algorithm[patent pending]

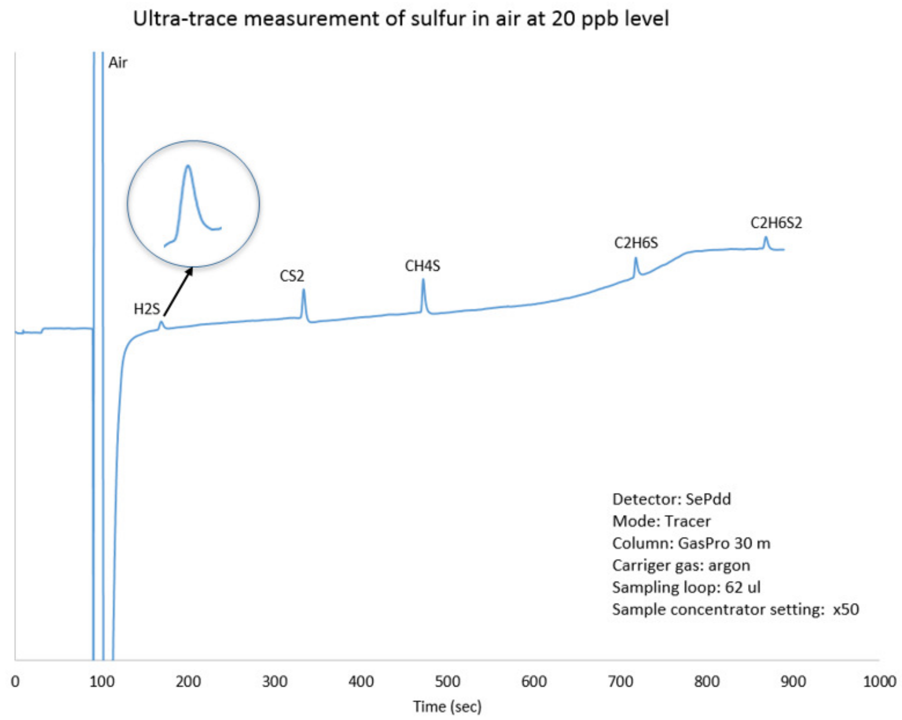


Figure 5 – Raw chromatogram Sulfur in air

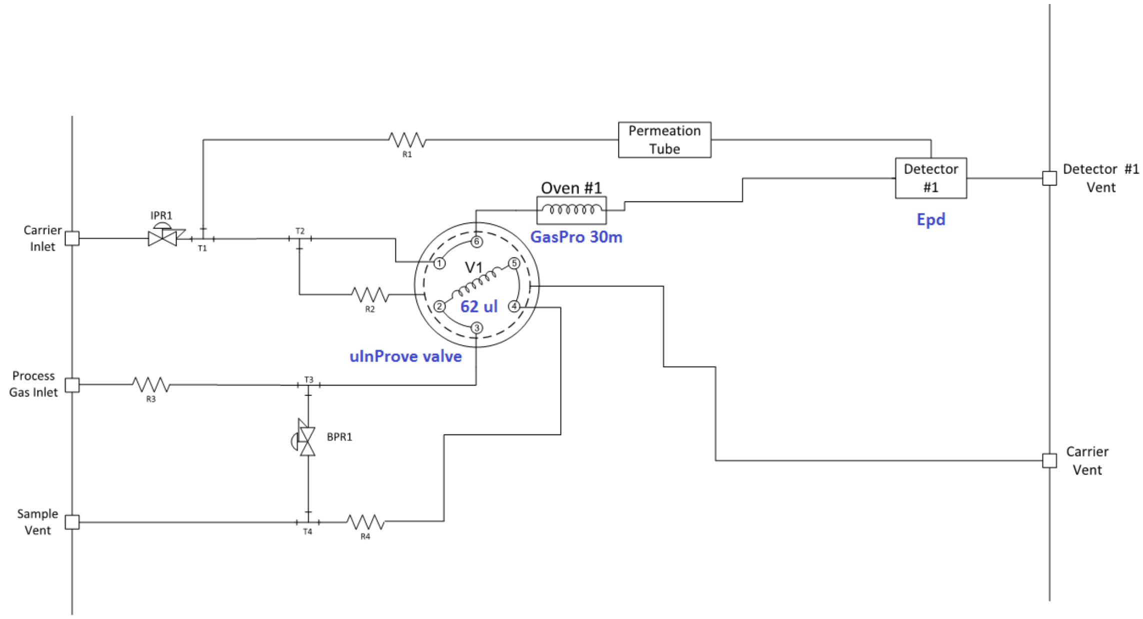


Figure 6 – Chromatographic configuration

CONCLUSION

In summary, the PLSV technology unique design features resolve the known problems associated with other technologies such as conical rotary and diaphragm valves. The PLSV allows the valve head to be inerted withour suffering from early failure and does not suffer from dead volume and pressure drop like the diaphragm valve. It is consequently a major breakthrough for ultra-trace sulfur analysis and many other applications.

REFERENCES

[1] U.S. Department of Energy, Hydrogen Fuel Quality Specifications for Fuel Cells in Road Vehicles, 2016.

[2] A. Lamontagne and Y. Gamache, AN-08 PLSV Technology – A Quantum Leap for Chromatographic Valve.

[3] Y. Gamaches, AB-04 – Things you should know about GC Diaphragm valves, AFP Cookbook vol. 1.4