Green Analytical Chemistry

Solid phase Microextraction

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What is green analytical chemistry?

The goal of green analytical chemistry is to use analytical procedures that generate less hazardous waste and that are safer to use and more benign to the environment.

- developing new analytical methodologies
- modifying an old method to incorporate procedures that either use less hazardous chemicals or use lesser amounts of hazardous chemicals.

Greening Pretreatment

1. Ultrasound
2. Microwave-Assisted Extraction (MAE)
3. Supercritical Fluid Extraction (SFE) and Superheated Water Extraction (SWE)
4. Membranes
5. Cloud Point Extraction (CPE)
6. Greening through Screening
7. Solid-phase extraction (SPE)
8. **Solid-phase microextraction (SPME)**

Greening Signal Acquisiton

1. Spectroscopy
2. Electrochemistry
3. Bioanalytical chemistry

Solid-phase Microextraction

- Solid-phase microextraction is a very simple and efficient, solventless sample preparation method, invented by Pawliszyn in 1989.
- SPME integrates sampling, extraction, concentration and sample introduction into a single solvent-free step.
- SPME reduces the time necessary for sample preparation, decreases purchase and disposal costs of solvents and can improve detection limits.

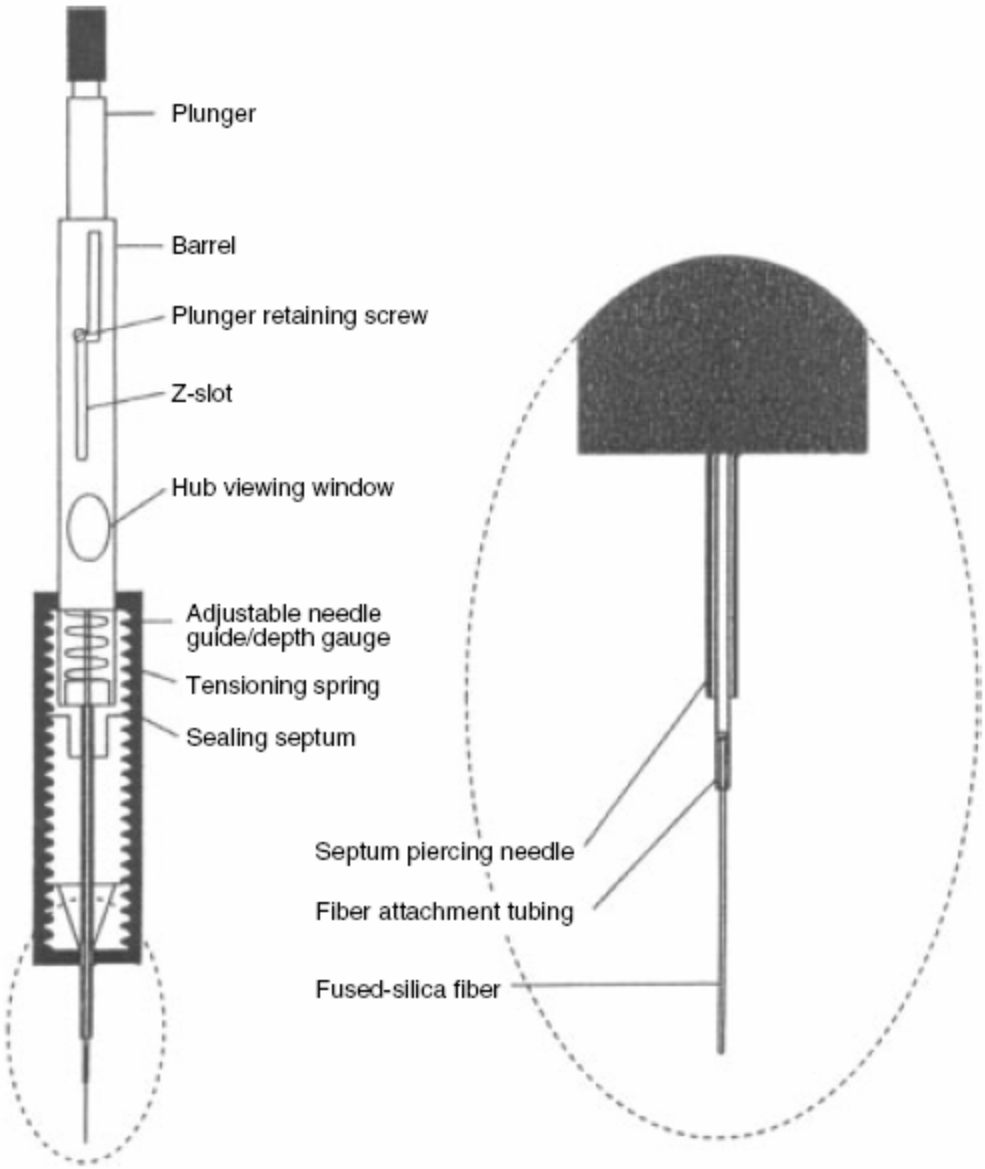
SPME Principles

A simple, effective adsorption/ desorption technique

- In SPME a small amount of extracting phase (fiber coating) associated with a solid support is placed in contact with the sample matrix for a predetermined amount of time. If the time is long enough, a concentration equilibrium is established between the sample matrix and the extraction phase.

- After extraction, SPME fiber is transferred to the injection port of separating instruments, like GC or HPLC, where desorption of the analyte takes place and analysis is carried out.

SUPELCO Bulletin **928**: 1



Schematic diagram of a commercial SPME device

Gyorgy Vas, Karoly Vekey. J. Mass Spectrom. 2004; **39**: 234

For liquid polymeric SPME coatings, the amount of analyte adsorbed by the coating at equilibrium is directly related to the concentration of the analyte in the sample:

$$n = \frac{K_{fs} V_f C_0 V_s}{K_{fs} V_f + V_s} \qquad (1)$$

where

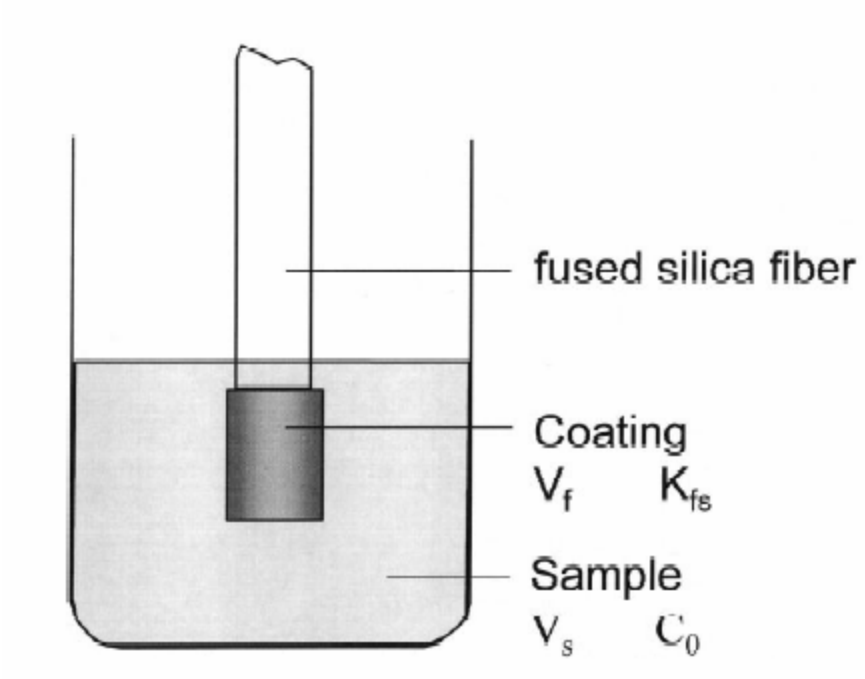
n = mass of analyte adsorbed by coating

C_0 = initial concentration of analyte in the sample

K_{fs} = partition coefficient for analyte between coating and sample matrix

V_f = volume of coating

V_s = volume of sample



$$n = \frac{K_{fs} V_f C_0 V_s}{K_{fs} V_f + V_s}$$

Microextraction with SPME

V_f : volume of fiber coating; K_{fs} :fiber/sample partition coefficient;
Vs:volume of sample; C_0: initial concentration of analyte in the sample

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when sample volume is very large, Equation (1) can be simplified to:

$$n = K_{fs} V_s C_0 \qquad (2)$$

The amount of extracted analyte is independent of the sample.

In practice, there is no need to collect a defined sample prior to analysis as the fiber can be exposed directly to the ambient air, water, production stream, etc.

The amount of extracted analyte will correspond directly to its concentration in the matrix, without being dependent on the sample volume.

Three Basic Types of Extractions

- Direct Immersion SPME

  In DI-SPME, the fiber is directly immersed in liquid samples.

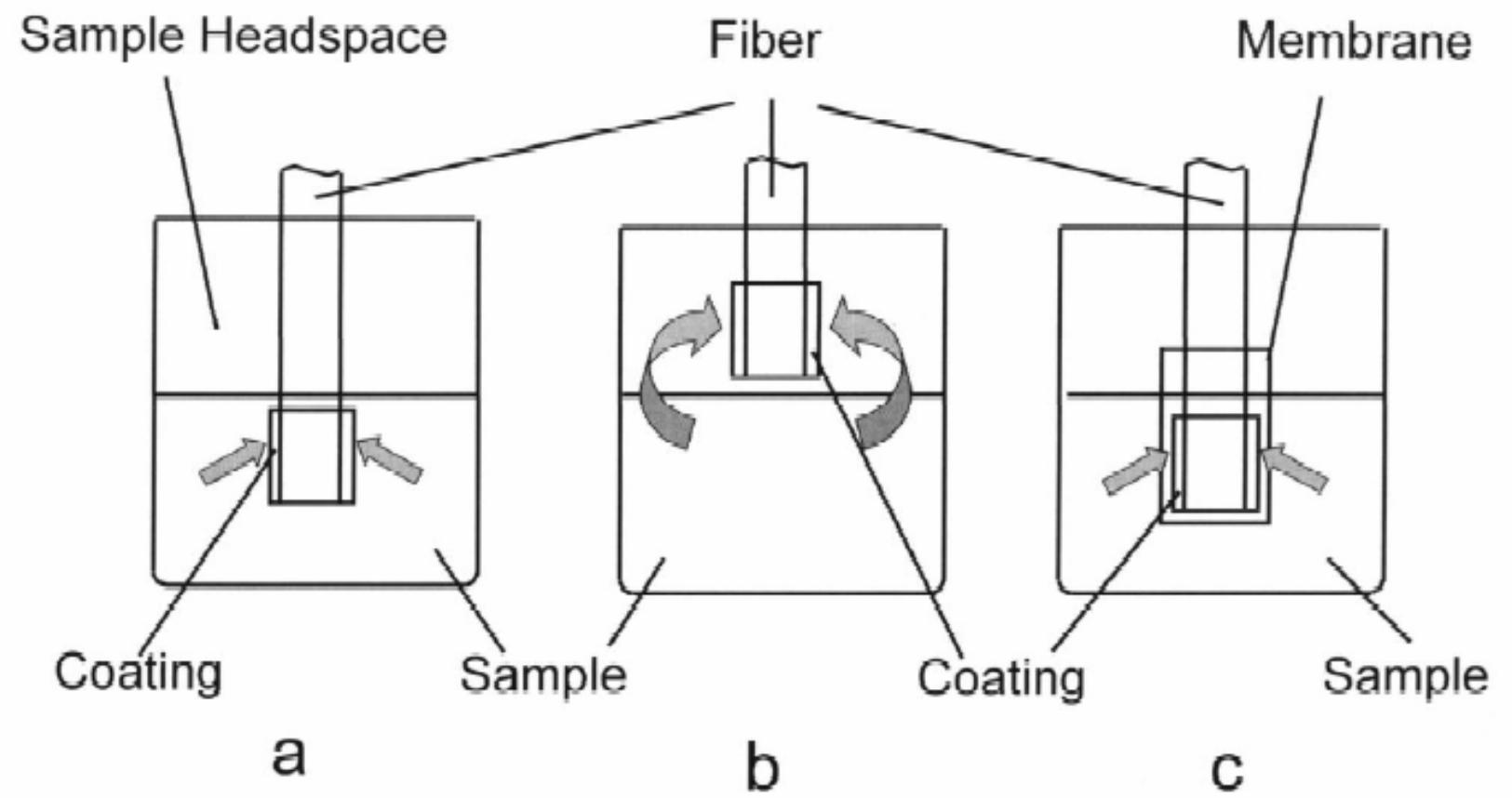
- Head Space SPME

  In HS-SPME, the fiber is exposed in the vapor phase above a gaseous, liquid or solid sample.

- Membrane-Protected SPME

  Indirect SPME extraction through a membrane

  The main purpose: protecting the fiber against damage



Modes of SPME Operation

(a) direct immersion SPME, (b) headspace SPME, (c) membrane-protected SPME

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Direct Immersion VS Head Space

- DI-SPME works best for low concentration water based sample matrices.

  Position the fiber just below the sample surface and maintain this position consistently for all extractions.

- HS-SPME is suitable for the analysis of VOCs.

  It is extremely important to keep the headspace volume constant and keep the fiber position at the same depth every time.

Optimizing Extraction Condition

- Fiber coating type and thickness
- Extraction time
- Extraction temperature
- Sample agitation
- Sample PH or salt concentration

Fiber Coating Type and Thickness

- The fiber is coated with a thin polymeric film, which concentrates the organic analytes.
- The chemistry of the SPME fiber plays a significant role in enhancing or discriminating against classes of compounds.
- The thickness affects both the equilibrium time and sensitivity of the method.
- The sampling fibers can be used multiple times.

Summary of commercially available SPME fibers

Fiber coating	Film thickness (um)	Polarity	Coating method	Maximum operating temperature	Technique	Compounds to be analysed
Polydimethysiloxane (PDMS)	100	Non-polar	Non-bonded	280	GC/HPLC	Volatiles
PDMS	30	Non-polar	Non-bonded	280	GC/HPLC	Non-polar semivolatiles
PDMS	7	Non-polar	Bonded	340	GC/HPLC	Medium-to non-polar semivolatiles
PDMS-divinylbenzene (DVB)	65	Bipolar	Cross-linked	270	GC	Polar volatiles
PDMS-DVB	60	Bipolar	Cross-linked	270	HPLC	General purpose
PDMS-DVB[a]	65	Bipolar	Cross-linked	270	GC	Polar volatiles
Polyacrylate (PA)	85	Polar	Cross-linked	320	GC/HPLC	Polar semivolatiles (phenols)
Carboxen-PDMS	75	Bipolar	Cross-linked	320	GC	Gases and volatiles
Carboxen-PDMS[a]	85	Bipolar	Cross-linked	320	GC	Gases and volatiles
Carbowax-DVB	65	Polar	Cross-linked	265	GC	Polar analytes (alcohols)
Carbowax-DVB[a]	70	Polar	Cross-linked	265	GC	Polar analytes (alcohols)
Carbowax-templated resin (TPR)	50	Polar	Cross-linked	240	HPLC	Surfactants
DVB-PDMS-Carboxen	50/30	Bipolar	Cross-linked	270	GC	Odours and flavours

[a] Stable flex type is on a 2 cm length fiber.

György Vas, Károly Vékey. J. Mass Spectrom. 2004; **39**: 236

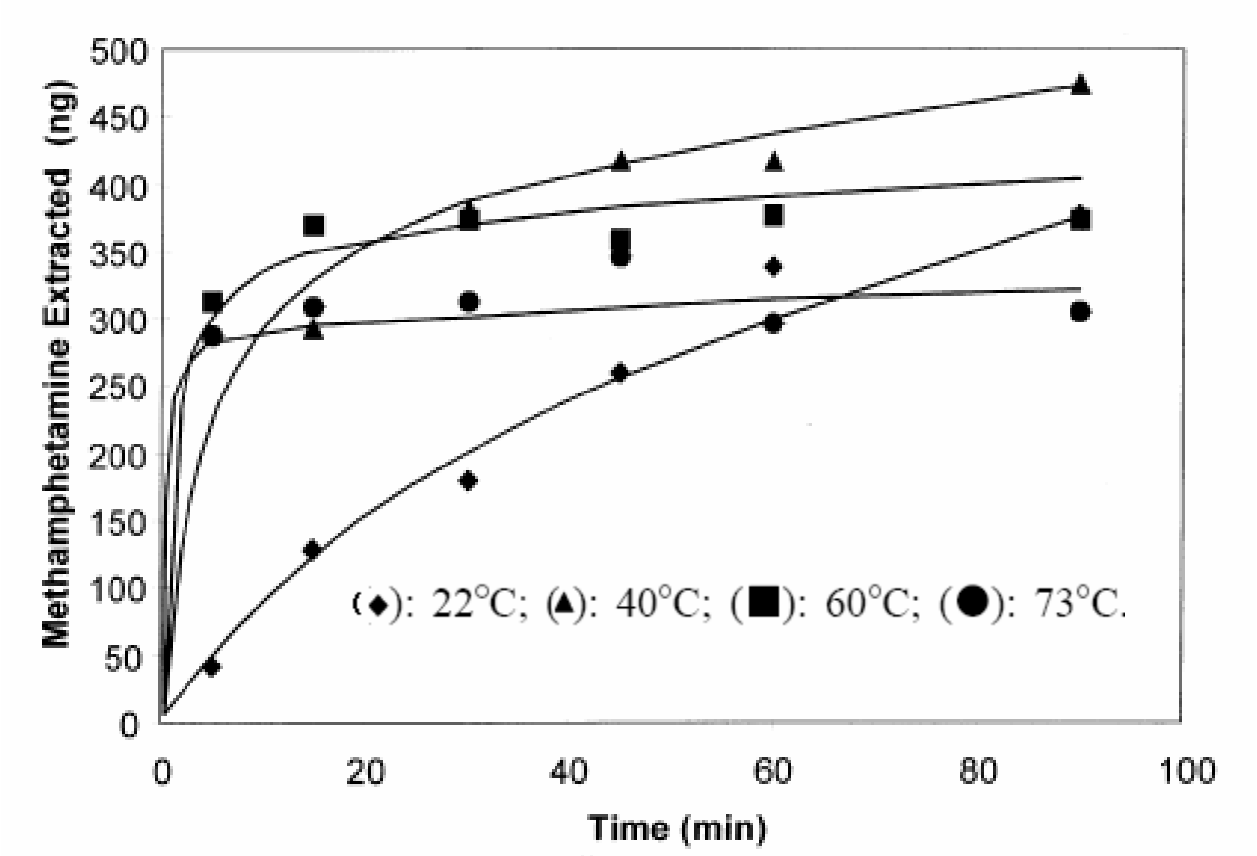
Extraction Time

- The extraction time depends on the size of the compounds, fiber coating, type of extraction used and sample concentration.
- Extraction times can be shorter when you are:
  - analyzing small compounds (<150 MW)
  - using thinner, absorbent type fiber coatings
  - using the headspace technique
  - working with high concentration samples (high ppb or ppm range).

Extractions typically take 15-20 minutes.

Extraction Temperature

- It is critical for accurate quantitation of the sample.
- The use of heat during headspace SPME will help release the analyte from the sample, improve sensitivity, and shorten the extraction time.
- You must use a constant temperature for all extractions to obtain good precision.



Effect of extraction temperature on equilibrium time and amount extracted, for headspace methamphetamine analysis

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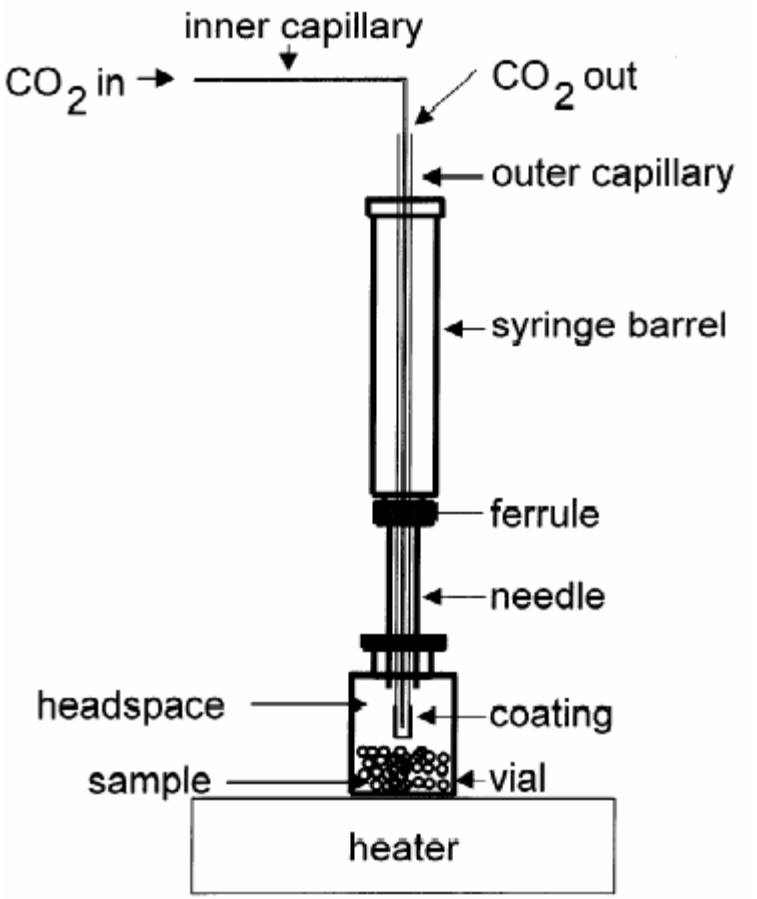
At elevated temperatures native analytes can effectively dissociate from the matrix and move into the headspace for rapid extraction by the fiber coatings.

However, the coating/sample distribution coefficient also decreases with an increase of temperature, resulting in a diminution in the equilibrium amount of analyte.

☹ *How to solve this problem?*

☺ To prevent loss of sensitivity, the coating can be cooled simultaneously with sample heating.

In this device, a fused-silica tubing is sealed and coated at one end (outer surface of the capillary). Liquid CO_2 is delivered via the inner capillary to the coated end of the outer capillary resulting in a coating temperature lower than that of the sample. This ‘‘cold finger’’ effect results in accumulation of the analytes at the tip of the fiber.



Design of internally cooled SPME device.

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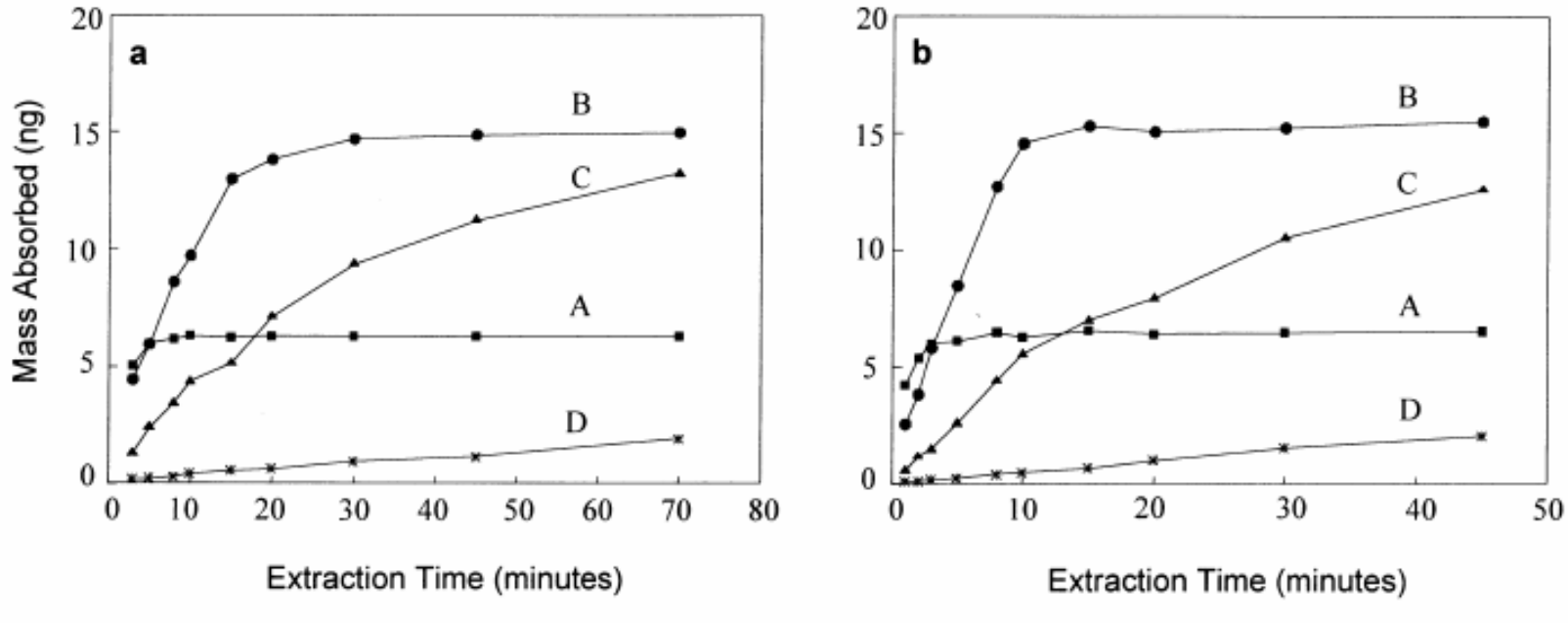
Sample Agitation

- Sample agitation is important to reduce the equilibrium time and improve the accuracy and precision, especially for higher molecular weight analytes with high diffusion coefficients.
- Stirring, sonication, and vibration are all suitable methods to agitate the sample.
- Maintain a consistent agitation between all extractions for good precision.



Extraction Time profile obtained for headspace SPME of several PAHs from aqueous samples at (a) 75% and (b)100% stirring rates

A, naphthalene; B, acenaphthene; C, phenanthrene; D, chrysene.

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Sample PH or Salt Concentration

- Adjusting the PH or adding salt can improve the extraction efficiency by changing the solubility of the analytes in the sample.
- You should buffer the PH of the sample to decrease analyte solubility, improve volatility of bases and acids, and to assure constant PH between extractions.
- The addition of 25%~30% (wt./vol.) NaCl will increase the ionic strength of the sample, which reduces analyte solubility.
- The addition of salt is especially helpful when analyzing polar analytes in water.

SPME Compares Well with Other Sample Preparation Techniques

	Detection Limit (MS)	Precision (% RSD)	Expense	Time	Solvent use	Simplicity
Purge & Trap	ppb	1-30	high	30 min	none	no
Stripping	ppt	3-20	high	2 hr	none	no
Headspace	ppm		low	30 min	none	yes
Liquid-Liquid Extraction	ppt	5-50	high	1 hr	1000 mL	yes
Solid phase extraction	ppt	7-15	medium	30 min	to 100 mL	yes
SPME	ppt	<1-12	low	5 min	none	yes

Combination

- The SPME technique can be routinely used in combination with gas chromatography (GC), high-performance liquid chromatography (HPLC) and capillary electrophoresis and places no restriction on MS.
- The SPME technique is ideally suited for MS applications, combining a simple and efficient sample preparation with versatile and sensitive detection.

Application of SPME in various fields of analytical chemistry

- Environmental applications
- Applications in food chemistry
- Analysis of wines and other alcoholic beverages
- Application to biological fluids
- Hair analysis
- Breath analysis–volatile metabolites of microorganisms

Environmental applications

- Determination of different compounds of air samples
- Pesticides, herbicides and other biologically active compounds in aqueous sample
- Determine aromatics and PAHs in sand and clay, VOCs, organometallic compounds, plasma and inorganic mercury samples in soil

Applications in food chemistry

- SPME is applied to the analysis of various components and contaminants in a range of different food sample.
- Aroma and flavor are among the most important analysis.

Analysis of wines and other alcoholic beverages

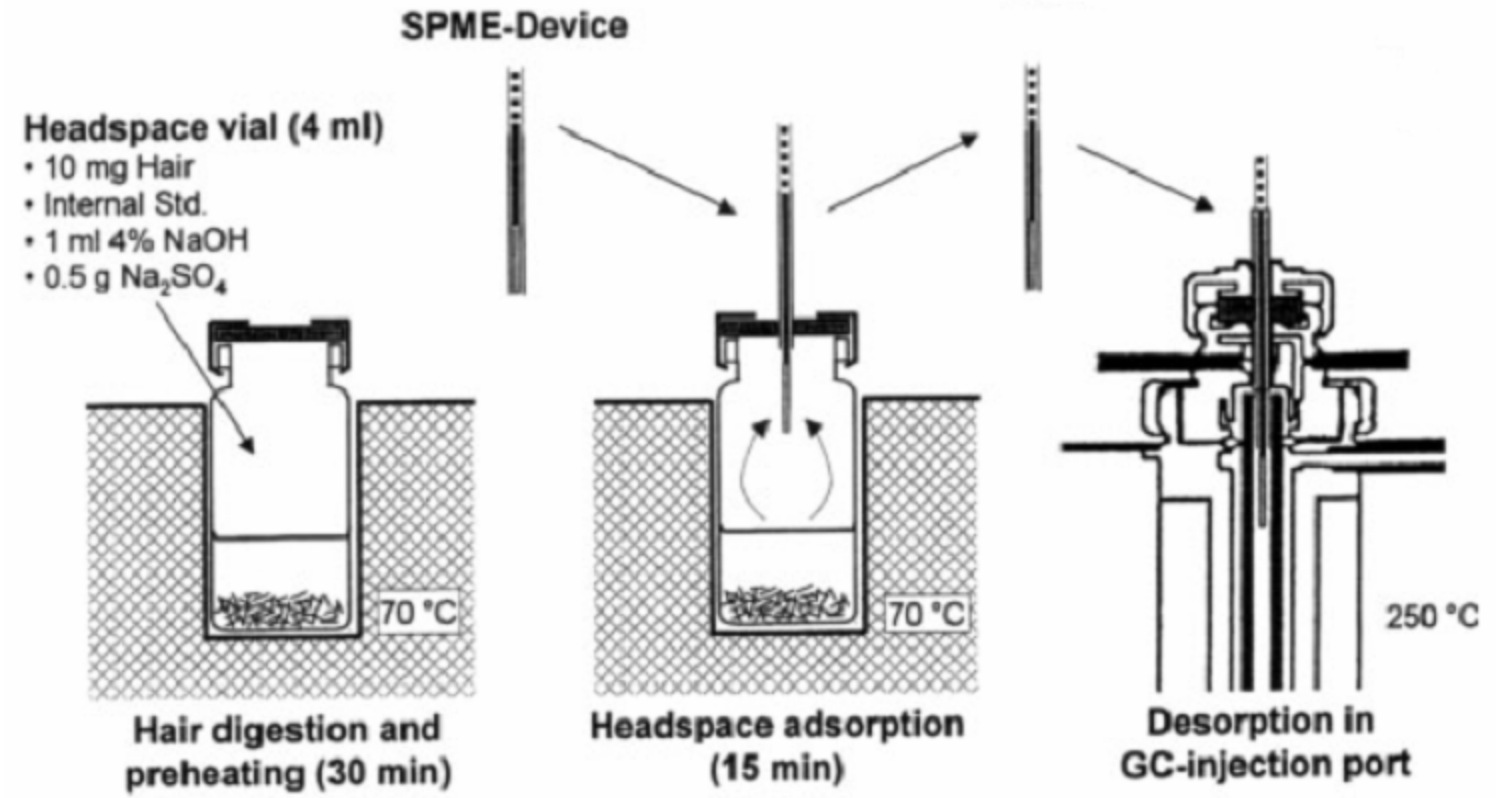
- Aromas are the most important components of wines.
- SPME can extract a few tens of different aroma components from wines.

Application to biological fluids

- SPME is one of the most promising sample preparation methods for biological samples.
- HS-SPME is ideal for the analysis of biological specimens, toxicology and environmental medicine, such as proteins.
- HS-SPME is suitable for the analysis of urine which is frequently used for drug screening, forensic purposes, monitoring workplace exposure to chemicals.

Hair analysis

- It is used for the long-term monitoring of drug and alcohol users.

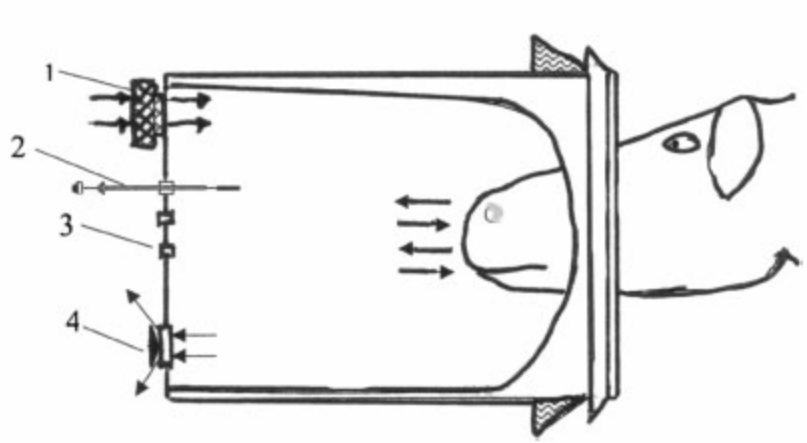


Schematic drawing of the HS-SPME sampling device for hair analysis

Gyorgy Vas, Karoly Vekey. J. Mass Spectrom. 2004; **39**: 248

Breath analysis–volatile metabolites of microorganisms

- HS-SPME is used to collect rapid on-site breath samples using DVB–Carboxen–PDMS (50 : 30) and 100 µm PDMS for the extraction of bovine breath gases



Schematic drawing of a face mask-like breath sampling device.

1: Ambient air filter; 2: SPME device; 3: septa; 4: one-way valve.

Gyorgy Vas, Karoly Vekey. J. Mass Spectrom. 2004; **39**: 249

Conclusion

- SPME affords a number of advantages in simplifying sample preparation, increasing reliability, selectivity, sensitivity and reducing the cost and time of analysis.
- The configurations and operation of the SPME devices are very simple.
- SPME is becoming widely used as an extraction and concentration step prior to MS analysis.
- SPME can integrate sampling with sample preparation which makes it suitable for on-site analysis and process monitoring.

Limitations of SPME

1. The volume of the polymer extraction phase is very small and requires extreme precision during manufacturing of the coating .
2. The quality of the fibers depends on the manufacturer, and

   sometimes the performance is different from batch to batch.
3. Some level of degradation of the fiber occurs during repeated usage.
4. The carry-over of the fiber is also a problem that in some cases is difficult to eliminate.
5. Fibers are fragile and can easily be broken.

Thank You