

Control Your "T"s for Better Quantitation with Solid Phase Microextraction (SPME)

Introduction

Traditional sample preparation methods try to completely remove the analytes of interest from the sample. SPME does not work this way. With SPME, the amount of analyte removed by the fiber is proportional to the concentration of the compound in the sample. This is true when the fiber and the sample reach equilibrium or before equilibrium, as long as you carefully control the sampling parameters. The ability to use SPME quantitatively before you reach equilibrium permits much shorter sampling times producing a fast, economical, and versatile technique. We discuss in this article why controlling the sampling parameters of time, temperature, and technique are important to improve your quantitation.

Time

The extraction time is a critical parameter in the SPME sampling process. Figure A shows the typical relationship of extraction time to analyte absorbed on the fiber. If you vary the time that you expose the fiber during sampling you will vary the analyte concentration on the fiber, until you reach equilibrium. Once the analyte is at equilibrium between the fiber and the sample, its concentration will become constant. Consequently, controlling your extraction time is critical when working in the pre-equilibrium period. Use a stopwatch to time each extraction precisely. Figure B shows the poor reproducibility obtained for aromatic compounds in water when the sampling parameters are not well controlled or monitored.

Temperature

Temperature also effects the equilibrium during extraction. If you increase the temperature, you change the equilibrium distribution of analytes in the sample and the headspace. During the sampling process, the fiber also establishes equilibrium with the sample and headspace. Variations in temperature will change the equilibrium and the resulting concentration of analyte on the fiber. You need to stabilize the sample at the determined optimal temperature before exposing the fiber. Be aware that variations in room temperature can cause non-reproducible results if you use an ambient sampling temperature. Use a calibrated thermometer along side the sample to insure a constant extraction temperature.

Technique

The technique used in sampling will also influence your reproducibility. A reliable,

Figure A. Absorption-Time Profile

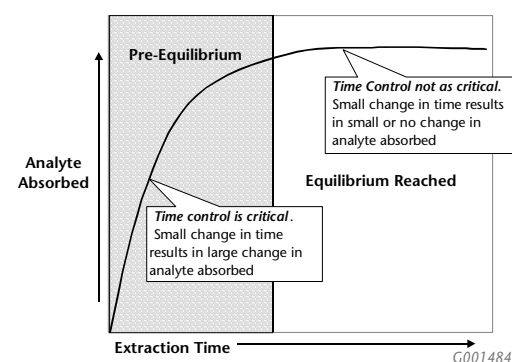


Figure B. Results from Not Controlling the "T"s

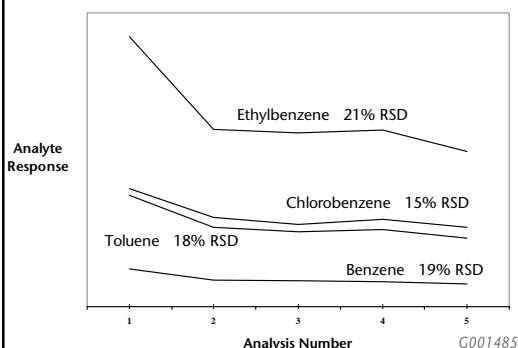
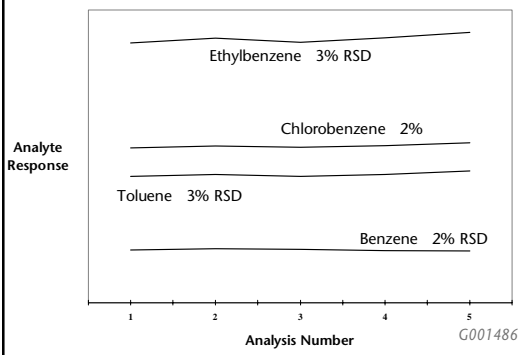


Figure C. Results from Controlling the "T"s



reproducible technique is important whether using a headspace or direct immersion sampling approach. Be consistent with your fiber position and applying agitation, salting, or pH adjustments. Figure C shows how dramatically you can improve reproducibility if you just pay

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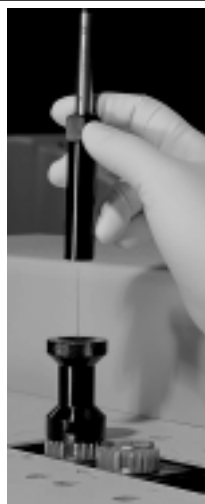
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SPME Sampling Stand with Heat/Stir Plate



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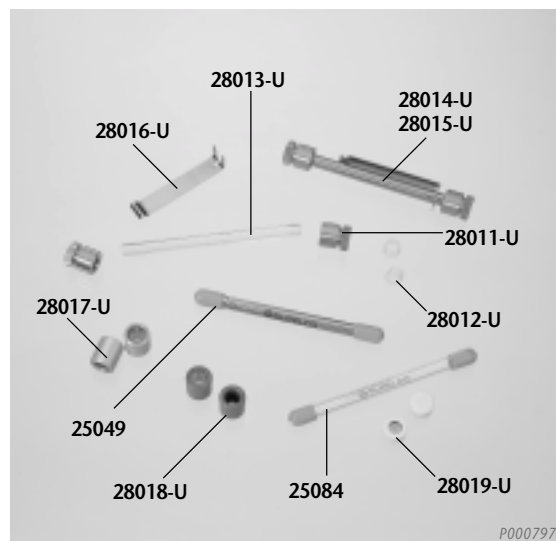
SPME Inlet Guide



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NEW PRODUCTS

Thermal Desorption Tube Accessories for PerkinElmer Equipment



P000797

PerkinElmer and Supelco offer a broad line of adsorption tubes for the PerkinElmer ATD-50 and ATD-400 and TurboMatrix thermal desorption instruments. Supelco now offers the complete line of PerkinElmer accessories. These accessories are manufactured by PerkinElmer and are now available through Supelco. We have all the products you will need for the new TurboMatrix instrument including the new brass end caps, replacement ferrules, clip holders, diffusion caps with and without membranes and empty glass and stainless steel tubes with brass caps. We are also offering for the ATD-50 and ATD-400 the PTFE end caps and empty glass and stainless steel tubes.

For more information on accessories available for PerkinElmer thermal desorption equipment, request T401093.

Accessories for PerkinElmer Thermal Desorption Tubes

TurboMatrix Tube Accessories	Qty.	Supelco Cat. No.
Brass Caps	20	28011-U
Replacement Teflon® PFE Ferrules for Caps	20	28012-U
Pen Clips for Tubes	10	28016-U
Diffusion Caps Standard	10	28017-U
Diffusion Caps with Membrane	10	28018-U
Empty Glass Tube with Brass Caps	10	28013-U
Empty SS Tube with Brass Caps	10	28014-U
Empty SS Tube with Brass Caps	50	28015-U

TATD Model 50 and 400 Accessories	Qty.	Supelco Cat. No.
PTFE Storage Caps	20	28019-U
Empty Tube Stainless Steel	1	25049
Empty Tube Glass	1	25084

SPME StableFlex Fiber Assortment Kits

The new SPME StableFlex Fiber Assortment Kits contain an excellent assortment of fibers for the beginner getting started with SPME or the experienced SPME user looking for improvement. The StableFlex fiber coating

bonds to a flexible fused silica core resulting in a resilient and durable fiber with outstanding reproducibility.

The assortment kits are available for both manual and automated use and include one each of the four StableFlex fiber chemistries.

65µm PDMS/DVB for volatile, amines, and nitroaromatics

50/30µm DVB/Carboxen/PDMS for flavors, volatiles, and semivolatiles

85µm Carboxen/PDMS for gases and low molecular weight compounds

70µm Carbowax/DVB for alcohols and polar compounds

SPME StableFlex Fiber Assortment Kit 1, Manual 57350-U

SPME StableFlex Fiber Assortment Kit 1, Automated . 57551-U

For more information, request T401070.

FEATURED PRODUCTS

SPME Optimization Accessories

SPME Sampling Stand

Holds eight vials while supporting the SPME syringe for consistent fiber immersion depth. Cat. No. 57333-U accommodates 4mL vials only; Cat. No. 57357-U accommodates 15mL vials. Order the 15mL vial puck (Cat. No. 57358-U) as a replacement for the 15mL unit, or to use 15mL vials with the 4mL unit.

for 4mL vials 57333-U

for 15mL vials 57357-U

Vial puck for 15mL vials 57358-U

Heat/Stir Plate

Fits compactly on the base of the SPME sampling stand. Heating range is 40-550°C, stirring range is 60-1200rpm.

Corning heat/stir plate, 120VAC Z262129

Corning heat/stir plate, 230VAC¹ Z262129

¹ CE approved.

Magnetic Stirring Bars

Fits 4mL vials, 10 x 3mm, pk. of 3, PTFE covered

..... Z11,8877-3EA

Thermometer

For monitoring sample temperature when using the SPME sampling stand and a heat/stir plate.

5" thermometer 57332

SPME Inlet Guide

Secures the SPME fiber holder in the injection port during the thermal desorption process. Interchangeable among Merlin Microseal[™] sealing system and most Varian and Hewlett-Packard chromatographs. 57356-U

For more information on any of the products above, request T101928. For a complete listing of PTFE and glass covered magnetic stirring bars, visit our website, www.sigmaaldrich.com/supelco

LCD Digital Stopwatch

Use to precisely time SPME extractions 23011

SPME BOOKS

Solid Phase Microextraction: A Practical Guide

Sue Ann Sheppers Wercinski, ed. 1999, 242pp. This reference book contains extensive descriptions of proven sampling methods for chemical analysis, focusing on SPME application. **26610-U**

Solid Phase Microextraction: Theory and Practice

Janus Pawliszyn, 1997, 241pp. This book describes the operating principles and construction of SPME devices, theory, method development, and applications. **26591-U**

Applications of Solid Phase Microextraction

Janus Pawliszyn, 1999, 653 pp. A compilation of 46 invited chapters describing applications of SPME for foods, forensics, environmental samples, and other areas. **26611-U**

Techniques for Analyzing Food Aroma

Ray Marsilli, ed. 1997, 371 pp. This book discusses the analytical methods for food flavors and aromas, showing how to select appropriate techniques for resolving the problems of major food trends. **26589-U**

SEMINARS

Solid Phase Microextraction (SPME) Seminar Series

Supelco gives customized SPME seminars at the customer's location for groups of ten or more. We design the seminars to your needs to address either the SPME beginner or experienced users. We will tailor the presentation to discuss specific problems or applications that are of special concern or interest to you.

☎ For more information on setting up an on-site SPME seminar, contact us at 888-550-5487.

SAMPLE PREPARATION PERFORMANCE TIP

The Role of Flow Rate in Solid Phase Extraction

All too often, one of the most neglected considerations in the practice of SPE is the control and optimization of flow rate. When developing an SPE method, many analysts pay close attention to such variables as solvent properties, matrix conditions, and pH; however, clear characterization of flow rate is often ill defined. Therefore, subsequent employment of the SPE procedure can often result in low and/or variable recoveries between run to run and user to user.

Flow rates affect analyte recovery, purity, and sampling throughput. In terms of recovery and reproducibility, many methods are especially flow rate sensitive to the load and elution steps; but much less sensitive to the condition, equilibration, and wash steps. The reason is independent of retention capacity, and much more to do with the kinetic sorptive properties of SPE. In other words, when the flow rate is too high for a given SPE step, mobile phase and analyte molecules pass through

NEW LITERATURE

Solid Phase Microextraction (SPME) Troubleshooting Guide

The guide presents a systematic approach to troubleshooting SPME problems. The guide will help you find a quick solution to many problems typically encountered. It also 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 remedies. By following these recommendations, you can save valuable time and money.

☎ For more information, request T101928

Solid Phase Microextraction (SPME) Quantitation Guide

The guide presents a practical introduction to quantitation using SPME based on your type of sample. We describe the factors that will influence your accuracy and precision and the different quantitation approaches that you can use. To help further, we provide specific examples for each of the different approaches discussed along with specific references for additional reading.

☎ For more information, request T101929

2001 Solid Phase Microextraction (SPME) Application Guide (Third Edition)

Searchable CD format includes over 750 applications, which are defined by analyte and matrix. There are 151 new references in the third edition. The guide helps the analytical chemist to choose the SPME fiber to use for their sample preparation problems. Most entries list the SPME conditions and instrumentation used for the application.

☎ For more information, request T199925



An Trinh -
LC Product Manager

All literature mentioned in this issue can be obtained from the website, www.sigma-aldrich.com/TheReporter, by completing the Literature Request section on the reply card, or by calling our Technical Service Department.

☎ For more information, request T197910 or T700002.

Trademarks and Registered Trademarks:

Microseal- Merlin Instrument Company
StableFlex- Sigma-Aldrich Co.
Teflon - E. I. du Pont de Nemours & Co., Inc.

Patents:

***SPME** - Technology licensed exclusively to Supelco. US patent #5,691,206; European patent #523092.

†**Microseal** - Merlin Instrument Co., US Patent#4,954,149

Control Your "T"s...

(continued from page 1)

close attention to time, temperature, and technique throughout the sampling procedure. For these extractions, unlike the previous set, we were careful to add the same amount of salt to each sample vial and to stir the sample at the same speed during each extraction. We used a SPME sampling stand to consistently position the fiber just above the vortex of the stirring water. This maximized our analyte absorption. We controlled the sampling temperature and monitored it with a thermometer. Lastly, we timed each extraction precisely with a stopwatch.

Conclusion

You can improve your reproducibility and quantitation with SPME through careful control and monitoring of time, temperature, and technique during sampling. SPME is a fast, economical, and versatile technique that can be very reproducible and quantitative if you pay attention to your "T"s.

☞ For additional information on SPME quantitation request T101929, T101928, and the SPME books by Dr. Janusz Pawliszyn 26591-U and 26611-U, listed on page three.

Visit our web site at www.sigma-aldrich.com/TheReporter for a longer version of this article.

CASE STUDY 3

SPME Beginner Improves Quantitation

A customer trying Solid Phase Microextraction* (SPME) for the first time was experiencing poor reproducibility. He wanted to extract aromatic compounds from a water sample. During the development of his extraction procedure, he experienced problems in the quantitation of the extracted analytes. The problems included broad tailing peaks, poor peak symmetry, and variation in detector response (Figure D).

The customer contacted Supelco Technical Service for assistance. The Technical Service chemist inquired if the customer had optimized his chromatographic conditions using a standard mixture. The customer had made up a mixture of the aromatics in methanol and injected it directly into the chromatograph. The result was no tailing peaks with good response. All the aromatics were sharp and well resolved. The Technical Service chemist also discovered he was using a wide-bore injection port liner, was not agitating or stabilizing the sample to room temperature before beginning, and was not precisely timing the extraction.

To overcome the problems, our technical service chemist worked with the customer to develop a routine in preparing the sample and the extraction procedure. He modified the extraction procedure by equilibrating each sample at room temperature and monitoring it with a calibrated thermometer. He consistently agitated the sample on a stir plate at the same setting and he positioned the fiber at the same height above the water with a sampling stand. Then he closely monitored the extraction time of each sample with a stopwatch. The customer also switched to the recommended SPME narrow-bore (0.75mm ID) injection port liner. Once the customer changed the liner and controlled his extraction parameters, he improved his peak shape, separation, and reproducibility (Figure E).

☞ For more information request the SPME Quantitation Guide T101929.

Sample: 10mL of water containing EPA 602 mixture of aromatics at 100ppb in 15mL vial
SPME Fiber: 100µm PDMS (Cat. No.: 57300-U)
Column: SPB-1 sulfur, 30m x 0.32mm ID x 4µm film
Cat. No.: 24158
Oven: 45°C (1 min), to 200°C at 15°C/min, hold 3 min.
Carrier: helium, 43cm/sec
Det: FID
Inj: Splitless, closed 2 min.

1. Benzene
2. Toluene
3. Chlorobenzene
4. Ethylbenzene
5. 1,3-Dichlorobenzene
6. 1,4-Dichlorobenzene
7. 1,2-Dichlorobenzene

Figure D. Initial Results

Average RSD's >15%

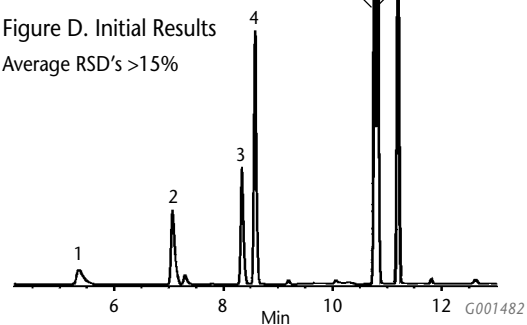
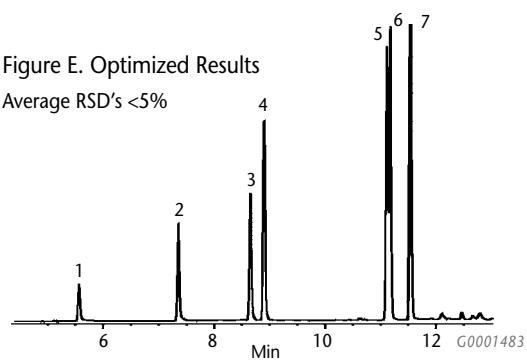


Figure E. Optimized Results

Average RSD's <5%



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