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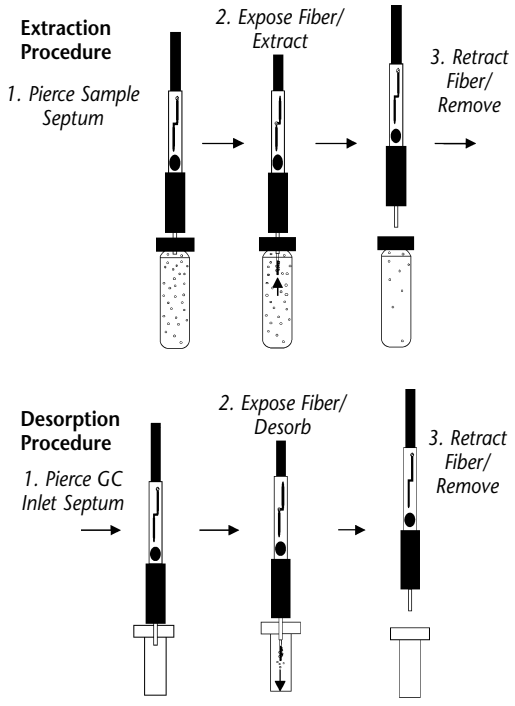
SPME - A Fast and Inexpensive Approach to Trace Organic Analysis

Abstract

Solid phase microextraction (SPME) is a simple and inexpensive sample extraction technique that can achieve very low levels of detection of trace organic compounds. Analysts whose task it is to measure compounds at trace levels will find their job to be much easier when they use SPME. SPME extracts and concentrates organic compounds from liquid or solid matrices without the use or expense of solvents. In addition, analysts do not always need sophisticated or expensive instrumentation. Today's chemists need simpler, faster, cheaper and easier ways of obtaining results. Your first and least expensive choice in selecting a technique for analyzing trace organics should be SPME.

In the article that follows, a practical example of how SPME provides all of the above is described for the real problem of detecting odor-causing compounds in drinking water.

Figure 1 – Solid Phase Microextraction – Extraction/ Desorption Process



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Trace Analysis Using SPME

SPME is a solvent-less extraction technique that involves the exposure of a chemically coated fiber to a gaseous or liquid sample or the headspace above a sample (Figure 1). Fiber coatings consist of a variety of polymers (stationary phase), solid adsorbents, or a combination of the two. Under controlled conditions, chemical compounds present in the sample extract onto the fiber coating. The next step is to desorb the fiber in the heated injection port of a GC or GC/MS for analysis. SPME can extract and release certain compounds having concentrations in the part-per-trillion (ppt) range [1].

Odors in Drinking Water

Odor is an important water quality – consumers know "bad" water when they smell it! Methyl-isoborneol (MIB) and geosmin are two naturally occurring compounds found in water. They are responsible for the "musty" odor occurring at certain times of the year. People can detect their presence in water at ppt levels. "Closed loop stripping" (CLS) followed by GC/MS has been the preferred technique for the extraction and analysis of MIB and geosmin in water. This technique, described in Ameri-

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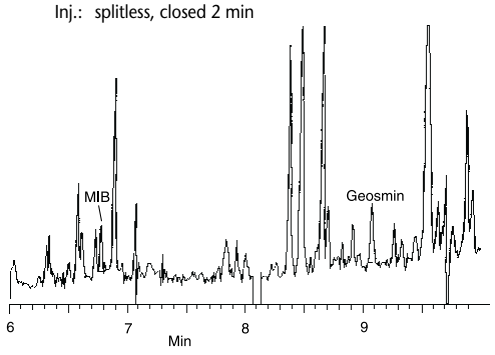
Figure 2 – Odor Agents at 1ppt in Water by SPME-GC/MS

Sample:	30mL of water containing MIB and geosmin at 1ppt and 25% NaCl in a 40mL vial, sample conditioned for 30 min at 65°C
SPME Fiber:	**divinylbenzene/Carboxen/polydimethylsiloxane**
Cat. No.:	**57348-U**
Extraction:	heated headspace, 65°C, 30 min, with rapid stirring
Desorption:	3 min, 250°C
Column:	**Meridian MDN-5, 30m x 0.25mm ID, 0.25µm film**
Cat. No.:	**24096**
Oven:	60°C (1 min) to 250°C at 15°C/min
Carrier:	helium, 35cm/sec
Det.:	MS, m/z = 75-180 at 0.6sec/scan (quantitation ions 95 and 112)
Inj.:	splitless, closed 2 min



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SP SamplePreparation issue

CONTENTS

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T201001

FEATURED PRODUCTS

Products for Odor Determination in Drinking Water

The new AWWA method 6040D describes the use of SPME for the determination of MIB and geosmin in water.

For more information, request T398147 – Solid Phase Microextraction of Odors in Drinking Water for Analysis by GC/MS.

40mL Vial Holder

P000690

SPME Products

DESCRIPTION	CAT. NO.
50/30µm Carboxen/DVB/PDMS Stableflex Fiber	**57348-U**
Manual SPME Holder	**57330-U**

SPME Accessories

To assist in heating the water sample, use 40mL sample vials with magnetic stirring bars heated in a six-position aluminum heating block on a heat/stir plate.

DESCRIPTION	CAT. NO.
40mL headspace vials, clear glass, 29x81mm (Pk. 100)	**27184**
Magnetic stirring bars, (Pk. of 3)	**Z118877-3EA**
40mL vial holder, six position, aluminum	**33313-U**
Corning heat/stir plate, 120 VAC	**Z262129**
Corning heat/stir plate, 230 VAC	**Z262137-1EA**

Odor Calibration Standards

The following calibration standards are specifically used in determining odors in drinking water.

Drinking Water Odor Calibration Standards – 100µg/mL in 1mL methanol

DESCRIPTION	CAT. NO.
(+-)-Geosmin	**47522-U**
2-Methylisoborneol	**47523-U**
(+-)-Geosmin and 2-Methylisoborneol	**47525-U**
2,4,6- Trichloroanisole	**47526-U**
2-Isopropyl-3-methoxpyrazine	**47527-U**
2-Isobutyl-3-methoxypyrazine	**47528-U**

Drinking Water Odor Standards Kit –
1mL of each standard listed above **47529-U**

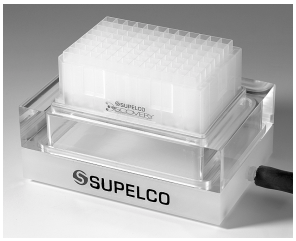
Capillary GC Column

The following capillary column provides the required separation while delivering low bleed performance for GC/MS analyses.

Low Bleed Capillary Column for GC/MS Analyses

DESCRIPTION	CAT. NO.
30m x 0.25mm x 0.25µm MDN-5	**24096**

Discovery SPE-96 Well Plate & PlatePrep Vacuum Manifold



Discovery® SPE-96 Well Plates

Discovery SPE-96 well plates are extensively tested and quality controlled for pharmaceutical and clinical applications. Included with each plate is a certificate of analysis that describes tests used to ensure reproducible raw silica and bonded silica properties. Each lot is tested for consistent carbon loading, cleanliness, hydrophobic selectivity, and capacity, as well as efficiency for extracting model acidic, neutral, and basic pharmaceuticals. Stringent guidelines regarding packing procedures have also been imposed to ensure consistent flow rates and sorbent bed weights.

Supelco 96-Well Plates and Accessories

96-Well Plates

Discovery DSC-18 SPE-96 Plate, 25mg/well **575601-U**
Discovery DSC-18 SPE-96 Plate, 50mg/well **575602-U**
Discovery DSC-18 SPE-96 Plate, 100mg/well **575603-U**
Discovery DSC-18Lt SPE-96 Plate, 25mg/well **575604-U**
Discovery DSC-18Lt SPE-96 Plate, 50mg/well **575605-U**
Discovery DSC-18Lt SPE-96 Plate, 100mg/well **575606-U**
Discovery DSC-Si SPE-96 Plate, 25mg/well **575607-U**
Discovery DSC-Si SPE-96 Plate, 50mg/well **575608-U**
Discovery DSC-Si SPE-96 Plate, 100mg/well **575609-U**
Discovery DSC-PS/DVB SPE-96 Plate, 25mg/well **575610-U**
Discovery DSC-PS/DVB SPE-96 Plate, 50mg/well **575611-U**

96-Well Plate Accessories

96 Sq. Well Collection Plates, 0.35mL, PP, 50/pk **575651-U**
96 Sq. Well Collection Plates, 1mL, PP, 50/pk **575652-U**
96 Sq. Well Collection Plates, 2mL, PP, 50/pk **575653-U**
Disposable Reservoir/Waste Tray, PVC, 25/pk **575654-U**
96 Sq. Well Piercable Cap Mats, 50/pk **575655-U**
Reagent Reservoir ..... **R9259 - 100ea.**
Cluster Tube Rack ..... **Z372226 - 1pak**

PlatePrep Manifold and Manifold Replacement Parts

96-Well Plate Starter Kit with Manifold **575650-U**
Contents of kit:
- 1 Plate Prep Manifold
- 1 96 Sq. Well Collection Plates, 2mL, PP
- 2 Disposable Reservoir/Waste Trays, PVC
- 1 96 Sq. Well Piercable Cap Mats
- 5 Reagent Reservoirs
- 1 Cluster Tube Rack

PlatePrep Vacuum Manifold **57192-U**
Acrylic Clear Top for Manifold **57193-U**
Polypropylene Base for Manifold **57194-U**
Gasket Kit for Manifold **57195-U**
Vacuum Gauge/Bleed Valve for Manifold **57161-U**

*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.*

LITERATURE

Solid Phase Microextraction

SPME Application Guide

This guide contains 110 new references and a total of over 600 references categorized by application, analyte/matrix, and extraction condition.

To request a copy of the SPME Guide, request T199925.

New SPME Methods

ASTM* D6438-99 – "Standard Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints and Coatings by Solid Phase Microextraction-Gas Chromatography", Vol. 6.01. This method is used for the determination of the listed compounds in paints and coatings by SPME headspace sampling and GC analysis.

ASTM* D6520-00 - "Standard Practice for the Solid Phase Microextraction (SPME) of Water and its Headspace for the Analysis of Volatile and Semi-Volatile Organic Compounds", Vol. 11.02. This practice covers the procedures for the extraction of volatile and semi-volatile organic compounds from water and its headspace using SPME.

*ASTM methods are not available from Supelco but may be obtained from ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, or at the ASTM Store on the ASTM web site, **www.astm.org**

AWWA Method 6040 – Constituent Concentration by Gas Extraction – published in Standard Methods for the Examination of Water and Wastewater, available from the American Water Works Association (AWWA), (**www.standardmethods.org**) (method not available from Supelco)

Journal Article

"Optimization of Extraction Conditions and Fiber Selection for Semivolatile Analytes Using Solid-Phase Microextraction". Journal of Chromatographic Science, Vol. 238, July, 2000. Bob Shirey, Supelco R/D Chemist, has written a research article that discusses the use of SPME for the extraction of semivolatiles from water samples.

For a reprint of Bob Shirey's paper, request T400234.

Discovery SPE-96 Well Plates

Four product profiles and an Application Note are available from Supelco on the Discovery DSC SPE-96 Plates. These profiles describe four of the phases currently available, how and for what compounds they may be used with, and the product specifications of each phase. The Application Note describes a number of bio-analytical applications using pharmaceutical compounds.

Discovery DSC-Si SPE-96 Plate - An acid washed silica. Our 96 well format enables you to quickly and effectively clean samples or remove baseline impurities in combinatorial chemistry applications.

For more information, request T400173.

Discovery DSC-PS/DVB SPE-96 Plate - A polystyrene-divinylbenzene material that retains hydrophobic compounds which contain some hydrophilic functionality, especially aromatics.

For more information, request T400174.

Discovery DSC-18 SPE-96 Plate - A polymerically bonded trifunctional C18 silica used to extract, isolate, purify and concentrate pharmaceuticals from biological fluids and other aqueous media.

For more information, request T400171.

Discovery DSC-18Lt SPE-96 Plate - A monomerically bonded C18 used to extract moderately polar to non-polar compounds from aqueous media, such as biological fluids.

For more information, request T400172.

Discovery SPE-96 Plates - We measure the recoveries of a number of acidic, basic, and neutral test analytes at various spike concentrations. In addition, we compare the effects of elution volume vs. recovery. Finally, we compare the performance of our Discovery SPE-96 well plates against competitor extraction plates.

For more information, request T300165, Application Note 165, Discovery SPE-96 Well Plates

SAMPLE PREPARATION PERFORMANCE TIP

Proper pH Selection Will Improve Your SPE Extractions

Analysts who have the task of developing cartridge or 96-well SPE applications can improve extractions through proper pH selection. Using pH to modify the form of the analyte can improve its retention, selectivity, and recovery. To improve retention of a basic compound when performing reverse phase SPE, adjust the pH of the sample matrix to at least 2 pH units above the target analyte's pKa. This will neutralize the analyte's basic ionizable functional groups further facilitating the non-polar retention mechanisms associated with reverse phase separations. Subsequent wash step(s) using an aqueous solution in conjunction with an organic modifier will often remove impurities co-extracted onto the sorbent bed. Increasing the pH of the wash solution can minimize compound loss when stronger wash solutions (higher organic concentration) are required. In contrast, a decrease in pH will aid in the elution of basic compounds of interest. In conclusion, one can dramatically increase extraction efficiency and recoveries by paying close attention to the proper pH selection when developing an SPE method.

For more information request T197910, Guide to Solid Phase Extraction, and T700002, Instructions for Using Discovery SPE-96 Well Plates.

An Trinh -
LC Product Manager

References for "SPME – A Fast and Inexpensive..."

(1) SPME Application Guide – T199925.

Trademarks and Registered Trademarks:

Carboxen, Discovery *- Sigma-Aldrich*

Patents:

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

SPME – A Fast and Inexpensive...

(continued from page 1)

can Water Works Association (AWWA) method 6040B, is very time consuming requiring several hours per sample.

SPME for Detection of Odor-Causing Compounds

SPME provides results comparable to CLS. An SPME fiber extracted the organics from the headspace of a water sample heated at 65°C. The sampling time was 30 minutes. The dual coated divinylbenzene-carboxen-PDMS fiber provided the best extraction and desorption results for MIB and geosmin. Figure 2 shows a chromatogram of the odor compounds desorbed from the SPME fiber. GC/MS ions 95 and 112 confirmed the identity of MIB and geosmin, respectively. Concentrations were determined to be 1ppt by standard addition. Recently, the AWWA approved a new method, 6040**D,** that uses SPME as an alternative to the CLS technique.

Conclusion

In summary, SPME is a simple and inexpensive sample extraction technique that can achieve very low levels of detection of trace organic compounds present in a variety of sample matrices. In this practical example, SPME provides results comparable to CLS for the extraction and detection of the compounds responsible for musty odors in drinking water at ppt levels in much less time. SPME is a simple, fast and low cost extraction technique that should be your first choice for evaluating a suitable technique for extracting and analyzing trace organic compounds from a variety of matrices.

For more information on the use of SPME for determination of MIB and geosmin in water, request T398147 – Solid Phase Microextraction of Odors in Drinking Water for Analysis by GC/MS.

CASE STUDY 1

Resolving Combichem Purification Problems

In recent years, advances in combinatorial chemistry (Combichem) have made a tremendous impact on the pharmaceutical industry by drastically accelerating the drug discovery process. The marriage of robotic liquid handlers, multi-well platforms, and well-established combinatorial techniques has allowed the simultaneous synthesis of large molecularly diverse arrays of potentially biologically active molecules. However, for each synthesis a purification step is required to remove the target molecule from reaction by-products, side-products, and excess reagents. Because many reactions contain ionic impurities and products that could be selectively extracted with ion-exchange resins, ion-exchange solid phase extraction (SPE) has become a routine procedure for purifying solution-phase combinatorial reactions. However, as more compounds are synthesized, there is a larger demand on parallel purification which typically involves the implementation of either smaller bed weights, tube sizes, and/or 96-well SPE. As bed weights scale-down, sufficient loading capacity becomes a major issue for many combinatorial chemists.

This concern was shared by Dr. Bart van Steen, Advanced Drug Discovery Support, Solvay Pharmaceuticals, The Netherlands. Both Supelco scientists and Dr. van Steen agreed that the majority of commercially available pre-packed ion-exchange SPE tubes and well plates contain silica-based sorbents that do not meet the capacity needs required in combinatorial chemistry. For example, most strong cation exchange silica-based sorbents are functionally bonded to either propylsulfonic acid or benzenesulfonic acid, both of which have an average binding capacity of 0.2 and 0.8meq/g, respectively. This translates to a typical loading capacity of just <10mg per well in a 96-well SPE plate. Because most combinatorial synthesis scales are in the range of 25-300mg, silica-based sorbents do not adequately address the capacity needs when scaling up to 24- and 96-well purification platforms. Upon confirming Dr. van Steen's capacity issues, Supelco and Solvay Pharmaceuticals partook in a joint effort in evaluating alternative ion-exchange materials and methods. Using a representative test compound in conjunction with an SPE method suggested by Solvay Pharmaceuticals, we discovered a resin that exceeded Solvay's expectations by providing capacity of 2.5meq/g, or approximately 30mg loading capacity when using a 75mg/well 96-well extraction platform. Unlike most silica-based ion exchange sorbents, this resin is styrene-divinylbenzene co-polymer functionally bonded to sulfonic acid, and stable across the entire pH range. The material comprises of whole spherical beads offering excellent kinetic and packing properties well suited for SPE. Upon determining the appropriate ion-exchange material, Supelco was able to assist Solvay by custom packing the resin into flangeless SPE cartridges and 96-well SPE plates that continue to serve an integral purification role within Solvay's Automated Molecular Assembly Plant, their high throughput Combichem facility.

For more information, email An Trinh at atrinh@sial.com

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