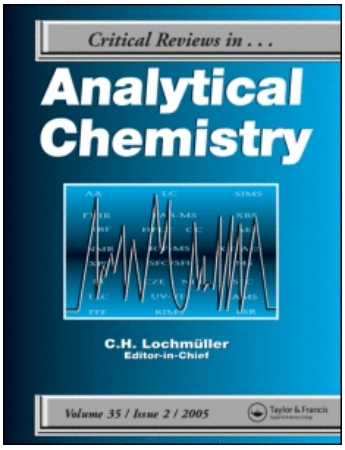

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Modern Techniques of Extraction of Organic Analytes from Environmental Matrices

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Online publication date: 18 June 2010

To cite this Article Rawa-Adkonis, Magdalena , Wolska, Lidia and Namieśnik, Jacek(2003) 'Modern Techniques of Extraction of Organic Analytes from Environmental Matrices', Critical Reviews in Analytical Chemistry, 33: 3, 199 — 248
To link to this Article: DOI: 10.1080/713609164
URL: http://dx.doi.org/10.1080/713609164

Critical Reviews in Analytical Chemistry, 33(3):199–248 (2003)

Modern Techniques of Extraction of Organic Analytes from Environmental Matrices

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ABSTRACT: Isolation and/or preconcentration of analytes from samples characterized by complicated composition of the matrices consist an essential step of analytical procedures used for determination of trace organic components.

Different analytical approaches used in analytical practice can be classified according to parameters as follow:

- labor and time consumption
- consumption of solvents and other reagents
- mode and efficiency of extraction process
- level of the automation of the operation

There are plenty of original works focused on elaboration of new techniques of extraction of wide spectrum of analytes.

This article deals with an trial of systematization of information available connected with new methodological and technical proposals in this field.

KEY WORDS: trace analysis**,** techniques of extraction, environmental samples.

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1040-8347/03/$.50

I. INTRODUCTION

Environmental demands and ecotoxicological considerations call for action in two principal directions:

- the search for environmental-friendly technologies that are characterized by the absence of or at least by low emission levels pollutants;
- the trend towards determination of board spectrum of analytes at low concentration levels (ppt or even ppb) in samples of varied matrix composition.

The latter approach has been facilitated by the introduction of a new generation of highly sensitive analytical devices and methods and by the development of new sample preparation procedure, that is, sample treatment prior to the final determination stage.

This line of action becomes particularly significant in modern environmental analysis. New detectors, although commercially available, are generally insufficiently sensitive to allow for the determination of the majority of analytes in environmental samples. For this reason, the optimization of the stages and operations associated with sample preparation becomes essential.[1]

In this respect, sample preparation comprises:

- isolation of the analytes from the original matrix and moving them to the receiving (secondary) matrix of simpler composition, with an optional enrichment of the analytes
- release of analytes previously kept in appropriate rap either in the isolation and/or enrichment stage
- removal of excess solvent and drying, purification, and fractionation of the extracts[2]

Most of these steps include the use of chromatographic techniques. These are most widely used for separation of mixtures into individual chemical species prior to the final determination. The operations involved in sample preparation are usually tedious and time-consuming and they are difficult to automate.

Today special attention is paid in environmental analysis to sample preparation methods that ensure reduction of amount of liquid solvents or even their complete elimination in the course of the analytical procedure. Further, the number of operations and processes involved in the sample preparation stage should be kept to a minimum.[3]

The issolation and/or preconcentration of analytes from samples characterized by the complex composition of the matrices consist of a very important stage of analytical procedures in the field of trace and environmental analytics. Our article focuses on new approaches in this field.

II. SOLID PHASE EXTRACTION (SPE)

Quite often general information can be found in the literature that the "romance" of researchers with the SPE technique started 20 years ago; however, this is not entirely true. The last 20 years have been characterized by a great interest in this technique, but the real beginning of SPE had place half a century ago in connection with trace analysis of organic contaminants in water. Since then hundreds of publications describing different SPE methods have been published. Also, many review papers and monographs on the subject were written.[4,5,6,7,8,9,10,11]

In the applications of the solid phase extraction technique into analytical practice, one can distinguish three very well-distinguished periods of time. They are as follows:[4]

- first attempts to apply of SPE technique ("active carbon period");
- the period of searching for more suitable sorbents;
- the period of technical development of SPE-based techniques for isolation and/or preconcenration of organic analytes from water samples;
- new directions in the application of SPE technique.

The usefulness of sorptive properties of solids in technological processes of water treatment has been known for long time.

Granulated Active Carbon, *GAC*, has been a popular sorptive material used in technological processes, but only later tests were conducted to

check whether the recovery of organic substances absorbed on GAC bed prior to analytical procedure and analyte identification was possible.

In 1951, *a pioneering work* on this subject was published by the employees of the U.S. Public Health Service, Cincinnati, OH.[12]

In the paper, a metal cylinder filled with 1200 to 1500 g of GAC was described, which served to enrich organic contaminants present in samples of filtered and unfiltered surface water. After filtering a known volume of water through the sorption trap, that is, active carbon filter, the trap was delivered to the laboratory. Then, the carbon bed was removed from the cylinder, dried in air, and extracted with diethyl ether in a Soxhlet apparatus. Organic compounds present in the obtained extract were classified into five groups, and some analytes were identified.

Since the publication of the above paper, many scientific centers have been conducting research on new methods for active carbon application in isolation and enrichment of organic analytes in water samples.

In their next publication,[13] the authors described the usage of a carbon filter of the dimensions 18 in × 3 in, designed to retain pesticides from hundreds of gallons of water filtered through the sorbent bed (the analytes were extracted with chloroform).

The important step in the development of SPE technique was the use a sorption tube containing a layer of active carbon that served as a trap for retaining analytes from water with the application of Closed Loop Stripping Analysis, CLSA.[14]

The main disadvantages of the carbon filters are as follows:

- irreversible adsorption
- chemical modification on the surface of the sorbent
- low recovery of analytes

The above negative characteristics caused that other materials were being sought in order to replace carbon with a sorbent devoid of these serious faults.

This period is connected with the intensive development of research procedures for novel types of sorptive materials (in an *off-line* mode) that lasted from the late 1960s until the beginning of 1980s, as follows:

- In the mid-1960s, the company Rohn & Haas introduced cross-linking polystyrene resin named Amberlite XAD-1.
- In 1996, the application of polymeric sorbent for isolating and enriching of organic contaminants in water samples was described for the first time.[15] A column 1 cm in diameter, containing a 7-cm-long XAD-2 sorbent bed, was used.
- In the following years, other sorbents from the XAD family, that is, XAD-2, XAD-4, XAD-7, XAD-8, were applied in analytical procedures.
- In 1972, a method for enriching organic contaminants in potable water was elaborated, based on the use of XAD-2 and XAD-7.[16]
- In 1973, a technique for extraction of organic analytes from water with the use of a sorption tube filled with Chromosorb 102 was described.[17]
- In 1974, a comprehensive study on the methodology for analyte enrichment with the use of XAD-2 was published.[18] It was concluded that this technique is useful for determining organic pollutants in water at the levels of 10 to 1000 ppb, while in the case of pesticides at the level of 20 ppt.
- In the next stage, the following sorbents were introduced to commercial markets, and therefore to analytical procedures:
- Porapak-type sorbents
- Chromosorb-type sorbents
- Tenax-GC; this sorbent found a particularly broad application in Purge and Trap (PT) technique
- In 1982, the first publication on the possible use of Tenax-GC as sorbent in a trap designed to directly retain analytes from a stream of liquid, which analytes were later directed to a chromatographic column (after thermal desorption), was published.[19]
- In this period of time, publications on the possible application of other types of sorbents (e.g., polyurethane foams, polypropylene, polytetra-fluoroethylene, and ion-exchange resins) in analytical procedures were written

- Chemically bound stationary phase, used to fill liquid chromatography columns, were also used to fill sorption tubes. The first papers on this subject were published in 1975.[20,21]
- New generations of carbon sorbents (carbon molecular sieves[22]) and graphitized carbon[23] were introduced. Thanks to the stringent quality of the production processes, sorbents of more homogenous structure and duplicable characteristics were produced

The introduction of a wide spectrum of sorptive materials into analytical procedures gave a new stimulus for the development of SPE methodology, as presented below:

- The introduction of commercially available extraction columns (e.g., Sep-Pak and Bond-Elut) used in an off-line mode. However, the undesirable phenomena and side-effects have been noted, such as
    - undesirable dilution (e.g., at the elution stage),
    - possibility of sample contamination.
- The idea of replacing off-line systems with on-line ones.[21] In an on-line system the analytes from the sorption trap are transferred directly onto a chromatographic column by a stream of carrier gas. In a simplified version, the analytes are directly enriched in the initial part of the column
- The introduction of on-line precolumn technology[20,24] that has occurred in connection with the development of two-dimensional liquid chromatography. A precolumn, which is equivalent to safety column in HPLC and can be replaced as frequently as needed, is a relatively inexpensive part of the equipment. Different types of sorbents are used to fill precolumns
- The application of two or more precolumns, set in a row, for isolation and enrichment of analytes.[25]
- The use of precolumn technology in gas chromatography (SPE-GC).[26] Due to the use of a six-way valve, it was possible to connect to the system a microcolumn filled with chemically bound silica phase (C8) in order to enrich pesticides and analytes from the PCB family in water samples. Next, the column was dried in a stream of helium, and analytes were eluted with hexane by using a retention trap
- The development of LC-GC technology in the end of 1980s
- Modern times: a period of dynamic development of SPE technology
- The application of new types of sorbents:
    - Porous graphitized carbon (PGC)[27]
    - PLRP-S[28]
    - Envi-Chrom P
    - Li Chrolut EN
    - Isolute EN
    - Chemically bound octadecyl phase (C18)[29]
    - Immunosorbents[30]
    - Molecularly Imprinted Polymers (MIPs)[31]
- The introduction of membrane extraction discs.[32] Speed discs contain PTFE matrix with embedded beads of an appropriate sorbent. The use of discs significantly reduces the time of analyte extraction. Speed discs are also used as precolumns in on-line SPE-HPLC systems[33]
- The application of extraction with supercritical liquids to release the retained analytes[34]
- The introduction of Solid Phase Microextraction (SPME)[35]

Solid phase extraction (SPE) has appeared as an alternative to liquid-liquid extraction owing to its simplicity, low cost and easy automation. However, the sorbent used in "classic" SPE is not highly selective, and therefore the analyte is retained together with other matrix compounds, which hinders its final determination by different analytical techniques (mainly chromatographic ones). Therefore, the development of complex applications using different washing solvents is necessary, thus reducing the inherent advantages of SPE.

There are several papers in which the application of solid phase extraction as a technique of isolation and preconcentration of analytes from different environmental matrices are described. In **Table 1** information on the recent applications of SPE techniques in analysis of environmental pollutants are collected.

TABLE 1
Recent Applications of Different Sorbents For Preconcentraction of Organic Contaminants from Air and Water Samples

Sorbent	Type of extraction device		Analytes	Matrice	Mode of		Technique of analysis	References
	cartridge	disc			extraction	desorption		
Polydimethylosiloxane (PDMS)	C		Nicotine	A	Off-line	TD	GC-NPD	[36]
			Volatile and semivolatile organic compounds	A	Off-line	TD	GC-MS	[37]
Sep-Pak C_{18}	C		13 pesticides	A, W	Off-line	E	GC-ECD HPLC-UV	[38]
Carbopack B/Carbosive SIII	C		Volatile organic compounds (8 analytes)	A	Off-line	TD	GC-FID GC-ITD	[39]
	C		Acidic pesticides	W	Off-line	E	GC-MS	[40]
Graphitized carbon black (GCB)		D	Polar pesticides and their transformation products	W	Off-line	E	LC-ESI-MS-MS	[41]
C_{18}	C		Polychlorinated organic compounds	W	Off-line	E	GC-ECD	[42]

TABLE 1 (Continued)
Recent Applications of Different Sorbents For Preconcentraction of Organic Contaminants from Air and Water Samples

C_{18}, C_{18}, C_{18}/OH	C		20 N-methyl carbonate pesticides and 12 of their polar metabolites	W	Off-line	E	HPLC	[43]
C_8		D	Atrazine, acetochlor, alachlor	W	Off-line	E	GC-NPD	[44]
ENVI-Carb Isolate ENV + LiChrolut EN	C		Antifouling pesticides and their byproducts	W	Off-line	E	HPLC- APCI-MS	[45]
C_{18}		D	12 pesticides	W	Off-line	E	GC-MS	[46]
XAD-2	C		Chlorobiphenyls, polycyclic aromatic hydrocarbons	W	Off-line	E	GC-ECD GC-MS	[47]
Isolute	C		Various pesticides with a wide range of polarities	W	Off-line	E	GC-MS GC-ECD	[48]
LC-18 EnviroPrep Octadecyl EnviroCarb Oasis HLB	C		Defoliants (tribufos, dimethipin, thidiazuron), herbicide (diuron), insecticide (methyl parathion)	W	Off-line	E	GC-NPD GC-MS HPLC-DAD	[49]
C_{18}	C		16 organochlorine pesticides	W	Off-line	E	LVI-GC-ED	[50]
Backerbond	C		22 pesticides	W	Off-line	E	GC-MS	[51]
C_{18}		D	18 pesticides	W	Off-line	E	GC-ECD	[52]

TABLE 1 (Continued)
Recent Applications of Different Sorbents For Preconcentraction of Organic Contaminants from Air and Water Samples

C_{18}		D	16 pesticides (triazines, organochlorine pesticides)	w	Off-line	E	GC-MS	[53]
C_{18}	C		36 pesticides	w	Off-line	E	GC-NPD GC-ECD GC-MS-MS	[54]
C_{18}	C		35 pesticides	w	On-line	E	LC-ESI-MS-MS	[55]
Zorbax SB C_{18} Zorbax RX PLRP-S	C		Neutral pesticides, phenalic compounds acidic herbicides	w	On-line	E	LC-MS LC-DAD	[56[
C_{18}	C		21 pesticides	w	Off-line	E	HPLC-ACPI-MS	[57]
Empore		D	17 pesticides	w	Off-line	E	GC-ED HPLC-UV GC-MS	[58]

TABLE 1 (Continued)
Recent Applications of Different Sorbents For Preconcentraction of Organic Contaminants from Air and Water Samples

ENVI-18	C		17 organophosphorous pesticides	W	Off-line	E	GC-FPD GC-EI-MS	[59]
ENVI-18	C		16 organochlorine pesticides, 17 organophosphorous pesticides	W	Off-line	E	GC-FPD GC-_ECD	[60]
ENVI-18	C		18 organochlorine pesticides, 21 PCB congeners 17 organophosphorous pesticides	W	Off-line	E	GC-FPD GC-_ECD GC-EI-MS	[61]
LiChlorut EN	C		Nitrophenols	W	Off-line	E	GC-MS	[62]
Hypersep Hypercarb supelclean ENVI-Carb	C		Quaternary ammonium herbicides	W	Off-line	E	CE	[63]
Abselut Nexus	C		Synthetic musk	W	Off-line	E	GC-MS	[64]
Empore		D	Methiocarb residues	W	Off-line	E	HPLC	[65]
Carbopack B	C		24 polar pesticides	W	Off-line	E	LVI-GC-MS GC-TSD	[66]

TABLE 1 (Continued)
Recent Applications of Different Sorbents For Preconcentraction of Organic Contaminants from Air and Water Samples

LiChlorut EN ENV+HR-P Oasis HLB	C		Halocetic acids	w	Off-line	E	LC-API-MS	[67]
Oasis HLB	C		2-aminoanthranceme,4-nitroquinoline-N-oxide	w	On-line	E	HPLC-UV RP-HPLC-DAD	[68]
onPac AG9-SC	C		oxyhalides	w	Off-line	E	IC-MS-Ms	[69]
BondElut C_{18}	C		Dibutyltin, diphenyltin, tributyltin, triphenyltin	w	On-line Off-line	E	LC-FD	[70]
Empore		D	Triazines	w	Off-line		LD-FTMS	[71]
SPEC (C_{18})		D	Polycyclic aromatic hydrocarbons	w	Off-line	E	LETRSS	[72,73]

LD-FTMS – **L**aser **D**esorption **F**ourier-**T**ransform **M**ass **S**pectrometry

LETRSS – solid-liquid extraction **L**aser-**E**xcited **T**ime **R**esolved **S**hopd'skii **S**pectrometry

The special attention should be paid on:

- The application of sorption tubes packed with polydimethylsiloxane (PDMS)[36,37,74] for preconcentration of organic analytes from air. In this case preconcentration occurs by sorption of the analytes into the bulk of the liquid phase instead of adsorption onto an active adsorbent surface. The most suitable stationary phase for this purpose is 100% polydimethylsiloxane. Preconcentration by sorption has some clear advantages over adsorption onto an active surface. In the sorption mode, polar solutes desorb fast at low temperatures due to the weak interaction of the analytes with the PDMS material. Moreover, PDMS is much more inert than a standard sorbent minimizing the losses of unstable and/or polar analytes. Another advantage of the PDMS phase is that its degradation products can be easily identified with the use of a mass spectrometric detector because they generate characteristic silicone mass fragments. Peaks originating from the sorbent can therefore not be mistaken as being from a sampled analyte. For practical purposes, the advantage of PDMS are that, since the analytes are retained in the bulk of this material, retention of the solutes on this phase is more reproducible than in the case of adsorbent
- Use of thick film open tubular traps as preconcentration devices for real gaseous and liquid samples.[75,76,77] These devices, however, suffer from two clear disadvantages:

  - low (total) volume capacity
  - low maximum allowable sorption flow rate

  In an attempt to overcome these problem a multichannel thick film silicone trap have been designed.[78]

- The application of extraction disc for *in situ* analysis of unfiltrated water.[52] A field method referred to as the "Solid Phase Extraction Empore Direct Immersion" (SPEEDI) is proposed that maximizes the automated sampling and extraction of organochlorine pesticides onto and from SPE discs through disc immersion and sample agitation. The SPEEDI method involves minimal solvent usage and sample manipulation. It is an effective technique of preconcentration for most semivolatile analytes without the necessity for filtration.
- Combination of solid phase extraction with laser desorption Furier transform mass spectrometry (LD-FTMS).[71] This technique is explored in conjunction with the use of membranes as SPE supports as an alternative in order to achieve a more direct route for analysis and to simplify the management of the aqueous samples. SPE membranes are inserted directly into the cell of a Fourier transform mass spectrometer for analysis after laser ionization. The LD FTMS technique has already proven its capacity for the analysis of organic compounds on different supports, for example, surfactants on textiles.[79]
- A novel approach for solid-liquid extraction laser-excited time resolved Shpol'skii spectrometry (LETRRS).[72,73] One reason to develop a new methodology for screening PAHs in environmental samples is the need for rapid and cost effective monitoring techniques for the routine analysis of numerous samples. The strong fluorescence emitted by PAHs in liquid solutions has prompted the development of several room temperature fluorescence methods. Similarly, several phosphorescence methods exist where PAHs are adsorbed on a solid substrate, and its phosphorescence is enhanced with a heavy atom salt. The main advantage of room temperature luminescence methods is their capability to provide through a simple experimental procedure PAHs screening at the semiquantitative level. Placing the PAH's solution or the solid substrate in the sample compartment of the instrument easily performs luminescence measurement. Unfortunately, the broad nature of room temperature luminescence spectra severely restrict PAH's direct determination in complex mixtures. Reducing the sample temperature almost always improves vibronic resolution of PAH's fluorescence and excitation spectrum. The temperature effect on PAH's fluorescence are especially pronounced

in the so-called Shpol'skii solvents as a result of a significant reduction of inhomogeneous band broadening. Under Shpol'skii conditions, the PAHs are frozen to 77 K or below in a uniform matrix, which is often an n-alkane. The combination of reduced thermal and inhomogeneous band broadening produces vibrationnaly resolved excitation and fluorescence spectra with unmatched information for PAH's identification

- Time-resolved laser-induced flurimetry for screening of PAHs on solid-phase extraction membranes. The first report on application this technique (TRLIF-SPE) has been published recently.[80] Octadecyl membrane are used with the dual purpose of extracting the pollutants from the water sample and serving as a solid substrate for fluorescence detection. The excitation of fluorescence is performed with a Nd: YAG pumped tunable dye laser pumped with a pulsed source for time-resolving spectral interference. This approach provides better limit of detection (LOD) and selectivity compared with other techniques

A. New Directions in the Application of Solid Phase Extraction

The literature studied led to the conclusion that there are some new approach in the field of application of solid phase extraction in analytical practice. They are described in the next part of this article.

1. Immunoassay (IMA)

Many methods of trace analysis require the use of complicated, labor-intensive and time-consuming techniques of sample preparation and pretreatment before proper analysis.

Therefore, the search for new methodologies that would become alternatives to the commonly used procedures, has been on form many years, at least within the scope of screening methods.

Immunoassay is not a novel solution because it has been in use already for many years in clinical diagnostics as a valid, sensitive, and selective method for determining low concentrations of organic compounds in blood, urine, and tissue samples.[81]

History:

1958—the publication of the first paper on immunological test designed to detect picograms of insulin in human blood samples of small volume.[82]

1977—R.S. Yalow received a Nobel Prize in Physiology and Medicine for the development of the test. In the following years, this new revolutionary technique found a wide application in biochemistry and clinical analytics.

1971—the introduction of immunological methods to environmental analysis.[83]

1992—the introduction of portable systems employing immunological methods for *in situ* measurements to laboratory practice.[84]

The increasing use of immunological tests in field research is associated with their certain characteristics, such as portable equipment and minimal requirements with respect to sample preparation.[85]

1995—the introduction of the first commercially available immunoassay for pesticide detection.[86]

a. The General Principle of Immunoassay

The term "immunoassay" is commonly defined as analytical procedures, with the use of antibodies for qualitative and quantitative determination of antigens.

In environmental analysis, the properties of immunoassay, which decide that it be used for fast and large-scale screening, have been recognized already.

The basic element of an immunoassay is the antibody that binds specifically with a molecule of antigen.

The antibodies from the gamma globulin group (IgG) are used in immunoassays.

The next stage in the development of immunological techniques is finding the proper marker that is used for the efficient detection of antibody-antigen complexes. The application of the following markers can be considered:

- radioactive isotopes
- enzymes
- co-enzymes
- fluorogenic

In general, the principle underlying the immunoassay can be described by the following reaction:

$$Ab + Ag + Ag^* \leftrightarrow AbAg + AbAg^*$$

where, Ab - antibody, Ag - antigen, Ag* - labeled antigen

The AbAg bond is relatively weak and can be of the following type:

- van der Waals bond
- electrostatic interactions that are most common
- hydrogen bond
- hydrophobic interactions

A precisely measured amount of labeled antigen (i.e., marker) is added to the sample containing analyte (i.e., antigen). Such a prepared sample is exposed to the material on whose surface-immobilized antibodies are present. As a result, antigen (i.e., analyte) and marker bind to antibodies. Unbound analyte and marker molecules are removed (e.g., by washing), and then the amount of marker that has been bound by antibodies is determined. This amount is proportional to the amount of antigen (i.e., analyte). The larger the amount of bound marker, the lesser the amount (i.e., concentration) of analyte (i.e., antigen) in the analyzed sample. Two basic types of immunoassay can be distinguished:

- Radio-immunoassay (RIA), where radioactive isotopes are used as markers.
- Enzyme immunoassay (EIA), where appropriate enzymes are used as markers.

b. Radio-Immunoassay

The introduction of radio-immunoassay revolutionized many areas of clinical and biological sciences. In radio-immunological techniques the isotopes, such as ^{125}I, ^{3}H, and ^{14}C, are used and that results in several inconvenient features associated in general with the application of radioactive elements. The most important ones are listed below:

- the necessity of radiological protection
- designation of special compartments for working with radioactive elements
- short half-life time of some radioactive isotopes used
- high cost of analytical equipment

The above inconvenient features and disadvantages caused that other methods, based on the use of different markers, were sought. An example of such an alternative solution is the application of enzymes that mediate fluorescence or chemiluminescence reactions.

c. Enzymatic Immunoassay

This technique, employing appropriate enzymes as markers, was used for the first time in environmental research in the early 1980s.

In most cases, antibodies are immobilized on a solid surface. Such surface, to which antibody or antigen bind, can consist of:

- test tube's wall
- microplate
- glass beads
- beads made of synthetic materials

The amount of antibody is limited; therefore, labeled and unlabeled antigens (i.e., analytes) compete for binding with it. Labeled and unlabeled antigens are retained by the immobilized antibodies.

After reaching the equilibrium, unbound antigen is removed by washing, and the amount of bound, enzyme-labeled antigen is determined, based on the level of enzymatic activity.

The principle of enzymatic immunoassay has been presented schematically in **Figure 1.**

Different modifications of EIA technique are known. One of the most popular is enzyme linked immunosorbent assay (ELISA). Frequently, this method is described as double antibody sandwich technique.

Antigen present in the analyzed sample is bound by the immobilized antibodies. Other enzyme-labeled antibodies are also present in the analyzed mixture. These antibodies also have affinity for the antigen (i.e., molecules of analyte) and bind to the immobilized antigen. After the removal of unbound antigen-enzyme conjugates the activity of the enzyme, which is proportional to the amount of antigen present in the analyzed sample, is determined. Schematic presentation of the principle of ELISA is shown in **Figure 2**.

A wide spectrum of enzymes has been used as markers in different EIA techniques. The majority of these enzymes form color complexes that can be easily quantified, mainly with the use of colorimetry, although other analytical techniques have been applied as well.

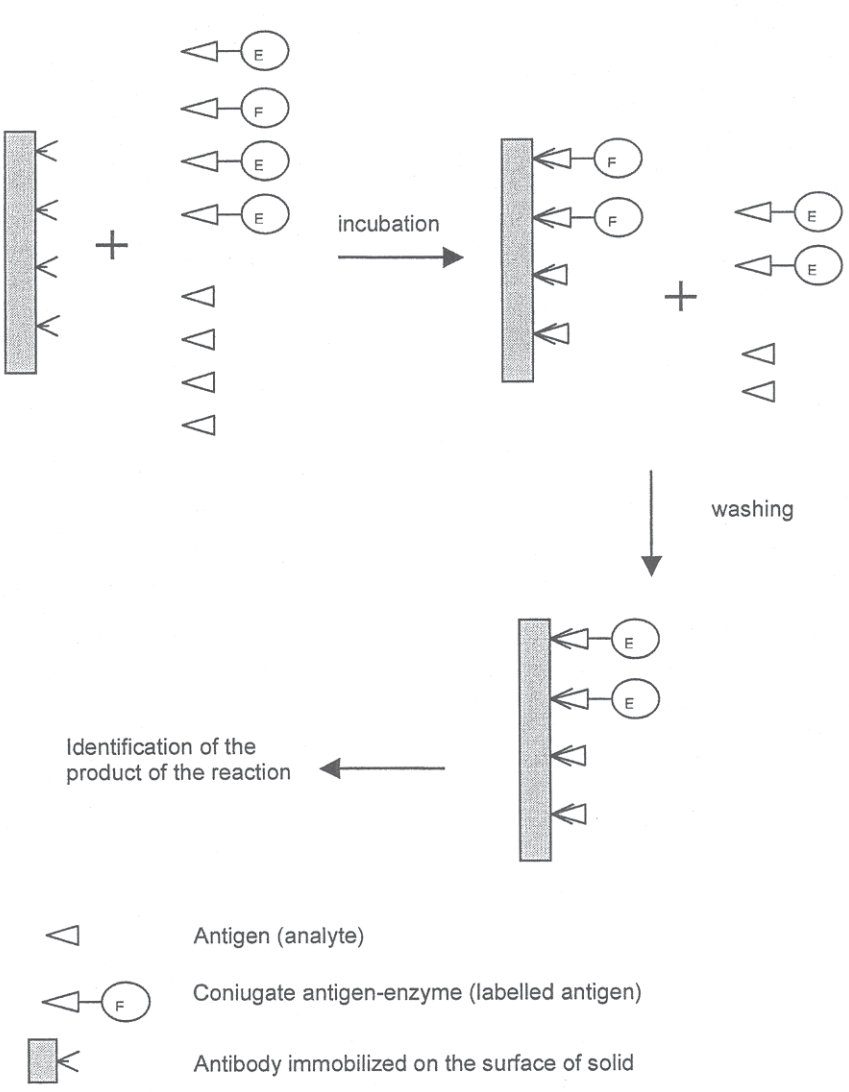

FIGURE 1. Schematic presentation of the principle of enzymatic immunoassay.

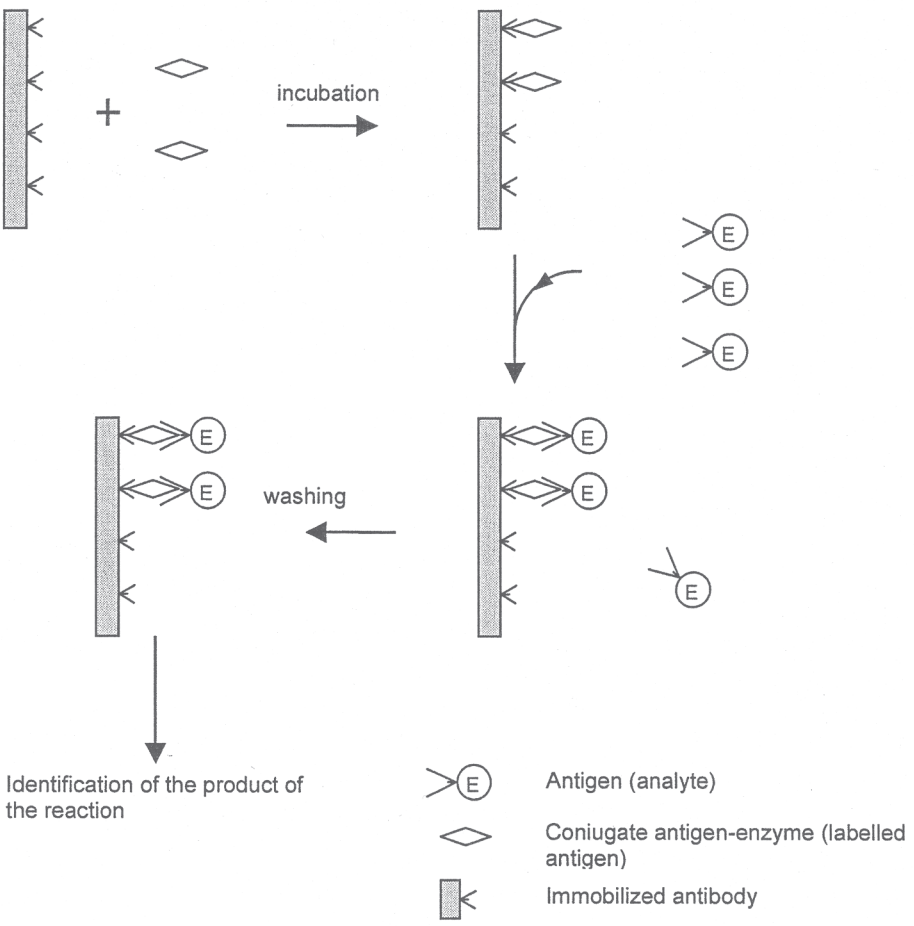

FIGURE 2. Schematic presentation of the principle of ELISA.

The most frequently used enzymatic markers are:

- alkaline phosphatase
- horseradish peroxidese
- β-galactosidase
- urease

The application of immunoassay in analytical procedures results in:

- reduction of labor-intensive and time-consuming pretreatment and purification of samples before proper analysis;
- decreased costs of analysis per unit, due to the minimized use of sophisticated monitoring and measuring equipment. The dimension of the financial problem can be reflected by the fact that just in the U.S. over 1 million USD is spent on environmental pollution monitoring.[81]

Example: At present, a particular challenge for the analytical chemists has been posed by dioxin (PCDD and PCDF) measurements in samples containing complex matrices. Cost of such analysis, which is labor intensive and time-consuming, ranges from 1000 to 2000 USD depending on the sample matrix. Most of the costs are incurred by painstaking and complicated extraction procedures and purification of the obtained extracts.

The application of RIA and EIA significantly speeds up and simplifies the flow of analytical procedure.

Different novel methods, developed in connection with the application of immunoassay, find broader use in various areas of chemical analysis, for example:

- Immunoaffinity Chromatography, IAC
- Flow Injection Immunoanalysis, FIIA
- immunosorbet-containing sampling devices used, for example, in SPE

d. Immunosorbents

Recently, antibodies immobilized on an adequate support, called immunosorbents, were proposed as selective sorbents for use in SPE applications[86,87,88] in order to overcome after mentioned drawbacks associated with typical nonspecific sorbents.

Different immunosorbents have been employed for the determination of pesticides,[89,90] drugs,[91,92] polyaromatic hydrocarbons,[93,94] etc. showing an excellent degree of clean up owing to the inherent selectivity of the antibodies used. However, obtaining antibodies is difficult and expensive (until now). Also, it is important to point out that after the antibodies have been obtained, they have to be immobilized on an suitable support, which may result in poor antibody orientation or even complete denaturation.

Because of these limitations, an alternative approach to the synthesis of host molecules that recognize targeted quest species has been developed. This new approach is called "molecular imprinting".

2. Molecularly Imprinted Polymers (MIPs)

Molecular imprinting is based on the preparation of a highly cross-linked polymer around a template (the analyte) in the presence of a suitable monomer.[95,88,96] The template and monomer(s) are first mixed in order to form a stable prepolymerization complex in a selected solvent. Subsequently, the polymerization is initiated in the presence of a suitable cross-linker. After polymerization, traditionally bulk polymerization, the polymer is ground and sieved to an appropriate particle size, and the template is removed, leaving cavities complementary in shape, size, and functionality. These cavities are able to selectively rebind, in given conditions, the analyte (the template) from the complex mixture. Molecularly imprinted polymers are called "tailor-made" binding sites for target molecules. The preparation of MIPs is easy and inexpensive, and they can be easily adapted to different analytical purposes. Important considerations in the design of these polymers have been reviewed by several authors.[97,95,98]

MIPs are being exploited in an increasing number of applications that include their applications as "tailor-made" separations materials, as antibody/receptor binding site mimics in recognition and assay systems, as enzyme mimics for catalytic applications, and as recognition elements in biosensors as well as facilitated chemical synthesis.

To date, their most extensively investigated application has been the separation materials in molecuraly imprinted solid phase extraction (MISPE).

As in other SPE procedures, a small account of imprinted polymer (typically 50 to 200 mg) in placed in a cartridge. The procedure of extraction of analytes with use of molecularly imprinted polymer bed is schematically presented on the **Figure 3.**

However, in MISPE the selection of solvent is dependent on the kind of template-monomer interactions that took place during polymerization.

Molecularly imprinted polymers have been applied for extraction of drugs,[99] pesticides,[100,101,102] phenolic compounds,[96] and amino acids[103] in techniques such as liquid chromatography,[104] thin layer chromatography,[103] and capillary electrochromatography.[99]

3. Stir Bar Sorptive Extraction (SBSE)

In 1999 a new technique of sportive extraction called stir bar sportive extraction (SBSE) was introduced into the analytical practice.[105] This

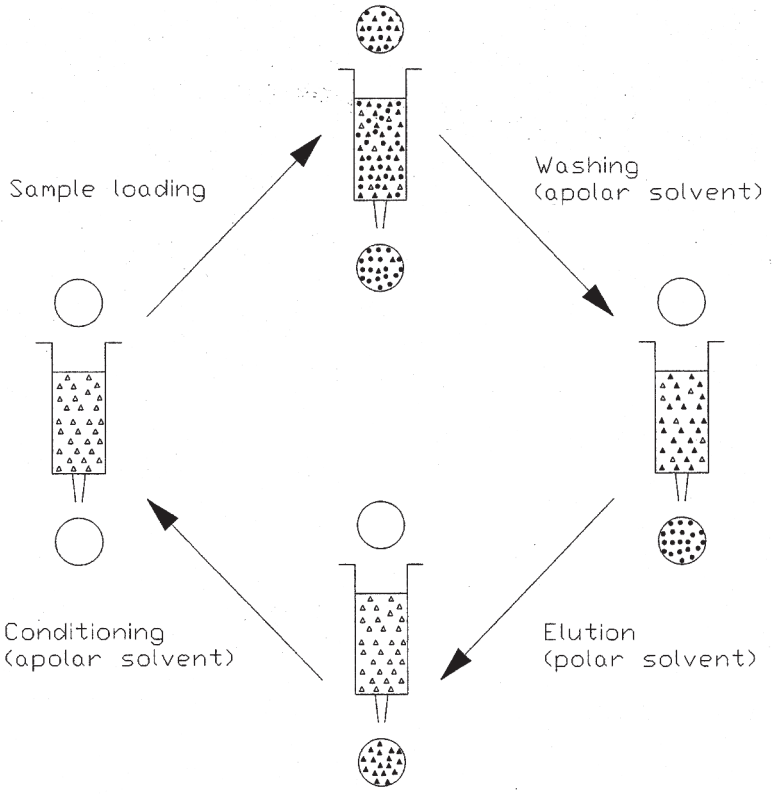

FIGURE 3. Schematic presentation of the molecularly imprinted solid phase extraction (MISPE) technique.

technique was developed to extract organic analytes from liquid samples and is based on the sorption of analytes onto a thick film of polydimethylsiloxane (PDMS) coated on an iron stir bar.[106,107,108,109,110]

The first stir bars were prepared by removing the Teflon® coating of existing stir bars, reducing the outer diameter of the magnet, and enveloping of magnet with a glass tube to give a 1.2 mm o.d. Silicone tubing with an internal diameter and an outer diameter of 3 mm was slide over the magnetic glass tube. However, as a stir plate is itself magnetic, the use of magnetic stir bar is not required. Nonmagnetic stir bars were prepared from stainless steel rods with an o.d. of 0.8 mm and a length of 40 mm. The total amount of PDMS material present on the 10- and 40-mm stir bars were 75.7 and 300.9 mg, respectively, which converts with the density of 0.825 g/ml to volumes of 92 and 365 µl, as the PDMS tubing contains ca. 40% (v/v) of fumed silica as filling material (determined with solid state NMR and TGA) the effective volumes of PDMS are 55 and 219 µl, respectively.

The stir bar is inserted into an aqueous sample, and extraction takes place during stirring. Because of the low phase ratio (volume of the water phase divided by the volume of PDMS phase), very high recoveries have been obtained especially for volatile compounds. The efficiency of the SBSE has been compared with other sportive techniques.[110]

This technique has been applied for the extraction of different types of organic compounds in aqueous,[107,108] wine,[109] and in fruits and vegetables.[106,110] Combined with thermodesorption–GC-MS,[108] it enables a low detection limit.

As an alternative, the stir bar can be desorbed by liquid extraction and the extract injected into the LC system.[107,109]

In the case of solid samples, there is a need of pretreatment based on accelerated solvent extraction.[106]

III. DEVELOPMENT OF EXTRACTION TECHNIQUES BASED ON APPLICATION OF SOLVENTS

In recent decades there have been major advances in the area of trace analytics, mainly reflecting the development in analytical instruments.[111]

As these sophisticated instruments are not capable of handling sample matrices directly, a sample is required.

Various methods are applied in order to prepare samples for analysis, which may generally be divided into physical, chemical, and physicochemical ones.[112] Depending on the matrix in which the analytes (organic and inorganic) are localized, the great interest is in extraction techniques.

The great need for change in analytical sample preparation has led to the development of new methods whose main advantages are

- speed
- negligible volume of solvents used (so called solvent-less sample preparation techniques)
- ability to allow analytes to be detected at very low concentrations

Initiated efforts to address the problems of large solvent consumption and poor automation have led to the development of the flow injection extraction (FIE) technique in 1978.[113,114] Typical FIE procedures involve the injection of an aqueous sample into an aqueous carrier stream that is merged with suitable reagent streams. Organic solvents are continuously inserted stream passes through the coil where extraction occurs. The organic phase is subsequently separated from the aqueous phase and led through a flow cell for measurement. FIE has the following advantages over liquid-liquid extraction:

- low cost
- high extraction speed
- reduced solvent and sample consumption

However, the amount of solvent used is still of the order of several hundreds microliters per analysis, and there are problems of deposition/adsorption of particles or dyes on the optical cell windows during analysis.

In 1990 a new technique called solid-phase microextraction (SPME) technique was introduced.[115] This technique is a completely solventless method. With SPME a thin fused silica fiber coated with sorbent or stationary phase is exposed to the sample or to its headspace and the target analytes partition from the sample matrix to the fiber coating. After extracting/preconcentrating for a set period of time, the fiber is transferred to the injection port of GC or to the suitable interface of HPLC, CE, or other analytical instruments for subsequent analysis. An important feature of this technique is that extraction and injection are incorporated onto the same fiber thus minimizing the analysis time. The main drawbacks of this technique are as follows:

- limited lifetime of fibers
- relatively high cost of fibers
- possibility of degradation of stationary phase of fiber with time
- danger of coelution of target analytes with peaks of degradated stationary phase

Nevertheless, a decade after its introduction, this technique proved to be a powerful alternative to traditional extraction techniques. To date, SPME has been used successfully for the analysis of gaseous, liquid, and solid samples containing a wide variety of analytes ranging from very volatiles to semivolatiles.

In the last few years efforts have been directed toward miniaturizing the LLE extraction procedure by greatly reducing the solvent to aqueous phase ratio, leading to the development of solvent microextraction methodologies. The new methodologies included in this approach fall into two categories:

- microextraction using immiscible liquid films, including liquid-liquid microextraction (LLME) (or liquid phase microextraction — LPME)

and liquid-liquid-liquid microextraction (back extraction — SME/BE);[116,117,118,119,120]
- single drop microextraction the extractant phase is a drop of a water-immiscible solvent.

With LPME, the analytes may be pre-concentrated significantly, based on the volume ratio between the sample and the acceptor phase. Thus, preconcentration values in the range 50 to 150 can be achieved. In addition sine 3 phase LPME (back-extraction) involves extraction from an aqueous sample through a water-immiscible organic phase and back into a new aqueous phase, substantial sample clean-up occurs.

The scheme of device for LPME is presented in **Figure 4**. The sample solution was filled into a small vial with a screw/septum. Two conventional medical syringe needles were inserted through the septum; one served to introduce the acceptor solution into the hollow fiber prior to extraction, whereas the second needle was utilized for the collection of acceptor phase after extraction. The ends of the two needles were collected into a piece of polypropylene hollow fiber. A sample was filled into the vial and alkaline solution was added to adjust pH into the alkaline region. For end extraction a new 8-cm length of hollow fiber was placed and between the two needles ends and subsequently dipped for 5 s into diethyl ether (this procedure served to fill the pores of the hollow fiber with organic solvent. The hollow was then exposed to ultrasonication

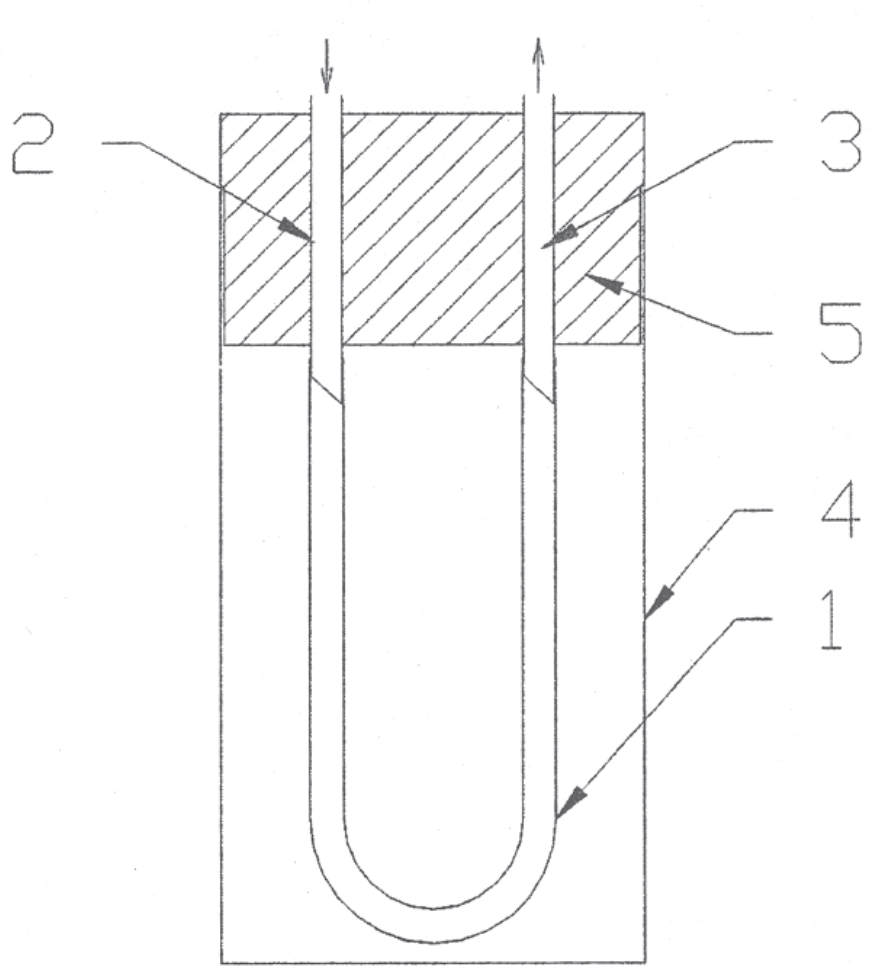

FIGURE 4. Schematic presentation of LPME device. 1 — hollow fiber with acceptor phase; 2 — needle for injection of acceptor phase; 3 — needle for collection of acceptor phase; 4 — vial; 5 — cap screw/silicone septum.

in a water bath to effectively remove any excess of diethyl ether on the outside of the fiber. After impregnation accepter phase (25 µl) was injected into the hollow fiber, and subsequently the fiber was placed in the sample solution. After extraction (60 min — in order to ensure equilibrium), the acceptor phase was flushed into a special vial. Each LPME device was only used for a single extraction.

The technique described is also known under acronym MMLLE (microporous membrane liquid-liquid extraction).[121]

Single drop extraction where the extraction phase is a drop of a solvent suspended in the aqueous phase.[122,123,124,121,125,126] In this case of water sample a solvent used should be water immiscible. New methods using a droplet of solution also has been applied to sample and determine soluble gases in the air.[127,128,129,130]

The main findings of his technique have been described in some review papers published recently[131,132,133]

In **Figure 5** a scheme of single drop microextraction system is presented (microdrop is suspended at the tip of microsyringe).

A. Micelle-Mediated Extraction as a Tool for the Separation and Preconcentration of Analytes

Generally, micellar systems have attracted considerable attention in the last few years as potential extracting media and continue to have a broad appeal for extraction applications. The use of preconcentraction steps based on phase separations by surfactant-based techniques provides a convenient alternative to more conventional extraction schemes.[134] Solutes that bind to micelles in solution are extracted to different extents, depending on the micelle-solute binding interactions. In principle, the micelle-mediated extraction technique involves cloud-point extraction (CPE), but there are also other extraction techniques from this group:

- Micellar enhanced ultrafiltration.[135] A large number of studies have demonstrated that that the separation of the micellar (pseudo)-phase from the aqueous can be achieved by ultrafiltration using membranes with a pore diameter smaller than the size of the micelle. This technique is referred to as micellar-enhanced ultrafiltration (MEUF). As in the case of CPE, the basis of the MEUF technique is the specific binding force between surfactants and analytes (metal ion).
- Reversed micellar phase extraction.[136] Reversed micelles are nanometric aggregates stabilized by surfactants in organic solvents. A reversed micellar solution is a thermodynamically stable mixture of water, oil, and surfactant, where the water regions are separated from oil by a monolayer of surfactants. Reversed micellar system have various capabilities such as extraction system of proteins, hydrophilic media for enzymes, and media for the preparation of functional materials or to perform heterogeneous reactions in nanometer-sized water pools.

Cloud point is the temperature above which aqueous solutions of nonionic and zwitterionic surfactants become turbid.[137] More specifically, the solutions separates into a surfactant-rich phase of small volume, composed almost totally of the surfactant and a diluted aqueous phase in which the surfactant concentration is close to the micelle concentration. This phenomenon has been said to be due to an increase in micellar size and dehydratation of hydrated outer micellar layers with the increase in temperature. Species that can interact with micellar systems either as such or after they have been derivatized can readily be concentrated in a small volume of the surfactant-rich phase after heating. Since its introduction for metal extraction in 1976,[138] the cloud point phenomenon has been properly investigated and exploited as a versatile, simple technique for the complexation and preconcentration of metal ions[139,140,141,136] as well as for the recovery of organic compounds of environmental concern (e.g., chlorophenols,[142] polychlorinated dibenzofurans,[143] weak organic bases,[144] triazines[145]).

Many revives have given the basic features and different aspects of the CPE technique and underpinned its viable, environmentally benign character as an alternative to a classic extraction method.[134,137,138,146,147]

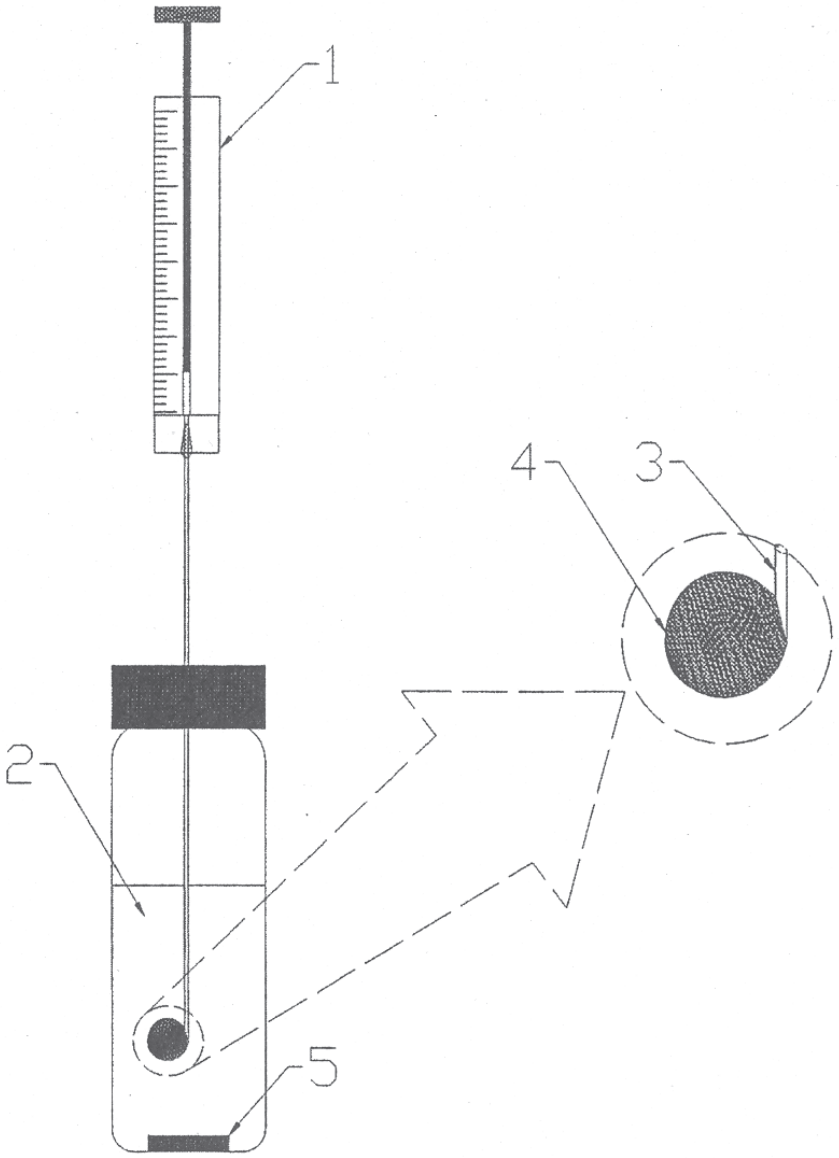

FIGURE 5. Schematic presentation of single-drop microextraction system: 1 — GC-microsyringe; 2 — aqueous sample; 3 — syringe needle; 4 — organic drop; 5 — stirrer.

B. Ultrasonic Extraction (USE)

In sonication, acoustic vibrations with frequencies above 20 kHz are applied to the sample, when this vibrations are transmitted through the liquid, cavitations occurs, that is, bubbles with a negative pressures are formed. Chemical compounds and particles are removed mechanically from the matrix surface and adsorption sites by the shock waves generated when the cavitation bubbles collapse.

Furthermore, implosion of cavities creates microenvironments with high pressures and temperatures. Because of this process, sonication can be used to decompose or oxidize organic compounds. Hence, when developing an extraction methods, care must be taken to avoid degradation of analytes.

Ultrasonic extraction can be performed by using the standard equipment in a laboratory, an ultrasonic bath. Therefore, advantage is the low initial cost. Further separation by the centrifugation or filtrations is required, however, after the extraction process, which is time consuming, and labor intensive.[148,149] Due to the sometimes inefficient recovery during a single batch extraction, it is performed in at least two steps, which generally results in higher solvent consumption compared with other extraction techniques.

Classic sonication technique (in static mode) is used both for the extraction of organic components[150] and inorganic species. During an ultrasonic extraction in static mode (described above) and a new method of extraction of analytes from solid samples is proposed.[151] It is called dynamic sonication assisted solvent extraction (DSASE). Dynamic extraction can be advantageous in this respect, because the analytes are removed as soon as they are transferred from the solid matrix to the solvent. Furthermore, in a dynamic system the sample is continuously exposed to fresh solvent, which promotes the transfer of analytes from the sample matrix to the solvent.

Samples to be extracted are inserted into the extraction cell and immersed in an ultrasonic bath. A suitable solvent is pumped through is pumped through the extraction cell and extracts are collected in a glass vials.

For the first time this new technique was applied to extract organophosphate esters from air sampling filters (in 3 min with an extraction volume of 600 µl of solvents.[151]

C. Accelerated Solvent Extraction (ASE)

The recently developed accelerated solvent extraction (ASE) — also referred to as pressurized fluid extraction (PFE) technique — offers an order of magnitude of additional reductions in solvent use with faster sample processing time, and with the potential of automated unattended extraction of multiple samples. Briefly, using ASE a solid sample is enclosed in a sample cell that is filled with an extraction solvent; after the cell is sealed, the sample is permeated by the extracting solvent under elevated temperature and pressure for short periods (5 to 10 min). Typically, the samples is extracted under static conditions, where the fluid is held in the cell for controlled time periods to allow sufficient contact between the solvent and the solid for efficient extraction. Alternatively, dynamic or flowthrough techniques can be used. Compressed gas is used to purge sample extract from the cell into a collection vessel. The ASE technique achieves rapid extraction with small volumes of conventional organic solvents by using high temperatures (up to 200°C) and high pressures (up to 20 MPa) to maintain the solvent in a liquid state. The use of liquid solvents at elevated temperatures and pressures enhances efficiency compared with extractions at or near room temperature and atmospheric pressure because of enhanced solubility and mass-transfer effects and the disruption of surface equilibrium. In a very short period of time some review papers with a very detailed description and evaluation of this technique of sample pretreatment have been published.[152,153,154] ASE has been used to extract various hydrophobic organic compounds from different environmental samples.[155,156,157,158,159]

Some studies have carried out comparisons between ASE and conventional techniques, such as supercritical fluid extraction (SFE) and Soxhlet extraction.[160] In the studies where techniques comparisons were made, the performance of ASE was consistently equivalent to or better than conventional techniques such as Soxhlet and sonication extraction.

D. Microwave Assisted Extraction (MAE)

Microwave-assisted extraction was introduced to the scientific community in 1986.[161] Microwaves, initially used in the food and agriculture industries for conditioning food products, have been used for sample digestion since the mid-1980s. Even more recently they have been also used to solvent extraction of organic analytes from solid samples. The enhancement is based on absorption of microwave energy by molecules of chemical compounds. Typically, microwave sources operating at 2.45 GHz are used. The solvents most used include dichloromethane and acetone-hexane mixtures.

Microwave-assisted extraction can be performed in two ways:

- pressurized MAE in closed vessels.[162–174] This first technique employs a microwave-transparent vessel for the extraction and a solvent of high dielectric constant. Such solvent absorb microwave radiation, and thus are heated to a temperature exceeding the solvent boiling points under standard conditions. Boiling does not occur because the vessel is pressurized. This mode of operation is very similar to ASE — elevated pressure and temperature facilitate extraction of the analyte from the sample.
- atmospheric MAE system.[164,175] The second technique employs solvents with low dielectric constants. Such solvents are essentially microwave-transparent, and thus absorb very little energy, and therefore extraction can be performed in open vessels. The temperature of the sample increases during extraction, because it usually contains water and other components with high dielectric constants. This led to an enhancement of this process. Because extraction conditions are milder, this mode of operation can be used to extract thermolabile analytes.

This technique is called Focused Microwaves (FMW), and it also give satisfactory results for polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine pesticides, and alkanes with some advantages of security, ease of manipulation.[176,177]

Microwave heating is very efficient and can basically be explained by the interactions of an electric field with charged particles and polar molecules in solution involving two mechanisms of energy absorption, that is, ionic conductance and dipole rotation. However, problems arise in MAE when using apolar solvents, because microwave energy can only be effectively absorbed by molecules having a dipole. For the extraction of organic contaminants this is a drawback, but this problem can be solved by increasing the polarity.

Commercially available instruments allow up to 16 samples within 15 to 30 min; the solvent consumption is 20 to 30 ml per sample.

Microwave-assisted extraction has several advantages:

- shorter heating and extraction time
- compact devices
- easy control of the sample-heating process
- reduction of the amount of solvent used for extraction
- efficient use of energy (which is consumed exclusively for heating of the sample and the solvent)

It should be pointed out that several additional operations must usually be performed before the final determination:

- separation of the extract from the matrix (by filtration or decanting)
- concentration of the extract (removed of excess of solvent)
- purification, drying of the extract

Using the dynamic approach for extraction is generally advantageous, especially with respect to the partitioning of the solvent into the extraction media. This can be highly efficient when fresh solvent is continuously introduced into the extraction cell, that is, the rate constant for description does not need to be large compared with the rate constant for the adsorption for efficient removal of the target solute.

Dynamic microwave-assisted extraction has been found to be an efficient technique.[172,173,178,179,180] In **Figure 6** a scheme of the DMAE-SPE system is presented.[181]

Another new approach is combination of the MAE with the use of an aqueous surfactant solution as extracting phase. This new technique is called microwave-assisted micellar extraction (MAME).[168] This procedure is based on the well-known solubilization capacity of aqueous micellar solutions toward water-insoluble or sparingly soluble organic compounds. As a general rule, nonionic surfactants are usually the most effective, showing larger solubilization capacities that rapidly increase, together with the solubilization kinetics as the cloud-point temperature of the solution is raised.[182]

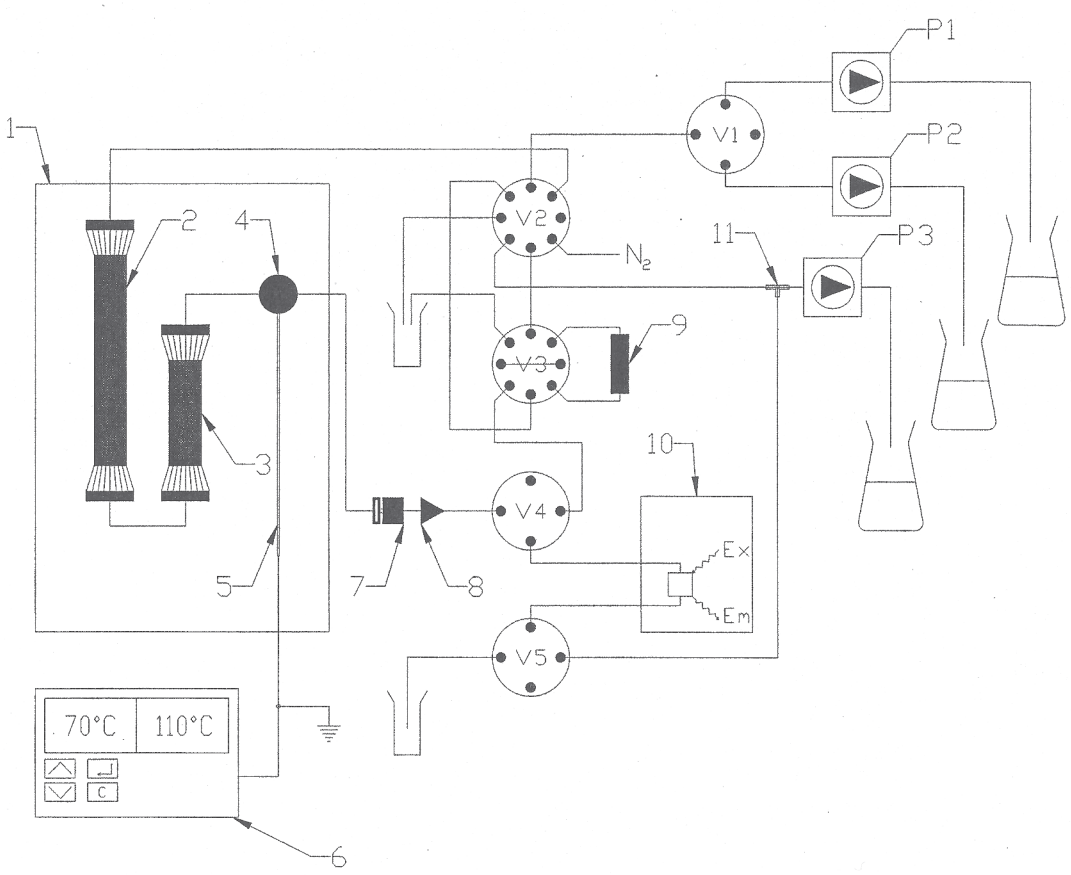

FIGURE 6. The DMEA-SPE system: 1 — microwave oven; 2 — preheating column; 3 — extraction cell; 4 — three-way PEEK connector; 5 — grounded K-thermocouple; 6 — temperature controller; 7 — in-line particulate filter; 8 — fused-silica restrictor; 9 — SPE column; 10 — fluorescence detector; 11 — mixing tee; V1 — V5 Valco valves; P1 — P3 HPLC pumps.

E. Pressurized Hot Water Extraction (PHWE)

The unique properties of water make it an interesting choice for the extraction medium. It is a cheap, nontoxic, and its physicochemical properties are easily adjusted by a change in temperature. The dielectric constant is the key parameter in interpreting solvent-solute interactions and can be related to polarity. The dielectric constant of water is high at room temperature (78.5), but it decreases with an increase in temperature. Low dielectric constant favors solubility of nonpolar compounds, and at high temperatures water can be used to extract these compounds. Nonpolar gases and organic compounds are fully miscible with water at a supercritical state. Nevertheless, the solubility of inorganic (ionic) compounds is decreased with increasing temperature, and also the possibility of hydrogen bonding between water molecules is lowered. Even though, in theory, supercritical water is an excellent solvent for all kinds of organic compounds, its high critical temperature (374°C), pressure (22.1 MPa), and corrosive nature have almost eliminated its use as an extraction medium. Fortunately, the solubility of many low-polarity compounds in water is high enough for their extraction at temperatures much lower than the critical temperature. Excellent results have been obtained at temperatures below 350°C and at pressures of 2 to 25 MPa. For example, the solubility of benzo(*a*)pyrene is in-

creased from negligible to over 1000 μg/g[183] when the temperature is increased from ambient to 250°C.

In many applications, temperature above 200°C must be used to achieve efficient extraction, and this requires special extraction vessels, valves, and sealing materials. Unfortunately, commercial equipment for PHWE technique is not available.

Typically, PHWE is performed in dynamic mode, and it means that the water is flushed continually through the extraction vessel. After the extraction, the water is cooled and the extracted analytes are collected either to an organic solvent or to a solid phase trap. The latter must be dried with gas flow, after which the analytes are eluted with suitable organic solvent. The benefit of the solid phase trap is that the elution can usually be performed with relatively small solvent volume, and often no preconcentration is needed. If, however, the extract is very dirty the solid phase trap may become blocked with extracted material and, for these samples, liquid collection is preferable.

Taking into account the extreme conditions in which HPWE is performed, this technique is not suitable for thermolabile analytes. Analytes may also react with each other or with water molecules during the extractions. Fortunately, most of the organic pollutants present in environmental matrices such as sediments and soils are persistent and their decomposition is not usually a problem even at higher temperatures. In addition, because the extraction process is dynamic, analytes are quickly released from the matrix and transferred from the hot oven to room temperature and exposed to the extraction conditions for only a short time.

PHWE is a promising, environmentally friendly technique, which effectively has been applied to a variety organic compounds and sample matrices, including:

- brominated flame retardants (BFRs) in sediment samples[184,185]
- nonylphenol polyethoxy carboxylates (NPECs) in industrial and municipal sludges[186]
- polycyclic aromatic hydrocarbons (PAHs) from sediments[187,188]
- polychlorinated biphenyls (PCBs) in soils and sediments[189,190]
- polychlorinated dibenzofurans (PCDFs) in soils and sediments[191]
- oxygenated compounds from plants material[192]
- herbicides in sediments[193]

F. Matrix Solid-Phase Dispersion (MSPD)

To use of SPE column and disks in analytical procedures, sample must be in a liquid, relatively nonviscous particulate-free and homogenous state. Many samples, however, start out in forms that are not directly applicable to SPE. This fact presents some unique problems for analysts trying to find the best process for rendering a sample into a suitable to analyse are solids and semisolids, many of which are of biological origin. An analyst must initially disrupt the gross architecture of these samples in preparation for SPE. This disruption ensures access to the solvents inside and outside the solid samples and provides samples that are adequately homogeneous for analysis. Disruption and homogenization also provide samples with a larger overall surface area, which provides more access for solvents and reagents used during the sample pretreatment step.

Classic techniques for sample disruption usually involve one or more of the following:[194]

- mincing
- shredding
- grinding
- pulverizing
- pressurizing

These techniques can be followed by or performed simultaneously with the addition of solvents, acids, bases, buffers, abrasive, salts, detergents, and chelating agents to cause an additional disruption of cellular and architectural composition and to initiate the process of extracting and separating various sample components from one another and from the analytes of choice.

A new technique for sample preparation was introduced into analytical practice in 1989.[195] This new technique, called matrix solid-phase dispersion, remedied many of the complications with dealing with solid samples and their subsequent

extraction using solid-phase materials. In this first version of the technique, a sample was placed in a glass mortar containing a bonded phase-solid support material (C-18 or octadecyl derivatized silica) and blended with the use of a glass pestle. The bonded phase-support served the following functions:[194,196,197]

- it acted as an abrasive that promoted disruption of the samples general architecture;
- the bonded phase acted as a liophilic, bound solvent that assisted in the sample disruption and lyses the cell membrane;
- the blended material was still capable of being packed into column and analytes could be eluted sequentially with solvents;
- the blended matrix and its distribution onto the bonded phase-support produced a unique column material allowed a new degree of sample fractionation.

The scanning electron microscopy examination of the blended tissue showed that the sample was distributed evenly over the surface bonded-phase support.[196] The sample is distributed completely and distributed over the surface as a function of interactions with the support, the bonded phase, and the tissue matrix components themselves to form a layered phase consisting of support — liophilic bonded-phase sample lipids and distribution of sample-associated compounds arranged in and on this phase based on their own relative polarities.

Thus, matrix solid-phase dispersion is different from classic SPE in that SPE samples must be in liquid form before addition to the column, matrix solid-phase dispersion can handle solid or viscous liquid samples directly. The interactions of the components of the system are greater in matrix solid-phase dispersion and different in part from SPE. The list of publications focused on the application of MSPD technique is very long, and the number of articles on this subject increases.[198,199,200] In most cases, the MSPD technique provides results equivalent to older "official" techniques. However, MSPD requires 95% less solvents and 90% less time. The use of smaller sizes and lower solvent consumption, purchase, and disposal combine to make MSPD competitive with order techniques of sample pretreatment.

G. Fluidized-Bed Extraction (FBE)

In 1997, a solid-fluid-fluidizing series extraction procedure, which provides for relative simple and cost-effective alternative, was presented.[201]

The principle of operation is as follows:[202]

The solid sample is loaded into extraction tube, which is equipped with a filter on a special disk at the bottom. The extraction solvent is filled into the basic vessel that contains a stirring bar. The heating-cooling block of the device is then warmed up to the chosen temperature (according to the boiling point of the solvent). The evaporated solvent penetrates the filter and condenses primarily at the cooling bar (stage a). The condensed solvent drips back into extraction material/mixed solvent and is recollected there. The constant flow of the solvent vapor from the basic vessel warms the mixture and vigorously fluidizes the vapor bubbles. Extraction at elevated temperature and fluidizing agitation both account for the effective extraction of analytes (stage b). Following the process stage "heating", the solvent is then recollected into extraction tube. For this purpose the system is programmed to turn off heating and to simultaneously cool down the basic heating-cooling block as well as the solvent contained in the basic vessel (stage c). Therefore, a vacuum is produced in the basic vessel as a result of the quick cooling process and the resultant differential pressure transport the extractive through the filter into the basic vessel (stage d). This sequence of stages may be cyclically repeated if it is necessary. The schematic presentation of the device for fluidized-bed extraction technique is given in **Figure 7**.

For the extraction of soil samples, a 2.5-g sample quantity was weighed into the extraction tube and mixed with 3 g of diatomite (to enhance the permeability of solid bed).[202]

This technique showed excellent results for the extraction of polychlorinated compounds[202] and also for the analysis of the 16 priority polycyclic aromatic hydrocarbons as listed by the U.S.

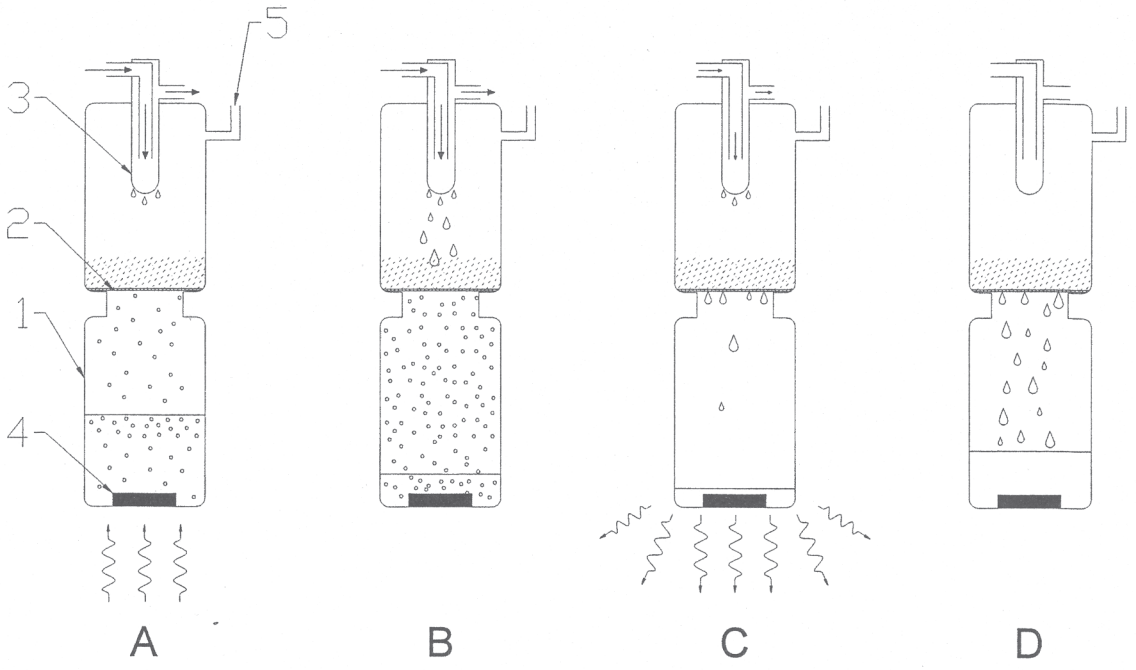

FIGURE 7. Schematic presentation of the principle of the FBE.

Environmental Protection Agency (EPA) in soil and sediment.[203]

IV. SUPERCRITICAL FLUID EXTRACTION (SFE)

The first observations that supercritical fluids dissolve unexpectedly large quantities of relatively nonvolatile materials were reported in the literature over 120 years ago.[204] It has been reported that metal halides became soluble in or precipitated from ethanol at a temperature above the critical temperature of ethanol (Tc = 234°C) when the pressure on the system was changed. Increasing the pressure caused the solutes to dissolve, whereas decreasing the pressure caused the dissolved material to nucleate and precipitate. In 1954 the feasibility of using liquid CO_2 just below the critical point as a solvent for many polar and nonpolar organic materials was established.[205] Intensive study of SFE in the 1970s and 1980s was generally confined to chemical processing applications such as the decoffeination of coffee.[206] The use of SFE for analytical purposes in the laboratory is now attracting increased attention all over the world.[207] Basically, SFE is designed to replace traditional multistep, time-consuming sample preparation techniques that use large quantities of organic solvents. Supercritical fluid extraction was the first technique that has provided a viable option to the conventional and widely used Soxhlet extraction.

A supercritical fluid is defined as any substance that is above its critical temperature and critical pressure. The critical temperature is the highest temperature at which a gas can be converted to a liquid by increasing the pressure. The critical pressure is the highest pressure at which a liquid can be converted to a traditional gas by an increase in liquid temperature. Above the critical pressure the properties of liquid and dense gas become identical. This highly dense gas is referred to as the supercritical fluid. Nonpolar materials have relatively low critical parameters (e.g., **CO_2: T_c = 31.3°C, P_c = 7295 kPa**), whereas polar compounds have high critical parameters (e.g., NH_3: **T_c = 132.5°C, P_c = 115.35 MPa**). Inasmuch as the ideal material for effecting SFE should have mild critical parameters, the most polar substances have not been given serious consideration for analytical SFE. Furthermore, this auxiliary material should also be relatively inert, inexpensive, highly pure, and nontoxic. Carbon dioxide best accommodates all these requirements.

Alternate materials (N_2O and various freons[208]) have been given limited consideration as supercritical fluids, even though certain of these, such as nitrous oxide, exhibit no greater solvating power than CO_2. A supercritical fluid exhibits physical-chemical properties intermediate between those of liquids and gases. Specifically, its relatively high (liquid-like) density gives good solvent power, while its relatively low viscosity and high diffusivity (gas-like) values provide appreciable penetrating power into the matrix. These latter two properties have been shown to give rise to higher rates of solute mass transfer into a supercritical fluid than into a liquid. Higher pressures are naturally required to attain liquid-like densities for temperatures further above the critical temperature. Furthermore, the vapor pressure difference at atmospheric pressure between CO_2 and typical solutes is considerably greater than that found for liquid solvent/solute pairs. This feature accounts for the ease by which the dissolved solute can be immediately separated from supercritical CO_2 after decompression, as opposed to miscible, less volatile liquid solvent-solute system. For this reasons, sample preparation via SFE can often be carried out at relatively moderate temperatures (<80°C), making the process amenable to thermally labile compounds. The possibility of more rapid extraction rates, increased extraction selectivity, greater extraction efficiency, and compatibility with on-line chromatographic and spectrometric instrumentation allow for further advantages. A schematic diagram of simple SFE apparatus is shown in **Figure 8.** High-pres-

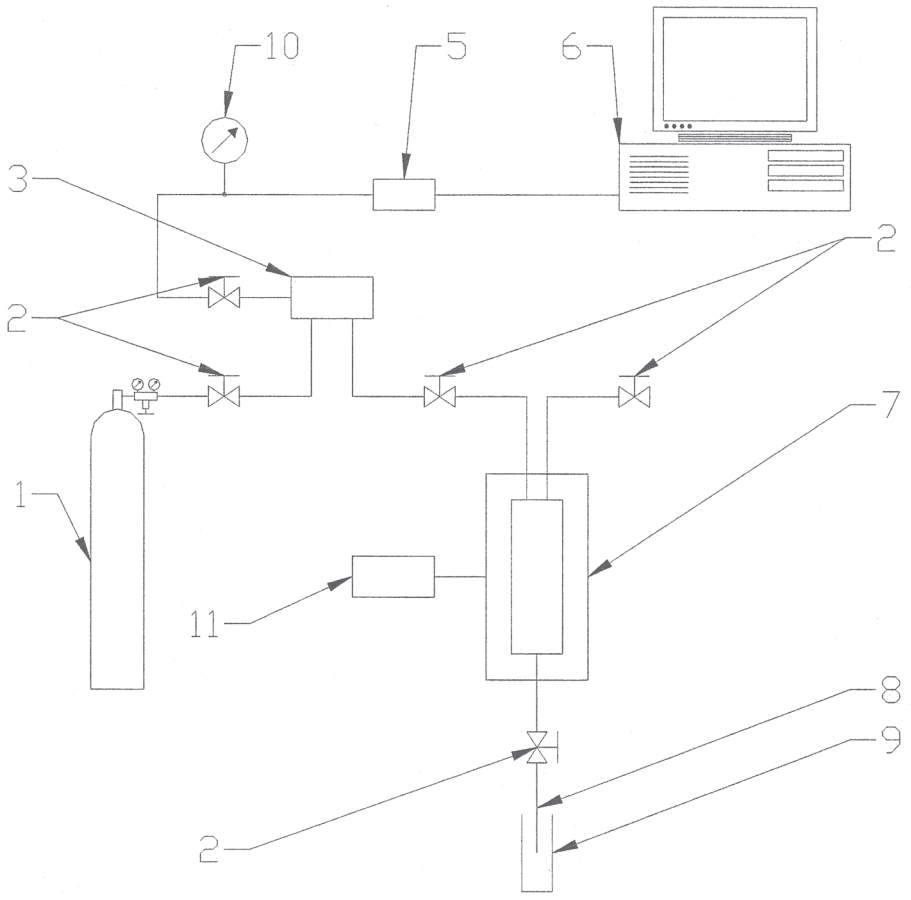

FIGURE 8. Schematic diagram of simple SFE apparatus. 1 — carbon dioxide pressurized cylinder; 2 — shut-off valve; 3 — high pressure syringe pump; 4 — three-way valve; 5 — pressure transducer; 6 — computer; 7 — extraction cell; 8 — fused silica capillary restrictor; 9 — collection vessel; 10 — pressure gauge; 11 — temperature controller.

TABLE 2
Conditions of Extraction of Soil Samples with the Application of Different Extraction Techniques

		Extraction technique			
		Soxhlet	PLE (ASE)	SFE	Subcritical water
Parameter	Sample size (g)	2	2	2	2
	Extraction solvent	CH_2Cl_2 - acetone	CH_2Cl_2 - acetone	Pure CO_2	Water
	Collection solvent	-	-	CH_2Cl_2	Toluene
	Pressure (MPa)	ambient	7	40	5
	Temperature (°C)	b.p. of solvent	100	150	300
	Flow-rate	15 min/cycle	1 ml/min	1 ml/min	1 ml/min
	Time	18 h	50 min	60 min	30 min
	Solvent volume (ml)	150	15	15	10

PLE – Pressurized Liquide Extraction

ASE – Accelerated Solvent Extraction

sure carbon dioxide is delivered through an on/off valve to the extraction vessel using a syringe pump operated in constant pressure mode in the range 5.2 to 30.0 MPa. The extraction cell is stainless steel, and the extraction processes are mainly carry out in it. The extraction can be processed in either a static or dynamic mode. Analytes are collected in suitable organic solvents by a fused silica capillary restrictor.

In **Table 2** conditions of extractions of soil samples with application of different extraction techniques are presented.[209]

There are review articles[207,210,211] treating the different aspects of introduction of supercritical fluid extraction technique into analytical practice. More detailed information connected with recent applications of the SFE technique to isolate analytes from various matrices are collected in **Table 3.**

Studies on new solutions in SFE and on the new application of this efficient extraction technique are continued. Special attention should be paid to:

- restrictor plugging in off-line SFE[212]
- new analyte collection method for off-line SFE based on mixing of expanding supercritical effluent with overheated organic solvent vapor[213]
- studies of collection capacity of a solid phase trap in SFE[214]
- design of SFE-GC system with quantitative transfer of extraction effluent to a megabore capillary column[215]

TABLE 3
Information on the Recent Application of the SFE Technique to Isolate Different Types of Organic Analytes from Environmental Samples

No	Matrice	Analytes	Mode of extraction					Analytical technique	Reference
			Static	Dynamic	Off – line	On – line	Automated		
1	SPE cartridge	Organic pollutants of intermediate polarity (in sewage)		+	+			GC, GC-MS	[217]
2	Activated carbon cartridge	m- Xylene		+	+				[218]
3	SPE cartridge (Florisil)	Polycyclic aromatic hydrocarbons and polychlorinated biphenyls (in air)		+	+			GC-ITMS	[219]
4	Biological samples	Polychlorinated biphenyls		+	+			GC-MS	[220]

TABLE 3 (Continued)
Information on the Recent Application of the SFE Technique to Isolate Different Types of Organic Analytes from Environmental Samples

5	Human adipose tissue	Polychlorinated biphenyls		+	+			GC-MS	[221]
6	White pine needles	Polycyclic aromatic hydrocarbons	+	+	+			GC-MS	[222]
7	Airborne particulates	Polycyclic aromatic hydrocarbons		+	+				[223]
8	Fly ash	Dioxins		+	+			HRGC-HRMS	[174]
9	Fly ash	Polychlorinated dibenzo-p-dioxins		+	+			HRGC-HRMS	[224]
10	Dust	Pesticides (carbosulfon and imidacloprid)						LC-UV	[225]

TABLE 3 (Continued)
Information on the Recent Application of the SFE Technique to Isolate Different Types of Organic Analytes from Environmental Samples

11	Urban dust (SRM 1649), marine sediment (SRM 1941)	Organic compounds		+	+			GC-MS	[212]
12	River sediments	Acidic herbicides	+		+			GC-ECD GC-MS	[212]
13	Marine sediments	Hydrocarbons, polychlorinated biphenyls, polycyclic aromatic hydrocarbons		+	+		+	GC-FID GC-ECD GC-MS	[226]

TABLE 3 (Continued)
Information on the Recent Application of the SFE Technique to Isolate Different Types of Organic Analytes from Environmental Samples

14	River sediment (NIST 1938), marine sediment (NIST 1944), harbour sediment (CRM 536), industrial soil (CRM 481), fresh water sediment	Polychlorinated biphenyls	+		+			GC-MS	[227]
15	Surfactant suspemsion soil extract	Polychlorinated biphenyls		+	+			GC-FID GC-MS	[228]
16	Water	Oil		+		+		FTIR	[229,230]
17	Sludge	Bisphenol A	+	+	+			GC-MS	[156]
18		Metal complexes		+	+			FAAS	[231]
19	Soil	Metals	+	+	+			AAS	[232]

TABLE 3 (Continued)
Information on the Recent Application of the SFE Technique to Isolate Different Types of Organic Analytes from Environmental Samples

20	Marine sediment	Polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls		+		+	+	SFC-CT-GC-MS	[233]

- application of SFE technique in physico-chemical studies (e.g., determination of partition coefficients)[216]

V. MEMBRANE EXTRACTION TECHNIQUES

In simple terms, a membrane can be a selective barrier between two phases (donor or feeding phase and acceptor or permeate phase). For mass transport to occur, a force must be applied to produce a flow. The absolute rate at which a species crosses a membrane is called permeability, and the ratio of rates of two different species is called selectivity.

Although membrane processes may vary widely regarding how they function and in their different applications, they all have some common characteristics that make them attractive as alternatives in the field of separation. Often they are faster, more efficient, and cheaper than other separation techniques. Additionally, in most cases, the processes are carried out at room temperature, which has undoubted advantages in the handling and separation of unstable or thermally labile species.

In the above context, this type of process is applied not only in the laboratory but also on an industrial scale (desalination of sea water, cleaning of industrial effluents).

Although synthetic membranes may be of a very different chemical nature and may display different properties, they can be classified in some groups described in more detailed manner in **Table 4**. In review articles published recently,[234,235] more detailed information is available.

All types of membranes can be used both in a flat configuration and in a tubular arrangement when the diameters of tubular membranes are in the micrometer range (between 200 and 500 μm external diameter, with walls at some 20 μm), they are known as hollow fibers.

The technical limitations of polymeric membranes have in recent years motivated the development of dense SiO_2 and metal membranes as well as porous inorganic membranes. Carbon molecular sieve membranes (CMSMs) prepared by the carbonization of polymeric precursors[236] have been studied in the last few years as a promising alternative to both inorganic and polymeric membranes. The CMSM's that have been reported so far have been prepared by pyrolysis, typically in an inert atmosphere, of either polymeric hollow fibers or thin polymeric films coated on porous support.

In membrane-based processes, separation is the result of the differences in the transport rates of chemical species through the interface. Transport through membranes is a nonequilibrium process in which flow can be related to the force that generated it. These forces are mainly due to:

- differences in concentration. The International Union of Pure and Applied Chemistry (IUPAC) recommends the term "dialysis" for all processes caused by these forces. The species than be separated may be gases or liquids[237]
- differences in pressure. The three separation processes through membranes in which transport is induced via application of pressure are microfiltration, ultrafiltration, and invert osmosis or hyperfiltration. They differ in the size of solutes retained by membrane:
    - between 1 and 10 Å in inverse osmosis
    - between 10 and 103 Å in ultrafiltration
    - between 103 and 105 Å in microfiltration
- differences in electrical potential. There are two processes based on application of difference in electrical potential:
    - electrodialysis. The system comprises a series of anionic and cationic exchange membranes that are arranged alternately between an anode and cathode. Electrodialysis can be used with both neutral and charged membrane
    - Donnan dialysis. It employs charged membrane, but no external potential difference is applied. One of two solutions separated be the membrane has a lower concentration of all species than the other one, giving rise to flow of one of the species (whose charge allow it to pass through the membrane). In this way a difference in potential is generated that must be compensated by the

TABLE 4
Classification of Membranes Used for Analytical Purposes

No.	Type of membrane	Description	Additional remarks
1	Microporous membranes	Membrane comprises of solid matrix with pore diameter ranging from 5 nm to more than 50 μm. The separation of analytes form mixture is generally accomplished by size-exclusion mechanism in which pore diameter and analyte size are the main parameter,	Difference between microporous and homogenous membranes depends on the limit imposed on the size of empty spaces that, to a greater or lesser extent, exist in all macroscopic structures.
2	Homogenous membranes	This type of membrane is also known as dense membranes and they comprise a film in which there are no pores. Transport through these membranes is governed not only by diffusion but also by solubility of the analytes in membrane. Homogenous membranes can be made of different materials and depending on this material are classified as follows: • metallic membranes, • glass membranes, • polymer membranes, • liquid membranes. Polymeric homogenous membranes can be prepared from a solution of polymer by evaporating off solvent or in the case of thermoplastic polymers by a process of fusion, extrusion and	From the poin of view of separation processes the most important are those made of polymer and liquid membranes.

TABLE 4 (Continued)
Classification of Membranes Used for Analytical Purposes

		solidification by cooling. Among the materials used for this type of membrane silicone is often used owing to its good permeability. Liquid membranes can be subdivided into 2 groups: - emulsions (ELM). Species with surfactant properties are usually used to stabilize the emulsions and hence this type of system is often referred to as "surfactant liquid membrane"; - supported liquid membranes (SLM) may be formed of surfactant species deposited on a support that they are unable to cross (externally supported) or formed by the confinement of a liquid phase within a macroporous support (internally supported).	The main advantage of liquid homogenous membranes as compared with polymer membranes is the greater diffusivity of species in a liquid medium.
3	Ion – exchange membranes	Ion – exchange membranes are composed of polymer base with fixed charges. Depending on the sign of fixed charge they can be classified as anionic and cationic. Among the most important processes used to prepare these membranes are: - dispersion of ion-exchange material in a polymer matrix; - polymerization of ionic monomers; - introduction of ionic groups in a polymer matrix. Among the materials most used are the copolymers olivinylbenzene-styrene and derivatives of fluorinated polymers such as Nafion. The selectivity of these membranes comes from the exclusion of ions with the same sign as the fixed charge at their permeability to ions with the charge with opposite that of fixed one.	In anionic membranes, the group most usedare quaternary ammonium ions although phosphonium and sulphonium groups are also used. In cationic exchange membranes, the group most used are sulphonic although phosphoric, carboxylic and arsenic groups can also be used.

TABLE 4 (Continued)
Classification of Membranes Used for Analytical Purposes

4	Asymmetric membranes	The form asymmetric membranes is used to refer to membranes that show an important variation in the cross-section of their structure. These membranes are useful for when asymmetry in the pores is required or when one needs an effective membrane that is as thin as possible on a high porous support in such a way that the rate of analyte transfer will be fast and mechanical resistance will increase considerably. Two types of asymmetric membranes can be considered: - integral asymmetric membranes; - composite asymmetric membranes. Structure of integral asymmetric membranes consist of very fine layer – the effective membrane with thickness of 0,1 – 10 μm and with total thickness of up to 100 or 200 μm. The second type of membranes comprises structures generated from two different materials. Those used most commonly are made of thin layer of polymer generated in situ on microporous base.	

passage of ions from the zone of lowest concentration to that of highest concentration (against the gradient).

In most cases, the analytical applications of membrane processes aim at simplifying the sample preparation step. In the next, different analytical techniques such as gas chromatography,[238] liquid chromatography,[239] ion chromatography,[240] electrophoresis,[241,239] flow injection analysis,[242] and photoacoustic techniques[243] can be used. For example, in the case of application of chromato-membrane cells for extraction procedures in FIA are as follows:

- small volumes of contacting phases (100 to 200 μl)
- fast adjustment of the distribution equilibrium (the distance to the phase boundary is always short)
- no problems with phase separation
- continuous mode of extraction or preconcentration
- completely automated sample pretreatment on request

Some extraction techniques based on the application of membrane processes, which very often are used in analytical practice. They are as follows:

- supported liquid membranes (SLM)[244,245,246,247] also with the application of immunologic trapping.[248] The extraction involves the partition-

ing of neutral compounds between the sample solution, continuously pumped alongside the membrane and the membrane. From the membrane, the reextraction takes place in a second aqueous phase, contacting antitodies specific for the target compound(s). Hence, there is a formation of an antibody-antigen complex at the heart of the sample preparation (ImmunoSLM). When the immunocomplex forms, the antigen can no longer redissolve in the organic membrane, thus being trapped in the acceptor. Consequently, the concentration gradient of free antigen over the membrane is ideally unaffected, this being the driving force of the process;

- membrane extraction with sorbent interface (MESI)[238,249,250,251,252] The membrane is a polymer hollow fiber, and the analytes are extracted from the surrounding liquid or gaseous sample. A gas inside the hollow fiber transports the analyte molecules into a cold sorbent tube where they are trapped. The analytes are thermally desorbed from the sorbent and directed to the analytical instrument (e.g., GC). There is also the possibility of using a catalytic reaction to trap the extracted analyte directly in the gas phase;
- on-line membrane extraction microtrap system (OLMEM).[253] In the OLMEM-GC technique, water or air sample continuously flowed into the membrane module and nitrogen flowed countercurrent at the permeate side to strip the permeated organic compounds into the vapor phase. The organic substances are transported to and concentrated in a micro-sorbent trap. After rapid thermal desorption are injected onto a chromatographic column
- permeation liquid membrane (PLM).[173] PLMs preconcentrate the analyte from the sample solution into a receiver solution. These two aqueous phases are separates by a hydrophobic liquid membrane that contains an analyte selective carrier. This technique allows the selective detection of wide range trace compounds (metal ions, carboxylic acids, and alcohols)
- membrane-assisted solvent extraction (MASE).[254] The operation of the extraction is based on a small-scale liquid-liquid extraction with a polymer membrane separating the aqueous phase (sample) from the organic phase
- pulse introduction membrane extraction (PIME),[255] which is also referred to as membrane purge-and-trap (M-P-T). A phase of sample is injected into membrane for extraction. The permeated organics are shipped by a flow of carrier gas, concentrated (using a microtrap) and injected (after desorption) into the analytical instrument. This concept can be used in gas chromatography, mass spectrometry, as well as other analytical techniques. The system does not need to read steady state; thus, errors associated with steady state requirements are eliminated
- single hollow fiber membrane with subsequent cryotrapping of analytes.[256,257] The system is similar to MESI and OLMEM ones
- silicone tubing probe combined with differential detection systems[258,259]
- application of hydrophobic membrane made of crosslinked poly(dimethylsiloxane) (PDMS) as an extraction medium for volatile organics compounds (VOCs) from water.[260] It was suggested that when the hydrophobic characteristics of a membrane system is greater, water molecules in the membrane tend to exist in the form of clusters, thereby the permeating size of water component increases, resulting in suppressing water permeation and increasing the enrichment factor for the organic components. This process is called pervaporation.[261]

A. Membrane Inlet Mass Spectrometry (MIMS)

Mass spectrometry (MS) has been slowly emerged as an environmental screening tool for several reasons. Mass spectrometer requires a sizeable capital investment. In addition, there is a lack of approved screening methods and a perception that MS instruments are too large, complex, and unreliable for practical use in the field.

These obstacles have diminished in recent years with improvements in instrumentation and wider acceptance of screening data by regulators. New analyzer technologies, such as quadrupole ion traps, have also become available that are

small and simple yet provide advanced analytical capabilities, such as MS/MS and selective low-pressure chemical ionization (CI).

Direct sampling mass spectrometry (DSMS) refers to the introduction of analytes from a sample directly into a mass spectrometer using simple interface with minimal sample preparation and without chromatographic separation.[262] This translates into:

- simplicity
- real-time response
- high sample throughput capability

Multiple inlet configurations permit the screening of most types of environmental samples for volatile and semivolatile organics. The basic information about the most common mass analyzers used for DSMS techniques are collected in **Table 5**.

There are four major types of inlets for DSMS instruments:

1. capillary restrictors consisted of a piece of deactivated fused-silica silica narrow-bore capillary that extends from atmosphere into the ion source

TABLE 5
Commonly Used Instruments for the DSMS Technique

		Type of MS unit				
		Linear quadrupole	**Triple quadrupole**	**Quadrupole ion trap**	**Time of flight**	**Magnetic sector**
Parameter	Ionization modes	EI, CI, API, GD	EI, CI, API, GD	EI, CI (low pressure), GD	EI, laser	EI
	Mass range [Da]	15 – 1000	15 – 1000	15 – 650	15 – 200+	15 – 200+
	Detection limits	ppt – ppm	ppt – ppm	ppq – ppm	ppb – ppt	ppm – ppt
	Benefits	Rugged, transportable, commercially available and field instruments	MS/MS capable	Rugged, transportable, MS/MS capable, very sensitive	Mechanically simple, high mass range possible	Rugged
	Limitations	Less sensitive than MS/MS	Field use requires large vehicle, complicated to operate	Ion-molecule reactions can make spectral interpretation difficult, limited dynamic range	Resolution can be poor	Mass range is limited and resolution can be poor on small instruments, moderate sensitivity

2. modular sampling devices
3. gas flow splitter. Modular sampling devices and gas flow splitter allow the inlet configuration to be quickly changed for sampling different media[263]
4. membrane inlets based on a use of synthetic membranes to extract analytes from a sample and directly introduce them into the spectrometer while blocking the flow of air and liquids[264]

The polymeric membrane is the only separation between the liquid or gaseous sample and the vacuum of a mass spectrometer. Analytes dissolve in the membrane, permeate through it, and finally evaporate into the mass spectrometer, where they are ionized and analyzed according to their m/z ratio. The most important steps of membrane inlet mass spectrometry are presented in chronologically order in **Table 6.**

Many reviews regarding the technique itself and its applications have been published already.[265,266,264,267,268]

In MIMS, the introduction of analyte into the mass spectrometer is a result of transport through a suitable polymer membrane. This permeation process involves absorption into the membrane, diffusion through the membrane, and evaporation from the membrane into vacuum. This three-stage process is often called prevaporation, and it is schematically presented in **Figure 9**.

Each step depends primarily on the molecular properties of the analyte and the membrane material. In addition, the temperature of the membrane can have a significant effect on permeation rates. The use of the right membrane thus can result in a large increase in mass fraction of analyte, relative to the mass fraction of the solvent that passes the membrane. There are a lot of data connected with the studies of the different materials for the membrane.[234,298,299,123,300,301] The membranes used typically are organic polymers such as polyethylene and Teflon® for gas monitoring and silicone-based polymers for organics in aqueous solutions and in air.

Mathematically, the permeation process can be described by the first law of diffusion (Flick's Law). Assuming that the constants for solvatation and diffusion are independent of partial pressure and the steady state flow through the membrane (J_{ss}) can be presented as follows, Eq. 1:

$$J_{ss}=A\cdot D\cdot S\cdot(P_s/L) \quad (1)$$

where:

J_{ss} — the steady state flow through the membrane [mol/s],
A — the membrane surface area (cm^2),
D — the diffusion constant,
S — the solubility constant (mol*torr-1*cm^{-3},
P_s — the vapor pressure of the analyte on the sample side of the membrane (torr),
L — thickness of the membrane (cm).

Nowadays, the MIMS technique becomes a very powerful tool in the analytical studies of different types of samples in order to determine a wide spectrum of analytes,[304,306,305,307] and the field of application is increasing constantly.

Membrane introduction mass spectrometry (MIMS) offers several important advantages compared with the other established air, water, and soil analysis methods. The main advantages are as follows:

- high-speed analysis
- solventless character of the technique
- low cost of analysis (per sample)
- direct technique analysis (without sample pretreatment)
- possibility of long-term continuous monitoring of different processes and experiments

VI. CONCLUSIONS

The techniques of extraction (isolation) and/or preconcentration of analytes are used in the analysis of trace components of gaseous, liquid, and solid samples. During this operation the transport of analytes from primary matrices (donor) to the secondary matrix (acceptor) takes place.

The advantages obtained in this manner are follows:

- transport of analytes to matrix characterized by simplicity of composition compared with

TABLE 6
The Most Important Steps in the Development of the MIMS Technique

No	Year	Development step (description)	Index
1	1963	First application of MIMS technique – for measurement of CO_2 and O_2 during photosynthesis and respiration.	[269]
2	1966	Monitoring (in vivo) of gases dissolved in blood.	[270]
3	1966	Application of membrane inlet as an interface between gas chromatograph and mass spectrometer.	[271]
4	1971	Demonstration that MIMS technique can be used to study electrochemical reactions .	[272]
5	1974	The first air monitoring application of MIMS (measurement of chemical warfare agents).	[273]
6	1974	The use of hollow fibre membrane for monitoring of wide spectrum of organic analytes in water and air.	[274]
7	1974	Introduction of small sample cell type of MIMS for measurements of oxygen kinetics in biochemical systems.	[275]
8	1975	Application of MIMS technique for monitoring of the process of fermentation	[276]
9	1975	Presentation of first portable quadrupole MS equipped with membrane separator.	[277]
10	1975	Application of membrane inlet as an interface between liquid chromatograph and mass spectrometer.	[278]
11	1976	New type of inlet with immobilized enzyme on the membrane.	[279]
12	1979	Observation of the influence of pH on the analyte responses of MIMS device.	[280]
13	1981	Description of transportable quadrupole mass spectrometer equipped with a membrane inlet (measurement organic solvents in human breath).	[281]
14	1986	Combining the MIMS device with stop flow technique (measurement of kinetics of enzyme catalyzed reactions).	[282]

TABLE 6 (Continued)
The Most Important Steps in the Development of the MIMS Technique

15	1987	Introduction into analytical practice an automatic MIMS system for industrial fermentation monitoring.	[283]
16	1987	Introduction of the direct insertion membrane probes.	[284]
17	1987	Design a removable direct insertion membrane probe (DIMP). Capillary membrane loop is mounted inside the ion source block exactly between two parallel filaments.	[284]
18	1990	Application of inlet utilizing a sheet silicone membrane.	[285]
19	1991	Introduction of a new type of membrane inlet called helium purge inlet utilizing a silicone capillary membrane. During the operation of a helium purge inlet the aqueous sample flows continuously over membrane while the inside of the capillary membrane is purged with helium directed to the ion source of a mass spectrometer.	[286]
20	1992	Introduction of technique reversed phase membrane inlet mass spectrometry (RP-MIMS). Normally in the case of application of MIMS technique organic compounds from water or air are measured. When reversed phase MIMS technique is applied impurities of organic solvents are measured. In this technique a sheet of microporous polypropylene membrane is used at the end f the direct insertion membrane probe. The microporous polypropylene membrane allows sufficient amount of the solvent to penetrate the membrane into the ion source for chemical ionization.	[287] [288]
21	1995	Invention of trap and release membrane introduction mass spectrometer (TR-MIMS). Tubular membrane is mounted inside the ion source. In this method the heat from the filament is utilized the thermally desorb the analytes from the membrane. The application of this unit allows detection of relatively polar SVOC's (pentachlorophenol, phenoxyacetic acid, caffeine) at ppb levels.	[133]

TABLE 6 (Continued)
The Most Important Steps in the Development of the MIMS Technique

22	1996	Application of cryotrap membrane introduction mass spectrometry (CT-MIMS) for analysis of VOC's in water at ppt level. The conventional MIMS probe is modified so that the membrane interface is placed a bit away from the ion source. A U-shaped trap tube is then inserted between the membrane interface and ion source. Cryotrapping is performed with liquid nitrogen and then retained analytes (after fast thermal desorption) were directed into the ion source region of a quadrupole mass spectrometer. The extra ordinary sensitivity of CT-MIMS system allows VOC's to be detected at very low concentration.	[289]
23	1998	Development of fully automatic MIMS measurement system for on-line industrial wastewater monitoring.	[290]
24	1998	Introduction of a new technique for analysis of VOC's in water and soil samples (Purge-and-Membrane Mass Spectrometry: PAM-MS). In this technique VOC's are purged form the sample with an inert gas and the stream is directed through a sheet membrane module. Analytes pervaporated through the membrane directly into the ion source of mass spectrometer.	[291]
25	1998	Introduction into analytical practice new analytical system based on: • tubular silicone multimembrane sampling unit, • cryogenic trap inlet device, • selective chemical ionization, • quadrupole ion trap. The system was applied for rapid determination of isoprene and others atmospheric important alkanes characterized by short lifetime.	[292]
26	1998	Developing a tubular silicon membrane interfaced sampling apparatus to screen BTEX compounds in water with a hand-held ion mobility spectrometer (IMS).	[293]
27	1998	Application of laser desorption MIMS.	[294]

TABLE 6 (Continued)
The Most Important Steps in the Development of the MIMS Technique

28	1999	Invention and application of desorption chemical ionization membrane inlet mass spectrometry (DCI-MIMS). In this first version of system a polar polyacrylonitryle membrane was used. The membrane of this type is highly permeable to water and the vapourisated water from the aqueous sample was used to create a water CJ plasma. In second-generation system a silicone membrane was used and the CJ gas was introduced into the ion source via a separate gas inlet line. The system allows to detect a highly polar (polyacrylonitryle membrane) as well as hydrophobic compounds of low volatility (silicone membrane).	[295] [296]
29	2000	Design of direct insertion membrane probe for trap and release membrane introduction mass spectrometry system (DIMP-TR-MIMS). The system has been applied for combined trace level determination (low or sub ppb range) of volatile (VOC's) and semivolatile organics compounds (SVOC's) in aqueous solutions.	[297]

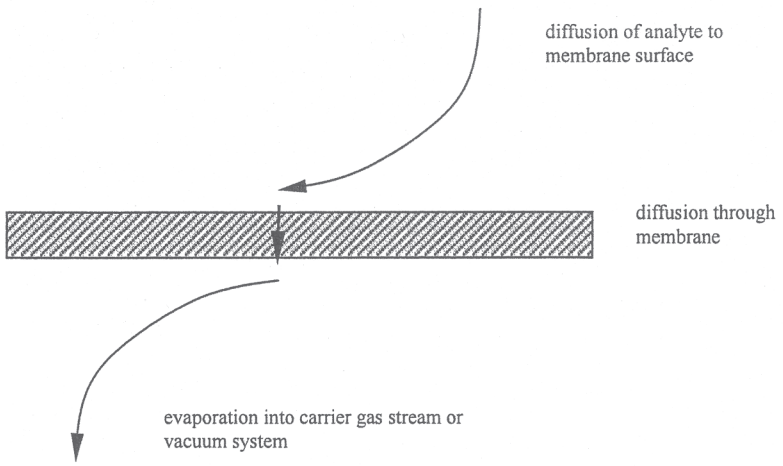

FIGURE 9. Schematic representation of the membrane prevaporation process.

primary matrices and more suitable and compatible with analytical technique used at the step of final determinations
- removal or at least reduction of interferences as a result of selective transfer of sample components to the acceptor matrices
- rise of the concentration of analite in acceptor matrix to the level over the limit of quantitation of the chosen analytical technique

Nevertheless, it should not be forgotten that the extraction and preconcentration of analytes can be a source of losses of contamination of the sample under investigation.

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