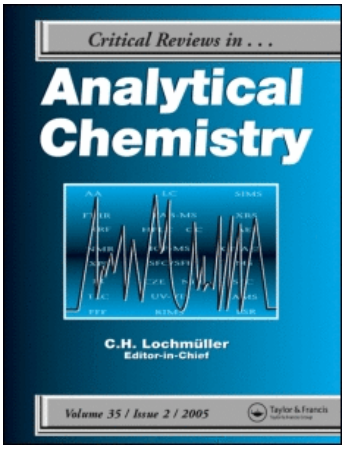

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Modern Techniques of Sample Preparation for Determination of Organic Analytes by Gas Chromatography

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Modern Techniques of Sample Preparation for Determination of Organic Analytes by Gas Chromatography

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The majority of techniques currently applied for isolation/enrichment of organic analytes from gaseous and liquid samples are based on extraction and utilize solid absorbents or organic solvents. While techniques fulfill their tasks, they reveal some important inconveniences. In the case of liquid-liquid extraction, the problem lies in consumption of considerable quantities of organic solvents, which is both environmentally unfavorable and increases the costs of the analytical procedure (storage and utilization costs of these solvents). In the case of techniques in which adsorbents are used, problems may arise when polar or high molecular mass compounds have to be analyzed, or when phenomena of incomplete desorption or artifacts formation (like decomposition of some sample components) may occur. Thus, a number of techniques with reduced solvent consumption (Liquid Phase Microextraction) or practically solventless techniques (e.g., absorption in liquid-like polymers) have been introduced over the past two decades. These techniques show many favorable characteristics; nevertheless, they also have their own limitations. In this paper, a review of the wide spectrum of sample preparation techniques with special attention paid to environment-friendly techniques is presented. The techniques are described from the point of view of analyte isolation mechanisms, and both theoretical and technical aspects are discussed.

Keywords sample preparation, organic analytes, isolation/enrichment, extraction, solventless techniques, gas chromatography

INTRODUCTION

When obtaining a sample for analysis, the first key decision for further course of action should be which technique of separation should be applied and, consequently, how to prepare the sample before the final determinations. Type of analytes and their concentration dictate the choice of the separation technique and the type of detector. It is also worth noting that due to high separation efficiency and compatibility with various kinds of detectors, gas chromatography is the first technique taken into consideration, even if an additional stage of analytes derivatization has to be included into the analytical procedure. On the other hand, the application of high-performance liquid chromatography (HPLC) is useful in cases of determination of non- and semivolatile, thermolabile analytes or those of high polarity, when effective isolation from aqueous matrices is impossible Liquid chromatography, both in the normal (NP-HPLC) and reversed phase system (RP-HPLC) can give us more freedom in the matrix selection (aqueous or organic). The use of the RP-HPLC technique is particularly attractive. It results from compatibility of this technique with popular analytes ionization techniques, like atmospheric pressure ionization (API), which in turn facilitates use of mass detectors.

After selecting the final determination technique (separation and detection system), the way of the sample preparation should be chosen. It is worth stressing that although the separation technique is selected first, it is of secondary importance in a given analytical procedure, at least in the sense that it is the stage of sample preparation that determines the quality of obtained results. There are no problems in associating the detector signal with the respective analytes and their quantities—no changes

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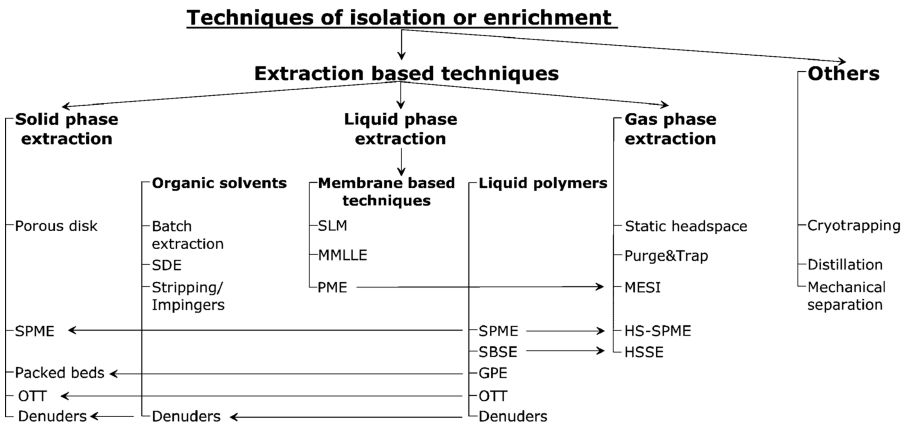

FIG. 1. Classification of sample preparation techniques according to the way of analyte isolation.

occur in the composition (both qualitative and quantitative) of the sample during chromatographic separation. On the contrary, in the case of sample preparation, the change of its composition results from the very nature of this process.

The basic goals of the sample preparation process are: analytes isolation from the primary matrix (if it can influence the final determination stage), analytes isolation from the interfering compounds present in the sample, matrix phase change (phase switching) to one suitable for the chosen chromatographic technique, (for example, aqueous samples or samples with high content of water vapor in the case of gas chromatography), and finally enrichment of analytes to allow their determination by the type of detector chosen. The critical decision for the analyst to make is which detector to use, depending on the expected composition of the sample. Thus, for example, in the case of process analysis, the matrix is usually well defined and several compounds are taken into consideration. It permits the simplification of the sample preparation process. In turn, in the case of analyses of environmental samples (which are usually heterogeneous and their composition may be very complex and difficult to predict), practically none of the abovementioned goals can be avoided.

The last group of parameters, which should be taken into consideration when making the decision of the sample preparation technique, consists of such information as the accessible quantity of sample, possibility of in situ sampling, etc. The number of samples to be analyzed is also of some importance—the question is whether the planned procedure will be unique or whether it will be used in carrying out multiple, even routine, analysis. In the latter case, the techniques facilitating automation and low cost per analysis are preferred. In general case, however, one should bear in mind the popular principle that the lack of the sample preparation stage in an analytical procedure is the best way of sample preparation. Any changes in the sample composition prior to the final determination should be minimized and possibly avoided. This is normally impossible; hence, one should attempt reducing the number of operations performed on the primary sample. This attitude is revealed, for example, in development of techniques that can unite the goals of analytes isolation and enrichment in a single stage.

In this paper we concentrate on techniques of samples preparation based on the partition mechanism and suitability for the determination of organic compounds by means of gas chromatography (Figure 1). The aim was to collect and characterize these techniques, which are the both most frequently used and, in the authors' opinion, most promising. A number of excellent review articles and books covering this subject have already been published. Their authors concentrated on the specific matrix types (1, 2) of techniques, for example liquid phase extraction (3), liquid phase microextraction (4), analyte isolation by the use of sorbents (5) or adsorbents (6) and sometimes a single chosen technique such as solid phase microextraction (SPME) (7, 8) or membrane extraction.

In this paper, the criteria of comparing the techniques of sample preparation are the underlying physicochemical principles and general aspects of constructing the respective devices. At the same time we discuss both the advantages and restrictions of these techniques and to show the direction in which they are presently developing. In our opinion, such an approach permits a clearer presentation of the possibilities of employing the given technique, even without enumerating all the particular existing applications.

THEORETICAL BACKGROUND OF THE SORPTION BASED METHODS

Equilibrium Mode

One of the goals of the sample preparation is to raise concentration of the analytes in the secondary sample, as compared with that in the primary sample. Analytes enrichment is carried out for two reasons. First, one must collect, in a volume of secondary sample suitable for the chosen chromatographic method, the amount of an analyte required by the detector. Second, is to increase the analyte concentration in relation to the other compounds present in the sample and, thereby, to reduce the limit

of quantification by improving signal-to-noise ratio. Taking this into consideration, the enrichment process can be described by two parameters: extraction efficiency R (Eq. [1]) and enrichment factor E (Eq. [2]).

$$R = \frac{n_e}{n_s} \quad [1]$$

$$E = \frac{C_e}{C_s} \quad [2]$$

where n_e and C_e are the amount and concentration of the analyte in the extract, respectively (equilibrium state not required), and n_s and C_s are the amount and concentration of analyte in the primary sample, respectively.

In the case of a two-phase system, the extraction process can be illustrated by the following scheme:

$$\text{Analyte (primary sample)} \overset{K_{e/s},\beta_{s/e}}{\longleftrightarrow} \text{Analyte (secondary sample)}$$

Quantities connecting concentrations of analytes in both phases in equilibrium state are: sample and extractant volumes ratio $\beta_{s/e} = \frac{V_s}{V_e}$ and distribution coefficient $K_{e/s}$, which is usually defined by the equation (not thermodynamic definition):

$$K_{e/s} = \frac{C_{e,eq}}{C_{s,eq}} \quad [3]$$

where $C_{e,eq}$ is analyte concentration in extract in the equilibrium state and $C_{s,eq}$ is analyte concentration in sample in the equilibrium state.

Taking into account the amount of analyte in the system at every moment of the extraction process is constant and equal to the quantity introduced to the system together with the primary sample, analyte distribution between system phases in equilibrium state can be described by the equation:

$$C_s V_s = C_{s,eq} V_s + C_{e,eq} V_e \quad [4]$$

Substituting Eq. [3] into Eq. [4], after rearranging we obtain an equation describing amount of extracted analyte in the equilibrium state:

$$n_{e,eq} = \frac{K_{e/s} V_e C_s V_s}{K_{e/s} V_p + V_s} \quad [5]$$

After substitution into Eq. [1] we get a relation between extraction efficiency (analyte recovery degree) and parameters describing the given system sample – analyte – extractant (10):

$$R = \frac{K_{e/s} V_e}{K_{e/s} V_e + V_s} \quad [6]$$

Subsequently the second essential parameter, i.e., enrichment factor we can calculate by the formula:

$$E = \frac{V_s}{V_e} R \quad [7]$$

The above-mentioned relationships are valid in every partitioning-based extraction process in a two-phase system, e.g., in liquid-liquid extraction techniques as well as in techniques where a liquid-like phase of immobilized polymer is used as an extractant (e.g., SPME, Stir Bar Sorptive Extraction (SBSE) and Open Tubular Trapping (OTT)).

In three-phase systems, an additional stage of the intermediate extraction has to comply. In such systems, organic solvents, inert gas (headspace) or polymeric membranes are used as the intermediate phase. The extraction process runs according to scheme:

$$\text{Analyte (primary sample)} \overset{K_{ie/s},\beta_{s/ie}}{\longleftrightarrow} \text{Analyte (intermediate extract)} \overset{K_{ss/ie},\beta_{ie/ss}}{\longleftrightarrow} \text{Analyte (secondary sample)}$$

Isolation techniques with the so-called back extraction and some membrane techniques are the examples of the systems of this type. According to the presented scheme, the partition mechanism decides both the equilibria; thus, the whole process depends on the ratio of volumes of the primary sample and the intermediate extractant ($\beta_{s/ie}$), the ratio of volumes of intermediate extractant and secondary sample ($\beta_{ie/ss}$), as well as distribution coefficients of analyte between the primary sample and the intermediate extractant ($K_{ie/s}$) and between the intermediate extractant and the secondary sample ($K_{ss/ie}$):

$$K_{ie/s} = \frac{C_{ie,eq}}{C_{s,eq}} \quad [8]$$

$$K_{ss/ie} = \frac{C_{ss,eq}}{C_{ie,eq}} \quad [9]$$

where $C_{ie,eq}$ is the analyte concentration in intermediate extract (phase) in equilibrium state.

Although the scheme presented here shows the course of extraction process in a complete way, from the practical point of view, the net result of the extraction process (i.e., the change of analyte concentration in the primary and secondary sample) is important as it is presented by the scheme:

$$\text{Analyte (primary sample)} \overset{K_{ss/s},\beta_{s/ie},\beta_{ie/ss}}{\longleftrightarrow} \text{Analyte (secondary sample)}$$

Consequently, calculating values of the recovery and the enrichment factors consideration overall distribution coefficient of analytes between primary and secondary samples ($K_{ss/s}$) should be taken into account, which can be calculated by means of Eq. [8] and Eq. [9] (11):

$$K_{ss/s} = \frac{C_{ss,eq}}{C_{s,eq}} = K_{ie/s} K_{ss/ie} \quad [10]$$

It is essential that both of phase volume ratios, $\beta_{s/ie}$ and $\beta_{ie/ss}$, influence the recovery and enrichment factors. It is because the analyte in equilibrium state is divided between all system phases according to the equation:

$$C_s V_s = C_{s,eq} V_s + C_{ie,eq} V_{ie} + C_{ss,eq} V_{ss} \quad [11]$$

where V_{ie} is the volume of the intermediate extractant.

Substituting $C_{ss,eq}$ from Eq. [10] and Eq. [9] into Eq. [11], leads to a relationship permitting the calculation of the amount of analyte in the secondary sample in the equilibrium state $n_{ss,eq}$ (11):

$$n_{ss,eq} = \frac{K_{ss/s}V_{ss}C_sV_s}{K_{ss/s}V_{ss} + K_{ie/s}V_{ie}} \quad [12]$$

Thus, the recovery factor for the three-phase system can be described by the following equation:

$$R = \frac{K_{ss/s}V_{ss}}{K_{ss/s}V_{ss} + K_{ie/s}V_{ie} + V_s} \quad [13]$$

Finally, similarly as in the case of Eq. [7], the enrichment factor value can be calculated using equation:

$$E = \frac{V_s}{V_{ss}}R \quad [14]$$

The relationships described for three-phase systems are valid for every technique if partitioning is a dominating mechanism of analyte isolation and if the process is carried out in the equilibrium mode.

Nonequilibrium Mode

Automation of the extraction process in connection with a large volume of the sorbent phase makes it reasonable to carry out the extraction process in the nonequilibrium mode. Employing this mode in the SPME technique is more difficult due to the small quantity of sorbent (sensitivity is restricted even in the equilibrium mode). On the other hand, techniques, such as e.g., SBSE, in spite of the fact that a sufficient quantity of sorbent is provided, are not suitable to perform nonequilibrium extractions due to difficulties in adequate control of the basic nonequilibrium mode parameter, i.e., extraction time. Furthermore the extraction time has an essential practical meaning and should be optimized (shortened) in situation, when carrying out many reproducible determinations is necessary. With restriction to the one-sample matrix, selection of adequate sorption time depends on such parameters as the kind of determined compounds (partition coefficient), analyte concentration (the lower concentration requires a longer sorption time or bigger sample volume to reach the limits of detection), as well as accessible sample volume (which can have an influence on the phase-volumes ratio (β)).

In the case of equilibrium mode extraction when a large volume of the stationary phase is utilized, it is reasonable to use the recovery factor that can be calculated with the following equation (12):

$$R = \frac{n_e}{n_s} = \frac{\left(\frac{K_{e/s}}{\beta_{s/e}}\right)}{1 + \left(\frac{K_{e/s}}{\beta_{s/e}}\right)} \quad [15]$$

The preceding equation may be used to predict extraction efficiency. It can be easily calculated that for a typical sample volume of 10 ml and extractant volume of 100 μl (e.g., SPME),

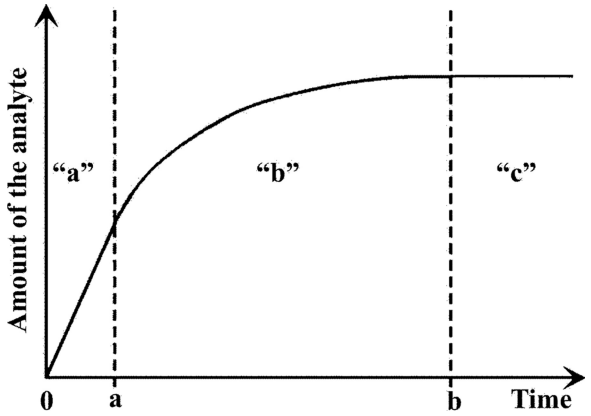

FIG. 2. Dependence of the amount (number of moles) of the analyte extracted on the extraction time: "a" is the linear part, "b" is the nonlinear part, "c" is equilibrium.

quantitative extraction ($R > 0.9$) of volatile and polar organic compounds ($\log K_{o/w}$ 2–3) is possible. Thus, quantitative determination can be achieved and calibration of the isolation stage is unnecessary. It should be taken into consideration, however, that the time needed to achieve the equilibrium state grows considerably with both thickness of the sorbent phase and the partition coefficient (10). For these reasons such an approach is rational only if it is necessary, e.g., when n_e (but after equilibration) calculated on the basis of Eq. [15] is close to the limit of detection of the detector used. Consequently, applying a sampling probe with a thick sorbent layer is more suitable to carry out extraction in a nonequilibrium mode (Figure 2, fields "a" and "b").

Selection of the proper extraction time is, of course, a compromise between sensitivity and time (throughput) of the analysis, but keeping in mind that this compromise concerns the range inaccessible for techniques utilizing probes with thin layer (and volume) of the sorbent. The range from $t = 0$ to $t = a$ in Figure 2 represents a specific case of nonequilibrium conditions, in which the amount of the adsorbed analyte increases linearly with time of the extraction. Additionally within this range, the extraction rate has the highest value restricted, according to Fick's first law, by the flux of the analyte through Nernst's diffusion layer:

$$F = -D_a \times \frac{dC_a}{dr} \quad [16]$$

where F is flux of the analyte through the diffusion layer, D_a is analyte diffusion coefficient in sample matrix, r is radius (thickness) of the diffusion layer, and dC_a/dr is the gradient of analyte concentration in the diffusion layer.

Thus, for the given initial analyte flux ($mol \cdot s^{-1} \cdot m^{-2}$), width of the time interval ($0 < t < a$) depends on both sorbent phase thickness and sample volume. For the most popular sampling probes of a cylindrical shape, kinetics of the sorption process are described by the diffusion differential equation in a form

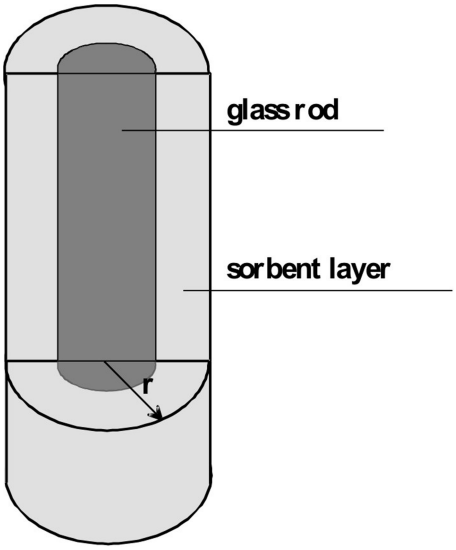

FIG. 3. Schematic diagram of a cylindrical probe used in the model discussed: r is the probe radius.

regarding cylindrical coordinates (see Figure 3) (13):

$$\frac{\partial C_A}{\partial r^2} + \frac{1}{r}\frac{\partial C_A}{\partial r} = \frac{1}{D}\frac{\partial C_A}{\partial t} \quad [17]$$

where r is radius of the sorbent layer, C_A is analyte concentration in sorbent layer, D is analyte diffusion coefficient in sorbent, and t is time.

To solve Eq. [17] it is necessary to determine boundary conditions of the extraction process (10):

a. Initial analyte concentration in a sorbent is equal zero:

$$C_A(r, t = 0) = 0 \quad [18]$$

b. Analyte concentration on the outer surface of sorbent layer (r_A) remains constant during the entire extraction time (characterized by the concentration of an analyte in the sample and diffusion coefficient):

$$C_A(r = r_A, t) = K_{e/s}C_s \quad [19]$$

c. The carrier (for example a fused silica rod), on which the sorbent layer is deposited, is impermeable to analytes (there is no adsorption and consequently no absorption of the analytes, r_r is the radius of the outer carrier surface):

$$\frac{\partial C_A}{\partial t}(r = r_r, t) = 0 \quad [20]$$

Such defined assumptions allow one to solve Eq. [17] to find analyte concentration profiles in sorbent coating for the given extraction time. Relative analyte concentrations profiles for two coatings of different thickness (100 μm—SPME-like, 400 μm—SBSE-like) are presented in Figure 4 (14). As may be seen, the slope of the concentration gradient in the coating decreases rapidly with time, which, accordingly to Eq. [16], results in a proportional decrease of analyte flux into the sorbent layer. In other words, flux of the analytes into the thicker layer is still high, while the thinner coating approaches the saturation state. The area under the curves corresponds to the extracted amount of an analyte in the sorbent for the given extraction time. Thus, integrating the series of theoretical concentrations profiles calculated for different extraction times allows us to find the course of the relationship between the amount of an extracted analyte and the extraction time (Figure 5) (14).

Also noticed is that increasing thickness of the sorbent layer increases the time when extraction rate is relatively high. Consequently, as long as the analyte flux into the sorbent layer is higher than analyte flux through the diffusion layer, the amount of the extracted analyte increases linearly with time. The additional condition that has to be fulfilled is constant concentration of an analyte in the sample (Eq. [16]). In the case of a finite sample volume this condition is fulfilled as long as significant

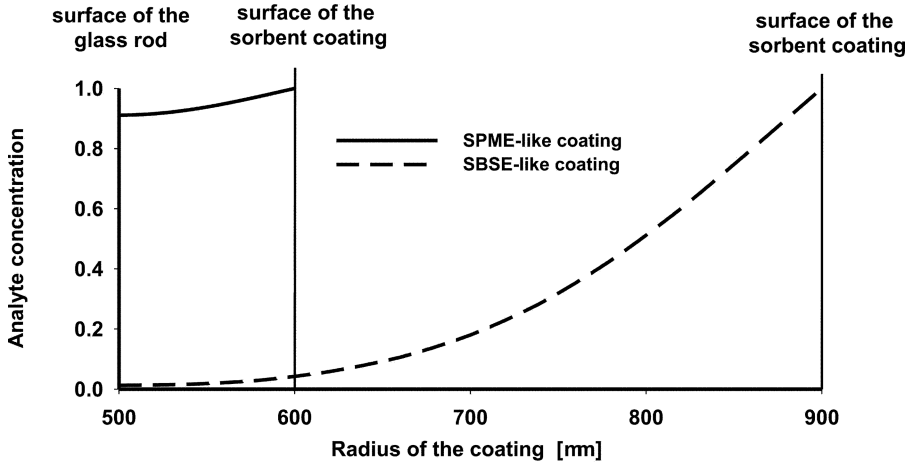

FIG. 4. Theoretical profiles of analyte concentrations in PDMS films of different thickness after the same time of extraction. Reprinted from (14) with permission from Elsevier.

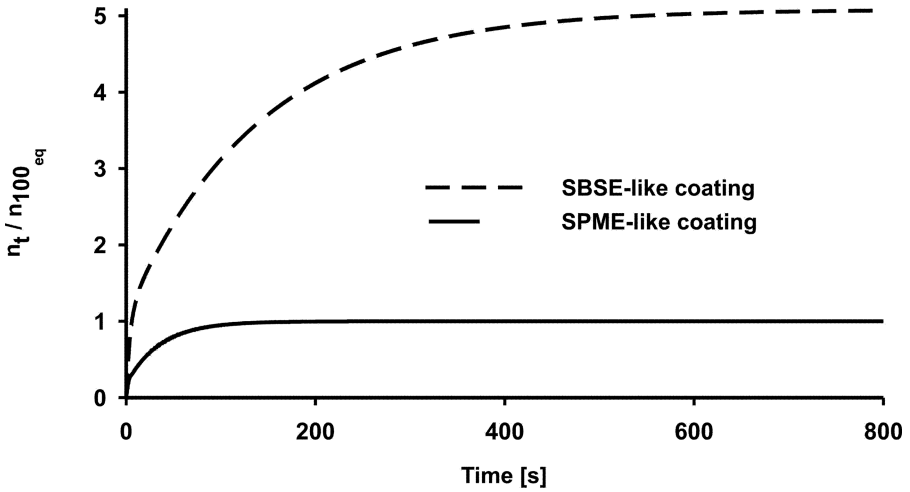

FIG. 5. Theoretical dependence of the amount of analyte in the sorbent (PDMS) film on the extraction time for two films of different thicknesses. Normalized values are shown: number 1 on the ordinate corresponds to the amount of analyte in a typical SPME film (100 μm) at equilibrium ($n_{SPME,eq}$). Reprinted from (14) with permission from Elsevier.

sample impoverishment in analyte ensues. This condition is also fulfilled in the situation when analytes are extracted from the flowing stream of the sample like a river or a pipeline (process analysis).

ADSORPTION-BASED TECHNIQUES

The peculiarity of sorbent-based techniques allows us to modify, depending on need, the methodology of carrying out the extraction process. Based on theoretical backgrounds mentioned earlier, we can widen the applicability range of the individual techniques by changing the method and mode of the extraction, e.g., to achieve lower detection limits or higher sample throughput. The change of extraction mode also has consequences in the calibration procedure. Here, the general characteristics of particular techniques and modes of analyte isolation are presented.

Static Techniques

The extraction process carried out as a static method means that, from the beginning of the process, the whole sample and whole sorbent are in contact. Additionally new portions of sample and sorbent are not added to the system until the end of extraction.

The static method can be applied in both equilibrium (Figure 6A) and nonequilibrium modes (Figure 6B). In the first case, extraction is carried out until the equilibrium state is reached. In this case the final analyte concentration in the sorbent phase is the highest of all concentrations possible to obtain for the given sample-sorbent system ($K_{e/s}$) under given conditions ($\beta_{s/e}$, temperature). In a situation, when recovery does not exceed 1%, the analyte concentration in the investigated sample can be calculated on the basis of a known value of partition from the equation (rearranged Eq. [3]):

$$C_{p,eq} = \frac{C_{e,eq}}{K_{e/s}} \qquad [21]$$

In the case of a favorable analyte partition coefficient and phase volume ratio β, it is more convenient to use Eq. [15] to check whether extraction can be exhaustive ($R \geq 0.9$). It is essential for the calibration procedure—the results obtained in the case of exhaustive extraction are quantitative by definition (only calibration of the detector is required). In the case of intermediate recoveries, analyte concentration in the sample has to be calculated from Eq. [5]. It should be emphasized that the enrichment factor, E, achievable by the static methods, depends on the distribution coefficient only up to a certain value. For the high $K_{e/s}$ values, an assumption about exhaustive extraction can be made; thus, the enrichment factor is equal to the phase ratio in reverse ($\beta_{s/e}$).

The static extraction method in the nonequilibrium state is terminated before the equilibrium state is achieved (Fig. 6B). In such a situation, the amount of the extracted analyte is lower than

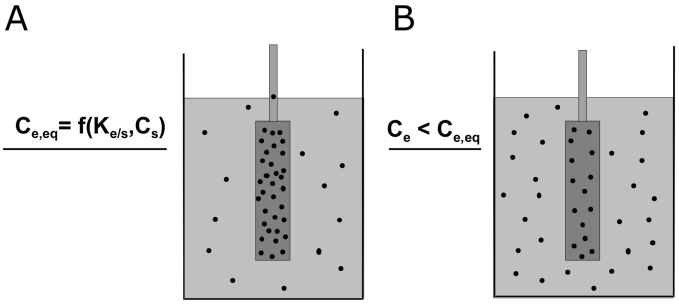

FIG. 6. Static method of analyte isolation: A, equilibrium mode; B, nonequilibrium mode (see text for details).

the result from Eq. [5], which has consequences in the analytical and calibration procedures. Because of the fact that the final concentration of analyte in sorbent cannot be unambiguously connected with the $K_{e/s}$ value, there is no need to know this parameter. On the other hand, some other parameters influencing the extraction process such as extraction time, mixing intensity, and probe position in the sample bulk (in the case of mechanical mixing) should be taken into consideration when designing an analytical procedure. On the other hand, significant shortening of extraction time is the serious advantage of the nonequilibrium mode. It is of essential importance particularly in process analysis when large volume of the sorbent is utilized and when analytes with high partition coefficients have to be analyzed.

Static extraction in the equilibrium mode is the most suitable technique based on the partition mechanism. Analytes become dissolved in the sorbent phase, thus disadvantageous processes of competition between analytes do not appear. In the case of adsorption, which proceeds on active centers only, processes of analytes exclusions (displacement) can occur; thus, analytes of lower affinity to adsorbent cannot be detected. This can also appear in cases when some of the analytes are present in the sample at significantly lower concentrations than the others. One of the possible solutions of this problem can be the nonequilibrium mode, using calibration based on the analyte diffusion rates (15). In this technique, very short extraction times, on the order of a few dozen seconds are applied, so the exclusion process cannot occur (the whole accessible adsorbent surface is not used). On the other hand, due to extremely short extraction time, repeatability of the obtained results is very low, which is probably caused by difficulties in controlling parameters determining the extraction kinetics (16).

Dynamic Techniques

In the dynamic techniques, new portions of the sample are constantly introduced to the system. Consequently, the extractant is in contact with the sample of original composition for the whole time of extraction. Extraction is often carried out in the equilibrium mode—due to continuous refreshing of the sample, the diffusion rate of analytes to the sorbent surface remains on a constant high level. Since the sample of unchanged composition takes part in equilibrium, to calculate the analyte concentration in the sample, we should know only the partition coefficient value (Eq. [3]).

Due to the geometry of the extraction devices, the dynamic methods are most often employed together with tubular traps: tubes packed with adsorbent bed, open tubular traps, denuders. As with static methods, dynamic methods can be applied in both the equilibrium mode and nonequilibrium mode (breakthrough mode). A diagram of the analyte isolation process course in both modes is presented in Figure 7. In the breakthrough mode the sample is passed through the trap until the earliest eluted analyte appears at the outlet of the trap, while in the equilibrium mode it is continued beyond the breakthrough point until equilibrium state in system is reached. The most important practical reason

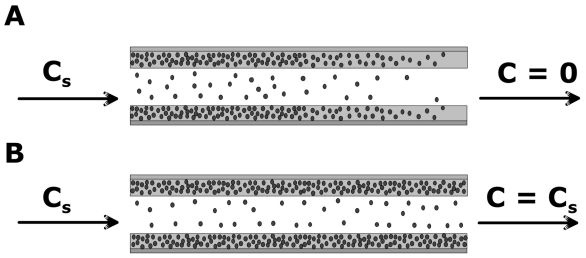

FIG. 7. Dynamic method of analyte isolation: A, nonequilibrium mode (breakthrough volume mode); B, equilibrium mode; C_s, analyte concentration in the primary sample; C, analyte concentration at the outlet of the trap.

to favor the breakthrough mode is the simplicity of the calibration procedure: analytes are retained quantitatively, so only the knowledge of the amount of the analyte in the trap and the volume of sample passed are needed to calculate the analyte concentration. Since breakthrough volume depends on both the sample flow rate through the trap and temperature, these parameters should be controlled. It should also be mentioned that sample flow rate through the trap should not be too high because of the decrease in the breakthrough volume (especially in the case of liquid samples). It is worth mentioning that analyte isolation in the equilibrium mode does not restrict the sample flow rate; furthermore, high flow rates accelerate reaching equilibrium. On the other hand, in the equilibrium mode extraction, partition coefficients values must be known, and the key parameters on which they depend must be kept under strict control.

Summarizing the choice of trapping medium, some general remarks should be considered respectively to the target analytes:

a. adsorbents are usually employed in the breakthrough mode because of their high retention power. Adsorbent application in equilibrium mode encounters difficulties connected with the exclusion/displacement phenomenon of analytes of lower affinity to the adsorbent;
b. absorbents are mostly employed in the equilibrium mode because of their low retention properties. Still, trials are carried out to employ sorbents in the breakthrough mode, e.g., by applying traps with the bed of absorbent or by increasing thickness of the coating in open tubular traps (17, 18).

EXTRACTION-BASED TECHNIQUES

Extraction techniques may be divided into three main types, depending on the kind of extractant phase: liquid-phase extraction, gas-phase extraction, and extraction in which solid adsorbents are applied. Previously, we described the techniques utilizing immobilized liquids as sorbents. The only reason for such an approach is based on instrumentation, while formally (extraction mechanism) they belong to a group of liquid-phase extraction techniques. To illustrate current trends and developments in techniques of sample preparation for GC analysis, we describe several relatively new techniques.

Large-Volume Injection Techniques

A complete understanding of both advantages and limitations of extraction techniques, as well as comparison of their applicability, requires a discussion of techniques of sample injection onto a chromatographic column. Generally, due to increase of sample volume during solvent evaporation, it is not possible to inject (with typical split/splitless injector) samples of volumes larger than 1–2 μl. On the other hand, detection limits of most of detectors are in the range 10^{-10}–10^{-12} g, which means that, e.g., for pesticides (acceptable concentration in water is ca. 0.1 $\mu g \cdot l^{-1}$), direct analysis requires samples of at least 1 ml.

Thus, the initial preconcentration of analytes seems to be necessary. On the other hand, to gather analyte amount sufficient for the detector, extraction from 1 ml of the sample should be carried out in volume ratio sample–extractant 1000:1 (assuming 100% extraction efficiency). That is practically impossible to achieve because of a small but measurable solubility of commonly applied organic extractants in water. To avoid restrictions of this kind a number of large-volume injection (LVI) techniques were developed (19). The three main LVI techniques can be distinguished as: analyte injection directly onto a chromatographic column (OC-I) (20), analyte loop-type injection (LT-I) (21), and injection in a programmable temperature vaporization of the sample (22) (PTV).

Common to all LVI techniques is almost total solvent evaporation before the sample reaches the head of the GC column. In this way the virtually enriched analytes are separated in a chromatographic column. The evaporation of solvent takes place in a deactivated capillary tube connected with the adequate GC column through a precolumn, trapping analytes (OC-I), or through a system of two valves (LT-I). In the case of the PTV technique, both processes of solvent evaporation and analyte trapping take place already in a PTV injector. Due to different instrumentation applied, LVI techniques differ in practical properties (19):

- *The OC-I Technique:* solvent is more volatile than the analyte and is initially removed by ventilation; thus, very precise and time-consuming calibration of the analytical procedure for specific applications is necessary. The subject of optimization is not only the sample evaporation point (below the corrected solvent boiling point) and a gas carrier rate of flow, but also a time of opening and closure of the ventilation valve. The latter is especially meaningful—a few seconds' delay in closing the ventilation valve can result in loss of a major part of volatile fractions of the analyte. Even so, the OC-I technique makes it possible to determine the analytes of the very diverse volatility in the case when very rigorous procedures are preserved.
- *The LT-I Technique:* the solvent evaporation process starts from the front of the injected sample. Consequently, the accumulating vapors of solvent (its overpressure) counteract the sample flow through the precolumn, which allows reducing the whole process control to the selection of suitable temperature of the GC oven (it must exceed the corrected solvent boiling point). The price to pay for simplicity of the calibration procedure is the loss of analytes of low and medium volatility (depending on solvent). The modified LT-I technique, using a co-eluent of lower volatility, makes it possible to determine the more volatile analytes. but unfortunately with such consequences in calibration procedure as in the OC-I techniques.
- *The PTV:* the injection of sample based on selective evaporation of solvent simultaneously with a trapping of less volatile analytes. Unlike the previous techniques mentioned, repeated trapping of analytes proceeds by the rapid cooling of the evaporated sample. The procedure of calibration is arduous and laborious as in the case of the OC-I—both the sample evaporation rate (the carrier gas temperature and its rate of flow) and the cooling temperature have to be adjusted. Even so, the determination of the analyte (of only slightly lower volatility than the solvent) is possible to perform (e.g., by application of injector liner packed with a suitable sorbent) (23).

In practice, application of LVI techniques allows injection of the samples of several milliliters (24). Unfortunately, direct injection of the original samples is limited to the very pure samples, i.e., without solid components and inorganic salts. In the case of aqueous samples, we should also take into consideration the relatively high boiling point of the water, which considerably restricts determination of analytes, even those of low volatility. On the other hand, limiting the necessity of extract concentration, the LVI techniques become an important supplement for liquid-phase extraction techniques (25, 26).

Liquid Phase Extraction

Here, the most frequently applied and most intensively developed technical solutions of the solvent extraction techniques are described. Special attention was paid to techniques compatible with gas chromatography as well as pro-environmental techniques that are alternative to those utilizing organic solvents.

Liquid–Liquid Extraction. Extraction using organic solvents is one of the oldest ways of sample preparation and purification. Organic compounds originally presented in the sample pass to an organic phase of extractant that is suitable for employing a capillary gas chromatography. For these reasons, liquid–liquid extraction (LLE) is very often referred to as the phase (matrix) switching technique. LLE is the simplest technique of phase switching. It is particularly popular in the case of isolating organic analytes from water samples. In the simplest form, extractant and sample are shaken in one container. Here, the analytes are transferred directly from the primary sample to the water immiscible organic phase. After equilibration, the analytes are distributed between phases, accordingly to Nernst's Law. The extraction efficiency (R) mentioned earlier depends

on the partition coefficient $K_{e/s}$ (determined by selection of the extractant) and on the volume phase ratio β (V_s/V_e) according to the following equation (19):

$$R = 1 - \frac{1}{1 + K_{e/s}(\frac{V_e}{V_s})} \quad [22]$$

The simplest way to increase the process efficiency is to carry out the few-stage extraction using a new portion of pure solvent. The other approach (allows for automation) is to merge the stream of the sample with the stream of extractant, and it may be carried out in both countercurrent and concurrent flow directions (27, 28).

The obtained extract can be analyzed directly by gas chromatography (for example with the use of LVI techniques), or if necessary, extract can be concentrated by partial evaporation of the solvent. However, it should be noticed that to achieve high extraction recoveries, usually large amounts of the organic extractant should be applied. The subsequent concentration of extract leads to a significant increase of the enrichment factor E. However, such operation (evaporation of solvent) can be the cause of loss of the more volatile analytes (29). The other common problem connected with the liquid–liquid extraction is a formation of emulsions, as a result of the intensive shaking/mixing during extraction. Also other drawbacks should be pointed out. The other essential faults of extraction are:

- The extraction is very often handmade, so sample preparation is very laborious,
- Many operations upon the sample are performed, which may cause loss of analyte or sample contamination, and
- The consumption of large amounts of organic solvents.

There were many attempts made to solve the first two problems, and developing automated procedures based on the flow of extractant and sample stream was one such attempt (30, 31). Unfortunately the third drawback cannot be eliminated from the LLE procedure for obvious reasons. An additional warrant to withdraw usage of the techniques based on the organic solvents arises with the Montreal Protocol postulating the elimination of these methods from analytical procedures (32). The use of large quantities of organic solvents is harmful not only environmentally, but it can be also harmful for laboratory workers. The problems and cost of organic waste are also significant and raise considerably the costs of the whole analytical procedure. On the other hand, liquid phase extraction can be a very useful technique of sample preparation in specific cases because of the large variety of accessible solvents.

Liquid-Phase Microextraction. Restrictions of conventional LLE techniques, mentioned previously, resulted in an origin of the new trend in the way of applying liquid solvents—liquid-phase microextraction (LPME). LPME techniques gain in significant limitation of the organic solvents consumption, simultaneously preserving the possibility of using a broad range of solvents. Liquid-phase microextraction techniques can be divided in to two main groups: the group of techniques where extractant forms a droplet exposed in the original sample, and techniques utilizing polymeric membranes (4, 9, 33).

Single Drop Extraction. In the Single Drop Extraction (SDE) technique, a portion of extractant is usually of 1 to 10 μl volume. Thus, two very essential parameters to characterize solvent are limited mutual solubility with water (sample) and surface tension sufficiently high to form a drop (e.g., example: toluene, n-octane) (34). The instrumentation differs in the way the single drop is obtained, the possibility of process automation and the extraction mode. The simplest solution is to suspend extractant drop at the end of a polytetrafluoroethylene (PTFE) rod and to dip it in the sample (35). When extraction is finished, only 1 μl of all the extract is drawn out with a microsyringe and injected directly into the gas chromatograph. In the other method, the typical microsyringe is used (Figure 8). The drop is formed at the end of the needle by pressing the plunger. Subsequently, after extraction, the solvent is withdrawn and may by immediately injected to the chromatograph (36, 37). Application of the microsyringe makes it possible to automate the extraction procedure. Additionally, full control of solvent volume increases analysis repeatability.

SDE is usually used as a static method in both equilibrium and nonequilibrium modes. However, the techniques of dynamic sampling with the forced flow of sample have also been developed. One of the reasons for developing these techniques is the relatively low extraction rate. It is due to an unfavorable geometry of the system (38); it is well known that the spherical shape shows the lowest surface-to-volume ratio. The extraction rate can be represented by the rate constant K (s^{-1}) (39):

$$\kappa = A\upsilon\left(\frac{K_{e/s}}{V_s} + \frac{1}{V_e}\right) \quad [23]$$

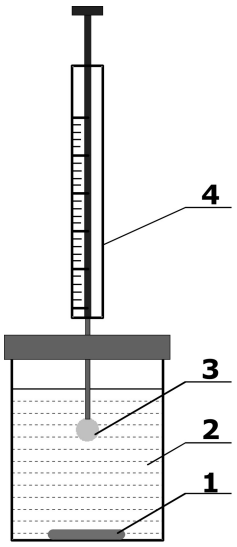

FIG. 8. Extraction of analytes using an SDE device: 1, stir bar; 2, sample; 3, hanging drop of the extracting agent; 4, syringe.

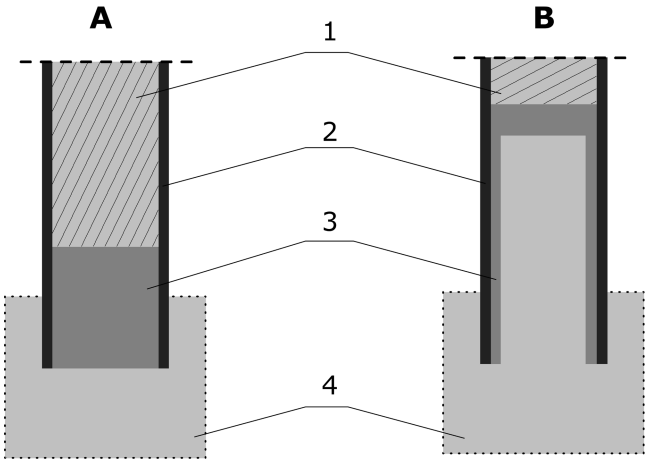

FIG. 9. Two stages of microextraction performed in a syringe needle: A, extraction with the needle filled completely with the extracting agent; B, extraction after formation of a film of the extracting agent on the inner surface of the needle by retraction of the syringe plunger: 1, plunger; 2, needle; 3, extracting agent; 4, sample.

where A is the interface area and υ is the coefficient describing transport of the analyte in the extractant.

Equation [23] shows that a higher extraction rate can be obtained as a result of increasing the interface area or by decreasing both extractant and sample volumes. In the case of LPME techniques, the reasonable solution is to increase the interface, while the extractant volume is already considerably limited. The scheme of the extraction process is shown in Figure 9 (40): first the needle of the microsyringe containing the small quantity of extractant (1–2 μl) is introduced into the sample, then a small volume of the sample is withdrawn into the microsyringe. At this moment, the extractant forms a thin layer on the inner wall of the syringe, which results in the significant increase in the interface area. Finally, the sample is pushed out of the syringe after a few seconds. This procedure can be repeated many times. When the extraction is accomplished, the extract (or part of it) may be injected directly into the GC column.

In the other solution accelerating extraction a small volume of extractant is introduced into the sample stream (41). Here, a drop of the extractant is formed and held at the end of the tube outlet. The sample flow is continued until the equilibrium state is reached. After extraction, part(s) of the extract is(are) sampled with a microsyringe and introduced to the GC.

The single-drop extraction techniques described here are two-phase systems, which are easy to use together with a GC because of the kind of solvent (organic liquid). The field of application of SDE techniques in the two-phase system is restricted to the hydrophobic compounds of the relatively high partition coefficients (about 1000), because of the small extractant volume. SDE techniques were applied to determine such compounds like chlorobenzenes, organic nitro compounds, chloroorganic pesticides, and progesterone (34, 40, 42, 43).

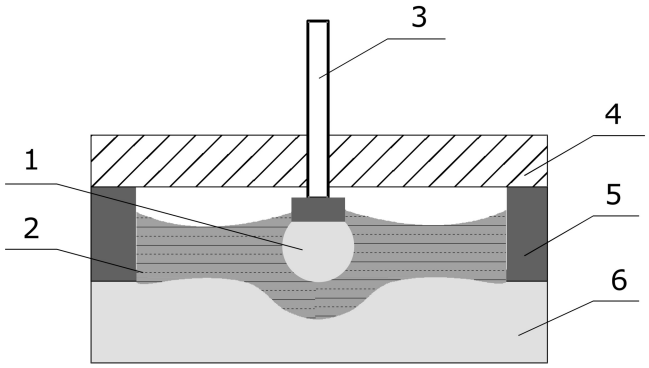

FIG. 10. Magnified fragment of the set for analyte extraction using an SDE device in a three phase system: 1, extracting agent (acceptor); 2, intermediate extracting agent (organic liquid); 3, syringe needle; 4, Teflon cover; 5, Teflon ring; 6, sample.

Aside from extraction in a two-phase system, SDE techniques in three-phase systems were also developed. These techniques are oriented toward final analysis by liquid chromatography or capillary electrophoresis. The field of application of this group of techniques is identical to the field of application of other liquid-phase extraction techniques in three-phase systems, e.g., the liquid-liquid-liquid extraction or membrane extraction. It refers mostly to these compounds, which can occur in ionic forms as organic bases and acids. An example of an SDE device for extraction in a three-phase system is shown in Figure 10 (44).

There are some advantages in the case of the SDE techniques except these mentioned above. The simplicity of extraction system and possibility of directly injecting the sample into the chromatograph are worth noting. It makes this technique like the SPME technique. However the SDE technique has some essential faults. First it needs very careful, precise and, consequently, time- and labor-consuming usage of the devices. Second, there are some difficulties holding the drop in place: the extension of extraction time and overly intensive mixing are not recommended, because the drop can dissolve or fall down [35]. Consequently, it decreases the efficiency or increases time of the extraction process.

Membrane Techniques. The second group (besides SDE) of liquid-phase microextraction techniques is a group of techniques based on the use of suitable membranes to separate both the sample and the extractant. In this instance, similar to the case of SDE techniques, the idea was to significantly reduce the quantity of organic chemicals used and to increase the analyte enrichment degree by means of reducing the phase volumes ratio. The increase of the range of applicable extractants is the additional advantage in the case of membrane technique. Extractant is trapped in pores of the polymer, so the requirement of mutual solubility of both extractant and water is not as restrictive as in the case of SDE techniques. Additionally, the use of membrane techniques makes it easy to automate the analytical procedure. Membrane techniques can be divided between the three basic groups:

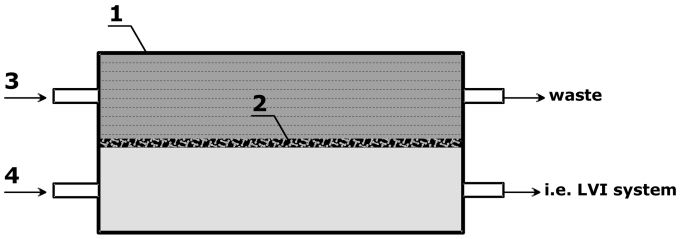

FIG. 11. Analyte extraction utilizing an MMLLE technique: 1, body of the MMLLE device; 2, porous membrane impregnated with an organic solvent; 3, direction of the sample flow; 4, direction of the extracting agent flow (in some cases immobile extracting agent is used).

- Supported Liquid Membrane (extraction) (SLM)—a distinguishing feature is the lack of contact between both the original sample (donor) and the secondary sample (acceptor); the polymeric membrane is used as a support for organic solvent (intermediate extractant) (45),
- Microporous Membrane Liquid-Liquid Extraction (MMLLE)—here, both donor and acceptor solutions are in direct contact through membrane pores (46),
- Polymeric Membrane Extraction (PME)—the membrane is made of silicone rubber. This technique can be qualified as SLM (water) or MMLLE (organic extractant), depending on the acceptor phase.

Membrane extraction can be carried out in different configurations (47):

- SLM: water–organic phase–water
- MMLLE: water–organic phase–organic phase
  organic phase–organic phase–water
- PME: water–polymer–water (SLM)
  water–polymer–organic phase (MMLLE)

The organic phase is trapped in the polymer pores by the capillary forces. The applied membranes are usually hydrophobic (e.g., polypropylene (48, 54)); consequently, the most frequently organic phase long-chained hydrocarbons used are undecane, kerosene, n-octanol, and dihexylether (48, 54).

In the case of systems with an organic acceptor (MMLLE), membrane pores are filled with the same organic solvent, thus the opportunity for direct extract injection to the gas chromatograph is created. This system works on the basis of the typical two-phase liquid-liquid extraction (Figure 11).

Volumes of extractant are considerably smaller then in conventional liquid-liquid extraction: in conventional LLE, the volume phase ratio β is in the range from 1 to 5, while in the liquid-phase microextraction, this ratio is in the range 20–200 (51); thus, high values of the enrichment factors E can be obtained. The inconvenience of two-phase membrane systems is the loss of the part of the analytes trapped within the extractant immobilized in pores of the membrane. Hence, the high value of the partition coefficient of analyte is needed to achieve the required recovery and enrichment factors (51).

Contrary to MMLLE, in SLM techniques, the extraction process runs in a three-phase system. The application of SLM techniques is restricted to ionic compounds because of the type of acceptor phase (water). Neutral compounds are also distributed between the phases of system but they do not undergo enrichment. The hypothetical extraction mechanism of compounds with acid or basic functional groups is presented in Figure 12. The basis of the SLM techniques is to obtain the analyte as donor in inactive-neutral form so that its extraction and transport through the membrane is possible. In the acceptor phase, the analyte should be converted to the ionic form, which prevents its re-entering the organic phase. In this way, extraction can run theoretically at a rate of 100%.

Thanks to this mechanism, selective extraction is also possible in view of the analytes' acidity/basicity constant.

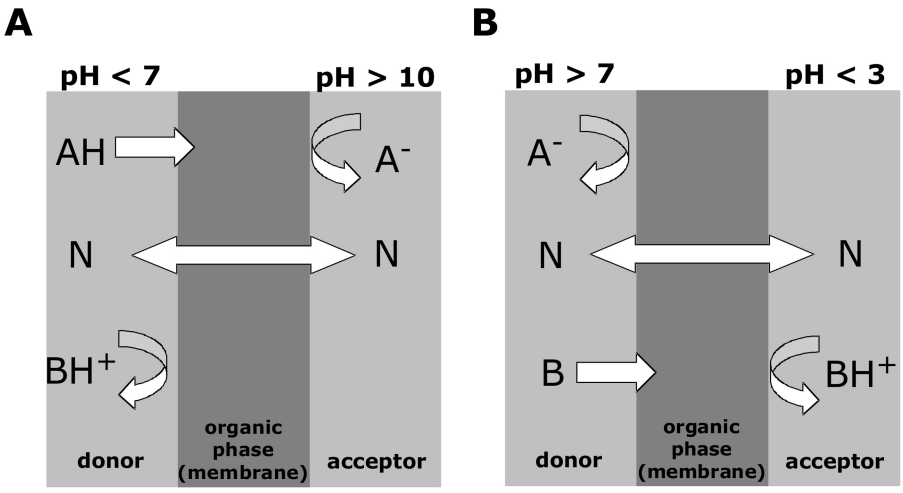

FIG. 12. Analyte extraction using an SLM technique: A, extraction of analytes with acid groups; B, extraction of analytes with basic groups.

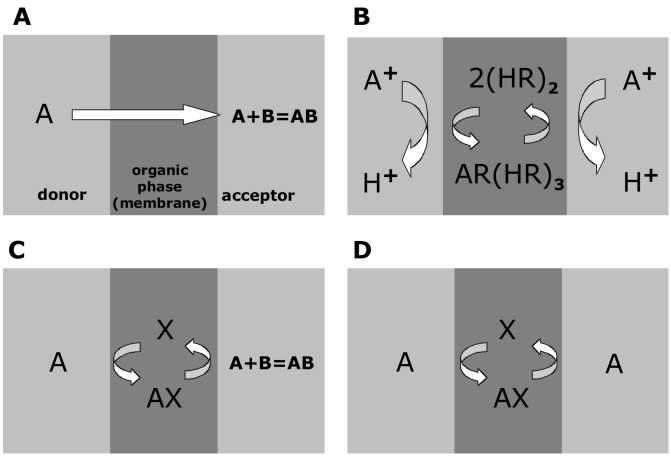

FIG. 13. Examples of analyte extraction mechanisms using an SLM technique: A, extraction with the analyte undergoing reaction in the acceptor phase; B, extraction with formation of ion pairs; C, extraction utilizing a compound being the analyte carrier in the organic phase with a subsequent reaction in the acceptor phase; D, extraction utilizing a compound being the analyte carrier in the organic phase.

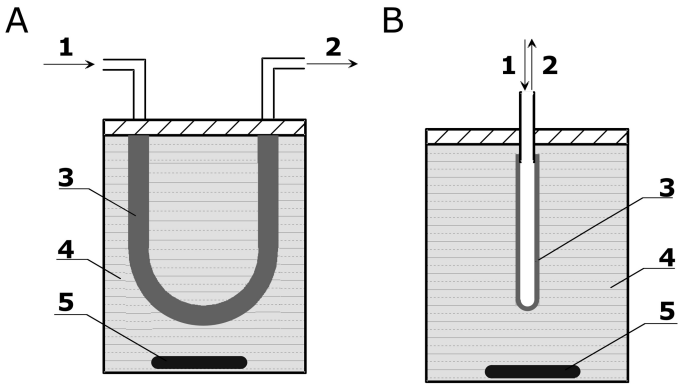

FIG. 14. Schematic diagrams of devices for extraction employing an HF-LPME technique: A, U-shaped polymeric tube, extraction can be performed in either static or dynamic (flow of the extracting agent) mode; B, polymeric tube mounted on a joint permitting dynamic introduction and removal of the extracting agent to and from the system. 1, direction of introducing the agent into the system; 2, removal of the agent from the system; 3, polymeric tube (membrane); 4, sample; 5, stir bar.

Consequently, a chemical modification of the environment of donor or acceptor plays an essential role in this technique. The efficiency of the whole process is governed by the partition coefficient between donor (original sample) and acceptor (secondary sample) phases, while the third phase of the polymeric membrane serves as a carrier medium. An achievement of high values of the analyte partition coefficient $K_{ss/os}$ is possible not only by adjustment of the pH of solutions but also by chemical reactions such as complex formation, ion pair formation, chelating, etc. (52, 53). Some freedom of choice of the adequate mechanism of extraction results in the significant increase of selectivity of the SLM technique.

The mechanisms of extraction in the three-phase system are presented schematically in Figure 13. From the scheme it maybe delivered that carrying out of the efficient extraction of analytes of an ionic form is possible, even when the partition coefficient donor—organic phase (polymer) is low if the partition coefficient organic phase-acceptor is high enough. It means that changing a two-phase system into a three-phase system is sufficient to make possible the enrichment of analytes of low $K_{ss/s}$ value (51).

There are many possibilities for building assemblies for membrane microextraction (9). Presently, a construction based on using a hollow fiber of the porous polymer (HP-LPME) is most frequently applied (48, 54). Schematic diagrams of devices for the HL-PME are presented in Figure 14. Advantages of this system are: low cost and easy exchange of the polymer tube, which allows avoiding the memory effect of membrane. The extraction itself can be easy to automate by using a typical automatic sampler (26). SLM techniques are most often used together with the HPLC or CE techniques because of the phase of acceptor (water). On the other hand, introducing to the procedure the additional step of phase-switching allows one to apply the SLM technique in combination with gas chromatography (55).

GAS-LIQUID EXTRACTION

From the point of view of the process mechanism, the extraction of organic analytes from gaseous matrices using liquid extractants can be carried out in two ways, depending on properties of the analyte:

analytes of high partition coefficients $K_{e/s}$—organic extractants can be applied directly—no additional modifications are needed. This process runs with the use of the partition mechanism as for typical extraction in the two-phase system;

analytes of low partition coefficients $K_{e/s}$—a preliminary derivatization is required to trap the analytes. The process efficiency depends on both rate and efficiency of the reaction of derivatization. The most frequently used matrix for derivatization agents is water, which is why derivatization techniques are usually applied together with HPLC.

From a technical point of view. two devices are most often used: impingers and denuders.

Impingers. Impinger extraction is carried out in direct contact of both gaseous and liquid phases. In the simplest setup, a gaseous sample is pumped through a tube with its outlet placed closely to the bottom of the flask filled with extractant. Extraction is carried out under conditions ensuring quantitative trapping of analytes in extractant—the gas stream coming out from the jet end of the tub impinges against the bottom of the flask, creating bubbles, which significantly increases the interphase surface, accelerating the extraction of analytes. Moreover, by choosing adequate reactants, analyte isolation may be carried

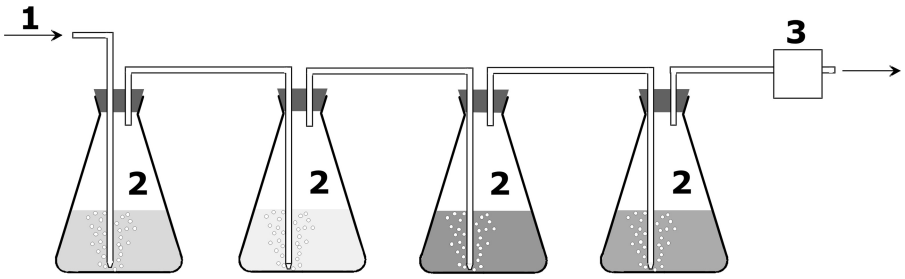

FIG. 15. Schematic diagram of a system employing an impinger technique of extraction: 1, direction of the gaseous sample flow; 2, flasks containing different extracting agents (arranged in series); 3, pump forcing the sample flow.

out selectively. Such solutions are also applied as multistage extractions, when the different, chemically active compounds are in consecutive washers (Fig. 15) (56).

The relatively high solvent consumption (also organic solvents if they are used) is a fundamental fault of impinger extraction. The sufficiently long time of contact of both gaseous and liquid phases is the basic condition of quantitative extraction. Therefore, the use of relatively large quantities of extractant is necessary (several to tens ml). As the result, the value of enrichment factor decreases significantly. The introduction of additional stage of sample concentration is necessary, which can result in analyte losses and potentially complicate the analytical procedure.

Denuders with Liquid Absorbents. Denuders are specific devices suitable to isolate analytes from the gaseous samples. Their specificity stems from the fact that they are designed especially for analysis of gaseous samples containing solid particles or aerosols (57). For heterogeneous samples the difficulties appear especially in the case of isolation techniques, in which sorptive devices of filter abilities are used. The presence of solid particles in the matrix can affect the results of determination of gaseous samples components in different ways (58, 59). In the case when analytes occur in both phases simultaneously, the deposition of the solid phase (on a bed or filter) takes place as the sample passes through sampler. The trapping of low, or liberation of more volatile, compounds can occur and consequently change composition of the investigated sample. In turn, isolation of the analytes where no filters are used causes the simultaneous trapping of analytes from both phases, and their collective determination leads to considerable errors (60). The principle of operation of denuders is schematically presented in Figure 16.

The essence of denudation phenomenon is a motion of particles and aerosoles being a result of the two forces:

- A force parallel to the direction of the gas stream, resulting from forced flow; and
- A force perpendicular to denuder walls, resulting from radial diffusion.

The process of isolation and enrichment of analytes takes place directly from the original matrix: analytes present in the gaseous phase due to the high diffusion coefficients reach the surface of the retaining medium, while solid particles and aerosols pass the tube practically without contacting the walls of the device.

Denuders based on a diffusion mechanism are often used to determine inorganic analytes (61–63). Few applications in the isolation of organic analytes are limited to compounds of low volatility (64, 65) or compounds enabling derivatization (66). Denuders based on the application of liquid extractants,

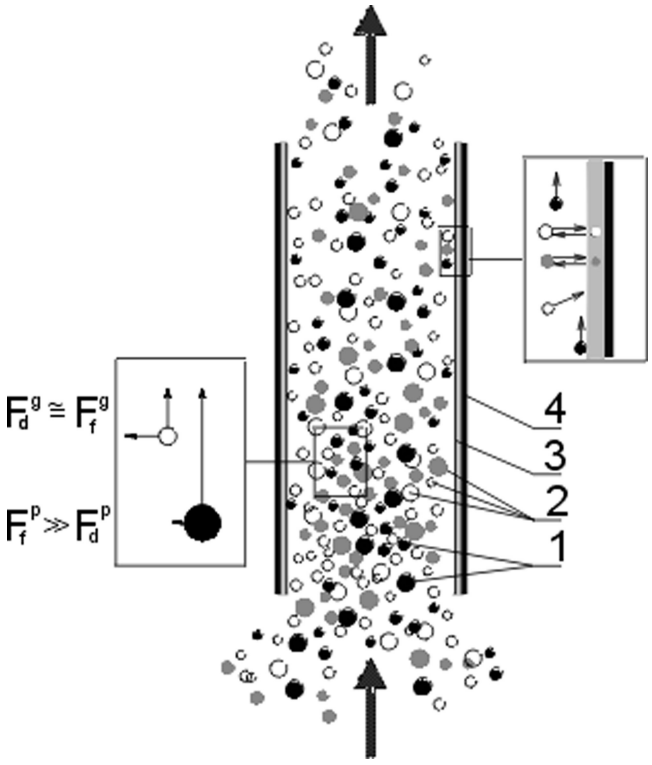

FIG. 16. Principle of the isolation of analytes utilizing the denudation phenomenon: 1, solid particles; 2, analyte in the gaseous phase; 3, film of the extracting agent; 4, denuder wall. F—forces acting on the molecules and particles in the gaseous phase, subscripts and superscripts denote: g, gaseous phase; p, solid particles (aerosols); d, diffusion component of the force; f, flow component of the force.

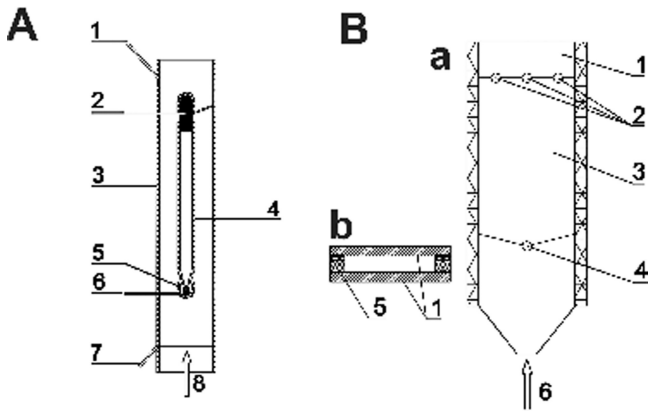

FIG. 17. Schematic diagrams of wet denuders: A: cylindrical configuration: 1, inlet of the extracting agent (outer wall); 2, inlet of the extracting agent (inner wall); 3, outer tube; 4, inner tube; 5, inner tube absorbate collector; 6, outlet of the absorbate; 7, outlet of the absorbate from the outer tube; 8, stream of the sample. B: parallel plates configuration: a, cross-section; b, longitudinal section; 1, glass plate; 2, inlet of the extracting agent; 3, part of the plate with porous surface; 4, outlet of the absorbate; 5, gasket; 6, stream of the sample.

known as wet denuders, are most often used in the configuration of parallel plates (67, 68) (Figure 17A), cylindrical (69–71) or annular (Figure 17B) (72). Generally, both gas and extractant streams are passed in countercurrent directions: the air stream is pumped at the bottom, while the liquid is delivered at the top of the device. The liquid solvent flowing down washes the device walls, forming a thin film. The wet annular denuders can operate also in the horizontal position—a film of the extractant is obtained by the rotation of the device rings (73, 74).

Another solution uses devices known as diffusive scrubbers (75–77). In denuders of this type, the gaseous sample and trapping medium are separated with a permeable membrane. The analyte isolation proceeds in two steps: denudation to the membrane surface and permeation. Both the ionic-exchangeable (cationic and anionic-exchangeable) (78) and the porous membranes are used, depending on the type of analyte (79, 80).

Gas-Phase Extraction

Gaseous-phase extraction techniques are the most frequently applied techniques for isolation of volatile organic compounds (VOC) in liquid and solid samples. One of the reasons is their natural compatibility with gas chromatography (81). There are a variety of different techniques utilizing gaseous media as an extractant. Among these, four play particularly important roles:

- Dynamic headspace analysis—gas-phase extraction with the simultaneous trapping of analytes (Purge &Trap, PT);
- Static headspace analysis (S-HS);

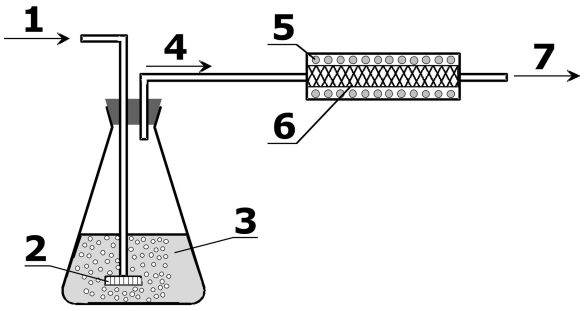

FIG. 18. Experimental set for the extraction of analytes using a PT technique: 1, direction of the stripping gas (inert gas); 2, porous glass frit; 3, sample: 4, gas containing enriched analytes; 5, heater permitting thermal desorption; 6, sorbent trap; 7, gas chromatograph.

- Headspace Solid Phase Microextraction (HS-SPME); and
- Membrane extraction techniques.

Next, the principles of these four techniques are discussed with regard to their field of application, sensitivity and possibility of automation.

Gaseous Phase Extraction with Simultaneous Analytes Trap. PT technique is the one most frequently used for determination of VOCs in liquid samples. It is also recommended by U.S. Environmental Protection Agency (EPA/SW-846-5030A and 8260A). The procedure of analyte isolation consists of two stages: analyte extraction (purge) from the sample by the stream of an inert gas and their subsequent trapping in a suitable trap. A general scheme of the PT device is presented in Figure 18.

There is a wide spectrum of analytical techniques applied as traps, from cryogenic traps (82) through traps packed with a suitable sorbent (83), to open tubular traps (84, 85). It is worth noting that in most cases, subsequent liberation of the analytes from the trap is carried out by thermal desorption, thus eliminating organic solvents from the analytical procedure. An inert gas is introduced to the sample by bubbling to increase the rate and efficiency of extraction. To achieve highly quantitative results, gas-phase extraction must be exhaustive. Otherwise, it is difficult to unambiguously relate an amount of extracted analyte to its concentration in the original sample. Consequently, significant volumes of an inert gas are usually required (dependent on the analyte's volatility). One drawback is that significant amounts of the water vapors are transferred to the trap, which raises the necessity of their elimination from the inert gas, since they can disturb further stages of the procedure (e.g., cryotraps) (82).

In view of the first procedure stage—gas-phase extraction, an application field of the PT techniques is limited to organic analytes of high volatility. On the other hand, the extraction procedure does not introduce any restrictions to analyte polarity (86, 87). Limits of quantification of the PT techniques depend, to some extent, on the chosen technique of analytes isolation from the inert gas stream. In the case the trap packed with sorbent

bed as well as in the open tubular trap the breakthrough volume is critical parameter, limiting volume of inert gas used in extraction. Overall it should be emphasized that among gas phase extraction techniques, the PT techniques allow to reach the lowest limits of detection on the level below ppt (88).

Static Headspace Analysis. Static techniques of the headspace analysis are the simplest among gas phase extraction techniques in regard to instrumentation. The classical solution is to place the sample into gastight container, leaving an empty space subsequently filled with the inert gas. After equilibration, a small volume of the gaseous extract is sampled and injected directly into the gas chromatograph. Such solution permits easy automation of the analytical procedure; however, this process in consequence of uncontrolled diffusion of analytes to the atmosphere is exposed to loss of analytes during gas sample handling.

On the other hand, application of the syringes equipped with a gastight valve (on the needle) allows avoiding analyte losses but at the same time the possibility to automate is lost. These restrictions are overcome in technique, based on the direct injection of the headspace sample to the gas chromatograph. A scheme of such assembly is presented in Figure 19. During the first stage, the excess volume of the inert gas is injected to the container containing the sample, creating overpressure. After the equilibrium state is established, the valve is opened and the column is filled with the expanding gas. The quantity of gas injected to the column can be controlled by means of the controlling the pressure in the chromatographic column.

If the headspace sample expands to both the precolumn and the cryogenic trap, a focusing of the analyte is achieved before its injection to the chromatographic column. The sensitivity of the S-HS technique depends on analyte concentration in the gaseous phase and volume of the headspace sample. Under given conditions, the concentration of the analyte in the headspace phase depends on its concentration in the original sample, on its partition coefficient between the phases and on the inert gas-sample volume ratio. One of the ways to adjust the extraction process to the expected analyte concentration in the sample is by changing the volume of the headspace phase.

For relatively high content of analytes in the sample, it is reasonable to decrease the volume of the headspace phase while the high concentration of the analyte in the headspace phase allows us to sample only the small volume of the gas. In such cases the gaseous sample can be injected directly into the chromatograph, omitting focusing and the removing the possible traces of water stages. On the other hand, samples with low analyte concentration required a larger volume of headspace phase, which in turn results in the necessity of the use of the analyte focusing stage. Additionally, if water samples are analyzed, it is necessary to introduce the procedure of water removal.

Considering the preceding limitations, compounds of relatively high volatility and present in the investigated sample on the ppb level are within the range of practical use of S-HS techniques (81). In some cases, to extend the S-HS application range with less volatile analytes, the temperature dependence of the partition coefficient can be used (82). On the other hand, sample heating increases water contents in the headspace phase; thus, its removal become necessary. Nevertheless in view of its simplicity, possibility of automation and compatibility with gas chromatography, S-HS techniques are widely used for the determination of VOCs in both the liquid and solid (being in contact with the liquid phase) samples. It should also be noticed that as for other PT techniques, the applicability of H-HS depends only on analyte volatility regardless of their polarity.

Headspace Solid Phase Microextraction. The HS-SPME technique is a modification of the previously described static headspace technique. The modification is by the introduction of an additional equilibration stage where analytes are distributed between sample headspace and sorbent of the SPME device. Technically it is achieved by simple introduction of the SPME fiber into a gastight vial and immersion into the headspace phase in contact with the sample (Figure 20). The extraction is carried out until the equilibrium state is reached. After extraction, analytes may be thermally desorbed in the body of the GC injector. Thus several problems of the S-HS techniques are avoided:

- since isolation and enrichment of analytes proceed in one stage, both analytical procedure and apparatus are simplified, analytes are trapped and subsequently transported to the GC using SPME device (inert gas serves

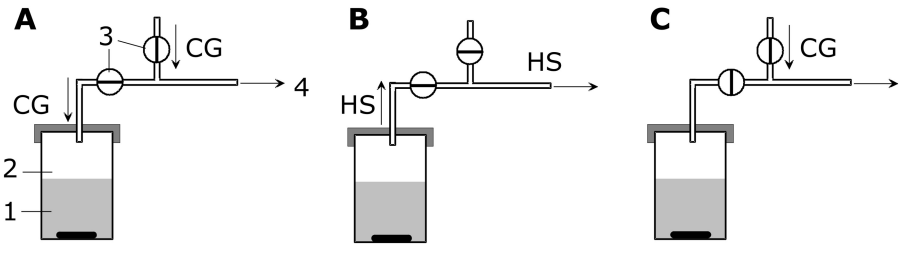

FIG. 19. Stages of a static headspace process using overpressure of the inert gas: A, pressurization of the tank containing the primary sample with carrier gas; B, introduction of headspace sample onto a chromatographic column; C, chromatographic separation; 1, sample; 2, headspace; 3, shut-off valves; 4, gas chromatograph; CG, stream of the inert gas (carrier gas); HS, stream of headspace phase.

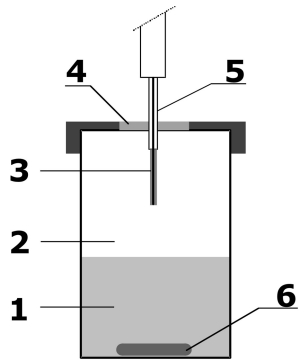

FIG. 20. Schematic diagram of an experimental set for extraction of analytes using an SPME-HS technique: 1, sample; 2, headspace; 3, SPME fiber; 4, membrane; 5, needle of the SPME device; 6, stir bar.

only as an intermediate extractant) what decreases the risk of the sample loss/contamination);
- if hydrophobic sorbent is used to trap analytes (e.g., PDMS) then the presence of water does not disturb analytical procedure.

Using a three-phase system instead of a two-phase system significantly changes the application range compared to the classical S-HS technique: it may decrease limits of detection of VOCs, then again gives the possibility of determination of low volatile compounds. Moreover, changing the type of the sorbent makes it possible to isolate analytes not only on the basis of their volatility, but also playing up the other physicochemical properties such as the polarity or presence of the specific functional groups.

The increase in the number of phases also brings some inconveniences, mainly in the calibration procedure. First, the final amounts of the analytes in the sorbents are the result of two equilibriums; thus, the very precise control of the volumes of all phases in the system is necessary (89). Furthermore, for sake of analysis repeatability, it is necessary to control many additional parameters influencing equilibrium state, such as extraction time, temperature, mixing rate, and the shape of vials with the investigated sample (90). Nevertheless HS-SPME is currently the most rapidly developing technique in the group of gaseous-phase extraction techniques (81).

Membrane Extraction with the Sorbent Interface. Membrane Extraction with the Sorbent Interface (MESI) is employed in analyte isolation both from the liquid and gaseous phases. The extraction is most often carried out by means of a silicone tube (membrane) immersed in the investigated sample. The inert extraction gas after passing the tube enter sorption trap (may be cooled) were extracted analytes are retained. The step of the analyte focusing is absolutely necessary as the gaseous extract is highly diluted. Extract dilution is caused by the small interphase surface and low diffusion rate of analytes through the membrane (for gaseous samples enrichment do not occur due to thermodynamic restrictions). Taking into account hydrophobicity of PDMS (gaseous extract do not contain water), all steps of the procedure, i.e., gas phase extraction, analytes trapping and GC analysis can proceed in series and (Figure 21). After extraction, analytes trapped in the sorptive tube are thermally desorbed and introduced with the stream of carrier gas onto the head of GC column. Additionally, absence of water allows focusing analytes using first segment of GC column, which significantly simplifies the setup.

Comparing to other gas-phase extraction techniques, membrane extraction with the sorbent interface considerably slows down the analytical procedure due to a limited rate of diffusion of the analytes to the surface and through the membrane. On the other hand, the MESI technique gives the possibility of carrying out the extraction process in a selective way (different types of the membrane). The lack of typical problems related to the presence of water in an investigated sample is also an unquestionable advantage of the MESI technique.

Sorptive Extraction

As was mentioned before, the use of organic solvents is one of the disadvantages of classic liquid-phase extraction techniques. It is inconvenient not only environmentally but also for practical reasons. In the case when solvents are used, the designing

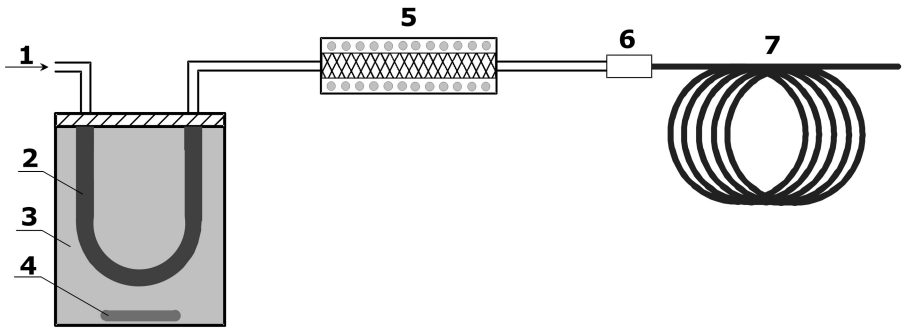

FIG. 21. Example of an experimental setup for the extraction of analytes using a MESI technique: 1, inlet of the inert gas; 2, polymeric membrane; 3, sample; 4, stir bar; 5, thermal desorber with a sorbent bed (usually equipped with a cooling system); 6, connecting element; 7, capillary chromatographic column.

of systems equipped with numerous pipelines and pumps is required, which significantly complicates the apparatuses and increases its cost. Moreover, operations are usually multistage, thus increasing the possibility of analyte losses or sample contamination. For these reasons, an urgent need exists to seek sample preparation techniques eliminating organic solvents from the analytical procedures. These changes were additionally forced by requirements included in the aforementioned Montreal Protocol. Research is carried out in two main directions: widening applications of adsorbents suitable for thermal desorption and isolation of analytes using absorbents. While, in both cases, the analytes are frequently released by extraction with organic solvents, taking into consideration the present trends. The aforementioned techniques are discussed here only in applications employing the sorption–thermal desorption systems.

Solid-Phase Extraction (Adsorbents) (SPE). Techniques in which analytes are accumulated on the surface of adequate solid adsorbent currently play a dominant role in the sample preparation process and are most often recommended for routine analyses. As mentioned before, one of the research goals in the usage of adsorbents is their application together with thermal desorption of analytes. In this context, one can distinguish several desirable adsorbent features: thermal stability and large specific surface. Possibly homogeneous and controlled surface properties with respect to the analyte–adsorbent interactions: nonspecific–addressed to the wide group of compounds; and specific–in applications focused on one type of analyte.

Generally, adsorbents can be divided into two main groups:

1. Adsorbents based on different forms of carbon, for example, active carbon, graphitized carbon and carbon molecular sieves. Characteristic feature of this group of adsorbents is their very high thermal stability (up to 450°C). These carbon adsorbents are also characterized by very high affinity towards organic compounds, resulting in excellent retention properties. Traps with these adsorbents are used for collection of a wide range of organic compounds of diverse volatility, starting from ethane (on molecular sieves) (91) up to chlorinated biphenyls (92). On the other hand, this strong affinity towards organics may become a problem during desorption. In spite of limitation of the number of active centers in the graphitization process, thermal desorption of less volatile compounds must be carried out at high temperatures, and it is often incomplete. Moreover, such extended heating times can result in thermal decomposition of analytes.
2. Polymeric adsorbents: were introduced to eliminate abovementioned problems related to carbon adsorbents. A variety of porous polymers are available, differing in both chemical (polarity, surface activity, etc.) and physical properties (thermal stability, specific surface) as for example Tenax, Chromosorb, and Porapak series (6). Optimized and precisely controlled composition of these polymers practically eliminates their catalytic activity and reduces interactions with interfering substances present in the sample (e.g., hydrophobic properties of Tenax). On the other hand, the use of polymeric adsorbents has also negative consequences–thermal desorption may lead to adsorbent decomposition and/or liberation of interfering compounds (for example benzene derivatives) (93).

The classification of adsorbents presented here is very simplified and covers only the most frequently used adsorbents. One can observe, however, the meaningful developments in solid-phase extraction techniques oriented towards specific analytical applications, like isolation of specific classes of compounds or even individual compounds (94). These achievements of several past years are principally results of employing advanced techniques of material engineering, permitting design of new types of adsorbents, characterized by both specific structure and surface interactions, like immunosorbents (95) or molecularly imprinted polymers (96, 97).

From a technical point of view, analyte isolation by means of adsorbents can be carried out in both the passive (98) and the dynamic modes (99). The former is suitable for sampling over longer periods of time, for example, in air pollution or workplace air monitoring (100). In the case of the dynamic mode, the sample is pumped/sucked through the trap (usually cylindrical) packed with the adsorbent bed. The flow rate and volume of the sample are adjusted to the capacity and retention power of the trap. The maximum sample volume that can be passed through the trap is determined by the breakthrough volume of the earliest eluted analyte of interest. The common solution is to combine in series traps packed with different adsorbents, which allows isolation of compounds varying in volatility and chemical properties (99).

ABSORPTION-BASED EXTRACTION

This group of techniques due to partition mechanism utilized allows avoiding some faults of the abovementioned adsorption based techniques: the use of organic solvents, incomplete desorption, thermal decomposition of analytes, artifacts formation. In the partition mechanism, analytes are dissolved in a liquid-like phase of polymer, thus their subsequent desorption may be performed under mild temperature conditions what eliminates the risk of analytes decomposition. Moreover, sorbents do not show the catalytic properties thanks to occurrence of merely unspecific interactions analyte–absorbent (the lack of active centers).

The most frequently used absorbent is polydimethylsiloxane. There are some reasons that favor the use of PDMS: it is generally applied as a stationary phase in gas chromatography (accessibility of physicochemical data); stable up to ca. 300°C; chemically inert (the lack of catalytic surfaces); it is possible to easily determine or to estimate theoretically the physicochemical properties (the partition coefficient of analyte); glass state transition temperature (−126°C) and melting point (−50°C) are significantly below the extraction temperature (100); PDMS has liquid properties (diffusion coefficient much higher than for

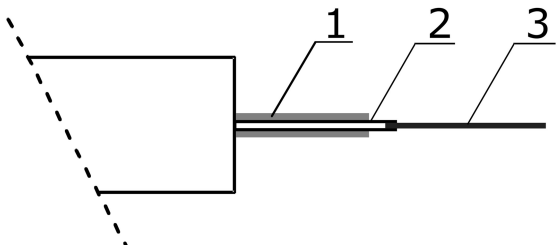

FIG. 22. Schematic diagram of the SPME device: 1, needle; 2, tube to which the quartz fiber is fixed; 3, the quartz fiber covered with the sorbent film (see text for details).

solids and Nernst's partition law can be used for the quantitative description).

Additionally, thermal desorption from PDMS-containing traps produces a very low baseline on chromatograms in blank tests. Moreover, it is easy to identify products of thermal decomposition (mainly low mass silanes) when mass detectors are used (101). Sorbent extraction techniques are presented, discussing principles and applications of such techniques as: Solid-Phase Microextraction, Stir Bar Sorptive Extraction, Open Tubular Traps, and Gum Phase Extraction (GPE).

Solid-Phase Microextraction

Solid-phase microextraction was introduced in the early 1990s (102). The SPME probe is made of fused silica fiber coated with a film of a suitable sorbent (usually 5–100 μm thick). The fiber is mounted in the needle of a syringe-like device (Figure 22) (7). This arrangement prevents mechanical damages to the fragile fiber, especially when the fiber is being introduced through a septum into the injection chamber of a GC. During sampling, the fiber is pushed out of the needle with a plunger and exposed to the sample bulk. Once extraction is completed, the fiber is retracted into the needle. Such a procedure allows not only for mechanical protection but also reduces possibility of analyte losses (desorption) or sorbent contamination when the probe is moved to the GC injection chamber. Concentration of the respective analytes in the original sample can be found on the basis of known values of their partition coefficients between the absorbent and sample matrix. An important practical aspect of this technique is the possibility of determination of the PDMS/sample partition coefficient on the basis of retention data of the chromatographic analysis. Partition coefficients of the analytes in the octanol/water or octanol/air systems can also be used as an approximation of the proper values.

The SPME technique finds its application in the analysis of samples of all types (gaseous, liquid and solid). In the case of liquid samples, the head-space analysis is often performed (11). An advantage of this technique is acceleration of the extraction process (high diffusion coefficients in the gaseous phase) and extended lifetime of the fiber (lack of contact with sample components, which can contaminate or block the sorbent, e.g., in analyses of biological samples) (103). The same procedure is often applied in analysis of solid samples (104). Until now, SPME has found many applications in analyses of numerous types of analytes, e.g., pesticides, drugs, herbicides, and a wide range of other organic environmental pollutants (7, 105, 106). Such common use is the result of undeniable advantages of the SPME—setup simplicity, low cost and easy automation of the analytical procedure. Nevertheless, SPME reveals also some drawbacks and limitations. Small dimensions of the SPME probe (advantageous for the aforementioned reasons) result in equally small volumes of sorbent films (ca. 0.7 μl). Consequently, it is often impossible, due to thermodynamic restrictions, to achieve sensitivity enabling quantitative determination of volatile or polar organic compounds, especially when analysis of trace or ultra-trace components has to be performed.

Stir Bar Sorptive Extraction

Stir bar sorptive extraction is one of the methods developed to avoid problems resulting from insufficient amounts of sorbent (12) (in a similar approach instead of stir bar segment of polydimethylsiloxane rod is used as a probe (107)). The aims of developing SBSE were to reach lower detection limits compared to other techniques and to decrease analyte losses caused by their adsorption on the glass stir bar (the most commonly applied technique of sample agitation). Increased amount of the sorbent in SBSE makes it reasonable to recovery using Eq. [15]. However this equation calculating analyte concentration in the original sample usually also serves to predict whether or not (given $K_{e/s}$ and $\beta_{s/e}$) the extraction process is exhaustive. Such knowledge may be very important for practical reasons. If expected recovery exceeds 90% (usually considered as an exhaustive) calibration of sampling probe is unnecessary as the results obtained are quantitative by definition.

In the SBSE technique, the extraction is carried out using a magnetic stir bar coated with polydimethylsiloxane (Figure 23) (108). During extraction, the stir bar is rotated with a magnetic stirrer to accelerate the analyte diffusion to the sorbent surface. After extraction the stir bar is carried to the specially designed thermal desorber (for GC analysis) (109, 110) or to the suitable

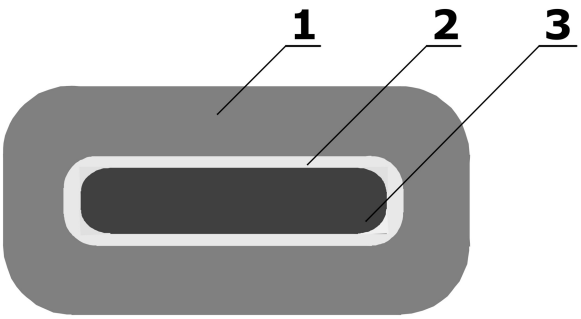

FIG. 23. Longitudinal section of the SBSE device: 1, sorbent layer; 2, glass body; 3, magnetic core.

extractant (LC or GC analysis) (111, 112). Stir bars are typically coated with the amount of sorbent of 50–250 μl, which in many cases is sufficient for exhaustive extraction (111, 113). A practical usefulness of the SBSE was tested extracting compounds of different types e.g., polycyclic aromatic hydrocarbons (112, 114), off-flavors (109), pesticides (113, 115) and organotin compounds (116) and from different matrixes, e.g., water, beer, yogurt, wine and biological fluids. The SBSE technique was also applied for the headspace phase analysis of liquid and solid samples (117, 118).

On the other hand, SBSE has one important drawback: such operations as sampler removal from the sample, its rinsing and drying (or solvents extraction, if necessary) are made manually at present. Until now only thermal desorption could be performed automatically; thus the whole analytical procedure is rather laborious.

Open Tubular Traps. Open tubular traps are made of a tube covered inside with a coating of analyte-retaining medium. Sampling consists in sample pumping or suction (gas samples) and is like the procedure applied in the case of traps packed with adsorbent beds. Adsorbents are also often applied as the trapping material, for example porous polymers (119) and carbon-based adsorbents (120, 121). In view of the earlier remarks concerning adsorbents, OTTs are discussed here using the example of traps with a polydimethylsiloxane stationary phase. The OTTs are similar to typical capillary columns used in gas chromatography, thus their connection to the GC systems is rather easy. Thanks to the open space inside, the traps show the low flow resistance (per unit of length), an important factor in analyses of gaseous samples.

In these applications the suction of sample is preferred, and a purpose of this solution is to avoid sample contamination or losses of analytes in the pumping devices. An overly high flow resistance can result in low sample flow, leading to meaningful extension of the sampling time. Besides, the open space left in the trap is also very advantageous in analyses of water samples and water-saturated gaseous samples. In such cases, complete removal of water from the trap can be achieved by passing a small volume of dry inert gas through the trap after sorption. The possible loss of the more volatile analytes can be avoided in this way.

The dimensions of the most frequently applied traps are: from 0.3 to 0.7 mm in diameter and from 1 to 3 m in length. The parameter that determines sampling capacity of the trap is its breakthrough volume, which can be expressed as (122):

$$V_B = V_M + (1 + k') \times \left(1 - \frac{2}{\sqrt{N}}\right) \qquad [24]$$

where V_B is breakthrough volume of the trap, V_M is dead volume of the trap, k' is the chromatographic capacity coefficient, and N is the number of theoretical plates.

Equation [24] explains why the thick coatings of sorbent should be employed. While the increase of the stationary phase thickness, according to van Deemter's equation, results in decrease of the number of theoretical plates (N), but there is a significant increase of the capacity coefficient value (k') at the same time. Thus, the open tubular traps with the thick film of stationary phase are preferred (122, 123). The other way of increase of the trapping properties of traps is an enlargement of their inside diameter with the maintenance of the stability of phases volume ratio in the trap at the same time (124). It results in both multiplying the trap breakthrough volume and lowering the pressure drop across the trap.

The OTT technique was applied in isolation/enrichment of the wide group of compounds diverse as to their polarity and volatility (17, 18, 65). It was used in analyses of gaseous, liquid and solid samples (head-space) (125). In the case of analysis of analytes from liquid samples, the head-space analysis was employed as well as the direct introduction of the liquid sample to the trap. In the latter case, this kind of trap results in some faults. The primary fault is the weak retention of analytes from the liquid phase, caused by the low diffusion coefficients in this phase. To allow for this effect, one should use very low sample flows through the trap, which extends the time of sampling significantly (19).

The sampling in the equilibrium mode can be employed as an alternative (127, 128). In this case there is no limitation of the flow rate, with the extra advantage of high flow rates significantly reducing the time needed to reach the equilibrium. On the other hand, knowledge of partition coefficients and control of parameters affecting them (for example—temperature) are necessary.

Gum-Phase Extraction (GPE) (Traps with a Sorbent Bed). In the case of the GPE technique, a bed consists of particles of 100% polydimethylsiloxane unlike in the case of traps containing the solid adsorbent bed. Problems related to incomplete desorption or decomposition of analytes during the thermal desorption are avoided in this way. This configuration also allows increasing significantly the quantity of trapping material as compared with the SPME and OTT techniques (better volumes ratio of phases (β) in a system) (129). When the GPE technique is used for analyses of water samples, the loss of more volatile analytes during drying the bed becomes a serious problem, despite the fact that the hydrophobic material is used as a sorbent (5). Hence, this technique finds its application, first of all, in gaseous samples analysis (130). However, especially in the case of samples saturated with water vapor, problems with water removal can appear.

The increase in the retention power of the trap is the basic advantage of the GPE technique. It is the consequence of decreasing the distance that the analyte has to cover to reach the sorbent surface and of increasing the sorbent surface (the interface). Consequently, the high flow rate values of the sample through the trap can be applied (to $2.5\,l \cdot min^{-1}$) (131). When the breakthrough volume is insufficient to accumulate such quantity of analyte, which is required by the type of detector chosen, the authors suggest employment of the equilibrium extraction mode (132).

SUMMARY

On the basis of this review of sample preparation techniques for determination of organic compounds, we can state that no universal technique exists. Each technique has some restrictions related to the type of analyte, matrix or the range of concentrations of analytes in the investigated sample. In principle, each sample type requires an individual approach. However, some basic trends appear in the development of these techniques. The trends are connected mainly with restrictions of the use of organic solvents in analytical procedure. This direction of development can be observed, first of all, in growing usage of techniques based on polymeric absorbents, chiefly polydimethylsiloxane. This group of techniques includes solid-phase microextraction, stir bar sorptive extraction and open tubular traps. On the other hand, in view of the nonpolar nature of this sorbent, employment of these techniques in analyses of polar analytes is limited.

Application of the membrane techniques seems to be more attractive in the context of polar analytes. These techniques (especially the version with the restricted quantity of analyte) allow us to achieve significant enrichment of analytes and high selectivity at the same time. The long analyte extraction time and the arduous calibration procedure can be a drawback in the case of the membrane techniques. On the other hand, these shortcomings appear only in the specific cases when the chromatographic separation is less time-consuming than the analyte extraction procedure. It should be mentioned that the time of extraction also begins to be a significant parameter in the case of techniques, in which the increased quantities of polymeric absorbents (for example, SBSE) are used. One should also note that almost all of the discussed techniques have a version that permits easy automation of at least some part of the analytical procedure, though it may be relatively difficult to achieve and rather expensive as in the case of the SDE and SBSE techniques.

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