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Achievements in solvent microextraction

Komise pro obhajoby doktorských disertací v oboru Analytická chemie

Jméno uchazeče: Vasil Andruch

Pracoviště uchazeče: Univerzita P.J. Šafárika

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List of symbols and abbreviations

BE, Back extraction;

CFME, Continuous-flow microextraction;

DDSME, Drop-to-drop microextraction;

DI-, Direct immersion;

DLLME, Dispersive liquid–liquid microextraction;

DLPME, Dispersive liquid-phase microextraction;

DSDME, Directly suspended droplet microextraction;

EA-, Effervescence assisted;

GAC, Green Analytical Chemistry;

HF-, Hollow-fiber;

HLLME, Homogenous liquid–liquid extraction;

HS-, Headspace;

LED, Light-emitting diode;

LLE, Liquid–liquid extraction;

LLLME, Liquid–liquid–liquid microextraction;

LPME, Liquid-phase microextraction;

SDME, Single drop microextraction;

SFODME, Solidification of floating organic drop microextraction;

SME, Solvent microextraction;

UA-, Ultrasound assisted;

UASEME, Ultrasound-assisted surfactant-enhanced microextraction;

USAEME, Ultrasound-assisted emulsification microextraction;

VA-, Vortex assisted;

VALLME, Vortex-assisted liquid–liquid microextraction;

VASEME, Vortex-assisted surfactant-enhanced emulsification liquid–liquid microextraction;

Introduction

The results included in this work and discussed herein were published in [1-21].

We are currently witnessing large and continuing progress in analytical instrumentation. However, despite this progress, sample pre-treatment is still an essential part of almost every analytical procedure. There are at least two major reasons for this: unsatisfactory sensitivity of analytical detectors and the significant impact of the matrix [22]. Thus, a sample pre-treatment procedure has to separate and to concentrate the analytes of interest at the same time [23]. There are a fairly large number of sample pre-treatment techniques, from which liquid-liquid extraction (LLE) is one of the most frequently used. Apart from the advantages which this method offers, it also has some disadvantages and limitations, such as the large consumption of organic solvents, which are often hazardous and associated with the generation of large amounts of waste.

First of all, we must ask what is Solvent microextraction anyway? SME is an extraction method that uses volumes of 100 μL or less of solvent [24]. Herein it is necessary to say that some authors classify their own methods as a microextraction even if it uses more than 100 μL of solvent. Secondly, we must ask why we actually need SME. At the turn of the 21st century, the 12 principles of so-called Green Chemistry were formulated by Anastas and Kirchhoff in their work *Origins, Current Status, and Future Challenges of Green Chemistry* [25]. According to the first principle "*It is better to prevent waste than to treat or clean up waste after it is formed*" [25]. The principles of Green Chemistry can and should be applied in the field of the analytical chemistry, because in some cases the chemicals used for analysis are even more hazardous than those which are being determined [26]. Therefore, a variety of ways were suggested to avoid the side effects of analytical procedures and to achieve the principles of Green Analytical Chemistry (GAC). These include, among others, miniaturization and automation [15] as well as improvements in analytical instrumentation [26]. The importance of GAC is evidenced by the number of review articles devoted to this topic [27-37]. Thirdly, we must ask what SME offers, that is, which SME methods are better than conventional extraction techniques. And last but not least, we must remember that SME is not a panacea; it also has disadvantages and limitations.

A brief history and classification of solvent microextraction

The history of SME/LPME begins in the 1990s with the works of Liu, Dasgupta, Jeannot, Cantwell, He, Lee, Pedersen-Bjergaard and Rasmussen [38-50].

Liu and Dasgupta demonstrated the usefulness of the liquid drop for the purposes of analytical chemistry as a sampling interface for soluble components of gaseous samples [38]. They introduced the droplet collector into a sequential injection analysis manifold and reported a procedure for determination of gaseous ammonia. According to the authors, the disadvantage of the proposed approach is that the droplets are not a quantitative collector. On the other hand, the benefits include the possibility of easy replacement of the collection droplet and the possibility of introduction of reagents [38]. Cardoso and Dasgupta [39] reported an approach in which a liquid film formed on a thin platinum wire guide was used as a collector for the determination of nitrogen dioxide at the parts-per-billion level. Two optical fibers were placed in contact with a liquid film. A green LED was used as the light source, and a home-built detector was used for the absorbance measurements. Liu and Dasgupta designed the dynamically growing and falling droplet-based gas sensor system using a windowless optical cell in which the gas sample flows through a cylindrical chamber containing a droplet of a reagent solution formed at the tip of a tube [40]. The reported system was applied for automated and continuous determination of gaseous chlorine using tetramethylbenzidine solution as a chromogenic reagent [40]. These authors also reported a drop-in-drop system in which an aqueous sample flows continuously around an organic microdrop, and the target analyte is extracted into organic phase [41]. The absorbance was measured using an LED source and an optical fiber based detector. The system was applied for the determination of sodium dodecyl sulfate extracted as an ion pair into chloroform.

Jeannot and Cantwell chose a different path; they located a microdrop of organic solvent at the end of a Teflon rod immersed in a stirred aqueous sample solution [42]. After the extraction, the organic phase is injected into the GC using a microsyringe. Later, they improved this approach and used a microsyringe needle instead of a Teflon rod as the supporting device for the extraction microdrop [43].

He and Lee [45] investigated two modes of liquid-phase microextraction (LPME) (static and dynamic) for the determination of two chlorobenzenes extracted into a single drop of toluene. Ma and Cantwell [47] designed a concept of SME with back extraction (BE) in which 30 μL octane is placed inside a small Teflon ring over a buffered aqueous sample. The acceptor phase, 0.50 μL of a buffered aqueous drop, is suspended in an organic solvent liquid membrane on the tip of a microsyringe needle. Under stirring conditions, the analytes are extracted into the organic phase and back-extracted into the buffered aqueous microdrop. Pedersen-Bjergaard and Rasmussen [48] designed a concept of a liquid–liquid–liquid microextraction (LLLME) for sample preparation of biological fluids. The target analytes are extracted from a buffered aqueous sample through the 1-octanol inside the pores of a polypropylene hollow fiber and finally into an acidic acceptor solution inside the hollow fiber. Besides preconcentration, this approach also works as a clean-up technique.

There are several classifications of solvent microextraction based on various principles [22, 24]. It is necessary to mention the following categories: (1) Single-drop microextraction, SDME, (2) Hollow-fiber liquid-phase microextraction, HF-LPME, (3) Solidification of floating organic drop microextraction, SFODME, (4) Homogenous liquid–liquid extraction (HLLME), and (5) Dispersive liquid–liquid microextraction, DLLME, among others.

Single-drop microextraction was begun by the work of Jeannot and Cantwell [42, 43]. There are different categories of this method; these include Direct immersion single-drop microextraction, DI-SDME; Headspace single-drop microextraction, HS-SDME; Solvent microextraction with simultaneous back-extraction, SME-BE, and/or Liquid–liquid–liquid microextraction, LLLME; Directly suspended droplet microextraction, DSDME; Continuous-flow microextraction, CFME; and Drop-to-drop microextraction, DDSME [22].

The most frequently reported methods are HS-SDME and DI-SDME. The method is commonly performed in a sealed vial containing a few milliliters of sample, reagents and a stir bar. The extraction solvent is located in a microsyringe. The syringe needle tip is held in position above (HS-) or below (DI-) the surface of the sample solution. The extraction solvent forms a drop suspended from the tip of the needle. After the extraction, the solvent

microdrop is withdrawn and subjected to instrumental analysis. Several variables which can influence the SDME procedure, including sample pH, ionic strength of sample solution, stirring rate, acceptor phase, microdrop volume, microdrop stability and sampling temperature, must be optimized.

Liquid–liquid–liquid microextraction is based on the extraction of the target analytes from a buffered aqueous sample solution (donor phase) into an organic phase and then back-extraction into a directly suspended droplet of aqueous solution (acceptor phase) without using any supporting device [51]. The method was used for the determination of 3-nitroaniline in water samples using 18-crown-6 ether and high-performance liquid chromatography [51]. Directly suspended droplet microextraction is based on the extraction of target analytes into a small volume of an immiscible organic solvent added to the surface of the sample solution, under stirring conditions [52, 53]. The method was applied for separation and determination of benzene, toluene, ethylbenzene and o-xylene compounds in water using a gas chromatography-flame ionization detector. DSDME offers more flexibility in the choice of the extraction solvent volume and stirring rate when compared with other droplet based techniques [52]. The advance of Drop-to-drop microextraction is its low solvent and sample consumption [54]. The method was used for determination of methoxyacetophenone isomers in water using gas chromatography-mass spectrometry [54]. In Continuous-flow microextraction, the solvent drop is held at the outlet tip of a PTFE tube connecting to the extraction chamber; thus the solvent drop interacts continuously with the sample solution [55, 56]. The technique was applied for the analysis of trace nitroaromatic compounds and chlorobenzenes [55] and volatile halohydrocarbons in water samples [56]. Various automated SDME procedures were also reported based on sequential injection system [57, 58] using a furnace autosampler arm [57] and a home-made flow-through microextraction cell [58]. The approaches were applied for the determination of cadmium and chromium in water samples through electrothermal atomic absorption spectrometric detection [57, 58]. The advances in single-drop microextraction are reviewed in several papers, for example [5, 16, 22].

Hollow-fiber liquid-phase microextraction originated from the work of Pedersen-Bjergaard and Rasmussen [48]. We must distinguish two modalities: (a) two-phase, and (b) three-phase. In the two-phase mode, HF-LPME, the target analytes are extracted from an aqueous sample into a water-immiscible organic solvent immobilized in the pores of a hollow fibre. In the three-phase mode, HF-LLLME, the target analytes are extracted from an aqueous sample through a water-immiscible solvent immobilized in the pores of a hollow fibre and then back extracted into the aqueous phase inside the hollow fibre.

In Solidification of floating organic drop microextraction, a few microliters of the extraction solvent is placed on the surface of the sample solution, and the magnetic stirrer is turned on. After the extraction, the sample vial cools in a beaker containing crushed ice, and the organic solvent solidifies. Next, the solidified solvent is transferred to another vial and melted immediately. Finally, the extractant phase is used for subsequent quantification by an analytical instrument [59]. The efficiency of SFODME is influenced by a number of variables, such as the nature and volume of the organic solvent, the temperature and volume of the sample solution, the stirring rate and the extraction time. However, the main limitation of the method lies in the requirements that the extraction solvent should have a melting point near room temperature. On the other hand, in contrast to DI-SDME, the stirring rates may be set much higher. In addition of conventional SFODME, several modes of this technique were reported, such as DLLME-SFO, UA-DLLME-SFO, UA-SFODME, VA-DLLME-SFO, or VA-SFODME. The advances in SFODME are reviewed in several papers, for example [18, 60, 61].

In Homogenous liquid–liquid extraction the phase separation can be achieved by temperature, salting-out effect and pH [62]. Effervescence-assisted extraction [63], sugaring-out extraction [64] and switchable solvent-based LPME [65] can also be assigned to this group.

Dispersive liquid–liquid microextraction was introduced by Rezaee and Assadi in 2006 [66, 67]. This method applies the ternary system containing an aqueous sample solution, an extraction solvent and a dispersive solvent. The extraction procedure is usually performed in a screw-cap test tube with a conical bottom which contains a few milliliters of the sample

solution with the pH and ionic strength set. When the appropriate mixture of extraction and dispersive solvent is rapidly injected into the aqueous sample solution, commonly using microsyringe, a cloudy state develops, and that means the formation of a large surface area between the extraction solvent and the aqueous sample, which enables a state of equilibrium to be rapidly achieved. After the separation of the phases, usually by centrifugation, the sedimented phase are withdrawn and subjected to detection by an instrumental method. The extraction solvents in DLLME, in addition to the general requirements of solvents in LLE, must fulfill to several special requirements, the most important of which is the requirement for its density to be higher than the density of water. Therefore, chlorobenzene, chloroform, carbon tetrachloride and tetrachloroethane are frequently used as the extraction solvent in DLLME. The dispersive solvents must be miscible with both water and the extraction solvent, meaning that methanol, ethanol, acetonitrile and acetone are commonly used. The method's benefits include mainly the quick achieving of the equilibrium state, the short extraction time, simplicity and low cost. Based on the increasing number of papers published on this topic, we can say that DLLME is today a very popular sample pretreatment technique (Fig. 1).

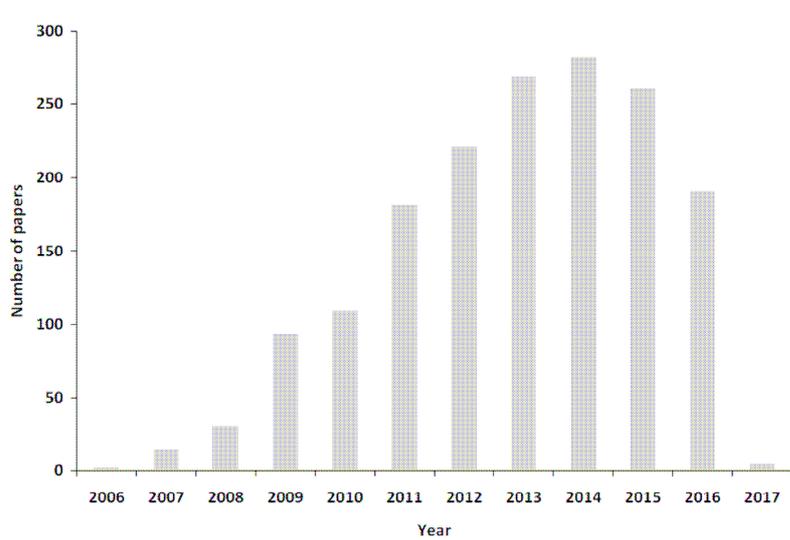


Fig. 1 Evolution of the number of publications devoted to dispersive liquid-liquid micro-extraction (Based on the www.scopus.com using keyword “Dispersive liquid-liquid microextraction or DLLME”)

Motivation

Like other analytical methods, SME methods, including DLLME, also have drawbacks and limitations. Therefore, the research activities discussed in this dissertation were focused, among other subjects, on solving these difficulties.

Characterization of the papers used in this dissertation

The results included in this work and discussed herein were published in [1-21]. The articles are given chronologically in the reference list. However, the thesis is arranged “topic-by-topic” for a better understanding of the achievements in the individual topics. The general topic of the research activities can be divided into the following narrower topics:

- development of dispersive liquid–liquid microextraction;
- automation of solvent microextraction;
- application of auxiliary energy in solvent microextraction;
- terminology of solvent microextraction.

The author has selected a set of 13 original and 8 review papers for the purpose of this dissertation. The research articles describe recent achievements in solvent microextraction and its automation. The review articles appeared during the solving of the research topics and are dedicated to a deeper analysis of the current state of the topic, a discussion of the solutions suggested by other authors and for a better understanding of the issue. All experiments were carried out by author’s PhD students, with the exception of [19, 20], and were financially supported by projects of the author (among others). The percentage contribution of the co-authors was calculated by simple dividing 100 by number of co-authors.

1. One of the serious difficulties of DLLME lies in requirements related to the extraction solvent, namely to have a density greater than that of water for simple phase separation, and to form a cloudy solution in the presence of the disperser solvent. Therefore, hazardous solvents such as halogenated hydrocarbons are used in the vast majority of them [6]. To solve this difficulty a few solutions were suggested by other groups, such as DLLME utilizing special extraction vessels [68-71], so called solvent-terminated DLLME (ST-DLLME) [72] and DLLME based on solidification of a floating organic droplet (DLLME-SFO) [73, 74]. Each of the reported solutions is clever; however, each is also characterized by some limitations, such as the procedures are sometimes tedious and laborious; they require a homemade device; withdrawal of a microvolume of the extraction solvent can be complicated; and the number of solvents with proper melting point for SFO is limited.

A novel approach to DLLME, based on the use of an auxiliary solvent for the adjustment of density, the so-called auxiliary-assisted dispersive liquid-liquid microextraction (AS-DLLME) was reported [1]. The procedure utilises a solvent system consisting of a dispersive solvent, an extraction solvent and an auxiliary solvent, which allows for the use of solvents having a density lower than that of water as an extraction solvent while preserving simple phase separation by centrifugation [1]ⁱ. Solvents having a density markedly higher than that of water can be considered as auxiliary solvents in order to make it possible to prepare a mixture of solvents with a density higher than that of the aqueous phase while using minimal volumes of auxiliary solvent [1]ⁱ.

Auxiliary-solvent assisted DLLME was used for development of methods for determination of various analytes, such as gold [1] copper [2], boron [3], silver [4], manganese [7], chromium [8], cadmium [10] and picric acid [11]. Based on the experience obtained during the preparation of these papers, a review article entitled *Recent advances in dispersive liquid-liquid microextraction using organic solvents lighter than water* [6] and *Five years of dispersive liquid-liquid microextraction* [9] were published.

2. Another difficulty of DLLME lies in the requirements related to the dispersive solvent. Dispersive solvent helps the extraction solvent form fine droplets in the aqueous sample and

affect the size and distribution of the droplets [6]. The dispersive solvent must be miscible with both the extraction solvent and the aqueous sample. Therefore, methanol, ethanol, acetone and acetonitrile are most commonly used in DLLME. However, one can find a few papers in which another kind of dispersive solvent, [75-79], has been employed. [10].

Tributylphosphate was tested as an alternative dispersive solvent. The solubility of tributylphosphate in water is very low; therefore we cannot consider it as a common dispersive solvent. The series of kinetic experiments were carried out for better understanding the role of tributylphosphate using a model analyte. It was found, that the nature of the solvent only slightly affects, the quality of the cloudy state. On the other hand, the ratio of the solvents in the mixture exhibits a more significant effect. The change in the ratio of the extraction solvent and tributylphosphate from 4:1 to 1:4 lead to the substantial increase in stability of the cloudy state over time. Consequently we cannot exclude the even partial dispersing effect of the tributylphosphate [10].

3. The next problem in DLLME lies in the detection step. The first articles about DLLME were devoted to the coupling of this technique with gas chromatography. The connection of DLLME with GC, HPLC, GF-AAS and FAAS is today commonplace (Fig. 3). However, the connection of SME with UV–Vis spectrophotometry is not widespread. The main reason being that the micro-volume of the extractant phase after the preconcentration procedure is typically not sufficient to perform a measurement in conventional UV–vis spectrophotometers [5]ⁱⁱ. Notwithstanding the coupling of SDME and DLLME with UV–vis spectrophotometric detection is still in the early stages of investigation and only a handful papers have thus far appeared, these techniques do seem to offer a valuable, desirable and efficient tool for analytical chemists. Such coupling expands the applicability of SDME and DLLME, and what is important, the instrumentation used is generally inexpensive and is commonly found in the majority of laboratories [5]ⁱⁱ.

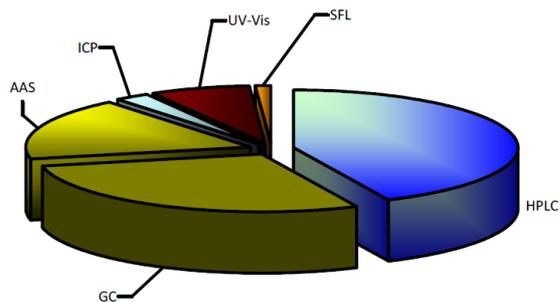


Fig. 3 Coupling of DLLME/DLPME to detection techniques (Based on more than 1500 articles from the Author's own database).

Various solutions were reported to solve difficulties with the absorbance measurement in the microvolume of the extraction phase, including evaporation and/or dilution of the extraction phase, use of fiber optic-linear array detection spectrophotometry (FO-LADS), digital colorimetry (DC) and cuvetteless microvolume spectrophotometry. Each of these solutions has both advantages and drawbacks.

Application of the commercially available micro-volume cells simultaneously with long path-lengths offers clear advantages over others: it does not require additional steps, such as evaporation; it does not decrease the sensitivity, unlike dilution of the sedimented phase; and last but not least, it does not require the use of homemade devices.

Based on the experience obtained during the preparation of the research papers devoted to coupling of DLLME with UV-Vis and AAS detection, two review articles [5, 12] were published. The recent achievements in coupling of headspace and direct immersion single-drop microextraction with chromatographic techniques [16] and in solidified floating organic drop microextraction [18] were discussed.

Apart from miniaturization, one interesting and challenging task for analytical chemists is automation, the direct coupling of the sample preparation step with the detection system. Automated systems offer a number of advantages, such as minimizing the errors associated with manual handling, reducing sample and reagent consumption and improving sensitivity and precision, among others [15]ⁱⁱⁱ.

An automated air-assisted LPME [14] and vigorous-injection assisted DLLME with stopped-flow spectrophotometric determination of chromium(VI) [14] and boron [17] were reported. Very recently two other approaches [19, 20] devoted to automated effervescence assisted DLLME for determination of antipyrine in saliva samples [19] and effervescence-assisted switchable solvent-based LPME for LC determination of ofloxacin in human urine samples [20] were reported. Based on the experience obtained during the preparation of the research papers, a review article entitled *Solvent microextraction: A review of recent efforts at automation* [15] was published in which the capabilities of automated liquid-phase microextraction techniques and the more recent advances were illustrated with selected examples.

Ultrasound and microwaves, as well as vortexing, magnetic stirring and shaker mixing can be considered as auxiliary energy. Ultrasonic energy has been applied in analytical chemistry mainly for pre-treatment of solid samples, ultrasonic-assisted derivatisation reactions, various other operations, such as nebulisation in atomic spectrometry, glassware cleaning and the removal of bubbles from solution; as well as detection. Although many articles have examined the application of ultrasound for the above-mentioned purposes, the number of articles devoted to investigating this energy in order to improve analytical reactions is limited [80].

Ultrasonic energy was applied for the determination of boron [3], with boron determination based on ion pair formation of tetrafluoroborate anion with dye reagent and the extraction of the ion pair formed into organic solvent with subsequent spectrophotometric detection as a model sample. The determination procedure involves two independent steps: (1) conversion of boric acid to tetrafluoroborate anion, and (2) complex formation and extraction of BF_4^- formed with a cation of dye reagent. The suggested ultrasound-assisted conversion was followed by both LLE [81] and DLLME [3] extraction. The main advantages of ultrasonication in comparison with conventional heating [81] are that the conversion process occurs much faster, thus decreasing reaction time, and that it does not lead to the heating of the sample, thus preventing the escape of volatile

products formed. The main advantages of DLLME in comparison with conventional LLE [81, 82] are the considerable decreasing of the consumption of hazardous organic solvents (thus making the procedure greener) and the significant shortening of the extraction time as a consequence of the large surface area formed between the aqueous and organic phases [3]^{iv}.

Very recently a review article was published entitled *Application of ultrasonic irradiation and vortex agitation in solvent microextraction* [13]. It was devoted to new, recently-developed microextraction procedures that do not require a disperser solvent and in which ultrasonic energy or vortex agitation is applied instead of a disperser solvent as a means of dispersing the extraction solvent, meaning the disperser solvent can be omitted from the extraction procedure.

The literature on dispersive solvent microextraction comprises a great many methodologies, different possibilities and a broad range of terminology, all of which greatly complicates the classification of these methods as well as the conditions to be specified in the procedure name, its acronym or both [21]^v. Ideally, the method name and its acronym should provide the reader sufficient information; however, it should also be as simple as possible and not burdened with unnecessary details [21]^v.

We should first distinguish between two techniques: (1) dispersive liquid–liquid microextraction (DLLME) that use a mixture of extraction and dispersive solvents and which in some instances, in addition to these two solvents, the formation of the cloudy solution is enhanced by adding supplementary reagents or applying supplementary energy, and (2) dispersive liquid-phase microextraction (DLPME), in which no dispersive solvent is used [21]^v.

The following acronyms were suggested: DLLME and DLPME for procedures with and without a dispersive solvent, respectively; UA- for ultrasound-assisted, VA- for vortex-assisted, MSA- for magnetic stirring-assisted, UDSA- for up-and-down shaker-assisted, AA- for air-assisted, PA- for pressured gas-assisted, and MW- for microwave-assisted, intended for additional energy; SA- for surfactant-assisted and EA- for effervescence-assisted, meant for an additional reagent; SD- for solvent-based deemulsification, -SID for salt-induced de-

emulsification, and FA- for flotation-assisted, used for phase separation; -SFO for solidification of floating organic drop, SM- for supramolecular solvent, and IL- for ionic liquid, designed for extraction solvent; as well as TC- for temperature controlled, and -BE for back extraction [21]^v.

Similar rules could be applied for methods without a dispersive solvent. However, several modifications are needed, because well established names and acronyms already exist for some procedures. In this context, ultrasound-assisted emulsification microextraction (USAEME), ultrasound-assisted surfactant-enhanced microextraction (UASEME), vortex-assisted liquid–liquid microextraction (VALLME) and vortex-assisted surfactant-enhanced emulsification liquid–liquid microextraction (VASEME) should be mentioned [21]^v.

Conclusion

This dissertation is devoted to Solvent microextraction (SME), also frequently called Liquid phase microextraction (LPME). The history, advantages and disadvantages of the selected SME techniques were briefly discussed in order to show the importance of this area of research and the necessity for further development of such microextraction methods for modern analytical chemistry. Like other analytical methods, SME methods including dispersive liquid–liquid microextraction (DLLME) and homogenous liquid–liquid extraction (HLLME) also have drawbacks and limitations. The research activities discussed in this dissertation were focused on solving these difficulties and can be divided into the following topics: development of DLLME, automation of SME, application of auxiliary energy in SME, and terminology of SME.

To solve the difficulty connected with requirements to the extraction solvent in conventional DLLME, so-called auxiliary-assisted DLLME was reported. The procedure utilises a solvent system consisting of a dispersive solvent, an extraction solvent and an auxiliary solvent, which allows for the use of solvents having a density lower than that of water as an extraction solvent while preserving simple phase separation by centrifugation. Tributylphosphate was suggested as an alternative to commonly used dispersive solvents in DLLME. The nature of the solvent only slightly affects the cloudy state. On the other hand, the ratio of the solvents in the mixture exhibits a more significant effect. Application of commercially available micro-volume cells simultaneously with long path-lengths offers clear advantages over other reported solutions for connection of SME with UV–Vis spectrophotometry: it does not require additional steps, such as evaporation; it does not decrease the sensitivity, unlike dilution of the sedimented phase; and last but not least, it does not require the use of homemade devices. Achievements in automation of microextraction were also presented: the automated air-assisted LPME, vigorous-injection assisted DLLME, automated effervescence assisted DLLME, and automated effervescence-assisted switchable solvent-based LPME procedures have been suggested. The current status of the DLLME terminology was presented with the goal of standardizing and simplifying the terminology.

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Summary

This dissertation is devoted to Solvent microextraction (SME), also frequently called Liquid phase microextraction (LPME). The history of solvent microextraction is briefly discussed in order to show the importance of this area of research and the necessity for further development of microextraction methods for modern analytical chemistry. The principle advantages and disadvantages as well as possible applications of selected solvent microextraction techniques, including Single-drop microextraction, Hollow-fiber liquid-phase microextraction, Solidification of floating organic drop microextraction, Homogenous liquid–liquid extraction (HLL) and Dispersive liquid–liquid microextraction (DLLME), were discussed. Based on evolution in the number of publications, one can say that DLLME is today a very popular sample pretreatment technique. The method's benefits mainly include the quick achieving of an equilibrium state, the short extraction time, simplicity and low cost. Of course, like other analytical methods, SME methods, including DLLME, also have drawbacks and limitations. Therefore, the research activities discussed in this dissertation were focused on solving these difficulties. The research activities can be divided into the following topics: development of DLLME, automation of SME, application of auxiliary energy in SME, and terminology of SME. The research articles are devoted to improving solvent microextraction techniques, mainly DLLME and HLL, as well as the automation of these techniques. The review articles appeared during the solving of the research topics and are dedicated to a deeper analysis of the current state of the topic, a discussion of the solutions suggested by other authors and for a better understanding of the issue.

The extraction solvent used in conventional DLLME must have a density greater than that of water. A novel approach based on the use of an auxiliary solvent for the adjustment of density, so-called auxiliary-assisted DLLME, was reported. The procedure utilises a solvent system consisting of a dispersive solvent, an extraction solvent and an auxiliary solvent, which allows for the use of solvents having a density lower than that of water as an extraction solvent while preserving simple phase separation by centrifugation. The dispersive solvent should help the extraction solvent form fine droplets in the aqueous sample and affect the size and distribution of the droplets. The main criterion for the selection of the dispersive solvent is its high miscibility in both the extraction solvent and the

aqueous sample. Tributylphosphate was suggested as an alternative to commonly used dispersive solvents. Since its solubility in water is very low, we cannot consider it as a common dispersive solvent. The nature of the solvent only slightly affects the cloudy state. On the other hand, the ratio of the solvents in the mixture exhibits a more significant effect. The connection of SME with UV–Vis spectrophotometry is not common. The main reason being that the micro-volume of the extractant phase after the preconcentration procedure is typically not sufficient to perform a measurement in conventional UV–vis spectrophotometers. Various solutions were reported to solve difficulties. Application of the commercially available micro-volume cells simultaneously with long path-lengths offers clear advantages over others: it does not require additional steps, such as evaporation; it does not decrease the sensitivity, unlike dilution of the sedimented phase; and last but not least, it does not require the use of homemade devices.

Achievements in the automation of liquid–liquid microextraction were also presented. Automated air-assisted LPME and vigorous-injection assisted DLLME with stopped-flow spectrophotometric detection were reported. The automated effervescence-assisted DLLME based on the aspiration of a sample and all required aqueous reagents into the manifold, followed by simultaneous counterflow injection of the extraction solvent, the mixture of the effervescence agent and the proton donor solution. Formation of carbon dioxide microbubbles generated *in situ* leads to the dispersion of the extraction solvent in the whole aqueous sample and extraction of the analyte into organic phase. Unlike the conventional DLLME, in the case of EA-DLLME, the addition of dispersive solvent, as well as, time consuming centrifugation step for disruption of the cloudy state is avoided. The phase separation was achieved by gentle bubbling of nitrogen. Moreover, an automated effervescence-assisted switchable solvent-based liquid phase microextraction procedure has been suggested.

The literature on dispersive solvent microextraction comprises a great many methodologies, different possibilities and a broad range of terminology, all of which greatly complicates the classification of these methods as well as the conditions to be specified in the procedure name, its acronym or both. The current status of this issue is presented with the goal of standardizing and simplifying the terminology.

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