CUSTODION® SPME Syringe User Guide

Torion® Technologies Inc.

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CUSTODION® SPME SYRINGE USER GUIDE

Portions adapted from Supelco Analytical Bulletin 928 (T101928)

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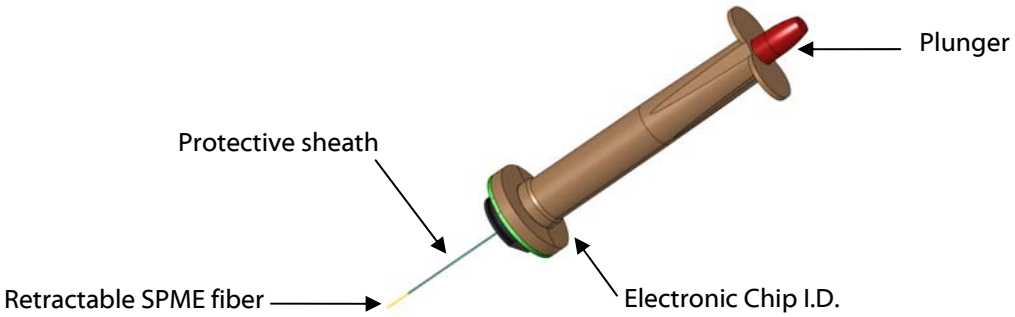
CUSTODION SPME Syringes

CUSTODION ASSEMBLY & PARTS

The SPME syringe designed for the GUARDION™-7 GC-TMS system as well as other GC and GC/MS systems is called the CUSTODION. The CUSTODION-10 and CUSTODION-11 versions include a memory chip that logs the syringe I.D. and other programmed information (metadata) about the sample. On the GUARDION-7 GC-TMS, the CUSTODION also triggers the injection and analysis to start on the GUARDION-7 without having to push a "start analysis" button.

The CUSTODION SPME syringe consists primarily of a barrel, plunger, spring, protective sheath, and SPME fiber.



Components:

Holder Assembly:	Ultem® plastic
Barrel and Plunger:	Stainless steel or Nitanol® metal alloy
SPME Fiber:	Fused silica or flexible Nitanol® metal alloy
Microchip:	EPROM add-only memory chip w/ 48-bit serial number C-10 - 64 Kbits memory capacity (250 samples) C-11 - 4 Kbits memory capacity (1 sample)

Physical Specifications:

Syringe Length:	7.2 in or 18.3 cm
Hand Grip Length:	4.0 in or 10.2 cm
Diameter:	1.375 in or 3.5 cm (widest)
Weight:	1.8 ounces (50 grams)
Film Thickness:	50-100 µm
Fiber Length:	active sample collection surface of SPME fiber - 1 or 2 cm in length
Barrel Gauge:	23 gauge metal alloy or 24 gauge StableFlex™ stainless steel

Available SPME Phases:

Divinylbenzene/Polydimethylsiloxane (DVB/PDMS) 65 µm d_f
Polydimethylsiloxane (PDMS) 100 µm d_f
Polyacrylate (PA) 85 µm d_f (only in Stable-Flex)
Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) 50/30 µm d_f
Carboxen/Polydimethylsiloxane (CAR/PDMS) 85 µm d_f
Carbowax/Polyethylene Glycol (PEG) 60 µm d_f (only in metal alloy)

Available Syringe Tips:

Tapered tip for use with regular septa
Blunt tip for use with Merlin® microseal

SPME TECHNOLOGY

Solid phase micro extraction, or SPME, is an innovative technology that is quick, easy, and reliable. SPME is a solvent-free extraction technique that combines extraction, collection, and concentration of analytes present for gas-phase, liquid, and dissolved solid samples. The active sample collection surface of the SPME fiber is 1 cm in length and is coated with a liquid polymer film or solid sorbent. The fiber's coating removes chemical compounds from the sample matrix by absorption in the case of liquid polymer coatings or by adsorption in the case of solid coatings. SPME technology provides the user with quick and convenient sampling and sample preparation in a single step. After sample collection, the SPME fiber is inserted directly into the heated injection port of a gas chromatograph (GC) for thermal desorption, separation, and detection. The CUSTODION SPME Syringe can be reliably used for on-site field sampling or in-laboratory applications with single handed operation.

GENERAL OPERATING INSTRUCTIONS

The CUSTODION Syringes are a series of novel SPME syringes that incorporate SUPELCO® Analytical's SPME fiber technology. The SPME syringes are fabricated with injection-molded components and the device resembles a ball-point pen. The Supelco SPME fiber assembly is housed inside the syringe. The push button trigger on top of the syringe enables the SPME fiber to be withdrawn into a protective sheath after sampling and while being inserted into the heated injection port of a GC or GC-MS. Target analytes in air, headspace, liquid or dissolved solid samples are quickly trapped on the SPME fiber, which is mounted inside the easy-to-operate syringe. The CUSTODION SPME Syringes are designed for easy single-handed operation even when wearing protective gloves.

The easy-to-use CUSTODION SPME Syringes are suitable for sample collection of analytes in air, liquids, and both headspace above solids and dissolved solids in liquids. Use of the CUSTODION SPME syringe involves the following steps:

1. Collect the sample by grasping the CUSTODION SPME syringe with your thumb positioned above the plunger.
2. Insert the SPME syringe needle into the sample or sample container (refer to the recommended sampling protocols beginning on page 11).
3. Depress the plunger to extend the SPME fiber either directly into the sample or the sample headspace. Expose the fiber for a sufficient amount of time to collect and concentrate the sample, depending on the expected analyte concentration(s). Short exposure times (5-30 s) are recommended for high concentrations, while longer exposure times (up to 30 min) may be required for low concentration samples. If organic solvents are to be sampled, headspace sampling is recommended. Refer to organic solvent compatibility information in this guide.
4. Do not to touch the SPME fiber on the sample container as this may damage the SPME fiber.
5. Once the sample is collected, depress the plunger to withdraw the SPME fiber back into the protective needle and remove the CUSTODION syringe from the sample or sample container.
6. Insert the CUSTODION syringe needle into the injection port of a GC or GC/MS.
7. Depress the plunger with your thumb to extend the SPME fiber and begin analyte desorption. Keep the SPME fiber extended for a sufficient amount of time to allow analyte(s) to desorb.
8. Depress the plunger again to draw the SPME fiber back into the CUSTODION syringe needle.
9. Remove the CUSTODION syringe from the injection port.

Tips for Sampling, Desorption, and Analysis Procedures

EXTRACTION PROCEDURE

Extraction time is critical for the sample to establish equilibrium with the SPME fiber coating. Extractions typically take 20 sec to 2 min, but can be as short as 1-10 sec, depending on the concentration(s) of the target analyte(s). Headspace extractions are usually shorter than direct immersion into liquids or dissolved solid extraction solvents. The extraction time will depend on the size and molecular weight of the compounds, fiber coating, type of extraction solvent used and sample concentration. Extraction times can be shorter when:

-Analyzing small compounds (<150 MW)
-Using thinner, absorbent type fiber coatings
-Using a headspace technique
-Working with high concentration samples (high ppb or ppm range)

Temperature of the sample is critical for accurate quantitation. A constant temperature must be used for all extractions to obtain good precision. The use of heat during headspace extractions will help release the analyte from the sample, improve sensitivity, and shorten the extraction time. Note that SPME headspace sampling requires lower temperatures than standard headspace applications. If the temperature is too high, then analytes may be driven off the fiber resulting in reduced overall sensitivity. This is particularly true when using liquid phase/absorbent type fibers such as PDMS. Generally, heating the sample is not required for immersion extractions. For some applications with non-volatile or high boiling semi volatile compounds, a small amount of heat applied to the sample can shorten the SPME equilibration time.

Agitation of the sample is important to reduce the equilibrium time and improve accuracy and precision. This is crucial when analyzing semivolatile compounds by immersion sampling. Maintain a consistent agitation between all extractions for good precision. Stirring, sonication, and vibration are all suitable methods to agitate the sample. Agitation can also be used with headspace extractions. The agitation will usually shorten the headspace extraction time and assure better precision across the sample analyses.

Adjusting the pH or adding salt can improve the extraction efficiency by changing the solubility of the analytes in the sample. The addition of 25-30% (w/v) NaCl will increase the ionic strength of the sample, which reduces solubility for organic analytes. The addition of salt is especially helpful when analyzing polar organic analytes in water. Buffering the pH of the sample will decrease analyte solubility, improve volatility of bases and acids, and assure constant pH between extractions. Acidic analytes can be buffered down to pH 2 and basic analytes up to pH 11. ***Note****: The Carbowax-DVB fiber coating should not be used at a pH above 9. Do not use mineral acids or hydroxide salts when adjusting the sample pH. Phosphate buffers at 0.1M are suitable to obtain a pH buffering range of 2 to 11.*

Headspace sampling sensitivity is best when the headspace volume is small. It is recommended to keep the headspace volume between 30% and 50% of the vial. When the headspace volume is small, the fiber extracts more sample faster and with greater efficiency. In some cases, a larger headspace volume can be used with high concentration samples. It is extremely important to keep the headspace volume and the vial size constant. Position the fiber at the same depth in the headspace each time to improve reproducibility. If the matrix contains proteins such as serum and blood, it is advisable to deproteinate the sample before headspace extraction.

Immersion sampling sensitivity is improved by filling the sampling vial to a minimum of 80%. The recommended sample volumes are 1mL to 5mL. Use the same volume for all extractions to achieve reproducible results. Immersion sampling works best for low concentration water based sample matrices. When using immersion for samples containing sugars, proteins, and particulate matter, rinse the fiber in water before desorption. This will extend fiber life and reduce injection port contamination. It is best not to immerse the fiber in oils, but if needed, the fiber can be wiped lightly before desorption. Position the fiber just below the sample surface for immersion sampling and maintain this position consistently for all extractions.

SAMPLING VIALS AND SEPTA CAN BE A SOURCE OF CONTAMINANTS AND ARE FREQUENTLY MISTAKEN AS A FIBER RELATED PROBLEM. IT IS RECOMMENDED TO BAKE OUT SEPTA AT 150°C FOR TWO HOURS BEFORE USE AND ALWAYS USE PRE-CLEANED VIALS FOR SPME SAMPLING.

DESORPTION PROCEDURE

For laboratory GC inlets, splitless injection is required with SPME to focus the analytes on the chromatographic column. Close the split vent valve during sample injection. GC systems with narrow-bore inlet liners (0.75mm ID) will reduce peak broadening in the chromatographic analysis by minimizing the dead volume during analyte transfer onto the GC column.

Pre-drilled, low bleed septa (Thermogreen™ LB-2) or a septum-less injector system (Merlin Microseal™) are recommended to reduce or eliminate coring of the injection port septa during sample desorption. Septa coring can result in interfering peaks, obstruction of the GC carrier gas flow, plugging of the GC injection port, poor chromatography, and SPME fiber breakage.

ANALYSIS PROCEDURE

If a problem source is determined to be the GC injection port, column, or detector, please refer to the manufacturer's documentation. Manufacturer user manuals often provide helpful tips to improve analysis procedures.

SPME PRODUCT RELATED ISSUES

SPME fiber breakage is a potential problem when applying excessive stress to the fiber during sampling or analysis. The use of StableFlex fibers are recommended for SPME application. StableFlex fibers are made with a flexible core, which is more durable and less likely to break if stressed. For SPME applications such as field sampling where excessive bending of the syringe needle is possible due to a harsh environment, the metal alloy syringe needle provides additional strength and flexibility.
Note: *Do not expose PDMS or PDMS-DVB coated fibers to non-polar solvents (hexane, dichloromethane (methylene chloride), diethyl ether, etc.). Do not expose Carbowax coated fibers to polar solvents (methanol, ethanol, etc.). If the fibers must be exposed to solvents, do not expose the fiber for extended periods (i.e., more than a few seconds in headspace). The fiber coating in both of these cases will swell and cause damage to the fiber upon retraction into the needle guide. The damage may include breakage, grooving, or stripping of the fiber coating. To avoid this problem, dilute the sample with water before extraction to reduce the organic solvent percentage to less than three percent (<3%, v/v).*

CUSTODION SPME Fiber Assemblies

CONDITIONING AND THERMAL CLEANING OF SPME FIBERS

Follow the conditioning guidelines in the table below to thermally clean the SPME fibers before use.

If a fiber becomes contaminated after use, these steps can be repeated if necessary. If the contamination is severe, the fiber can be thermally cleaned for an extended period of time at a temperature 20°C below the listed conditioning temperature in the table below. If the steps do not clean the fiber, solvent cleaning can be attempted. Please follow the guidelines for solvent cleaning of specific fiber coatings (see next section).

Temperature, pH and Conditioning Guidelines for SPME Fiber Coatings

Fiber Coating	Film Thickness	pH	Maximum Temperature (°C)	Recommended Operating Temperature (°C)	Conditioning Temperature (°C)	Conditioning Time (Hrs)
PDMS	100 µm	2-10	280	200-280	250	0.5
PDMS	30 µm	2-11	280	200-280	250	0.5
PDMS	7 µm	2-11	340	220-320	320	1
PDMS/DVB	65 µm	2-11	270	200-270	150	0.5
Polyacrylate	85 µm	2-11	320	220-300	280	1
Carboxen/PDMS	75 µm	2-11	320	250-310	300	1
PEG	60 µm	2-9	250	200-250	240	0.5
DVB/CAR/PDMS	50/30 µm	2-11	270	230-270	270	1
Carbopack™ Z	15 µm	2-10	340	250-340	320	0.5
Carbowax/DVB	70 µm	2-9	250	200-240	230	0.5

Note 1: *When conditioning in a GC injection port, be sure to open the split vent to reduce the amount of impurities entering the column. For the GUARDION-7, the GC injector is optimized for SPME injection and no setting changes are required. Always ramp the column temperature after fiber conditioning to remove any contaminants that may have entered the GC column.*

Note 2: *Make sure that the injection port contains an appropriate liner. We strongly urge that you insert a liner designed for SPME use with a narrow I.D. between 0.75 mm and 1.0 mm I.D. for the GC inlet. Do not insert a SPME fiber into a liner containing glass wool. If the fiber contacts the wool, the coating could be damaged.*

GENERAL PRECAUTIONS, SOLVENT CLEANING AND COMPATIBILITY FOR SPME FIBER COATINGS

PDMS (Polydimethylsiloxane) Absorbent Fiber Coatings

1. For solvent cleaning, PDMS fibers can be immersed in water soluble organic solvents such as methanol, acetonitrile, acetone or ethanol, especially if it is a mixture of water with the organic solvent. The addition of water helps to reduce swelling. Usually 15-30 min. should be sufficient for cleaning the fibers.
2. Do not place PDMS fibers in non-polar solvents or samples containing percent levels of non-polar solvents such as hexane, methylene chloride (dichloromethane) and diethyl ether.
3. Heated headspace extraction of samples with high concentration (>100 ppm) of non-polar solvents and terpenes can swell PDMS coatings. The 30 μm PDMS is less likely to be stripped than the 100 μm PDMS when the fiber is retracted. Consider this fiber as an option when evaluating such samples.

PEG (Polyethylene Glycol, Carbowax) Fiber Coating

1. For solvent cleaning PEG fibers, place the fibers in a 1% methanol:water solution containing a minimum of 15% NaCl for 15 to 30 min. It is important to have the salt present when soaking as this reduces swelling of the PEG coating.
2. PEG fibers can be immersed in hydrocarbon solvents and will not swell.
3. It is highly recommended that PEG fibers not be immersed in samples with water-soluble organic concentrations above 1% (total water soluble organic) unless the water sample contains at least 15% NaCl or other salts. The degree of swelling will vary depending upon the solvent(s) in the water. In many cases there will not be sufficient swelling to damage the fiber, but in some cases the fiber coating can be stripped or damaged when the fiber is retracted.
4. It is recommended that the PEG fiber should not be exposed to the headspace of samples with a water-soluble organic concentration higher than 2%. The organic analytes will be concentrated in the heated headspace and can swell the phase which can result in stripping when the fiber is retracted into the needle.
5. Methanol may be produced when the fiber is exposed to acidic samples. This is due to the presence of an inhibitor in the starting material. Most of the inhibitor has been removed, but several additional extractions in an acidic solution will remove the remaining amount of inhibitor that may be present. Solvent cleaning (step 1) is usually sufficient for removal of the inhibitor from the fiber coating.

Polyacrylate Fiber Coating

1. For cleaning, soak the fiber in a water miscible organic solvent for 30 min, followed by immersion in water to reduce any swelling. It is best to place the fiber in water prior to retracting the fiber.
2. The polyacrylate fiber can be immersed in aliphatic hydrocarbon solvents without swelling.
3. The polyacrylate coating may darken with use. This is not un-usual and does not hinder fiber performance, unless the coating becomes black. This indicates that oxygen is present in the injection port. If the fiber is desorbed at 280 °C or lower, the coloration will be reduced.

Adsorbent/Particle Type Fibers

1. Carboxen 1006 used in Carboxen-containing SPME fibers can retain solvents in the micropores, so it is generally not advisable to soak this fiber in solvents. Multiple desorption cycles may be required to remove the solvent. Fibers will not greatly swell in water soluble organic solvents.
2. For PDMS-DVB fibers, follow the guidelines for PDMS fibers.

Blank Analysis

Prior to running a fiber blank analysis, be sure that the GC column has been thermally cleaned to the desired upper temperature of your method.

Note 1: *Do not soak any SPME fiber in chlorinated solvents.*

Note 2: *All SPME fiber coatings are bonded. However, bonded fibers will still swell in certain solvents. In some cases the swelling is sufficient that when the fiber is retracted into the needle, the needle can strip off the fiber coating. The swelling may occur in both headspace and liquid immersion modes. In some samples the organics can be concentrated in the headspace and swell the fiber even more than if the fiber was immersed in liquid. It is important to determine compatibility of samples with the fiber coatings.*

CUSTODION SPME Recommended Sampling Protocols

AIR SAMPLING

1. Collect air samples into a clean, sterile Tedlar bag or similar. Other sampling methods may include direct SPME exposure to an air flow or open area (air duct, room, open container), headspace directly above a sample located in an open space (outside of a package), or the headspace inside of a container (bag, closed container with a sampling port).
2. Unscrew the syringe needle protective cap from the CUSTODION syringe.
3. If required, pierce the sample container using the syringe needle. Ensure that the SPME fiber is retracted into the syringe needle before piercing the septa. In this position, the green indicator in the thumb mechanism on the CUSTODION will be visible.
4. Position the tip of the syringe needle at least 1.5-2 cm above any solid surface (wall of container, solid sample) to prevent damage to the SPME fiber.
5. Expose the SPME fiber by depressing the top of the CUSTODION push button plunger assembly. This will extend the 1 cm SPME fiber from the tip of the syringe needle. The green indicator in the plunger mechanism will no longer be visible.
6. Sample the headspace for an amount of time that is suitable for the expected concentration of analyte(s) in the sample. If the sample concentration(s) is (are) unknown, it is recommended to begin sampling at short durations (i.e., 10 sec) and increase the sample exposure time only if anticipated target analyte results are not observed upon analysis. ***Note:*** *Heating the sample may be useful to liberate volatile compounds. However, this may also lead to degradation for certain analytes.*
7. After sample exposure, retract the SPME fiber into the syringe by depressing the CUSTODION plunger assembly once again. The green indicator will now be visible through the thumb assembly.
8. If not immediately analyzing the sample, reinstall the CUSTODION protective cap. Store syringe under refrigerated or cool conditions for best preservation of collected sample.

HEADSPACE SAMPLING (LIQUIDS AND SOLIDS)

1. Collect the liquid or solid sample into a clean, sterile sample vial fitted with a septum top.
2. Unscrew the syringe needle protective cap from the CUSTODION syringe.
3. Pierce the top of the sample vial using the syringe needle. Ensure that the SPME fiber is retracted into the syringe needle before piercing the septa. In this position, the green indicator in the thumb mechanism on the CUSTODION will be visible.
4. Position the tip of the syringe needle at least 1.5-2 cm above the sample surface to prevent touching the sample with the SPME fiber.
5. Expose the SPME fiber by depressing the top of the CUSTODION push button plunger assembly. This will extend the 1 cm SPME fiber from the tip of the syringe needle. The green indicator in the plunger mechanism will no longer be visible.
6. Sample the headspace for an amount of time that is suitable for the expected concentration of analyte(s) in the sample. If the sample concentration(s) is (are) unknown, it is recommended to begin sampling at short durations (i.e., 10 sec) and increase the sample exposure time only if anticipated target analyte results are not observed upon analysis. ***Note:*** *Heating the sample may be useful to liberate volatile compounds. However, this may also lead to degradation for certain analytes.*
7. After sample exposure, retract the SPME fiber into the syringe by depressing the CUSTODION plunger assembly once again. The green indicator will now be visible through the thumb assembly.
8. If not immediately analyzing the sample, reinstall the CUSTODION protective cap. Store syringe under refrigerated or cool conditions for best preservation of collected sample.

IMMERSION SAMPLING (LIQUIDS AND DISSOLVED SOLIDS)

1. Collect the liquid or solid sample into a clean, sterile sample vial fitted with a septum top.
2. If the sample is a solid, dissolve the sample in a suitable solvent (water or methanol, etc.) for the analyte(s) of interest. ***Note****: If the solvent is an organic solvent, ensure the solvent will not swell the fiber coating. Refer to the fiber compatibility notes on pages 4-5 of this guide for more information.*
2. Unscrew the protective cover from the end of the CUSTODION syringe.
3. Ensure that the SPME is retracted before piercing the septa. In this position, the green indicator in the plunger mechanism will be visible.
4. Pierce the top of the sample vial using the syringe needle.
5. Position the tip of the syringe needle at or below the sample surface, provided the total sample depth is at least 1 cm deep. For samples with smaller volumes, the sample vial may need to be tilted at an angle to allow for full immersion of the 1 cm SPME fiber.
6. Expose the SPME fiber from the syringe by pressing down on the top of the CUSTODION plunger assembly. This will extend the 1 cm SPME fiber. The green indicator in the plunger mechanism will no longer be visible.

7. Sample the liquid for a time suitable for the expected concentration of analyte(s) in the sample. Agitate the sample (shaking, sonication, etc.) for a short period of time (i.e., 10 sec). If the sample concentration is unknown, it is recommended to begin sampling at short durations (i.e., 10 sec) and increase the sample time only if anticipated results are not observed upon analysis.
8. If the sample contains dissolved solids, rinse the fiber with water after sample exposure and before desorption. This will extend fiber life and reduce GC injection port contamination.
9. Retract the SPME fiber into the syringe by depressing the CUSTODION plunger assembly once again. The green indicator in the plunger mechanism will be visible.
9. If not immediately analyzing the sample, reinstall the CUSTODION protective cap. Store syringe under cool conditions for best preservation of collected sample.

Special note:

Solvent compatibility: Do not expose PDMS or PDMS-DVB coated fibers to non-polar solvents (hexane, dichloromethane (methylene chloride), diethyl ether, etc.). Do not expose Carbowax coated fibers to polar solvents (methanol, ethanol, etc.). If the fibers must be exposed to these solvents, do not expose the fiber for extended periods (i.e., more than a few seconds in headspace). The fiber coating in both of these cases will swell and cause damage to the fiber upon retraction into the needle guide. The damage may include breakage, grooving, or stripping of the fiber coating. To avoid this problem, dilute the sample with water before extraction to reduce the organic solvent percentage to less than three percent (<3%, v/v).

Solid Phase Microextraction Troubleshooting Guide

HOW TO LOCATE & SOLVE PROBLEMS

Solid phase micro extraction (SPME) is an innovative, solvent free technology that is fast, economical, and versatile. SPME has gained wide spread acceptance as the technique of preference for many applications. As with any analytical process however, problems occur on occasion. The most important step in correcting a problem when it occurs is identifying the root cause as quickly as possible. The systematic approach to troubleshooting described in this guide will allow for a quick solution to many problems. This guide contains helpful tips to prevent problems before they occur, as well as a troubleshooting table listing the symptoms of common problems, the possible causes, and suggested fixes. By following these recommendations, valuable time and money can be saved.

TROUBLESHOOTING SUGGESTIONS

Troubleshooting can be facilitated by closely observing and keeping complete records of the conditions under which the SPME syringe has been used. Understanding the system performance history as related to the fiber, sampling, desorption, inlet, column, detector response, etc., is important for effective troubleshooting. Thorough documentation of system maintenance is equally important when determining what variables have changed, and when. Troubleshooting is more effective when the following items are available:

- New backup CUSTODION SPME syringe with fiber
- Pre-tested or control CUSTODION SPME fiber with known performance
- Pre-tested or control GC column with known performance
- All associated product instruction sheets and instrument manuals

ISOLATING THE PROBLEM SOURCE

Establish a Systematic Approach

Carefully note the symptoms encountered (e.g., no peaks detected, extraneous peaks detected, etc.), then find these in the troubleshooting table beginning on page 16. Next to each symptom are listed possible causes for what is being observed. Review the possible causes and systematically address each one through the remedy listed. Start the elimination process with the most probable cause based upon the specific situation, then work through the remedies systematically. A shotgun approach to applying multiple remedies at the same time, while appearing to be the fastest approach, is usually the least effective.

Understanding the cause and effect relationship with the changes made and determining the actual root cause of the problem is the most beneficial and effective approach. The troubleshooting table contains most of the problems encountered with SPME, but every situation or application cannot be anticipated. If a problem not covered in the table is found, the cause can still be determined and a solution found by systematically isolating the problem into one of four areas: sampling, desorption, analysis, or product. The following is a general scheme for isolating the problem.

Step 1: Eliminate the sample matrix from the process by sampling a clean matrix (reagent water or sand) spiked with a known reference standard. Sample this control with the identical sampling conditions used previously.

Step 2: Analyze the sampled fiber under the identical desorption and instrument conditions used previously. If the results show the problem persists, then proceed to step three. If the problem disappears, it has been demonstrated that the SPME fiber and desorption process are not the likely causes of the problem. The most likely cause of the problem is the sample matrix and its effect on the equilibrium or fiber. Experiment with the sampling conditions (headspace vs. immersion, time, temperature, pH, salt, agitation, etc.) to determine the optimal parameters for the matrix. Just as with any sample preparation technique, changes in the sample matrix will influence precision, accuracy, and chromatographic results.

Step 3: If the problem persists after removing the sample matrix from the process, begin systematically removing the remaining possible sources of the problem. These include:

- SPME fiber condition – examine the SPME fiber to ensure it is not missing, damaged, or worn. The fiber color should be similar or slightly darker than when first used. Change CUSTODION Syringes if necessary.
- Sampling vial - change the vial and associated septum and make sure baked or pre-cleaned sampling vials and septa are used.
- Fiber - change to a control fiber with known performance if available, or switch to a new, conditioned fiber. In addition, the sampling step can be eliminated by directly desorbing the fiber to isolate the problem as it relates to product versus sampling.
- Fiber position - make sure the fiber is positioned properly during the headspace or immersion sampling step.

Troubleshooting Table

Problem / Symptom	Possible Cause	Remedy
1. No peaks seen in GC analysis	1. Instrument problems (A)	1. Inject standard mixture to verify detector response
	2. The split vent was left open (D)	2. Run splitless injection
	3. The analyte concentration is too low to be detected (S)	3. Start with known concentration (1ppm) of analyte in deionized water mixture. Optimize extraction by adjusting extraction time, temperature and chemical condition of pH and salt
	4. Solvents present in sample competing with SPME extraction (S)	4. Minimize solvents in the sample to <3% by dilution in water
	5. Headspace volume too large to establish equilibrium with fiber (S)	5. Reduce headspace to 50% or less, agitate sample vigorously, or increase the sampling temperature
	6. Coating on fiber deteriorated (P)	6. Replace fiber. Fibers are reusable and will last for 50 injections on average
	7. Incorrect SPME fiber used for extraction (P)	7. This is beyond the scope of this guide. Please contact technical support (801.705.6600) for assistance if you are experiencing problems selecting the appropriate fiber for your application
	8. Leaking injection port (septum or connection) (D)	8. Replace septum and tighten nut properly
	9. Leaking sample vial (S)	9. Replace vial septum and seal cap properly
	10. Loss during transport from the field (S)	10. If the fiber will be stored for more than one day, it is recommended that it be stored at sub-ambient temperature. This reduces the chance of breakdown and loss of sample that can occur at higher temperatures
2. Extraneous peaks in analysis	1. Septa used in sampling vial or injection port outgassing organic contaminants (S/A)	1. Prebake the vial septa for 2 hours at 68°C prior to use. Use low-bleed septa to minimize injection port septum bleed
	2. Fiber is not preconditioned prior to sampling (P)	2. Precondition fiber at the recommended conditioning temperature. Once fiber is preconditioned, only 1-2 minutes is required to clean the fiber prior to sampling
	3. Inlet liner is contaminated or contains septa particles (D)	3. Replace the inlet liner. Use pre-drilled septum or a septum-less injector system (e.g. Merlin Microseal)
	4. GC column is collecting analytes on the front of the column because it is not heated high enough in sample analysis (A)	4. Complete GC analysis temperature program before injecting another SPME extract and keep column at 150°C when not in use
	5. Interfering peaks co-elute with analytes of interest (A)	5. Change GC column temperature program rate
	6. Carryover from previous analysis of the fiber (P)	6. Bake out fiber at the recommended conditions for several minutes (analyte dependent)
	7. Cross-contamination from laboratory air (S)	7. Do not expose the fiber to the laboratory environment at any time during the sampling or injection steps. Analyze control blanks using the same handling process as the sample to determine if technique or laboratory cross-contamination is present
	8. Cross-contamination during transport from the field (S)	8. If the fiber will be stored for more than one day, it is recommended that it be stored at sub-ambient temperature. This reduces the chance of sample cross-contamination

A=Analysis related D=Desorption related P=Product related S=Sampling related

Problem / Symptom	Possible Cause	Remedy
3. Fiber will not retract or sticks in holder needle	1. The end of the needle is plugged with a piece of septum (D)	1. Injection port septum nut is over tightened. Loosen the nut slightly to allow for improved injection. Use the pre-drilled injection port septa or a septum-less injector system (e.g. Merlin Microseal)
	2. The fiber was exposed to solvents that caused swelling of coating (S)	2. Do not expose PDMS coated fibers to non-polar solvents such as pentane, methylene chloride, or diethyl ether. Do not expose Carbowax fibers to polar solvents.
	3. Syringe malfunction.	3. Replace CUSTODION syringe.
4. Needle bends during injection into sample vial or GC injection port	1. Improper manual sampling technique (S)	1. To prevent the needle from bending with doing manual SPME sampling, follow this procedure: ▪ Hold the SPME assembly on top of the sampling vial with the bottom of the CUSTODION flush with the top of the vial cap. ▪ Hold the sampling vial and CUSTODION securely with one hand ▪ Expose the fiber and perform sampling as usual
	2. Improper manual desorption (injection)technique (D)	2. To prevent the needle from bending when doing manual SPME injections, follow this procedure: ▪ Position the CUSTODION on top of the GC injection port or in the SPME inlet guide with the bottom of the CUSTODION flush with the top of the injection or guide ▪ Hold the CUSTODION securely with one hand ▪ Expose the fiber and perform sample desorption as usual
	3. Vial or injection port septum is too tight (S/D)	3. Loosen slightly the vial closure or injection port nut
	4. Septa in sample vial/injection port is too thick or coated with thick Teflon® coating (S/D)	4. Use LB-2 septa for injection port or silicone septa with <10mil Teflon on sampling vials. Shorten the amount of exposed needle on SPME holder to 0.5 inch or (~1cm) before puncturing the vial septa. Adjust the holder needle setting to the desired depth for sampling. Do not use butyl rubber style septa
	5. GC inlet liner is too narrow or packed with adsorbent material (D)	5. Use larger splitless inlet liners (0.75mm ID or larger) without glass wool or adsorbents
	6. Needle is out of alignment with injection port or sample vial (S/D)	6. Reference auto injector manual on alignment
5. Fiber breaks	1. Fiber was not retracted into the protective needle after removal from sample vial or injection port (S/D)	1. Retract fiber into protective needle during insertion into vial/injection port and removal
	2. End of the needle is plugged with a piece of septum (D)	2. Injection port septum nut is over tightened. Loosen the nut slightly to allow for improved injection. Use pre-drilled injection port septa or a septum-less injector system (e.g. Merlin Microseal)

A=Analysis related D=Desorption related P=Product related S=Sampling related

Problem / Symptom	Possible Cause	Remedy
6. Reproducibility is poor	1. Time and temperature variations during sampling (S)	1. Control time of extraction and temperature. Use a timing device and calibrated thermometer to ensure reproducible results. Note that room temperature fluctuations will influence the ambient sample temperature
	2. Fiber not consistently positioned at the same depth during sampling (S)	2. Position fiber just below sample surface for immersion sampling and at a consistent position above the sample during headspace sampling
	3. pH or salt conditions varying during sampling (S)	3. Apply any pH or salt adjustments made to the samples uniformly across all extractions
	4. Equilibrium is not reached during extraction (S)	4. Determine minimum time for equilibrium using a standard mixture and controlled extraction conditions. Note that full equilibrium is not required to be reached for all applications to achieve reproducible results
	5. Varying organic content in the samples (S)	5. Dilute samples to minimize solvent interference or use headspace sampling to minimize solvent effect. Use internal standards, surrogates, or the standard addition technique to compensate for variations in sample matrix
	6. Varying headspace in sample vials during headspace extraction (S)	6. Minimize headspace volume to 50% or less and agitate the sample. Maintain the same headspace volume and agitation conditions across all extractions
	7. Solid samples not releasing analytes for extraction (S)	7. Grind solid into small particles, add to water, and apply head and agitation
	8. Competing analyte displaces compound of interest/or interferes (S)	8. Reduce the extraction time to minimize displacement or interference
	9. Not reproducing desorption conditions (D)	9. Verify that the fiber position (depth), desorption time, temperature, and splitless conditions are consistent. If available, use an automated SPME system to improve reproducibility
	10. Not using agitation during sampling or apply it inconsistently (S)	10. Use a stir bar or sonication system to agitate the sample during sampling. Maintain consistent agitation conditions for all standards and samples
	11. Inconsistent sample volumes (S)	11. Maintain consistent volumes for all standards and samples
7. Fiber discolored	1. Fiber is oxidized during fiber conditioning or sample injection into GC (S/D)	1. Minimize oxygen in carrier gas, and condition fibers in oxygen free gas flow. Reduce the injection port temperature to the recommended maximum setting. Carbowax/DVB coatings are especially sensitive to temperature (<260°C is recommended)
	2. Heating during injection (D/P)	2. Does not usually affect the performance of the fiber. Always minimize the oxygen content in the GC carrier gas to avoid oxidizing the fiber coating. The polyacrylate coated fiber will discolor above 280°C. Carbowax may slightly darken during Use, however, if the fiber turns brown, lower the injection port temperature (265°C is the recommended maximum) check the system for leaks
8. Number of injections from the fiber is less than previously obtained	1. Fiber is oxidized during fiber conditioning or sample injection into GC (S/D)	1. Minimize oxygen in carrier gas, condition fibers in oxygen free gas flow. Reduce injection port temperature to the recommended fiber maximum
	2. Coating on fiber deteriorated (P)	2. Replace fiber. Fibers are reusable and will last for 50 injections on average
	3. Fiber was exposed to solvents that cause swelling of coating (S)	3. Do not expose PDMS coated fibers to non-polar solvents such as pentane, methylene chloride, or diethyl ether. Do not expose Carbowax fibers to polar solvents

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ABBREVIATIONS

C	centigrade
CAR/PDMS	Carboxen/Polydimethylsiloxane
cm	centimeter
d_f	coating thickness
DVB/CAR/PDMS	Divinylbenzene/Carboxen/Polydimethylsiloxane
DVB/PDMS	Divinylbenzene/Polydimethylsiloxane
GC	gas chromatography
I.D.	internal diameter
M	molarity
µm	micrometers (microns)
Min	minute
mL	milliliter
MS	mass spectrometry
MW	molecular weight
NaCl	sodium chloride
PA	Polyacrylate
PDMS	polydimethylsiloxane
PEG	polyethylene glycol (Carbowax)
Sec	second
SPME	solid phase micro extraction
Syringe I.D.	syringe identification (serial number)
v/v	volume-to-volume
w/v	weight-to-volume