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Reviews

Solid Phase Microextraction as a Method for Preparing Environmental Samples

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Abstract

A new technique for sample preparation, Solid Phase Microextraction (SPME), is described. Theoretical and practical aspects and the particular possibility of using this technique in environmental analyses are discussed (application for analytical determination in different matrix). This paper will show many advantages as well as faults of SPME.

Keywords: Solid Phase Microextraction (SPME), matrix

Introduction

Contamination of air, water, soil and other matrixes by some organic compounds is trouble not only for ecological and analytical chemists. Some changes in the ecological system and violation of its equilibrium about agriculture, household and industry are reasons for continuous pollution of water, soil, food, etc. Therefore, with regard to ecological, social and economic results, it is very important to complete environmental protection. Preventing environmental degradation is a connection between continuous control and monitoring of pollution. For this reason, application of modern analytical techniques based on migration processes in gases, liquids, solid and on the phase boundary made detection level and lowering quantity of samples [1].

The range of different analytical techniques used is dependent not only on characteristics and kinds of determination matter (analyte), but with the choice of adequate and selective method of analysis. These methods enable isolation, purification and enrichment of analyte [1]. It is easy to state that among sample preparations are physical, physico-chemical and chemical methods. In this area, the leading ones were physico-chemical methods based on phase boundary effects: liquid-liquid, liquid-solid, gas-liquid and gas-solid phases. One of the most frequently applied techniques based on the phase boundary processes is static and dynamic headspace (HD) [1], as well as the purge and trap technique (PT) [1]. Two of these techniques are applied to isolate and determine volatile organic contaminations in liquid and solid environmental matrices [1].

From the literature it is known that sample preparation are the most time-consuming stage of determination analysis (60-70 %), 15-20 % is time for final determination and 15-20 % time for analysis spent for determination and validation of the results.

The first classical technique of extraction was liquid-liqud extraction (LLE) [1], followed by solid phase extraction (SPE) [1-4] and microwave extraction (ME) [5, 6], and, finally, supercritical extraction (SFE) [7, 8]. Obviously, among methods we can include headspace technique (HS) as well as the purge and trap technique (PT). Alternative on HS and SPE is modern, propagated by Pawliszyn, solid phase microextraction (SPME) [9, 10, 11, 12]. This uses a fused silica fiber, coated with an adsorbent, that is mounted on a modified chromatographic syringe to extract samples and pass analytes directly into gas chromatography (GC) and a high performance liquid chromatography (HPLC) heated injector. The coated fiber (like a "sponge") concentrates the organic analytes on its surface so they can be transfered to the GC instruments. While in the injector, analytes are thermally desorbed and transferred to the GC column for analysis. Temperature programmable *split-splitless* and *on-column* injectors have all been used for SPME desorption. This technique determines organic micropollutants in water, which permits extraction without any solvent. It requires sample volumes of around 2 ml and is

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easily automated, thus reducing sample handling. Sample extraction is possible in just 10 minutes [13]. It has been proven to be time efficient and sensitive. By sampling from the headspace above sample matrices, SPME can be used to extract target analytes from very complex matrices such as sludge, wastewater and soil [9]. SPME has been successfully used for analyzing volatile organic compounds, polyaromatic hydrocarbons (PAHs) [10], polichlorinated biphenyls (PCBs) [10], and phenol and its derivatives in aqueous samples [9].

The ideal sample preparation method should be fast, inexpensive, solvent free, partable, relatively independent of the instrument design, and amennable to automation [14]. It should also be applicable to gaseous and liquid samples as well as have a large linear dynamic range while retaining excellent detection limits. The trends in modern trace analysis are shown in Fig. 1.

Furthermore, it should be able to function as a screening technique or to be used in the quantitive analysis of selected compounds or classes of compounds. Solid phase microextraction meets most of these criteria. This method has been applied to volatile and nonvolatile compounds, can be used for gaseous and liquid samples, is linear over four orders of magnitude, can be used with any gas chromatograph (GC) and/or gas chromatograph – mass spectrometer (GC/MS) can be completely automated [10-12].

SPME can attain detection limits of 15 ppt (parts per trillion) and lower for both volatile and nonvolatile compounds. Thus this technique can be used by the United States Environmental Protection Agency (EPA) and by the Ontario Municipal Industrial Strategy for Abatement (MISA) program [15]. No solvents are used in this sample preparation process, and no sample work-up is required. Sampling times are short (typically 2-15 min). The process has been mathematically modeled, and the effect of the matrix, the extraction temperature, and chromatographic conditions on the precision and accuracy of automated SPME have been determined.

In the current paper the theoretical and practical aspects of solid phase microextraction have been discussed in detail. Some application will be presented as a potential advantage compared to other extraction techniques.

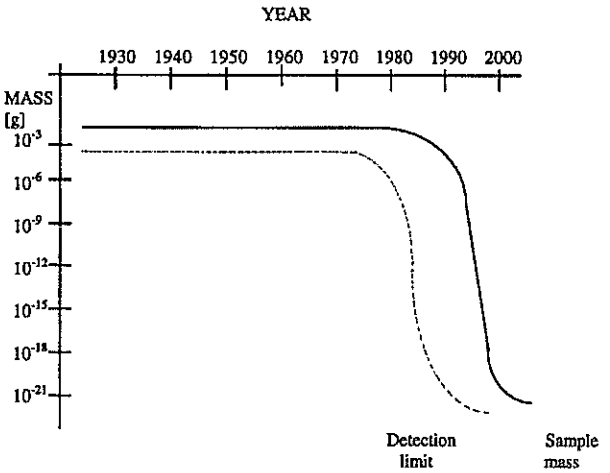


Fig. 1. Trends in modern trace analysis

Theoretical Aspects

As mentioned before, the base of the SPME technique is classical headspace analysis by GC. The samples to be analyzed are solid solutions, homogeneous solid solutions or non-homogeneous materials, Py_i either fluidic or non-fluidic. When the sample is a homogeneous liquid solution with two or more components it is convenient to define the distribution constant of the analytes, taking into account either the variables of state of the system or the mass balance of the analytes between the condensed and gaseous phases.

The thermodynamic expression for the distribution constant (K_i^*) can be derived from the expresion of Henry's law ($Py_i = k_H x_i$) [16] as:

$$K_i^* = \frac{x_i}{Py_i} \, ql \tag{1}$$

where: x_i and y_i are the molar fractions of the analyte i distributed between the condensed and gaseous phase, respectively, at overall pressure P. The distribution constant defined in this manner (K_i^*) is the inverse of Henry's law constant (k_H).

Considering the non-ideality of the system, it is necessary to know the variations of the above terms, taking into account the activity (γ_i) and fugacity (ν_i) coefficients for the analyte i in the system at a given temperature T and overall pressure P:

$$(\nu_i)_p Py_i = \gamma_i (\nu_i^0)_{p_i^0} (P_i^0)_p X_i \tag{2}$$

where: $(\nu_i)_p$ is the fugacity coefficient of the analyte i in the headspace gas at pressure P, $(\nu_i^0)_{p_i^0}$ is the fugacity coefficient of pure substance i at its saturation vapour pressure p_i^0, $(P_i^0)_p$ is the saturation vapour pressure of substance i at the overall external pressure P and γ_i is the Raoult-law activity coefficient of analyte i.

The distribution constant (K_i), defined in terms of the equilibrium mass/volume concentrations in the condensed and gaseous phase, can be expressed as:

$$K_i = \frac{C_{iL}}{C_{iG}} = \frac{W_{iL}/V_L}{W_{iG}/V_G} \tag{3}$$

where: C_{iL} and C_{iG} are the concentration of analyte i, W_{iL} and W_{iG} are the masses of analyte i, and V_L and V_G are the volumes of the condensed and gaseous phases in the system, respectively. K_i can be written by employing known thermodynamic definitions and neglecting the non-ideality of the gaseouse phase and the compressibility of the condensed phase effects as:

$$K_i = \frac{RTd_L}{\gamma_i p_i^0 M_L} \tag{4}$$

where: R is the ideal gas constant, d_L and M_L are the density and the molar mass of the condensed phase.

The static haedspace technique fails when trace components or components with very low vapour pressures are analyzed [16]. In these instances, the concentration of the analytes in the gaseous phase can be increased by:

(a) raising the temperature, which increases the saturated vapour pressure (p_i^0) of the pure trace component. This increase in the temperature of the system can be effected in such a way that the value of K_i might be approximately zero and thus it is not necessary to know it;

(b) increasing the value of the activity coefficients by adding an electrolyte or a non-elecrolyte. Other ways, e.g. variation of the pH of the solution, could increase the values of these coefficients.

SPME involves a few simple steps. The fiber is withdrawn into the needle of the syringe, and the fiber is lowered into the sample by depressing the plunger. Organic analytes partition from the water into the stationary phase until equilibrium is reached (Fig. 2). The plunger is then withdrawn, and the analytes are thermally desorbed in the injectors, which have all been used for SPME desorption [16].

The amount of analyte adsorbed on the fiber at equilibrium and at infinite volume is linear dependent on the analyte's concentration in solution according to the following equation:

$$n_s = KV_1C_2^0 \tag{5}$$

where: n_s is the number of moles of analyte absorbed by the stationary phase, K is the distribution constant of an analyte partitioning between the stationary and aqueous phase, V_1 is the volume of the stationary phase, and C_2 is the initial analyte concentration in the water.

In a finite volume of sample, such as 2-5 ml, the sample can be significantly depleted, and the amount absorbed becomes:

$$n_s = \frac{KV_1V_2C_2^0}{KV_1 + V_2} \tag{6}$$

where: V_2 is the volume of sample.

The dynamics of the absorption process have been mathematically modeled for both stirred and unstirred solutions. The amount of sample adsorbed as a function of time (the extraction profile) can be derived by solving Fick's second law of diffusion (rate of change concentration of diffusion analyte in definite measuring point). Fick's second law presents eq. 7:

$$\frac{\sigma c}{\sigma t} = D\,\frac{\sigma^2 c}{\sigma x^2} \tag{7}$$

where: c is concentration of diffusion analyte, t is time of diffusion, D is coefficient of diffusion.

Fig. 2 shows calculated absorption for a perfectly stirred solution.

Assuming perfect agitation, after time:

$$t = 0.5\ (b - a)^2/D_1 \tag{8}$$

where: D_1 is the diffusion of the analyte in the coating, and (b – a) is the coating thickeness as defined in Fig. 2 – extraction efficiency is larger than 90 %.

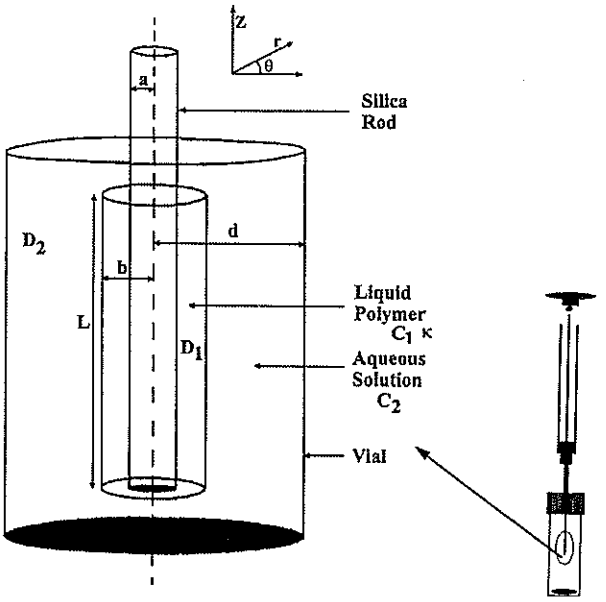


Fig. 2. Graphic representation of the coated fiber inserted into a finite volume of unstirred solution according to [11], where: k is the coating/water distribution constant of the analyte, D_1 is the diffusion coefficient of the analyte in the coating, D_2 is the diffusion coefficient of the analyte in the water, C_1 is the concentration of analyte in the coating, C_2 is the concentration of analyte in the water, L is the height of the cylinder exposed to solution, a is the radius of the silica fiber, b is the radius of the coated fiber, and d is the radius of the analyte container.

This model predicts that rapid extractions of lower than 1 min. are possible if the solution is completely mixed. Without mixing, the time required to reach equilibrium is limited by diffusion in water. With inefficient mixing, an unstirred layer of water remains next to the fiber, which limits the rate of absorption because analytes must first diffuse across this static layer. In practice, stirring with a magnetic stir bar fails to provide perfect mixing, so the static water layer increases equilibration time from theoretical 15 s to a few minutes. The mass absorbed depends on the distribution constant and the volume of the stationary phase. The equilibration time depends on the distribution constant of the analyte, with a larger distribution costant, more analyte must diffuse through the static layer.

The concentration profile in the coating as a function of time for diffusion of analyte into the fiber coating from perfectly agitated solution of infinite volume is described by:

$$C_1(r,\ t) = \kappa C^0{}_2 + (C^0{}_1 - \kappa C^0{}_2)\ \pi \sum_{m=0}^{\infty} \exp\ (-\ \alpha^2{}_m\ D_1 t\ \cdot$$

$$\cdot\ \frac{J_1(\alpha_m b)J_1(\alpha_m a)}{J^2{}_0(\alpha_m b) - J^2{}_1(\alpha_m a)}\ [Y_0(\alpha_m r)J_1(\alpha_m a) - Y_0(\alpha_m a)J_0(\alpha_m r)] \tag{9}$$

where: α_m's are the roots of:

$$J_o(\alpha b)Y_1(\alpha a) - J_1(\alpha a)Y_1(\alpha b) \tag{10}$$

and J, Y are Bessel functions [11]. There used cylindrical coordinates which is easier to solve because of cylindrical symmetry in the system (Fig. 2).

The solution to the above differential equation with the appropriate boundary conditions corresponding to experimental configuration will describe the concentration profile of the analyte in the system as a function of radius. Then the total mass absorbed by the coating as a function of time can be calculated by integrating the concentration profile along the radius:

$$M = 2\pi L \int_a^b C_1(r,t)\, r\,dr \qquad (11)$$

where: L is the height of the cylinder, "a" is the radius of the silica rod, and "b" is the radius of the coated fiber.

The resulting relationship can be easily verified experimentally by determing the mass of the analyte adsorbed by the fiber after the fiber has been extracting for a settled time.

In the coating expressed as a fraction of the maximum mass extracted at equilibrium, approximately 50 % of the maximum amount is extracted after 0.1 time units while it takes about 5 times longer to extract about 90 % of the maximum amount. This relationship can be described mathematically by integrating the concentration of analytes in the fiber by distribution function (eq. 9) over the radius and thus obtaining the mass adsorbed by the coating as a function of time [11].

The relationship described by eq. 11 is shown in Fig. 3 and is referred to as the time exposure profile of the fiber for diffusion of analyte into the fiber coating from a perfectly agitated solution of infinite volume. The profile of this dependence corresponds exactly to typical adsorption isotherm (the Langmuir type) [17].

About 90 % of M_1^{∞} is adsorbed after time corresponding to $D_1t / (b - a)^2 = 0.5$. In practical situations the equlibrium

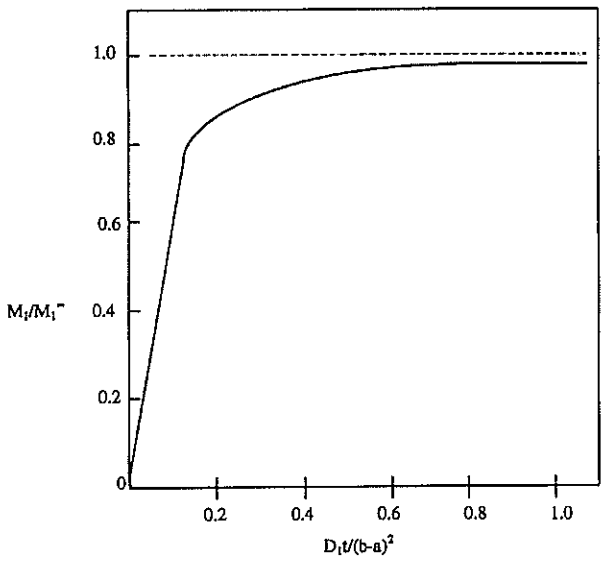


Fig. 3. Mass adsorbed from a perfectly agitated solution of infinite volume

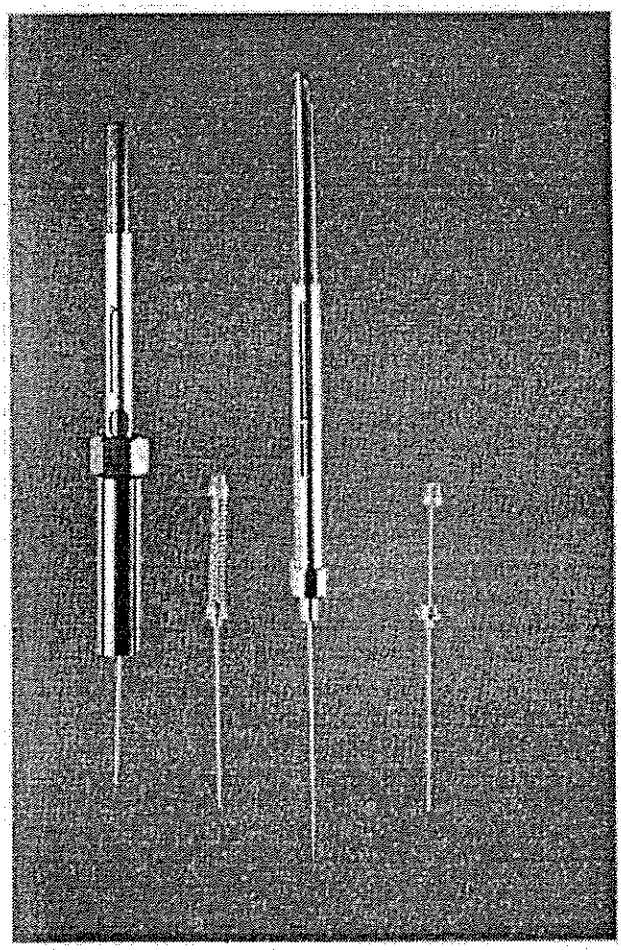


Fig. 4. SPME apparatus proposed by Supelco Inc, [63]; a) for manual sampling, b) for AutoSampler

time for a perfectly agitated solution can be calculated from this relationship by substituting specific diffusion coefficients and fiber thicknesses [11].

SPME Device

In SPME, a stationary phase-coated fused silica fiber is introduced into the water sample, and organic analytes adsorb on the phase. The analytes are desorbed from the fiber to the capillary GC column and to HPLC also by the heated chromatographic injection port. No solvents or complicated apparatus are required. Manual and autosampler units are presented in Fig. 4.

The SPME device consists of a holder, fused silica fiber contained inside a syringe, inserts and inlet liners put in GC aparatus, vial for extraction with hole caps, and teflon (PTFE) of silica septa (Fig. 5).

The metal plunger assembly is removed and replaced with a fused silica optical fiber. The syringe is used to introduce the fiber into the injector of a gas chromatograph and protects the fiber from damage during storage.

Optical fibers are used in this technique because they are inexpensive and are made of chemically inert fused silica, the same material used to make capillary GC

Table 1. The species of SPME cover fibers proposed by Supelco [63]

Fiber coating	Thickness (μm)	Target analyte	Matrix	Method Load
Polydimethylsiloxane	100	Volatiles	Gas Water Soil	Sub ppb 0.001-3 ppb 0.002-1 ppb
Polydimethylsiloxane	30	Nonpolar semivolatiles	Water/Soil	Low ppt
Polydimethylsiloxane	7	Mid-to nonpolar semivolatiles	Gas Water Soil	Low ppb
Polydimethylsiloxane/ divinylbenzene	65	Polar volatiles	Water	Low ppb
Carbowax/ divinylbenzene	65	Polar analytes	Water	Low ppb
Polyacrylate	85	Polar semivolatiles	Water Water	0.004-0.2 ppb Low ppt

columns. They have a small diameter, which allows convenient introduction into a chromatographic injector. These fibers coated with polymers such as polydimethylsiloxane of various thickness are available commercially and can be used directly in extractions. The uncoated fiber [18] can also be used or a variety of common chromatographic stationary phases can be attached to its surface [19]. This technique can be applied succesfully to the analysis of volatile chlorinated organics such as chlorinated organic solvents and substituted benzenes as well as nonvolatile chlorinated biphenyls.

Supelco Inc. [63] offers some fiber covers, shown in Table 1.

Applications

The SPME technique offers many chances to extract many compounds (semivolative, volative and nonvolative) from various matrixes: water, soil, drugs, urine, blood. Table 2 presents applications of SPME.

Conclusions

SPME has attracted increasing attention in the field of environmental analysis for its simplicity, efficiency, good precision, low detection limit, and easy automation. SPME uses a fine-fused silica fiber coated with a polimeric

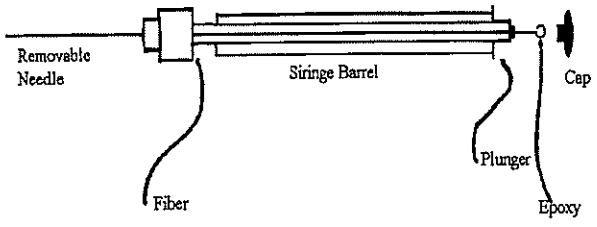


Fig. 5. Construction of SPME device by Pawliszyn et al. [18].

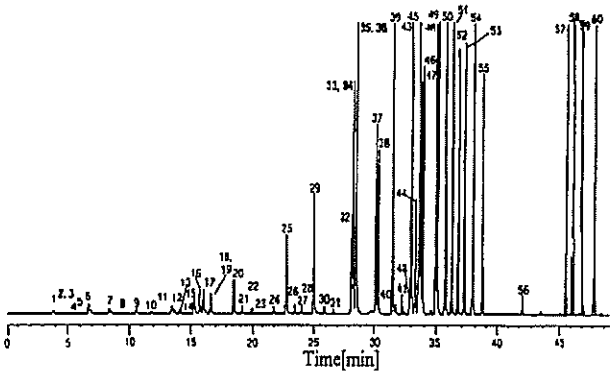


Fig. 6. Example of chromatogram of volatile analytes extracted using SPME (Supelco trade literature "SPME 1995")

coating to extract organic compounds from environmental matrix and directly transfer them into the injector of a gas chromatograph (GC) for thermal desorption and analysis.

The SPME technique is a new isolation method which can be used to extract a wide range of organic compounds, volatile or semivolatile, from various matrices such as air, water, and soil. This technique also has the ability to concentrate trace compounds from the matrix into the fiber coating since the fiber coating has a very small volume.

The SPME device not only combines the extraction and concentration together but also directly transfers the absorbed compounds into a GC injector. The selective absorption of the fiber coating prevents a substantial amount of oxygen and moisture from getting into the GC column. These features in the SPME technique provide major advantages over previous headspace technique.

Compared with direct SPME sampling from aqueus phase, the headspace SPME technique can be used to sample target organic compounds in very complex matrixes such as oily or greasy water and human blood. In those cases, the direct SPME sampling will lead to fiber coating enclosed by grease or impaired by large protein molecules. By sampling from the headspace, these problems can easily be avoided.

SPME has many very important advantages: speed, sensitivity, economy, and versatility, which are shown in Tab. 3.

SPME is used with success for determining many compounds in one sample (Fig. 6). The numerated peaks correspond to sixty compounds Supelco ("SPME 1995"). These compounds belong to different groups: chlorinated hydrocarbons, BTEX, substituted monoaromatic hydrocarbons. The sample is spiked drinking water (50 ppb each analyte); fiber: polydimethylsiloxane, 100 μm film; sampling: 20 ml, 5 min.; desorption: 6 min., 220°C, split/splitless; column: VOCOL™, 60 m × 0.25mm ID, 1.5 μm; oven: 35°C (4 min) to 200°C at 4°C/min; carrier: helium, 2 ml/min.

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Table 2. Applications of SPME

Compounds	Phase-coated fibers	Procedure	Literature
1	2	3	4
BTEX (benzene, toluene, etyhyl, benzyne, xylene, isomers)	Polydimethylsiloxane: 7 μm and 100 μm	Sample - water and wastewater; The fiber was placed in direct contact with the stirred sample during 10 min at room temperature. Finally, the fiber was placed in the GC injector at 150 °C during 2 min. Split mode injection with 1:1 split ratio was used.	11, 12, 13, 15, 18, 20, 21, 22, 24, 25, 26, 27, 28, 29, 30, 32, 34, 36, 39, 43, 47, 48, 49, 51, 52, 62
Phenols	Polydimethylsiloxane 100 μm Polyacrylate 85 μm	Sample - water and wastewater; Phenolics was investigated from headspace over water. All analytes were done with 40 ml EPA vials equipped with 1-in stir bars. The injector was maintained at 200°C and desorption times of 2 and 7 min were used for the polydimethylsiloxane and polyarylate fibers respectively. The detector was maintained at 275°C, with a nitrogen make-up gas flow of 23 ml/min, hydrogen 30 ml/min, and air at 280 ml/min range 12 and attenuation 32.	29, 30, 35, 41
PAHs	Polydimethylsiloxane 7 μm	Extraction of semivolatile PAHs and phthalate compounds from spike water samples ranging from 10 to 200 ppb. Sampling; 4 ml, 15 min. The fiber is introduced into the samples.	10, 28, 30, 36, 37
VOCs	Polydimethylsiloxane 100 μm	Sample: 50 ppb each analyte in water. Sampling: 20 ml, 5 min Extraction from the sample by immersing, Desorption: 6 min, 220°C at 4 °C/min. (spliter vent closed 6 min then vented at 100 ml/min).	15, 20, 24, 26
PCBs	Polydimethylsiloxane 30 μm	Sample: water; concentration were 45, 26, 11 μg/l. The fiber was expsed 1 min. Desorption; He carier, 29 cm/s; N_2 make-up, 24 ml/min; injector, 300°C; detector, 325°C; oven, 15°C, rate 10°C/min to 300°C, hold for minutes.	18
Dioxane	Polydimethylsiloxane 100 μm	Sample: pharmaceutical drug substance and raw materials. Detection limits range from 0.06 μg/ml to 0.3 μg/ml. Analysis by headspace and immersion.	Supelco Publications # 62 Order T394062
Phenicylidine	Polydimethylsiloxane 100 μm	Sample: human body fluids. SPME fiber was exposed to the headspace of the vial for 30 min at 90°C.	55
Mineral oil hydrocarbons	Polydimethylsiloxane 100 μm	Sample: drinking water. Detection: FID or MS. By this method a concentration down to 1 μg/l can be detected and assures an accurate quantitation of MOHCs at the set limit of 10 μg/l drinking water.	57
Ethanol Acetone Isoprene	Polydimethylsiloxane 100 μm Polyacrylate 85 μm	Sample: human breath. Range 2% - 6% could depending.	58
Amphetamines	Polydimethylsiloxane 100 μm	Sample: 1 ml urine + 100 μg each analyte, 5 μg d_5-methamphetamine, 0.7 g K_2CO_3 in 12 ml vial. Extraction: headspace, 80°C, 5 min (after 20 min sample warming period). Desorption: 3 min, 250°C. Det. FID, 250°C.	Supelco Publications # 83 Order T395083

Compounds	Phase-coated fibers	Procedure	Literature
1	2	3	4
Pesticides	Polydimethylsiloxane 30 µm	Sample: agricultural soil premixed with water and fortified at 0.1 - 2.5 mg/kg with five different pesticides. Recoveries between 2 and 72%.	56, 59, 60, 61
THM	Polydimethylsiloxane 100 µm	Sampling: swimming pool water and air directly above water surface. The isolation was carried out at ambient temperature. The series of extraction periods from 1 to 90 min were examined.	40

Table 3. Comparision of different sample preparation techniques

Technique	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
LLE	ppt	5-50	high	1 hr.	1000 ml	yes
SPE	ppt	7-15	medium	30 min.	up to 100 ml	yes
SPME	**ppt**	**<1-12**	**low**	**5 min.**	**none**	yes

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