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Developing microwave-assisted ionic liquid microextraction for the detection and tracking of hydrophobic pesticides in complex environmental matrices†

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In the present study, we have developed a novel dispersive liquid–liquid microextraction (DLLME) based on microwave-assisted DLLME (MADLLME) using ionic liquids for the separation of environmentally-relevant pyrethroid pesticides from various aqueous milieux. High-performance liquid chromatography (HPLC) was employed for the detection and quantitative tracking of the pesticides. Six different ILs were preliminarily tested as extraction solvents against four representative model pyrethroids. The optimization of the current method was derived by consideration of the dispersal solvent, ionic liquid choice, extraction container material, aqueous-phase pH, and microwave conditions (particularly, the applied power and irradiation time). Optimal results were achieved using methanol as a dispersal solvent with trioctylmethylammonium bis(trifluoromethylsulfonyl)imide ($[N_{8881}][Tf_2N]$) as the extraction solvent at a microwave power of 200 W for 60 s. A number of spiked food samples (*e.g.*, honey, milk, assorted fruits) were also tested using MADLLME, with excellent recoveries achieved from these complex matrices as compared to DLLME alone.

Introduction

Pyrethroids, synthetic spin-offs of natural pyrethrin insecticides, are neurotoxic pesticides used to control agricultural and domestic insects.[1–6] Compared to natural pyrethrins, pyrethroids possess enhanced photostabilities, resulting in longer environmental residence times of up to several months before they undergo degradation.[7] In terms of functionality, pyrethroids contain ester and carbonyl moieties, and frequently aromatic rings, nitriles, and a dimethylcyclopropane ring as well (see Fig. 1 for illustrative examples). In all, some 1000 unique pyrethroid structures are known; some of these are very divergent from the original pyrethrin form which inspired them, including variants lacking the dimethylcyclopropane ring.[8] Currently, pyrethroids comprise the most prevalent household insecticide for both indoor and outdoor use.[5] While they are not intentionally sprayed into waterways, pyrethroids can enter lakes, ponds, rivers, and other marine bodies through runoff from agricultural fields.[8] Unfortunately, pyrethroids are highly toxic to aquatic invertebrates; plus fish are extremely sensitive to their neurotoxic effects.[9] Some studies have also shown that exposure to pyrethroids may have a negative influence on human health.[10] It is thus increasingly important to quantify and track pyrethroids throughout the environment and within edible sources.[11–14]

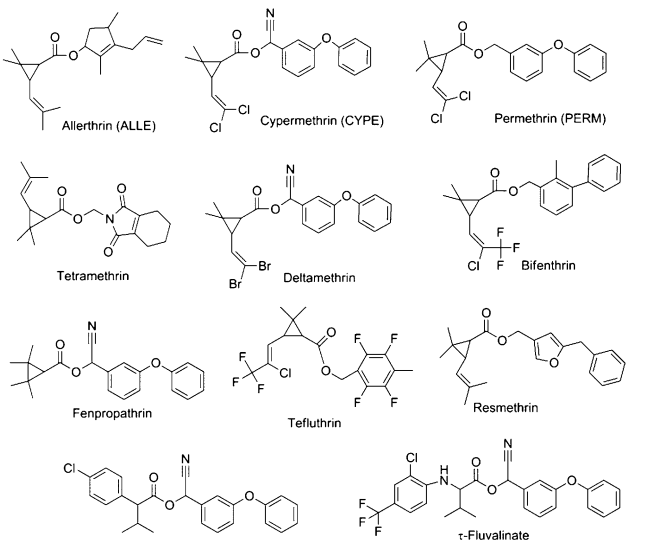

Fig. 1 Chemical structures of some key pyrethroids. The three pyrethroids for which abbreviations are provided were the focus of this analytical study.

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† Electronic supplementary information (ESI) available: Tabulated peak retention times of the pyrethroids and HPLC chromatograms of DLLME and MADLLME extracts of spiked food samples. See DOI: 10.1039/c3ra41139g

The separation of pyrethroids from environmental matrices has been investigated recently using dispersive liquid–liquid microextraction (DLLME).[8,12,15,16] This technique is based on a ternary system: *viz.*, an aqueous phase initially containing the analyte, a hydrophobic extraction solvent, and a dispersing solvent.[17] Typically, a mixture of the extracting solvent and the disperser solvent is injected into the aqueous phase resulting in fine droplets (*i.e.*, high interfacial surface area) of the extraction solvent, affording an enrichment of the target component within the extracting solvent phase.[15,18] The extraction phase containing the target analyte is then separated from the aqueous phase, usually by centrifugation. A serious limitation, however, is the fact that most extraction solvents used for this purpose are volatile organic compounds (VOCs, including chlorobenzene, chloroform, carbon disulphide, and carbon tetrachloride) and are hazardous or toxic.[15]

A prominent alternative to VOCs which has been proposed is the class of solvents known as ionic liquids (ILs), which are organic molten salts possessing melting points below 100 °C. ILs are beneficial alternatives due to their striking properties, such as near-zero vapour pressure, large liquidus range, electrical conductivity, and high thermal conductivity.[19–22] Most conspicuously, ILs can be made task-specific because their properties can be broadly tailored by realizing different cation–anion combinations.[23,24]

Indeed, DLLME performed using an IL as the extraction phase has been recently reported.[25–29] In one example, Zhou and co-workers used a temperature variation of DLLME, wherein temperature swing alone serves to disperse the extraction phase, to extract organophosphorus pesticides from aqueous phases using the IL 1-hexyl-3-methylimidazolium hexafluorophosphate [hmim][PF_6].[25] Following this, Yao and Anderson developed a DLLME method which combined a metathesis reaction for the *in situ* formation of the IL-based extraction phase with the simultaneous extraction of aromatic compounds from water.[27] Anderson and co-workers further developed DLLME by employing tris(pentafluoroethyl)trifluorophosphate (FAP) anion-based ILs for the extraction of emerging contaminates (mostly pharmaceutical compounds) from water samples.[26] Most recently, they extracted deoxyribonucleic acid (DNA) with six novel ILs, reaching an extraction efficiency as high as 97%.[28] In order to improve the efficiency of IL-based DLLME, many assistance-based techniques have been investigated.[16,29,30] In assisted DLLME, the extraction phase is first dispersed within the aqueous phase followed by an applied external stimulus, such as heat, ultrasound, or microwave energy, to increase the extraction efficiency.[17]

Towards applying IL-based DLLME to the extraction of pyrethroids, Zhou *et al.* investigated temperature-assisted IL-based DLLME using the IL 1-octyl-3-methylimidazolium hexafluorophosphate [omim][PF_6] as the extraction phase followed by high performance liquid chromatography (HPLC) to determine the levels of pyrethroids extracted.[31] Also, Zhang *et al.* compared conventional DLLME, temperature-controlled DLLME, and ultrasound-assisted DLLME for the extraction of pyrethroid pesticides from honey samples. Two ILs, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] and [hmim][PF_6] were investigated, with the highest extraction efficiencies being reported for ultrasound assistance.[16] However, both these studies used the undesirable PF_6^- anion which, when contacting an aqueous phase, is known to result in some hydrolysis, generating highly toxic hydrogen fluoride (HF).[32,33]

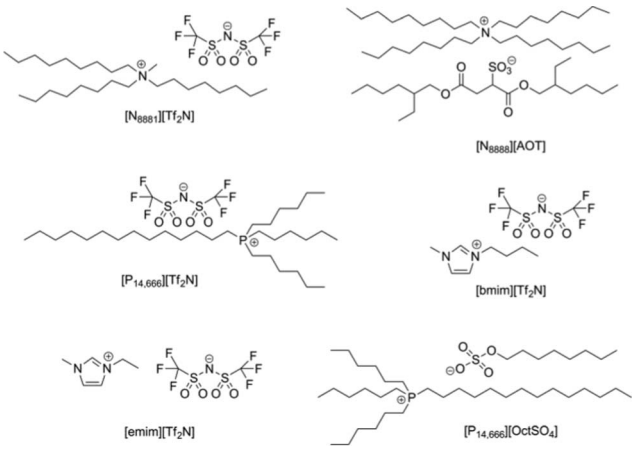

Fig. 2 The six ILs tested for pyrethroid separation.

In the present study, we investigate six non-PF_6^- ILs (Fig. 2) for the DLLME of three exemplary pyrethroid compounds followed by HPLC detection. We investigate both conventional and microwave-assisted DLLME (MADLLME). MADLLE is an efficient technique that has been used for the extraction and pre-concentration of numerous organic compounds from various matrices.[30,34,35] Yet, to the best of our knowledge, simultaneous IL-based MADLLME has not previously been applied to pyrethroid extractions. The high polarity (polarizability) and ionic nature of ILs makes them excellent absorbers of microwave energy, suggesting their suitability for microwave-assisted chemistry.[36–39] In particular, due to the high microwave cross sections possessed by ILs, very high heating rates can be obtained which may, in turn, lead to higher extraction efficiencies for MADLLE applications. IL-based MADLLME has, in fact, demonstrated better extraction efficiencies for compounds such as phthalic acid esters[30] and triazine herbicides.[40] However, these studies did not investigate the mechanism behind the microwave/IL interactions which led to these higher efficiencies. In the present study, we evaluate and optimize various factors that may impact microextraction efficiency and then apply our optimized method for the successful analysis of real world samples.

Experimental

Reagents and materials

The pyrethroids allerthrin (ALLE), cypermethrin (CYPE), and permethrin (PERM) were purchased from Sigma-Aldrich (St.

Louis, MO, USA) and used as received. HPLC-grade methanol, acetonitrile, and hydrochloric acid solution were purchased from Sigma-Aldrich (St. Louis, MO, USA). $[N_{8888}]Br$ and $[P_{14,666}]Cl$ salts were obtained from Sigma and Cytec, respectively. AOT (dioctyl sulfosuccinate sodium salt, 98%) and $OctSO_4$ (sodium octyl sulfate, ~95%) precursors were obtained from Sigma and $LiTf_2N$ was from 3 M. Stock solutions (500 mg L^{-1}) of each pyrethroid were prepared in methanol, protected from light, and stored at 4 °C. Stock solutions were used to prepare dilute aqueous pyrethroid solutions of known concentration for subsequent extraction and calibration experiments.

Ionic liquid synthesis

The synthesis of $[emim][Tf_2N]$, $[bmim][Tf_2N]$, and $[N_{8881}][Tf_2N]$ followed previously reported methods,[41–43] heeding certain precautions outlined earlier for achieving "spec-grade" fluids.[44] For the remaining ILs, metathesis was carried out using commercially sourced anions following established approaches.[45]

Conventional DLLME

Pyrethroid samples for DLLME were prepared by diluting the appropriate amount of pyrethroid stock solution with deionized water to a total volume of 5 mL in either a plastic centrifuge tube or a pre-cleaned glass test tube. Each IL was dissolved in methanol (the disperser solvent used throughout these studies) in a 24 : 80 v/v (IL/MeOH) ratio. For conventional DLLME, 260 μL of the IL/methanol solution was injected into the prepared pyrethroid solution and mixed using a HulaMixer™ Sample Mixer (Life Technologies) for 5 min. After mixing, the sample was centrifuged at 3500 rpm for 10 min to separate the aqueous and IL phases. Then 20 μL of the IL phase was removed and diluted with 1000 μL of methanol. Then, 50 μL of this final solution was subjected to HPLC analysis for pyrethroid separation.

Microwave-assisted DLLME (MADLLME)

MADLLME was carried out using a CEM Discover microwave (Matthews, NC, USA). Samples were prepared as described above for conventional DLLME except that a 10 mL glass microwave vial was used. After injecting 260 μL of the IL/methanol mixture, the samples were microwave at a fixed power for a specified period of time (30–120 s) while stirring in sealed microwave vials. Temperature, microwave power, and pressure were recorded during each run. The samples were then centrifuged at 3500 rpm for 10 min to separate the aqueous and IL phases. Then, 20 μL of the IL phase was removed and diluted with 1000 μL of methanol. Finally, 50 μL of this solution was used for HPLC analysis to detect pyrethroid compounds.

High-performance liquid chromatography (HPLC)

HPLC chromatographic analysis was carried out on a Beckman HPLC system equipped with a System Gold 126 Solvent Module and System Gold 168 Diode Array Detector (DAD). The separation was performed on a Waters Symmetry Shield RP18 Column (5 μm; 4.6 mm × 250 mm) using acetonitrile-water solution (70 : 30, v/v) as the mobile phase. The flow rate was set at 1 mL min^{-1} and the column temperature at 25 °C. The wavelength of the DAD was 230 nm and the data were collected and processed by 32 Karat Software. Calibration curves relating peak area to pyrethroid concentration were constructed by injecting 50 μL of pyrethoid dissolved in methanol at concentrations ranging from 1 to 100 mg L^{-1}. Table S1 and Fig. S1 in the Electronic Supplementary Information (ESI†) display the peak retention times for each pyrethroid compound under our HPLC experimental conditions.

Preparation of food samples

Almond milk

Organic almond milk (Pacific Foods of Oregon, Inc.; Tualatin, OR, USA) was purchased from a local supermarket. 1.0 g of almond milk was diluted with 10 mL deionized water, stirred until a homogeneous solution formed, and then filtered through a 0.45-μm nylon syringe filter to remove any large particulates. Almond milk samples were stored in the refrigerator at 4 °C.

Honey

Raw & unfiltered honey (Ambrosia Honey Co.; Longmont, CO) was purchased from a local supermarket. 1.0 g of honey was diluted with 10 mL deionized water, stirred until a homogeneous amber solution formed, and then filtered through a 0.45 μm membrane. Prepared raw honey samples were stored in the refrigerator at 4 °C.

Tap water

Water used for analysis was drawn directly from the tap in the laboratory (house water), filtered through a 0.45 μm syringe filter, and then stored in the refrigerator at 4 °C.

Assorted fruits

Three kinds of organically-grown ("pesticide-free") fruit (*i.e.*, apple, peach, and grapes) were purchased from a local supermarket. A 10 g sample of each fruit was cut into small pieces, and allowed to dry for 30 min in a 15 ml centrifuge tube. After drying, 15 mL of a methanol/deionized water (1 : 1, v/v) solution was added followed by sonication for 30 min. The fruit samples were then centrifuged for 30 min at 4000 rpm. The supernatant was collected, filtered through a 0.45 μm syringe membrane, and promptly stored in the refrigerator at 4 °C.

Results and discussion

DLLME optimization

Conventional DLLME was performed using deionized water spiked with pyrethroids at a concentration of 50 mg L^{-1}. Several factors were examined for their potential influence on conventional DLLME and MADLLME, including adsorption of the pyrethroids to the vessel walls, degradation of the pyrethroids under microwave energy (of particular relevance

is microwave power and total irradiation time), and the aqueous-phase pH.

Narrowing the pool of ILs

The ideal IL for DLLME and MADLLME must satisfy several requirements: low aqueous solubility, higher density than water, and high extraction efficiency for lipophilic organic compounds. Within our set of six contender ILs, based on preliminary experiments, $[N_{8888}][AOT]$, $[P_{14,666}][octSO_4]$, and $[emim][Tf_2N]$ were removed from further consideration due to their inadequate phase separation from the aqueous layer following centrifugation.

Effect of container wall material

The rapid extraction method, DLLME, may minimize adsorption derived errors, but cannot prevent them entirely. Since pyrethroids are hydrophobic in nature, their recoveries may be affected by their adsorption onto container surfaces, particularly glass walls.[8,46,47] Since the vials designed for our microwave reactor are indeed glass, we investigated the possible effect of glass *vs.* polypropylene (PP) as the container material under conventional DLLME. DLLME was performed using PP centrifuge tubes alongside the use of glass test tubes. These tests were run using pyrethroid concentrations of 50 mg L^{-1} for the three ILs still under consideration (*vide supra*). When the IL $[N_{8881}][Tf_2N]$ was used for DLLME, the recoveries for the pyrethroids were improved by 6%, 43%, and 10% for ALLE, CYPE, and PERM, respectively, when glass was used in place of PP, as shown in Fig. 3A. However, this trend did not hold for the two remaining ILs. For $[bmim][Tf_2N]$, the recoveries of ALLE and CYPE actually decreased by 40% and 58%, respectively, when glass containers were used, while the recovery of PERM increased by 17% (Fig. 3B). The behaviour changed yet again for $[P_{14,666}][Tf_2N]$, with recoveries improving only for ALLE (by 28%) when proceeding from PP to glass. Nonetheless, a dramatic concomitant decrease of 77% was observed for PERM in this case (Fig. 3C). Seeing that $[N_{8881}][Tf_2N]$ consistently yielded better recovery efficiencies across all three pyrethroids tested when using glass containers for extraction (as well as less container-to-container variability), $[N_{8881}][Tf_2N]$ was selected as the extraction phase for subsequent MADLLME studies.

Checking pyrethroid stability under microwave irradiation

Although synthetic pyrethroids were originally developed to maintain their insecticide activity while prolonging stability and environmental residence time,[12] it remained important to assess pyrethroid degradation under conditions of microwave irradiation required for this investigation. Pyrethroid degradation could be detected, for example, by the emergence of additional peaks in the HPLC chromatogram following the application of microwave energy. In the current study, we saw no additional peaks in the HPLC chromatogram nor drift in retention times for ALLE or PERM when MADLLME was performed. However, two additional peaks appeared for CYPE after the application of microwaves. The original peak for CYPE with a retention time of 24 min is hereafter denoted as peak 1 (Fig. 4 and 5), with the two emergent peaks (labeled as peaks 2 and 3) having retention times of 9.2 and 6.4 min,

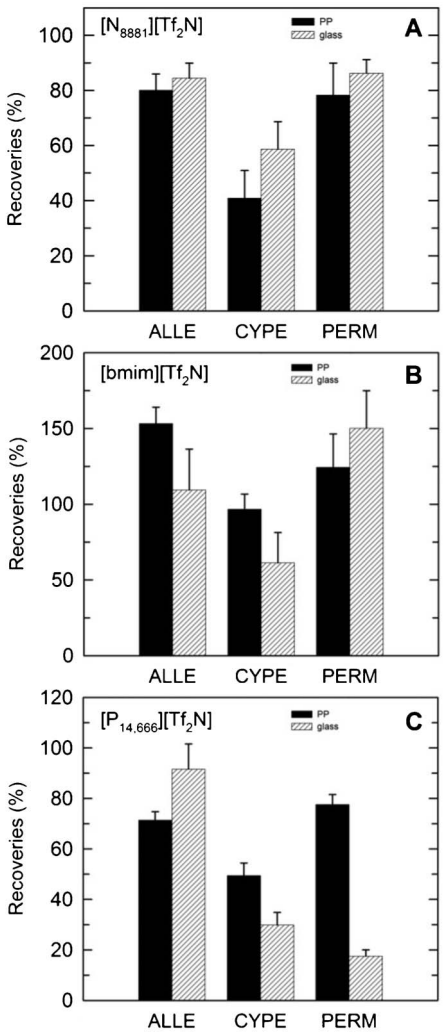

Fig. 3 Container material effects on DLLME extraction of ALLE, CYPE, and PERM using different candidate ILs (Panels A–C). In all experiments, the three pyrethroids were each present at 50 mg L^{-1} in deionized water.

respectively. Although their precise origin is not yet known, it is important to note that these additional peaks appeared often after DLLME as well, suggesting their formation may not

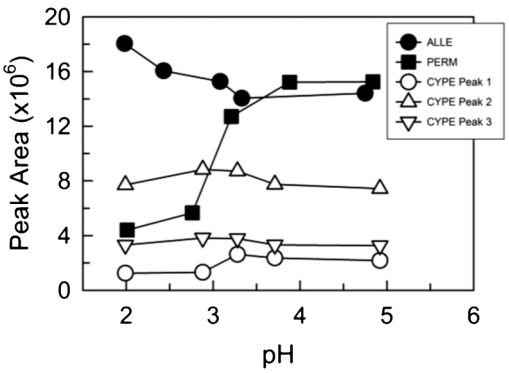

Fig. 4 pH-dependent efficiency of conventional DLLME extraction using $[N_{8881}][Tf_2N]$ for initial pyrethroid concentrations of 50 mg L^{-1}.

be entirely linked to the use of microwaves. In fact, CYPE is known to degrade into α-cyano-3-phenoxybenzyl alcohol and 3-phenoxybenzoic acid in soil with degradation as high as 80% after 14 days.[48] Instead of ruling out CYPE for further study at this point, we decided to track all three peaks arising from CYPE and its degradation products for our optimization studies in order to reflect less-than-ideal real world degradation scenarios.

Effect of aqueous-phase pH

The pH of the analyte solution may influence microextraction efficiencies by affecting the ionic state of the analytes.[16,29,30] In this study, the effect of pH on the DLMME extraction efficiency was explored by adjusting the pH of the aqueous pyrethroid solution by the addition of hydrochloric acid. As shown in Fig. 4, the peak area of ALLE decreases slightly (~20%) upon increasing the pH from 2 to 5, while the peak area of PERM nearly quadruples between pH 2 and 4. The peak areas for all three CYPE peaks remain relatively constant over much of this range. Considering the pH-dependent behaviour of all three analytes, all further experiments were conducted by adjusting the aqueous pH to 5.

Selecting optimal microwave conditions

In this study, the effects of microwave power and time on extraction efficiency were studied in order to optimize the microwave conditions for MADLLME using $[N_{8881}][Tf_2N]$. The recovered HPLC peak areas for ALLE, CYPE, or PERM for microwave powers between 100 and 300 W for 60 s of irradiation are provided in Fig. 5A. The largest peak area was observed at 200 W for all pyrethroid components. The exact reason for the slight increase observed at 200 W is unclear. From a thermal perspective, the temperature reached after 60 s of microwave treatment for each trial increased as applied power increased (Fig. S2A, ESI†). Therefore, extraction efficiency is not directly correlated with temperature, a somewhat surprising result. It is also worth noting that HPLC degradation peaks for CYPE were present at all microwave irradiation powers tested. Using a microwave power of 200 W, the influence of microwave irradiation time from 30–120 s was investigated next (Fig. 5B). From these studies, the highest peak areas were obtained for 60 s of irradiation. Again, there was not a direct relationship between temperature (*i.e.*, irradiation time; see Fig. S2B, ESI†) and extraction efficiency. From these power- and time-variable experiments, optimal microwave conditions for our MADLLME method of 200 W and 60 s were identified.

Comparison of conventional DLLME and MADLLME

The recovery of pyrethroids using conventional DLLME was compared to MADLLME using the optimal conditions identified above (200 W for 60 s). For these studies, pyrethroid concentrations of 50 mg L^{-1} were used at pH 5 with $[N_{8881}][Tf_2N]$ as the extraction solvent. The concentration for CYPE in these MADLLME studies was determined exclusively from the HPLC peak originating from CYPE alone (peak 1) and not the degradation product peaks. From Fig. 6, modest improvements in pyrethroid recovery can be seen for both ALLE and PERM by employing MADLLME. Although higher

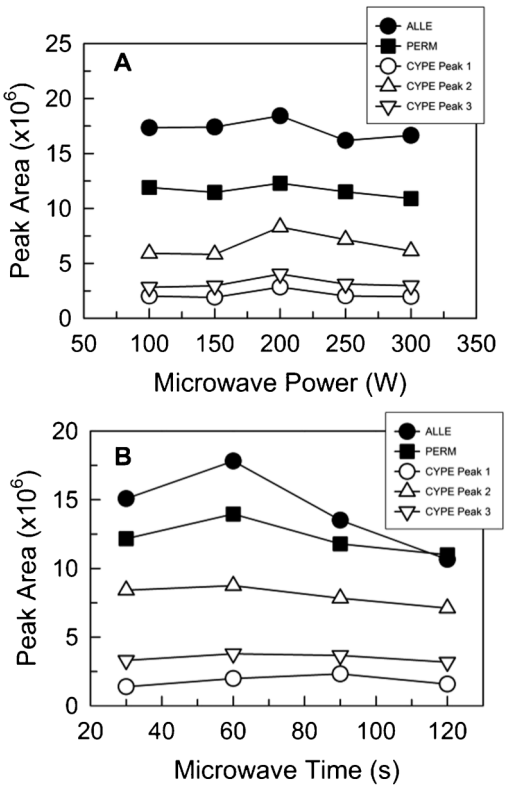

Fig. 5 Effect of (A) microwave power (irradiation time fixed at 60 s) and (B) microwave irradiation time (at a power of 200 W) on the recovered HPLC peak areas for pyrethroids after MADLLME using $[N_{8881}][Tf_2N]$ as extracting phase for starting pyrethroid concentrations of 50 mg L^{-1} each in deionized water.

recoveries were achieved for CYPE by using conventional DLLME, the lower recovery for MADLLME can be traced to degradation of the CYPE under microwave irradiation, as degradation peaks were not employed in the quantification of CYPE. In cases where degradation is not operative, however,

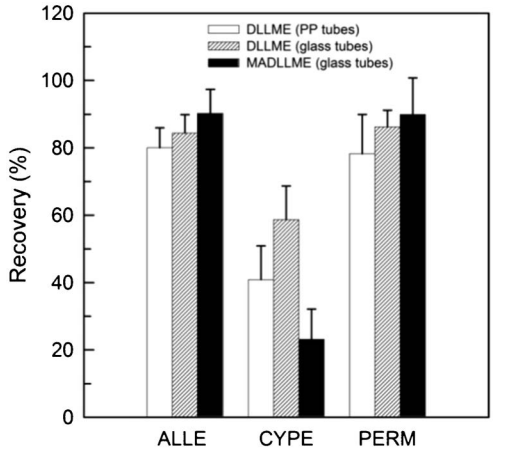

Fig. 6 Comparison of conventional DLLME and MADLLME using pyrethroid concentrations of 50 mg L^{-1} in deionized water with the IL $[N_{8881}][Tf_2N]$ as extracting solvent.

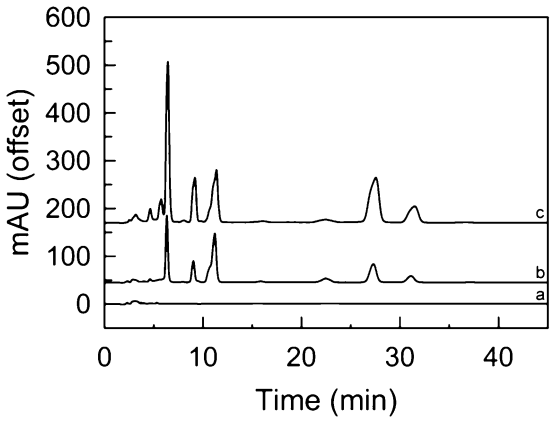

Fig. 7 Typical chromatograms after DLLME of (a) unadulterated almond milk, (b) DLLME of almond milk spiked with pyrethroids (ALLE, PERM, and CYPE), and (c) MADLLME of almond milk spiked with the same pyrethroids. The pyrethroid concentrations were 25 mg L^{-1} and the IL extraction phase was $[N_{8881}][Tf_2N]$. For MADLLME, the microwave power was 200 W for a total microwave-assisted extraction time of 60 s.

MADLLME presents a real advantage in that extraction can be performed efficiently, within a minute or less.

Analysis of real world samples

To evaluate our optimized MADLLME process (microwave conditions: 200 W; 60 s) using $[N_{8881}][Tf_2N]$ to extract real world samples, almond milk, raw honey, tap water, and a variety of fruit samples were analysed. Fig. 7 presents illustrative HPLC chromatograms following DLLME and MADLLME extractions of unadulterated almond milk alongside results for almond milk spiked with ALLE, PERM, and CYPE. The corresponding HPLC chromatograms for raw honey, tap water, and representative fruit samples are provided in Fig. S3–S7 of the ESI.†

As can be seen, for the unadulterated samples, no ALLE, CYPE, and PERM pyrethroids were detectable after DLLME, as no significant peaks were found at the retention times indicative of these pyrethroids. We next spiked the various food samples with 25 mg L^{-1} each of ALLE, CYPE, and PERM. To evaluate the precision and accuracy of the proposed MADLLME method, the spiked samples were analysed using both conventional DLMME and optimized MADLLME. For determination of recovered CYPE concentrations, only the peak with a retention time of 24 min corresponding to the native CYPE was used. Fig. 8 shows the recoveries obtained for both methods in all of the real world samples tested. The pyrethroid recoveries in all samples were greater using optimized MADLLME with the exception of CYPE in almond milk for which the recovery of both methods was statistically equivalent. The highest and most consistent recoveries were observed for PERM with recoveries approaching 100%. CYPE showed the lowest recoveries and degradation peaks for CYPE were observed in all HPLC traces, whether or not microwave assistance was used. The variability observed in recoveries across the different samples and the three pyrethroids studied may be due in part to the complexity of the samples involved. The food solutions may, for instance, contain proteins, lipids,

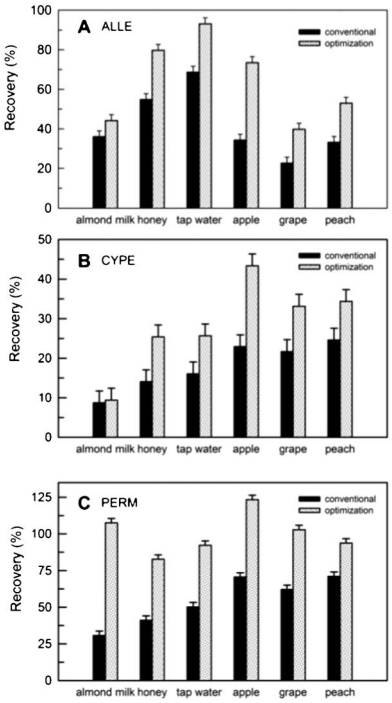

Fig. 8 Recoveries for pyrethroids from real world samples using the IL $[N_{8881}][Tf_2N]$ for DLLME *versus* MADLLME.

vitamins, or minerals that may impact the extraction (or chemistry) of the pyrethroid compounds. Looking at the HPLC trace for the non-spiked peach extract (Fig. S7, ESI†), one can clearly observe a prominent peak for an unidentified analyte extracted from the peach flesh by the $[N_{8881}][Tf_2N]$ that elutes near 9 min. Such matrix effects could surely play a role in extraction, in general, but they are in no way specific to or more pronounced in MADLLME. Indeed, overall, these studies illustrate some clear advantages offered by employing ILs in MADLLME for the extraction of pyrethroids from complex matrices.

Conclusions

In this study, a novel method of IL-based MADLLME followed by HPLC analysis was introduced for the recovery and detection of hydrophobic pyrethroid pesticides. This method is applicable to complicated real world matrices, as illustrated by the examples of tap water, almond milk, honey, and flesh from several representative fruits. By using the IL $[N_{8881}][Tf_2N]$ as the extraction solvent, excellent recoveries were achieved in our hands under the optimal microwave extraction conditions of 200 W applied for 60 s. Overall, this work highlights the advantages of conjoining the attractive features of ILs and microwave-based extraction as a powerful tool for hydrophobic targets. This approach is expected to be a general one and may find wide application in environmental monitoring as well as aspects of health and security, particularly in addressing issues in food safety.

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