

SPME Adsorbent Fibers with a Nitinol-Core for an Enhanced Fiber Reproducibility

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Introduction

In late 2019, the Supelco[®] Nitinol-core coated fibers were introduced as the adsorbent fibers for Solid Phase Micro Extractions (SPME). These Nitinol-core coated fibers have higher durability and reproducibility than their fused silica fiber counterparts and offer customers a higher degree of confidence and performance. To demonstrate the improved durability and reproducibility of the Nitinol-core fibers, a study was designed using adsorbent SPME coated fibers on both Nitinol-core and fused silica core. The adsorbent (“particle”) type SPME fiber coating provides multiple interactions/mechanisms between the sample analytes and the coating. This often improves the retention/sensitivity of analytes towards the adsorbent (“particle”) coatings in comparison to the absorbent (“film”) fiber coatings. The multiple interaction/mechanisms of these SPME fibers require accurate and precise coating depositions to ensure a robust and reproducible fiber. In this article, the performance enhancements of the Nitinol-core coated adsorbent fibers are compared with the fused silica adsorbent fibers, in terms of their reproducibility, inertness, and durability.

Results of the Study

Coating process

The manufacturing process of the Nitinol-core fibers allows for monitoring of the coating thickness and ovality throughout the entire process. This ensures the deposition of precise film thickness along with inter-lot and intra-lot consistency. **Table 1** shows the results of measurements from multiple coating lots. The number of typical measurements on the final coating is between 400-600.

Table 1. Variability of Measurements of Multiple Fiber Coatings Lots

Fiber Lot	Diameter Measurements		Coating Thickness	
	µm	RSD	µm	RSD
2049-10	282.5	0.37%	77.9	0.68%
2049-11	283.3	0.39%	78.2	0.70%
2049-13	278.7	0.26%	75.9	0.28%
2049-46	277.0	0.19%	75.0	0.35%
2049-47	276.2	0.24%	74.6	0.24%
2049-48	282.2	0.13%	77.6	0.24%
2049-57	281.7	0.38%	77.4	0.38%
2049-74	277.3	0.39%	75.2	0.88%
2049-75	277.8	0.39%	74.9	0.88%
Average	279.6	0.29%	76.3	
Std. Dev.	2.76		1.38	
RSD	0.99%*		1.81%*	

*Inter-lot Variability
#Intra-lot Variability

The inter-lot and intra-lot variabilities were observed to be less than 1% RSD and the variation in average coating thickness in the 9 fiber lots was less than $\pm 1.5 \mu\text{m}$.

Ovality or noncircularity of a coated fiber is its degree of deviation from the perfect circularity of the cross-section. Ovality is measured in percentage and based on the diameter of the coated fiber. A coated fiber with less than 1% ovality is considered circular. A more circularity of the shape causes a more equal migration of the analytes into the fiber.

Table 2. shows the average ovality values of 9 fiber lots

Ovality Measurements		
9 Fiber Lots	Fiber	μm
Average	277.4	0.62%

- X-Y - The average difference in μm based on 2 diameter measurements at 90° angles
- Diameter - Ovality is measured in percent by dividing "X-Y" value by the fiber diameter times 100 * X-Y μm /diameter μm X 100

Analytical Testing Results

Method Precision

The QC testing of the coated fiber should be an accurate measurement of its performance. The components of the test mix must measure various characteristics of the adsorbents using reliable testing methods.

With every adsorbent, there exists a balance between its extraction efficiency and desorption efficiency. Hence it is essential for a test mixture to contain both difficult to retain analytes as well as analytes that are difficult to desorb. Different classes of analytes showing retention by different adsorption mechanisms are useful. In this example, we have identified a 4-component mixture that meets the criteria.

To validate the method, an autosampler with fiber exchange capability was employed. This allowed for multiple extractions per fiber (4) and the testing of multiple fibers per lot in an automated manner. 4 extractions per fiber allows the advantageous calculation of precision (using area counts) of the different analytes.

Table 3 shows the average of the precision of repeated extractions from over 200 fibers (800 extractions). Fibers used had DVB/PDMS and Carboxen[®]/PDMS coatings on fused silica and Nitinol-cores

Isobutyl acetate	Toluene	n-Butanol	o-Xylene	Average of 4
2.03% RSD	2.04% RSD	1.92% RSD	1.80% RSD	1.95% RSD

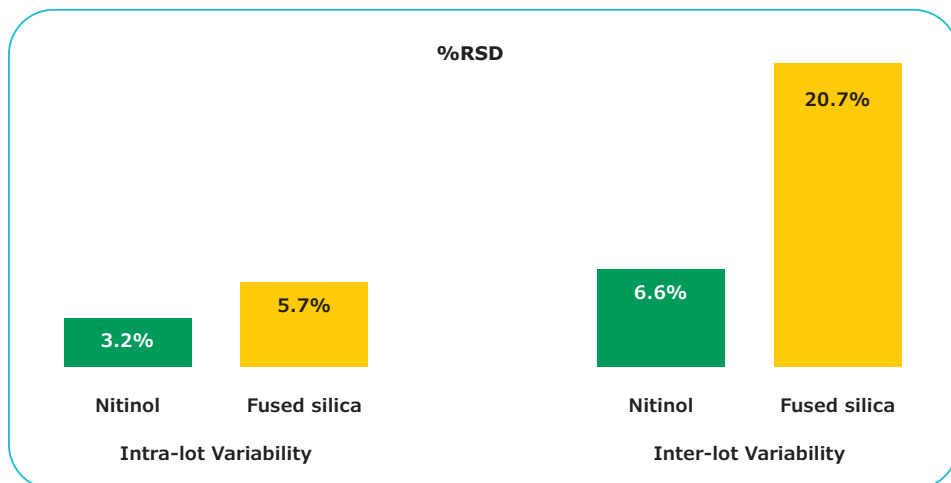
The results indicate that the method is highly reproducible and reliable.

Comparison of Fiber Cores

Fourteen fiber-coating lots of Carboxen®/PDMS fibers with a Nitinol-core and fourteen coating lots on fused silica core fibers were evaluated with the automated QC testing method. For each core, the RSD per analyte was determined from the total extractions of the fibers per given lot. The overall RSD per given lot was the average value of the 4 analyte RSD values. The intra-lot RSD values of all the lots of each core type were averaged to obtain the overall intra-lot values per core type.

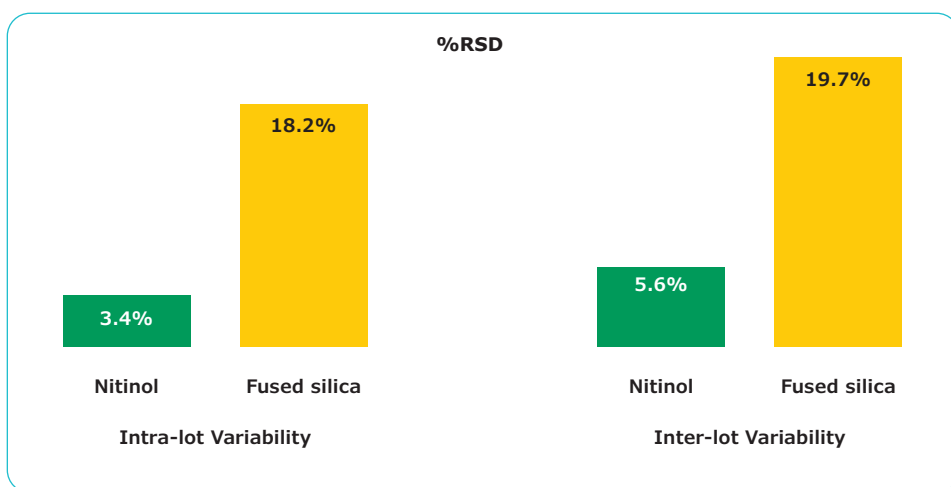
The inter-lot values were obtained by determining the RSD values per analyte from all of the extractions from the 14 lots per each core type. The RSD values of the 4 analytes were averaged to obtain the overall inter-lot variability per core type.

Figure 1 shows the results of the intra-lot and inter-lot variability of the 2 fiber cores with Carboxen®/PDMS coating.



The results showed that there was 48.7% reduction for intra-lot variability and a 68.1% reduction in inter-lot variability with fibers coated on a Nitinol-core compared to the fibers coated on fused silica (FS) core.

Figure 2 shows the results of variability between the fiber cores for the DVB/PDMS coating. The calculations were obtained from eight fiber lots on fused silica and eight lots on Nitinol-cores following the same procedure that was used to calculate the Carboxen®/PDMS coating variability.



The results show that there was an 81.3% reduction in intra-lot variability and a 71.7% reduction in inter-lot variability for Nitinol-core coated fibers as compared to fused silica core coated fibers. Typically, intra-lot variability is significantly lower than the inter-lot variability. However, variability for PDMS-DVB coatings on fused silica was similar between and within the lots. But, this was not the case with the Carboxen® coatings on the fused silica core. Carboxen® material is a much stronger adsorbent compared to DVB, with a higher percentage of micropores and a narrower average micropore diameter of 12 Å versus DVB with a value of 18 Å. The coating thickness variability is less of a factor for Carboxen® coated fibers compared to DVB coated fibers. The retention of analytes on a weaker adsorbent is more dependent on the coating thickness than the retention on a stronger adsorbent. Slight variations in the coating thickness are more easily observed with the weaker adsorbent. Since the coating on the Nitinol-core fibers is more tightly controlled than on fused silica core fibers, their variability is significantly lower than the fused silica core fibers. This indicates the testing process to be highly sensitive at detecting variations in the coating and an assurance of high quality and reproducible fibers.

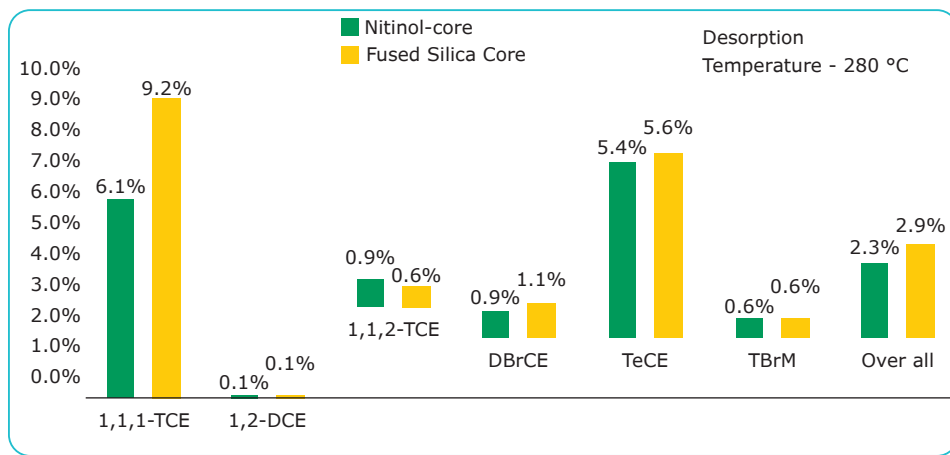
Inertness

An inert fiber core is essential to deliver reproducible and reliable results. An active core can catalyze the breakdown of some analytes during the desorption process. This not only decrease the response of the analytes but also create artifacts that were originally not present in the sample. Alkyl halides tend to be susceptible to degradation especially when the fiber is used at a desorption temperature of above 250 °C. The higher the temperature, the greater the breakdown.

Fused silica is typically used as a benchmark for high inertness, and hence coatings on fused silica cores were compared to the coatings on Nitinol-core. Nitinol is a combination of titanium and nickel and comprises over 99.99% of the composition. The material is used in the medical industry for the production of highly inert devices such as stents.

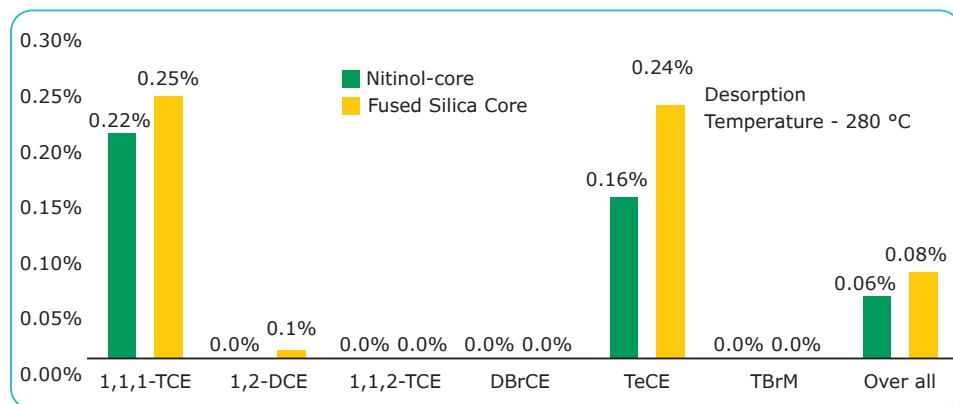
In this study, the extraction and desorption of haloalkanes was used for the comparison of cores. In most cases, the breakdown occurs with the loss of a HCl or HBr molecule and the formation of an unsaturated haloalkene. Since the samples were not spiked with haloalkenes, the presence of haloalkenes in the analysis was considered to be a result of the breakdown of haloalkanes. Both the Carboxen®/PDMS coating and the DVB/PDMS coating were compared on both the fiber cores. **Figures 3 and 4** show the average percentage of breakdown by core type with Carboxen®/PDMS and DVB/PDMS coatings, respectively. The average is based on four extractions per fiber coating and core type, using a mixture of alkyl halides.

Figure 3. The average percentage of breakdown of haloalkanes by Carboxen®/PDMS (n=4) core type



1,1,1-TCE = 1,1,1-trichloroethane; 1,2-DCE = 1,2-dichloroethane; 1,1,2-TCE = 1,1,2-trichloroethane; DBrCE = dibromochloroethane; TeCE = sum of 1,1,1,2- & 1,1,1,1-tetrachloroethane; TBrM = Bromoform; Overall = Average breakdown of all haloalkanes

Figure 4. The average percentage of breakdown of haloalkanes by core type-DVB/PDMS (n=4)



1,1,1-TCE = 1,1,1-trichloroethane; 1,2-DCE=1,2-dichloroethane; 1,1,2-TCE=1,1,2-trichloroethane; DBrCE=dibromochloroethane; TeCE=sum of 1,1,1,2- & 1,1,1,1-tetrachloroethane; TBrM=Bromoform; Overall=Average breakdown of all haloalkanes

The results show that the core types are similar and that the primary cause of the breakdown of the analytes is the desorption temperature. Both core types appear to be inert.

Analyte Recovery Performance

The Nitinol-core fibers showed an equivalent recovery and inertness as compared to the fused silica fibers, while providing superior durability and robustness. For users currently using the adsorbent coatings with a fused silica core but with concerns about the fiber performance, this testing has shown that there is a minimal difference in the analyte recovery between the two core types having the same coating. To demonstrate the similarity in recoveries, a group of alkyl halides was extracted four times with the two adsorbent coatings on both the fiber cores. **Table 4** shows the average response obtained and the percent difference between the fiber cores for each coating type.

Table 4. Comparison of Analyte Response (Peak Area) between Fiber Cores and Coatings

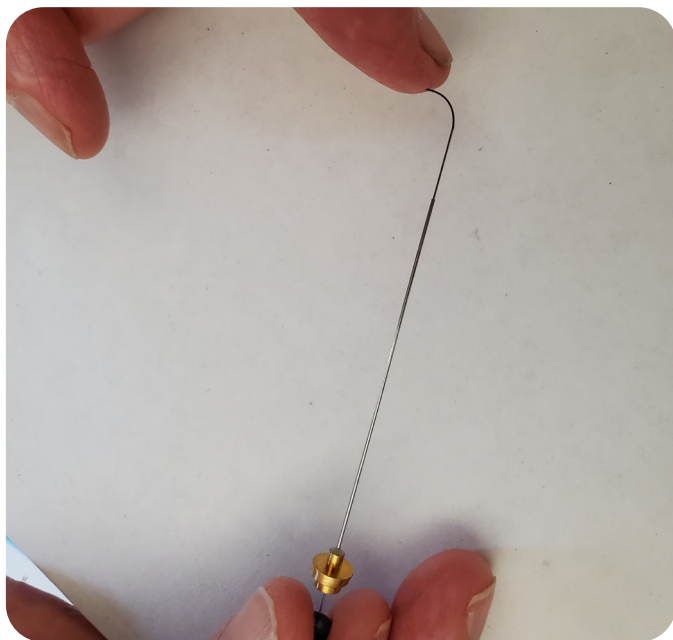
Analyte	DVB/PDMS Coatings			Carboxen®/PDMS Coating		
	Nitinol	Fused silica	Percent Difference	Nitinol	Fused silica	Percent Difference
1,1,1-trichloroethane	8088154	7912758	2.2%	29939050	31422213	-5.0%
1,2-dichloroethane	4293384	4117080	4.1%	26590648	24668157	7.2%
1,1,2-trichloroethane	11273578	11725096	-4.0%	22329364	20896864	6.4%
dibromochloromethane	17196101	17801539	-3.5%	28040335	26462127	5.6%
1,1,1,2-tetrachloroethane	21794638	22258723	-2.1%	25229513	23347665	7.5%
tribromomethane	20050799	20789889	-3.7%	21482461	19892605	7.4%
1,1,2,2-tetrachloroethane	25324934	25937177	-2.4%	24819794	24055163	3.1%

The difference in the analyte response between the two core types is similar to what one would expect to see between fibers having different coatings with the same core type.

Durability

The Nitinol-core fibers provide an increased mechanical stability and durability, resulting in a more durable fiber with increased number of extractions per fiber. The mechanical stability and shape memory of Nitinol-core fibers allow them to be highly flexible while maintaining their original shape. **Figure 5** shows a picture of the fiber flexed at an 90° angle without being broken. The fiber was flexed 180° until it touched the inner rod and it returned to its original form without any breakage. A fused silica fiber typically breaks when flexed at any angle between 30°- 45°.

Figure 5. Flexing of a Nitinol Fiber at a 90° Angle



Fibers become more variable when the coating is damaged. The proprietary coating process creates an extremely well bonded coating that is less easily damaged, resulting in more reproducible results over time.

CONCLUSIONS

The Nitinol-core fibers with adsorbent coatings have been proved to be highly reproducible for the following reasons observed:

- Coated fiber diameter variability of less than 1% RSD and a coating thickness variation of less than 1.5 µm within lots. Coating thickness variation within lots <1.5 µm
- An improved intra-lot reproducibility as compared to the fused silica; for carboxen® fibers, the variability was 48.7% lower and for DVB fibers, 81.3% lower
- An improved inter-lot reproducibility as compared to fused silica; for carboxen fibers, the variability was 68.1% lower and for DVB fibers, 71.7% lower
- QC testing performance - Repeatable extractions, with RSD of <2% using test probes for the measurement of different adsorption mechanisms
- Good fiber inertness – similar or better than fused silica fiber cores
- High durability - Nearly unbreakable flexible fibers with well bonded smooth coatings
- Similar analyte recoveries between core types for the same coating

These results demonstrate that the users of adsorbent fibers having a fused silica core can easily transfer their methods for the same coatings onto the Nitinol-core versions, while taking benefits of improved consistency, durability, and robustness.

Materials

Sampling Mode and Needle Size						
Fiber Coating and Thickness	Fiber Core/ Assembly Type	Hub Description	Manual Holder/ (w/spring)		Autosampler	
			23 Ga*	24 Ga*	23 Ga*	24 Ga*
Carboxen®/Polydimethylsiloxane (CAR/PDMS)						
75 µm CAR/PDMS	NIT/SS	Black Metallic	57901-U	57904-U	57907-U	57908-U
Polydimethylsiloxane/Divinylbenzene (PDMS/DVB)						
65 µm PDMS/DVB	NIT/SS	Blue Metallic	57916-U	57921-U	57923-U	57931-U

Merck KGaA
Frankfurter Strasse 250
64293 Darmstadt, Germany

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