CHIMICA ANALITICA II
CON LABORATORIO

(AA 2016-17)

8 C.F.U. - Laurea triennale in Chimica

Sistemi eterogenei
Estrazioni di analiti
da un liquido a un solido

Metodi di estrazione con ***trasferimento dell'analita dalla fase liquida alla fase solida:***

SPE - solid phase extraction

SPME - solid phase micro extraction

SBSE - stir bar sorptive extraction

Estrazione su fase solida
SPE

- Processo di estrazione che coinvolge un liquido ed una fase solida.
- Il campione passa attraverso una fase stazionaria e gli analiti sono separati secondo quanto ciascuno di essi è ripartito o adsorbito dalla fase stazionaria.

L'obbiettivo è:

Ritenere l'analita sulla fase o eluirlo rapidamente

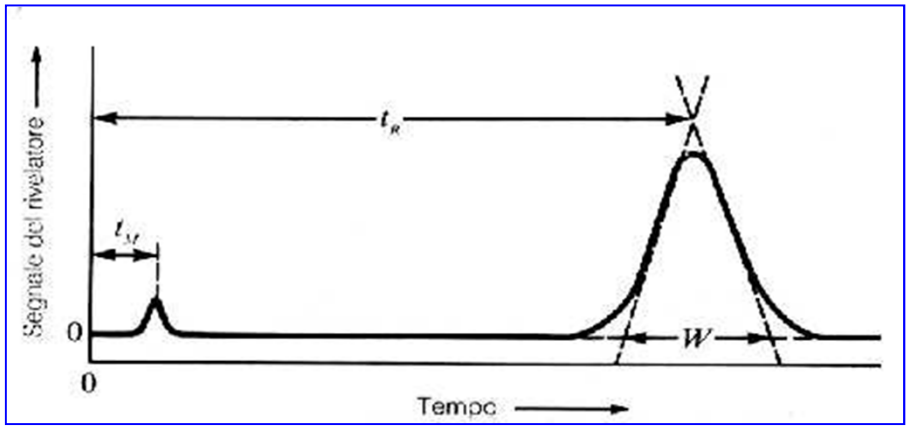
Il fattore di capacità k, che in cromatografia di eluizione è compreso tra 1 e 10, in SPE deve essere per la ritenzione >1000 e per l'eluizione <0.001

Un parametro importante che viene usato molto spesso per descrivere la velocità di migrazione dell'analita lungo la colonna è il fattore di capacità, k'.

$$k'_A = \frac{\text{n° totale di moli di A nella fase stazionaria}}{\text{n° totale di moli di A nella fase mobile}} = \frac{K_A \cdot V_S}{V_M}$$

Si dimostra che k' può essere ricavato dai parametri del cromatogramma:

$$k'_A = \frac{t_R - t_M}{t_M}$$



Due sostanze saranno separabili se presentano valori diversi di k'.

La selettività quantifica l'entità della separazione fra due specie: riguarda la capacità di un sistema cromatografico di distinguere fra due componenti ed è dipendente dalla distribuzione relativa delle specie fra la fase mobile e quella stazionaria, con $(t_R)_B > (t_R)_A$.

$$\alpha = \frac{k'_B}{k'_A} = \frac{(t_R)_B - t_M}{(t_R)_A - t_M}$$

Fundamentals of Sample Preparation

Extraction for SVOC and Non-VOC from Liquid or Solid Samples

Solid Phase Extraction (SPE)

- SPE uses a cartridge or disc
- May be performed a one time use syringe or a multiple cartridge unit

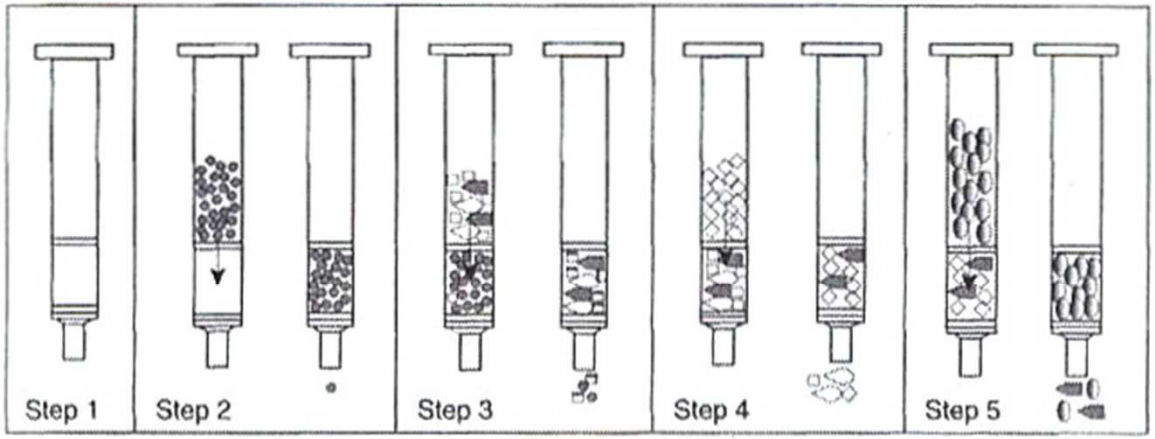


Figure 7.7 Five steps of solid phase extraction: (a) Select the proper SPE tube or disk from various commercially available SPEs, (b) Condition the SPE tube or disk, (c) Add the sample; (d) Wash the packing; (e) Elute the compounds of interest (Courtesy of Supelco)

Fundamentals of Sample Preparation for Environmental Analysis

Extraction for SVOC and Non-VOC from Liquid or Solid Samples

Solid Phase Extraction (SPE)

- SPE retains analyte from a flowing liquid sample on solid sorbent, analyte is recovered via elution from the sorbent
- Phase types:
  - Reverse phase
  - Normal phase
  - Ion exchange
  - Adsorption

Meccanismi di ritenzione

- Legame ad idrogeno
- Interazioni dipolo-dipolo
- Forze di dispersione idrofobiche
- Interazioni elettrostatiche (ioniche)

NON-POLARI		
C18	Octadecil	Si-C18H37
CB	Octil	Si-C8H17
C2	Etil	Si-C2H5
CH	Cicloesil	Si-C6H11
PH	Fenil	Si-C6H5
POLARI		
CN	Cianopropil	$Si\text{-}CH_2CH_2CH_2CN$
2OH	Diolo	$Si\text{-}CH_2CH_2CH_2\text{-}0\text{-}CH_2CHOH\text{-}CH_2OH$
SI	Silica	Si-OH
NH2	Aminopropil	$Si\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$
SCAMBIO IONICO		
PRS	Solfonilpropil	$Si\text{-}CH_2CH_2CH_2\text{-}SO_3^-$
CBA	Carbossimetil	$Si\text{-}CH_2\text{-}COO^-$
DEA	Dietilaminopropil	$Si\text{-}CH_2CH_2CH_2NH(CH_2CH_3)_2$
SAX	Trimetilaminopropil	$Si\text{-}CH_2CH_2CH_2N\ \text{-}(CH_3)_3$

Fundamentals of Sample Preparation for Environmental Analysis

Extraction for SVOC and Non-VOC from Liquid or Solid Samples

Solid Phase Extraction (SPE)

- Nonpolar:
  - Reverse phase C18 (octadecyl bonded silica) and C8 (octyl bonded silica) are most commonly used for hydrophobic analytes
- Polar:
  - Normal phase SPE uses cyanopropyl bonded, diol bonded, or amino propyl bonded silica (used for polar analytes such as cationic compounds and organic acids)
- Electrostatic:
  - Ionic Exchange SPE is based on electrostatics uses quaternary amine, sulfonic acid, or carboxylic acid bonded silica
- Adsorption type SPE uses unmodified materials such as alumina, Florosil, resins

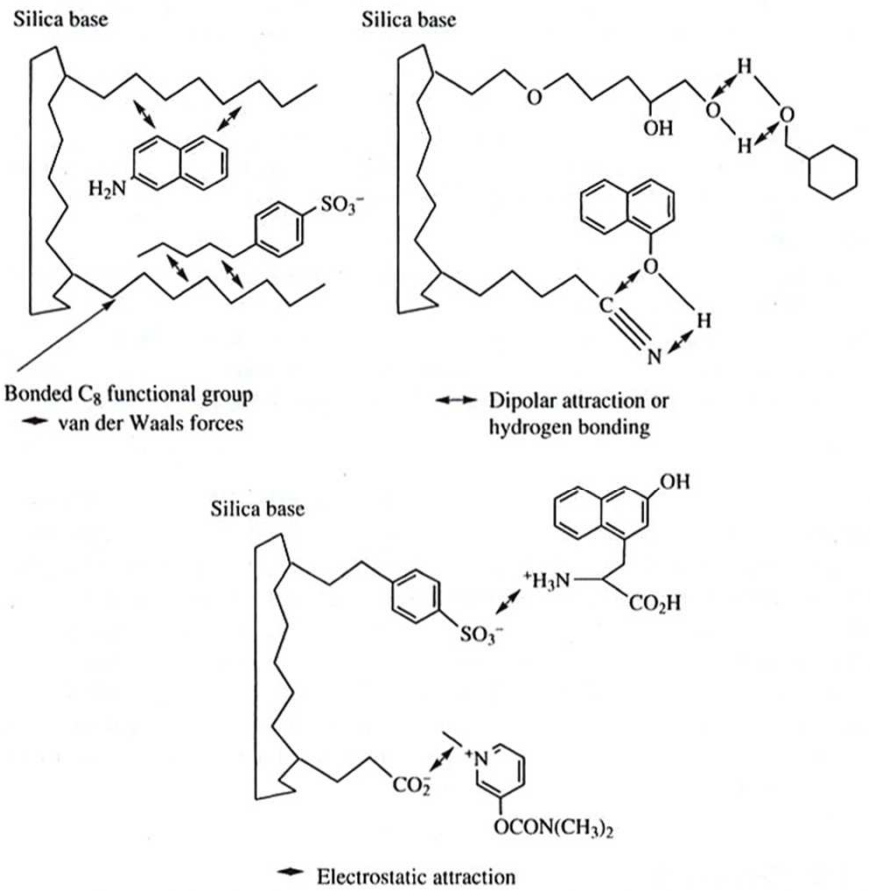
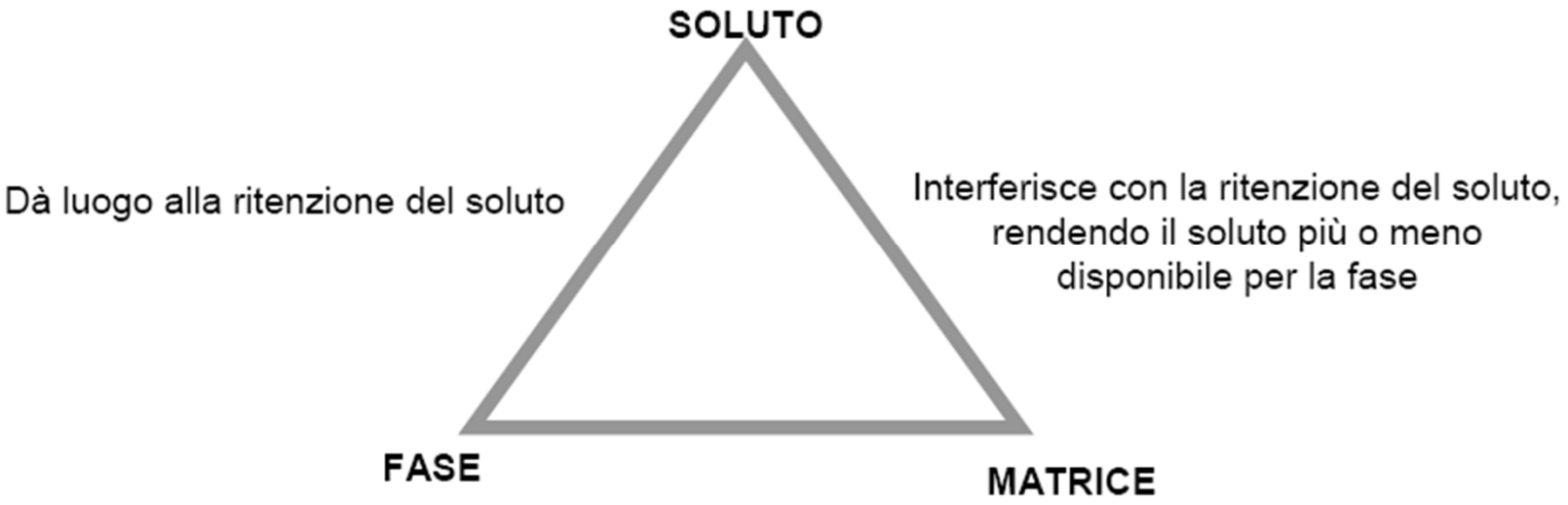


Figure 7.6 Solid-phase extraction using nonpolar, polar, and electrostatic interactions (Reprinted with permission from *American Laboratory*, 24(12):37–42. © 1992 by International Scientific Communications Inc.)

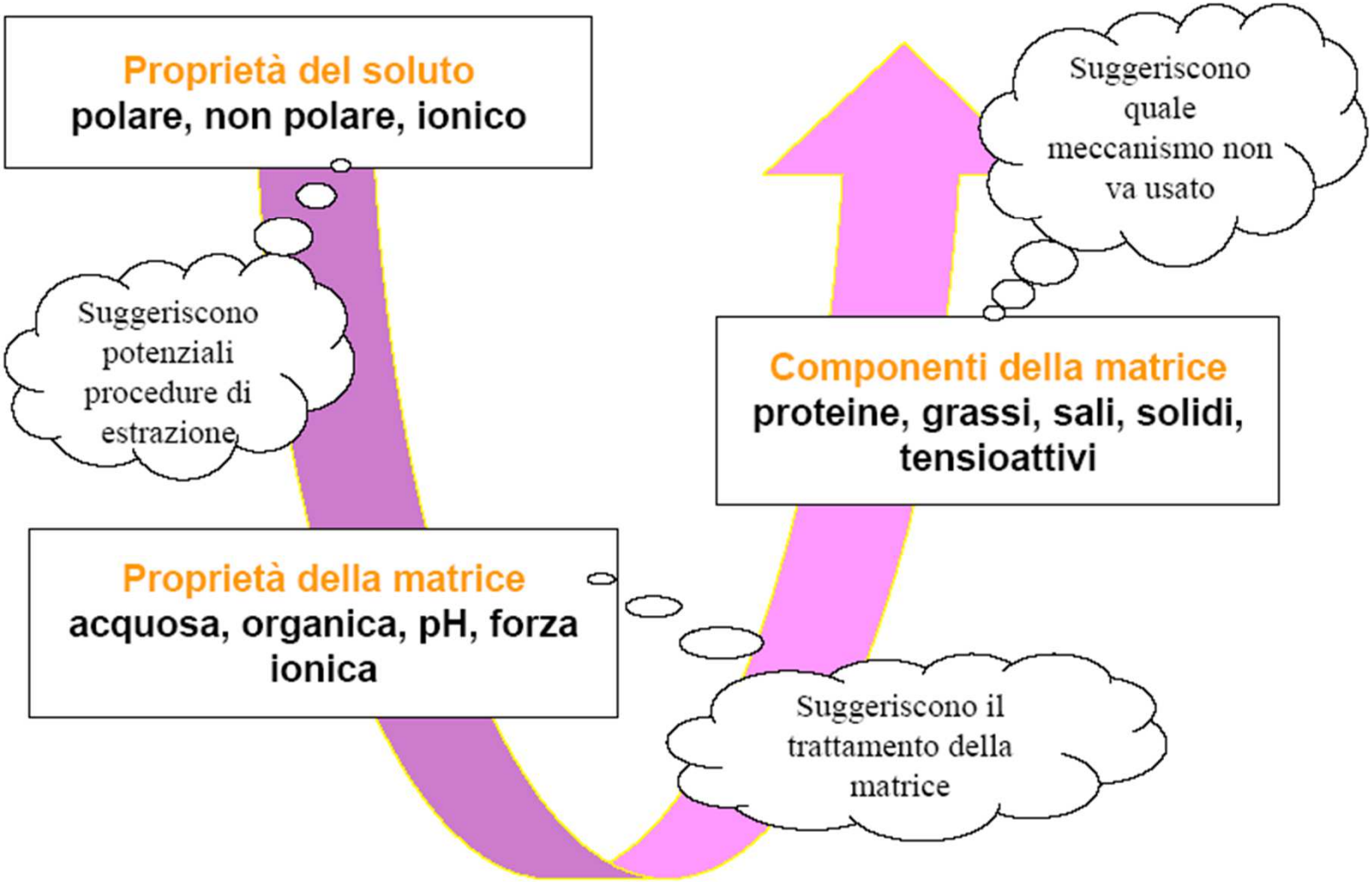
L’ambiente di estrazione

Nell’estrazione in fase solida il campione è considerato composto da **SOLUTO** e **MATRICE**.
Durante l’estrazione tre simultanee interazioni devono essere considerate.

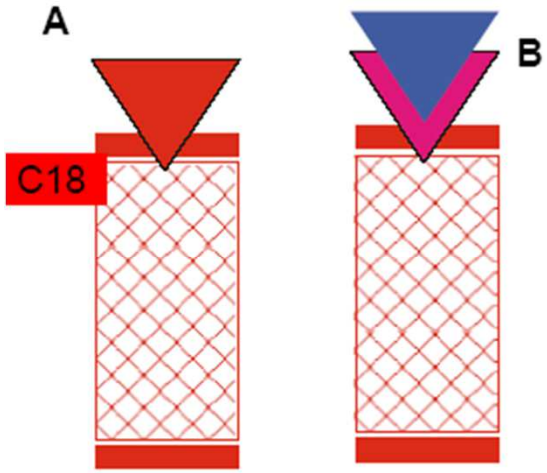
1. SOLUTO-FASE
2. SOLUTO-MATRICE
3. FASE-MATRICE

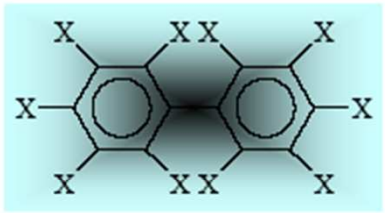


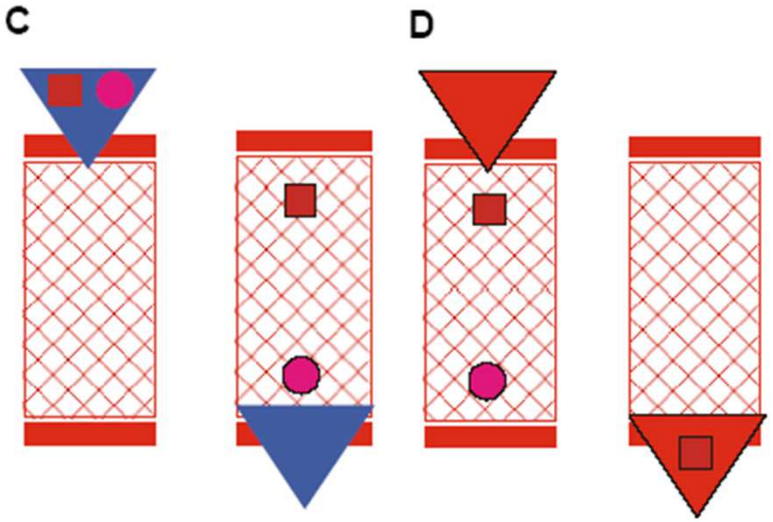
Scelta della fase



SPE: bifenili policlorurati



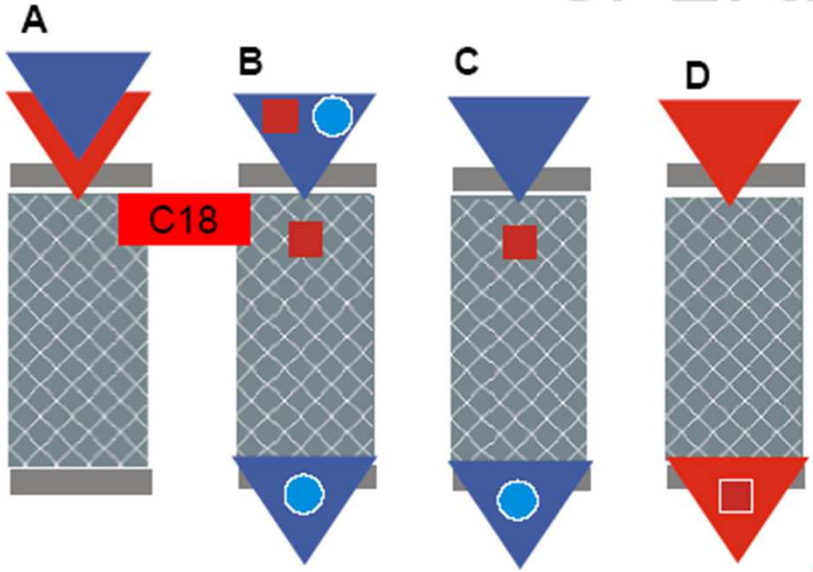


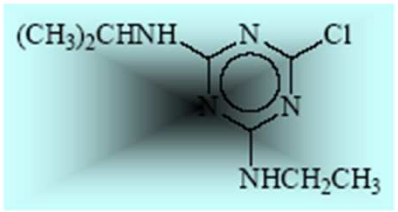


PCB's da acqua

A. Condizionamento: esano,
B. Condizionamento: metanolo, acqua
C. Applicazione del campione
D. Eluizione : esano

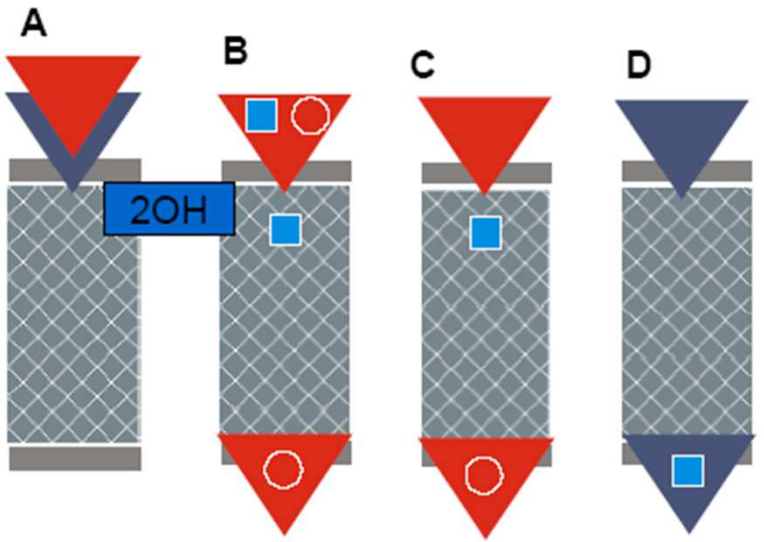
SPE: atrazina





Atrazina da tessuti

A. Condizionamento: metanolo, acqua
B. Applicazione del campione
C. Lavaggio: acqua
D. Eluizione: metanolo



Atrazina da olio vegetale

A. Condizionamento: metanolo,esano
B. Applicazione del campione
C. Lavaggio: esano
D. Eluizione: metanolo

Fundamentals of Sample Preparation for Environmental Analysis

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Solid Phase Extraction (SPE)

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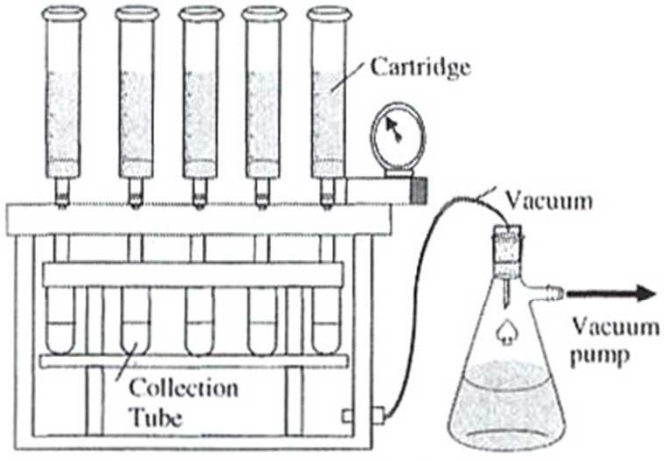


Figure 7.8 Vacuum manifold for solid phase extraction (SPE) of multiple cartridge units

(c) Automation is possible for SPE, resulting in reduced analytical cost, time, and labor.

Altri metodi di estrazione basati sull’assorbimento

SPME - Microestrazione in fase solida

SBSE - estrazione per assorbimento basata su ancoretta agitatrice

ESTRAZIONE E PRECONCENTRAZIONE DI SOSTANZE VOLATILI

Microestrazione in fase solida (Solid Phase Microextraction (SPME))

Questa tecnica abbastanza recente, ha acquisito popolarità negli ultimi anni grazie a:

1. semplicità
2. velocità
3. sensibilità

Il metodo è stato introdotto nei primi anni '90 dal Prof. Janusz Pawliszyn dell'Università di Waterloo in Ontario, Canada.

Vengono utilizzati **piccoli segmenti di fibre di silice fusa ricoperte di un opportuno materiale** (es. Polidimetilsilossano) **sigillati in un sistema "a siringa".**

Con questa tecnica si possono estrarre sostanze volatili o semi-volatili da varie matrici e attraverso il sitema a siringa è possibile iniettarle direttamente nel cromatografo (GC o HPLC).

Non sono necessari solventi. L'estrazione dell'analita e la preconcentrazione avvengono in un unico step.

Siringhe SPME sono commercializzate da varie ditte quali Supelco, Inc and Varian e vengono utilizzate per numerosi composti in un'ampia varietà di matrici.

Chi ha scoperto la SPME?

- La Solid Phase Microextraction è stata inventata nel 1990 da Dr. Janusz Pawliszyn e dai suoi colleghi dell'Università di Waterloo in Canada.

- Ha inventato questa tecnica per "soddisfare la richiesta di un metodo di preparazione del campione veloce, "solvent-free", impiegabile sul campo", che per l'industria significa più veloce e più efficiente.

http://www.spme.uwaterloo.ca/

Cos'è una SPME?

- **SPME è una tecnica di adsorbimento/desorbimento o partizione "solvent-free" .**

- SI appoggia sull'uso di fibre rivestite per isolare e concentrare analiti su un diversi materiali di rivestimento, che possono esser opportunamente selezionati.

- Dopo l'estrazione, le fibre sono trasferite a uno strumento analitico per la separazione e la quantificazione degli analiti investigati (*target analytes*).

- Ciò è possibile grazie all'impiego di un dispositivo simile a una siringa, il quale protegge il campione durante il trasferimento fino allo strumento.

- Il dispositivo a forma di siringa protegge la fibra durante la conservazione dell'estratto.

Di più a proposito della SPME

- La SPME è anche una tecnica di microestrazione che, comparata a volume del campione, contiene un quantitativo di solvente di estrazione molto piccolo.

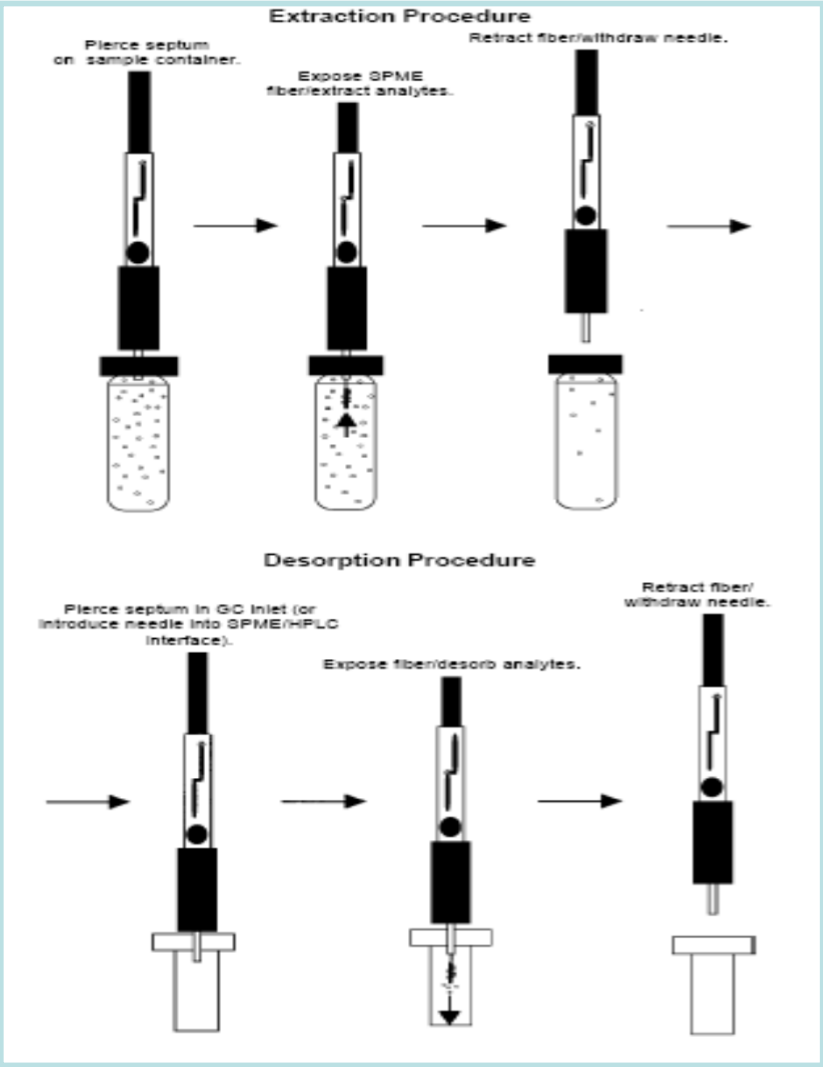
- La SPME permette di raggiungere un equilibrio tra la matrice da campionare e la fase estraente, piuttosto che perseguire una rimozione esaustiva/completa degli analiti verso la fase estraente.
  - La fase estraente è attaccata in modo permanente al supporto/fibra che può esser fatto di diversi materiali (silice, metallo).

- Il quantitativo di analita adsorbito dalla fibra dipende dallo spessore del rivestimento ("*coating*") e dalla costante di distribuzione dell'analita tra campione e "*coating*".

- Il tempo di estrazione dipende dalla lunghezza del tempo richiesto per ottenere estrazioni precise per gli analiti "*target"* con le costanti di distribuzione più sfavorevoli.

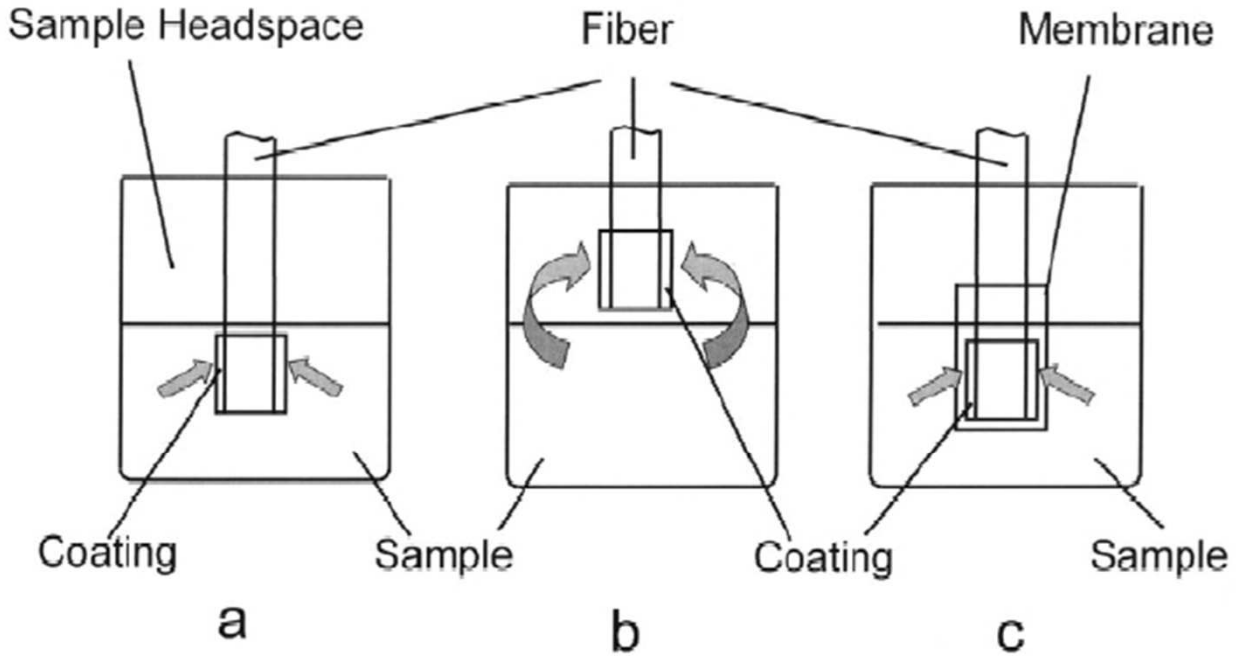
- **La selettività può essere modificata, alterando il tipo di fibra impiegata per rispondere alle caratteristiche degli analiti di interesse.**
  - **I composti volatili richiedono un rivestimento ("coating") spesso e gli analiti semivolatili un rivestimento sottile.**

Come funziona la SPME?



- First, you draw the fiber into the needle.
- The needle is then passed through the septum that seals the vial.
- You then depress the plunger to expose the fiber to your sample or headspace above the sample.
- Organic analytes are then adsorbed to the coating on the fiber.
- After adsorption equilibrium is attained, which can be anywhere **from 2 minutes to 1.5 hours**, the fiber is drawn back into the needle and is withdrawn from the sample vial.
- Finally, the needle is introduced into the GC injector or SPME/HPLC interface, where adsorbed analytes are thermally desorbed and delivered to the instruments column.

Estrazione per immersione o in spazio di testa



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

H. Lord, J. Pawliszyn J. Chromatogr. A **885** (2000) 161

Raggiungere l'equilibrio

L'estrazione è considerata completa quando raggiunge l'equilibrio e le condizioni possono essere descritte dalla segente equazione in cui :

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

n=massa dell'analita assorbito sul rivestimento
C_0=concentrazione iniziale dell'analita
K_{fs}= coefficiente di partizione per l'analita tra il rivestimento e la matrice del campione
V_f= volume del rivestimento

V_s= volume del campione

- Questa equazione mostra la relazione tra la concentrazione dell'analita nel campione e il quantitativo estratto dalla fibra rivestita.
- Se il quantitativo di analita estratto sulla fibra è una porzione insignificante di quello presente nel campione (in pratica **se Vs >>Vf**), questa equazione si semplifica a **$n=K_{fs}V_fC_0$** , in cui il quantitativo di analita estratto è indipendente dal volume di campione.
- Ciò significa che:
  - Non c'è bisogno di raccogliere un quantitativo definito di campione prima dell'analisi. La fibra può essere esposta alla matrice che si deve analizzare e
  - Il quantitativo di analita estratto corrisponderà direttamente alla sua concentrazione nella matrice.
- Ciò consente di evitare gli errori associati alla perdita di analita per decomposizione o per assorbimento sulle pareti del contenitore di campionamento.

Components of a Manual SPME Holder

Adjustable needle guide/depth gauge

Plunger

The O ring

Plain Hub

Plunger retaining Screw

Septum piercing needle

Where fiber is exposed in headspace/liquid sample

“holder” manuale per SPME

Other SPME holders available

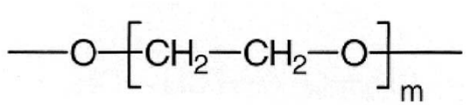
SPME Portable Field Sampler

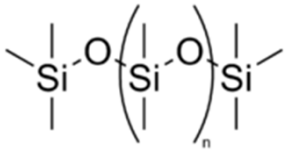
Contains an internal septum that stores your fiber after sampling by sealing it.

Great for field work

Comes with

- a PDMS/Carbowax fiber for trace-level volatile analysis
- Or a PDMS fiber for concentrating polar analytes



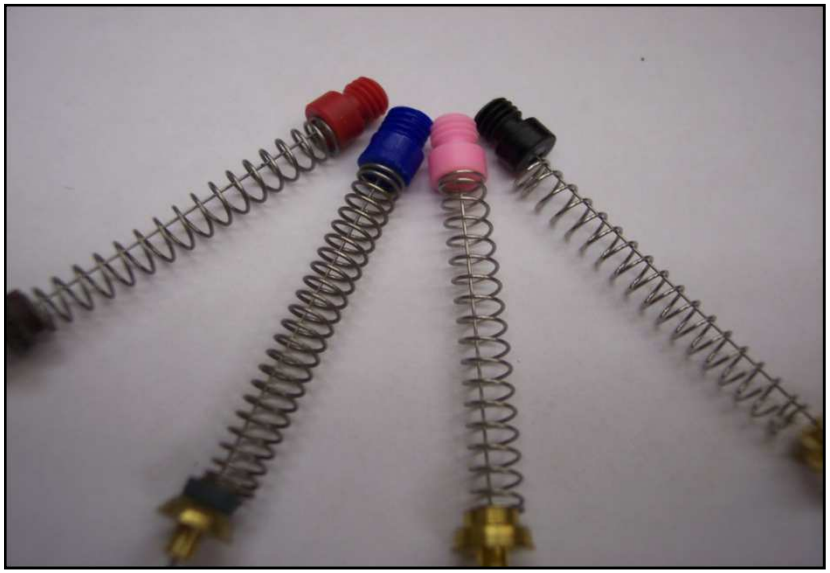


- **This holder is used with an autosampler or an SPME/HPLC interface…requires an upgrade kit for autosampler use.**
- **Contains a needle that moves freely for control by an automated system, and for depth regulation in the interface desorption chamber.**

Fibre SPME disponibili

Rivestimenti disponibili per le fibre:

- PDMS
- PDMS/DVB
- Poliacrilato
- CAR/PDMS
- CW/DVB
- CW/TPR
- StableFlex DVB/CAR/PDMS



- **Diverse Fasi disponibili:**
  - **Non-legate**
    - **Stabili con acqua e alcuni solventi organici miscibili con acqua**
    - **Può verificarsi un moderato rigonfiamento**
    - **Non usare MAI con solventi organici non polari**
  - **Legate**
    - **Stabili con TUTTI i solventi organici**
    - **Può verificarsi un moderato rigonfiamento con solventi non polari**
  - **Parzialmente Crosslinked (con legami a ponte)**
    - **Stabili con la maggior parte dei solventi organici miscibili con acqua**
    - **Può esser stabile in alcuni solventi non polari, ma si può aver rigonfiamento**
  - **Altamente Crosslinked**

Fibre StableFlex

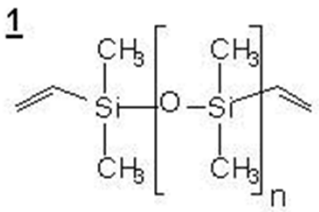
- These type of fibers are coated on a **flexible fused silica core** instead of the standard fused silica core used on the other fibers.
- This **coating partially bonds to the flexible core** which results in:
  - a **more stable coating**
  - a more durable and longer lasting fiber
- These special coated fibers are for GC use only .
- They also have the same **temperature, conditioning, and cleaning** requirements as the other fiber of its same coating and thickness.
- These are available in every coating EXCEPT for PDMS, Polyacrylate, and CW/TPR.

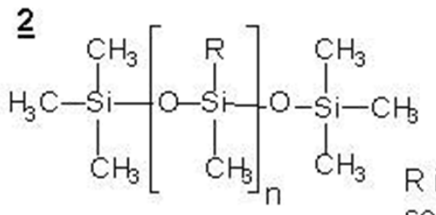
Polydimethylsiloxane (PDMS)

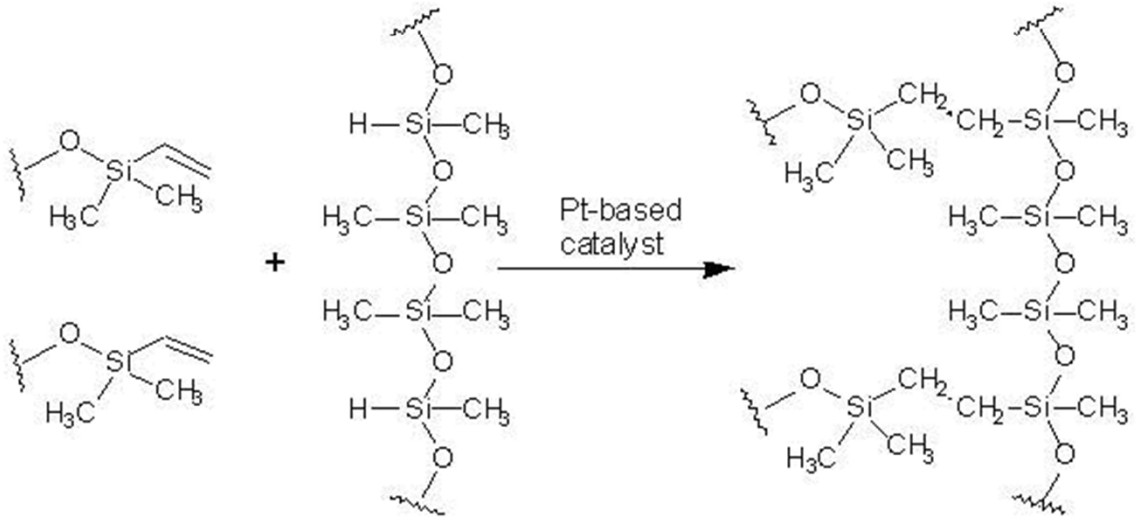
Film Thickness	Description	Hub Description	Recommened use
100µm	Non-bonded	**Red**	Volatiles on GC/HPLC
30µm	Non-bonded	**Yellow**	Nonpolar semivolatiles on GC/HPLC
7µm	Bonded	**Green**	Moderately polar to nonpolar semivolatiles on GC/HPLC

siloxane oligomers

siloxane cross-linkers







Polydimethylsiloxane/Divinylbenzene (PDMS/DVB)

Film Thickness	Description	Hub Description	Recommened use
65µm	Partially crosslinked	**Blue**	Polar volatiles on GC
60µm*	Partially crosslinked	**Brown**	General purpose on HPLC
StableFlex Fiber 65µm	Highly crosslinked	**Pink**	GC

*** This fiber is more durable due to it not containing any epoxy**

Polyacrylate

Film Thickness	Description	Hub Description	Recommened use
85µm	Partially crosslinked	white	Polar semivolatiles on GC/HPLC

Carboxen/Polydimethylsiloxane (CAR/PDMS)

Film Thickness	Description	Hub Description	Recommened use
75µm	Partially Crosslinked	**Black**	Trace-level volatiles on GC
StableFlex Fiber 85µm	Highly crosslinked	**Lt.Blue**	GC

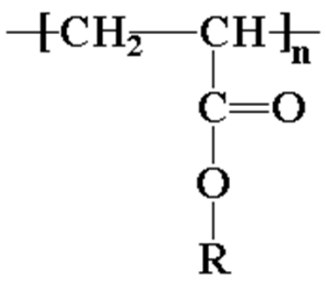
Carbowax/Divinylbenzene (CW/DVB)

Film Thickness	Description	Hub Description	Recommened use
65µm	Partially crosslinked	**Orange**	Polar analytes on GC

Carbowax/Templated Resin (CW/TPR)

Film Thickness	Description	Hub Description	Recommened use
50µm*	Partially crosslinked	**Purple**	Surfactants on HPLC

*** This fiber is more durable due to it not containing any epoxy**



StableFlex Divinylbenzene/Carboxen/PDMS (DVB/CAR/PDMS)

Film Thickness	Description	Hub Description	Recommened use
50/30µm	Highly crosslinked	Gray	GC

Recommended Temperature and Conditioning for GC Use

Phase	Thickness	Maximum Temperature	Operating Temperature	Conditioning Temperature	Time (Hrs.)
PDMS	100µm		280° C	200° C-270° C	250° C 1
	30µm	280° C	200° C-270° C	250° C	1
	7µm	340° C	220° C-320° C	320° C	2-4
PDMS/DVB	65µm	270° C	200° C-270° C	260° C	0.5
Polyacrylate	85µm	320° C	220° C-310° C	300° C	2
CAR/PDMS	75µm	320° C	240° C-300° C	280° C	0.5
CW/DVB	65µm	265° C	200° C-260° C	250° C	0.5
DVB/CAR/PDMS	50/30µm	270° C	230° C-270° C	270° C	4

Note that the Polyacrylate, or white fiber, will turn brown as a result of condition and will not hurt the performance of the fiber.

Maintenance on SPME

- Chlorinated solvents my dissolve the epoxy that holds the fiber so DO NOT USE CHLORINATED SOLVENTS EVER.
- Use caution when handling PDMS/DVB and CW/DVB fibers because the coating can be inadvertently stripped off.
- Cleaning your fiber depends on the fiber phase coating:
  - Bonded can be taken to maximum temperature and thermally cleaned for 1 hour to overnight, or can be rinsed in an organic solvent and then thermally cleaned.
  - Non-bonded can only be thermally cleaned and can be taken to the maximum temperature for 1 to 2 hours or baked overnight at 10-20 degrees under the maximum temperature.
    - If not clean after this treatment, thermally treat it for 30 minutes at 20 degrees above the maximum temperature.
  - Partially bonded fibers can be rinsed in water-miscible organic solvents.

Sampling with SPME

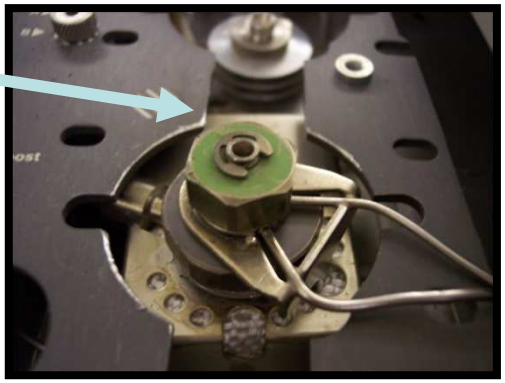
- Consistent **sampling time, temperature, and fiber immersion depth** are crucial to this technique when it comes to high accuracy and precision.
- **Equilibrium is attained more rapidly in headspace than in immersion** because the analytes can diffuse more rapidly to the coating on the fiber.
- The thicker the fiber coating, the more analytes that are extracted, which is proven in the figure below.

	Relative Recovery (%)		
Analyte*	100µm Coat	30µm Coat	7µm Coat
Benzene	2	1	<1
Toluene	5	1	<1
Ethylbenzene	6	4	1
1,3-Dichlorobenzene	15	5	1
Naphthalene	13	4	1
Acenaphthylene	19	8	3
Fluorene	29	18	6
Phenanthrene	37	27	16
Anthracene	49	38	32
Pyrene	69	54	47
Benzo(a)anthracene	105	91	96
Chrysene	100	100	100
Benzo(b)fluoranthene	104	111	120
Benzo(a)pyrene	119	127	131
Indeno(1,2,3-cd)pyrene	61	140	148
Benzo(ghi)perylene	61	117	122

*Listed in order from smaller to larger molecular weights
SPME: polydimethylsiloxane-coated fibers, immersion sampling, 15 min

Injecting and Running a Sample on GC

This is where you inject your SPME needle on the GC-MS



Advantages of SPME

- During desorbtion of the analyte, the polymeric phase is cleaned and ready for reuse.
- Absence of solvent makes SPME
  - environmentally friendly
  - separation is faster
  - throughput increases and allows for use of simpler instruments
- Small in size
  - great for field work.
  - Amount of extracting phase is small and equilibrium of system is not disturbed
  - Very small objects can be studied
- High sensitivity and limit of determination
- All extracted analytes are transferred to the analytical instrument
- Can sample directly into a sample or the headspace above sample.

- **Range of analytes that can be analyzed include volatile, semivolatile, nonvolatile, and inorganic species.**
- **coupled with other instruments besides GC like CE, LC, and MS.**
- **When compared to similar extraction methods, SPME has a better detection limit, precision, cost, time, solvent use, and**

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	1000mL	yes
Solid Phase Extraction					
ppt	7-15	medium	30 min	to 100mL	yes
SPME					
ppt	<1-12	low	5 min	none	yes

Table provided by J. Pawliszyn, University of Waterloo, Waterloo, Ontario, Canada.

Disadvantages of SPME

- Can get relatively expensive if one is not careful with fibers due to the cost being roughly 90€ per fiber.

- Polymer coating is fragile, easily broken, and have limited lifetime.

- Also a monopoly with Supelco being the only suppliers of the fibers so cost continuously increases.

- Its main limitation is its reduced concentration capability due to the small volume of polymer coating on the fiber, which is being addressed and researched further by Dr. Pawliszyn.

Why SPME?

- It can be used to analyze various types of analytes from gaseous, liquid, and solid samples instead of specializing in just one type like LLE or Headspace.
- Very cheap compared to other extraction methods.
- Reduces sample preparation times and disposal costs due to being solvent-free, also a bonus for the environment.
- Improves detection limits.
- A very simple methods that almost anyone could perform.

Different fields using SPME

- Applications SPME is applied to include:
  - Food and drug
  - Environmental
  - Clinical/Forensics

Choosing Best Sample Preparation Technique

- Sample preparation constitutes for over 80% of your total analysis time so an effective sample is desired, especially by the food and drug industry where time is money.

- The following is desired in sample preparation of pharmaceuticals:
  - Loss of very little sample
  - Good yield recovery of analyte of interest
  - Coexisting compounds removed efficiently
  - Procedure can be performed conveniently and quickly
  - Cost of analysis is kept to a minimum

Comparing Extraction Methods for Pharmaceutical Analysis

SPE and LLE in drug analysis:

- Both complicated and time-consuming, which limits the number of samples
- Prone to sample loss due to being multi-step
- Require large sample amount
- Require an organic solvent
- Difficult in automating these procedures
- Additional cost for waste treatment

SPME, as we have heard in previous slides, prevents all of these common drawbacks listed for SPE and LLE.

Similar Microextraction Techniques used for Pharmaceutical Analysis

- Stir Bar Sorptive Extraction (SBSE)
- Fiber SPME-main focus of this presentation
- In-Tube SPME
- Solid Phase Dynamic Extraction (SPDE)

SBSE

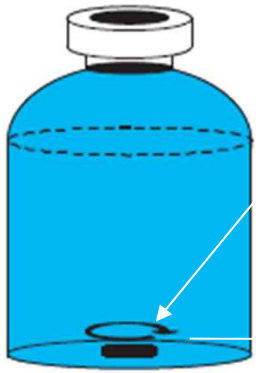
- Stir bar sorptive extraction, or SBSE, is a very similar technique to SPME.
- It is a technique that is used for the analysis on both volatile and semivolatile organic compounds in aqueous environmental samples.
- When compared to SPME, SBSE has higher recoveries and higher sensitivity.
- The extraction is performed by placing the stir bar in the sample for 30-120 minutes.
  - After extraction, stir bar is placed in a glass thermal desorption tube that is placed in a thermal or liquid desorption unit to be thermally desorbed and analyzed.

SBSE (Twister™)

- **Preparativa: circa 2’ a campione**
- **Volume richiesto: da 10 a 100 ml**
- **Assenza di manipolazioni**

PDMS

Ancoretta magnetica

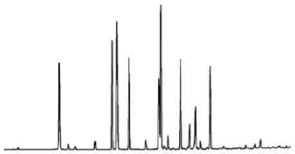


Rivestimento in vetro

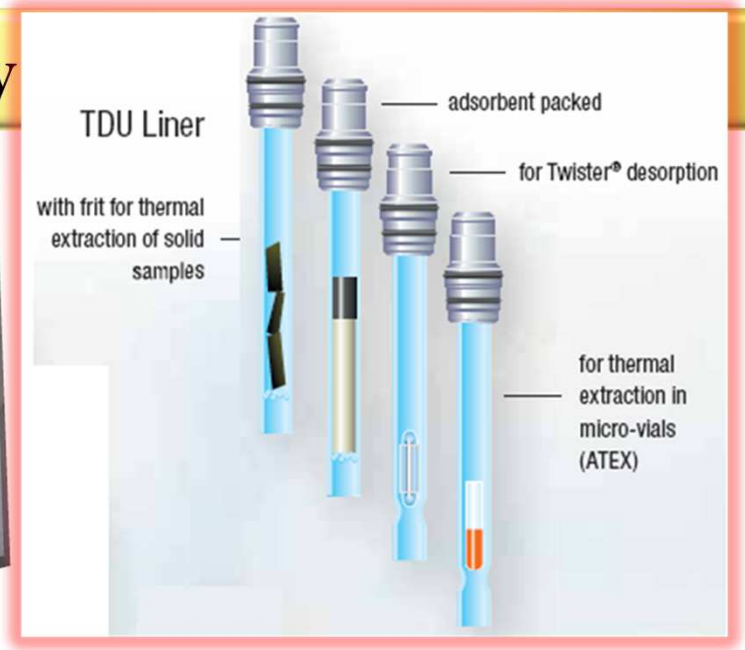
Stir Bar Sorbtive Extraction

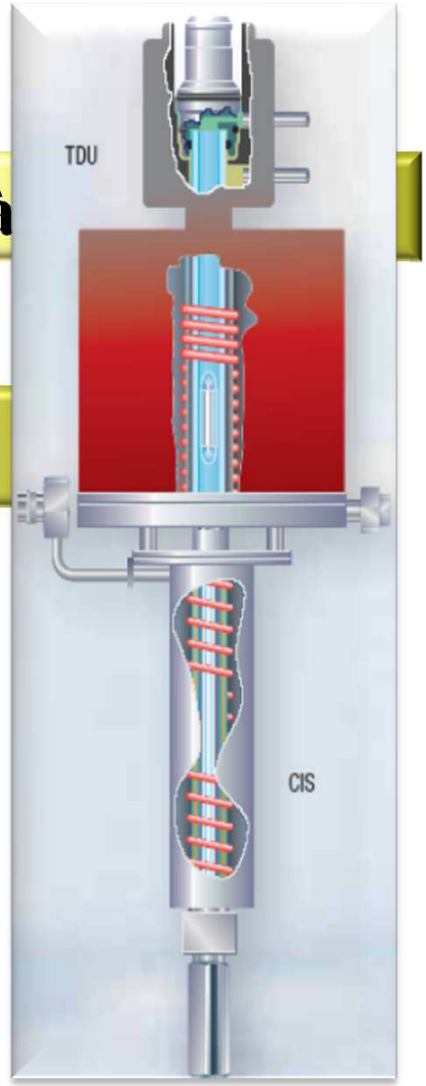
Desorbimento

Cromatografia

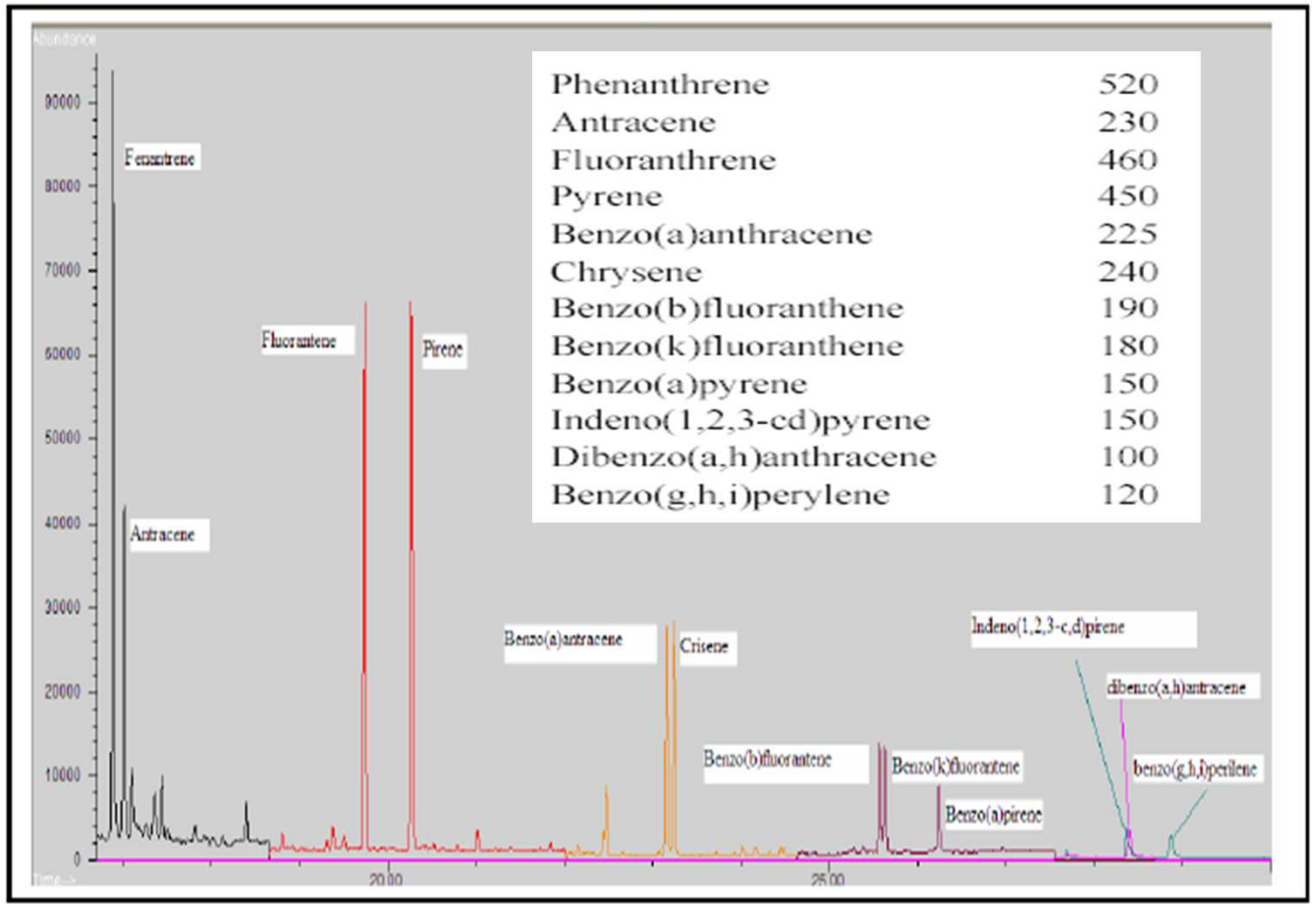


Analisi SVOC (alta produttività





PAHs in water



Rapporti S/N;
standard da 0,50 ng/l

Applicazione routinaria

#	Compound	r^2 (20 – 600 ppt)	LOD (ppt)	LOQ (ppt)
1	alpha-HCH	0.991	0.50	1.7
2	beta-HCH	0.996	1.80	5.9
3	Lindane	0.994	0.30	1
4	delta-HCH	0.998	1.50	5
5	Heptachlor	0.996	1.00	3.4
6	Aldrin	0.991	0.70	2.4
7	Heptachlor epoxide	0.995	0.20	0.7
8	Endosulfan I	0.992	10.70	36.1
9	Dieldrin	0.993	0.70	2.4
10	Endrin	0.993	0.90	2.9
11	Endosulfan II	0.992	2.10	35.7
12	Endosulfan Sulfate	0.994	3.50	12
13	Endrin ketone	0.994	1.70	5.7
14	Metoxichlor	0.995	0.10	0.4
15	*p,p*'-DDT	0.997	0.80	2.5
16	*p,p*'-DDE	0.998	0.40	1.4
17	*p,p*'-DDD	0.997	0.10	0.4

#	Compound	r^2 (20 – 600 ppt)	LOD (ppt)	LOQ (ppt)
18	Simazine	0.999	8.60	28.6
19	Atrazine	0.999	0.30	0.9
20	Ametryn	0.991	0.30	1.1
21	Trietazine	0.996	0.10	0.4
22	Terbutryn	0.992	0.50	1.8
23	Terbuthylazine	0.997	0.30	0.9
24	Propazine	0.996	0.20	0.6
25	Prometryn	0.996	0.20	0.7
26	Diazinon	0.998	0.20	0.6
27	Methyl-parathion	0.99	0.80	2.7
28	Parathion	0.991	0.20	0.8
29	Ethion	0.992	0.10	0.5
30	Fluoranthene	0.996	0.04	0.1
31	Benzo[*a*]pyrene	0.992	0.70	2.4
32	Benzo[*ghi*]perylene	0.991	1.50	4.9
33	Benzo[*k*]fluoranthene	0.993	0.70	2.3
34	Indeno[123-*cd*]pyrene	0.991	1.50	4.8
35	Benzo[*b*]fluoranthene	0.991	0.60	1.9

Elevata frammentazione di massa

Polarità considerevole ($\log(K_{o/w}) = 2.4$)

Solid-Phase Dynamic Extraction

This technique is for vapor and liquid samples.

Dynamic sampling is performed by passing the headspace through the tube using a syringe.

The analytes are then concentrated onto PDMS and activated carbon, which are coated onto the inside wall of the needle.

This technique permits operation under dynamic conditions while keeping the headspace volume constant.

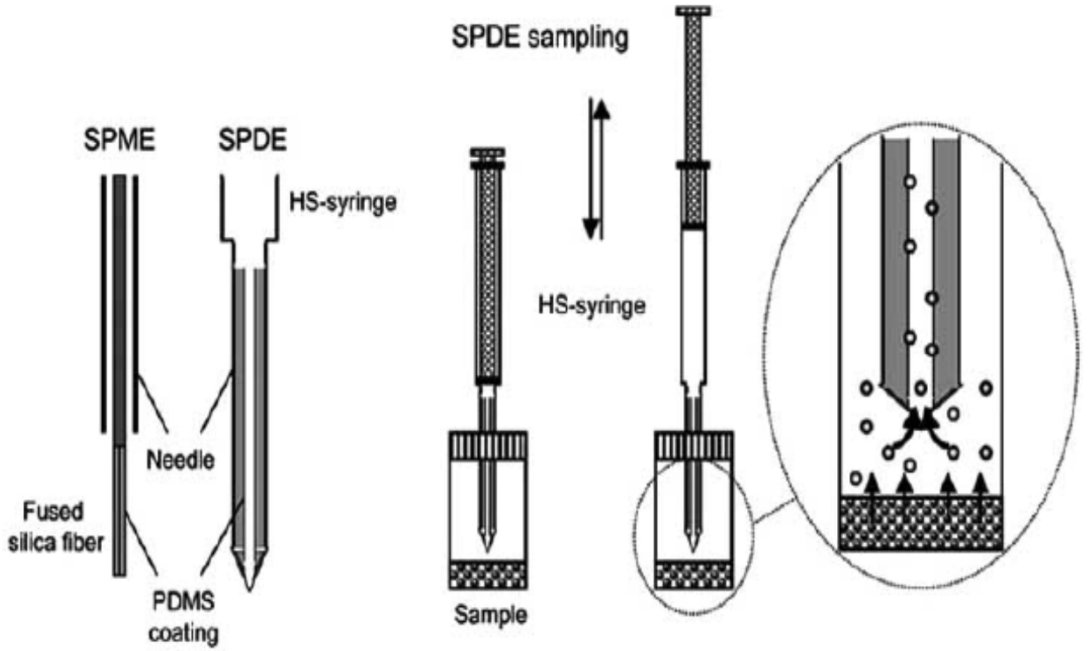


Fig. (4). Schematic representation of SPME and SPDE devices, and extraction process by SPDE.

Trapped analytes are then recovered by heat desorption directly into a GC injector body, which was shown to you in a previous slide.

A great advantage of this technique over SPME is the robustness of the capillary and the fact that it is nearly impossible to damage this mechanically.

This has been used to analyze volatile compounds, pesticides, and some drugs successfully.

The only drawback to this technique is that it tends to have carryover because the analytes tend to remain in the inside needle wall after heat desorption.

Applications of drug analysis using SPME and related microextraction techniques

Analyte	Matrix	Extraction device [a]	Extraction mode [b]	Hyphenated analysis [c]
Cannabinoids	Hair	PDMS-fiber	DI	GC-MS
Cannabinoids	Hair	PDMS-fiber	HS + OFD	GC-MS
Cannabinoids	Hair	PDMS-coated syringe	HS-SPDE	GC-MS
Cannabinoids	Saliva	PDMS-fiber	DI	GC-MS
Amphetamines	Hair	PDMS-fiber	D + HS	GC-MS
Amphetamines, designer drugs	Hair	PDMS-coated syringe	HS-SPDE	GC-MS
Amphetamines, designer drugs	Hair	PDMS-fiber	HS + OFD	GC-MS
Amphetamine-like drugs	Hair, saliva	PDMS-fiber	HS	GC-MS
Amphetamines, MDA, MDMA, MDEA	Hair, urine	PPY-coated	IT	LC-MS
Amphetamine, fenfluramines	Blood	PDMS-fiber	D + DI	GC-MS
Amphetamines	Blood	PDMS-fiber	HS	GC-MS
Amphetamines, MDA, MDMA, MDEA	Serum	PDMS-fiber	D + HS	GC-MS
Amphetamines, MDMA	Urine	PDMS-fiber	DI	GC-MS
Amphetamines, MDA, MDMA, MDEA	Urine	PDMS-fiber	HS	GC-MS
Amphetamines, MDA, MDMA, MDEA	Urine	Omegawax 250 capillary	IT	LC-MS
Amphetamine-related drugs	Urine	PDMS-fiber	D + HS	GC-MS
Amphetamines, MDA, MDMA, MDEA	Urine	PDMS-fiber	D + DI	FAI-MS-MS
Amphetamines	Urine	PDMS-fiber	D + HS	GC-MS
Amphetamines	Urine	PDMS-fiber	HS	GC-FID
Amphetamine, MDMA	Urine	CW/TPR-fiber	DI + OFD D + DI	HPLC-FLD
Amphetamines	Drugs	PDMS-fiber	DI + OFD	GC-MS
Recreational drugs	Hair	PDMS-fiber	HS	GC-MS
Cocaine, benzoylecgonine	Hair	PDMS-fiber	DI	GC-MS
Cocaine, Cocaethylene	Sweat	PDMS-fiber	DI	GC-MS
Illicit drugs	Hair	PDMS-coated syringe	HS-SPDE	GC-MS
Illicit drugs	Saliva	PDMS-fiber	HS / DI	GC-MS
Illicit drugs	Serum, urine	PA-fiber	HS	GC-MS
Methadone	Hair	PDMS-fiber	DI	GC-MS
Methadone, metabolite	Hair	PDMS/DVB-fiber	HS	GC-MS
Methadone	Saliva	PDMS-fiber	DI	GC-MS
Methadone, metabolite	Plasma	PDMS-fiber	DI	GC-MS

Applications of drug analysis using SPME and related microextraction techniques

Nitrous oxide, isoflurane, halothane	Urine	DVB- carboxen / PDMS-fiber	HS	GC-MS
Halothane	Blood	PDMS-fiber	HS	GC-MS
Lidocaine	Hair	CW/DVB-fiber	HS	GC-MS
Lidocaine	Plasma	PDMS-fiber	DI	GC-FID
Lidocaine	Urine	PDMS-fiber	DI	MS-MS
Local anesthetics	Plasma	Silica C2-packed syringe	MEPS	GC-MS
Thiopental, pentobarbital	Hair	CW/TPR-fiber	DI	GC-MS-MS
Brabiturates	Blood, urine	PA-fiber	DI	GC-MS
Midazolam	Plasma	PA-fiber	DI	GC-MS
Lamotrigine, drugs	Plasma	CW/DVB-fiber	DI	GC-TSD
Clozapine	Plasma	PDMS-fiber	DI	GC-NPD
Delorazepam	Urine	CW/TPR, PDMS/DVB-fiber	DI	HPLC-UV
Benzodiazepines	Serum	Supel-Q plot capillary	IT	LC-MS
Benzodiazepines	Serum	ADS-packed capillary	IT	HPLC-UV
Benzodiazepines	Blood	ADS- fiber	DI	HPLC-UV
Benzodiazepine & metabolites	Urine	PDMS, PDMS/DVB-fiber	DI	GC-ECD
Benzodiazepines	Urine	ADS-fiber	DI	HPLC-UV
Carphedon	Urine	CW/DVB-fiber	DI	GC-FID
Phenothiazines	Blood, urine	PA-fiber	DI	LC-MS-MS
Levomepromazine	Plasma	PDMS-fiber	DI	GC-NPD
Amitriptyline	Urine	PDMS-fiber	DI	HPLC-UV
Tricyclic antidepressants	Urine	Wire-packed DB-1 capillary	IT	HPLC-UV
Tricyclic antidepressants	Urine	Zylon DB-1 capillary	IT	CE-UV
Amitraz	Plasma	PDMS-fiber	DI	GC-TSD
Sufentanil	Plasma	PDMS/DVB-fiber	DI	GC-MS
β-Blockers	Serum, urine	Omegawax 250 capillary	IT	LC-MS
β-Blockers	Serum, urine	PPY-coated capillary	IT	LC-MS
Propranolol	Serum	MIP-packed capillary	IT	HPLC-UV
Verapamil	Cell culture	PPY-coated capillary	IT	LC-MS
Ranitidine	Urine, tablet	Omegawax 250 capillary	IT	LC-MS
Rivastigmine	Plasma	PDMS/DVB-fiber	HS	GC-MS
Thymol	Plasma	PDMS/DVB-fiber	HS	GC-FID
Menthol	Plasma, urine	PDMS/DVB-fiber	HS	GC-MS
Methylxanthines	Blood, urine	CW/DVB-fiber	DI	GC-NPD
Xanthines	Serum	Monolithic capillary	IT	HPLC-UV
Busulphan	Plasma	CW/DVB-fiber	DI	GC-MS
Tetracyclines	Milk	CW/TPR-fiber	DI	LC-MS
Mycophenolic acid	Serum	CW/TPR-fiber	DI	HPLC-UV

Results from Pharmaceutical Studies with SPME-Hair Samples

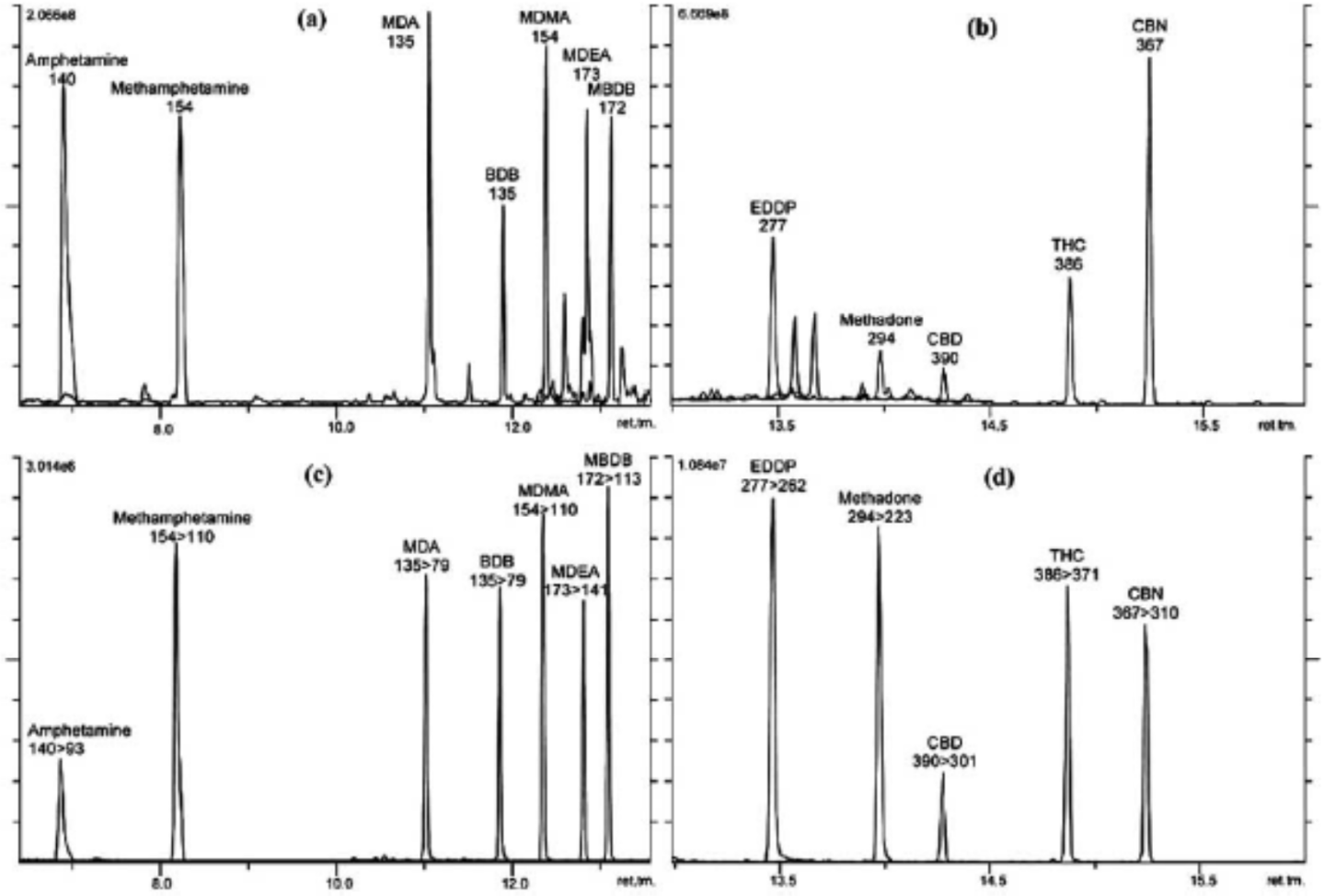


Fig. (7). Positive ion HS-SPDE GC-MS SIM chromatograms (a, b) and corresponding HS-SPDE GC-MS-MS MRM chromatograms (c, d) of identical spiked hair samples containing 1 ng/mg of the analytes. Reprinted with permission from reference [82]. (© 2003 John Wiely & Sons).

More Results from Pharmaceutical Studies with SPME-Urine treated with drugs

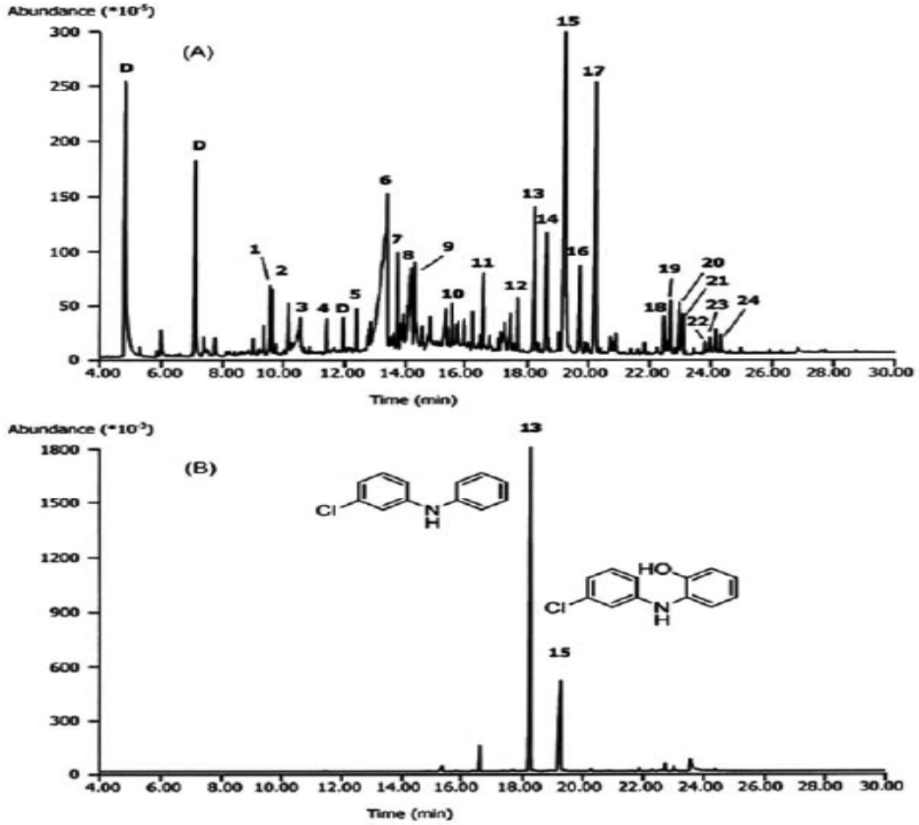
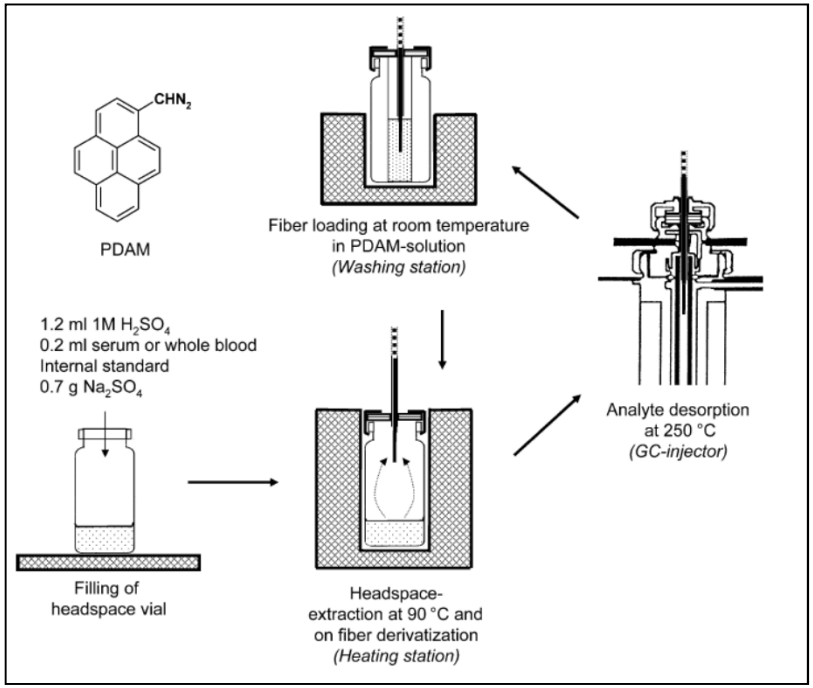


Fig. (10). SBSE thermal desorption CGC–MS analysis of 5 mL of urine from a patient being treated with drugs. (A) Total ion chromatogram, (B) extracted ion chromatogram at m/z 229 of clomipramine metabolites. GC conditions: capillary column, a 30 m × 0.25 mm I.D., 0.25 μm d_f HP-5MS column (Agilent Technologies); oven temperature, programmed from 50 to 320°C at a rate of 10°C/min. MS conditions: Agilent 5973 mass spectrometric detector operated in the scan mode (m/z 40–500). Peaks: 1=4-vinyl-2-methoxyphenol, 2=eugenol, 3=decanoic acid, 4=cis-eugenol, 5=ethyl 4-ethoxybenzoate, 6=dodecanoic acid, 7=cadinene, 8=junipene, 9=bulnesol, 10=citronilide, 11=benzylsalicylate, 12=cannabichromene, 13=clomipramine metabolite I, 14=methadone metabolite I, 15=clomipramine metabolite II, 16=methadone, 17=androstenol, 18=diazepam, 19=androsterone, 20=epiandrosterone, 21=nordiazepam, 22=temazepam, 23=O-methyloxazepam, 24=allopregnanediol, 25=bromazepam. Reprinted with permission from reference [129]. (© 2003 Elsevier Science).

Clinical/Forensic Application

- **Used for the detection and quantitative determination of illicit and therapeutic drugs, pesticides, solvents, and other poisons from blood, urine, hair, and human tissue.**
- **Samples were brought into a homogeneous aqueous solution by pretreatment of homogenization, protein precipitation, or centrifugation.**
- **Hair is first digested by NaOH or extracted with a suitable solvent.**
- **SPME conditions were determined by structure and properties of the analyte.**



- This figure was an on-fiber derivitization for determination of fluoroacetic acid from blood.
- Pyrenyldiazomethane (PDAM) was loaded onto the fiber from n-hexane solution in the washing station of the sample.
- During headspace extraction, acid was on-fiber-transformed into pyrenylmethyl fluoroacetate, which was then measured by GC-MS with high sensitivity.

List of Forensic Toxicology Applications

Table 2 Applications of SPME for analysis of toxic compounds

Substance	Matrix	SPME mode	Coating	Extraction conditions	Detection	LOD (ng/ml or ng/mg[a])	Remarks
Solvents, inhalation narcotics							
31 volatile compounds	Blood	HS-SPME	75 μm CAR/PDMS	NaF, Na_2CO_3, 40 °C, 6 min	GC-MS	0.005–0.12	Spiked samples
Halothane	Blood a. o.	HS-SPME	100 μm PDMS	$(NH_4)_2SO_4$,H_2SO_4 100 °C, 15 min	GC-MS	4	2 homicides
Chloroform	Blood a. o.	HS-SPME	100 μm PDMS	$(NH_4)_2SO_4$, 100 °C, 15 min	GC-MS	–	Sniffing fatality
Toluene	Blood a. o	HS-SPME	100 μm PDMS	$(NH_4)_2SO_4$, 100 °C,15 min	GC-MS	–	Sniffing fatality
o-Xylene, *m*-xylene, *p*-xylene	Blood a. o	HS-SPME	100 μm PDMS	$(NH_4)_2SO_4$, 100 °C,15 min	GC-MS	–	Sniffing fatality
Dichloromethane	Urine	HS-SPME	75 μm CAR/PDMS	NaCl, 22 °C, 30 min	GC-MS	0.005	Accident
Trichloroethylene	Urine	HS-SPME	75 μm CAR/PDMS	NaCl, 22 °C, 30 min	GC-MS	0.005	Workplace occupation
Perchloroethylene	Urine	HS-SPME	75 μm CAR/PDMS	NaCl, 22 °C, 30 min	GC-MS	0.005	Workplace occupation
Trichloroethylene	Blood a. o.	HS-SPME	100 μm PDMS	No additives, 60 °C,1 min	GC-ECD	5	Fatal poisoning
Tetrachloroethylene	Blood a. o	HS-SPME	100 μm PDMS	No additives, 60 °C,1 min	GC-ECD	3	Fatal poisoning
Toluene	Blood, urine	HS-SPME	100 μm PDMS	Dilution 1:3 H_2O, 60 °C, 1 min	GC-MS	–	Glue sniffer
3 isomeric dichlorobenzenes	Blood	HS-SPME	100 μm PDMS	No additives, 30 °C, 15 min	GC-MS	20	Poisoning case
Amphetamines and related substances							
A, MA	Blood	HS-SPME	100 μm PDMS	Borate buffer, 90 °C, 30 min	GC-MS	0.5	Derivatized with PFBBr
A, MA	Urine	HS-SPME	100 μm PDMS	KOH, NaCl, 100 °C, 20 min	GC-MS	0.3	Derivatized with HFBA
A, MA	Oral fluid	DI-SPME	100 μm PDMS	$NaHCO_3$,K_2CO_3, RT, 20 min	GC-MS	0.5–5	Derivatized with BCF
A, MA	Hair	HS-SPDE	50 μm PDMS	NaOH, 50 °C, 50 cycles, 1 ml	GC-MS	0.04–0.05	Derivatized with MBTFA
MDMA, MDE, MDA	Urine	DI-SPME	100 μm PDMS	pH 10.8, RT, 16 min	GC-MS	5–15	Derivatized with PCF
MDMA, MDE, MDA	Hair	HS-SPDE	50 μm PDMS	NaOH, 50 °C, 50 cycles, 1 ml	GC-MS	0.03–0.19	Derivatized with MBTFA
MDMA, MDE, MDA	Oral fluid	DI-SPME	30 μm PDMS	NaOH, NaCl, RT, 30 min	GC-MS	1–5	
MBDB, BDB	Hair	HS-SPDE	50 μm PDMS	NaOH, 50 °C, 50 cycles, 1 ml	GC-MS	0.07–0.18	Derivatized with MBTFA
Fenfluramine	Blood	HS-SPME	100 μm PDMS	K_2CO_3, NaCl, 80 °C, 15 min	GC-MS	5	Derivatized with ECF
Selegiline/ norselegiline	Blood, urine	HS-SPME	DVB/CAR/ PDMS	NaOH, NaCl, 90 °C, 25 min	GC-MS	0.01–0.05	Parkinson disease patient
Cocaine and metabolites							
Cocaine, cocaethylene	Plasma	DI-SPME	100 μm PDMS	pH 9, NaCl, RT, 25 min	GC-MS	11–19	Drug abusers
Cocaine, cocaethylene	Urine	DI-SPME	100 μm PDMS	pH 9–10, RT, 20 min	GC-MS	5	Patient in withdrawal treatment
Cocaine, cocaethylene	Hair	DI-SPME	100 μm PDMS	pH 8.5, NaCl, RT, 25 min	GC-MS	0.1	Digested with pronase dithiothreitol
Cocaine, cocaethylene	Sweat patches	DI-SPME	100 μm PDMS	pH 5, RT, 20 min	GC-MS	12.5 ng/patch	PharmCheck™ sweat patch
Benzoylecgonine	Urine	DI-SPME	100 μm PDMS	pH 7, 55 °C, 10 min	GC-MS	0.03	Derivatized with HCF, confirmed with Meth.
Benzoylecgonine	Hair	DI-SPME	100 μm PDMS	pH 9–10, RT, 20 min	GC-MS	0.5	MeOH extractoin, derivatized with BCF
Cannabinoids							
THC, CBD, CBN	Oral fluid	DI-SPME	30 μm PDMS	No reagents, RT, 30 min	GC-MS	1	
THC, CBD, CBN	Hair	HS-SPDE	50 μm PDMS	Na_2CO_3, 90 °C, 20 min	GC-MS	0.09–0.14	Derivatized with MSTFA
THC, CBD, CBN	Hair	HS-SPME	100 μm PDMS	Extr. residue, 125 °C, 20 min	GC-MS	0.01	Derivatized with BSTFA/TMCS

List of Forensic Toxicology Applications cont'd

Table 2 (continued)

Substance	Matrix	SPME mode	Coating	Extraction conditions	Detection	LOD (ng/ml or ng/mg[a])	Remarks
Opioids and related substances							
Methadone, EDDP	Plasma	DI-SPME	100 μm PDMS	pH 9, RT, 30 min	GC-MS	5–9	Methadone patients
Methadone, EDDP	Urine	DI-SPME	100 μm PDMS	pH 11, NaCl, RT, 30 min	GC-NPD	1	Drug addicts
Methadone, EDDP	Oral fluid	DI-SPME	100 μm PDMS	pH 9.2, NaCl, RT, 30 min	GC-MS	8–40	Methadone patients
Methadone, EDDP, EMDP	Hair	HS-SPME	65 μm PDMS/DVB	NaOH, HCl, 110 °C, 20 min	GC-MS	0.03–0.05	Drug fatalities
Methadone, EDDP	Hair	HS-SPDE	50 μm PDMS	Na_2CO_3, 90 °C, 20 min	GC-MS-MS	0.006–0.009	Derivatized with MBTFA
Tramadol	Plasma	HS-SPME	65 μm PDMS/DVB	NaOH, 100 °C, 30 min	GC-MS	0.2	Healthy volunteers
Tramadol	Hair	HS-SPME	85 μm PA	NaOH, 90 °C, 20 min	GC-MS	0.1	Chronic treatment
Fentanyl	Plasma	HS-SPME	PDMS, own preparation	pH 12, 85 °C, 30 min	GC-MS	0.01	Fentanyl patch treatment
Sufentanil	Plasma	DI-SPME	PDMS/DVB	pH 10.6, NaCl, RT, 30 min	GC-MS	0.4	Intensive care patients
Ethanol and alcohol markers							
Ethanol	Blood, urine	HS-SPME	85 μm PA	$(NH_4)_2SO_4$, 60 °C, 1 min	GC-FID	1,000	Postmortem samples
Fatty acid ethyl esters	Hair	HS-SPME	65 μm PDMS/DVB	pH 7.4, Na_2SO_4, 90 °C, 30 min	GC-MS	0.01–0.04	Detection of alcohol abuse
Fatty acid ethyl esters	Skin surface lipids	HS-SPME	65 μm PDMS/DVB	pH 7.4, Na_2SO_4, 90 °C, 30 min	GC-MS	0.3–1	Wipe and patch test
γ-Hydroxybutyric acid							
GHB, GBL	Plasma, urine	HS-SPME	CW/TPR, CAR/PDMS	H_2SO_4, Na_2SO_4, 65 °C, 15 min	GC-MS	50–100	Conversion of GHB to GBL
GHB	Water	DI-SPME	70 μm CW/DVB	No additives, RT, 15 min	GC-MS	1,500	Derivatized with BSTFA/TMCS
GHB	Urine	DI-SPME	100 μm PDMS	pH 7, 40 °C, 20 min	GC-MS	200	Derivatized with HCF/pyridine
Benzodiazepines							
Benzophenones	Urine	DI-SPME	100 μm PDMS	pH 9.4, RT, 30 min	GC-ECD	80–160	Hydrolysis of 8 benzodiazepines
6 benzodiazepines	Urine, serum	DI-SPME	85 μm PA with octanol	pH 6.0, NaCl, RT, 15 min	GC-NPD	3–140	Volunteer
7 benzodiazepines	Urine, serum	In-tube SPME	Supelco-Q-plot capillary	pH 8.5, 10 draw/eject cycles	LC-ESI-MS	0.2–2	60 cm capsule, spiked samples
4 benzodiazepines	Whole blood	DI-SPME	ADS-coated fiber	No additives, RT, 30 min	LC-ESI-MS	20–35	Volunteers
Midazolam	Plasma	DI-SPME	85 μm PA	pH 6.5, 50 °C, 10 min	GC-MS	1	
Delorazepam	Urine, serum	DI-SPME	65 μm PDMS/DVP	pH 6.5 or 7.4, RT, 30 min	HPLC-DAD	5	Study of albumin interaction
Various therapeutic drugs							
8 barbiturates	Urine	DI-SPME	65 μm CW/DVB	NaCl, RT, 20 min	GC-MS	1	Patient sample
7 barbiturates	Blood, urine	DI-SPME	85 μm PA	pH 6-7, 60 °C, 60 min	GC-MS	50–600	Patient sample
Thiopental, pentobarbital	Hair	DI-SPME	50 μm CW/TPR	pH 5–6, 30 °C, 20 min	GC-MS-MS	0.05–0.07	DFSA case
Ketamine	Hair	HS-SPME	100 μm PDMS	K_2CO, 90 °C, 5 min	GC-MS	0.7	Hair extraction 1 M HCl
Propofol	Blood, tissues	HS-SPME,	100 μm PDMS	100 °C, 25 min	GC-MS	–	Death case
4 tricyclic antidepressants	Urine	In-tube SPME	20 cm, 0.25μm PDMS	pH 12, 10 min, 80 μl/min	HPLC-UV	5	Wire in-tube configuration
4 tricyclic antidepressants	Plasma	DI-SPME	65 μm PDMS/DVB	pH 10, 65 °C, 40 min	HPLC-DAD	50–75	Spiked samples

List of Forensic Toxicology Applications cont'd

Table 2 (continued)

Substance	Matrix	SPME mode	Coating	Extraction conditions	Detection	LOD (ng/ml or ng/mg[a])	Remarks
4 tricyclic antidepressants	Blood	HS-SPME	100 μm PDMS	NaOH, 100 °C	GC-FID	30–50	Animal experiments
3 tetracyclic antidepressants	Blood	HS-SPME	100 μm PDMS	NaOH, 120 °C, 45 min	GC-MS	5–25	Death case
7 tricylic or tetracyclic antidepressants	Hair	HS-SPME	100 μm PDMS	$NaHCO_3$, NaCl, 100 °C, 30 min	GC-MS	0.03–0.10	Death cases, metabolized with MCF
6 SSRI antidepressants	Urine	DI-SPME	65 μm PDMS/DVB	$NaHCO_3$ NaCl, 100 °C, 30 min	GC-MS	0.4	Patient sample, derivatized with acetanhydride
Fluoxetine, norfluoxetine	Plasma	DI-SPME	65 μm PDMS/DVB	pH 9.0, 50 °C, 30 min	HPLC-UV	5–10	Spiked samples
11 phenothiazines	Blood, urine	DI-SPME	85 μm PA	pH 8, $KClO_4$, 40 °C,60 min	LC-MS-MS	0.2–200	Volunteer samples
L-Mepromazine	Plasma	DI-SPME	100 μm PDMS	NaOH, NaCl, 30 °C, 30 min	GC-NPD	2	Spiked samples
Clozapine	Plasma	DI-SPME	100 μm PDMS	NaOH, NaCl, 30 °C, 30 min	GC-NPD	30	Patient samples
5 local anesthetics	Blood	HS-SPME	100 μm PDMS	NaOH, 120 °C, 45 min	GC-MS	10–500	Death case
Lidocaine	Hair	HS-SPME	65 μm CW/DVB	NaOH,Na_2SO_4, 70 °C,30 min	GC-MS	0.1	Drug fatalities
Lidocaine	Plasma	DI-SPME	100 μm PDMS	pH 9.5, NaCl, RT, 45 min	GC-FID	5	Spiked samples
6 antiepileptics	Plasma	DI-SPME	65 μm CW/DVB	pH 7.0, NaCl, 30 °C, 15 min	GC-TSD	50–200	Therapeutic drug monitoring
5 anticonvulsants	Plasma	DI-SPME	50 μm CW/TPR	pH 5.0, NaCl, 30 °C, 30 min	HPLC-DAD	2,000	Spiked samples
Valproic acid	Plasma	HS-SPME	100 μm PDMS	NaCl, 80 °C, 20 min	GC-MS	300	In-sample-derivatized with IBCF/ethanol
9 beta-blockers	Serum, urine	In-tube SPME	Omegawax 250 capillary	pH 8.5, RT, 15 draw/eject cycles	LC-MS	0.1–1.2	Spiked and patient samples
Verapamil, gallopamil	Plasma, urine	In-tube SPME	PPY, 3 times coated	pH 11, 40 draw/eject cycles	LC-MS	2–6	Metabolism study
Clenbuterol	Water	DI-SPME	85 μm PA	pH 12, RT, 60 min	GC-MS	0.2	On-fiber-derivatized with HMDS
Naproxen and metabolites	Urine	DI-SPME	100 μm CW/TPR	pH 3, NaCl, 20 °C, 30 min	HPLC-UV	30	Patient samples
Ibuprofen and glucuronide	Urine	DI-SPME	PDMS/DVB	pH 3.8, NaCl, RT, 30 min	HPLC-UV	250	Patient samples
11 corticosteroids	Urine	DI-SPME	65 μm CW/TPR	NaCl, RT, 15 min	LC-MS	4–30	Spiked samples
Sterols	Serum	DI-SPME	85 μm PA	KCl, 90 °C, 90 min	GC-FID	250–1,100	On-fiber-derivatized with BSTFA
Pesticides and chemical warfare agents							
22 organophosphorous pesticides	Blood	HS-SPME	100 μm PDMS	$(NH_4)_2SO_4$,H_2SO_4, 120 °C, 15 min	GC-MS	10–300	Spiked samples
5 organophosphorous pesticides	Blood, tissues	HS-SPME	85 μm PA	NaCl, 70 °C, 20 min	GC-NPD	2–55	Postmortem samples
Parathion-methyl/-ethyl	Blood	HS-SPME	100 μm PDMS	$(NH_4)_2SO_4$,H_2SO_4, 90 °C, 15 min	GC-MS	20–50	Spiked samples
Parathion, paraoxon	Blood, urine	DI-SPME	65 μm CW/DVB	Dilution 1:10 H_2O, 60 °C, 60 min	GC-MS	3–25	25 poisoning cases
Parathion-methyl	Blood, tissues	HS-SPME	85 μm PA	NaCl, 70 °C, 20 min	GC-MS	1	Death case
Malthion	Blood	HS-SPME	100 μm PDMS	$(NH_4)_2SO_4$,H_2SO_4, 90 °C, 15 min	GC-MS	1,000	Death case
Quinalphos	Blood, urine	DI-SPME	65 μm CW/DVB	Dilution 1:10 H_2O, 60 °C, 60 min	GC-MS	2-10	36 authentic samples
Fluoroacetic acid	Serum, urine	HS-SPME	DVB/CAR/PDMS	H_2SO_4, Na_2SO_4, 90 °C, 30 min	GC-MS	20	Derivatized with pyrenyldiazomethane
Fluoroacetamide	Blood, urine	DI-SPME	100 μm PDMS	pH 7.0, TEABr, 70 °C, 25 min	GC-MS	1,000	Fatal poisoning
Chlorovinylarsounous acid	Urine	HS-SPME	100 μm PDMS	NH_4Ac, 70 °C, 10 min	GC-MS	0.007	Derivatized with 1,3-propanedithiol

List of Forensic Toxicology Applications cont'd

Table 2 (continued)

Substance	Matrix	SPME mode	Coating	Extraction conditions	Detection	LOD (ng/ml or ng/mg[a])	Remarks	References
Other poisons								
Cyanide	Whole blood	HS-SPME	75 μm CAR/PDMS	H_3PO_4, Na_2SO_4, 30 °C, 10 min	GC-MS	10	Fire victim	[192]
Sulfide	Blood	DI-SPME	100 μm PDMS	RT, 20 min	GC-MS	10	In-sample-derivatized with PFBBr	[193]
Strychnine	Blood	DI-SPME	65 μm CW/DVB	Dilution 1:10 H_2O, RT, 20 min	GC-MS	7	3 poisonings	[194]
Lead	Whole blood	HS-SPME	70 μm PDMS-DVB	pH 4, RT, 10 min	GC-FID	4	In-sample-derivatized with STEB	[195]

[a] The limit of detection (*LOD*) is given in nanograms per milliliter for blood, serum, plasma, urine and oral fluid and in nanograms per milligram for hair.

A amphetamine, *ADS* alkyldiol–silica particles, *a.o.* and others, *BCF* butylchloroformate, *BDB* 1-(1,3-benzodioxol-5-yl)-2-butanamine, *BSTFA N,O*-bis(trimethylsilyl)trifluoroacetamide, *CAR* Carboxen, *CBD* cannabidiol, *CBN* cannabinol, *CW* carbowax, *DAD* photodiode array detection, *DFSA* drug-facilitated sexual assault, *DI* direct immersion, *DVB* divinylbenzene, *ECD* electron capture detection, *ECF* ethylchloroformate, *EDDP* 2-ethylene-1,5-dimethyl-3,3-diphenylpyrrolidine, *EMDP* 2-ethyl-5-methyl-3,3-diphenyl-1-pyrroline, *ESI* electrospray ionization, *FID* flame ionization detection, *GC* gas chromatography, *GHB* γ-hydroxybutyric acid, *GBL* γ-hydroxybutyrolactone, *HCF* hexylchloroformate, *HFBA* heptafluorobutyric anhydride, *HMDS* hexamethyldisilazane, *HPLC* high-performance liquid chromatography, *HS* headspace, *IBCF* isobutylchloroformate, *LC* liquid chromatography, *MA* methamphetamine, *MBDB N*-methyl-1-(1,3-benzodioxol-5-yl)-2-butanamine, *MBTFA N*-methylbis(trifluoroacetamide), *MCF* methylchloroformate, *MDA* methylenedioxyamphetamine, *MDE* methylenedioxyethamphetamine, *MDMA* methylenedioxymethamphetamine, *MS* mass spectrometry, *NPD* nitrogen-phosphorous detection, *PA* polyacrylate, *PCF* propylchloroformate, *PFBBr* pentafluorobenzyl bromide, *PDMS* polydimethylsiloxane, *PPY* polypyrrole coating, *RT* room temperature, *SSRI* selective serotonin reuptake inhibitor, *STEB* sodium tetraethylborate, *TEABr* tetraethylammonium bromide, *THC* Δ^9-tetrahydrocannabinol, *TMCS* trimethylchlorosilane, *TPR* templated resin, *TSD* thermionic-specific detection, *UV* variable-wavelength UV detection

Gadgets used in Forensics that are associated with SPME

TuffSyringe TS100

This device preserves sample and prevents contamination of SPME fiber as well as inadvertent operation.
Cost of this device is $245.

Conditioner 1X

This precisely measure and controls temperature from 0° to 350 ° and can clean other needles/syringes in addition to SPME fibers.
Cost of this device is $1875.

SafePorter SP200/SP201

This transports/stores SPME holders and is constructed of machined aluminum that allows for the sample/holder to remain safe even if run over by a car.
It also contains a dual o-ring that creats a hermetic seal to preserve and protect SPME holder/sample.
Cost of the SP200 (comes with a septum) is $145 and the SP201 (without septum) is $135.

Environmental Application

- **Air sample**
  - Analytes are extracted by the fiber wither by direct exposure or by use of the headspace method.
  - Most applications involve the use of a commercial SPME fiber, but a dialuminum trioxide-coated fiber has been used for VOC sampling.
  - On-site air sampling can be performed by the equilibrium methods or by the non-equalibrium method, with quantification by use of calibration plots from a standard gas generating system of standard gas mixture as opposed to using equations.
  - rapid air sampling can be performed with controlled air-flow rate
- **Water samples**
  - Can be performed by direct immerion (DI), headspace (HS), or in-tube method.
  - The air inside needle must be completely replaced by water and effects of extracted analytes on the external wall of the needle should be avoided.
  - The in-tube SPME has been used for analysis of BTEX, PAH, pesticides, and herbicides in aqueous samples.
  - The fibers have also been used to analyze environmental pollutants in aqueous samples and have been accompanied by ultrasounds or microwaves.
  - Traditional calibration methods have been used for most applications.
- **Soil and sediment samples**
  - Performed by HS or DI methods and applications have been assisted by sonication, microwaves or by heater or cooling fiber.
  - Traditional calibrations but some exhaustive calibration methods have been used in quantification of BTEX in soil samples.
  - A hollow-fiber membrane-protected SPME has also been used for determination of herbicides in sewage-sludge samples.

List of Environmental Applications -gas

Table 2 Applications of SPME in environmental analysis of gas samples

Analytes	Extraction method	Fiber/Capillary	Detection
Organic pollutants	Static indoor air sampling	PDMS	GC–MS
Toluene	Static indoor, outdoor air sampling	CAR, fiber retracted device	GC–MS, FID
BTEX, hexane	Static indoor air sampling	PDMS–DVB	GC–PID, FID, DELCD
BTEX	Static air sampling	CAR–PDMS	GC–MS
BTEX	Static outdoor air sampling	CAR–PDMS	GC–FID
VOC	Static indoor air sampling	CAR–PDMS	GC–MS
VOC	Static indoor air sampling	PDMS, CAR–PDMS PDMS–DVB,	GC–FID
VOC	Static indoor, outdoor air sampling	CAR–PDMS, fiber retracted device	GC–MS
VOC	Static indoor air sampling	γ-Al_2O_3 coated fiber	GC–FID
VOC, formaldehyde	Static indoor air sampling	PDMS, PDMS–DVB	GC–PID, FID, DELCD
Formaldehyde	Static indoor air sampling	PDMS–DVB, on-fiber derivatization	GC–FID
Pesticides	Dynamic indoor air sampling	PDMS	GC–MS
Odorants	Static air sampling (landfills)	DVB–CAR–PDMS	GC–MS
Malodorous sulfur compounds	Static air sampling	CAR–PDMS	GC–PFPD
Organophosphate triesters	Dynamic indoor air sampling	PDMS	GC–NPD
VSC	Static air sampling	PDMS–CAR, fiber retracted device	GC–PFPD
Dodecane	Static indoor air sampling	PDMS, fiber retracted device	GC–PID, FID, DELCD
Isocyanates	Static air sampling	PDMS–DBV, fiber retracted device, on-fiber derivatization	HPLC–MS
n-Valeraldehyde	Static air sampling	PDMS–DVB, fiber retracted device, on-fiber derivatization	GC–FID
Chlorobenzenes	SPE followed by HS-SPME	CW–PDMS, PDMS–DVB	GC–ECD, GC–MS
PCB	SPE followed by HS-SPME	PDMS, PDMS–DVB	GC–ECD, GC–MS
Sarin	Dynamic air sampling	PDMS–DVB	GC–MS
C_5–C_{15} *n*-alkanes	Static air sampling	PDMS–DVB	GC–FID
Hydrocarbons, formaldehyde	Static air sampling	PDMS, PDMS–DVB, fiber retracted device	GC–FID
BTEX	Controlled air flow rate	CAR–PDMS, 65 μm PDMS–DVB	GC–FID
VOC	Controlled air flow rate	PDMS–DVB	GC–MS, FID
Organophosphate triesters	Controlled air flow rate	PDMS	GC–NPD
VOC	Controlled air flow rate	PDMS–DVB	GC–FID
BTEX	Controlled air flow rate	CAR–PDMS, PDMS–DVB	GC–MS, FID

List of Environmental Applications-aqueous

Table 3 Applications of SPME in environmental analysis of aqueous samples

Analytes	Extraction method	Fiber/Capillary	Detection
BTEX	HS	CAR–PDMS	GC–FID
BTEX	HS	PPY-coated gold wire	GC–FID
BTEX, benzenes	HS	PDMS–DVB–CAR	GC–FID
BTEX and ethers	HS	PDMS–DVB	GC–MS
BTEX, naphthalene, chlorinated hydrocarbons	HS	PDMS, PA	MCC–UV-IMS
PAH	DI, ultrasound treatment	PDMS	GC–MS
PAH	In-tube SPME	PDMS-coated capillary	HPLC
PAH	DI	PDMS	HPLC–FLD
PAH	In-tube SPME	PDMS-coated capillary	GC–MS
PAH	In-tube SPME	PPY-coated capillary	HPLC–UV
PAH	Static water sampling	PDMS, fiber retracted device	GC–MS
PAH	HS	PPY–DS	GC–MS, FID
PCB	HS, microwave assisted	PDMS	GC–ECD
PCB, pesticides	Static water sampling	PDMS	GC–MS
Pesticides	In-tube SPME	PPY-coated capillary	HPLC–ESI-MS
Pesticides	In-tube SPME	Omegawax 250	HPLC–UV
Pesticides	In-tube SPME	Super-Q PLOT	LC–UV
Pesticides	HS	PA	GC–MS
Pesticides	DI	PDMS–DVB	GC–MS–MS
Pesticides	DI	PDMS–DVB	GC–MS
Pesticides	DI	CW–DVB, CAR–PDMS, DVB–CAR–PDMS	GC–ECD, GC–MS
Pesticides	DI	PDMS, PA	GC–MS, GC–ICP-MS
Pesticides	DI	PA	GC–MS
Pesticides	HS, microwave assisted	DVB–CAR–PDMS	GC–ECD
Pesticides	DI	PDMS–DVB	HPLC
Pesticides	HS	Polymethylphenylvinylsiloxane, sol–gel	GC–ECD
Herbicides	DI	PDMS–DVB, CW–TPR	HPLC
Herbicides	DI	PA	GC–MS
Herbicides	DI	PDMS–DVB	MEKC
Herbicides	In-tube SPME	DB-WAX	LC–MS
Phenols	HS	Polyaniline-coated fiber	GC–FID
Phenols	HS	C[4]/OH-TSO-coated fiber	GC–FID
Phenols	HS	PDMS–DVB, DVB, derivatization	GC–FID
Organotin compounds	HS	CAR–PDMS, derivatization	GC–PFPD
Organotin compounds	HS	PDMS, derivatization	GC–FID
Organotin compounds	Headspace	PDMS, derivatization	GC–MS
Organometallic compounds	HS	PDMS, DVB–CAR–PDMS, derivatization	GC–MS
Organometallic compounds	HS	PDMS, derivatization	GC–MS
Methylmercury, mercury(II)	DI	PDMS	GC–MS
Chlorinated hydrocarbons	HS	Activated carbon fiber	GC–MS
Chlorohydrocarbons	HS	Activated carbon fiber	GC–MS
Explosives	DI	CW–DVB	GC–ECD
Explosives	DI	CAR	HPLC–UV
VOC, MTBE, etc.	HS	PDMS, CAR–PDMS, PDMS–DVB	GC–MS
MTBE	HS	CAR–PDMS	GC–MS
Triazines	DI	CW/templated resin, PDMS–DVB	HPLC
Triazines	DI	PDMS–DVB	GC–MS
Methylamine	DI	CW–TPR, derivatization	HPLC
Iodophenols	DI	CAR–PDMS	CE–ICP-MS

Analytes	Extraction method	Fiber/Capillary	Detection
Chromium	DI, HS	PDMS, derivatization	GC–ECD, MS, GC–ICP-MS
Alkanethiols, Dihydrogen sulfide	Direct	PDMS–DVB, derivatization	GC–MS
Aromatic amines	DI	PDMS–DVB, derivatization	GC–MS
Odorous trihalogenated anisoles	HS-SPME	PDMS	GC–MS
DCP, MITC	Direct	PA	GC–ECD–NPD
Chlorophenols	Headspace	PA	GC–FID
Aldehydes	HS	PDMS–DVB, derivatization	GC–MS
PBDE, PBB	HS	PDMS, PA	GC–MS–MS
Organic pollutants	Static water sampling	PDMS	GC–MS
BTEX	Controlled water flow rate	CAR–PDMS, PDMS–DVB	GC–MS, FID

List of Environmental Applications-soil/sediment

Table 4 Applications of SPME in environmental analysis of soil and sediment samples

Analytes	Extraction method	Fiber/Capillary	Detection
PBP	Static sampling (sediment)	PDMS	GC–ECD
TNT and its degradation products	Static sampling (sediment)	PA	HPLC
Organic pollutants	Static sampling (Soil)	PDMS	GC–MS
BTEX	Headspace, cooled fiber	PDMS	GC–MS
BTEX	HS (sand)	CAR–PDMS	GC–MS
BTEX	Multiple HS (soil)	CAR–PDMS	GC–FID
Organotin compounds	Headspace (sediment)	PDMS, derivatization	GC–MS
PAH	Direct SPME (sediment)	PDMS	GC–MS
PAH	DI, microwave-assisted (sediment)	PDMS, PA	GC–MS
DCP, MITC	Headspace (soil)	PA	GC–ECD/NPD
2-Chloroethyl ethyl sulfide	Headspace (soil)	Acrylate/silicone co-polymer coating, sol–gel	GC
PCDD/F	HS (soil), sample heating, ultrasonic device	PDMS, cooling device	GC–MS–MS
Butyltin compounds	HS (sediment), sonication	PDMS	GC/MIP AED
Explosives	DI (sediment), sonication	CW–DVB	GC–ECD
Methylphosphonates	HS (soil)	PDMS, PDMS–DVB	IMS
Fungicides	HS (soil)	PA	GC–MS
Fungicides	DI-SPME followed water extraction (soil)	PA, ultrasonic	GC–MS
Herbicides	HFM-SPME (sewage sludge)	PDMS–DVB	GC–MS
Chlorobenzenes	DI (soil)	PDMS	GC–ECD
Chlorophenols	HS (soil), microwave-assisted	PA	GC–ECD

Conclusion

- SPME is a solvent-free microextraction technique that is:
  - Cost efficient
  - Simple to understand and use
  - High sensitivity
  - Low detection limits
  - Can be used to sample analytes of many types
  - Used in many areas of industry

References

1. http://www.spme.uwaterloo.ca/SPMEdata/spmedata.html
2. Pawliszyn, J. Solid Phase Microextraction : Theory and Practice. (1997) Publisher: (VCH, New York, N. Y.), 275
3. Arthur, C.L., Killam, L., Buchholz, K.D., Potter, D., Chai, M., Zhang, Z., Pawliszyn, J., Solid-Phase Microextraction: An Attractive Alternative, Environmental Lab. 11 (1992) 10-15
4. Z. Zhang and J. Pawliszyn, Headspace Solid Phase Microextraction. Anal. Chem. 65 (1993) 1843-852
5. Z. Zhang, M. J. Yang and J. Pawliszyn, Solid Phase Microextraction: A New Solvent-Free Alternative for Sample Preparation, Anal. Chem. 66 (1994) 844A-853A
6. R. Eisert and K. J. Levsen, Determination of Pesticides in Aqueous Samples by Solid-Phase Microextraction In-Line Coupled to Gas Chromatography-Mass Spectrometry, J. Am. Soc. Mass Spectrom. 6 (1995) 1119-1130
7. Z. Zhang and J. Pawliszyn, Sampling Volatile Organic Compounds Using a Modified Solid Phase Microextraction Device, J. High Res. Chromatogr. 19 (1996) 155-160
8. Kataoka,H. Recent Advances in Solid-Phase Microextraction and Related Techniques for Pharmaceutical and Biomedical Analysis. Current Pharmaceutical Analysis. 1 (2005) 65-84
9. Pragst, F. Application of solid-phase microextraction in analytical toxicology. Anal Bioanal Chem. 388 (2007) 1393-1414
10. Vuckovic, D., E. Cudjoe, D. Hein, and J. Pawliszyn. Automation of Solid-Phase Microextraction in High-Throughput Format and Application to Drug Analysis. Anal. Chem. 80 (2008) 6870-6880
11. Webster, G. R. Barrie; Sarna, Leonard P.; Graham, Kristina N. Solid phase microextraction. Tech. Aquat. Toxicol. (1996) 459-477