Chromacol Vial Septa Selection.

For Autosamplers

- ***Sealing of Autosampler vials***

The material used for sealing the sample within the vial is often overlooked as a part of the analytical process. It can have a significant effect on the overall performance of the system.

Sealed 2-SV vial with insert

- ***Evaporation and Sample Loss***

Without effective seals the loss of volatile components from any mixture will affect the precision of results. Especially important with samples presented for GC analysis

- ***Septa material: -***

The compatibility of any solvent with the seal has to be considered. Although most septa have a protective layer strong solvents can affect all the flexible elastomers.

- ***Cap and Septa combinations***

The seals have to be held in place the type of closure will have some effect on the seal integrity.

- ***Piercing needles***

The type of needle used to pierce the seal during sampling can physically damage seals and produce unwanted fragments of material that can block connecting tubing and contaminate samples.

Replacement syringe for HP GC autosampler

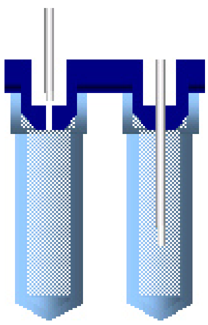
- ***Thickness***

Most vial septa thickness is measured in mm. The thicker seals give improved resealability. Most caps will take septa within a narrow range of thickness. Too thick a seal may give problems with cap fit.

Septa Hardness

- The hardness testing of plastics is most commonly measured by the Shore (Durometer) test. This method measures the resistance of plastics toward indentation and provides an empirical hardness value.

- Shore Hardness, is the preferred method for rubbers/elastomers and is also commonly used for 'softer' plastics such as polyolefins, fluoropolymers, and vinyl.
- This is measured using either the Shore A or Shore D scale. The Shore A scale is used for 'softer' rubbers while the Shore D scale is used for 'harder' ones. Most septa hardness values are stated in Shore A. The exception is that some PTFE and PE hardness is stated as Shore D.
- The results obtained from this test are a useful measure of relative resistance to piercing of various grades of polymers. This gives guidance on the type of needle that will penetrate the seal and whether thinner gauge needles may be used.



Silicone mat piercing

Penetration Force

- The force required to pierce any septum will also be affected by the thickness of the seal and the type of needle. Independent studies have shown that silicone septa are more easily pierced than chlorobutyl or butyl septa of similar hardness.

Elastomeric materials

The materials used in autosampler seals are selected for their ability to seal the liquid within the vial and their chemical resistance.

Rubbers of different types and compositions are the elastomers of choice for most applications. Reference may be made to a number of rubber types.

- Natural Rubber: - Natural cis-polyisoprene. Made partly from natural latex. Has a random structure. Usually red or red-orange in colour. Hardness is dependent on the degree of cross-linking that is formed by the vulcanization process. This introduces sulphur as the cross-linking agent. Harder versions may have higher sulphur content.
- Silicone rubber: - polysiloxanes are formed with silicone chains replacing the carbon chains of other natural and synthetic rubbers. Has high temperature stability so suitable for headspace applications and can be sterilized by autoclaving. It is softer than most natural or synthetic rubbers and has excellent resealing properties.
- Chlorobutyl rubber: -Neoprene, used widely for bungs and stoppers. The presence of chlorine limits its use with ECD detectors but it has excellent chemical resistance.
- Butyl rubber: - (Isombutylene-isoprene copolymer). A synthetic rubber with good chemical resistance.

Elastomeric Fluoropolymers

- Examples are Kel-F®, Viton®, Kalrez®. Excellent resistance to chemicals including strong oxidizing agents but more expensive and formulations are harder than all rubbers.

Chromacol Seal Types

Seal Material	Shore Hardness	Thickness	Seal Material	Shore Hardness	Thickness
–V1 Viton®	62	1mm	**–ST3 Light Blue Silicone/ PTFE**	45	3mm
			–ST3HT Red Silicone/ PTFE	45	3mm
–AC7 Natural Rubber/PTFE	60	1mm	**–ST2 White Silicone/Red PTFE**	57	2mm
–8RT1 Natural Rubber/PTFE	58	1mm	**–ST18 White Silicone/Red PTFE**	57	1.8mm
–CBT1 Chlorobutyl/PTFE	52	1mm	**–ST15 White Silicone/Red PTFE**	57	1.5mm
–CBT3 Chlorobutyl/PTFE	52	3mm	**–ST1 White Silicone/Red PTFE**	57	1mm
–6RT1/AC6 Natural Rubber/PTFE	38	1mm	**–ST14 Blue Silicone/PTFE**	50	1.4mm
–B3P Grey Butyl Plug	52	3mm	**–ST101 Blue Silicone/PTFE**	30	1mm
			–ST143 White Silicone/PTFE	20	1.4mm
–TST1 Red PTFE/White Silicone/Red PTFE	57	1mm	**–ST144 Blue Silicone/Red PTFE**	20	1.4mm

The importance of PTFE

- PTFE layers protect the majority of rubber seals as the PTFE acts as a chemically resistant barrier against chemical attack.
- Making a sandwich of silicone rubber between two layers of PTFE produces a seal extremely resistant to “coring” from open ended piercing needles or probes.
- PTFE seals give excellent resistance to chemical attack but do not reseal after piercing. This makes them unsuitable for applications requiring multiple standard injections.

Non-elastomeric plugs.

Polypropylene, Polyethylene and PTFE are use to make a range of single use plugs and caps. These do not reseal and will lose solvent if left after injection.

Chromacol Product Guide

Technical Challenges

Coring:-

This is usually caused by the action of the autosampler-piercing needle. As the needle descends it should normally cleanly cut the top of the elastomer, force its way through the seal and exit through the protective PTFE layer. It then enters the sample before starting to extract the liquid injection volume.

- The needle does not enter correctly and slices the elastomer.
- The slice may either enter the needle orifice or be pushed down into the sample
- The result is a blockage of the sample path leading to under delivery of sample.
- If fragments reach the sample the analysis will show a contamination peak.

Some auto samplers are more prone to this phenomenon than others. Conical finish needles are more likely to core. Side entry needles are less prone to the problem. Softer seals are more likely to be affected.

Needle Types

Solutions

There are a number of ways to reduce the incidence of coring.

- Make sure the vial is not over crimped or screw caps are not over tightened.
- Make sure that the syringe needle is of the correct type and is not damaged. Even a slight nick on the tip may start the process.
- Use sandwich septa with two layers of PTFE enclosing the softer elastomer.
- Consider a pre-slit septa if the problem persists.

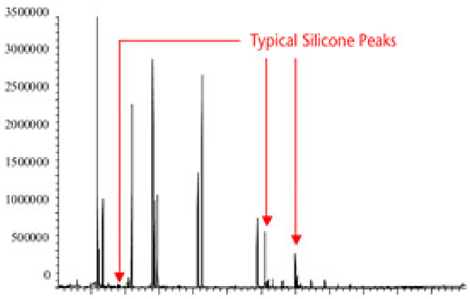
MS Detectors: -

The advantage of these detectors is the ability to show the presence of all the mixture components in the Total Ion mode. The disadvantage is that it can also show the presence of unwanted contaminants introduced from sources such as the injection solvent, the vial septa and the connecting tubing.
The ability to show these components previously missed by techniques such as UV-Vis spectroscopy and FID can interfere with analyte peaks and reduce result confidence.

Solutions

There are a number of ways to reduce this contamination threat

- Use a high-grade silicone seal with a clean PTFE protective face.
- If septa have been in store consider baking the caps at 150C in a drying oven to remove volatile contaminants.



GC-MS trace with silicone fragments

Vacuum generation:-

As the aim is to produce a sealed vessel that will not leak it may be a surprise to realize that too good a seal can reduce the precision of the injector. This perverse effect is due to the formation of a slight vacuum as the sample is withdrawn through the injection or piercing needle. This vacuum can prevent all the required volume entering the sampling system

Solutions

There are a number of ways to remove this effect

- Make sure that the vial is not overfilled with sample
- Do not take more than 50uL of sample for each injection.
- Use a pre-slit seal that will allow the pressure to equalize more rapidly.

Storage:-

It may be required to keep samples stored until the analytical process is complete. If the sample is to be retained for a number of days or perhaps weeks it is necessary to ensure that the solvents used will not escape from the sealed vial or cause damage to the seal material.

Problem Solvents:-

Dichloromethane and other chlorinated solvents do attack most rubbers. Viton® is used where prolonged contact with the solvent is unavoidable.

DMSO is a polar solvent with a huge appetite for water. DMSO volumes can increase by up to 20% if left in a humid atmosphere. The seal must prevent not just DMSO evaporation but also water permeation. A robust PTFE layer is required with thicker rubber and silicone rubber seals preferred.

THF will dissolve most polymers and only the fluoropolymers show much resistance. This limits storage options, as it is volatile and potentially explosive if non-stabilized. Viton® gives some resistance but multiple PTFE discs may need to be used. (Polypropylene and Polyethylene Plastic caps can also be damaged)

Pentane has such a low boiling point that even slight warming will lead to volatile loss. When used in GC a secure rubber/PTFE seal is required.

Solid Storage Screw Caps

A PTFE lined cap with no injection hole may be preferred for screw top vials. Such PTFE lined caps are available in sizes from 8mm to 24mm

Summary Recommendations

Chromacol Seal Type	Method Compatibility	Vial
-AC7	Crimp Cap General HPLC and GC. Agilent A/S compatible	Crimp
-ST1	General HPLC and GC where silicone is preferred.	Screw and Snap
-8RT1	General HPLC and GC where rubber is preferred.	Screw and Snap
-ST101	LC-MS and GC-MS recommended. Shimadzu LC and GC compatible.	Crimp, Screw and Snap
-ST1X/-ST101X	Pre-slit septa for blunt needle penetration and anti-vacuum operation for PE and Merck-Hitachi HPLC systems.	Crimp, Screw and Snap
-SCST	Solid top storage cap.	Screw
-TST1	Anti-coring septa. Gilson preferred.	Crimp, Screw and Snap
-V1	Chlorinated solvents GC-FID	Crimp and Screw

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