Qualification of Headspace High Performance Septa by Headspace GC/MS

Technical Overview

Introduction

Headspace (HS) coupled with gas chromatography (GC) provides quantitative and qualitative information about the volatile components that are present in complex sample matrices. The Agilent 7697A Headspace Sampler is part of Agilent's line of gas chromatography products. Together with the market-leading 7890A GC, it has been demonstrated to provide industry leading performance [1,2].

As the Agilent 7697A Headspace Sampler, with tray, offers the capability of heating samples up to 300 °C [3], the application of the 7697A Headspace Sampler has been extended to high temperature analyses, such as investigating polymeric materials. At high temperature, a wider range of volatile components can be released from the matrix, thus providing more qualitative fingerprint information as well as potentially increasing the scope of quantitative work.

Currently, PTFE/silicone-based vial septa are widely used for headspace analyses but they are not recommended for use above 200 °C. When using these septa at high temperature, a series of siloxanes from the septa are seen. The intensity of the siloxane peaks increases significantly in the headspace as temperature increases, and they eventually become the predominant volatile species. These interference peaks significantly impact the reliability and efficiency of headspace analysis at high temperature, especially for qualitative or semi quantitative analyses.

An alternative headspace vial septum was investigated, to reduce siloxane interferences from the septum at high temperature, and improve the reliability of high temperature headspace analysis. These septa are referred to as High Performance septa. To demonstrate and qualify their performance, HS background at high temperature and pressure were monitored, and the chemical compatibility with common solvents used in headspace applications was investigated. Results showed that the High Performance HS septa provided significantly cleaner HS backgrounds at various HS vial-equilibration temperatures (up to 300 °C). The chemical compatibility was also favorable. High Performance septa are the recommended option for reliable and efficient HS/GC analyses at high temperature.

Experimental

Screw caps and crimp caps with High Performance septa were tested for blank background and solvent compatibility at various pressure and temperature conditions. Stainless steel crimp/screw caps were used to reinforce the seal to the vial and prevent leaks during high temperature equilibrium. Three manufacturer lots of septa were tested for lot-to-lot consistency. In addition, PTFE/silicone HS septa from 3 vendors were tested for comparison under the same conditions as the High Performance septa.

Chemical solvents and reagents

All reagents and solvents were HPLC or analytical grade. Milli-Q water was used. Dimethyl sulfoxide, N,N-dimethylformamide, and N,N-dimethylacetamide were purchased from Sigma-Aldrich (St Louis, MO, USA). Toluene was from Honeywell B&J (Muskegon, MI, USA). Acetic acid and triethylamine were purchased from EMD (Darmstadt, Germany). 1,3-Dimethyl-2-imidazolidinone was from Fluka (Switzerland). 10% Acetic acid in water was prepared by mixing 10 mL acetic acid, glacial, and 90 mL Mill-Q water.

Vial blank and solvent blank

Vial blank samples were prepared by capping the empty 20 mL headspace crimp top vials or screw top vials directly; no effort was made to purge the vials with an inert gas prior to capping. These vial blank samples were used for blank background and potential septa contamination evaluation. Solvent blank samples were prepared by adding 1 mL of solvent blank into a vial and then capping the vial. For DMI, only 5 µL of solvent was added to reduce possible contamination of the GC/MS system.

Instrumentation

All testing was done on an Agilent 7890A GC equipped with an Agilent 7697A Headspace Sampler and Agilent 5975C Series GC/MSD. Table 1 lists the instrument conditions and Table 2 lists flow path consumable supplies.

Table 1. Instrument conditions for Agilent HS/GC/MS system used for high performance septa qualification tests.

HS sampler:	Agilent 7697A Headspace Sampler
Temperature:	Oven/Loop and Valve/Transfer line temperature varied from 85-300 °C for different tests
Time:	GC cycle time: 32 min, vial equilibrate time: 30 min, pressure equilibration time: 0.1 min, inject time: 0.5 min
Configuration:	Vial pressurization gas type: He, sample loop volume: 1 mL, standby flow: 20 mL/min
Vial:	Fill mode: flow to pressure, fill pressure: varied from 15-75 psi for different tests, fill flow: 50 mL/min, custom loop fill mode, loop fill ramp rate: 20 psi/min, loop final pressure: 10 psi, vial size: 20 mL, shaking: once
Carrier:	GC controlled
Advanced function:	Purge flow: 100 mL/min, purge time: 1 min
GC:	Agilent 7890A Series GC
Carrier gas:	Helium, constant flow at 2.5 mL/min
Inlet:	Split mode: 250 °C, split ratio: 10:1
Oven profile:	40 °C for 1.5 min, then to 325 °C at 15 °C/min, hold for 2.5 min
Analytical column:	Agilent DB-5ms Ultra Inert, 30 m × 0.25 mm, 0.25 µm (p/n 122-5532UI)
MSD;	Agilent 5975C Series GC/MSD inert with performance electronics
Vacuum pump:	Performance turbo
Mode:	Scan
Tune file:	Atune.u
EM voltage:	Atune voltage
Transfer line temperature:	250 °C
Source temperature:	230 °C
Quad temperature:	150 °C
Solvent delay:	None
Scan mass range:	25-570 amu and 35-550 amu

Table 2. Flow path supplies.

Vials:	Headspace 20 mL crimp top clear vial, 100/pk (p/n 5182-0837) Headspace 20 mL screw top clear vial, 100/pk (p/n 5188-2753)
Vial caps:	High Performance septa w/ steel crimp caps, 100/pk (p/n 5190-3987) High Performance septa w/ steel screw caps, 100/pk (p/n 5190-3986)
Crimper:	20 mm Electronic Crimper (p/n 5190-3189)
Decapper:	20 mm Electronic Decapper (p/n 5190-3191)
Transfer line:	FS deactivated tubing, 0.53 mm x 5 m (p/n 160-2535-5)
Transfer line ferrule:	Ferrule polyimide graphite 1/32 in (p/n 0100-2595)
Fitting:	Fitting-internal reducer 1/16-1/32 in (p/n 0100-2594)
GC inlet septum:	Advanced Green Non-Stick 11 mm (p/n 5183-4759)
GC inlet ferrules:	0.4 mm id, 85/15 Vespel/graphite (p/n 5181-3323)
O-rings:	Non-stick liner O-ring (p/n 5188-5365)
Inlet seal:	Gold plated inlet seal with washer (p/n 5188-5367)
Inlet liners:	Direct liner 2 mm id, deactivated (p/n 5181-8818)

Results and Discussion

The purpose of this study was to qualify the ability of High Performance HS septa to provide cleaner HS chromatographic backgrounds at stringent headspace conditions, and demonstrate compatibility with common headspace solvents.

To test for chromatographic purity, vial blanks were evaluated at different temperature and pressure conditions. The oven/loop & valve/transfer line temperatures were tested at 85, 150, 250, and 300 °C. For each temperature all 3 zones were set to the same temperature. The vials were tested at initial pressures of 15, 50, and 75 psi, and always depressurized to 10 psi to fill the sample loop prior injection with the 6-port valve.

Eight solvents were evaluated in the headspace solvent compatibility test. The solvents represented a range of properties and customer applications and included water, 10% acetic acid in water, triethylamine (TEA), toluene, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC) and 1,3-dimethyl-2-imidazolidinone (DMI).

There are 2 configurations of High Performance septa: High Performance septa with steel screw caps (p/n 5190-3896) and High Performance septa with steel crimp caps (p/n 5190-3897). Steel caps are used to reinforce the seal of cap/septum to vial, thus preventing vial leakage and sample loss during sample heating and injection. The screw cap configuration provides added ease-of-use by avoiding the need to crimp a steel cap. An electronic crimper and decapper are strongly recommended when using the steel crimp caps due to the hardness of the steel.

Chromatographic purity

The commonly used PTFE/silicone HS septa are typically specified for use up to 200 °C, because at high temperature (>200 °C), septum contaminates begin to dramatically leach out of the silicone layer. A series of siloxane peaks are detectable when using PTFE/silicone HS septa at high temperature. The intensity of the siloxane peaks increases significantly in the headspace sample as the vial temperature increases and they eventually become the predominant volatile species, as shown in Figure 1.

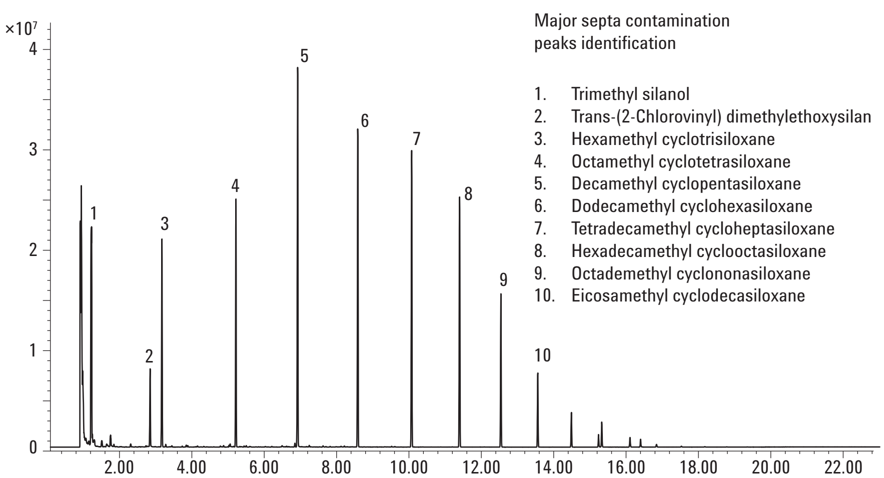

Figure 1. GC/MS HS chromatogram of vial blank with PTFE/silicone headspace septum heated to 300 °C shows that the PTFE/silicone septum causes significant contamination when heated at high temperature.

High Performance headspace septa directly address septum contamination at high temperature by significantly reducing the amount of siloxanes that leach out of the material. The reduction in background siloxanes improves HS chromatographic purity. Figure 2 shows the comparison of vial HS blank chromatograms from PTFE/silicone headspace septa from several competitors with High Performance septa. As shown in the figure, the High Performance septa provided low HS chromatographic background at 300 °C.

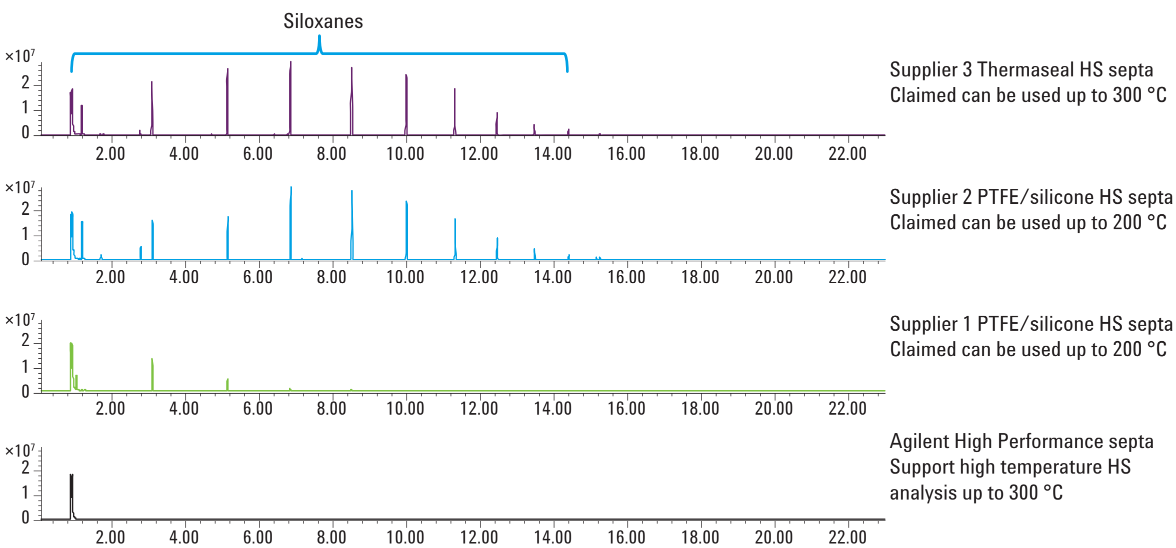

Figure 2. GC/MS chromatographic comparison of vial blank with different PTFE/silicone headspace septa and High Performance septum. Vials were equilibrated at 300 °C for 30 min. By using High Performance septa, the vial blank chromatogram clearly shows a significantly cleaner HS chromatographic background.

Additional temperatures and pressures were also used to evaluate the High Performance septa. The resulting chromatograms from blank vials at these temperatures and pressures are shown in Figures 3 and 4. In Figure 3, the different temperatures were tested by pressurizing all of the vials to 15 psi then venting them down to 10 psi before injection using the six-port valve. In Figure 4, the different initial vial pressures were tested with oven/loop and valve/transfer line temperature of 300 °C. The insets in Figures 3 and 4 represent expanded portions of the baselines to clearly show the small abundance scale. The insets show that there are fewer and lower siloxane peaks, even at 300 °C.

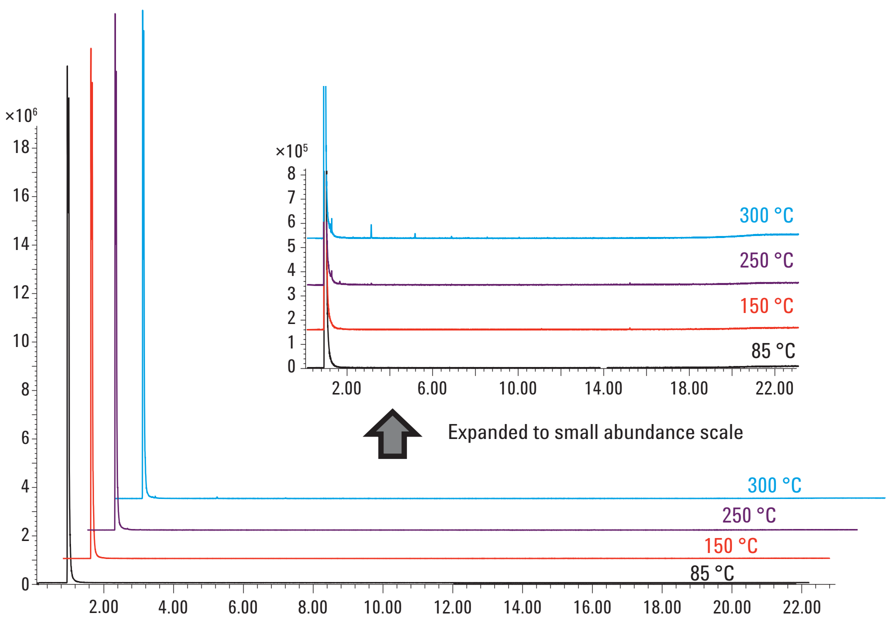

Figure 3. GC/MS chromatogram comparison of vial blanks with High Performance septa at different temperatures. Vial blanks were equilibrated at each temperature for 30 min and initially pressurized to 15 psi but then vented to 10 psi prior to injection.

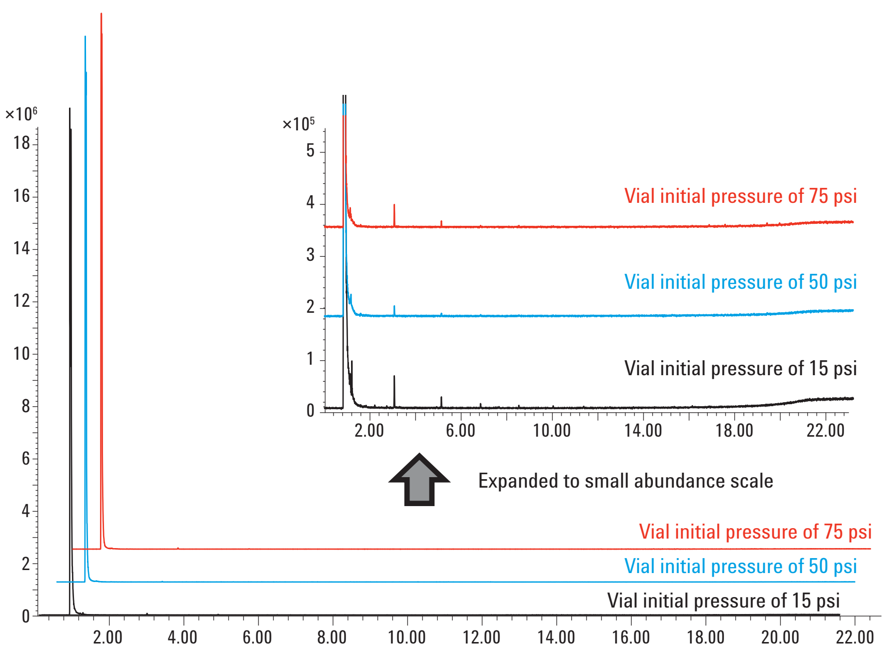

Figure 4. GC/MS chromatogram comparison of vial blanks with High Performance septa at different pressures. The pressure represents the initial pressure each vial was charged to prior to venting. All vials were vented to 10 psi before injection. Vials were equilibrated at 300 °C for 30 min.

A generous MS scan range, 25-570 amu, was used to obtain as much information as possible and also to monitor the air peak for leakage during the test. A second MS scan range, 35-550 amu, was included in the testing to show that the inclusion of N2 (28) and O2 (32) did not obscure the system sensitivity for any trace level peak detection. As shown in Figure 5, cleaner HS background was also achieved under the 35 550 amu condition with minimal interference peaks, indicating that the previous wider scan range did not prevent any potential contamination peaks from being detected.

Chemical compatibility

Eight common headspace solvents/solutions were tested for the chemical compatibility of High Performance septa. Different methods were used for each solvent in the compatibility tests, according to solvent boiling point and purity. Usually, a 7697 HS oven temperature 15 °C below the solvent boiling point was used to heat the samples. One exception was for the 10% acetic acid; the boiling point of water was used because water was the primary component in the solution. Another exception was DMI, where the boiling point of DMI is 225 °C but 150 °C was used in the test for 2 reasons: first, to prevent column contamination and unnecessary column degradation by DMI, and second, to operate at a temperature where contaminants from the PTFE/silicone septa, used for comparison, would be minimal. To be consistent, an initial vial pressure of 15 psi and a final pressure of 10 psi were used. Table 3 summarizes the method conditions for the solvent compatibility tests.

Table 3. Solvent computability test methods (equilibration time = 30 min, vial pressure = 15 psi).

Solvent	Boiling Point (°C)	Oven/Loop & Valve/ Transfer Line Temperature (°C)	Volume of Sample in 20 mL Vial
Water	100	85/95/105	1 mL
10 % acetic acid in water	Assume 100	85/95/105	1 mL
TEA	88.7	73/83/93	1 mL
Toluene	111	96/106/116	1 mL
DMF	153	138/148/158	1 mL
DMSO	189	174/184/194	1 mL
DMAC	165	150/160/170	1 mL
DMI	225	150/160/170	5 µL

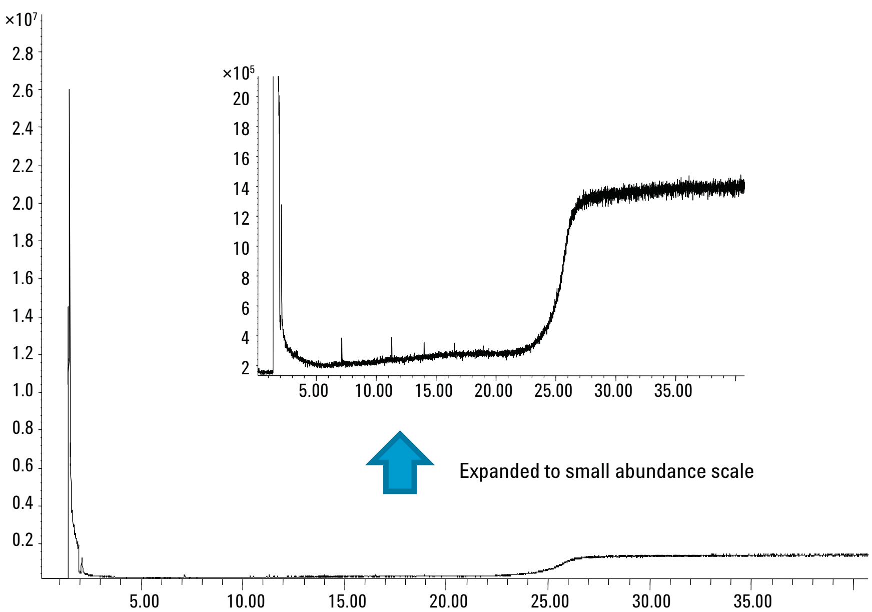

Figure 5. GC/MS chromatogram of HS background with High Performance septum. Vials were equilibrated at 300 °C for 30 min and data were acquired with MS scan range of 35-550 amu.

The instrument conditions were kept constant for a given solvent, and 3 kinds of PTFE/silicone headspace septa from different suppliers were tested along with the High Performance septa. In Figure 6, the cleanest PTFE/silicone septa solvent blank HS chromatograms were compared to the corresponding High Performance septa solvent blank chromatograms. In all of these solvent blank HS chromatograms, the solvent blank peak was always the largest peak. Minor impurities from the solvents were also observed in the chromatograms. As shown in Figure 6, the High Performance septa can provide identical solvent blank HS chromatograms compared to the PTFE/silicone headspace septa. The chemical compatibility of the High Performance septa indicated that they were compatible with common headspace solvents and were equivalent to the performance of PTFE/silicone septa in low- to mid-temperature headspace applications.

Conclusions

The qualification tests for the High Performance septa on the Agilent 7697HS-GC/MS system demonstrated that these septa can provide significantly cleaner HS chromatographic background at high temperatures (up to 300 °C), compared to their PTFE/silicone counterparts at headspace oven equilibration times up to 30 min. In addition, the High Performance septa displayed favorable chemical compatibility with common headspace solvents. The High Performance septa support the feature functions of the Agilent 7697A Headspace Sampler for high temperature applications. They improve the accuracy and reliability of qualitative and quantitative information that can be acquired by significantly reducing the amount of contaminants introduced from vial septa into the sample headspace. High Performance septa can also be used as replacements for the currently used PTFE/silicone septa for low- to mid-temperature HS applications by providing identical or better chromatographic purity, with or without solvents.

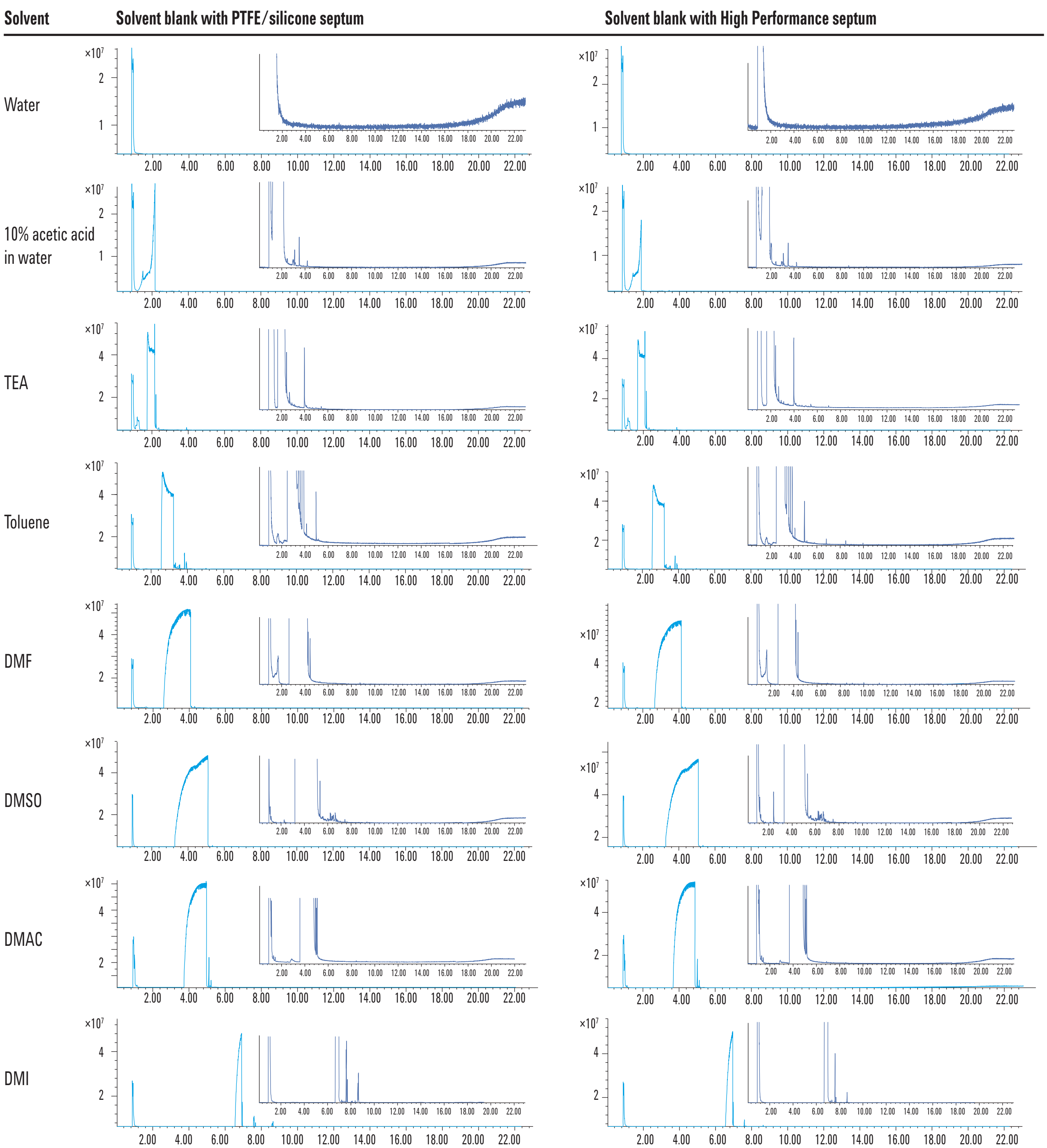

Figure 6. GC/MS HS chromatograms of solvent blanks with PTFE/silicone septum and High Performance septum. The High Performance septum results do not indicate any incompatibilities with common headspace solvents.

References

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