Vials, Caps, Septa & Various Products in Comparison

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1. Abstract

Today there are a wide range of different vials, caps and septa for headspace and SPME analysis available on the market. For the user it is not always easy to choose the right product for his particular application. In many cases there is only a limited amount of supplier information available for the various vials, caps and septa supplied. Sometimes when a mixed variety of products is used, recommended combinations are broken up. This can lead to unsatisfactory analytical results, time consuming investigations and loss in confidence.

In order to compare the different products, it was necessary to develop a standard headspace method. The analytical test has to be a fast, reliable and quasi matrix independent test procedure. The selection of a septum shall not only fulfil the application requirements.

Also the hardness of the septum itself is an important criteria. Until today the only information given from the septum manufacturer/supplier has been the " o Shore A" value. This value is actually not in relation to the final septum. The "o Shore A" is a degree of hardness for the rubber manufacturer. A new test procedure shall give a reliable degree of the hardness of a septum as used for the headspace or SPME analysis.

2. Introduction

Have you ever asked yourself following questions?

- Which septum will be suitable for my application?
- Which cap fits together with the vial and septum?
- Which vial is shall be selected for the headspace or the SPME technique?
- Which combination is suitable for the instrumentation?
- How can I test and compare my headspace or SPME equipment?
- How can I find out the hardness of the septum, without destroying a SPME Fiber?

If you asked yourself these questions in the past, then I assume that you have been confronted with the whole complexity of the headspace and SPME technique already.

Do you know the frustration of wanting to start a new series of analysis and then finding that you have run out of caps? You are then forced to use anything that has been hiding away in a drawer for ages, and of course you will then not be satisfied with the next days data analysis.

Another often heard comment from the lab personnel is that the "purchasing guys" had to save-a-penny and delivered something unwanted in the lab. Not knowing how critical it is if a proven combination of "vials-caps-septa" is broken up, can mean that if one component does not fit properly, your analytical results could be totally bizarre.

Due to the fact, that the PAL System uses a magnet to transport the vials, the questions became even more important. Of course steel material is the first answer if one thinks about magnetic force. The steel caps have been in the market for years. Are they really as good as caps made of different material? How can I keep the magnetic transport if I change to a different material?

The market responded. Caps made out of aluminum with a magnetic inlay have been invented. Also a new approach has been taken with the new concept of a screw vial/cap combination.

Another important question is, how can one compare the equipment? Is it possible to define a simple test which can be reproduced in the lab? Yes such tests do exist and one approach will be described below.

I mentioned above the hardness of the septum. The only hint for the hardness from the supplier side has been the "degree shore A" (o shore A). This value is more or less invalid for the user. Reasons and a possible way how to approach this issue will be explained.

3. Experimental Test Conditions

3.1 Gas Chromatographic Conditions:

GC Agilent 6890:

- Injector: split/splitless, Liner: Single Taper 4 mm ID, silanized glass wool packing (P/N HP 5062-3587)
  Temperature: 250°C
  Split Ratio = 1:100
- Detector: FID
  Temperature 300°C
  Fuel Gases: Make-up Gas N2 25 ± 2 ml/min, Air 400 ± 30 ml/min, H2 30 ± 2 ml/min
- Column: Retention Gap (uncoated fused silica column).
  Length 5m, OD 0.375 mm, ID 0.10 mm
  Supplier: BGB Switzerland, P/N: BGB TSP 1003755
  Column Oven Temperature: 200 0C, Runtime 1,0 min
  Carrier Gas: Helium 0.1 ml/min, approx. 14 psi column head pressure.

Data Acquisition System: Agilent ChemStation Rev. 6.03

3.2 Combi PAL Method Parameters Settings:

CYCLE	HS-Inj	Fill Speed	100µl/s
SYRINGE	2.5HS	Pullup Del	1 sec
Sample Volume	500 µl	Inject to	GC Inj1
Incubat Temp	80 °C	Inject Speed	500 µl/s
Incubat Time	7 minutes	Pre Inj Del	500 ms
Agi Speed	250 rpm	Pst Inj Del	1 sec
Agi On Time	5 sec	Syr Flushing	90 sec
Agi Off Time	2 sec	GC-Runtime	60 sec
Syringe Temp	85°C		

Table 1

Syringe:
Hamilton Art Nr 203084 / CTC Art. Nr.: SyrC HS 2.5 -23-5

3.3 Sample Preparation

Test Sample: Iso-Octane, puriss.,
Microcaps Glass Capillary held with tweezers, filled and put into 20mL headspace vial, sealed immediately.

3.4 Test Procedure:

For the test, 2 series of vials with 7 samples each were prepared. The first series was analyzed immediately after preparation. The second series was kept at room temperature 22 ± 2 °C for 24 hours. The loss of iso-Octane was determined (1st minus 2nd series) and expressed in percent. The relative standard deviation, s-rel (%), was then calculated.

4. Selected Material for Test-Series

4.1 Selected Vials for Test-Series

Flat Neck Vial
Supplier: La-Pha-Pack P/N: 20 09 0873
MicroLiter P/N: 20-2100

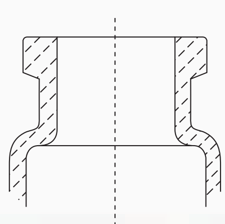


Figure 1.

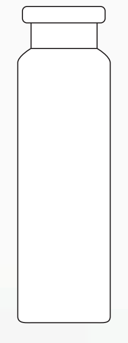


Figure 2.

Conical Neck Vial
Supplier: Chromacol P/N: 20-CV

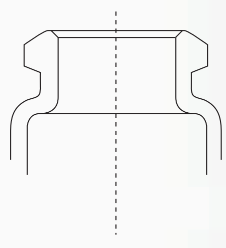


Figure 3.

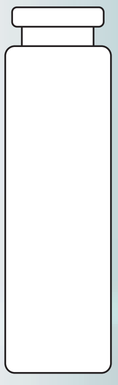


Figure 4.

SPME Neck Vial
Supplier: La-Pha-Pack P/N: 20 09 122

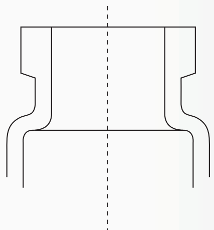


Figure 5.

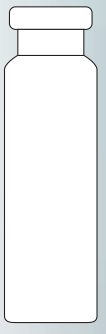


Figure 6.

Screw Neck Vial
Supplier: La-Pha-Pack
Clear Glass P/N: 18 09 1307
Amber Glass P/N: 18 09 1311

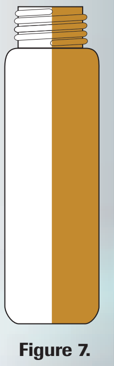


Figure 7.

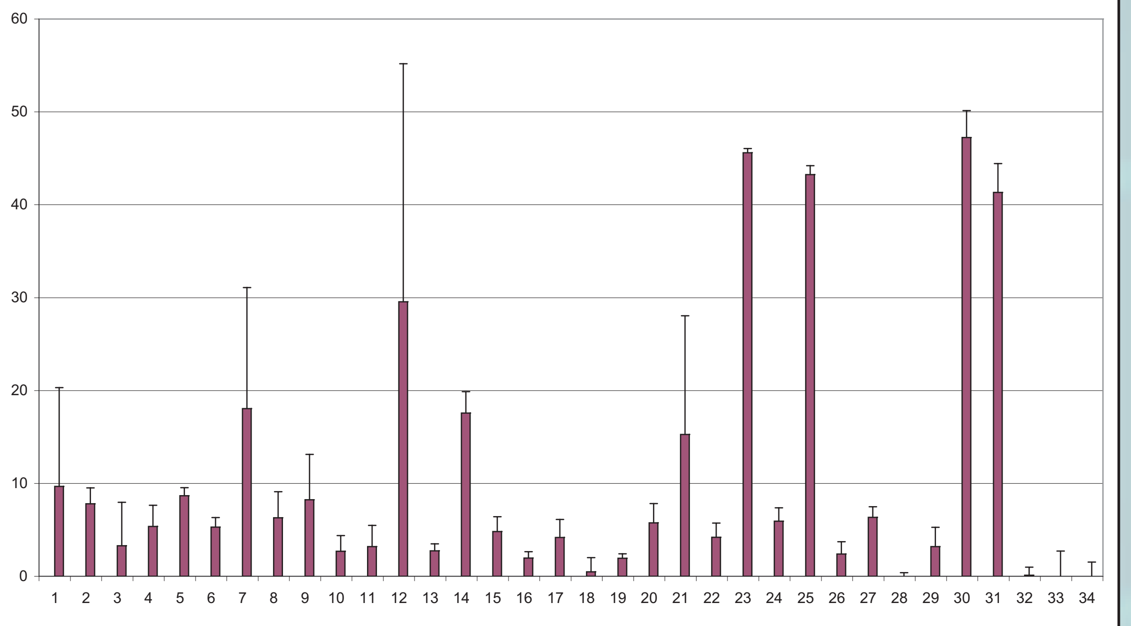
4.2 Selected Caps for the Test-Series

- Steel Magnetic Caps
  Steel Blank
  Steel with special alloy, gold lacquered
  Center hole 5 and 8 mm
- Aluminum Magnetic Caps
  Aluminum with magnetic inlay
  Steel washer in-between Septum and Cap (MicroLiter)
  Center hole 8 mm
- Magnetic Screw Cap
  Center hole 8 mm

4.2 Selected Septa Material for the Test-Series

- Silicone Rubber
  With PTFE layer, various thickness' and qualities
- Viton
  Without PTFE layer
- PharmaFix, Chloro/Bromobutyl Rubber (Polymer)
  With PTFE layer
- Butyl-red Polymer
  Without PTFE layer
- PTFE Membrane
  Thin PTFE Membrane,
  Chromacol P/N: 20-LLX

5. Summary Results: Loss of iso-Octane (%) after 24 hours at Room Temperature | Test #



Graphic 1: Loss of iso-Octane (%). Error Range expressed aas relative standard deviation (%)

*T	Vial Type			Cap Type					Septa Type					Analytical Results	
#	Suppl.	Vial P/N	Vial Type	Supplier	Cap P/N	Cap Material	Cap Type	Cap Hole mm	Supplier	Septa P/N	Septa Type	Septa Thickness mm	Septa Hardness o Shore A	rel StdDev s-rel (%) (2nd Series)	Loss of iso-Octane %
1	1	20 CV	conical	2	20 03 1200*	Steel, golden	Crimp	8	2	20 02 0035	Pharmafix, Chlorbutyl Teflon	3	50	10,6	9,7
2	1	20 CV	conical	2	20 03 0975*	Steel, golden	Crimp	8	2	20 02 0141	Silicone transp. blue, PTFE white	3	35	1,7	7,8
3	2	20 09 0873	flat	2	20 03 1200*	Steel, golden	Crimp	8	2	20 02 0035	Pharmafix, Chlorbutyl Teflon	3	50	4,7	3,3
4	2	20 09 0873	flat	2	20 03 0975*	Steel, golden	Crimp	8	2	20 02 0141	Silicone transp. blue, PTFE white	3	35	2,3	5,4
5	1	20 CV	conical	1	20 MCBC	Aluminium/Tin	Crimp	8	1	20-ST3	Silicon Blue, PTFE	3	35	0,9	8,7
6	2	20 09 0873	flat	1	20 MCBC	Aluminium/Tin	Crimp	8	1	20-ST3	Silicon Blue, PTFE	3	35	1,0	5,3
7	1	20 CV	conical	1	8007-MCB	Steel, blank	Crimp	8	1	8008-RU/Te	Pharmafix, Chlorbutyl Teflon	3	50	13,0	18,1
8	1	20 CV	conical	1	20 MCBC	Aluminium/Tin	Crimp	8	1	8008-RU/Te	Pharmafix, Chlorbutyl Teflon	3	50	2,8	6,3
9	2	20 09 0873	flat	1	8007-MCB	Steel, blank	Crimp	8	1	8008-RU/Te	Pharmafix, Chlorbutyl Teflon	3	50	4,9	8,2
10	2	20 09 0873	flat	1	20 MCBC	Aluminium/Tin	Crimp	8	1	8008-RU/Te	Pharmafix, Chlorbutyl Teflon	3	50	1,7	2,7
11	1	20 CV	conical	1	20 MCBC	Aluminium/Tin	Crimp	8	1	20-ST3HT106		3	45	2,3	3,2
12	1	20 CV	conical	2	20 03 0665*	Steel, golden	Crimp	5	2	20 02 0141	Silicone transp. blue, PTFE white	3	35	25,6	29,5
13	2	20 09 0873	flat	1	20 MCBC	Aluminium/Tin	Crimp	8	1	20-ST3HT106		3	45	0,8	2,7
14	2	20 09 0873	flat	3	20 03 0665*	Steel, golden	Crimp	5	2	20 02 0141	Silicone transp. blue, PTFE white	3	35	2,3	17,6
15	1	20 CV	conical	3	20-0050*	Steel, golden	Crimp	5	3	ML 20-0050M	Silicone blue, PTFE transp.	3	45	1,6	4,8
16	2	20 CV	conical	1	20 MCBC	Aluminium/Tin	Crimp	8	4	n/m	Silicone white, PTFE white	3	45	0,7	2,0
17	2	20 09 0873	flat	3	ML 20-0050M*	Steel, golden	Crimp	5	3	ML 20-0050M	Silicone blue, PTFE transp.	3	45	1,9	4,2
18	2	20 09 0873	flat	1	20 MCBC	Aluminium/Tin	Crimp	8	4	n/m	Silicone white, PTFE white	3	45	1,5	0,5
19	1	20 CV	conical	3	20-0050AT*	Aluminium (Washer, green)	Crimp	8	3	20-0050AT	Silicone blue, PTFE transp.	3	45	0,5	1,9
20	1	20 CV	conical	3	20-0051ML*	Steel, golden	Crimp	8	3	20-0051 ML	Silicone white, PTFE	3	45	2,1	5,7
21	2	20 09 0873	flat	3	20-0050AT*	Aluminium (Washer, green)	Crimp	8	3	20-0050AT	Silicone blue, PTFE transp.	3	45	12,8	15,3
22	2	20 09 0873	flat	3	20-0051 ML	Steel, golden	Crimp	8	3	20-0051 ML	Silicone white, PTFE	3	45	1,5	4,2
23	1	20 CV	conical	3	20-0020M*	Steel, golden	Crimp	5	3	20-0020M	Butyl, black	3	50	0,5	45,6
24	1	20 CV	conical	3	20-0030M*	Steel, golden	Crimp	5	3	20-0030M	Butyl, PTFE black	3	50	1,4	5,9
25	2	20 09 0873	flat	3	20-0020M*	Steel, golden	Crimp	5	3	20-0020M	Butyl, black	3	50	1,0	43,2
26	2	20 09 0873	flat	2	20 03 06665	Steel, golden	Crimp	5	3	20-0030M	Butyl, PTFE black	3	50	1,3	2,4
27	2	20 09 1222	SPME	2	20 03 1295*	Steel, golden	Crimp	8	2	20 03 1295	Viton black	0,5	75	1,1	6,3
28	2	20 09 1222	SPME	2	20 03 1295*	Steel, golden	Crimp	8	2	20 02 1295	Viton black	1	75	0,4	0,0
29	2	20 09 1222	SPME	2	20 03 1246*	Steel, golden	Crimp	8	2	20 02 1244	Silicone white, PTFE blue	1,5	60	2,1	3,2
30	2	20 09 0873	flat	1	20 MCBC	Aluminium/Tin	Crimp	8	1	20LLX	Teflon			2,9	47,2
31	2	20 CV	conical	1	20 MCBC	Aluminium/Tin	Crimp	8	1	20LLX	Teflon			3,1	41,3
32	2	18 09 1307	Screw	2	18 03 1414*	Steel	Screw	8	2	17 02 1318	Silicone white, PTFE blue	1,5	60	0,9	0,1
33	2	18 09 1307	Screw	2	18 03 1309*	Steel	Screw	8	2	17 02 1417	Silicone transp. blue, PTFE white	1,3	35	2,7	0,0
34	2	18 09 1307	Screw	2	18 03 1416*	Steel	Screw	8	2	17 02 1415	Butyl red, PTFE grey	1,6	55	1,5	0,0

Supplier 1: Chromacol Supplier 2: La-Pha-Pak Supplier 3: Microliter Supplier 4: not named * P/N for Cap and Septum in combination

5. Summary of the Tests Vials-Caps-Septa/Recommended Combinations

Summarising the results, one can make the following statements:

5.1 Vials

Conical Neck Shape, Crimp Vial
The vial should not be used in combinations with tested steel caps. It has been designed and developed for the Aluminum crimp cap. The vial type has been misused in the past in combination with steel caps.

Flat Neck Shape, Crimp Vial
This form of the vial neck does forgive a little more in cases where the combination is not ideal. Nevertheless are steel caps also not recommended in this combination.

SPME Neck Shape, Crimp
The SPME Fiber-Needle is not an ideal tool to penetrate a septum. This form of the vial neck shape allows to use a thinner septum for the penetration of the fiber. The septum and the steel cap have to be matched. The vial neck shape does give good results with the tested combinations. A possible, untested, improvement could be the combination of the Aluminum cap with the recommended Septa.

Screw Cap
This new approach for vials for the Headspace and SPME technique is a good alternative for everybody who does not like the crimping and even less the decapping of the vials. The results with the recommended combinations are excellent.

5.2 Caps

Steel caps, crimp type, 5 mm center hole
The results have been discouraging. This cap is since a long time on the market and it has never been improved over the years. It would be no surprise if this crimp cap would slowly disappear.

Steel caps, crimp type, 8 mm center hole
In combination with the SPME vial neck it gives good results. Otherwise is the cap is not recommended - or at least one has to validate the method very carefully.

Aluminum caps with Magnetic Inlay, 8 mm center hole
This rather new developed crimp cap is an excellent replacement for the often used steel cap. Highly recommended for all crimp vials.

Aluminum caps with steel washer inserted
This approach is actually an excellent idea to overcome the shortness of the steel cap and still providing a magnetic transport possibility. Today it can be considered as replaced by the Aluminum cap with the magnetic inlay.
Working in the routine one can often observe that the cap is not crimped in a proper way. If the crimper tool is not perfectly positioned, the cap can move slightly before beeing crimping. The washer is harder than the Aluminum. It will deform the top surface of the cap. This will result in mechanical disturbance moving the vials across the CombiPAL and bring them back into the Vial Tray.

Screw Caps
The recommended and tested combinations give excellent results. The caps are tight and easy to handle. Sealing and opening process is not comparable and much easier than the crimping and decapping process. The crimp tool uncertainty is eliminated.

5.3 Septa

The selection of the Septum material is highly application driven. It has not been the purpose of this work to test this aspect. It is important that the septum thickness and softness will be matched with the cap and the vial. Only with the ideal combination can reliable and trustful results be achieved.

Silicone Septa with Teflon Layer
Good results can be achieved. The combination of the cap and vial is important.

*PharmaFix Septum, Chloro/*Bromobutyl with PTFE layer
The Pharma-Fix septum is made of a vulcanised Chloro/Bromobutyl rubber which forms a collar joint to seal with the glass rim. Embedded is a thick Teflon layer, centred in the contacting area for the analytical sample. The septum has a normal thickness of 3 mm but the collar does add up to the total thickness. Therefore it is highly critical to select a matching cap. See Result of test 7, Graphic 11.
Furthermore is the hardness of the septum extremely high. The rubber material is filled and the PTFE layer is with 0.21 mm almost double as thick as the layers of the most common septa. It is impossible to penetrate the septum with the SPME Fiber. Even the headspace syringe needle can be too weak. The septum is not only hard but the rubber is so tight that the needle almost sticks to the septum. Withdrawing the needle from the vial can be a problem if the injection unit is not maintained properly (short tension cord of CombiPAL injection unit).

Septum #70175, Silicone white, PTFE layer
This septum can give a good seal. The drawback is the hardness of the septum. The above described problems with the PharmaFix septum applies as well to this septum.
To hard for SPME and a good potential source for problems in the routine analysis.

6. Hardness of the Septum/"o Shore A" Versus Penetration Force

For the user it is critical to know the hardness of a septum. The only available information for the customer is the hardness expressed in "o shore A".

The "shore-test" is a standardized test from the rubber industry. A steel ball is dropped on a rubber or polymer piece, specified in size and thickness.

The degree of beveling of the rubber is expressed in "o shore A". This test procedure is valuable for the manufacturer of the rubber/polymer industry. For the purpose of a Headspace or SPME Vial Septum it does not give any hint on the hardness of the septum. The thickness of the septum and the Teflon layer, the Teflon layer itself are not considered in this test.

Realizing this shortness of a correct and valuable information for the user, one started developing a new test. The needle, as used for the Headspace or SPME technique, will penetrate in a controlled manner into a septum which is crimped on a vial. The penetration force will be expressed in Newton.

The speed and height of the needle for the penetration is defined and constant. The septum is crimped to simulate the real situation in the practice.

The goal has been to develop a test which is understandable and will give comparable results. It should be possible to define an upper limit of the septum hardness (expressed in Newton) to be able to judge the penetration feasibility for a needle, headspace and SPME technique.

Preliminary results are given in the table below. This test is at the time of writing this article in the stage of fine tuning and all measurements will be repeated. This publication shall give a rough estimate, corrections will follow.

Septum	Thickness mm	"Hardness" O Shore A	Headspace Needle Gauge 23 Pointstyle 5 Penetration in Newton	SPME Needle Gauge 23 Pointstyle 3 Penetration in Newton
Silicone Blue transp./PTFE white	3.0	35	7.0	15.5
PharmaFix, Chlorbutyl, Teflon	3.0	50	14.0	23.0
Butyl, PTFE grey	3.0	50	13.0	20.0
Silicon white, PTFE blue	1.5	60	4.0	7.5
Viton black	1.0	75	9.0	16.0
Natural rubber, PTFE red-orange	1.3	55	8.0	14.5
Silicon blue, PTFE blue	1.5	60	3.0	9.0
Silicon white, PTFE blue	1.5	60	4.0	11.0
Butyl red, PTFE grey	1.6	55	9.0	14.0
Teflon Membrane	0.0	0	2.0	7.0
Silicone high temperature	3.0	35	8.0	12.0
Silcone blue, PTFE	3.0	35	5.5	13.0
Chlorbutyl	3.0	50	17.0	26.0
Silcone white, PTFE white	3.0	45	5.5	15.0
Butyl, PTFE black	3.0	50	14.0	24.5
Silicone blue, PTFE transp.	3.0	45	6.0	14.5
Silicone blue, PTFE transp.	3.0	45	6.0	11.0
Silicone white, PTFE	3.0	45	6.5	15.5
Butyl black	3.0	50	11.5	19.0

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A special thank you goes to Werner Reifferscheidt and his crew to develop the machine for the penetration test. All test requirements and needs shall be forwarded directly to La-Pha-Pack.

Supplier and Manufacturer Companies:

Chromacol Ltd.
enquiries@chromacol.com
http://www.chromacol.com

La-Pha-Pack Werner Reifferscheidt GmbH
Service@La-Pha-Pack.com
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7. Conclusions

The aim of this work has been to make suppliers, purchasing responsible persons and the user in the lab aware, that one has to pay more attention to the details of the equipments.

One has to admit that not all information's have been available. The main drawback for this lack is that the "scientific community" has not been able to agree on a standard test yet. I hope that his work will encourage everybody to use the same test procedure as described in this paper. Recalling the main advantages, like speed, practically matrix independency and very little chromatographic influence, should be convincing enough to follow the proposed path.

The main result is easy to remember:
There is not a vial, cap or septum which will give a bad result – the combination of the three parts will give the only valid answer.

Finally it is not acceptable anymore to express the hardness of a septum in "o Shore A".

Every septum being on the market or will come new on the market, shall be tested with the described procedure. The benefit will be that a user can compare the hardness of the final septum as applied. This will prevent needle bending and frustration in the routine work.