Technical Overview

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Solid Phase Microextraction Fundamentals

Solid phase microextraction (SPME)

Solid phase microextraction (SPME) is a solvent-free sample preparation technology. Based on the principle of adsorption or absorption and desorption, SPME uses a coated fiber or Arrow to concentrate volatile and semivolatile compounds from a sample. In SPME, analytes establish equilibria among the sample matrix, the headspace above the sample, and the polymer-coated fused phase. There are two categories of SPME extractions: headspace (most common) and direct immersion (DI), where the SPME fiber or Arrow is immersed into the aqueous sample (application specific).

The SPME analysis consists of two processes:

1. Partitioning of analytes between the coating and the sample (Figure 1)

   This process consists of inserting the SPME device into the sample matrix and exposing the phase to the sample. The target analytes are either adsorbed or absorbed (phase dependent) from the sample to the phase. After reaching the equilibrium state, the phase is retracted into the needle and removed from the sample vessel.

2. Desorption of concentrated analyte into the analytical instrument

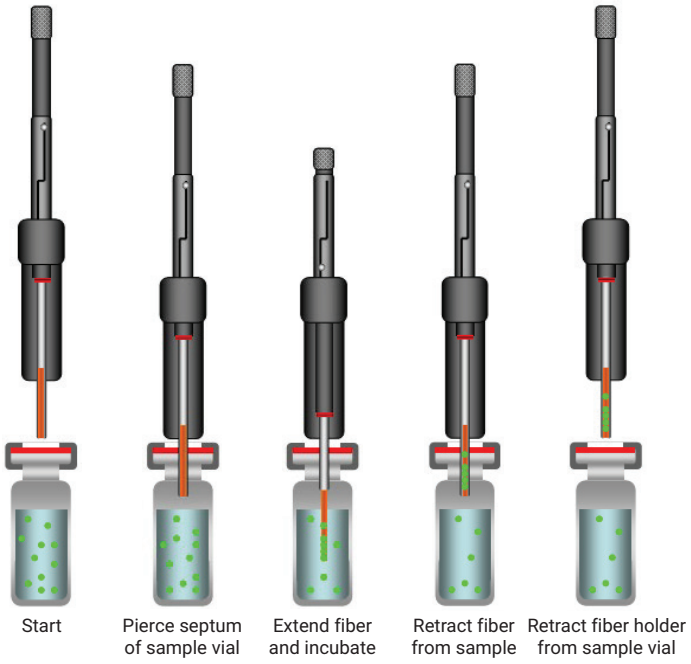

Figure 1. SPME process - direct immersion (DI) example shown.

SPME fibers and SPME Arrows

Invented in the early 1990s by Prof. Pawliszyn from the University of Waterloo in Ontario, Canada, SPME was introduced as a chemically modified fused silica fiber. Over the past few decades, SPME has become one of the most widely used extraction technologies for environmental, food, and clinical analyses. However, the technology remained almost unchanged with some drawbacks, such as the limited mechanical stability and small phase volumes. In 2016, a new patented technology for microextraction—combining trace-level sensitivity with high mechanical robustness—was launched, the PAL SPME Arrow. The PAL SPME Arrow has an outside diameter of 1.1 or 1.5 mm, resulting in large sorption phase surfaces and volumes, and an arrow-shaped tip, which allows for smoother penetration of vial and injector septa.

SPME fiber advantages:

- Original proven design
- Solvent-free
- Easy to automate
- Nondestructive to samples
- Fibers are reusable
- Compatible with GC or HPLC instrumentation

All Agilent SPME fibers have a standard length of 10 mm and a 23-gauge needle. The SPME fiber possesses a 100 µm × 10 mm, 0.6 µL sorption phase (Figure 2).

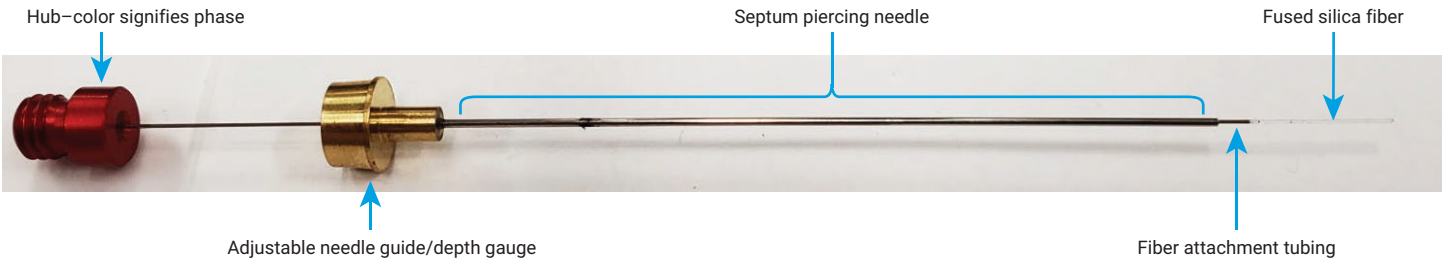

Figure 2. Characteristics of the SPME fiber (Agilent SPME fiber, PDMS-100/10-P3, red, 3/pk, p/n 5191-5872).

SPME Arrow advantages:

- Same as SPME fibers with the added benefits of:
- Larger sorption phase surface
- Increased phase volume
- Longer lifetime

All Agilent SPME Arrows have a standard length of 20 mm with either a 1.1 or 1.5 mm outside diameter (od) needle (Figure 3). SPME Arrows feature larger sorption phase surfaces (up to 6×) and volumes (up to 20×).

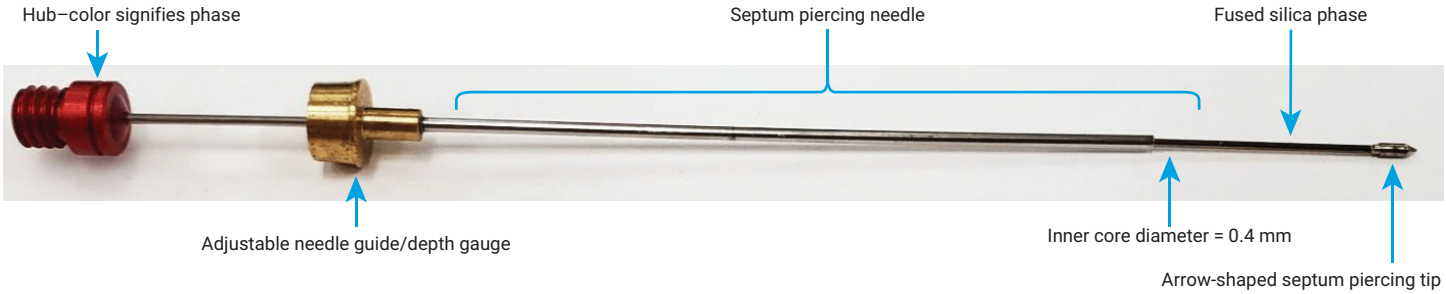

Figure 3. Characteristics of the SPME Arrow (Agilent SPME Arrow, PDMS (polydimethylsiloxane), 1.10 mm, 100 µm, red, 3/pk, p/n 5191-5862).

Choosing an SPME phase

There are several criteria that should be considered when choosing an SPME phase. These criteria include molecular weight of the target analytes, polarity of the target analytes, concentration, and the complexity of the matrix.

- Molecular weight (MW) of the analyte

  The MW of an analyte determines how rapidly it can move in and out of the phase coating and through the sample. A smaller analyte will diffuse more quickly and will require a shorter equilibration time. A larger analyte will migrate through the coating and sample more slowly and take a longer time to reach equilibrium.

- Analyte polarity (Figure 4)

  Polar coatings can be more selective for polar analytes, like phenols and esters, and can be less selective for nonpolar analytes.

- Analyte concentration (Figure 5)
  - For absorbent phases, the quantity of the analyte extracted is directly proportional to the volume of the phase. The thicker the film of the coating, the more analyte can be extracted from the sample.
  - Adsorption type fibers are better for extracting analytes present at low concentration levels and often provide lower detection limits for many analytes.
- Complexity of the matrix

  The PDMS coating is the most robust option for directly analyzing complex matrices, making it preferred regardless of the sensitivity of this coating toward the analytes of interest.[1]

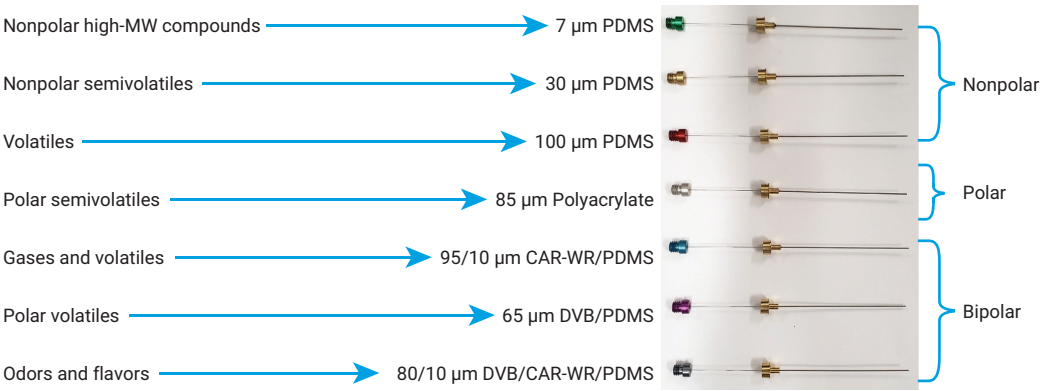

Figure 4. Agilent SPME fiber phases and their associated polarities.

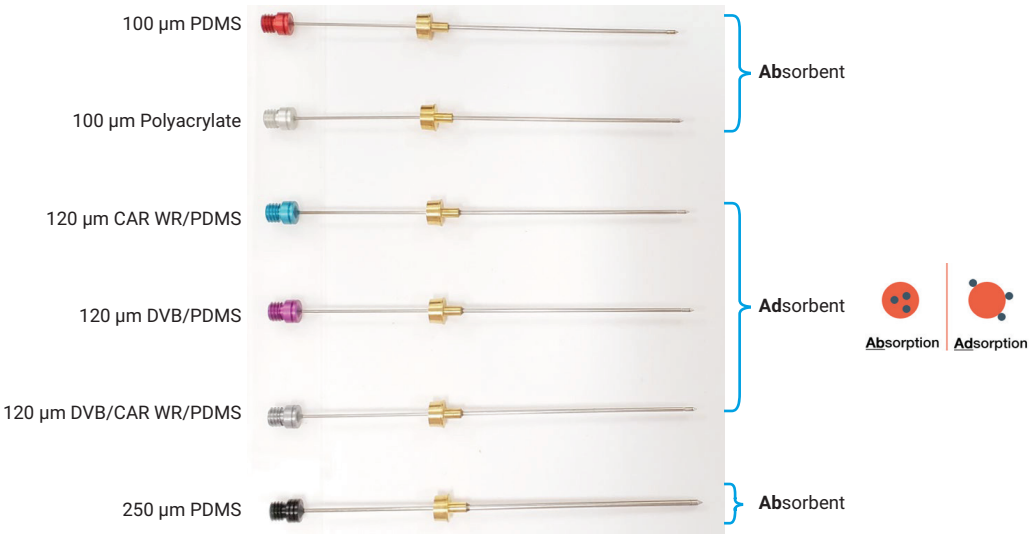

Figure 5. Agilent SPME Arrow phases and their associated material properties.

General phase recommendations:

- Nonpolar and volatile compounds usually require the 100 µm PDMS phase.
- CWR/PDMS effectively concentrates low molecular weight compounds.
- Larger molecular weight or semivolatile compounds are more effectively extracted with a 30 or 7 µm PDMS phase.
- To extract polar analytes from polar samples, use an 85 µm PA coated phase.
- Volatile polar analytes, such as alcohols or amines, are adsorbed more effectively and released fast with a 65 µm PDMS/DVB phase.
- For trace-level volatile analysis, the 75 µm PDMS/CWR phase is recommended.
- A 50/30 µm DVB/CWR/PDMS phase is optimal for a wide range of analytes (C3 to C20).
- General-purpose phase for HPLC analysis is the 60 µm PDMS/DVB phase.

SPME sample recovery

Changing the sample extraction method such as extending the equilibrium time or adding salt to the sample before to extraction affects sample recovery. Each condition and influence (Figure 6) are application dependent. Therefore, method development is an important part to any SPME application.

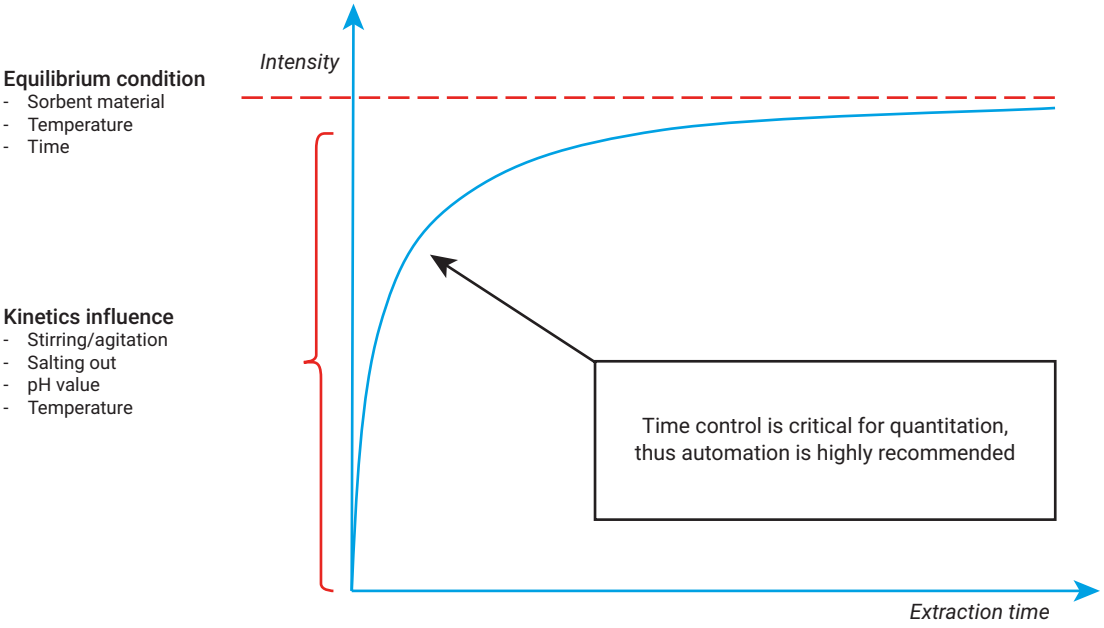

Figure 6. Physical factors affecting sample recovery by SPME.

Besides choosing the right coating and coating thickness, the sample temperature is also an important parameter in optimizing the method sensitivity. Generally, increasing the sample temperature will increase the sensitivity for the higher boiling components, but decrease the sensitivity for the lower boiling components. Temperature also affects the equilibrium during extraction; increasing the temperature will decrease the equilibration time.

One of the most common influences used in SPME applications is "salting out".[2] This involves adding a saturated amount of salt (commonly NaCl) to the sample to lower the partition coefficient (K) of target analytes to increase their concentration in the headspace. Salting out in turn provides an increase in extraction efficiency for many analytes, particularly for polar compounds and organic volatiles. However, it should be noted that salting out does not help in every application.

Direct immersion (DI)[3]

For complex or dirty samples (food and soil samples), headspace SPME is frequently chosen. However, the more hydrophilic and low volatility compounds—with relatively slower kinetics in solution—suffer higher resistance to transportation to the headspace. Thus, headspace sampling involving semivolatile and polar compounds is not always efficient. The extraction efficiency for polar and semivolatile compounds improves drastically when DI-SPME is performed. In DI-SPME, the diffusion coefficients through the matrix, which define the mass transfer properties of the extraction mode, are similar for all small molecules present in the system (Figure 7). The polyacrylate (PA) phase is most commonly used when analyzing nonvolatile polar analytes from clean matrices[4] (Figure 8).

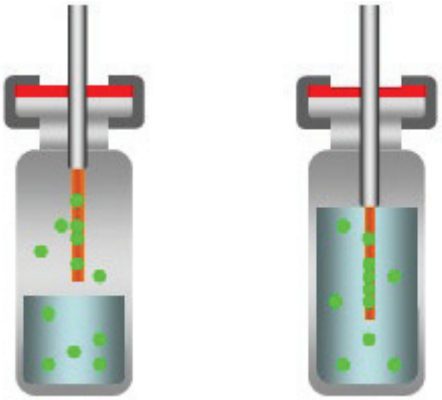

Figure 7. Headspace sampling and direct immersion fiber positioning.

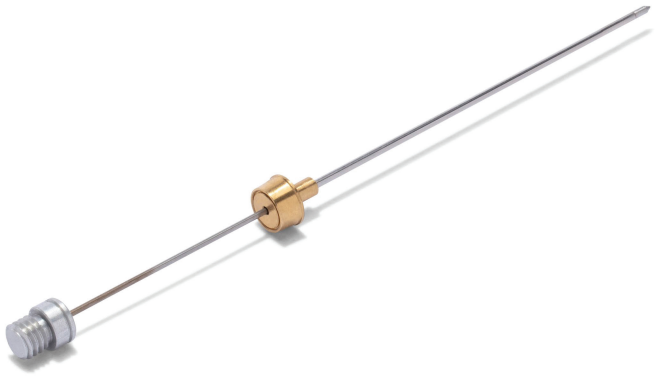

Figure 8. Agilent SPME Arrow, acrylate (polyacrylate), 1.10 mm, 100 µm, gray, 3/pk (p/n 5191-5858).

Despite the advantages presented in terms of extraction efficiency, solid porous phases show certain drawbacks associated with deterioration of the phase surface due to direct exposure to complex matrices for extended periods of time. Surface saturation of the solid porous phase is also possible due to adsorption from matrices containing a high concentration of target analytes or interferences. DI-SPME may be cumbersome, especially when dealing with complex matrices. However, when used correctly with rinses and proper conditioning, the lifetime of the phase can be extended.

All SPME phases may swell when exposed to certain solvents (particularly for chlorinated solvents). For example, PDMS swells in contact with nonpolar solvents (such as hydrocarbons, toluene, and dichloromethane).

When considering swelling, it should be noted that the CWR/PDMS phase is less prone to artifacts related to coating saturation compared to the PDMS/DVB and the DVB/CWR/PDMS phases (under the same working conditions). This is because the CWR particles have a higher surface area compared to those of DVB, thus CWR/PDMS has a greater total phase volume than PDMS/DVB.[5] The CWR/PDMS phase also has narrow micropores small enough to accommodate smaller analytes, and therefore, tends to have a higher affinity for low molecular weight and polar compounds compared to the PDMS/DVB phase.[5] With a larger sorption phase and volume the 1.5 mm od, CWR/PDMS SPME Arrows provide an optimal solution for DI-SPME analyses (Figure 9).

Figure 9. Agilent Smart SPME Arrow, carbon WR/PDMS (carbon wide range, polydimethylsiloxane), 1.50 mm, 120 µm, light blue, 3/pk (p/n 5610-5863).

The Agilent SPME portfolio

Agilent offers high-quality products for solid phase microextraction (SPME) sample preparation. Agilent supplies SPME Arrows and fibers in packs of three and related accessories, including fiber holders and inlet guides.

Table 1. SPME fibers and Arrows in the Agilent SPME product portfolio.

Part Number	Fiber/Arrow	Smart	Product Description	Fiber Gauge/ Arrow od	Phase Length	Phase Thickness	Color	Pack
5191-5877, G7371-67001	Both	No	Manual injection kit for SPME fiber and SPME Arrow	NA	NA	NA	NA	1 each
5191-5876	Fiber	No	Acrylate (polyacrylate)	23	10 mm	85 µm	Gray	3 pack
5610-5876	Fiber	Yes		23	10 mm	86 µm	Gray	3 pack
5191-5858	Arrow	No		1.1 mm	20 mm	100 µm	Gray	3 pack
5610-5858	Arrow	Yes		1.10 mm	20 mm	100 µm	Gray	3 pack
5191-5875	Fiber	No	Carbon WR/PDMS (carbon wide range/PDMS)	23	10 mm	95 µm	Dark blue	3 pack
5610-5875	Fiber	Yes		23	10 mm	95 µm	Dark blue	3 pack
5191-5859	Arrow	No		1.1 mm	20 mm	120 µm	Light blue	3 pack
5191-5863	Arrow	No		1.5 mm	20 mm	120 µm	Light blue	3 pack
5610-5859	Arrow	Yes		1.10 mm	20 mm	120 µm	Light blue	3 pack
5610-5863	Arrow	Yes		1.50 mm	20 mm	120 µm	Light blue	3 pack
5191-5874	Fiber	No	DVB/carbon WR/PDMS	23	10 mm	80 µm	Dark gray	3 pack
5610-5874	Fiber	Yes		23	10 mm	80 µm	Dark gray	3 pack
5191-5861	Arrow	No		1.1 mm	20 mm	120 µm	Dark gray	3 pack
5191-5864	Arrow	No		1.5 mm	20 mm	120 µm	Dark gray	3 pack
5610-5861	Arrow	Yes		1.10 mm	20 mm	120 µm	Dark gray	3 pack
5610-5864	Arrow	Yes		1.50 mm	20 mm	120 µm	Dark gray	3 pack
5191-5870	Fiber	No	PDMS (polydimethylsiloxane)	23	10 mm	7 µm	Green	3 pack
5610-5870	Fiber	Yes		23	10 mm	7 µm	Green	3 pack
5191-5871	Fiber	No		23	10 mm	30 µm	Yellow	3 pack
5610-5871	Fiber	Yes		23	10 mm	30 µm	Yellow	3 pack
5191-5872	Fiber	No		23	10 mm	100 µm	Red	3 pack
5610-5872	Fiber	Yes		23	10 mm	100 µm	Red	3 pack
5191-5862	Arrow	No		1.1 mm	20 mm	100 µm	Red	3 pack
5191-5866	Arrow	No		1.5 mm	20 mm	100 µm	Red	3 pack
5610-5862	Arrow	Yes		1.10 mm	20 mm	100 µm	Red	3 pack
5610-5866	Arrow	Yes		1.50 mm	20 mm	100 µm	Red	3 pack
5191-5867	Arrow	No		1.5 mm	20 mm	250 µm	Black	3 pack
5610-5867	Arrow	Yes		1.50 mm	20 mm	250 µm	Black	3 pack
5191-5873	Fiber	No	PDMS/DVB (PDMS/divinylbenzene)	23	10 mm	65 µm	Violet	3 pack
5610-5873	Fiber	Yes		23	10 mm	65 µm	Violet	3 pack
5191-5860	Arrow	No		1.1 mm	20 mm	120 µm	Violet	3 pack
5191-5865	Arrow	No		1.5 mm	20 mm	120 µm	Violet	3 pack
5610-5860	Arrow	Yes		1.10 mm	20 mm	120 µm	Violet	3 pack
5610-5865	Arrow	Yes		1.50 mm	20 mm	120 µm	Violet	3 pack

Table 2. Agilent SPME fiber and Arrow variety kits.

Part Number	Fiber/Arrow	Smart	Product Description	Fiber Gauge/ Arrow od	Phase Length	Phase Thickness	Color	Pack
5191-5879	Fiber	No	SPME fiber selection set 2 – PDMS (7 µm, 30 µm, and 100 µm), DVB/CWR/PDMS (80 µm), DVB/PDMS (65 µm)	23	10 mm	Multiple	Multiple	5 pack
5610-5879	Fiber	Yes	Smart SPME fiber selection set 2 – PDMS (7 µm, 30 µm, and 100 µm); polyacrylate (85 µm); CWR/PDMS (95 µm)	23	10 mm	Multiple	Multiple	5 pack
5191-5878	Fiber	No	SPME fiber selection set 1 – PDMS (100 µm), polyacrylate (85 µm), CWR/PDMS (95 µm), DVB/PDMS (65 µm), DVB/CWR/PDMS (80 µm)	23	10 mm	Multiple	Multiple	5 pack
5610-5878	Fiber	Yes	Smart SPME fiber selection set 1 – PDMS (100 µm), polyacrylate (85 µm), CWR/PDMS (95 µm), DVB/PDMS (65 µm), DVB/CWR/PDMS (80 µm)	23	10 mm	Multiple	Multiple	5 pack
5191-5869	Arrow	No	SPME Arrow selection set 2 – PDMS (1.10 mm, 100 µm); polyacrylate (1.10 mm, 100 µm); CWR/PDMS (1.10 mm, 120 µm); DVB/PDMS (1.10 mm, 120 µm); DVB/CWR/PDMS (1.10 mm, 120 µm)	1.1 mm	20 mm	Multiple	Multiple	5 pack
5610-5869	Arrow	Yes	Smart SPME Arrow selection set 2 – Smart SPME Arrow, PDMS (1.10 mm, 100 µm); Smart SPME Arrow polyacrylate (1.10 mm, 100 µm); Smart SPME Arrow, CWR/PDMS (1.10 mm, 120 µm); Smart SPME Arrow, DVB/PDMS (1.10 mm, 120 µm); Smart SPME Arrow, DVB/CWR/PDMS (1.10 mm, 120 µm)	1.10 mm	20 mm	Multiple	Multiple	5 pack
5191-5868	Arrow	No	SPME Arrow selection set 1 – PDMS (1.10 mm, 100 µm); polyacrylate (1.10 mm, 100 µm); CWR/PDMS (1.10 mm, 120 µm); DVB/PDMS (1.10 mm, 120 µm); PDMS (1.50 mm, 250 µm)	Multiple	20 mm	Multiple	Multiple	5 pack
5610-5868	Arrow	Yes	Smart SPME Arrow selection set 1 – Smart SPME Arrow, PDMS (1.10 mm, 100 µm); Smart SPME Arrow polyacrylate (1.10 mm, 100 µm); Smart SPME Arrow, CWR/PDMS (1.10 mm, 120 µm); Smart SPME Arrow, DVB/PDMS (1.10 mm, 120 µm); Smart SPME Arrow, PDMS, (1.50 mm, 250 µm)	Multiple	20 mm	Multiple	Multiple	5 pack

Table 3. Recommended Agilent SPME consumables and supplies.

Part Number	Product Description
5191-5877	SPME fiber or Arrow manual injection kit
392609902	Merlin microseal SPME replacement microseal, for Varian/Bruker 1079 GCs, 23 gauge
5182-3442	Merlin microseal starter kit, general purpose (100 psi), includes nut and microseal
5182-3444	Merlin microseal general purpose (100 psi) replacement microseal
5182-3445	Merlin microseal 100 psi nut
5182-3446	Merlin microseal nut for use with SPME arrows
5182-3447	Replacement microseals for use with 1.1 mm arrow SPME probes
5182-3448	Replacement microseals for use with 1.5 mm arrow SPME probes
5183-4757	Inlet septa, bleed and temperature optimized (BTO), nonstick, 11 mm
5183-4759	Inlet septa, advanced green, nonstick, 11 mm
5190-4048	Inlet liner, Ultra Inert, splitless, straight, 0.75 mm id, for SPME
5190-6168	Inlet liner, Ultra Inert, splitless, straight, 2 mm id
5182-0837	Vial, crimp top, headspace, clear, flat bottom, 20 mL, 23 × 75 mm, 100/pk
5188-2753	Vial, screw top, headspace, clear, 20 mL, 23 × 75 mm, 100/pk; vial size: 22.75 × 75 mm (18 mm cap)
5188-6537	Vial, screw top, headspace, amber, round bottom, 20 mL, 23 × 75 mm, 100/pk; vial size: 22.75 × 75 mm (18 mm cap)
5190-2239	Vial, crimp top, headspace, amber, round bottom, certified, 20 mL, 23 × 75 mm, 100/pk
5190-2286	Vial, crimp top, headspace, amber, graduation marks and write-on spot, flat bottom, certified, 20 mL, 23 × 75 mm, 100/pk
5188-2759	Caps/septa, screw, headspace, steel, high-temperature septa, certified, 18 mm, 100/pk; cap size: 18 mm
8010-0165	Caps/septa, crimp, headspace, 20 mm, silver magnetic, tan PTFE/silicone, 100/pk; cap size: 20 mm
8010-0420	Caps/septa, crimp, headspace, 20 mm, bimetal magnetic, PTFE/silicone septa, 100/pk; cap size: 20 mm
G3450-60638	8860/8890 inlet weldment for SPME arrow
G3452-60930	7890 turn top assy enlarged id, inert
G4585-60633	9000 inlet weldment for SPME arrow
G7371-67001	PAL3 alignment ring (grey) f S/SL inlet
G6500-88020	Magnet for 10/20 mL vial transport, used with PAL series automatic liquid sampler systems (PAL XT system)
G6500-88043	Split/splitless adapter ring, used with PAL series automatic liquid sampler systems (PAL XT system)

References

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Printed in the USA, February 13, 2023
5994-5775EN

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