

Green Aspects of Sample Preparation – a Need for Solvent Reduction

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Abstract

Growing public concern over protecting our environment obligates chemists, including analytical chemists, to change chemical activity in such a way that it will be conducted in an environmentally friendly manner. The article provides an overview of green chemistry issues relating to sample preparation techniques, concentrating especially on the green advantages of so-called solventless sample preparation. Current sample preparation techniques, fulfilling the demands of green chemistry standards, are presented, along with consideration of their features and advantages.

Keywords: green chemistry, green analytical chemistry, sample preparation

Introduction

The activities of chemists and chemical engineers, both in industry and in laboratories, can adversely affect the quality of the natural environment. Growing public concern over protecting our environment obligates chemists to change their attitude towards activities so that they will be conducted in an environmentally friendly manner. In 1991 the concept of Green Chemistry [1], commonly presented through the Twelve Principles [2], was introduced to implement such an idea into everyday life. Since that time, university teams, independent research groups, industry, scientific societies and governmental agencies, frequently cooperating together, presented different approaches to decrease pollution in order to reduce threats to health and the environment.

The irony is that the analytical methods used to assess the state of environmental pollution and analytical chemists in laboratories, through uncontrolled disposal of reagents and solvents or chemical waste, may in fact be the source of emission of a great amount of pollutants

that negatively influence the environment. This is connected with the necessity of using considerable amounts of chemical compounds in successive steps of applied analytical procedures. Sampling and especially preparation for their final determination is frequently connected with the formation of large amounts of pollutants (vapors, wastes of reagents and solvents, solid waste). Therefore, it is necessary to introduce the rules of green chemistry into chemical laboratories on a large scale.

Considering the Twelve Principles of Green Chemistry it is easy to indicate the directions that may decide about the “green” character of analytical chemistry [3]. The following issues should be treated as priorities:

- eliminating or minimizing the use of chemical reagents, particularly organic solvents, from analytical methods,
- eliminating from analytical procedures chemicals with high toxicity and ecotoxicity,
- reducing steps that demand much labor and energy, in particular analytical methods (per single analyte),
- reducing the impact of chemicals on human health.

Our paper focuses on the role of so-called solventless techniques of sample preparation in contemporary envi-

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ronmental analysis. The great interest in this approach is due to both ecotoxicological and economic aspects: emission of sometimes toxic solvents into the environment is avoided; solvents of high purity are expensive and so are costs of recycling, e.g. by distillation.

The discussion considers the principal features and advantages of the techniques currently in use. Examples of application of each method are also given.

Reduction of Solvents from Analytical Procedures (Solventless Sample Preparation)

There is an urgent necessity to evaluate employed analytical procedures not only in respect to the reagents, instrumental costs and analytical parameters but also on the basis of their negative influence on the environment. A good tool for such an evaluation may be a Life Cycle Assessment (LCA). The constant development of a new solventless technique is a good example of the activities in this field. The following direct analytical techniques (a sample preparation step is not necessary) may be treated as a typical example of procedures that are more friendly for the environment: X-ray fluorescence [4], surface acoustic wave (SAW) [5] used for the determination of volatile organic compounds (VOCs) and immunoassay [6]. Also, other techniques in which the amount of reagents and solvents is eliminated or minimized (calculated per one analytical cycle) belong to environmentally benign procedures, e.g.:

- solid phase extraction (SPE) [7],
- accelerated solvent extraction (ASE) [8],
- solid phase microextraction (SPME) [9],
- stir bar sorptive extraction (SBSE) [10],
- thin-film microextraction [11],
- single drop microextraction (SDME) [12]
- liquid phase microextraction (LPME) [13],
- supercritical fluid extraction (SFE) [14]
- extraction in automated Soxhlet apparatus [15]
- vacuum distillation of volatile organic compounds [16]
- mass spectrometry with membrane interface (MIMS) [17].

Techniques that reduce solvent consumption during sample preparation also are becoming popular, e.g. microwave accelerated extraction (MAE), supercritical fluid extraction (SFE) and pressurized hot water extraction (PHWE). SFE, when only pure carbon dioxide is applied, is also considered a solventless technique, but in many applications a small volume of organic solvent is needed in the trapping step or during elution from the trap. Furthermore, other applications require a modifier in the extraction step.

The next important challenge of green analytical chemistry is in-process monitoring. Developing and using in-line or on-line analyzers allows us to determine analytes in real time, enabling us to detect disturbances in the course of a process in the initial steps. Such a mean

of analysis gives rapid information and provides a chance for proper reaction – stopping the technological process or changing the operational parameters, and improves overall efficiency.

The application of green chemistry rules while designing greener analytical methods is the key toward diminishing the negative effect of analytical chemistry on the environment. The same ingeniousness and novelty applied earlier to obtain excellent sensitivity, precision and accuracy is now used to abate or eliminate the application of hazardous substances in analytics. Below, some modern analytical techniques are presented.

Accelerated Solvent Extraction (ASE)

Recently developed accelerated solvent extraction (ASE) – also referred to as pressurized fluid extraction (PFE) – 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 temperatures and pressure for short periods (5 to 10 min) (Fig. 1). Typically, the samples are 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 flow-through techniques can be used. Compressed gas is used to purge a 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

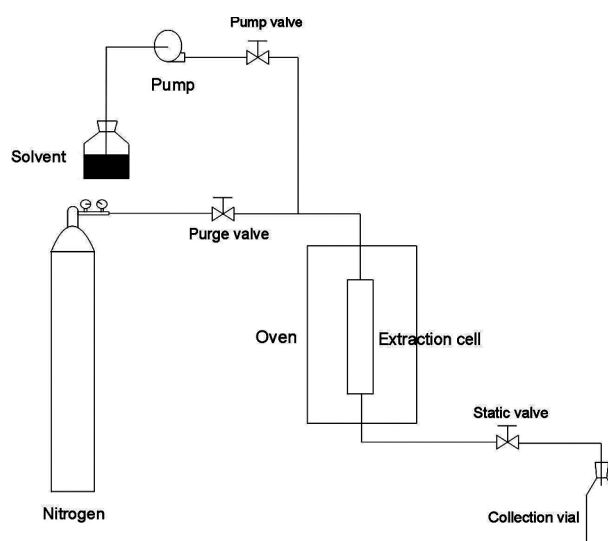


Fig. 1. Schematic diagram of accelerated solvent extraction system.

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 [18]. ASE has been used to extract various hydrophobic organic compounds from different environmental samples [19]. Some studies have carried out comparisons between ASE and conventional techniques, such as supercritical fluid extraction (SFE) and Soxhlet extraction. In the studies where technique comparisons were made, the performance of ASE was consistently equivalent to or better than conventional technique, such as Soxhlet and sonication extraction.

Solid Phase Microextraction (SPME)

SPME is a fast, universal, sensitive, solventless and economical method of sample preparation for analysis using gas chromatography (GC) or high performance liquid chromatography (HPLC) (Fig. 2). This technique allows one to reach detection limits at a level of 5-50 ppt for volatile, semivolatile and nonvolatile compounds. The approximate time of sample preparation using SPME is usually in the range 2-15 min. [20].

The effectiveness of analyte preconcentration using SPME depends on many parameters, such as: *type of fiber, stirring of sample, time of extraction, ionic strength, etc.*

The sensitivity of the technique depends mainly on the value of the partition coefficient of analytes partitioned between a sample and a stationary phase of a fiber. The efficiency of preconcentration depends not only on type

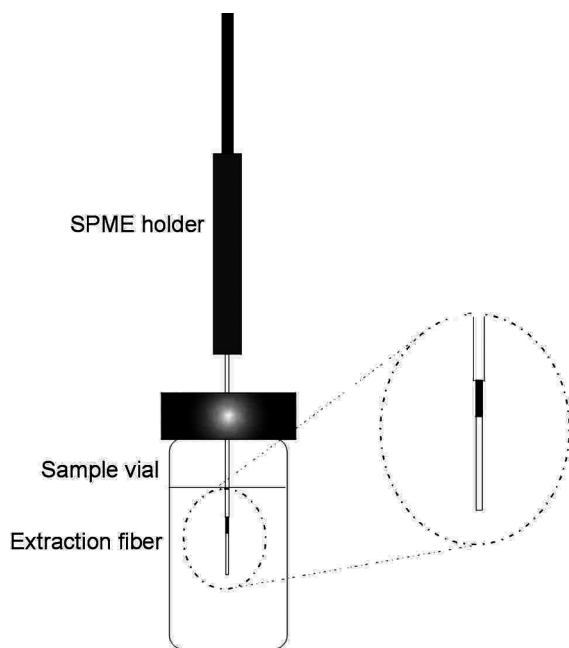


Fig. 2. Schematic diagram of solid phase microextraction system (SPME).

of fiber used but also on its thickness (amount). The type of fiber affects the amount and character of sorbed species [21]. The general rule “like dissolves like”, i.e. polar compounds are sorbed on polar fibers and nonpolar on nonpolar ones. A broad range of standard fibers are available on the market.

A great number of compounds can be determined using this technique. It enables the isolation of pesticides from different matrices [22], solvent residues [23] and an analysis of such complex mixtures as aroma compounds [24].

The exposure of a fiber may be realized in two modes, by direct immersing the SPME fiber into the liquid sample analyzed (direct immersion SPME) or by exposing the fiber to the headspace (HS-SPME). In the second approach, the fiber is inserted into the headspace, above a liquid or solid sample.

The sampling of volatile analytes from samples possessing complex matrices is usually realized in HS-SPME mode. The second variant gives decidedly better results in the determination of aroma components [25] and other volatile components [26]. The HS-SPME technique prolongs the life of the fiber used, because it is not in direct contact with the sample. On the other hand, the extraction of less volatile compounds is also possible directly from the solution – DI-SPME. But in this case, the fiber deteriorates quicker, increasing the cost of analysis. Therefore, when possible, headspace sampling is employed.

A 100 μm polydimethylsiloxane (PDMS) [27] and DVB-PDMS [28] are undoubtedly the most frequent and most universal fibers. The preferred final method of analysis of enriched compounds is usually gas chromatography coupled with mass spectrometry (GC-MS) [29]. Sometimes, as an alternative method, high performance liquid chromatography (HPLC) is used [30].

Stir Bar Sorptive Extraction (SBSE)

In 1999 a new technique of sorptive extraction called stir bar sorptive extraction (SBSE) was introduced into analytical practice [31]. This 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

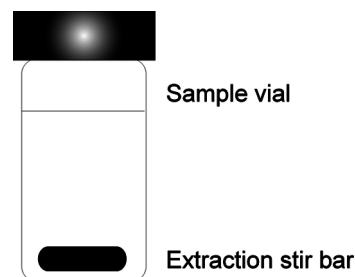


Fig. 3. Schematic diagram of stir bar sorptive extraction (SBSE).

[32] (Fig. 3). First, the stir bars were prepared by removing the Teflon® coating of existing stir bars, reducing the outer diameter of the magnet, and enveloping the 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 slid over the magnetic glass tube. However, as a stir plate is itself magnetic, the use of a 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 a 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 were obtained, especially for volatile compounds. The efficiency of SBSE has been compared with other sorptive techniques [33]. This technique has been applied for the extraction of different types of organic compounds in aqueous solutions [34], wine [35] and in fruits and vegetables [36]. Combined with thermodesorption-GC-MS [37], it enables a low detection limit. As an alternative, the analytes from the stir bar can be desorbed by liquid extraction and the extract injected into the LC system [38].

Thin-Film Microextraction

To obtain a higher volume of the extraction phase the surface area of the polymer is extended, which has been done by using membranes instead of fiber coatings. The use of a thin membrane has the advantage that enhanced extraction efficiency and hence high sensitivity can be achieved without suffering from elevated equilibrium times, as happens when using thick phase coated stir bars. A cross-linked commercial PDMS membrane [11] was successfully evaluated for extraction of PAH in headspace mode. An in-house prepared membrane of poly(dimethylsiloxane) [39] was applied to both non polar PAH extraction and to polar phenolic compounds. A commercial porous polysulphone hollow fiber membrane coated with a variety of hydroxylated polymethacrylate compounds [40], has increased swelling tendency when used in water. This is an advantage over classical SPME for extraction of alkyl-substituted phenols in seawater samples. One of the drawbacks of the system is the necessity of a thermal desorption system or high volume GC injector.

Single Drop Microextraction (SDME)

In 1997 Jeannot and Cantwell [41] and He and Lee

[42] independently introduced a simple kind of microextraction in which an organic drop hangs from the tip of a GC syringe needle (Fig. 4). SDME is a simple method of reducing solvent consumption. However, the small amounts of solvent used in SDME are an advantage of this extraction. Pure solvents or mixtures can be used for selective extraction of different organic species. Therefore, this technique represents a cheap and attractive alternative to SPME requiring a standard GC syringe only. SPME does not give a solvent peak in GC but analyte desorption from the polymer in a hot injector is significantly slower than solvent evaporation, resulting in peaks with a tendency to tail. Alternatively, stirring the sample increases extraction efficiency by SPME, but stirring or sonification of samples in SDME experiments caused damage to the organic drop. Consequently, these two methods cannot be applied together with SDME. Adequate precision, linearity and repeatability indicate that this virtually solventless extraction is a reliable method for routine analysis.

A review of SDME including 27 references [12], resumes the investigation carried out in this nowadays fast growing field until 2002. In a more recent work, a benzyl alcohol microdrop was found to be the optimum solvent for the extraction of solvent residuals from vegetable oils [44]. Octanol provided optimum extraction efficiency for a variety of short chain alcohols [45] from water samples. The field of applications has even been extended to the determination of metal-organic compounds, such as tributyltin [46], which was extracted into a decane microdrop. Using hexane as a solvent, volatile halohydrocarbons could be extracted in this way from aqueous samples [47], with LOD's as low as 0.001 $\mu\text{g dm}^{-3}$ for CCl_4 using GC with electron capture detection. An ionic liquid (1-octyl-3-methylimidazo-

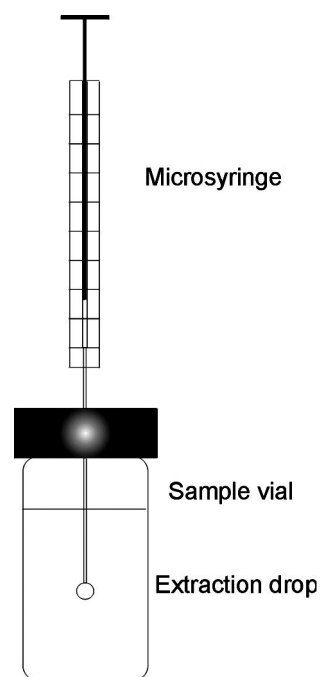


Fig. 4. Schematic diagram of single drop microextraction (SDME).

lium hexafluorophosphate) as extraction solvent was found to be suitable for the extraction of substituted phenols [48] and for formaldehyde in mushrooms [49], after derivatization with 2,4-dinitrophenylhydrazine. In spite of being a virtually solventless, inexpensive, fast and simple method for analyte extraction and/or preconcentration, frequent problems with drop stability and lack of sensitivity have been reported. A further development trying to overcome these limitations is microliter-size liquid membrane in between sample and microdrop (Fig 5). The former consists of octane and the latter of water, a simultaneous extraction/back extraction process was reported [50].

Liquid Phase Microextraction (LPME)

This technique can be considered as a further development of SDME. Illustratively the organic phase is inside the lumen of the fiber. The principle of the disposable LPME device is illustrated in Fig 6. The sample solution is filled into a vial with a screw top/silicone septum. Two conventional medical syringe needles (guiding needles) were inserted through the silicon septum in the screw top and the two ends were connected to each other by a piece of Q3/2 Accurel KM polypropylene hollow fiber. The latter served to contain the microliter volume of extracting solution. For extraction in combination with GC the hollow fibre was filled with *n*-octanol. For extraction in combination with CE or HPLC the hollow fiber mounted on the guiding needles was first dipped for 5 s into *n*-octanol to immobilize the solvent in pores. Following this, the fiber was placed in the sample and extraction was performed. After extraction the acceptor solution was collected in microvials by appli-

cation of small head pressure on one of the guiding steel needles for automated analysis by GC or CE.

The disposable nature of the hollow fiber eliminates the possibility of carry-over effects and cross-contamination, thus providing enhanced reproducibility. Further, the small pore size prevents large molecules and particles present in the donor solution from entering the acceptor phase, providing effective matrix/analyte separation. Details on hollow fiber configurations, LPME sampling modes and different parameters to be taken into account during method optimization were reviewed in 2003 by Psillakis et al. [51], another review focuses on the use of LPME for drug analysis [52]. An insight in basic extraction principles, technical set-up, recovery, enrichment, extraction speed, selectivity and applications can be found in a review given by Rasmussen et al. [53]. A disadvantage of LPME is a lack of precision, which may be caused by the completely manual operation, from fiber preparation and conditioning to the handling of extract.

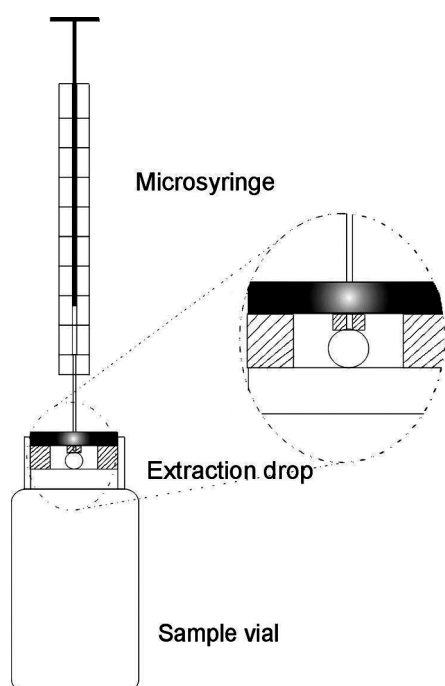


Fig. 5. Schematic diagram of single drop microextraction (SDME) with a microliter size liquid membrane.

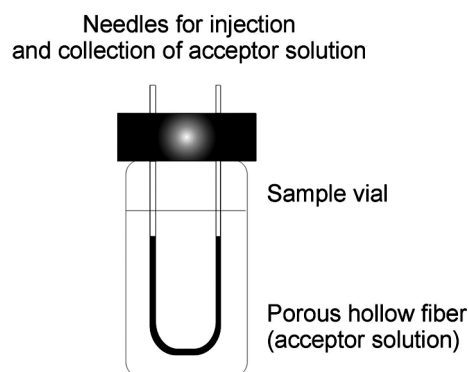


Fig. 6. Schematic diagram of a liquid phase microextraction (LPME) unit.

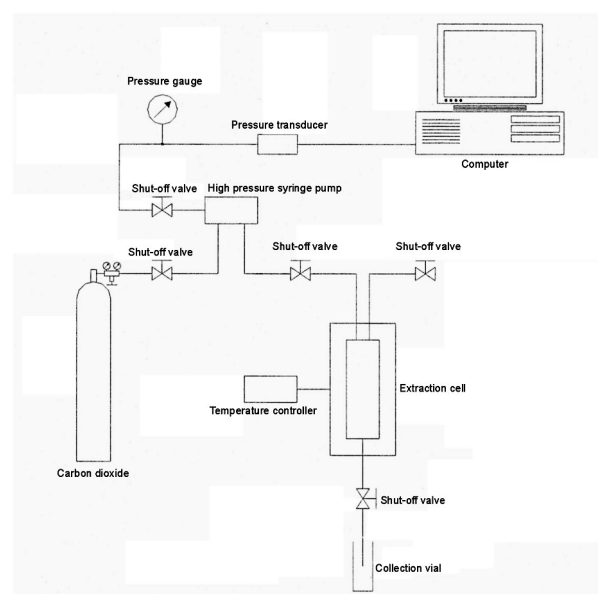


Fig 7. Schematic diagram of supercritical fluid extraction apparatus (SFE).

Supercritical Fluid Extraction (SFE)

The superior solvation qualities of supercritical fluids over liquids have been known for more than a century when, in 1879, Hannay and Hogarth investigated the solubility of different inorganic salts in supercritical ethanol. It was not until the late 1960s that the potential of extraction with supercritical fluids was recognized.

Several liquids or gases can be brought into the supercritical phase. Different solvents, as an extraction medium for the use in analytical-scale SFE, can be selected. Carbon dioxide is most commonly used as an SFE medium because of its desirable properties and easy handling. CO₂

is relatively inexpensive and commercially available at a purity grade acceptable for most analytical applications. Another advantage of carbon dioxide is that the polarity can easily be adjusted by adding modifiers, for example methanol, to the supercritical fluid or the extraction vessel.

Supercritical fluid extraction is superior to traditional extraction and clean up for organic compounds in samples in every aspect: solvent use is reduced to a minimum, analysis time is reduced to 2-3 hours, large sample put through is possible by using automated systems (Fig 7), the repeatability is better than the traditional analysis, optimization for different compound classes is possible,

Table 1. Recent applications of SFE to isolate different types of organic analytes from environmental samples.

No [Ref.]	Matrix	Analytes	Mode of extraction					Analytical technique
			Static	Dynamic	Off-line	On-line	Automated	
1 [60]	SPE cartridge	Organic pollutants of intermediate polarity (in sewage)		+	+			GC, GC-MS
2 [61]	Activated carbon cartridge	m-xylene		+	+			
3 [62]	SPE cartridge (Florisol)	Polycyclic aromatic hydrocarbons and polychlorinated biphenyls (in air)		+	+			GC-ITMS
4 [63]	Biological samples	Polychlorinated biphenyls		+	+			
5 [64]	Human adipose tissue	Polychlorinated biphenyls		+	+			GC-MS
6 [65]	White pine needles	Polycyclic aromatic hydrocarbons	+	+	+			GC-M
7 [66]	Airborne particulates	Polycyclic aromatic hydrocarbons		+	+			
8 [67]	Fly ash	Dioxins		+	+			HRGC-HRMS
10 [68]	Dust	Pesticides (carbosulfon and imidacloprid)						LC-UV
11 [69]	Urban dust, marine sediment	Organic compounds		+	+			GC-MS
12 [69]	River sediments	Acidic herbicides	+		+			GC-ECD, GC-MS
13 [70]	Marine sediments	Hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyls		+	+		+	GC-FID GC-ECD GC-MS
14 [71]	River sediment, marine sediment, harbour sediment, industrial soil, fresh water sediment	Polychlorinated biphenyls	+		+			GC-MS
15 [72]	Surfactant suspension soil extract	Polychlorinated biphenyls		+	+			GC-FID GC-MS
16 [73]	Water	Oil		+		+		FTIR
17 [74]	Sludge	Bisphenol A	+	+	+			GC-MS
18 [75]		Metal complexes		+	+			FAAS
19 [76]	Soil	Metals	+	+	+			AAS
20 [77]	Marine sediment	Polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls		+		+	+	SFC-CT- GC-MS

simultaneous analyses of many different organic compounds in one sample is possible.

The considerable reduction in analysis time and cost open the possibility of performing large monitoring studies that include many different compounds.

There are review articles [54] treating the different aspects of introduction of supercritical fluid extraction into analytical practice. More detailed information connected with recent applications of the SFE technique to isolate analytes from various matrices are collected in Table 1.

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

- restrictor plugging in off-line SFE [55],
- new analyte collection method for off-line SFE based on mixing expanding supercritical effluent with overheated organic solvent vapor [56],
- studies of collection capacity of a solid phase trap in SFE [57],
- design of SFE-GC system with quantitative transfer of extraction effluent to a megabore capillary column [58],

Table 2. Contribution of the Analytical Chemistry Department of Gdańsk University of Technology to the popularization of green chemistry ideas.

No [Ref.]	Title of publication	Popularization of Green Chemistry idea	Reviews concerning reduction of solvents in sample preparation	Papers presenting original research and development
1 [78]	Application of solid-phase microextraction for determination of organic vapours in gaseous matrices			+
2 [79]	Solventless sample preparation techniques in environmental analysis		+	
3 [80]	Studies on the use of commercial capillary gas chromatographic columns as diffusion denuders			+
4 [81]	Solid-phase microextraction – a convenient tool for the determination of organic pollutants in environmental matrices		+	
5 [82]	Comparison of extraction techniques for gas chromatographic determination of volatile carbonyl compounds in alcohols			+
6 [83]	Green analytical chemistry – some remarks	+		
7 [84]	Optimisation of operational parameters of extraction solid samples using accelerated solvent extraction (ASE)			+
8 [85]	Studies on extraction efficiency of new SPME fibres with respect to typical air organic pollutants			+
9 [86]	Some remarks on gas chromatographic challenges in the context of green analytical chemistry	+		
10 [87]	Modern techniques of extraction of organic analytes from environmental matrices		+	
11 [88]	Evaluation of headspace solid-phase microextraction for the analysis of volatile carbonyl compounds in spirits and alcoholic beverages			+
12 [89]	Determination of volatile aliphatic amines in air by solid-phase microextraction coupled with gas chromatography with flame ionization detection			+
13 [90]	Applicability of glass fiber as a support material for generation of gaseous standard mixtures using thermal decomposition of the surface compound. Calibration of analytical equipment			+
14 [91]	Extraction of acid herbicides from soil by means of accelerated solvent extraction			+
15 [92]	A review of theoretical and practical aspects of solid-phase microextraction in food analysis	+	+	
16 [93]	Determination of organo-tin compounds in biological samples using accelerated solvent extraction, sodium tetraethylborate ethylation, and multicapillary gas chromatography-flame photometric detection			+
17 [94]	New techniques of sample preparation for determination of organic compounds using Gas Chromatography		+	
18 [95]	Green Chemistry	+		
19 [96]	Challenges of Green Chemistry in monitoring and air protection	+		

- application of SFE in physico-chemical studies (e.g., determination of partition coefficients) [59],

Conclusions

Green Chemistry is not a new branch of science. It is a new philosophical approach that through its application and extension of principles can contribute to sustainable development. It is easy to find many interesting examples of the use of green chemistry rules. Also in chemical laboratories new analytical methodologies are still being developed which may be realized according to green chemistry standards. They are useful in conducting chemical processes and in the evaluation of their effects on the environment. In Table 2, exemplary publications from our department are presented. More information can be found on: <http://www.pg.gda.pl/chem/Katedry/Analityczna/analit.htm>.

The techniques of sample preparation, extraction (isolation) and/or preconcentration of analytes are usually 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. Nevertheless, it should not be forgotten that the extraction and preconcentration steps can be a source of environmental pollution. Techniques of sample preparation introduced in the article have the following advantages:

- they are solvent free or virtually solvent free – solvent usage per one analysis is reduced to a minimum,
- the transport of analytes to the matrix is characterized by simplicity of composition compared with primary matrices and more suitable and compatible with the 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,
- increase of the concentration of analytes in the acceptor matrix to the level over the limit of quantitation of the chosen analytical technique.

SPME with commercially available fibers is the most popular technique, where for a limited number of coatings, a high number of applications are reported. Additionally other SPME related techniques have been introduced as an analytical toolkit.

Techniques that are reducing solvent consumption during sample preparation also have gained popularity, e.g. pressurized hot water extraction (PHWE). This technique has replaced conventional organic solvents in a variety of extraction processes [97,98]. Because PHWE employs water as an environmentally benign solvent it can also be classified as a “solventless” technique. Selective extraction can be achieved by temperature tuning. Usually temperatures below the critical value of water, but usually above 100°C are employed. In work in liquid phase, pressure must be enough to prevent the water from vapor-

izing. In vapour phase some pressure is generally needed for effective transportation of the water. High temperature increases the initial desorption of the compounds from the sample particles. In addition, fast diffusion, low viscosity and low surface tension are achieved at higher temperatures. On the other hand, thermally labile compounds may be destroyed and the amount of coextracted compounds may be greater than at lower temperatures.

The increased popularity of the above-mentioned techniques for isolation and enrichment procedures is not only due to their proecological character but also to the fact that they provide the required sensitivity (up to ppt level). Furthermore, most of these techniques can be automated and quite easily coupled with “green” final methods of analysis, i.e. gas chromatography. Some efforts are still being undertaken to decrease sample preparation time in order to gain compatibility of the given preparation method with high speed chromatography.

Introducing these technique to everyday practice into laboratories is an important step in diminishing the negative effects of analytical chemistry on the environment.

References

1. RITTER S.K. Green Chemistry. Chem. Eng. News **79** (29), 27, **2001**.
2. ANASTAS P.T., WARNER J.C. Green Chemistry: Theory and Practise. Oxford University Press, Oxford **1998**
3. (a) ANASTAS T. Green Chemistry and the Role of Analytical Methodology Development, Crit. Rev. Anal. Chem. **29**(3), 167, **1999**. (b) WARDENCKI W., CURYŁO J., NAMIEŚNIK J. Green Chemistry – Current and Future Issues. Pol. J. Environ. Stud. **4**, 389, **2005**. (c) NAMIEŚNIK J., WARDENCKI W. Solventless Sample Preparation Techniques in Environmental Analysis. J. High Resol. Chromatogr., **23**, 297, **2000**.
4. (a) BAMFORD S.A., WĘGRZYNEK D., CHINEA-CANO E., MARKOWICZ A. Application of X ray fluorescence techniques for the determination of hazardous and essential trace elements in environmental and biological materials, Nukleonika, **49**(3), 87, **2004**. (b) ALVAREZ J., MARCO M.L., ARROYO J., GREAVES E.D., RIVAS R. Determination of calcium, potassium, manganese, iron, copper and zinc levels in representative samples of two onion cultivars using total reflection X-ray fluorescence and ultrasound extraction procedure. Spectrochim. Acta, Part B, **58B**(12), 2183, **2003**.
5. (a) BISWAS S., HEINDSELMEN K., WOHLTJEN H., STAFF C. Differentiation of vegetable oils and determination of sunflower oil oxidation using a surface acoustic wave sensing device. Food Control. **15**(1), 19, **2004**. (b) MARTIN S.P., LAMB D.J., LYNCH J.M., REDDY S.M. Enzyme-based determination of cholesterol using the quartz crystal acoustic wave sensor. Anal. Chim. Acta. **487**(1), 91, **2003**.
6. (a) SEIFERT M. Effect-oriented analysis for the determination of estrogenic compounds, Chimia. **57**(1/2), 37, **2003**. (b) NICHKOVA M., EUN-KEE P., KOIVUNEN M.E., KAMITA S.G., GEE S.J., CHUANG J., VAN EMON J.M., HAMMOCK B.D. Immunochemical determination of dioxins in

- sediment and serum samples. *Talanta*. **63**(5), 1213, **2004**, (c) KUMAR K., THOMPSON A., SINGH A.K., CHANDER Y., YOGESH, GUPTA S. C. Enzyme-linked immunosorbent assay for ultra trace determination of antibiotics in aqueous samples. *J. Environ. Qual.* **33**(1), 250, **2004**.
7. (a) ALUMBAUGH R.E., GIEG L.M., FIELD J.A. Determination of alkylbenzene metabolites in groundwater by solid-phase extraction and liquid chromatography-tandem mass spectrometry. *J. Chromatogr. A.* **1042**, 89, **2004**. (b) DĄBROWSKA H., DĄBROWSKI Ł., BIZIUK M., GACA J., NAMIEŚNIK J. Solid-phase extraction clean-up of soil and sediment extracts for the determination of various types of pollutants in a single run. *J. Chromatogr. A.* **1003**, 29, **2003**.
 8. GIERGIELEWICZ-MOŻAJSKA H., DĄBROWSKI Ł., NAMIEŚNIK J. Accelerated Solvent Extraction (ASE) in the analysis of environmental solid samples – some aspects of theory and practice. *Crit. Rev. Anal. Chem.* **31**, 149, **2001**.
 9. WARDENCKI W., MICHULEC M., CURYŁO J. A review of theoretical and practical aspects of solid-phase microextraction in food analysis. *J. Food Sci. Technol.* **39**, 703, **2004**.
 10. BENANOU D., ACOBAS F., DE ROUBIN M.R. Optimization of stir bar sorptive extraction applied to the determination of odorous compounds in drinking water. *Water Sci. Technol.* **49**(9), 161, **2004**.
 11. BRUHEIM I., LIU X.C., PAWLISZYN J. Thin-film microextraction. *Anal. Chem.* **75**, 43, **2003**.
 12. PSILLAKIS E., KALOGERAKIS N. Solid-phase microextraction versus single-drop microextraction for the analysis of nitroaromatic explosives in water samples. *J. Chromatogr. A.* **938**, 113, **2001**.
 13. ZHAO L., LEE H.K., Liquid-phase microextraction combined with hollow fiber as a sample preparation technique prior to gas chromatography/mass spectrometry. *Anal. Chem.* **74**(11), 2486, **2002**.
 14. (a) SHIMMO M., PIIA A., HARTONEM K., HYOTYLAINEN T., PATERO J., KULMALA M., RIEKKOLA M.L. Identification of organic compounds in atmospheric aerosol particles by on-line supercritical fluid extraction-liquid chromatography-gas chromatography-mass spectrometry. *J. Chromatogr. A.* **1022**, 151, **2004**. (b) WANG S., LIN Y., WAI C.M. Supercritical Fluid Extraction of Toxic Heavy Metals from Solid and Aqueous Matrices. *Sep. Sci. Technol.* **38**, 2279, **2003**.
 15. U.S. EPA., Method 3541 Automated Soxhlet Extraction 1.0. Scope and application 1.1.
 16. AKHTAR J., DURRANI S.K., CHUGHTAI, NAZIR A., MUNIR M., MUHAMMAD B. Determination of oxygen and nitrogen impurities in magnesium metal by vacuum distillation and ICP-OES techniques *Turkish J. Chem.* **26**(5), 681, **2002**.
 17. FERREIRA B.S., VAN KEULEN F., DA FONSECA M.M.M. A microporous membrane interface for the monitoring of dissolved gaseous and volatile compounds by on-line mass spectrometry. *J. Membr. Sci.* **208**(1-2), 49, **2002**.
 18. (a) BRUMLEY W.C. Techniques for Handling Environmental Samples with Potential for Capillary Electrophoresis. *J. Chromatogr. Sci.* **33**, 670, **1995**. (b) DĄBROWSKI A., GIERGIELEWICZ-MOŻAJSKA H., BIZIUK M., GACA J., NAMIEŚNIK J. Some Aspects of the Analysis of Environmental Pollutants in Sediments using Pressurized Liquid Extraction and Gas Chromatography – Mass Spectrometry. *J. Chromatogr. A.* **957**, 59, **2002**.
 19. (a) GALLAGHER P.A., MURRAY S., WEI X., SCHWEGEL C.A., CREED J.T. An evaluation of sample dispersion media used accelerated solvent extraction for the extraction and recovery of arsenicals from LFB and DORM-2. *J. Anal. At. Spectrom.* **17**, 581, **2002**. (b) LEE H.B., PEART T.E. Determination of Bisphenol A in Sewage Effluent and Sludge by Solid-Phase and Supercritical Fluid Extraction and Gas Chromatography/Mass Spectrometry. *J. AOAC Int.* **83**, 290, **2002**. (c) FERRER I., FURLOG E.T. Accelerated Solvent Extraction Followed by On-line Solid-Phase Extraction Coupled to Ion Trap LC/MS/MS for analysis of Benzalkonium Chlorides in Sediment Samples. *Anal. Chem.* **74**, 1275, **2002**.
 20. (a) PAWLISZYN J., in *Solid Phase Microextraction. Theory and Practice*. New York, **1997**. (b) ZHANG Z., PAWLISZYN J. Headspace Solid-Phase Microextraction. *Anal. Chem.* **65**, 1843, **1999**. (c) Supelco, Note56, **1998**.
 21. GÓRECKI T., YU X., PAWLISZYN J. Theory of analyte extraction by selected porous polymer SPME fibres. *Analyst.* **124**, 643, **1999**.
 22. (a) SIMPLICIO A.L., BOAS L.V. Validation of a solid-phase microextraction method for the determination of organophosphorus pesticides in fruits and fruit juice. *J. Chromatogr. A.* **833**, 35, **1999**. (b) HWANG B.H., LEE M.R., Solid phase microextraction for organochlorine pesticide residues analysis in Chinese herbal formulations. *J. Chromatogr. A.* **898**, 245, **2000**.
 23. (a) GRIMALDI R., DE PAZ F., RIVARA L., DE PIANE L. Enrichment of aromatic solvents present in virgin olive oils and their subsequent stripping and determination by GC-MS. *Boll. Chim. Igien.* **50**, 115, **1999**. (b) EVANS T.J., BUTZKE C.E., EBELER S.E. Analysis of 2,4,6-trichloroanisole in wines using solid-phase microextraction coupled to gas chromatography mass spectrometry. *J. Chromatogr. A.* **786**, 293, **1999**.
 24. (a) JAILLAIS B., BERTRAND V., AUGER J. Sample preparation of atmospheric aerosol for the determination of carbonyl compounds. *Talanta*. **48**, 747, **1999**. (b) MATICH A.M., ROWAN D.D., BANKS N.H. Solid phase microextraction for quantitative headspace sampling of apple volatiles. *Anal. Chem.* **68**, 4114, **1996**.
 25. (a) WAN X.M., STEVENSON R.J., CHEN X.D., MELTON L.D. Application of solid phase microextraction to Kiwi-fruit volatile flavour compound analysis during ripening process. *Food Res. Int.* **32**, 175, **1999**. (b) AUGUSTO F., PIRES VALENTE A.S., DOS SANTOS T.E., RIVELLINO S.R. Screening of brazilian fruit aromas using solid-phase microextraction-gas chromatography-mass spectrometry. *J. Chromatogr. A.* **873**, 117, **2000**.
 26. (a) LIGOR M., BUSZEWSKI B. Determination of mentol and menthone and pharmaceutical products by solid-phase microextraction-gas-chromatography. *J. Chromatogr. A.* **847**,

- 161, 1999. (b) BELTRAN J., LÓPEZ F.J., HERNANDEZ F. Solid phase microextraction (SPME) in pesticide residue analysis. A review (2000). *J. Chromatogr. A.* **885**, 389, 2000.
27. (a) SIMPLICIO A.L., BOAS V. Validation of a solid-phase microextraction method for the determination of organophosphorus pesticides in fruits and fruit juice. *J. Chromatogr. A.* **833**, 35, 1999. (b) FERNANDEZ M., PADRON C., MARCONI L., GHINI S., COLOMBO R., SABATINI A.G., GIROTTI S. Determination of organophosphorus pesticides in honeybees after solid-phase microextraction. *J. Chromatogr. A.* **922**, 257, 2001.
28. (a) FITZGERALD G., JAMES K.J., MACNAMARA K., STACK M.A. Characterisation of whiskeys using solid-phase microextraction with gas chromatography-mass spectrometry. *J. Chromatogr. A.* **896**, 351, 2000. (b) BICCHI C., DRIGO S., RUBIOLO P. Influence of fibre coating in headspace solid-phase microextraction-gas chromatographic analysis of aromatic and medicinal plants. *J. Chromatogr. A.* **892**, 469, 2000.
29. (a) HWANG B.H., LEE M.R. Solid-phase microextraction for organochlorine pesticide residues analysis in Chinese herbal formulations. *J. Chromatogr. A.* **898**, 245, 2000. (b) VERHOEVEN H., BEUERLE T., SCHWAB W. Solid-Phase Microextraction: Artefact Formation and its Avoidance. *Chromatographia.* **46**, 63, 1997.
30. (a) WU J., XIE W., PAWLISZYN J., Automated in-tube solid phase microextraction coupled with HPLC-ES-MS for the determination of catechins and caffeine in tea. *Analyst.* **125**, 2216, 2000 (b) EISERT R., JACKSON S., KROTZKY A. Application of on-site solid-phase microextraction in aquatic dissipation studies of profoxydim in rice. *J. Chromatogr. A.* **909**, 29, 2001.
31. BALTUSSEN E., SANDRA P., DAVID F., CRAMERS C. Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: theory and principles. *J. Microcolumn Sep.* **11**, 737, 1999.
32. (a) WENNRICH L., POPP P., BREUSTE J. Comparison of Isotopic Dilution Methods for Determination of Theophylline in the Plasma and Saliva of Infants and Children *Chromatographia.* **53**, 380, 2001. (b) POPP P., BAUER C., WENNRICH L. Application of stir bar sorptive extraction in combination with column liquid chromatography for the determination of polycyclic aromatic hydrocarbons in water samples. *Anal. Chim. Acta.* **436**, 1, 2001 (c) KOLAHGAR B., HOFFMANN A., HEIDEN A.C. Application of stir bar sorptive extraction to the determination of polycyclic aromatic hydrocarbons in aqueous samples. *J. Chromatogr. A.* **963**, 225, 2002.
33. BLASCO C., FONT G., PICO Y. Comparison of microextraction procedures to determine pesticides in oranges by liquid chromatography-mass spectrometry. *J. Chromatogr. A.* **970**, 201, 2002.
34. (a) POPP P., BAUER C., WENNRICH L. Application of stir bar sorptive extraction in combination with column liquid chromatography for the determination of polycyclic aromatic hydrocarbons in water samples. *Anal. Chim. Acta* **436**, 1, 2001. (b) KOLAHGAR B., HOFFMANN A., HEIDEN A.C. Application of stir bar sorptive extraction to the determination of polycyclic aromatic hydrocarbons in aqueous samples. *J. Chromatogr. A.* **963**, 225, 2002.
35. SANDRAP, TIENPONT B., VERCAMMEN J., TREDoux A., SANDRA T., DAVID F. Stir bar sorptive extraction applied to the determination of dicarboximide fungicides in wine. *J. Chromatogr. A.* **928**, 117, 2001.
36. (a) WENNRICH L., POPP P., BREUSTE P. *Chromatographia.* **53**, 380, 2001. (b) BLASCO C., FONT G., PICO Y. Comparison of microextraction procedures to determine pesticides in oranges by liquid chromatography-mass spectrometry. *J. Chromatogr. A.* **970**, 201, 2002.
37. KOLAHGAR B., HOFFMANN A., HEIDEN A.C. Application of stir bar sorptive extraction to the determination of polycyclic aromatic hydrocarbons in aqueous samples. *J. Chromatogr. A.* **963**, 225, 2002.
38. POPP P., BAUER C., WENNRICH L. Application of stir bar sorptive extraction in combination with column liquid chromatography for the determination of polycyclic aromatic hydrocarbons in water samples. *Anal. Chim. Acta* **436**, 1, 2001.
39. HU Y., YANG Y., HUANG J., Li G. Preparation and application of poly(dimethylsiloxane)/ β -cyclodextrin solid-phase microextraction membrane. *Anal. Chim. Acta* **543**, 17, 2005.
40. BASHER C., PARTHIBAN A., JAYARAMAN A., LEE H.K., VALIYAVEETIL S. Determination of alkylphenols and bisphenol-A. A comparative investigation of functional polymer-coated membrane microextraction and solid-phase microextraction techniques. *J. Chromatogr. A.* **1087**, 274, 2005.
41. JEANNOT M.A., CANTWELL A.A. Mass Transfer Characteristics of Solvent Extraction into a Single Drop at the Tip of a Syringe Needle. *Anal. Chem.* **69**, 235, 1997.
42. HE Y., LEE H.K. Application of a 32-Microband Electrode Array Detection System for Liquid Chromatography Analysis. *Anal. Chem.* **69**, 463, 1997.
43. YAMINI Y., HOJJATI M., HAJI-HOSSEINI M., SHAMSI-PUR M. Headspace solvent microextraction. A new method applied to the preconcentration of 2-butoxyethanol from aqueous solutions into a single microdrop. *Talanta* **62**, 265, 2004.
44. MICHULEC M., WARDENCKI W. Selected aspects of chromatographic solvents residues determination using HS, SPME and SDE techniques for isolation and preconcentration of analyte, in book of abstracts of 11th International Symposium on Separation Sciences, September 12-14, 2005, Pardubice, Czech Republic.
45. SARAJI M. Dynamic headspace liquid-phase microextraction of alcohols. *J. Chromatogr. A.* **1062**, 15, 2005.
46. ARTHUR C.L., PAWLISZYN J. Solid Phase Microextraction with Thermal Desorption Using Fused Silica Optical fibers. *Anal. Chem.* **62**, 2145, 1990.
47. LI Y., ZHANG T., LIANG P. Application of continuous-flow liquid-phase microextraction to the analysis of volatile halohydrocarbons in water. *Anal. Chim. Acta* **536**, 245, 2005.
48. LIU J.F., CHI Y.G., JIANG G.B., TAI C., PENG J.F., HU J.T. Ionic liquid-based liquid-phase microextraction, a new

- sample enrichment procedure for liquid chromatography. *J. Chromatogr. A.* **1026**, 143, **2004**.
49. LIU J. F., PENG J.F., CHI Y.G., JIANG G.B. Determination of formaldehyde in shiitake mushroom by ionic liquid-based phase microextraction coupled with liquid chromatography. *Talanta* **65**, 705, **2005**.
50. MA M., CANTWELL F.L. Solvent Microextraction with Simultaneous Back Extraction for Sample Cleanup and Preconcentration: Preconcentration into a Single Microdrop. *Anal. Chem.* **71**, 388, **1999**.
51. PSILLAKIS E., KALOGERAKIS N. Developments in liquid-phase microextraction. *Trends Anal. Chem.* **22**, 565, **2003**.
52. PEDERSEN-BJERGAARD S., RASMUSSEN K.E. Bioanalysis of drugs by liquid-phase microextraction. *J. Chromatogr. B.* **817**, 3, **2005**.
53. RASMUNSEN K.E., PEDERSEN-BJERGAARD S. Developments in hollow fibre-based, liquid-phase microextraction. *Trends Anal. Chem.* **23**, 1, **2004**.
54. (a) HEDRICK J.L., MULCAHEY L.J. Supercritical fluid extraction. *Microchim. Acta* **108**, 115, **1992**. (b) KIRSCHNER C.H., TAYLOR L.T. Recent advances in sample introduction for supercritical fluid chromatography. *J. High. Resolut. Chromatogr.* **16**, 73, **1993**.
55. PAGE S.H., BENNER B.A., SMALL J.A., CHOQUETTE S.J. Application of stir bar sorptive extraction in combination with column liquid chromatography for the determination of polycyclic aromatic hydrocarbons in water samples. *J. Supercrit. Fluids*, **14**, 257, **1999**.
56. VEJROSTA J., KARASEK P., PLANETA J. Analyte Collection in Off-line Supercritical Fluid Extraction. *Anal. Chem.* **71**, 905, **1999**.
57. BJÖRKLUND E., MATHIASSEN L., PERSSON P., JÄREMO M. Collection capacity of a solid phase trap in supercritical fluid extraction for the extraction of lipids from a model fat sample. *J. Liq. Chrom. Rel. Technol.* **24**, 2133, **2001**.
58. STONE M.A., TAYLOR L.T. SPE-GC with Quantitative Transfer of the Extraction Effluent to a Megabore Capillary Column. *Anal. Chem.* **72**, 3085, **2000**.
59. KARASEK P., POL J., PLANETA J., ROTH M., VEJROSTA J., WICAR S. Partition Coefficients of Environmentally Important Phenols in a Supercritical carbon Dioxide-Water System from Cocurrent Extraction without Analysis of the Compressible Phase. *Anal. Chem.* **74**, 4294, **2002**.
60. YOU J., LAO W., WANG G. Analysis of organic pollutants in sewage by supercritical fluid extraction. *Chromatographia* **49**, 399, **1999**.
61. BENKHEDDA J., JAUBERT J.N., BARTH D., ZETZL C., BRUNNER G. Adsorption and desorption of m-xylene from supercritical carbon dioxide on activated carbon. *Sep. Sci. Technol.*, **36**, 2197, **2001**.
62. MADEN A.J., HAYWARD M.J. Sheet Materials for Use as Membrane Introduction Mass Spectrometry. *Anal. Chem.* **68**, 1805, **1996**.
63. WHITWORTH D.J., ACHTERBERG E.P., HERZL V., NIMMO M., GLEDHILL M., WORSFOLD P.J. Development of a simple extraction procedure using ligand competition for biogeochemically available metals of estuarine suspended particulate matter. *Anal. Chim. Acta* **392**, 3, **1999**.
64. VAN BAVEL B., DAHL P., KARISSON L., HARDELL L., RAPPE CH., LINDSTÖM G. Supercritical fluid extraction of PCBs from human adipose tissue for HRGC/LRMS analysis. *Chemosphere*. **30**, 1229, **1995**.
65. LANG Q., HUNT F., WAI Ch. M. Supercritical fluid extraction of polycyclic aromatic hydrocarbons from pine (*Pinus strobus*) needles and its implications. *J. Environ. Monit.* **2**, 639, **2000**.
66. ODA J. Application of supercritical fluid extraction for the analysis of polycyclic aromatic hydrocarbons in airborne particulates. *Bunseki Kagaku*. **48**, 595, **1999**.
67. WINDAL I., EPPE G., GRIDELET A.C., DE PAUW E. Supercritical fluid extraction of polychlorinated dibenzo-p-dioxins from fly ash: the importance of fly ash origin and composition on extraction efficiency. *J. Chromatogr. A.* **819**, 187, **1998**.
68. ESKILSSON C.S., MATHIASSEN I. Supercritical fluid extraction of the pesticides carbosulfan and imidacloprid from process dust waste. *J. Agric. Food Chem.* **48**, 5159, **2000**.
69. PAGE S.H., BENNER B.A. JR., SMALL J.A., CHOQUETTE S.J. Application of stir bar sorptive extraction in combination with column liquid chromatography for the determination of polycyclic aromatic hydrocarbons in water samples. *J. Supercrit. Fluids*, **14**, 257, **1999**.
70. BERG B.E., LUND H.S., KRINGSTAD A., KVERNHEIM A.L. Routine analysis of hydrocarbons, PCB and PAH in marine sediments using supercritical CO₂ extraction. *Chemosphere* **38**, 587, **1999**.
71. BJÖRKLUND E., BØWADT S., MATHIASSEN L., HAWTHORNE S.B. Determining PCB sorption/desorption behavior on sediments using selective supercritical fluid extraction. 1. Desorption from historically contaminated samples. *Environ. Sci. Technol.* **33**, 2193, **1999**.
72. WU Q., MARSHALL W.D. Extractions of polychlorinated biphenyl (PCB) compounds from surfactant suspension/soil extracts with dechlorination on-line. *J. Environ. Monit.* **3**, 499, **2001**.
73. (a) MINTY B., RAMSEY E.D., DAVIES I. Development of an automated method for determining oil in water by direct aqueous supercritical fluid extraction coupled on-line with infrared spectroscopy. *Analyst* **125**, 2356, **2000**. (b) MINTY B., RAMSEY E.D., DAVIES I., JAMES D.I., O'BRIEN P.M., LITTLEWOOD M.I. Analysis of oil in water at the low ppm level using direct supercritical fluid extraction coupled online with infrared spectroscopy. *Anal. Commun.* **35**, 277, **1998**.
74. LEE H.B., PEART T.E. Determination of Bisphenol A in Sewage Effluent and Sludge by Solid-Phase and Supercritical Fluid Extraction and Gas Chromatography/Mass Spectrometry. *J. AOAC Int.* **83**, 290, **2002**.
75. ÖZEL M.Z., BARTLE K.D., CLIFFORD A.A., BURFORD M.D. Extraction, solubility and stability of metal complexes using stainless steel supercritical fluid extraction system. *Anal. Chim. Acta* **417**, 177, **2000**.
76. ELSHANI S., SMART N.G., LIN Y., WAI CH.M. Application of supercritical fluids to the reactive extraction and analysis of toxic heavy metals from environmental matrices – system optimization. *Sep. Sci. Technol.* **36**, 1197, **2001**.

77. FUOCO R., CECCARINI A., ONOR M., MARRARA L. Analysis of priority pollutants in environmental samples by on-line supercritical fluid chromatography cleanup-cryotrap-gas chromatography-mass spectrometry. *J. Chromatogr. A*, **846**, 387, **1999**.
78. NAMIEŚNIK J., ZYGMUNT B., JASTRZĘBSKA A. Application of solid-phase microextraction for determination of organic vapours in gaseous matrices. *J. Chromatogr. A* **885**, 405, **2000**.
79. NAMIEŚNIK J., WARDENCKI W. Solventless sample preparation techniques In environmental analysis. *J. High Resol. Chromatogr.* **23**, 297, **2000**.
80. DUDEK M., WOLSKA L., PILARCZYK M., ZYGMUNT B., NAMIEŚNIK J. Studies on the use of commercial capillary gas chromatographic columns as diffusion denuders. *J. High Resol. Chromatogr.* **23**, 449, **2000**.
81. ZYGMUNT B., JASTRZĘBSKA A., NAMIEŚNIK J. Solid-phase microextraction – a convenient tool for determination of organic pollutants in environmental matrices. *Crit. Rev. Anal. Chem.*, **31**, 1, **2001**.
82. WARDENCKI W., ORLITA J., NAMIEŚNIK J. Comparison of extraction techniques for gas chromatographic determination of volatile carbonyl compounds in alcohols. *Fresenius J. Anal. Chem.* **369**, 661, **2001**.
83. NAMIEŚNIK J. Green analytical chemistry – some remarks. *J. Sep. Sci.* **24**, 151, **2001**.
84. DĄBROWSKI Ł., GIERGIELEWICZ-MOŻAJSKA H., BIZIUK M., NAMIEŚNIK J. Optimisation of operational parameters of extraction solid samples using accelerated solvent extraction (ASE). *Chem. Inż. Ekol.* **8**, 801, **2001**.
85. JASTRZĘBSKA A., LIGOR M., ZYGMUNT B., BUSZEWSKI B., NAMIEŚNIK J., Studies on extraction efficiency of new SPME fibres with respect to typical air organic pollutants. *Chem. Inż. Ekol.* **8**, 851, **2001**.
86. WARDENCKI W., NAMIEŚNIK J. Some remarks on gas chromatographic challenges in the context of green analytical chemistry. *Pol. J. Environ. Stud.* **11**, 185, **2002**.
87. RAWA-ADKONIS M., WOLSKA L., NAMIEŚNIK J. Modern techniques of extraction of organic analytes from environmental matrices. *Crit. Rev. Anal. Chem.* **33**, 199, **2003**.
88. WARDENCKI W., SOWIŃSKI P., CURYŁO J. Evaluation of headspace solid-phase microextraction for the analysis of volatile carbonyl compounds in spiritus and alcoholic beverages. *J. Chromatogr. A* **984**, 89, **2003**.
89. NAMIEŚNIK J., JASTRZĘBSKA A., ZYGMUNT B. Determination of volatile aliphatic amines In air by solid-phase microextraction coupled with gas chromatography with flame ionization detection. *J. Chromatogr. A*, **1016**, 1, **2003**.
90. ŚWITAJ-ZAWADKA A., PRZYK E., SZCZYGELSKA-TAO J., WÓJCIK J., BIERNAT J.F., NAMIEŚNIK J., ZYGMUNT B. Applicability of glass fiber as a support material for generation of gaseous standard mixtures using thermal decomposition of the surface compound calibration of analytical equipment. *J. Sep. Sci.* **26**, 1057, **2003**.
91. KREMER E., ROMPA M., ZYGMUNT B. Extraction of Acidic Herbicides for soil by means of accelerated solvent extraction. *Chromatographia* **60**, 169, **2004**.
92. W. WARDENCKI, M. MICHULEC, J. CURYŁO, A review on theoretical and practical aspects of solid-phase microextraction In food analysis, *Intern. J. Food Sci. Technol.*, **39**, 703, **2004**.
93. WASIK A., CIESIELSKI T. Determination of organotin compounds In biological samples using accelerated solvent extraction, sodium tetraethylborate ethylation. *Anal. Bioanal. Chem.* **378**, 1357, **2004**.
94. KŁOSKOWSKI A., PILARCZYK M., NAMIEŚNIK J. Nowoczesne techniki przygotowania próbki do oznaczania analitów organicznych z zastosowaniem chromatografii gazowej. *Chem. Inż. Ekol.* **11**, 284, **2004**.
95. CURYŁO J., NAMIEŚNIK J. Green Chemistry. *Ekoprofit*, **2**(70), 80, **2004**. [in Polish].
96. CURYŁO J., WARDENCKI W., NAMIEŚNIK J. Challenges of Green Chemistry in monitoring and air protection. *Zabrze*, **2004**. [In Polish].
97. KRONHOLM J., REVILLA-RUIZ P., PORRAS S.P., HARTONEN K., CARABIAS-MARTINEZ R. AND RIEKKOLA M-L. Comparison of gas chromatography-mass spectrometry and capillary electrophoresis in analysis of phenolic compounds, extracted from solid matrices with pressurized hot water. *J. Chromatogr. A* **1022**, 916, **2004**.
98. DENG C., YAO N., WANG A. AND ZHANG X., Determination of essential oil in a traditional Chinese medicine, *Fructus amon* by pressurized hot water extraction followed by liquid-phase microextraction and gas chromatography-mass spectrometry, *Anal. Chim. Acta* **536** 237, **2004**.