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One-step in-syringe ionic liquid-based dispersive liquid–liquid microextraction

Marta Cruz-Vera, Rafael Lucena, Soledad Cárdenas, Miguel Valcárcel*

Department of Analytical Chemistry, Marie Curie Building(Annex), Campus de Rabanales, University of Cordoba, E-14071 Córdoba, Spain

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ABSTRACT

Dispersive liquid–liquid microextraction (DLLME) has been proved to be a powerful tool for the rapid sample treatment of liquid samples providing at the same time high enrichment factors and extraction recoveries. A new, simple and easy to handle one step in-syringe set-up for DLLME is presented and critically discussed in this paper. The novel approach avoids the centrifugation step, typically off-line and time consuming, opening-up a new horizon on DLLME automation. The suitability of the proposal is evaluated by means of the determination of non-steroidal anti-inflammatory drugs in urine by liquid chromatography/ultraviolet detection. In the presented approach an ionic liquid is used as extractant. The target drugs can be determined in urine within the concentration range 0.02–10 μg mL^{-1}, allowing their determination at therapeutic and toxic levels. Limits of detection were in the range from 8.3 ng mL^{-1} (indomethacin) to 32 ng mL^{-1} (ketoprofen). The repeatability of the proposed method expressed as RSD ($n = 5$) varied between 2.5% (for ketoprofen) and 8.6% (for indomethacin).

1. Introduction

Despite the great evolution experimented by analytical sciences in the last years, sample pre-treatment is still an unavoidable step in most analytical procedures due to the complexity of the sample, the low concentration of the target analytes, the presence of great number of potential interferences and even the incompatibility with the detection system. In this general context, the development of new techniques (or the improvement of the existing ones) which answer these main requirements has become a key trend in analytical chemistry.

Liquid-phase microextraction (LPME) emerged in the mid late 90s when Jeannot and Cantwell proposed for the first time the use of organic solvents in the low-microliter range as extractant in liquid–liquid extraction (LLE) [1]. In 1997, Jeannot and Cantwell [2], and almost simultaneously, He and Lee [3], proposed a new configuration based on the use of a conventional microsyringe as extraction unit. In this case, a drop of extractant located on the tip of the microsyringe is getting in touch with the sample allowing the extraction of the analytes. From this initial point, LPME has evolved and different extraction modes have been developed. Within these procedures, hollow fiber protected liquid-phase microextraction [4], proposed by Pedersen-Bjergaard and Rasmussen in 1999, has gained great importance in recent years.

From the practical point of view, most of the LPME-based techniques are non-equilibrium procedures since the time required to reach this state is too large. This fact is owing to the small contact surface between the sample and the extractant which negatively affects the sample throughput and the enrichment factors. Rezaee et al. proposed in 2006 a new extraction mode called dispersive liquid–liquid microextraction (DLLME) [5] which faced up these limitations. In this mode, the extraction is performed between the sample and a cloud of fine extractant drops formed when the mixture of extraction and disperser solvents is injected in the aqueous sample. The contact surface between phases is markedly increased reducing the extraction times and increasing the enrichment factors. DLLME has been successfully used for the determination of different pollutants such as, organophosphorous pesticides [6], chlorobenzenes [7], trihalomethanes [8], chlorophenols [9], flame retardants [10] and even metals like cadmium [11] and lead [12] in water. The versatility of DLLME makes its use possible in other analytical fields. In this sense, DLLME has been proposed for the determination of volatile phenols in wine [13], chloramphenicol in honey [14] and fungicides in apple [15].

According to the classical DLLME foundation, the extractant solvent should be immiscible with water and denser than it in order to favour the phase separation, always by centrifugation, after the extraction. Therefore only a few solvents, mainly halogenated hydrocarbons, have been extensively used in this modality, although the use of solvents with densities lower than water has been recently proposed [16].

Some ionic liquids (ILs), which are promising solvents in LPME [17–21], are suitable to be used in DLLME procedures as they accomplish these classical basic requirements. Moreover, their extraction

* Corresponding author. Tel.: +34 957 218 616; fax: +34 957 218 616.
E-mail address: qa1meobj@uco.es (M. Valcárcel).

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capability to a wide range of compounds is well documented [22]. In fact, ILs have been recently proposed as extractants in these procedures [23–26].

The objective of this paper is to present a new extraction alternative which avoids the centrifugation step, a typically off-line process, opening-up a new horizon for the automation of DLLME. The new simple and easy to handle approach uses a 10 mL-plastic syringe as extraction unit and a microsyringe for extractant addition and recovery. The new proposal is evaluated using ILs as solvents for the extraction of non-steroidal anti-inflammatory drugs (NSAIDs) from urine samples. All the variables affecting the DLLME procedure have been deeply studied and the analytical figures of merit have been established. After a recovery study, the proposal has been applied to the determination of the target analytes in urine samples obtained from patients under treatment with these drugs.

2. Experimental

2.1. Reagents and samples

All reagents were of analytical grade or better. Methanol, acetonitrile, ethanol, acetic acid and acetone (Scharlab, Barcelona, Spain) were evaluated as disperser solvents. 1-Butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$) from Merck (Darmstadt, Germany), was evaluated as extractant in the DLLME procedure since its extraction capability to substances with aromatic structures is well-founded.

Non-steroidal anti-inflammatory drugs (NSAIDs): flurbiprofen, naproxen, ketoprofen and indomethacin were purchased from Sigma–Aldrich (Madrid, Spain). Stock standard solutions of each analyte were prepared in methanol at a concentration of $5\,g\,L^{-1}$ and stored at 4 °C. Working solutions of the NSAIDs were prepared by dilution of the stocks in Milli-Q ultra pure water (Millipore Corp., Madrid, Spain).

Blank urine samples were collected from healthy individuals and stored in polytetrafluoroethylene (PTFE) flasks at −20 °C until analysis. Prior to the dispersive liquid-phase microextraction, each sample was adjusted to pH 3.0 with diluted hydrochloric acid (Panreac, Barcelona, Spain) and filtered through a disposable nylon filter (0.45 μm of pore size, Millipore, Madrid, Spain). In order to evaluate the proposed method, samples collected from individuals treated with NSAIDs, sampled at different times before oral administration, were analyzed.

2.2. Chromatographic system and conditions

Chromatographic analyses were performed on an HP1100 series liquid chromatograph (Agilent, Palo Alto, CA) equipped with a binary high-pressure pump for mobile phase delivery, a high-pressure injection valve (Rheodyne 7725, Cotati, CA) fitted with a 20 μL loop, and a single wavelength photometer (HP1100 series) for analytes' determination. Data analysis was performed using HP ChemStation software.

Chromatographic separation was achieved on a LiChrosorb C_{18} (4.6 mm × 150 mm) column (Supelco, Madrid, Spain) using

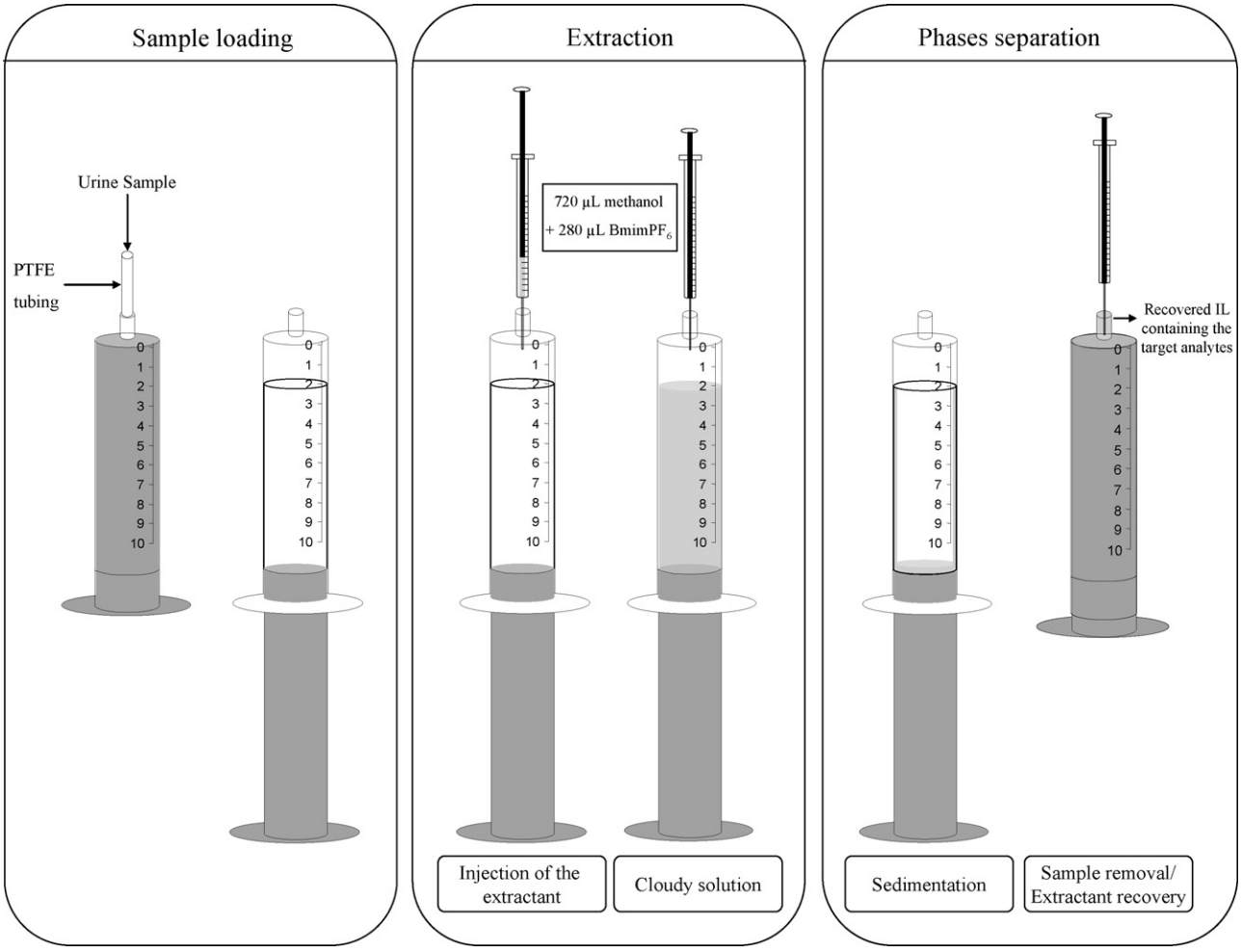

Fig. 1. Experimental set-up proposed for in-syringe ionic liquid-based dispersive liquid–liquid microextraction.

methanol/water/acetic acid 60/40/20 (v/v/v) as mobile phase. The flow rate was maintained at 0.9 mL min^{-1} and the analytes were monitored at 254 nm.

2.3. In-syringe dispersive liquid–liquid microextraction manifold and procedure

The proposed extraction system is quite simple requiring only a 10-mL plastic syringe as extraction unit, a 1000-μL glass syringe for the injection of the extractant/disperser mixture and for extractant recovering. The general scheme of the extraction process is depicted in Fig. 1 and consists of three well-defined steps, namely: sample loading, extraction and phases separation. At the beginning, a specific volume of standard solution or urine sample (typically 10 mL) is aspirated in the 10 mL-syringe by means of a PTFE tubing adapted to the tip of the syringe. Then, 1000 μL of the extraction mixture, containing 720 μL of disperser solvent (methanol) and 280 μL of the extractant ($BmimPF_6$), are sprayed by using the 1000-μL glass syringe, a cloudy solution being immediately formed. Later on, the plunger of the 10 mL-syringe is slowly moved to the initial point allowing the recovery of the IL from the wall and the lower part of the syringe while the urine sample is removed from the unit. Finally, the IL phase containing the target analytes can be easily recovered from the syringe tip. Different adapters can be coupled to the syringe tip depending on the expected volume to be recovered. The whole process takes less than 5 min.

For chromatographic analysis, the recovered IL containing the target analytes is diluted 1:1 (v/v) in mobile phase.

2.4. Analytical parameters

Two main parameters have been employed for the evaluation of the proposed configuration, namely: extraction recovery and enrichment factor. Extraction recovery (ER) was defined as the percentage of total analyte which was extracted to IL phase. For the discussion of the results, the IL phase will be denoted as recovered phase.

$$\mathrm{ER} = \frac{C_{\mathrm{rec}} \times V_{\mathrm{rec}}}{C_0 \times V_{\mathrm{aq}}} \times 100$$

where C_{rec} and C_0 are the concentration of the analyte in the IL phase and the initial concentration in the sample, respectively. V_{rec} and V_{aq} are the volumes of the phases involved. In other sense, the enrichment factor (EF) is defined as:

$$\mathrm{EF} = \frac{C_{\mathrm{rec}}}{C_0}$$

Finally, a normalized EF value can be defined for practical purposes taking into account the fact that the recovered phases should be diluted in mobile phase for chromatographic analysis. In this sense, normalized EF (EF°) is defined as:

$$EF^{\circ} = \frac{(C_{\mathrm{rec}} \times V_{\mathrm{rec}})}{(V_{\mathrm{rec}} + V_{\mathrm{m}})} \times \frac{1}{C_0}$$

V_{m} being the volume of mobile phase required for the dilution of the recovered phase. Taking into consideration the analytical procedure:

$$\mathrm{EF}^{\circ} = \frac{\mathrm{EF}}{2}$$

3. Results and discussion

The practical application of ILs in DLLME is limited by two facts. On the one hand, their high viscosity requires a deep optimization of the extractant/disperser mixture. On the other hand, the final phase separation is problematic as the IL tends to remain on the surface of the extraction vial, requiring a large time of centrifugation to sediment it. In this paper, a new experimental set-up which faces up this final shortcoming is proposed. The success of the experimental set-up relies on its capability to recover the IL after the extraction procedure avoiding the centrifugation step.

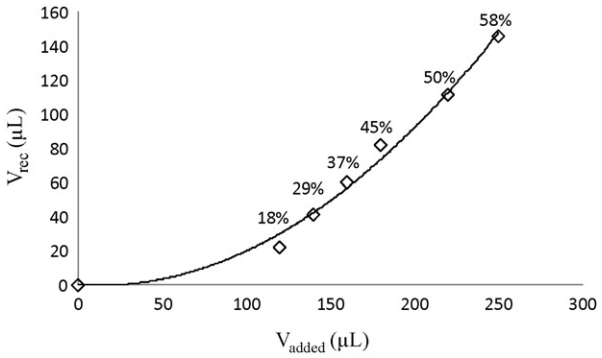

Fig. 2. Relationship between the volume of ionic liquid added and recovered after the extraction procedure, using the proposed experimental set-up. Data obtained using methanol as dispersant solvent and $BmimPF_6$ as extractant.

3.1. Design of the extraction manifold

Initially a 10-mL plastic syringe was selected as extraction unit on account of its lower price and availability. Also, its disposable nature will reduce the potential contamination between samples if required. The volume of the extraction unit will also yield high preconcentration factors as higher sample/extractant volume ratios can be achieved. The sample can be easily loaded by means of a PTFE tubing located between the vial and the syringe tip. The volume of the extractant was controlled by means of a 1 mL glass microsyringe. The efficiency of the system was evaluated by studying the relationship between the IL added and recovered, before and after the extraction, respectively. For this purpose, mixtures containing methanol as disperser solvent and $BmimPF_6$ as extractant were selected. In this sense, 500 μL of methanol containing different amounts of IL (between 125 and 250 μL) was added to 5 mL of milli-Q water, the final volume of IL being measured. Fig. 2 represents the graph obtained when the recovered volume (V_{rec}) is represented against the added volume (V_{added}), also indicating the percentage of recovered volume for each extractant volume added. A non-linear relationship is observed which indicates that the percentage of recovered volume depends on the IL initially added with the disperser solvent. This fact can be ascribed to the partial solubilization of the IL in water. This effect is less marked when higher volumes are added since the aqueous phase is saturated with the IL.

Once the relationship between the volumes recovered and added in the extraction process was established, the repeatability of this procedure was evaluated. For this aim, seven consecutive extractions were performed using 500 μL of methanol containing 130 μL of IL, the final volume being measured. $BmimPF_6$ recovery after extraction presents a relative standard deviation of 3.5%. In the light of the obtained results, the proposed set-up allows the repeatable recovery of the IL after the dispersion.

3.2. Selection of the disperser solvent

The disperser solvent should be miscible with both the extraction solvent and the aqueous phase. According to the supplier's information and experimental assays, different solvents (methanol, ethanol, acetonitrile, acetic acid and acetone) fulfil both

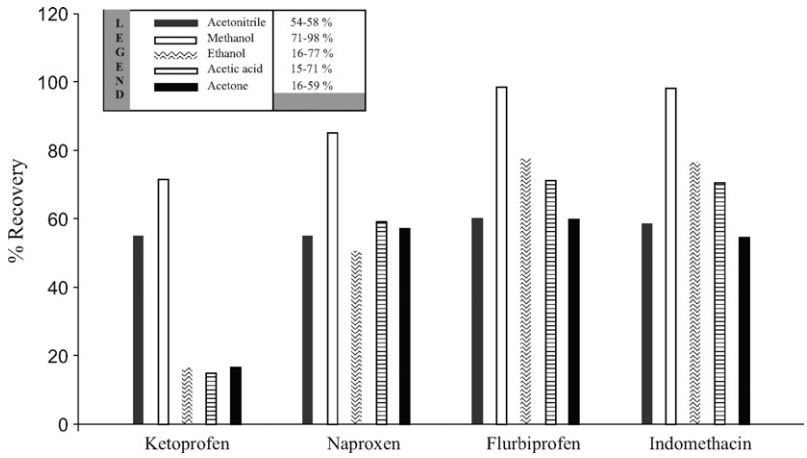

Fig. 3. Efficiency of different disperser solvents evaluated for the extraction of NSAIDs.

considerations and therefore they were taken into consideration. A series of standard solutions, adjusted at pH 3 and containing the analytes at 0.2 μg mL^{-1}, were studied by using 500 μL of each disperser solvent containing 130 μL of $BmimPF_6$. The results are graphically summarized in Fig. 3. The lowest precision was obtained for ethanol since some instability (tendency to phase separation) was observed within the mixture. According to the recovery values obtained for the analytes, methanol was selected as disperser solvent. This higher recovery can also be attributed to the better dispersion obtained in methanol which also results in a lower recovered volume of IL.

3.3. Optimization of the extraction medium

The effect of the IL volume on the DLLME was evaluated. As previously described, ILs present a high viscosity which can negatively affect the dispersion process. In order to study this influence, 5 mL of an aqueous solution containing the analytes at a concentration of 0.2 μg mL^{-1} was extracted with 500 μL of the extraction mixture containing different volumes of disperser and extraction solvents. The influence of the IL volume present in the disperser/extractant mixture on the enrichment factor and extraction recovery is depicted in Fig. 4. As expected, the enrichment factors decrease for all the analytes assayed with the volume of IL added since the volume of recovered phase increased. However, a special behaviour is observed for the extraction recovery as it increases with the extractant/disperser volume ratio up to 0.6 with a slight decrease over this value. This behaviour has not been described for other organic solvents and even for ionic liquids in the conventional approach for DLLME, since in almost all the applications the recovery value increases or remains constant. The fact observed in this experience can be ascribed to the high viscosity of the $bmimPF_6$. In fact, when large volumes of IL are used, the disperser is not enough to satisfactorily disperse the IL. In this sense, less fine droplets of extractant are formed reducing the extraction efficiency.

The disperser/extractant volume ratio was selected according to not only the extraction recovery and the enrichment factor but also the repeatability of the IL volume recovered. The optimum mixture composition contains 360 μL of methanol and 140 μL of IL. Despite of the fact lower ratios can provide a better enrichment factor, V_{rec} is less reproducible when low amounts of extractant are employed.

Once the composition of the extraction medium has been optimized, its volume has to be taken into consideration. Different volumes, in the interval 0.5–1.5 mL were evaluated, by calculating the extraction recovery and enrichment factor. The experimental data show an increasing extraction recovery whereas the enrichment factor decreases with the volume of extraction medium. According to the results, the optimum value for the volume of extraction medium was fixed to 1 mL as a compromise between ER and EF values.

3.4. Optimization of the sample conditions

The extraction of the target analytes can be affected by the sample matrix. This effect was evaluated through the influence

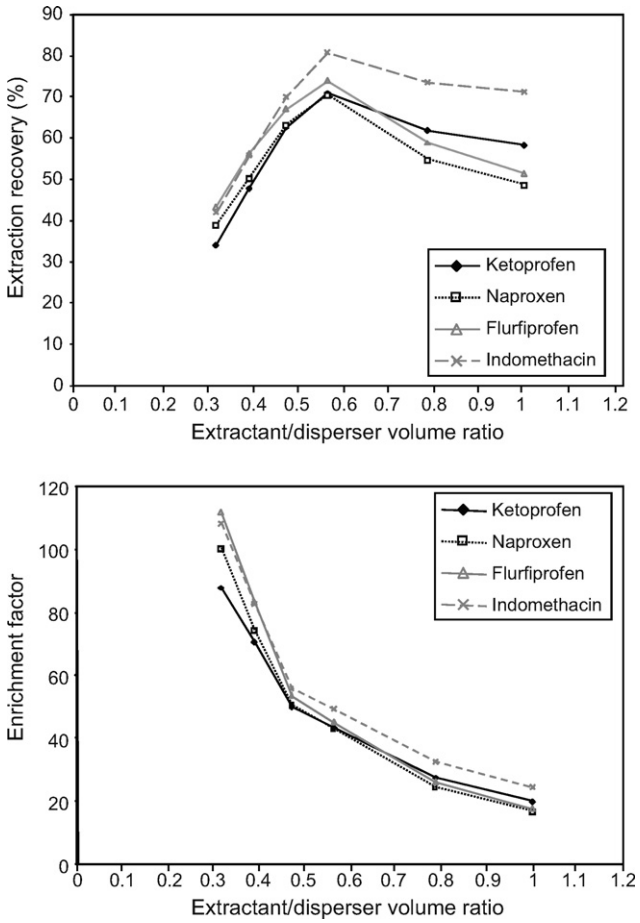

Fig. 4. Effect of the composition of the extractant (in terms of the extractant/disperser volume ratio) on the extraction recovery and enrichment factor for all the target analytes.

Table 1
Extraction parameters obtained for the target analytes by the proposed configuration using standards.

Compounds	ER[a] ± SD[b]	EF[c] ± SD[b]	EF°[d] ± SD[b]
Ketoprofen	36.8 ± 0.9	73.7 ± 1.4	36.8 ± 0.7
Naproxen	38.3 ± 0.9	76.6 ± 1.3	38.3 ± 0.6
Flurbiprofen	42.2 ± 1.0	84.4 ± 1.5	42.2 ± 0.7
Indomethacin	42.3 ± 1.0	84.6 ± 1.4	42.3 ± 0.6

[a] ER, extraction recovery.
[b] SD, standard deviation obtained for four levels of concentration by triplicate.
[c] EF, enrichment factor.
[d] EF°, normalized enrichment factor.

Table 2
Analytical figures of merit of the in-syringe DLLME developed for the determination of NSAIDs in urine samples.

	Linear range ($\mu g\,mL^{-1}$)	LOD[a] ($ng\,mL^{-1}$)	RSD[b] (%)	RR[c] (%)
Ketoprofen	0.08–10	32.0	2.5	99.6
Naproxen	0.02–10	9.2	3.6	100.6
Flurbiprofen	0.04–10	16.3	8.1	107.0
Indomethacin	0.02–10	8.3	8.6	106.0

[a] LD, limit of detection.
[b] RSD, relative standard deviation.
[c] RR, relative recovery.

of the sample dilution on the analytical signal. For this purpose a blank urine sample, spiked with the analytes at a concentration of 0.2 $\mu g\,mL^{-1}$, was diluted at different ratios (from 1:0 to 1:4) with an aqueous standard prepared at the same concentration in order to keep the amount of analytes present in the mixtures constant. Aliquots of 5 mL of the diluted samples were extracted following the proposed configuration, the final extracts being analyzed later on. The recovery remained almost constant in the whole interval assayed (except naproxen) and for simplicity urine samples were not diluted before the extraction process.

The effect of the sample volume in the extraction of the analytes was evaluated by extracting different volumes of the same spiked urine sample (0.2 $\mu g\,mL^{-1}$) according to the proposed extraction procedure. As expected, the enrichment factor increases with the sample volume in the range 2–10 mL. Finally, 10 mL was selected as the optimum sample volume as it provides the highest enrichment factors while maintaining acceptable recovery values.

3.5. Effect of the extraction time

In DLLME, extraction time is defined as interval time between injection of the mixture of disperser solvent (methanol) and extraction solvent ($BmimPF_6$) and the phase's separation. This parameter was evaluated in the range of 0–60 min. Negligible effect of the extraction time on the peak area of the analytes was observed. This fact indicates that the transference of the analytes from the sample to the extraction medium is fast. In fact, when the extraction mixture is dispersed into the aqueous phase (sample), a cloud of fine drops of extractant is created increasing the contact surface between phases. Therefore, the equilibrium state is quickly achieved which results to be one of the main advantages of DLLME procedures.

3.6. Analytical performance of the method

The proposed configuration was characterized according to the extraction parameters as well as the analytical figures of merit. Table 1 summarizes the extraction parameters (ER and EF) calculated for the target analytes under the optimal experimental conditions using the equations described previously. Both parameters were evaluated at four levels of concentration. In this sense, enrichment factors varied between 73.7 (for ketoprofen) and 84.6 (for indomethacin). Moreover the extraction recoveries varied between 36.8 (for ketoprofen) and 42.3 (for indomethacin).

Table 2 lists the figures of merit (calibration linear ranges, limits of detection, precision and relative recovery) of the proposed method for the four NSAIDs selected. The calibration graphs were constructed by analyzing aqueous standards containing the analytes at five concentration levels in the range 0.01–10 $\mu g\,mL^{-1}$. The standards, previously adjusted to pH 3, were extracted according to the novel experimental set-up working under optimal conditions. The obtained extracts were subsequently analyzed by liquid chromatography. Good linear relationships between the corresponding peak areas and the concentration were obtained for all the analytes ($R > 0.999$).

Limits of detection, calculated according to the $S/N = 3$ ratio, were in the range from 8.3 $ng\,mL^{-1}$ (for indomethacin) to 32 $ng\,mL^{-1}$ (for ketoprofen). The precision of the method, expressed as relative standard deviation, was calculated from five replicates of a urine sample containing the analytes at concentration of 0.2 $\mu g\,mL^{-1}$. The values varied between 2.5% (for ketoprofen) and 8.6% (for indomethacin).

Recovery studies were performed by analyzing diverse free-analytes urine samples spiked with the analytes at five different concentration levels (0.05, 0.2, 1, 5 and 10 $\mu g\,mL^{-1}$). The obtained peak areas for each analyte were interpolated in the calibration graphs constructed using standards. In this case the relative recoveries (urine relative to aqueous standards) were calculated by the known equation: %RR = [(analyte found)/(analyte added)] × 100. The average values are summarized in Table 2. In Fig. 5, two chromatograms obtained for blank and spiked urine sample (0.2 $\mu g\,mL^{-1}$) are presented.

3.7. Analysis of samples

Finally the proposed method was applied to the determination of the NSAIDs in urine samples. Several urine samples collected from individuals treated with NSAIDs were analyzed. Prior to the DLLME, each sample was adjusted to pH 3 and filtered through a disposable nylon filter. The obtained results are shown in Table 3, indicating some information about the dosage and the sampling procedure as well.

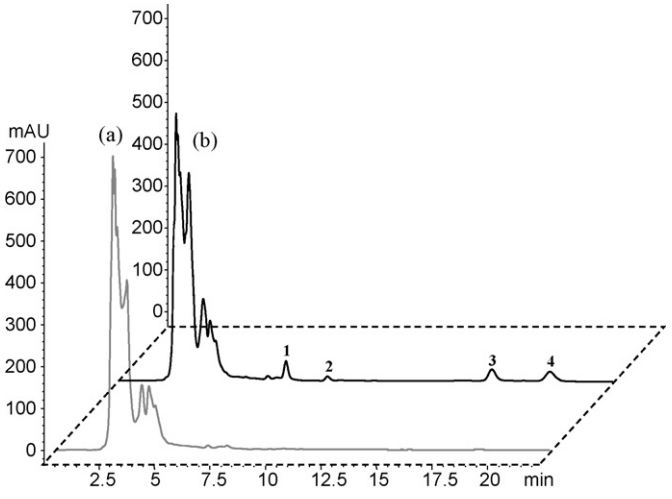

Fig. 5. Chromatograms obtained for a (a) blank and a (b) spiked (0.2 $\mu g\,mL^{-1}$) urine sample after the DLLME procedure. Peaks of interest: (1) Ketoprofen, (2) Naproxen, (3) Flurbiprofen and (4) Indomethacin.

Table 3
Analysis of urine samples using the in-syringe dispersive liquid–liquid microextraction procedure.

Sample	Administration		Sampling		Results	
	NSAID[a]	Dosage[b]	Time[c]	Volume[d]	NSAID[e]	Concentration ± SD[f]
1	Ketoprofen	100	40	240	–	n.d.[g]
2	Ketoprofen	100	70	240	Ketoprofen	d.[h]
3	Ketoprofen	100	120	120	Ketoprofen	d.[h]
4	Ketoprofen	100	240	80	Ketoprofen	7.0 ± 0.2
5	Naproxen	600	80	100	Naproxen	2.11 ± 0.08
6	Naproxen	600	260	120	Naproxen	4.3 ± 0.2
7	Naproxen	600	380	100	Naproxen	0.90 ± 0.04
8	Indomethacin	50	80	100	–	n.d.[g]
9	Indomethacin	50	120	80	Indomethacin	0.55 ± 0.03
10	Indomethacin	50	240	80	Indomethacin	0.88 ± 0.06

[a] Non-steroidal anti-inflammatory drug administrated to the voluntary.
[b] Amount of drug administrated via oral (mg).
[c] Sampling time after administration (min).
[d] Volume of urine sampled (mL).
[e] Non-steroidal anti-inflammatory drug found in the sample.
[f] Concentration of the drug ($\mu g\,mL^{-1}$) in the sample. SD, standard deviation ($n = 3$).
[g] n.d., non detected.
[h] d., detected. Concentration between limits of detection and quantification.

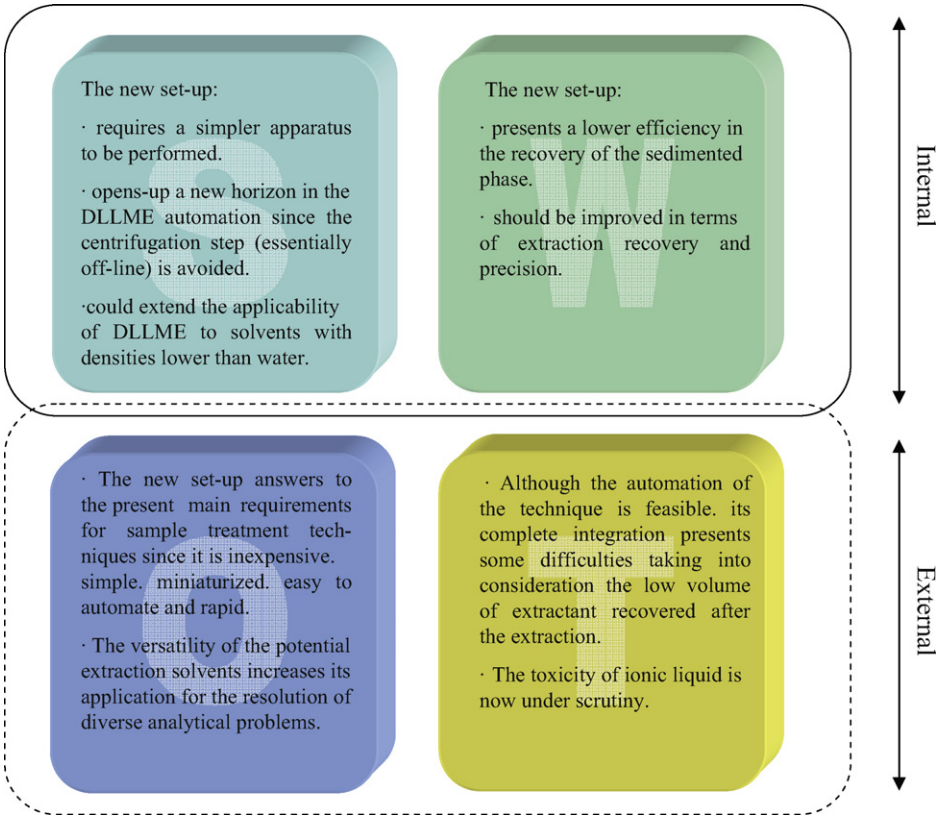

Fig. 6. SWOT analysis of the proposed set-up for DLLME. Strengths and weaknesses are obtained after a critical evaluation of the proposal. Opportunities and threats are obtained taking into consideration the main requirements for sample treatment technique.

4. Conclusions

A new experimental set-up for dispersive liquid–liquid microextraction is presented and critically evaluated. The main advantages and disadvantages of the proposal have been established following a SWOT (strengths, weakness, opportunities and threats) analysis. This analysis, summarized in Fig. 6, will be useful to identify the trends of further investigations.

The new experimental set-up requires a simple apparatus to be performed, only a conventional plastic syringe being used as extraction unit. This simple configuration avoids the centrifugation step, which is time consuming and essentially off-line, allowing reducing the extraction time (mainly when ILs are used as solvents) and making easier the automation of the procedure than the conventional approach. Essentially, phase separation can be automated using a typical syringe pump. In addition, the centrifugation step restricted the use of solvents in DLLME, since only solvents denser than water can be employed. The new approach can overcome this restriction by changing the orientation of the syringe during the phase separation step.

The above mentioned strengths of the new procedure answer some of the main requirements for sample pre-treatment

techniques such as simplicity, versatility, expeditiousness and low price.

Despite the evident advantages of the new proposal, some aspects have to be improved in order to make it competitive to other approaches. First of all, the efficiency in the recovery of extractant phase must be increased, since this reduced efficiency has an evident influence on the extraction recovery. In fact, the extraction conditions are selected as a compromise between "dispersive conditions" and "extractant recovery". On the one hand, when good extractant dispersion is achieved an excellent extraction is accomplished. On the other hand, when the dispersion is very efficient, the recovery of the extractant is more difficult. These opposite facts may explain the low extraction recovery obtained in the experimental section (between 30 and 40%). Meanwhile, although it is acceptable, the precision of the procedure must be improved.

Finally, the non-toxicity of ILs is nowadays in question and some studies have recently received broad attention [27].

According to the SWOT analysis, further investigation will be focused on:

(1) Automation of the overall process using sequential injection procedures.
(2) Extension of the DLLME to solvents with lower density than water following the trend recently proposed by Anthemidis and Ioannou [16].
(3) Improvement of the extraction recoveries and precision of the procedure.

Acknowledgment

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References

[1] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 68 (1996) 2236.
[2] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 69 (1997) 235.
[3] Y. He, H.K. Lee, Anal. Chem. 69 (1997) 4634.
[4] S. Pedersen-Bjergaard, K.E. Rasmussen, Anal. Chem. 71 (1999) 2650.
[5] M. Rezaee, Y. Assadi, M.M. Hosseini, E. Agnee, F. Ahmadi, S. Berijani, J. Chromatogr. A 1116 (2006) 1.
[6] S. Berijani, Y. Assadi, M. Anbia, M.R. Milani Hosseini, E. Aghaee, J. Chromatogr. A 1123 (2006) 1.
[7] R. Rahnama Kozani, Y. Assadi, F. Sheminari, M.R. Milani Hosseini, M.R. Jamali, Talanta 72 (2007) 387.
[8] R. Rahnama Kozani, Y. Assadi, F. Sheminari, M.R. Milani Hosseini, M.R. Jamali, Chromatographia 66 (2007) 81.
[9] N. Fattahi, Y. Assadi, M.R. Milani Hosseini, E.Z. Jahromi, J. Chromatogr. A 1157 (2007) 23.
[10] M. García-López, I. Rodríguez, R. Cela, J. Chromatogr. A 1166 (2007) 9.
[11] E.Z. Jahromi, A. Bidari, Y. Assadi, M.R. Milani Hosseini, M.R. Jamali, Anal. Chim. Acta 585 (2007) 305.
[12] M.T. Nasari, M.R. Milani Hosseini, Y. Assadi, A. Kiani, Talanta 75 (2008) 56.
[13] L. Fariña, E. Boido, F. Carrau, E. Dellacassa, J. Chromatogr. A 1157 (2007) 46.
[14] H. Chen, J. Ying, H. Chen, J. Huang, L. Liao, Chromatographia 68 (2008) 629.
[15] X. Zang, J. Wang, O. Wang, M. Wang, J. Ma, G. Xi, Z. Wang, Anal. Bioanal. Chem. 392 (2008) 749.
[16] A.N. Anthemidis, K.I.G. Ioannou, Talanta 79 (2009) 86.
[17] J.F. Liu, G.B. Jiang, Y.G. Chi, Y.Q. Cai, Q.X. Zhou, J.T. Hu, Anal. Chem. 75 (2003) 5870.
[18] M. Cruz-Vera, R. Lucena, S. Cárdenas, M. Valcárcel, J. Chromatogr. A 1202 (2008) 1.
[19] E. Aguilera-Herrador, R. Lucena, S. Cárdenas, M. Valcárcel, Anal. Chem. 80 (2008) 793.
[20] L. Vidal, A. Chisvert, A. Canals, A. Salvador, J. Chromatogr. A 1174 (2007) 95.
[21] A. Chisvert, I.P. Román, L. Vidal, A. Canals, J. Chromatogr. A 1216 (2009) 1290.
[22] R. Liu, J. Liu, Y. Yin, X. Hu, G. Jiang, Anal. Bioanal. Chem. 393 (2009) 871.
[23] Q. Zhou, H. Bai, G. Xie, J. Xiao, J. Chromatogr. A 1177 (2008) 43.
[24] Q. Zhou, H. Bai, G. Xie, J. Xiao, J. Chromatogr. A 1188 (2008) 148.
[25] Y. Chang Fan, Z. Liang Hu, M. Lan Chen, C. Shen Tu, Y. Zhu, Chin. Chem. Lett. 19 (2008) 985.
[26] Y. Liu, E. Zhao, W. Zhu, H. Gao, Z. Zhou, J. Chromatogr. A 1216 (2008) 885.
[27] D. Zhao, Y. Liao, Z. Zhang, Clean 35 (2007) 42.