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Supercritical Fluid Chromatography - The role of pump seals

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Liquid and supercritical fluid chromatography are now mainstay technologies in most analytical laboratories. These technologies are centred on the column and the stationary phase, which ultimately drive the separation, however this is not the most expensive component of the separation system. The most expensive component of a typical system are the pumps, which are designed to deliver a very accurate flow over a range of volumetric flow rates within a certain pressure range. The pumping systems do not differ between HPLC and SFC substantially, although there may be some modifications to ensure that the supercritical fluid is not in a gaseous state when the system is started.

There are a few designs of SFC/HPLC pumps on the market but all of them work on a piston moving through a seal, Figure 1, with the seal being a critical component to ensure that liquid is delivered to the correct place. This article will look into a little more detail into how a seal works and also what observations can be made as the seal begins to wear.

The action of the piston displaces a volume of liquid onto the column via a series of connectors and ultimately to the detector. The use of check valves ensures that the delivery of the fluid is in the correct direction i.e. onto the column and not into the mobile phase reservoirs. The design of the seal, and the material that are used for the seal ensures the optimum performance of the pumping system. Many analysts will not give the seal a second glance and will replace as a matter of course when a particular observation is occurring. However, since it can be the cause of a lot of angst it is worthwhile determining how the seal works, why it fails and what can be done to increase the operational lifetime of the seal.

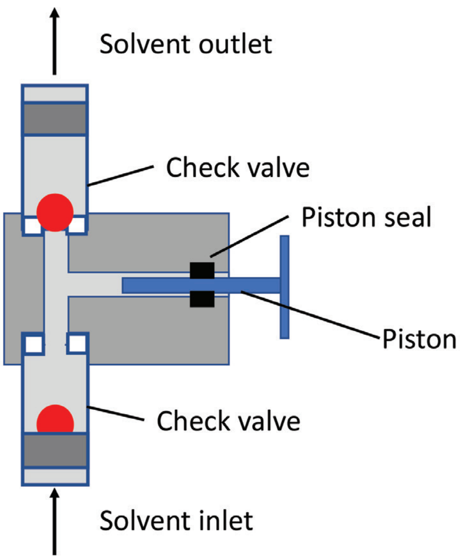

Figure 1: The general schematic design of a piston and pump seal

A seal fails when it is not fully in contact with the piston, for the reasons explained below, which creates a gap for the liquid to leak through. The analyst will see a variety of different issues, from fluid leaking from the pump, to lower than anticipated back pressure readings on the system, or an increase in the retention times, but not in retention factors. For analytical chromatography systems where the flow is reasonably high the leak can normally be seen as a gradual build-up of residual mobile phase around the pump head, or possibly even salt deposits. If dealing with capillary chromatography where the flow is very low, it may not be feasible to see a build-up of liquid, as the rate of evaporation may well match the rate of leakage. The use of tissues can potentially highlight some leaks with the system, however monitoring of the pressure may be a better troubleshooting aid. When the mobile phase is not a liquid, and instead is a gas at room temperature and at atmospheric pressure, as in SFC, this presents even bigger challenges, and in this scenario monitoring of the back pressure will give a good indication if the fluid delivery system is working as it should be.

It should be noted at this point, however, that a leak does not have to occur at a pump seal, and a systematic approach should be taken to identify where the leak is by monitoring the pressure at various components of the chromatographic system. This can be achieved by gradually removing components from the fluidic flow in HPLC, unfortunately the same approach cannot be used in SFC due to the depressurisation of the mobile phase into a gas.

It is thus important that the pump seal is in full contact with the piston, throughout all of the motion of the piston, to ensure that the mobile phase fluid does not leak [1]. This then raises an interesting question, since clearly it is possible for the piston to move through the seal, so how is it then possible that the fluid does not move through with the piston? The answer to this question is that the sealing process isn't perfect, and indeed a thin film of liquid (mobile phase) remains on the piston surface. This liquid flow is very low indeed and so undetectable however it plays an important role in lubricating the interface between the seal and the piston. This ultimately reduces the wear on the seal. Running a pump with no liquid in the lines will create a lot of friction between the seal and the piston, which will greatly affect the lifetime of the seal. It is thus important for this reason not to run pumps without any liquid. When the mobile phase exists as a gas at standard temperatures and pressures, such as carbon dioxide, this has the potential to cause significant issues with the longevity of pump seals.

The use of involatile buffers, or buffers at high concentrations can result in a degree of precipitation occurring of salt crystals. If this occurs within the film between the seal and the piston then this will cause increased wear and tear on both the piston and the seal. The seal is made of a softer material and a build-up of precipitated salts will cause an increase in the rate of deterioration of the pump seal. If involatile salts or high salt concentrations do have to be used for an assay it is highly recommended that the pumps are flushed with water to ensure that there is no build-up of precipitation that would cause issues with the pump seal. Although this may not be directly applicable to SFC, it is useful information to have, as some commercially available SFC systems can also be run as HPLC systems.

The pump piston is made of a very hard chemically inert substance, typically sapphire or a ceramic material, and this ensures that an accurate displacement volume can be maintained and also helps with the sealing process, as well as clearly making the longevity of the pumping system better. The piston also has to be unreactive to the wide range of solvents and pHs that are typically used in HPLC and SFC. The pump seal is made of a polymer, with the polymer having a wide range of solvent compatibility as well as mechanical stability. Black pump seals, which are probably the most commonly used, are made from graphite filled PTFE and will have a spring inserted, see Figure 2. Another type of seal is the yellow or clear seals which are made of ultra-high molecular weight polyethylene. The colour comes from the addition of a yellow dye. For aqueous-type eluents the yellow seal will give a dramatically longer seal life, however the dye may cause some problems with high sensitivity detectors. The yellow seals will typically also operate well above 10,000 psi, although it should be noted that the temperature range is only up to 80°C compared to the black seals which go up to 315°C.

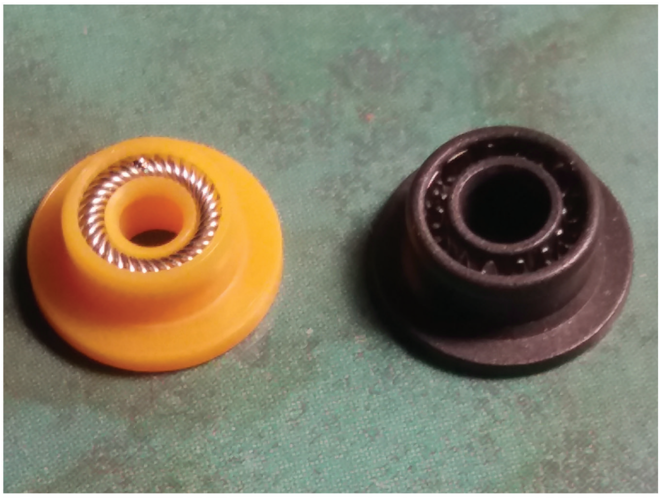

Figure 2: Two common pump seals, a high molecular weight polyethylene for UHPLC and a PTFE filled graphite for lower pressure.

The spring is also referred to as an energiser and is there to ensure that there is pressure placed on sealing face of the pump seal at all times [2]. At high pressures the solvent will push against the seal causing it to push against the piston, however at lower pressures (typically less than 100 psi) this may not occur and so the spring ensures that a seal is maintained even at low pressures. The term energise is often used when discussing the state of a seal at elevated pressures. When considering the typical operation of a chromatography system, there will be start/stop conditions where the system is at low or zero pressure. If the seal allows some amount of leakage at low pressure, it becomes possible for that leakage level to increase as the pressure builds, since the seal will not be correctly energised. This phenomenon is called 'blow-by'. Once it occurs in a system, it's difficult to get the seal to seat and seal correctly. When using SFC or HPLC pumps this is very much the manner in which these systems are operated. The spring therefore ensures that it is possible to turn the pumps on and off without causing blow-by. For pumps operating at high pressures, it is critical to ensure that the pump seal is seated correctly on installation, as it is very difficult to correct for any misalignment when the pump is in operation.

The spring material (typically Hastelloy) is inert to a wide range of solvents and for standard systems it will compromise a canted coil spring. The canted (slanted) coil, Figure 3, spring offers some very interesting properties that other springs don't display. Once the canted coil spring begins to be deflected, due to external pressures being exerted on it, it has a relatively flat force curve in the middle of its travel, which allows for a consistent load over a very broad deflection range. This spring type is also resistant to damage unless it's stretched, which in the confines of an SFC or HPLC pump is not realistic. Unlike other types of springs which can be yielded when over-compressed, the canted coil is almost impervious to this. A hard stop will be reached once the coils are "butted" preserving the spring functionality. Another key factor is the ability to control the load where friction forces need to be kept to a minimum. As the seal wears, with a relatively flat load curve, those friction forces will remain at the desired level throughout the life of the seal.

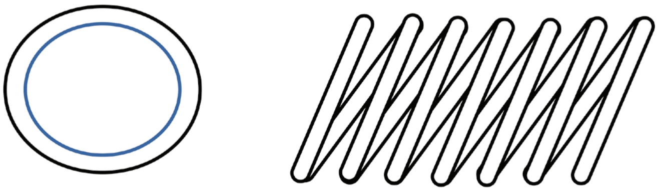

Figure 3: Picture of a canted or slanted spring.

The type of seal material used is important to avoid the seal swelling during operation. Thus, the PTFE seals will swell slightly in THF, and if the user is alternating between THF and methanol water mobile phases this will cause issues with the seal lifetime. As the seal wears very small amounts of the seal may erode due to the frictional forces present during the pumping process. Ideally these should be washed away from the piston to avoid further damage to either the seal or possibly the piston, or possibly blocking the check valves. It is therefore recommended that a seal wash is used. This is simply a flow of liquid that removes debris from the low pressure part of the pump system, thus extending lifetime of the seal.

The installation of pump seals is very important as the initial seal may well define the future operation of the pump, as was described previously. In this case it is important to follow the manufacturers instructions, removing very carefully the old seal, washing with a suitable solvent to remove any debris from the piston and the housing, and then making sure that the new seal is correctly seated, to ensure that blow-by does not occur.

Conclusion

Pump seals can seem to be a trivial component with the fluidics of a pump delivery system. They are small compared to other components, and most of the time are not visible to the separation scientist. However, the use of pump seals in HPLC and SFC is ubiquitous and without these components modern separation science would be very different. This article has highlighted how to identify if there is a potential problem with the seals and finally how to look after the seals from the installation to the general operational care of them when in use. Separation science has proved itself to be critical in aiding mankind develop new drugs, investigate the possibilities of life in far off worlds and determine our very well being. There are several components that are needed for this technology to work successfully and without doubt one of the most understated is the humble pump seal.

References

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2. https://www.balseal.com/seal/static?gclid=CjwKCAjwgISIBhBfEiwALE19SZogIutVGwj6CsyH6n9UfdojwRJGp7qaKY0BwYczSmiW6BQBytN49RoCKfsQAvD_BwE