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Bell-shaped extraction device assisted liquid–liquid microextraction technique and its optimization using response-surface methodology

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ABSTRACT

We have developed a new microextraction technique for equilibrium, non-exhaustive analyte preconcentration from aqueous solutions into organic solvents lighter than water. The key point of the method is application of specially designed and optimized bell-shaped extraction device, BSED. The technique has been tested and applied to the preconcentration of selected volatile and semi volatile compounds which were determined by gas chromatography/mass spectrometry in spiked water samples. The significant parameters of the extraction have been found using chemometric procedures and these parameters were optimized using the central composite design (CCD) for two solvents. The analyte preconcentration factors were in a range from 8.3 to 161.8 (repeatability from 7 to 14%) for heptane, and 50.0–105.0 (repeatability from 0 to 5%) for tert-butyl acetate. The reproducibility of the technique was within 1–8%. The values of limits of detection and determination were 0.1–3.3 ng mL^{-1} for heptane and 0.3–10.7 ng mL^{-1} for tert-butyl acetate. The new microextraction technique has been found to be a cheap, simple and flexible alternative to the common procedures, such as SPME or LLME. This BSED–LLME technique can also be combined with other separation methods, e.g., HPLC or CE.

1. Introduction

Microextraction techniques have recently become very efficient approaches to sample pretreatment. Their main advantages lie in substantial limitation of the use of organic, and often toxic, solvents, in small production of other wastes and in acceleration of the sample pretreatment step. Therefore, they are much cheaper, less harmful to the environment and fit to the framework of "green analytical chemistry" [1].

Very many publications deal with various principles and procedures of liquid–liquid microextractions (LLME) and the great variety of abbreviated names of the techniques used makes the field somewhat difficult to survey [2,3]. In general, LLME procedures can be classified in terms of many criteria, e.g., into two- and three-phase ones [4], into those employing liquid films (e.g., hollow-fibre liquid–liquid microextraction, HFMLLE [5]) or drops of extraction solvents (e.g., single-drop microextraction, SDME [6]) and directly suspended droplet microextraction, DSME [7]). Further procedures are based on homogeneous systems of two liquids (dispersion liquid–liquid microextraction, DLLME [8]). The selection of a suitable technique depends on the properties of the sample and on the analytical measuring method used. All the LLME techniques suffer from various drawbacks, such as a slow diffusion of the analyte into the solvent static layer (HFMLLE), a high cost and limited lifetime of some parts of the extraction system (HFMLLE, solid-phase microextraction – SPME), a very small volume of the resultant extract permitting only a single analysis (SDME), high demands on manipulation of a single drop of the solvent (SDME), or the use of halogenated solvents (DLLME).

The newly by us developed microextraction technique described in the present paper belongs among two-phase, equilibrium, non-exhausting LLME procedures designed for aqueous sample solutions and is free of most of the drawbacks mentioned above. We call it "the bell-shaped extraction device assisted LLME (BSED–LLME)", because of the extraction device characteristic shape. This technique is based on the extraction of an aqueous solution with a volume of units to tens of mL with a rather small volume of an extraction solvent (tens to hundreds of μL). The solvent is contained in the BSED for the whole extraction time. The important condition is that this solvent must have a density smaller than that of water, in order that it always forms the upper layer of the two-phase system. There are many solvents and their mixtures meeting this condition and thus the extraction procedure is flexible and the extraction conditions can readily match the properties of the analytes to be determined. The extraction starts with introduction of the solvent into the BSED which contains it through the whole procedure, in spite of intense stirring of the sample solution. Due to intense stirring, the extraction solvent is spread in a thin layer over a large area of the sample solution vortex and thus the extraction is accelerated. The specific BSED shape makes it possible

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to collect the solvent reproducibly, with almost no loss, at the end of the extraction.

To test the possibilities of this technique, the optimum conditions must be found for attainment of the maximum extraction efficiency. For this purpose, sophisticated multifactorial statistical methods, e.g., response surface methodology (RSM) [9], are recently gradually replacing the common one-factor-at-a-time (OFAT) procedures [9], because they are much more effective and make it also possible to find possible interactions among the individual parameters. Therefore, we used the RSM method in the present work. The RSM procedure can be divided into three principal steps: (a) screening, to find the parameters (e.g., temperature, volume, rate) which exert statistically significant influence on the response studied (e.g., extraction efficiency, peak area, etc.); (b) modeling, to find a mathematical description of the system response as a function (mostly polynomial one) of the statistically significant parameters; and (c) optimization, to specify the combination of the parameters yielding the optimum response [10].

This paper describes a new, simple and cheap microextraction technique, based on the use of a newly developed bell-shaped extraction device (BSED–LLME), combined with the GC–MS separation method. The experimental conditions have been optimized and the method has been applied to determination of some organic compounds in samples of drinking and mineral waters. The analytes selected are characterized by various polarities and thus by various solubilities in water (toluene, ethylbenzene, mesitylene, phenol, nitrobenzene, octanol, naphthalene and dimethyl phthalate) and represent examples of common volatile and medium volatile pollutants. Two extraction agents with different polarities have been used, heptane and tert-butyl acetate. Statistical methods have been employed, the Plackett–Burman design for screening and the central composite design for modeling and optimization [9], thus determining the precision, linearity and repeatability of the BSED–LLME method. The limits of detection and determination have been obtained, as well as the enrichment factors (the ratios of the final analyte concentrations in the extraction solvents to the original analyte concentrations in the samples). Analyses of drinking and mineral water samples have then been carried out.

2. Materials and methods

2.1. Chemicals and standard solutions

Ethylbenzene, nitrobenzene, octanol and dimethylphthalate (all 99%, Sigma–Aldrich, Germany), toluene and phenol (both p.a., Lachema, Czech Republic), mesitylene (99%, Fluka, Germany), methylhexadecanoate (GC standard, Polyscience, USA), NaCl (p.a., Lach-Ner, Czech Republic) were used as received. Methanol (p.a., Lachema), heptane (99.5%, Fluka) and tert-butyl acetate (99%, Sigma Aldrich) were used as the solvents. Water was purified (18.2 MΩ) using a Mille-Q Plus (Millipore, USA).

The stock solutions of the analytes (1 mg mL^{-1}) were prepared in methanol and the working solutions were obtained daily by appropriate dilution with bidistilled water. Methylhexadecanoate was used as the internal standard in the extraction solvents, at a concentration of 100.2 μg mL^{-1}. All the stock solutions were stored at a temperature of 4 °C.

2.2. Microextraction procedure

A volume of 10 mL of an aqueous solution containing the analytes was introduced into a 16 mL glass vessel, 7 cm high, 2 cm in diameter, provided with a screw cap. The solutions were prepared immediately prior to the experiments. A small magnetic rod (6 mm diameter, 14 mm length) was inserted into the vessel

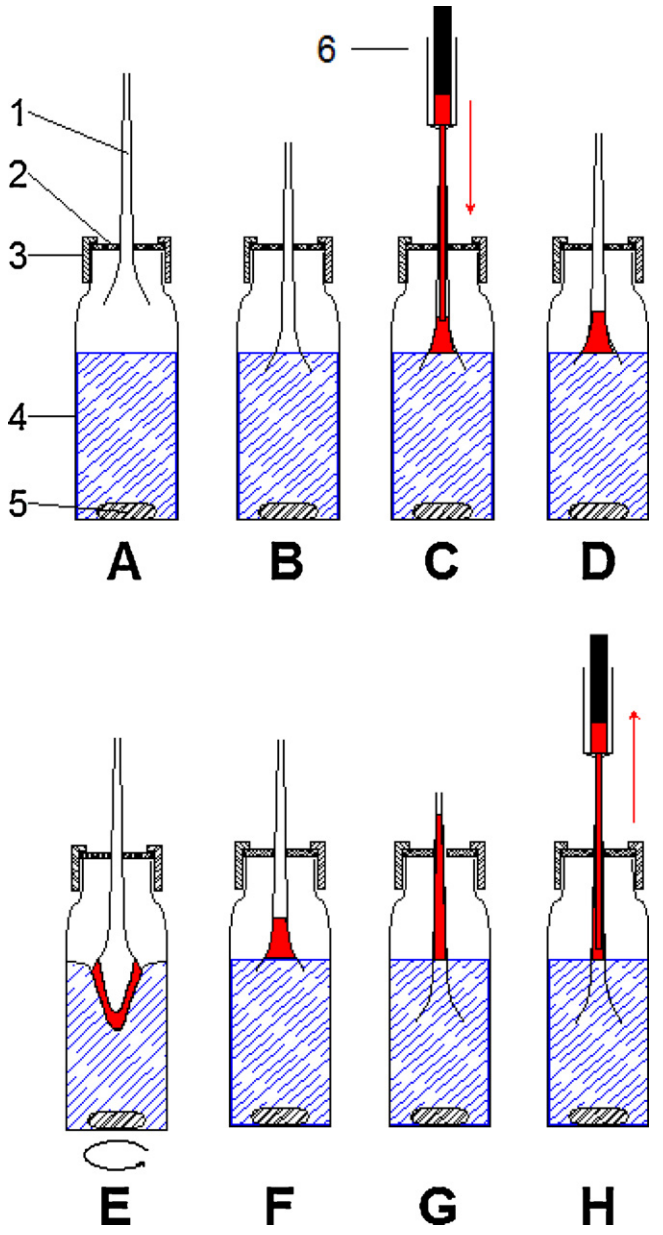

Fig. 1. Steps of the liquid–liquid microextraction with the bell-shaped extraction device (BSED–LLME). 1 – bell-shaped extraction device (BSED), 2–silicon rubber septum, 3 – screw cap, 4 – glass vial with aqueous sample, 5 – stirring bar, 6 – microsyringe with the extraction solvent; for (A)–(H) see the text.

which was then fixed on a Heidolph MR 3001 (BRD) magnetic stirrer. The vessel was closed with the screw cap through which passed the bell-shaped extraction device (BSED), made of transparent polypropylene (Fig. 1A and Fig. S1). The widened BSED end was immersed into the sample solution, with the sample solution level reaching the half height of the widened BSED part (Fig. 1B and Fig. S2). Using a 250 μL syringe (Hamilton, USA), the required volume of the extraction solvent with IS added was injected into the upper, narrow part of the BSED (Fig. 1C and D and Fig. S3). The extraction itself was started by switching on the stirring; a stable vortex developed after a slow (within 2–3 s) increase of the stirring rate (Fig. 1E and Fig. S4). The layer of the organic solvent was maintained on the surface of the whirling aqueous solution and the analytes were extracted from the aqueous into the organic phase.

The maximum stirring rate, at which the organic layer still remained compact, had to be found prior to the experiments (a

value of ca. 1000 rpm in the present work). The time of microextraction followed from the results of optimization of the experimental conditions (see below). By gradually decreasing the stirring rate (within 2–3 s), the defined layer of the organic layer was re-established inside the BSED (Fig. 1F). By shifting the BSED by ca. 0.5 cm down, into the aqueous solution, the organic solvent was pressed up, into the narrow part (Fig. 1G), could be collected by the syringe and transferred to the GC autosampler (Fig. 1H) for the GC–MS analysis.

The analyte concentrations in water were selected so that their concentrations in the organic phase were located in a lower part of the calibration dependence (100–10000 ng mL^{-1}). The syringe and the BSED were rinsed with pentane, acetone, distilled water and acetone again, to avoid analyte transfers between the experiments. The BSED and the BSED–LLME microextraction method are patented for commercial applications.

2.3. Instrumentation

GC–MS analyses were performed using a GC 17A gas chromatograph (Shimadzu, Japan), equipped with a detector GCMS-QP 5050A detector (Shimadzu). A DB-5ms capillary column (32 m × 0.25 mm ID, coated with 5% diphenyl-95% dimethylpolysiloxane, 0.25 μm (Agilent Technologies, USA) was used to separate the analytes. Helium (99.999%, Linde, Czech Republic) was used as the carrier gas at a constant linear flow velocity of 40 cm s^{-1}. Samples (2.5 μL) were injected by an autosampler (AOC-20i, Shimadzu) in the split mode (split ratio, 1/25) at a temperature of 250 °C. The column temperature was maintained at 50 °C for 5 min, then it was ramped at 30 °C min^{-1} to 250 °C and maintained for 3 min. The total analysis time was 14.67 min. The temperature of the transfer line to the MS detector was 275 °C. The mass spectrometer was operated in the EI mode (70 eV), and the SIM mode was used for quantification. The target *m/z* values of analytes were as follows (quantifier/qualifiers): toluene 91/92 + 65, ethylbenzene 91/106 + 51, mesitylene 105/120 + 77, phenol 94/66 + 39, octanol 56/55 + 41, nitrobenzene 77/51 + 123, naphthalene 128/51 + 64, dimethylphthalate 163/77 + 194 and methylhexadecanoate 74/87 + 43). The GC Solutions program (Shimadzu), ver. 2.30 was used for the data acquisition and evaluation. Screw–top glass vials of 16 mL volume (7 cm height and 2 cm diameter), magnetic stirrer (Heidolph MR3001, Germany) and 250 μL microsyringe (Hamilton, USA) were used for the microextraction.

2.4. Software

The construction and analyses of the experimental design and the response surfaces were carried out using the Minitab 16 statistical package (Minitab Inc., USA).

3. Results and discussion

3.1. Bell-shaped extraction device (BSED)

The BSED development aims at attaining the highest possible extraction efficiency with minimum time and material requirements. The device should permit extractions of sample solutions with volumes of the order of 10 mL with substantially smaller volumes of organic solvents, those of the order of tens to hundreds of microlitres. These general demands have led to the optimized shape and size (Fig. 2, the first one from the left was finally used in the work) of the device for extraction from 15 mL vials, 20–27 mm in diameter. There is an advantage in the possibility of scaling these dimensions in dependence on the volume of the sample to be extracted, on condition that the ratio of the vial and the device internal diameters (ID) remains within a range of ca. 1.8–2.5.

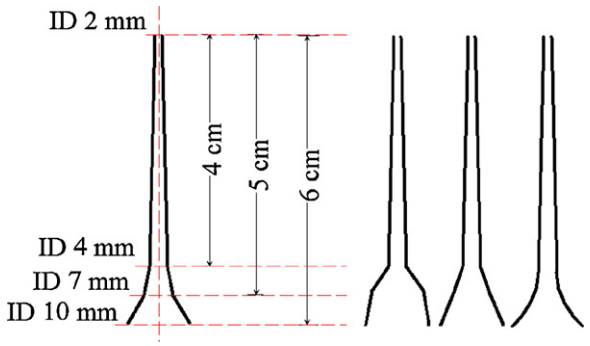

Fig. 2. Dimensions of optimized BSDE and its shape variants tested (the first one from the left was finally used in the work).

We have optimized the device shape to attain a maximum possible stirring rate and to maintain simple introduction and removal of the extraction solvent. Several funnel and bell shapes of the device have been tested and the resultant optimal shape can be seen in Fig. 2. To make the device transparent, glass, polyethylene and polypropylene materials have been tested and the last one has been found most suitable. The whole this study has been carried out with 10 BSED prototypes, assuming single use of the device. The BSED cost rougly equals that of a common pipet tip.

3.2. Optimization of the experimental conditions

The experimental conditions have been optimized using heptane as the extraction solvent. The five parameters evaluated have been selected on the basis of the literature [11], the experience of the present authors and the results of the preliminary experiments and they involve the extraction time, the extraction agent volume, the ionic strength of the aqueous solution extracted (additions of NaCl), the stirring rate and the diameter of the extraction vessel. The laboratory temperature (23 °C) has been maintained and the maximum response, defined as the sum of the peak relative areas in relation to the analyte IS values, has been sought.

3.2.1. Screening

To screen the parameters, the Plackett–Burman design has been used, which is based on ignoring the interactions among the individual factors and on determination of only the main effects [12,13]. Two coded values have been attributed to each parameter, the low (−1) and the high (+1) ones (Table 1). Dummy factors have been added to the test parameters, in order to estimate the experimental error in the statistical evaluation [14]. A coded table has been created using the Minitab 16 program and two eight-membered sets of measurements have been performed according this table, in random orders. The results have been evaluated using the ANOVA test, determining the main effects at a significance level of 95%. The result can be seen on the Pareto graph (Fig. 3).

This test of the parameter significance has indicated that the extraction agent volume and the extraction time have the greatest influence on the system response. The Pareto graph indicates that the additions of NaCl exerts a small effect on the overall analyte extractions, but these graphs for the individual analytes (not shown in this paper) have demonstrated that NaCl additions significantly affect the extraction of more polar extractants (phenol, dimethyl phthalate). Therefore, this parameter has also been included in the optimization by the CCD method. Surprisingly, the lowest effect on the extraction efficiency is due to the stirring rate, which has been expected to enhance the extractant transfer between the phases due to increase in the interface area and in the extractant transport rate toward the interface. Apparently, even a low stirring rate (500 rpm), which is required for the formation of a visible

Table 1
Experimental parameters and their levels used in the screening by the Plackett–Burman design for heptane as the extraction solvent in BSED–LLME.

Parameter	Level	
	Low (−1)	High (+1)
X_1 – extraction volume (μl)	100	300
X_2 – extraction time (min)	5	20
X_3 – dummy 1	−1	+1
X_4 – amount of NaCl (g)	0	2
X_5 – vial diameter of (cm)	2	2.7
X_6 – dummy 2	−1	+1
X_7 – stirring rate (rpm)	500	1000

Run	X_1	X_2	X_3	X_4	X_5	X_6	X_7
1	−1	1	1	−1	1	−1	−1
2	1	−1	1	−1	−1	1	−1
3	−1	−1	−1	−1	1	1	1
4	−1	−1	1	1	−1	−1	1
5	−1	1	−1	1	−1	1	−1
6	1	1	−1	−1	−1	−1	1
7	1	−1	−1	1	1	−1	−1
8	1	1	1	1	1	1	1

vortex, suffices for rapid extractant transfer. Growing stirring rate also increases the danger of separation of heptane droplets from the lower part of the vortex and their dispersion in the aqueous phase. It has been found that the limiting stirring rate for the maintenance of a stable vortex equals 1000 rpm. The diameter of the extraction vessel (20 or 27 mm) has also been found insignificant. Consequently, these two relatively insignificant parameters have been adjusted to 1000 rpm and 20 mm in further measurements.

3.2.2. Modeling

To optimize the operational parameters (extraction time, extraction agent volume and the amount of the salt added), the rotatable central composite design (CCD) [13] has been employed. Table 2 summarizes the levels of these parameters, the low and high values being denoted (−1) and (+1), respectively, zero corresponding to the central point and "star" points being denoted as α (see reference [13]). The list of 20 measurements (8 – factorial, 6 – central, 6 – star) is further given, according to the CCD plan, with combinations of the parameter levels. To evaluate this system by the ANOVA method, the following functional polynomial dependence has been used:

$$R = a + b \cdot X_1 + c \cdot X_2 + d \cdot X_4 + e \cdot X_1^2 + f \cdot X_2^2 + g \cdot X_4^2 + h \cdot X_1 \cdot X_2 + i \cdot X_1 \cdot X_4 + j \cdot X_2 \cdot X_4 \quad (1)$$

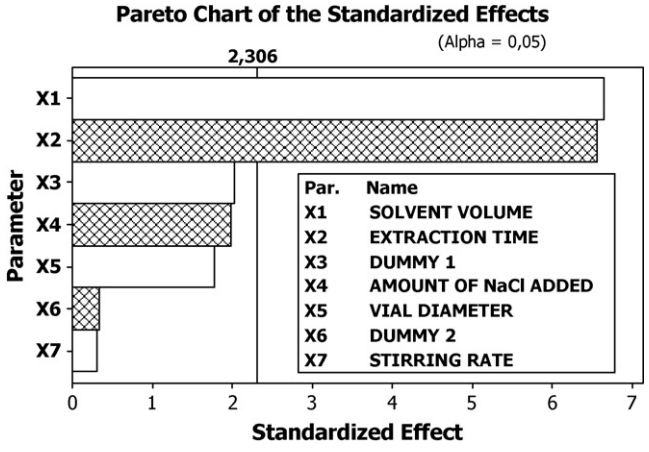

Fig. 3. Standardized main effect Pareto chart for the Plackett–Burman design. Vertical line in the chart defines the 95% confidence level.

where R is the response, X_i are the individual factors (Table 2) and a to j are the coefficient of the polynomial equation. This dependence involves both the possible curvature of the response surface (the quadratic terms) and the possible interactions among the parameters ($X_i \cdot X_j$ products).

On treating the results for the sum of the analyte peak relative areas by the Minilab 16 program and on exclusion of insignificant contributions to the response, the following quadratic equation,

$$R = 2.39 - 0.18 \cdot X_1 + 0.84 \cdot X_2 - 0.41 \cdot X_4 - 0.19 \cdot X_2^2 - 0.31 \cdot X_2 \cdot X_4 \quad (R^2 = 0.9792) \quad (2)$$

is obtained.

It follows from this equation that the response surface is curved and the interaction between the extraction time and the ionic strength parameters is significant. The lack of fit test has been insignificant at the 5% level and the determination coefficient, R^2, value indicates that there is an excellent agreement between the experimental data and the model created.

Response surfaces plots (Figs. S1–S6) showing the interrelationships of statistically significant parameters with the response for heptane and tert-butyl acetate are presented as Supplementary data.

3.2.3. Optimization

The system has been optimized in the Minilab 16 program, using the desirability function [15], to find the combination of the significant parameters which yields the maximum response value. The following optimum parameters have been obtained: extraction time, 29.5 min, extraction agent volume, 90 μL, NaCl addition, zero.

The same procedure (screening, modeling and optimization) has been carried out for the identical set of analytes, but with tert-butyl acetate, as the extraction solvent of a higher polarity. The extraction time and the stirring rate have been found to be significant and the equation,

$$R = 10.56 + 2.85 \cdot X_2 + 2.73 \cdot X_7 + 2.02 \cdot X_7^2 \quad (R^2 = 0.7624) \quad (3)$$

has resulted for the response. The agreement between the experiment and the model is somewhat poorer than in the previous case, but it can still be considered as satisfactory. The optimum parameters for tert-butyl acetate extraction equal 24 min. for the extraction time, and, again, no addition of sodium chloride. Surprisingly, the tert-butyl acetate volume has not been found to be a significant parameter, and, from practical point of view, 150 μL of the solvent have been used. This solvent is partially soluble in water (0.8%,

Table 2
Experimental parameters, their levels and modeling experimental plan of the central composite design for heptane as the extraction solvent in BSED–LLME.

Parameter	Level				
	Star point −α (1.68)	Low (−1)	Central (0)	High (+1)	Star point +α (1.68)
X_1 – extraction volume (μl)	90	100	115	130	140
X_2 – extraction time (min)	2.5	8	16	24	29.5
X_4 – amount of NaCl (g)	0.00	0.41	1.01	1.61	2.02

Run	X_1	X_2	X_4	Run	X_1	X_2	X_4
1	0	1.68	0	11	1	−1	−1
2	1.68	0	0	12	−1	1	1
3	0	0	0	13	0	0	0
4	1	1	−1	14	0	0	0
5	0	0	−1.68	15	1	1	1
6	0	0	1.68	16	0	0	0
7	1	−1	1	17	−1	−1	−1
8	0	−1.68	0	18	0	0	0
9	0	0	0	19	−1	1	−1
10	−1	−1	1	20	−1.68	0	0

Table 3
Limits of detection and quantification, and enrichment factors of the BSED–LLME method.

Extraction solvent	Compound	MLOD (ng mL^{-1})	MLOQ (ng mL^{-1})	R^2 of calibration curve	Concentration in water (ng mL^{-1})	Enrichment factor	R.S.D. of Enrichment factor (%)
Heptane	Toluene	0.3	0.9	0.9999	4.5	84.4	9
	Ethylbenzene	0.1	0.3	0.9997	3.8	136.8	7
	Mesitylene	0.7	2.2	0.9984	3.0	66.7	14
	Naphthalene	0.2	0.8	0.9993	2.0	75.0	13
	DMP	3.3	10.7	0.9995	30	8.3	7
Tert-butyl acetate	Toluene	0.4	1.2	0.9999	2.8	64.3	0
	Ethylbenzene	0.2	0.7	0.9997	2.4	54.2	1
	Mesitylene	0.8	2.7	0.9984	3.4	55.9	3
	Naphthalene	0.2	0.5	0.9993	2.0	105.0	5
	DMP	0.5	1.7	0.9995	3.4	52.9	5

MLOD, MLOQ are the limits of detection and quantitation of the method, respectively.
R.S.D. is the relative standard deviation for $n = 3$.

w/w) and thus a part of its volume is "lost" in the sample solution. In extraction with 150 μL of the solvent, roughly one half of this volume can be collected after the procedure. The results are unaffected, because a nonpolar IS (methyl hexadecanoate) is contained in the extraction solvent and it does not dissolve in the aqueous sample solution.

3.3. Testing of the BSED–LLME Method

To test the quantification, calibration plots for the individual standards in heptane have been obtained within a concentration range from 100 to 10,000 ng mL^{-1} (five concentration points), using GC–MS measurements. The signal-to-noise ratios for the lowest analyte concentrations have yielded the method limits of detection (MLOD) and quantitation (MLOQ) on multiplication by 3 and 10, respectively (Table 3). The calibration straight lines have further been used to determine the enrichment factors, EF (the enrichment factor is defined as the ratio between the analyte concentration in the sedimented phase and the initial concentration of analyte within the sample) [16], for the analytes in distilled water under the optimum experimental conditions (Table 3). The analyte concentrations are in a range from 2 to 4.5 ng mL^{-1} and the corresponding EF values are between 52.9 (dimethylphthalate – tert-butyl acetate) and 136.8 (ethylbenzene – heptane). This value has been low (8.3) only for dimethyl phthalate (DMP) combined with heptane, apparently due to the great difference in their polarities.

Table 4
Enrichment factors of the BSED–LLME method using two extraction solvents in spiked aqueous samples with different matrices.

Extraction solvent	Compound	Concentration in sample (ng mL^{-1})	Enrichment factor		
			Distilled water	Tap water	Mineral water
Heptane	Toluene	4.5	84.4[a]	52.2[a]	60.0[a]
	Ethylbenzene	3.8	136.8[a]	123.7[a]	161.8[a]
	Mesitylene	3.0	66.7	36.7	40.0
	Naphthalene	2.0	75.0	50.0	65.0
	DMP	30	8.3	8.3	6.7
Tert-butyl acetate	Toluene	2.8	64.3	75.0	56.3
	Ethylbenzene	2.4	54.2	54.2	50.0
	Mesitylene	3.4	55.9	73.5	67.6
	Naphthalene	2.0	105.0	95.0	105.0
	DMP	3.4	52.9[a]	61.8	58.8[a]

[a] This is a statistically significant difference.

Table 5
Comparison of enrichment factors for selected analytes obtained by different microextraction techniques.

Method	Toluene	Ethylbenzene	Mesitylene	Naphthalene	Ref.
DI–SDME–GC–FID	54.4	57.3			[17]
HS–SDME–GC–FID	206.6	387.7			[17]
DLLME–GC–FID	231	309			[18]
DSDME–GC–FID	254.88	275.44			[19]
HF-LPME–GC–FID	98.09	66.45			[20]
Fiber in tube–GC–FID	361	290	224		[21]
HS–SPME–GC–FID	16.7	16.1			[22]
RHF-LPME–GC–MS			35.1		[23]
SDME–GC–MS			18.1		[23]
SPME–GC–MS			127.8		[23]
HFH-LPME–GC–MS				160	[24]
HFH-LLLME–GC–MS				210	[25]

DI – direct immersion, HS – headspace, SDME – single drop microextraction, DLLME – dispersive liquid–liquid microextraction, DSDME – directly suspended droplet microextraction, HF-LPME – hollow fiber liquid phase microextraction, SPME – solid phase microextraction, RHF-LPME – revolving hollow fiber liquid phase microextraction, HFH-LLLME – hollow fiber-protected ionic liquid–liquid–liquid microextraction.

Therefore, the DMP concentration has been increased to 30 ng mL^{-1} (Tables 3 and 4).

The enrichment factor has not been reliably determined for phenol, nitrobenzene and octanol with any of the organic solvents used, because their peaks obtained in the separation procedure used are highly non-symmetrical and prevent reliable determinations at very low concentrations. Solvents with higher polarities and/or another separation system will be tested for these substances.

The EF reproducibility, in terms of R.S.D. ($n = 3$), varies within 7–14% for heptane and 0–5% for tert-butyl acetate. The measuring repeatability is between 1 and 8%. The BSED–LLME method attains EF values which are fully comparable with those of other microextraction methods, as can be seen in Table 5 containing some literature data. The extraction times are also similar to those provided by other microextraction procedures, even if the present authors expected shorter times due to intense stirring in the device.

3.4. Analyses of drinking and mineral water samples

To estimate the sample matrix effects on the EF values, some samples of drinking water from public supplies and of mineral water (Mattoni, CZ) have been analyzed. The analytes studied have not been present in these waters and thus the samples have been spiked with them and then subjected to extractions with heptane and tert-butyl acetate. Table 4 summarizes the EF values obtained, varying from 6.7 (DMP – heptane) to 161.8 (ethylbenzene – heptane). It can be seen that the sample matrix exerts statistically significant influence on the extraction of toluene and ethylbenzene with heptane and on that of DMP with tert-butyl acetate. No statistically significant EF differences have been found for the other analytes and samples studied. Therefore, the internal standard or standard addition techniques can be recommended for BSED–LLME determinations of the analytes studied in real samples.

4. Conclusion

This paper describes a new, non-exhausting, equilibrium approach to liquid–liquid microextraction, employing a newly developed bell-shaped extraction device (BSED) combined with GC–MS measurements. The method has been effectively optimized, employing multifactorial statistical procedures (RSM and CCD), and tested on determinations of organic pollutants in drinking and mineral waters.

The main advantages of this new method (BSED–LLME) involve simple and rapid manipulation with the extraction solvent and aqueous sample, great flexibility in the selection of the organic extraction solvent in dependence on the nature of the analytes to be determined, minimum toxicity to the environment and low costs. This new method is an efficient alternative to the standard techniques, such as SPE, SPME and other kinds of LLME. The BSED–LLME method can be combined not only with GC measurements, but also with other high-performance separations, such as HPLC or CE.

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Appendix A. Supplementary data

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