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Extensible automated dispersive liquid–liquid microextraction

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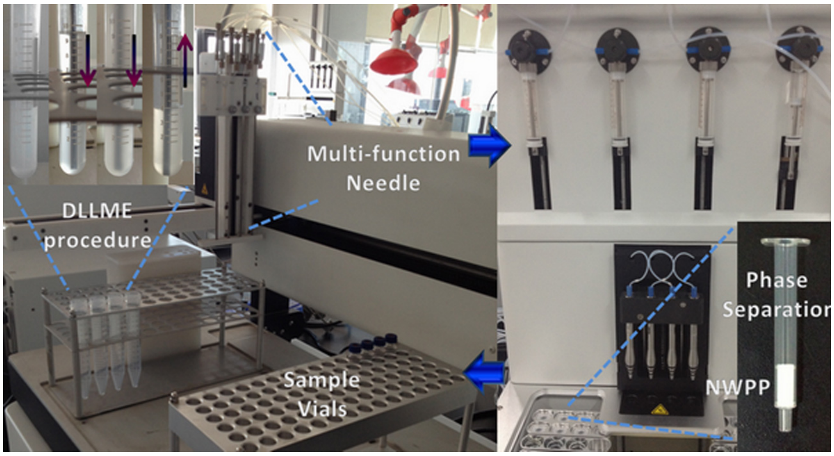
HIGHLIGHTS

- An extensible automated dispersive liquid–liquid microextraction was developed.
- A fully automatic SPE workstation with a modified operation program was used.
- Ionic liquid-based in situ DLLME was used as model method.
- SPE columns packed with nonwoven polypropylene fiber was used for phase separation.
- The approach was applied to the determination of benzoylurea insecticides in water.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a convenient and extensible automated ionic liquid-based in situ dispersive liquid–liquid microextraction (automated IL-based in situ DLLME) was developed. 1-Octyl-3-methylimidazolium bis[(trifluoromethane)sulfonyl]imide ($[C_8MIM]NTf_2$) is formed through the reaction between $[C_8MIM]Cl$ and lithium bis[(trifluoromethane)sulfonyl]imide ($LiNTf_2$) to extract the analytes. Using a fully automatic SPE workstation, special SPE columns packed with nonwoven polypropylene (NWPP) fiber, and a modified operation program, the procedures of the IL-based in situ DLLME, including the collection of a water sample, injection of an ion exchange solvent, phase separation of the emulsified solution, elution of the retained extraction phase, and collection of the eluent into vials, can be performed automatically. The developed approach, coupled with high-performance liquid chromatography–diode array detection (HPLC–DAD), was successfully applied to the detection and concentration determination of benzoylurea (BU) insecticides in water samples. Parameters affecting the extraction performance were investigated and optimized. Under the optimized conditions, the proposed method achieved extraction recoveries of 80% to 89% for water samples. The limits of detection (LODs) of the method were in the range of 0.16–0.45 ng mL^{-1}. The intra-column and inter-column relative standard deviations (RSDs) were <8.6%. Good linearity ($r > 0.9986$) was obtained over the calibration range from 2 to 500 ng mL^{-1}. The proposed method opens a new avenue for automated DLLME that not only greatly expands the range of viable extractants, especially functional ILs but also enhances its application for various detection methods. Furthermore, multiple samples can be processed simultaneously, which accelerates the sample preparation and allows the examination of a large number of samples.

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1. Introduction

In recent years, liquid–liquid extraction (LLE), the most accepted and widely used sample preparation procedure, has been challenged by miniaturized, efficient, and economical methods, such as liquid phase microextraction (LPME) [1–4] and solid phase microextraction (SPME) [5–7]. LPME provides relatively high enrichment factors for analytes due to its very high sample-to-solvent ratio, which thus allows the detection of analytes at low concentrations [8,9].

DLLME [10] is one of the most recently developed LPME methods. In DLLME, a small amount of extractant is dispersed in the sample via the quick injection of the extractant/dispersant mixture into the sample. An emulsified solution is formed and quickly reaches equilibrium, which dramatically shortens the extraction time. DLLME has been widely applied in the detection of pesticides [11–14], organic [15,16] and inorganic environmental contaminants [17,18], and pharmaceuticals [19–21] in various matrices.

However, unlike SPME and single-drop microextraction (SDME) [22,23], which were automated long ago [24–28], automated DLLME requires further development, mainly because the DLLME procedure involves more elaborate manual operations than other techniques. These operations are difficult to perform in common devices. The study of automated DLLME began with the flow-injection analysis (FIA) [29,30] and sequential-injection analysis (SIA) techniques [31,32], which employ a multi-position valve and a syringe pump as the core block. These techniques are devoted to overcoming the limitations of DLLME, such as low analysis throughput, a laborious procedure, and manual glassware cleaning or disposal. Automated in-syringe DLLME [33–35] was then developed to concomitantly overcome these limitations. Guo and Lee [36] reported an automated DLLME–GC/MS approach using a GC/MS instrument equipped with a CTC CombiPal autosampler; their method was the first to use commercial equipment to achieve the automation of DLLME and detection. Yamini et al. developed several on-line approaches for phase separation in different extraction methods coupled to an analysis instrument, which accelerated the development of on-line phase separation techniques [37–39]. These techniques represent a breakthrough in automated DLLME.

In the present work, a convenient and extensible automated DLLME procedure using commercial instrumentation has been developed. All DLLME steps have been performed by a fully automatic SPE workstation and special SPE columns. The specificity of the SPE columns is due to the nonwoven polypropylene (NWPP) fibers used as the column packing matterial, which was used in automated DLLME for the first time in the present work. The NWPP-based SPE columns functioned similarly to PTFE filters used in on-line emulsification liquid phase microextraction (ELPME) [38,39]. A PTFE in-line filter was used to separate the organic and aqueous phases in an on-line ELPME approach due to its hydrophobic and oleophilic properties. Similarly, NWPP sheets are commercial synthetic organic fibers with densities in the range of 0.94–0.96 $\mathrm{g\,cm^{-3}}$ [40]. Due to its hydrophobic and oleophilic properties, NWPP is the most commonly used commercial sorbent in oil spill cleanup [41–43]. The adsorption capacity of PP for oil is 8–19 $\mathrm{g\,g^{-1}}$, whereas the water uptake for PP sorbents is 0.1–0.2 $\mathrm{g\,g^{-1}}$. PP sorbents thus exhibit excellent oil/water selectivity [43,44]. Therefore, when an emulsified extraction solution is loaded onto an SPE column packed with NWPP, the aqueous phase passes through completely while the extraction phase is retained in the packing material, which allows extractant enrichment and phase separation to proceed simultaneously. Then, the extraction phase can be eluted using a proper eluent and transferred to the sample vial for instrumental analysis.

Using an SPE column as an absorbing device is conducive to popularizing the corresponding automated DLLME procedure due to the maturity and general use of automatic SPE instruments [45]. A fully automatic SPE workstation can fulfill the entire SPE process automatically, including conditioning, sample loading, washing, elution, air drying, and sample switching, without human intervention. Because automatic SPE processing is suitable for the examination of a large number of samples, an increasing number of research groups are using this equipment in their research and routine analyses.

In the present research, by programming and modifying the operating program, the entire DLLME process, including the collection of the aqueous sample, injection of the dispersive solvent and extractant, transfer and loading of the extraction solution, phase separation, elution, concentration and transfer of the eluent, can be accomplished continuously, repetitively, and automatically on an automatic SPE workstation. Thus, an alternative automation of the DLLME procedure is realized. Moreover, the commercial automatic SPE workstation makes the innovative approach convenient, extensible, and simple to apply to routine analysis by research groups worldwide.

Ionic liquids (ILs), composed of organic cations and various anions, are a class of non-molecular ionic solvents with low melting points ($<100\,^{\circ}\mathrm{C}$). ILs can be regarded as “green” solvents [46,47] because of their negligible vapor pressure, chemical and thermal stability, and good solubility in both organic and inorganic solvents, among other properties. ILs have been utilized in the field of microextractions [48], and IL-based DLLME methods have been extensively developed and applied [49,50]. However, the ILs suitable for DLLME are a very small fraction of all IL types reported, primarily because many ILs possess a similar density as water, rendering them incompatible with the extractants used in DLLME. The high viscosity of ILs also makes some of the manual steps difficult. In the proposed method, these density and viscosity requirements are avoided, which eliminates the obstacles to the application of ILs in DLLME and widens the range of ILs that can be implemented in DLLME and automated DLLME. Thus, IL-based DLLME was selected as the model method for the innovative approach developed herein.

IL-based in situ DLLME [51,52] is a simple, fast, and efficient DLLME that depends on the formation of hydrophobic IL and simultaneous extraction. The hydrophobic IL is formed to extract the analytes through the reaction between its corresponding hydrophilic IL and ion exchange reagent. Lithium bis[(trifluoromethane)sulfonyl]imide ($\mathrm{LiNTf_2}$) and lithium fluoroalkyl-phosphate (LiFAP) [53] are commonly used ion exchange reagents. The outstanding features of the IL-based in situ method are its simple operation and high extraction efficiency. Thus, IL-based in situ DLLME has been selected as the model method for the development of automated IL-based in situ DLLME. Taking the experimental cost into consideration, $\mathrm{LiNTf_2}$ was chosen as the ion exchange reagent.

As powerful insect growth regulators, benzoylurea (BU) insecticides are widely used to control numerous pest species in agricultural activities [54]. BU insecticides have some attractive properties, such as high selectivity, potent biological activity, rapid degradation, and low acute toxicity to mammals. However, strong interest in product safety has hindered its greater commercial development. The residues in the environment and foods resulting from the widespread use of BUs could lead to chronic exposure and long-term toxicity effects [55,56]. Therefore, rapid, simple, and sensitive analytical techniques are necessary for evaluating the risk of BUs to human health. Some novel sample preparation methods, such as solid phase extraction and dispersive liquid-phase microextraction [56,57], have been developed for the detection of BU insecticides. In the present study, the feasibility of the