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REVIEW

Review of Ionic Liquids in Microextraction Analysis of Pesticide Residues in Fruit and Vegetable Samples

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Abstract

The objective of this work is to provide a critical review of the use of ionic liquids in the microextraction of pesticide residues in fruits and vegetables. It includes an assessment of the advantages and limitations of current applications of ionic liquids in microextraction techniques. The review also aims to illustrate the impact of ionic liquids on the development of novel sorbent materials for analytical applications. The unique physicochemical properties of ionic liquids make them ideal sorbents in separation techniques. Their number of applications in analytical separation has increased considerably over the past 5 years. Therefore, this review focuses on the synthesis, purification, functionalization, and application of ionic liquids for pesticide residue analysis in fruits and vegetables with different sample preparation procedures, covering articles published in the literature since their first application in 2009.

Keywords Microextraction techniques · Ionic liquids · Pesticide residues · Fruits and vegetables

Introduction

Analytical measurement techniques have undergone tremendous growth in recent times [1], as evidenced by the development of various sample preparation methods using microextraction techniques [2–15]. Analytical measurement, which involves steps including sampling, sample preparation, separation, quantification, and data analysis, is performed in order to obtain useful information on the presence or absence of substances in environmental samples [16–19]. The sample preparation step is carried out to extract, isolate, concentrate, and enrich target analytes by removing interference. This step has been identified as the bottleneck in analytical measurement and has also been shown to consume the most analytical time and labor [1, 18, 20–22].

Sample preparation is a crucial step in any analytical procedure and must be carefully conducted in order to obtain accurate and reliable analytical results [23, 24], since most of the available analytical instruments cannot handle samples directly, due to the low concentration of the analytes and possible matrix interference [1, 21, 25]. An efficient sample preparation technique should ensure minimum sample loss by limiting the number of steps, and should have high sample throughput, low operational cost, and effective removal of matrix component interference, with high reproducibility and recovery [24, 26].

With the global movement toward environmental sustainability, sample preparation has evolved into the use of less toxic and more environmentally friendly sorbents, prompting the need to develop chemical sorbents which will generate less hazardous materials [27], in line with the use of microliter volumes of extraction sorbents in microextraction techniques [28]. To achieve the synthesis of environmentally friendly sorbent materials, all 12 principles of green chemistry must be met [29, 30], the most important of which is the use of renewable raw materials, where economically and technically possible, to prevent continued depletion of resources. This will help to prevent waste, while avoiding the costs associated with waste cleanup.

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Sol–gel-based sorbents [31–33], molecularly imprinted polymers [34, 35], and carbon nanotubes [36, 37] have been employed as environmentally friendly sorbent materials for the extraction of pesticide residues and other contaminants from complex matrices using microextraction techniques. This paper critically reviews the advantages and limitations of the use of IL-based sorbents in the extraction of pesticide residues in fruit and vegetable samples using microextraction techniques. Specific microextraction techniques have been reviewed in our previous papers [6, 38] and will not be discussed here.

Ionic Liquids (ILs)

ILs are eco-friendly, nonmolecular solvents, which consist of molten organic salts composed entirely of a combination of organic cations (nitrogen and phosphorus atom-containing compounds) and various organic or inorganic anions that are liquid at temperatures below 100 °C, while ILs that are liquid at or below room temperature are referred to as room-temperature ionic liquids (RTILs) [27, 39–48]. They contain hydrocarbon tails organized in three-dimensional networks of ions and can be divided into aprotic and protic ILs [49, 50]. As they have a structure which can be designed to produce specific desired properties, they are said to be tunable and are therefore considered "designer solvents" [51–54]. The first air- and water-stable ILs were reported in 1998 [55], and this opened a floodgate of research into ILs. The unique physicochemical properties of ILs, which include low melting point, electrical conductivity, extended liquid-state temperature range, wide electrical window, elevated thermal stability, high extractability, miscibility with other solvents, ability to undergo solvation interaction, air and moisture stability, negligible vapor pressure, low flammability, variable viscosity, and easily tunable physical and chemical properties [47, 48, 56–71], make them ideal for use as sorbents in separation techniques. ILs are green solvents because of their low flammability and low vapor pressure at room temperature (they do not release volatile organic compounds into the atmosphere [72, 73].

Most ILs have asymmetrically N-substituted nitrogen-containing cations such as *N*-alkylimidazolium, *N*-alkylpyrrolidinium, and *N*-alkylpyridinium; others are tetraalkylammonium, tetraalkylsulfonium, and tetraalkyphosphonium, and halogen-based organic or inorganic anions such as halides, tetrafluoroborate (BF_4), hexafluorophosphate (PF_6), alkylsulfates (RSO_4), bis(trifluoromethylsulfonyl)imides (Tf_2N), trifluromethanesulfonate (TfO), tosylate (TOS), and trifluoroethanoate [40, 41, 44, 46, 61, 64, 74–76] (Table 1). The low melting point of ILs with respect to other molten salts such as NaCl is due to the relative size of the two ions and their low symmetry [77]. Compared with the cations, the anions have a major impact on the thermal stability of ILs, and those with organic anions are found to be more thermally stable than those with inorganic anions [78]).

Table 1 Common cations and anions used in the synthesis of ILs

Cations	Anions
N-Alkylimidazolium	Halides
N-Alkylpyrrolidinium	Tetrafluoroborate
N-Alkylpyridinium	Hexafluorophosphate
Tetraalkylammonium	Alkylsulfates
Tetraalkylsulfonium	Bis(trifluoromethylsulfonyl)imides
Tetraalkyphosphonium	Trifluromethanesulfonate
	Tosylate
	Trifluoroethanoate

Synthesis and Purification of ILs

The synthesis of ILs sometimes involves the use of a large volume of toxic organic solvents. IL synthesis can be qualified as green synthesis only if both the IL products and their preparation comply with the 12 principles of green chemistry [29, 30]. The synthesis of ILs involves the formation of the desired cation, typically through simple alkylation followed by anion exchange through protonation to form the desired product, although in some cases only one of the two steps is required. ILs can be prepared through different routes, including anion exchange reactions (acid-base neutralization reactions and anion metathesis), quaternization (alkylation reactions), direct combination, and microwave or ultrasonic irradiation [30, 79–83]. ILs are also synthesized through a supercritical CO_2 route [84] and through the use of renewable starting materials [85, 86].

The required purity of the synthesized IL depends on its application. For use in the extraction of environmental contaminants, ultrapure ILs are required. Most impurities in ILs—which can be from the starting materials or reaction media, or can occur through contamination from the reactions undertaken—affect their physical properties. Impurities can be reduced or eliminated by purifying the starting materials, purifying the ILs at each stage of synthesis, and purifying the final IL products through drying, heating under vacuum, filtration, distillation, washing, and the use of ion-exchange resins [81].

Ionic Liquid Hybrids

IL hybrids involve the use of ILs as functionalization and dispersion agents for other materials such as sol–gel, carbon nanotubes (CNTs), Nafion membranes, graphenes, and

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deep eutectic solvents (DES) [75, 87–92], where the ILs act as solid support extractants. The functionalization results in controlled modification of the surface properties of both materials [42, 53, 93, 94], with the advantage of facile recycling and reuse [95]. The discovery by Fukushima et al. [96] that RTILs could be used to disperse CNTs resulted in further research on the preparation of CNT-IL hybrids and CNT-sol–gel hybrids using various methods. Essentially, ILs are coated on the outer surface of the materials via covalent or non-covalent methods [42] to form a protective layer around the nanoparticles, thereby enhancing their thermal and chemical stability. The functionalization of ILs with different materials depends on their inter- and/or intramolecular attraction, and can lead to the formation of different hybrid materials [93].

ILs help to enhance the physicochemical properties of nanoparticles and improve their stability through intermolecular interactions [93], leading to the formation of novel functional materials that share the properties of both the ILs and nanomaterials [97, 98]. The physicochemical properties of nanomaterials can also be modified and improved by functionalization with ILs, while the interaction of ILs and nanomaterials can lead to the formation of superior properties of stand-alone IL materials [97, 99]. The properties of ILs that make them important candidates for nanoparticle or microparticle preparation include melting and decomposition temperature, polarity, density, transport properties, surface and interfacial tension, and surface activity [53].

ILs have served as important materials in sol–gel applications as solvents, pore templates, drying-control chemical additives, and cracking and shrinking reduction agents [88, 100]. Due to the multiple interactions of ILs with various environmental analytes through dipole–dipole interaction, hydrogen-bond basicity, and dispersion forces, ILs coupled with other extraction sorbents have been used for the extraction of a wide range of analytes [90, 93]. Incorporation of paramagnetic components into ILs leads to the formation of magnetic ILs (MILs). The paramagnetic components are incorporated in either the anion or the cation, which are often composed of transition element or lanthanide metal ions [101].

The functionalization of ILs with other materials has helped to improve the extraction performance of several techniques for the analysis of pesticide residues. The use of an RTIL-mediated sol–gel monolith in analytical chemistry was first explored by Yan et al. for the preparation of a molecularly imprinted silica-based sol–gel-prepared monolith hybrid for the analysis of racemic mixtures of naproxen and zolmitriptan [102]. The use of IL-functionalized materials for microextraction of analytes from complex matrices appears promising, as they are stable and tunable, with better extraction efficiency and selectivity and improved preconcentration effects. The use of IL-mediated materials has yet to be fully explored in the microextraction of pesticide residues in food samples.

Application of ILs in Pesticide Residues Analysis

The choice of solvents for extraction depends on the combination of physical properties and solvation characteristics [46]. Knowledge of the physical properties of an IL and the phase behavior with gases, liquids, and solids (including inorganic salts) is important for its evaluation and selection for different applications as well as process design [103]. ILs can be easily coupled to microextraction techniques [104] and therefore have been used by several researchers for microextraction analysis of pesticide residues in water and other environmental samples [90, 105–144]. The application of ILs for pesticide residue analysis in fruit and vegetable samples is the focus of this review.

Pioneering research on the use of ILs as dispersive liquid-liquid microextraction solvent (IL-DLLME) was carried out by Ravelo-Perez et al. [145] for the analysis of eight pesticide residues (thiophanate-methyl, carbofuran, carbaryl, tebuconazole, iprodione, oxyfluorfen, hexythiazox, and fenazaquin), belonging to different chemical families, in banana samples using high-performance liquid chromatography (HPLC) with diode array detection (DAD). The extraction parameters were optimized using an experimental design. The banana sample was prepared by spiking 1 g of previously homogenized banana (1 kg) with a known volume of pesticide standard mixture in a centrifuge tube and mixing. The mixture was left at room temperature for 30 min, followed by the addition of 5 mL acetonitrile, with vigorous shaking by hand for 1 min. A buffer-salt mixture was then added to induce phase separation and pesticide partitioning. The tube was shaken on a vortex mixer for 1 min and sonicated for 5 min, then centrifuged for 10 min at 4000 rpm. The supernatant was filtered and the residue further redissolved in 10 mL Milli-Q water, after which the mixture obtained was placed in a 15-mL glass centrifuge tube, followed by the addition of 88 mg of extractant solvent (1-hexyl-3-methylimidazolium hexafluorophosphate [$C_6MIM(PF_6)$]) and 714 µL of dispersive solvent (methanol). The mixture was then centrifuged at 4000 rpm for 20 min, after which the upper aqueous phase was removed with a syringe, and the dispersed sedimented IL particles (20 µL) were dissolved in acetonitrile to produce a final volume of 125 µL. A 20-µL aliquot was then injected into the HPLC for analysis. The matrix effect was determined by comparing the calibration curves of the matrix-matched banana extract with the standard solution. The average recovery of spiked banana ranged from 53 to 97%, with relative standard deviation (RSD) ranging from 2.7 to 8.7%. The linearity

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ranged from 0.010 to 6.83 μg kg^{-1} [correlation coefficient (r^2) greater than 0.99], and the limit of detection (LOD) ranged from 0.32 to 4.66 μg kg^{-1}, which was below the harmonized maximum residue limit (MRL) established by the European Union (EU). The Student *t* test was used to assess the accuracy of the method by comparing the recovery of the investigated pesticide, and no significant difference was observed between the real and experimental values, with accuracy ranging from 92 to 106%.

A room-temperature IL-based DLLME method was developed for the determination of eight multi-class pesticides (thiophanate-methyl, carbofuran, carbaryl, tebuconazole, iprodione, oxyfluorfen, hexythiazox, and fenazaquin) in table grape and plum samples [146]. The sample preparation and the DLLME procedures followed the same steps as previously reported [145], which were found to be satisfactory when applied to table grape and plum samples. The extracted analytes were separated and detected by HPLC-DAD. The calibration curves for standard and fortified table grape and plum (matrix-matched calibration) samples were compared in order to determine matrix effects, and matrix effects were found in the two samples. Therefore, a calibration curve was constructed using a matrix-matched standard in order to take the matrix effects into consideration. The average recovery ranged from 72 to 100% (RSD = 1.4–9.1) and 64–105% (RSD = 1.9–8.6) in the table grape and plum samples, respectively, while the linearity in both samples ranged from 0.010 to 6.83 μg kg^{-1}, with a correlation coefficient greater than 0.99. The LOD ranged from 0.651 to 5.44 μg kg^{-1} and 0.902 to 6.33 μg kg^{-1} in table grape and plum samples, respectively. The Student *t* test was used to assess the accuracy of the method by comparing the recovery of the investigated pesticide, and there was no significant difference between the real and experimental values, with accuracy ranging from 88 to 106%, clearly demonstrating the feasibility of the proposed method for the analysis of the selected pesticides in both samples. Analysis of real samples (six table grape and six plum samples) showed the presence of carbaryl and iprodione in the two samples, but at concentrations below the EU MRLs.

A simple and rapid method was developed for the determination of seven carbamate pesticides (methomyl propoxur, carbofuran, carbaryl, isoprocarb, methiocarb, and promecarb) in five fruit samples using IL as extraction solvent prior to analysis with HPLC. The fruit samples were prepared by cutting the edible part and blending with a commercial food mixer. After blending, a 25-g aliquot of each fruit sample was measured into a Teflon centrifuge tube, followed by the addition of 25 mL of acetonitrile, with shaking at 200 rpm for 1 h. The extract was then evaporated using a rotary evaporator at 45 °C until the volume was reduced to 2–3 mL. The residue was dissolved with deionized water to a final volume of 25 mL and filtered. A 3-mL aliquot of the filtrate was measured into a test tube, followed by the addition at room temperature of 100 μL 1-butyl-3-methylimidazolium hexafluorophosphate [C_4MIM(PF_6)], and the mixture was shaken for 7 min. The target analytes were extracted as a fine droplet, which was withdrawn with a microsyringe and then diluted with 50 μL of acetonitrile and injected into the HPLC system. The analytical performance determined using optimized extraction conditions gave linearity of 0.02–8 μg mL^{-1} (RSD > 0.99), LOD ranging from 2 to 4 μg mL^{-1}, and average recovery of 81–118% (RSD = 4–10.2%). Analysis of real samples showed the presence of the investigated pesticides in the fruit samples, although at concentrations lower than the MRL set by the Thai Agricultural Commodity and Food Standard (TACFS, 9002-2008). The method was compared with the cloud-point extraction technique [147] in terms of linear range, LOD, and RSD, and was found to yield better analytical performance for all the target pesticides, but could not identify methomyl because its peak could not be separated from the IL peak [148].

An IL-based vortex-assisted DLLME method coupled to HPLC-DAD for the analysis of six organophosphorus pesticide (OPP) residues in apple and pear was developed by Zhang et al. [149]. The apple and pear samples were washed, homogenized, and centrifuged to obtain the fruit juice, and 5-g aliquots of the fruit juices were separately mixed with 5 mL of water and transferred into 15-mL centrifuge tubes. The mixtures were left for 1 min, after which 1 mL of methanol and 0.0623 g of 1-octyl-3-methylimidazolium hexafluorophosphate [C_8MIM(PF_6)] were added to the fruit juice samples, leading to the formation of a cloudy solution. The solution was shaken vigorously on a vortex agitator at 2000 rpm for 1 min and then centrifuged for 5 min at 4000 rpm. The upper aqueous phase was carefully discarded, and the sedimented IL phase was withdrawn using a 50-mL microsyringe and subjected to HPLC analysis. The IL used in this study was selected based on its good extractability of the target analytes, immiscibility with water, and good chromatographic behavior. Factors affecting DLLME (e.g., dispersion solvent, vortex time, salt addition, and pH) were carefully optimized using a one-factor-at-a-time (OFAT) design, which has been discouraged [150, 151]. The figures of merit for the proposed method gave a linear range of 2–100 μg kg^{-1} ($r^2 > 0.99$), average recovery of 69.8–109.1% (RSD = 2.3–5.7%), and LOD ranging from 0.061 to 0.73 μg kg^{-1}. The method was used to determine the presence of the target analytes in apple and pear, and the analysis revealed that the analytes were present in the samples but at levels below the LOD for the proposed method. These results showed that the IL-based vortex-assisted DLLME technique is simple, precise, and reliable.

A new IL (1,3-dibutylimidazolium hexafluorophosphate [BBIM(PF_6)])-based DLLME method was developed for the determination of OPP (fenitrothion, parathion, fenthion, and

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phoxim) residues in water and fruit samples. Pear samples were squeezed using a juice extractor, and the pear juice was filtered through a 0.45-μm membrane filter and then diluted at a ratio of 1:3 with doubly distilled water. About 5 mL of the diluted sample was placed in a 10-mL conical-bottom glass centrifuge tube, followed by the addition of 0.6 mL of methanol as dispersive solvent and 50 μL of [BBIM][PF_6] (0.0620 g) as extractant solvent. The analytes in the aqueous phase were extracted into droplets of the IL [BBIM(PF_6)], and the cloudy solution was further separated by centrifugation at 4000 rpm for 5 min, after which the enriched analytes in the IL phase were withdrawn by microsyringe and determined by HPLC. The performance of the proposed method was compared with other IL-based DLLME techniques, and it was observed that the use of [BBIM(PF_6)] gave better recovery and enrichment factor (EF) than [HMIM(PF_6)]. Factors affecting extraction efficiency were evaluated and optimized using an OFAT design. The performance of the proposed method determined using the optimized parameters showed linearity ranging from 5 to 1000 μg L^{-1}, with a correlation coefficient greater than 0.999. The average recovery was in the range of 78.6–86.9, with RSD of 1.1–2.7, and the LOD varied from 0.01 to 0.05 μg L^{-1}, which was lower than the EU MRL of 0.1 μg L^{-1}. Analysis of real pear samples showed the absence of the investigated pesticides in the sample, and the recovery values confirmed the validity of the proposed method [152].

A solid-phase microextraction (SPME) fiber chemically linked with IL was synthesized for simultaneous sampling and determination of seven pyrethroid pesticides (fenpropathrin, permethrin, cypermethrin, flucythrinate, fenvalerate, deltamethrin) in vegetable samples. The IL-linked fiber was prepared by removing an approximately 1-cm segment of polyimide using a flame torch, followed by dipping in 1 mol L^{-1} of NaOH. The fiber was then washed with water and 0.1 mol L^{-1} of HCl, followed by washing with methanol and then water. The fiber was air-dried at room temperature and was vertically inserted into a mixture of γ-methacryloxypropyltrimethoxysilane (γ-MAPS) and methanol (1:1, v/v) at 40 °C for 16 h. A 50-mg aliquot of IL (1-vinyl-3-hexadecylimidazolium hexafluorophosphate [ViHDIM(PF_6)]), was measured into a 5-mL vial containing 2 mL methanol and was dissolved ultrasonically. After dissolution, 2,2-azobisisobutyronitrile (AIBN), used as polymerization initiator, was added and the fiber was dipped into solution in the sample vial with a polytetrafluoroethylene (PTFE) capsule. The vial was placed in a water bath at 60 °C for 24 h. Finally, the IL-linked fiber was dried at room temperature and inserted into a laboratory-made SPME device. The IL-linked fiber was conditioned at 260 °C for 30 min in the gas chromatograph (GC) injection port prior to its use in the extraction, in order to eliminate residual solvents. A 10-g portion of fresh vegetable samples was cut into pieces and placed in 50-mL centrifuge tubes, followed by spiking with the pesticide standard at three different concentrations (1, 5, and 10 μg kg^{-1}) and drying for 30 min. After drying, 15 mL of a mixture of *n*-hexane/acetone (1:1 v/v) was added and mixed ultrasonically for 30 min and then centrifuged for 30 min at 4000 rpm. The supernatant layer was transferred into a flask and uploaded onto a Florisil SPE cartridge and eluted by 20 mL *n*-hexane. The eluate was collected and evaporated to dryness in a vacuum evaporator at 45 °C, and 10 mL of *n*-hexane was then added to dissolve the residue, which was exposed to an SPME IL-linked fiber coupled to a gas chromatography electron capture detector (GC-ECD). The efficiency of the IL-linked fiber was investigated under the optimized SPME conditions, and the analytical performance was evaluated. The linearity ranged from 0.10 to 100 μg L^{-1} ($r^2 \geq 0.9904$), with LOD of 0.21–0.49 μg kg^{-1}, and relative recovery ranging from 67.40 to 93.52% (RSD = 3.61–13.76). The synthesized fiber was compared with a polydimethylsiloxane (PDMS)-coated fiber, and was found to have a peak area about 20% higher than the PDMS, which was attributed to the phenyl group present in the IL-linked SPME coating, leading to π–π interaction with the pyrethroids. The target analytes were not detected in the vegetable samples [153].

An IL-supported magnetic dispersive solid-phase microextraction (IL-DLLME) method was developed for the determination of acaricides in fruit juice samples. The IL-DLLME extraction procedure involved the injection of 50-μL aliquots of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C_6MIM(NTf_2)] into 10 mL of water in a conical-bottom test tube, and the mixture was then sonicated for 2 min to accelerate the formation of droplets of the extractant solvents and to enhance the transfer of analytes. This was followed by the addition of 40 mg of S-BaFe magnetic nanoparticles (MNPs), and the mixture was then shaken vigorously with a vortex agitator for 90 s at 2800 rpm. The [C_6MIM(NTf_2)] was extracted by the MNP after a high-speed stirring procedure. The nanoparticles were concentrated by holding a magnet around the test tube, and the MNPs were sedimented and the sample solution carefully removed using a drip tube and microsyringe. Acetonitrile (50 μL) was then injected into the test tube to desorb IL from the MNPs by sonication for 2 min. Finally, the nanoparticles were isolated from the solution with a magnet, and 10 μL of the organic solvent was collected and injected into an HPLC system for analysis. Factors affecting the extraction (volume of IL, dosage of MNPs, sonication time, vortex time, salt addition, and desorption time) were optimized. The performance of the method was evaluated under the optimized conditions, and the analytes were found to exhibit good linearity, ranging from 0.5 to 500 ng mL^{-1} ($r^2 > 0.997$), with accuracy of 88–99.3% (RSD = 1.2–5.3%) and LOD of 0.05–53 ng mL^{-1}. The method was compared

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with other reported methods and was found to be superior because of the use of ILs without the addition of any toxic solvents, and recovery and LOD were found to be comparable to those of other SPME techniques [154].

An IL-based, totally organic solvent-free emulsification microextraction (TEME) method was developed for the analysis of three acaricides (chlorfenapyr, spirodiclofen, and fenpyroximate) in fruit juice (grape, peach, and orange) samples. The efficiency of seven different ILs was determined by a comprehensive comparison of their physical properties. The fruit juice samples were prepared by measuring a 30-mL aliquot into a centrifuge tube, followed by centrifugation at 4000 rpm for 10 min. The supernatant was then filtered through a 0.22-µm membrane, and 10 mL of homogeneous spiked sample solution was placed in a 15-mL screw-cap conical-bottom PTFE tube. This was followed by rapid injection of 53 µL of [C_6MIM(NTf_2)] and subjection to ultrasonic treatment for 2 min. The conical tube was then heated in a temperature-controlled water bath at 60 °C for 2 min, after which the tube was cooled with ice water and simultaneously subjected to additional ultrasonic treatment. The fine droplet was then centrifuged at 4000 rpm for 10 min and the IL was carefully withdrawn with a syringe. An aliquot of 10 mL of the IL phase was injected into an HPLC system for analysis. The performance of the method under optimized conditions gave linearity ranging from 0.1 to 600 µg L^{-1}, LOD of 21.1 –61.4 ng L^{-1}, and relative recovery of 91.9–103.7% (RSD = 2.0–4.8%). The proposed method was compared with other microextraction methods and was found to have comparable or better analytical performance, and was then applied for the analysis of real fruit juice samples [155].

A method for the sensitive determination of pyrethroid residues in tomato samples was developed using IL-based DLLME. The technique involved the use of a hydrophobic IL (1-butyl-3-methylimidazolium hexafluorophosphate [C_5MIM(PF_6)] as extractant solvent and acetonitrile as the dispersive solvent. The tomato samples were prepared by homogenizing previously cleaned samples in a disintegrator, and the tomato juice was filtered several times through filter paper. A 10-mL aliquot of the filtrate was placed in a screw-cap conical glass tube, and the pH of the sample was adjusted to 2 by the addition of acetic acid. The solution was then injected with 0.5 mL of methanol containing 100 µL of [C_5MIM(PF_6)], leading to the formation of a cloudy solution. The tube was immersed in an ultrasonic cleaner and then centrifuged for 10 min at 4000 rpm. The upper aqueous phase was removed with a syringe and the lower sedimented phase was diluted with 100 µL of methanol and filtered through a 0.45-µm filter membrane, after which 10 µL of the filtrate was injected into an HPLC for analysis. All factors affecting the extraction efficiency were optimized and the optimal conditions were used to evaluate the performance of the method. The linearity was found to range from 0.05 to 1.5 µg kg^{-1} ($r^2 \geq 0.997$), with relative recovery of 83.9–97.7% (RSD = 1.7–4.5), while the LOD ranged from 8.1 to 14.3 µg kg^{-1}, and the EF from 43 to 48. The proposed method was compared with other methods including liquid-liquid microextraction, matrix-assisted extraction, solid-phase extraction (SPE), and SPME, and was found to be more advantageous in terms of the use of a nontoxic micro-volume of IL as an extractant solvent and high sample throughput [156].

An IL-assisted liquid-phase microextraction technique based on the solidification of floating organic droplets (ILSFOD-LLME) was developed for the determination of seven benzoylurea insecticides (diflubenzuron, triflumuron, hexaflumuron, lufenuron, chlorfluazuron, and diafenthiuron) in fruit juices. An aliquot of the fresh fruit juices (50 mL) was accurately measured into a centrifuge tube and centrifuged for 10 min at 4000 rpm, and the supernatant was subsequently filtered through a 0.22-µm membrane. After filtration, an 8-mL aliquot of the filtrate, spiked with the target analytes at different concentrations, was introduced into a 10-mL glass vessel containing a 15-mm-long magnetic stirrer, and the glass vessel, sealed with black screw cap (to maintain the temperature at 45 °C), was affixed to the magnetic stirrer. A microsyringe was used to introduce 50 µL of 1-dodecanol (extractant solvent) and 10 µL of IL [$P_{14,6,6,6}$(PF_6)] (dispersive solvent). The final collection work was assisted by a bell-shaped collection device (BSCD). At 25 min, the vessel cap was replaced with another screw cap which was connected to the BSCD. The stirring was then stopped at 30 min, and the organic layer containing the analytes was pressed into the BSCD automatically. The vessel with the BSCD was dipped in an ice bath for 5 min, leading to the solidification of the mixed extractant. The extractant in the BSCD was transferred into a conical vial by a trimmed straw and then diluted with 40 µL of ethanol and analyzed with HPLC. The factors affecting the ILSFOD-LLME efficiency were investigated and optimized using OFAT and experimental design (orthogonal screening), and they were found to be in agreement. The optimized value of each parameter was used to estimate the figures of merit for the proposed method. The linearity ranged from 0.5 to 500 ng mL^{-1}, with a correlation coefficient greater than 0.996. The relative recovery ranged from 75.6 to 113.9% (RSD = 0.1–7.3), and the LOD from 0.03 to 0.28 ng mL^{-1}, while the EF ranged from 160 to 246. The proposed method was compared with other extraction methods in terms of solvent used, extraction time, linearity range, and LOD, and was found to be more advantageous in the use of a smaller volume of solvent, wider linear range, and lower LOD [157].

An IL-calixarene SPME fiber was prepared and evaluated for its efficiency in the determination of four triazine (atrazine, simazine, ametryn, and cyanazine) herbicides in fruit and vegetable samples. A sol–gel method was adopted

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in order to strengthen the connection between the coating and the fiber. The sol–gel solution was prepared by dissolving 90 mg of hydroxyl-terminated silicone oil (HO-TSO), 100 µL of tetraethoxysilane (TEOS), and 10 mg of polymethylhydrosiloxane (PMHS) in 100 µL of acetone, followed by the addition of a solution of 1 mg of 4-tert-butylcalix[4] arene dissolved in 9 mg of IL (1-vinyl-3-butylimidazolium ditrifluoro methyl sulfimide). The mixture was thoroughly mixed by ultrasonic agitation for 5 min, after which 80 µL of trifluoroacetic acid (TFA) was added, with continued mixing by ultrasonic agitation for another 5 min, followed by agitation at 5000 rpm for 5 min. The clear supernatant of the sol solution was then transferred to another clear vial for fiber coating. The coating was obtained by vertically dipping the fiber into the sol solution several times and then placing the coated fiber into the desiccator for 12 h at room temperature, followed by oven drying for 1 h at 150 °C. The fruit and vegetable samples were separately crushed with a fruit pulper to produce juice and scum. A 2-g portion of the crushed samples was transferred into a 50-mL Teflon centrifuge tube, followed by the addition of 20 mL of acetone, and the mixture was extracted in a water bath oscillator for 10 min and then centrifuged for 5 min. The supernatant obtained was concentrated to a small volume using a rotary evaporator and then dissolved in 1 mL of methanol, reconstituted to 10 mL with NaH_2PO_4 buffer solution, and centrifuged again. The obtained supernatant was collected and filtered through a 0.45-µm filter, and 1.2 mL of the filtrate was subjected to an SPME procedure (direct immersion, extraction temperature and time of 60 °C and 20 min, respectively). The analytical figures of merit obtained using the SPME-optimized parameter yielded linearity of 25–5000 µg kg^{-1}, ($r^2 \geq 0.996$), with limit of quantification (LOQ) and LOD of 11–43.3 µg kg^{-1} and 3.3–13.0 µg kg^{-1}, respectively, and average recovery of 71.5–96.9% (RSD = 4.4–9.9). Although the proposed method was not compared with similar SPME methods using commercial fiber coatings, it was found to be effective for the determination of triazines in fruit and vegetable samples [158].

An IL-based manual-shaking-enhanced ultrasound-assisted emulsification microextraction (IL-MSUSAEME) method was developed for the determination of three fungicide residues (pyrimethanil, fludioxonil, and cyprodinil) in apple and grape juice samples. Apple and grape juices were filtered through a 0.22-µm cellulose filter, and a 5-mL aliquot containing 1% NaCl (w/v) was placed in a 15-mL screw-cap conical-bottom glass tube and the pH adjusted to 5. Then, 30 µL of 1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [$C_2MIM(NTf_{2]})$] and 50 µmol L^{-1} of surfactant (NP-10) were added as extraction solvent and emulsifier, respectively. The tube was then shaken vigorously by hand for 15 s at a uniform speed (30 times), and immediately subjected to ultrasonication for 1 min to form a cloudy emulsion. Next, the mixture was centrifuged at 3800 rpm for 5 min, and an IL sediment formed at the bottom of the tube. The liquid sample was removed with a syringe and the IL sediment was diluted with 50 µL of methanol. The IL sediment was then transferred into a 200-µL glass insert-pipe inserted into a 1-mL autosampler vial, and 20 µL was injected into an HPLC for analysis. The effects of extraction solvent (comparing three different ILs), extraction solvent volume, types and concentration of surfactant, manual shaking, ultrasonic extraction time, addition of NaCl, and pH were determined and optimized. The proposed method was validated using the optimized parameters, and gave good linearity, ranging from 5 to 400 µg L^{-1} ($r^2 \geq 0.9986$), average recovery of 61.4–86% (RSD = 1.8–9.7%), and LOD of 0.4–1.6 µg L^{-1}. The method was used to analyze real vegetable samples, and the target analytes were not detected, showing that no analyte was present or was present at concentrations below the LOD of the method. The IL-MSUSAEME method was compared with matrix solid-phase dispersion, SPME, DLLME, ultrasound-assisted dispersive liquid-liquid microextraction (UA-DLLME), ultrasound-assisted-IL/IL-DLLME (UA-IL/IL-DLLME), temperature-controlled IL-DLLME (TC-IL-DLLME), and IL-UAEME in terms of solvent use and extraction time, and was found to have higher sample throughput [159].

A novel polythiophene-IL-modified clay composite SPME fiber was prepared and applied for the analysis of multi-class endocrine disruptor pesticide residues (chlorpyrifos, penconazole, procymidone, bromopropylate, and lambda-cyhalothrin). Montmorillonite (Mmt) clay intercalated with IL was co-deposited with polythiophene (PTh) polymer and was coated electrochemically on an SPME fiber. This was prepared by direct electrodeposition of PTh-IL-Mmt composite film on the surface of a stainless steel wire electrode from a 0.1 M $NaClO_4$ solution containing 0.3 M thiophene and 0.88 mg IL-modified clay in acetonitrile solution. The stainless steel wire was then immersed in acetone in a test tube, placed in an ultrasonic bath for 15 min, and subsequently washed with distilled water. The coated stainless steel wire was then washed with methanol, acetone, and water, dried under nitrogen gas flow, and heated in an oven for 20 min at 100 °C. A 5-mL aliquot of the sample was placed in a 20-mL glass vial with a PTFE-silicon septum, followed by the addition of 0.5 g of NaCl. The vial was sealed and placed on a laboratory-made headspace analysis water bath vessel at a temperature of 80 °C (extraction temperature). The coated fiber was inserted into the headspace of the sample vial, and the SPME procedure was carried out for 10 min at a stirring rate of 1000 rpm. The significance of eight factors affecting the SPME technique was estimated using a Plackett–Burman design (PBD), and the significant factors were optimized using a Box–Behnken design (BBD), while the insignificant factors were kept constant.

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Under the optimized conditions, the method was used for the analysis of two kinds of grapes and for validation of the method. The linearity ranged from 0.01 to 30 μg L^{-1} ($r^2 \geq$ 0.987), with recovery of 88.7–101.7%, RSD of 7.1–17.8%, and LOD of 0.002–0.667 μg L^{-1}. Some of the target pesticides were found in juice samples but were below the MRLs established by the Turkish Food Codex Regulation residue level and thus found to pose no health risks [160].

An environmentally friendly method was developed for the analysis of six triazole fungicides (triazolone, triadimenol, epoxiconazole, flusilazole, tebuconazole, and diniconazole) in pear, apple, and grape samples using the quick, easy, cheap, effective, rugged, and safe (QuEChERS) technique combined with IL-based DLLME prior to HPLC analysis. The QuEChERS-DLLME involved weighing about 5 g of chopped and homogenized samples into a 50-mL fluorinated ethylene polypropylene centrifuge tube, followed by the addition of 5 mL acetonitrile. The mixture was shaken vigorously by hand for 3 min, after which the tube was kept in a refrigerator for 15 min at −20 °C. Then, 2 g of anhydrous $MgSO_4$ and 0.5 g of NaCl were added and the tube was shaken vigorously again by hand for 1 min and centrifuged for 5 min at 10,000 rpm. The upper layer was decanted into another centrifuge tube containing 50 mg primary and secondary amine (PSA) and vortexed for 1 min, then centrifuged for 5 min at 4000 rpm. About 430 μL of the upper layer was transferred into a centrifuge tube, followed by the addition of 63.7 μL of IL [C_6MIM(PF_6)] and vortexing for 1 min. The mixture was rapidly injected into 5 g of deionized water in a centrifuge tube, spun vigorously for 1.7 min, and centrifuged for 5 min at 4000 rpm. The sedimented phase was removed and mixed with methanol (1:1, v/v) in a trace incubator. The factors affecting the QuEChERS-DLLME were optimized using response surface methodology, and the method was validated under the optimal conditions. The linearity of the method ranged from 10 to 10,000 μg L^{-1}, with a correlation coefficient greater than 0.997, recovery of 63.8–119.1%, RSD of 1.1–2.6%, and LOD of 3.4–26.8 μg L^{-1}. The method was compared with different DLLME techniques for the determination of triazole fungicides in terms of the number of analytes, LOD, and recovery, and the proposed method was found to be able to extract a higher number of triazole fungicides but with comparable LOD and recovery [161].

A silica nanoparticle-polyethylene glycol-IL SPME fiber was fabricated using sol–gel technology for the determination of five multi-class pesticide residues (terbuthylazine, desethylatrazine, phorate, parathion, and phosmet) in tomato samples. The SPME fiber was prepared using a porous Cu coated with polyethylene glycol (PEG) and 1-butyl-4-methylpyridinium tetrafluoroborate [C_4MPy(BF_4)]. The efficiency of different SPME-coated fibers, including polydimethylsiloxane (PDMS), PDMS-ILs, PDMS-IL-silica nanoparticles (PDMS-IL-sNP), polyacrylate (PA), PEG-IL, PEG, and PEG-IL-sNP, was compared, and PEG-IL-sNP was found to be most effective. The SPME fibers were conditioned in the GC inlet at 260 °C for 60 min. The tomato sample was chopped and homogenized, and 50 mL of the homogenized sample was then mixed with a known amount of standard solution in a 100-mL flask and brought up to the mark with distilled water. The mixture was placed in an ultrasonic bath for 30 min, after which 10 mL of the top solution was transferred into a Falcon tube, blended to smoothness, and centrifuged for 10 min at 8000 rpm. An aliquot of the supernatant was then transferred into a glass vial, and the fabricated fiber was inserted for 45 min at 30 °C. All factors affecting SPME performance were optimized, and the optimal conditions were used for method validation and for the analysis of real tomato samples. The method gave linearity between 60 and 1000 μg kg^{-1} ($r^2 \geq 0.987$), the LOD ranged from 20 to 90 μg kg^{-1}, and the RSD ranged from 1.2 to 4.6%. Although it was not compared with other published methods, the proposed method was found to be reliable and reproducible [162].

You et al. [163] developed a novel and simple method for the analysis of five fungicides (pyrimethanil, fludioxonil, azoxystrobin, cyprodinil, and pyraclostrobin) in apple, grape, and pear juice samples, using an IL-based air-assisted liquid-liquid microextraction (IL-AA-LLME) technique. The AA-LLME procedure involved measuring of 5 mL of aqueous sample into a 15-mL screw-cap glass test tube, followed by the addition of 1% (w/v) of NaCl and 40 μL of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [C_6MIM(NTf_6)]. The mixture was rapidly drawn from the tube into a 10-mL glass syringe and then reinjected into the tube using a syringe needle. The action was repeated until the solution became turbid, and the IL was dispersed into the aqueous sample as a fine droplet. The test tube was centrifuged for 3 min at 2535 rpm, and the dispersed fine droplet settled at the bottom of the tube. The upper aqueous layer was removed with a pipette, and the IL phase was then dissolved in 50 μL of methanol, and 20 μL was injected into an HPLC system for analysis. The effects of several parameters related to extraction efficiency were investigated using an OFAT approach. Under the optimal conditions, the analytical performance yielded good linearity in the range of 5–400 μg L^{-1} ($r^2 \geq 0.9987$), relative recovery of 74.9–115.4% (RSD = 1.2–10.1%), and LOD ranging from 0.4 to 1.8 μg L^{-1}. The proposed method was found to show several advantages over other microextraction techniques for the determination of pesticide residues in juice samples, in terms of extraction time or use of dispersive solvent.

An ionogel-based IL-coated fiber was developed for SPME of OPP residues in wine and fruit juice samples. An 80-mL aliquot of the juice sample was placed in a 100-mL conical glass flask and spiked with the pesticide standard

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solution to a concentration of 5 μg L^{-1} for each pesticide. This was followed by the addition of 40 g of NaCl and insertion of a 2-cm-long PTFE stir bar, and the flask was sealed with a cap. The conical flask was affixed to a magnetic stirrer and mixed at 550 rpm. After homogeneous mixing, a [C_{16}MIM(NTf_2)]-coated fiber was introduced into the flask and exposed to the headspace above the sample matrix for 50 min at 60 °C, after which the fiber was desorbed into a GC port for analysis. The factors affecting SPME were investigated and optimized, and the optimized conditions were used for method validation. The proposed method showed good linearity, ranging from 0.01 to 10 ng L^{-1}, with a correlation coefficient greater than 0.999 for most of the investigated pesticides. The relative recovery ranged from 56 to 109% (RSD = 2–21%) and the LOD from 0.57 to 4.13 ng L^{-1}. The uncertainty of the method was determined, and the expanded uncertainty of all the target pesticides ranged from 3.1 to 18.8%, showing the ruggedness of the proposed method [164].

A multivariate method for the analysis of eight pesticide residues (propamocarb, carbaryl, baycarb, thiobencarb, metalaxyl, thiamethoxam, diazinon, and dursban) in fruit and vegetable samples was proposed by Lawal et al. [165], using QuEChERS-IL-based DLLME. The sample solution was prepared by measuring 20 g of previously homogenized sample and 15 mL of acetonitrile into a 50-mL centrifuge tube. The mixture was then spiked with a known amount of pesticide standards and vortexed for 1 min, followed by the addition of 6 g $MgSO_4$ and 1.5 g of NaOAc. The tube was shaken vigorously for 1 min and then centrifuged for 2 min at 4000 rpm. The supernatant (1.5 mL) was transferred to a 2-mL centrifuge tube containing 150 mg of $MgSO_4$ and 50 mg of PSA, and the tube was centrifuged for 5 min at 4000 rpm. The resulting supernatant was transferred into a 15-mL centrifuge tube containing 10% NaCl (w/v), and centrifuged for 5 min at 7000 rpm, followed by the addition of 130 μL of IL [C_6MIM(PF_6)]. The sediment was mixed with 500 μL of methanol, and the resulting solution was subjected to LC-MS analysis. The optimal extraction conditions were determined using a PBD (to determine the significant factors) and BBD (for optimization of the significant factors). The method validation determined using the optimal values yielded linearity of 5–300 μg kg^{-1} ($r^2 \geq 0.99$), average recovery of 89–138%, and RSD of 0–18%, with LOD ranging from 0.01 to 0.39 μg kg^{-1}. The values were found to be within the recommended range, and the matrix effect was found to be negligible, which was as a result of the extensive cleanup of the matrix. The measurement of uncertainties was also estimated and found to be within the recommended limits.

Lawal et al. [165] used the QuEChERS-IL-based DLLME method described in their previous paper for the analysis of eight pesticide residues in five fruit and vegetable samples. The parameters were also optimized using an experimental design. The analytical figures of merit were found to be satisfactory, with linearity range from 5 to 400 μg kg^{-1}, and a coefficient of regression greater than 0.99. The LOD ranged from 0.02 to 0.32 μg kg^{-1}, which was lower than the lowest calibration level and EU MRL. The relative recovery of 82–137% and RSD of 0–19% were found to be within the SANTE-11813 [166] guidelines. The estimated matrix effect showed very weak matric interference for all samples, which was attributed to the effective extraction/cleanup of matrix interference by the proposed method [167].

A DLLME method was developed using IL as extraction solvent for the determination of seven fungicide residues (pyrimethanil, fenarimol, epoxiconazole, kresoxim-methyl, cyprodinil, prochloraz, and diniconazole) in fruit juice. A 5-mL aliquot of the fruit juice was diluted with deionized water (1:1, v/v) containing 0.2 mg L^{-1} of fungicide standard and placed into a 10-mL screw-cap conical-bottom glass tube, followed by rapid injection of 0.5 mL of methanol (dispersive solvent) containing 60 μL of [C_6MIM(PF_6)] (extraction solvent). The mixture was vortexed for 1 min, leading to the formation of a cloudy solution consisting of very fine droplets of IL dispersed into the aqueous sample. The mixture was then centrifuged at 4000 rpm for 5 min, after which the sediment containing the dispersed IL particles was removed and dissolved in methanol to 50 μL, and 10 μL of the solution was injected into an HPLC system. Parameter optimization was performed using a univariate design, and the optimal conditions were used for method validation. The linearity ranged from 0.2 to 2 mg L^{-1}, with a correlation coefficient greater than 0.99 and LOD of 3.1–10.2 μg L^{-1}. The recovery ranged from 61.40 to 93.10, with RSD in the range of 2.5–10.1%. The recovery of pyrimethanil was found to be unsatisfactory, probably because of the extraction pH of 4, as it was discovered that pyrimethanil could be effectively extracted at pH 6. The efficiency of the proposed method was also determined by comparing the peak areas of IL-DLLME with tetrachloride (CCl_4) and trichloromethane ($CHCl_3$) as extraction solvents, and the results revealed that the peak areas obtained with IL were higher than those of CCl_4 and $CHCl_3$, showing the advantages of IL over the other extraction solvents [168].

A microwave-assisted (MA) IL microextraction method was developed for the detection and tracking of three pyrethroid pesticides (allethrin, cypermethrin, and permethrin) in complex environmental matrices. Organically grown pesticide-free fruit samples were used for method development. A 10-g portion of each fruit sample was cut into pieces and allowed to dry for 30 min in a 15-mL centrifuge tube, followed by the addition of 15 mL of a mixture of methanol and deionized water (1:1, v/v). The mixture was then centrifuged for 30 min at 4000 rpm. The supernatant was collected, filtered through a 0.45-μm syringe membrane, and stored in a

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refrigerator at 4 °C. For conventional DLLME, 5 mL of the filtrate was transferred into a plastic centrifuge tube, and 260 µL IL [(N_{8881})(NTf_2)] dissolved in methanol [24:80 v/v (IL/MeOH)] was injected and mixed. After mixing, the sample was centrifuged for 10 min at 3500 rpm, after which 20 µL of the IL was removed and diluted with 1000 µL of methanol, and 50 µL of the final solution was injected into an HPLC system. For MA-DLLME, the filtrate was transferred into a 10-mL glass microwave vial, followed by injection of 260 µL of the IL/MeOH mixture, and the mixture was microwaved for 120 s while stirring. The sample was then centrifuged at 3500 rpm for 10 min, and the IL layer (20 µL) was removed and dissolved in 1000 µL of methanol. A 50-µL aliquot was injected into the HPLC system for analysis. Several factors affecting DLLME were examined, including adsorption of target analytes on the walls of the vessel, degradation of the analytes under microwave energy, and total irradiation time, as they affect the extraction efficiency of MA-DLLME as compared with conventional DLLME. The recoveries of the two DLLMEs were compared under optimal conditions, and the results showed that MA-DLLME gave better recovery for allethrin and permethrin (40–125%) than cypermethrin (35–45%), while the conventional DLLME gave better recovery for cypermethrin. The lower recovery of cypermethrin for MA-DLLME was traced to its degradation under microwave irradiation [169].

A method was developed by Ruan et al. for the determination of two benzoylurea insecticides (diflubenzuron and chlorbenzuron) in grape and peach samples using the QuEChERS technique, followed by cleanup with IL-based DLLME. The fruit samples were crushed homogeneously and stored at −20 °C prior to analysis. A 10-g portion of the homogenized and spiked sample was weighed into a 50-mL PTFE centrifuge tube and extracted with 20 mL of acetonitrile for 10 min in an ultrasonic cleaner. Next, 3 g of anhydrous Na_2SO_4 and 1.5 g of NaCl were added, and the mixture was vortexed for 1 min and then centrifuged at 3000 rpm for 5 min. A 10-mL aliquot of the supernatant was then concentrated to dryness using a rotary evaporator at 40 °C and was reconstituted with 1.6 mL of acetonitrile and transferred for cleanup by mixing with 100 mg of PSA and 150 mg of $MgSO_4$. It was then vortexed for 1 min and centrifuged for 5 min at 3000 rpm. The supernatant was collected and filtered through a 0.22-µm cellulose membrane filter. A 1.1-mL aliquot of the filtrate was transferred into a centrifuge tube containing 90 µL of IL [C_6MIM(PF_6)] and then vortexed for 1 min. The mixture was rapidly injected into a 10-mL centrifuge tube containing 5 mL of 10% NaCl solution and vortexed for 90 s, followed by centrifugation for 5 min at 5000 rpm. The aqueous phase was removed using a Pasteur pipette, and the IL phase was redissolved with 50 µL of methanol and vortexed for 60 s, after which 20 µL was injected into an HPLC system. The method validated using optimized extraction conditions gave linearity ranging from 0.01 to 0.5 µg mL^{-1}, with a correlation coefficient greater than 0.999 and relative recovery of 98.6–109.3% (RSD = 0.5–5.2%). The LOD for the target analytes in the two samples was found to be 5 µg kg^{-1}. A comparison of the proposed method with other published methods in terms of sample mass, recovery, and LOD showed that the proposed method exhibited satisfactory extraction performance, with better LOD. The satisfactory performance was attributed to the higher EF obtained from the IL-DLLME [170].

A simple, rapid, and effective method was developed based on IL-vortex-assisted liquid-liquid microextraction (VA-LLME) for the simultaneous determination of four neonicotinoid insecticides (clothianidin, imidacloprid, acetamiprid, and thiacloprid) in fruit samples. A fruit sample was homogenized, and a 30-mL aliquot of the juice was filtered through Whatman filter paper, after which the filtrate was further filtered through a 0.45-µm nylon membrane filter. A 10-mL aliquot of the filtrate was measured into a conical-bottom tube, followed by the addition of 1.5 g of Na_2SO_4 and 150 µL of [C_6MIM(PF_6)]. The mixture was then vortexed for 30 s and the analytes were extracted into the IL droplet. The aqueous layer was removed, and the IL layer was redissolved with 50 µg L^{-1} of acetonitrile to reduce the viscosity of the solution, and 20 µL was then injected into an HPLC system. The VA-LLME conditions were optimized using a univariate design, and the optimal conditions were used for method validation. The method yielded linearity ranging from 2 to 1000 ng mL^{-1}, with a correlation coefficient greater than 0.999 and LOD of 0.25–0.30 ng µg mL^{-1}. The relative recovery ranged from 92 to 108%, with RSD of 1.3–6.9% and an EF of 100 for all the target pesticides. The method was found to exhibit satisfactory analytical features in terms of recovery, RSD, EF, linearity, and LOD compared with other techniques such as DLLME and SPE for the analysis of neonicotinoid insecticides in fruit and vegetable samples. The proposed method was also found to be reproducible, low-cost, rapid, and simple [171].

A novel material was developed for SPME of organochlorine pesticides [α-hexachlorocyclohexane, β-hexachlorocyclohexane, δ-hexachlorocyclohexane, heptachlor, aldrin, dieldrin, 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene, and 1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane] in apple and peach juice samples. The method involved incorporating porous aromatic frameworks (PAF) with IL (1-(triethoxysilyl)propyl-3-aminopropyl hexafluorophosphate [ESC_4APIM(PF_6)]) as SPME fiber coating. The PAF was performed using a method described by Ben et al. [172], while the PAF/IL composite was prepared by weighing 100 mg of PAF into a three-necked round-bottom flask containing 15 mL of concentrated nitric acid, and the mixture was refluxed at 50 °C overnight. After cooling to room temperature, the mixture was filtered, washed with

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water, and dried in a vacuum oven. Next, 100 mg of the resulting solid was weighed into the refluxing apparatus, followed by the addition of 1080 mg of anhydrous tin chloride and 50 mL of tetrahydrofuran (THF), with refluxing at 50 °C for 24 h. The resulting solid mixture was filtered and the residue was washed with 10% NaOH, water, and diethyl ether, and then dried under vacuum. A 100-mg portion of the dried solid and 1020 mg of 1-(triethoxysilyl)-propyl-3-aminopropyl hexafluorophosphate were dispersed in 60 mL of dimethylformamide (DMF) containing 15% (v/v) of poly(ethylene glycol)diglycidyl ether (PEGDE). The yellow suspension was refluxed at 80 °C for 24 h and then centrifuged. The yellow product obtained was washed with anhydrous ethanol to remove excess PEGDE and was dried under vacuum at 120 °C to obtain PAF/IL composites. The SPME fiber previously treated with acetone, washed with ethanol, and dried was vertically dipped in epoxy resin glue for 30 s. The excess resin glue was wiped with a glass sheet and the fiber was inserted into a centrifuge tube filled with PAF/IL composite, rotated for 60 s, and then extracted. After solidification at room temperature, the fiber was dried under vacuum at 80 °C for 8 h, and later passed through a microsyringe to prepare a homemade fiber [173].

The prepared fiber was then exposed to the headspace of the sample matrix prepared by filtering 2 mL of the juice sample and brought up to 10 mL with acetone. The mixture was homogenized for 30 min in an ultrasonic cleaner and centrifuged at high speed for 15 min. The solvent of the supernatant was then removed by rotary evaporator and the residue dissolved in 10 mL of methanol for SPME analysis. The extraction time, temperature, salt addition, and desorption time were optimized, and the optimal conditions were used for method validation. Student's *t* test was used to prove the rationality of the optimal conditions. The data revealed that the optimal values and the nearest values of experimental conditions showed a significant difference ($p < 0.05$), and the results were found to be consistent with experimental results. The method linearity ranged from 1 to 500 μg L^{-1}, with a correlation coefficient greater than 0.993. The relative recovery ranged from 76.1 to 121.3%, and RSD from 0.5 to 6.1%, while the LOD ranged from 0.11 to 029 μg L^{-1}. The EF of the prepared PAF/IL-coated fiber was compared with fiber coated with only PAF, and the results showed higher EF for the PAF/IL fiber than the PAF-coated fiber. The proposed method was also compared with commercial SPME fiber coating in terms of LOD and EF, and showed comparable or better results [173].

A method was proposed for the determination of six triazole fungicides (triazolone, triadimenol, epoxiconazole, flusilazole, tebuconazole, and diniconazole) in fruit juice samples using IL-based vortex-assisted dispersive liquid-liquid microextraction (VA-DLLME). The sample matrix was prepared by diluting the homogenized sample with deionized water (1:1, 1:1, and 1:4 for peach, apple, and orange, respectively) and filtered. A 5-mL portion of the filtrate was placed in a 15-mL sharp-bottom centrifuge tube containing 4% NaCl (w/v), followed by rapid addition of a mixture of 250 μL acetonitrile and 70 μL IL [$C_6MIM(PF_6)$] to form a cloudy solution. The solution was vortexed for 2 min and centrifuged at 4000 rpm for 5 min, and the IL was precipitated in the bottom. The upper aqueous layer was removed with a pipette, and the IL phase (40 μL) was redissolved with 80 μL methanol for HPLC analysis. The factors affecting extraction efficiency were optimized using OFAT design, and the optimal conditions were used for method validation. The linearity ranged from 10 to 15,000 μg L^{-1} with a correlation coefficient greater than 0.997. The recovery ranged from 71 to 104.5% (RSD = 1.4–11.8%) and the LOD ranged from 0.4 to 6.7 μg L^{-1}. The proposed method was compared with other LLME and SPME methods for the analysis of triazole in fruit samples in terms of LOD and recovery, and it was found to give comparable or better values [174].

An efficient, sensitive, rapid, reliable, and green analytical method was developed for the analysis of three neonicotinoid insecticides in fruit juice and vegetable samples using Ringer tablet-based IL-DLLME. The juice samples were filtered, and the filtrate was diluted with HPLC-grade water at a ratio of 1:2, while the vegetable samples were crushed, and 50 mL of the juice produced was centrifuged at 1118 rpm for 10 min. The clear supernatant was diluted at a ratio of 1:5 with HPLC-grade water. A 10-mL aliquot of the diluted sample was spiked with 50 ng mL^{-1} of each analyte in a 15-mL conical-bottom glass test tube, followed by the addition of 63 μL of IL [$C_6MIM(PF_6)$] and 0.9 g of Ringer tablets (mixture of 2.25 g NaCl, 0.105 g KCl, 0.12 g $CaCl_2$, and 0.05 g $NaHCO_3$). After the IL had penetrated the pores of the Ringer tablets, the tablets were transferred into aqueous solution. The mixture was then shaken manually and the tablets dissolved in the aqueous solution, resulting in dispersion of the IL and leading to the formation of a cloudy solution. The mixture was then centrifuged for 4 min at 1118 rpm, and the IL settled in the bottom. The IL phase (10 μL) was withdrawn and injected into an HPLC system. The figures of merit determined under univariate-optimized conditions gave linearity of 0.41 to 5000 ng mL^{-1} ($r^2 \geq 0.998$). The relative recovery ranged from 66 to 84%, with RSD of 4–6% and LOD of 0.12–0.33 ng mL^{-1}. The performance of the proposed method was compared with other methods used in the determination of the selected pesticides in fruits and vegetables, including SPE and DLLME, in terms of LOD, linearity, and RSD, and the proposed technique was found to have a wider linear range and lower LOD and RSD, demonstrating the sensitivity of the method [175].

An ultrasound-assisted DLLME based on solidification of IL sediment (UA-SSIL-DLLME) was developed for the

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determination of triazole fungicides (epoxiconazole, uniconazole, tebuconazole, and hexaconazole) in fruit juice samples. An IL was prepared in situ by weighing 0.038 g of tributyl(octyl)phosphonium bromide in a test tube followed by the addition of 10 mL of sample (diluted with pure water at a ratio of 1:1), filtered through a 0.45-μm membrane, and shaken. A 300-μL aliquot of potassium hexaphosphate solution was rapidly added to the mixture, resulting in the formation of a white turbid solution. The solution was immersed in an ultrasonic bath at 50 W for 5 min, and the emulsion formed was centrifuged at 7000 rpm for 15 min. The tube was cooled in an ice bath until the IL phase was deposited at the bottom. The aqueous phase was decanted and the solidified IL phase was diluted with 40 μL of methanol, and 10 μL of the solution was injected into an HPLC system. The method validated under optimized conditions gave linearity ranging from 5 to 500 μg L^{-1} ($r^2 > 0.999$). The relative recovery for the method in three fruit juice samples ranged from 75.41 to 108.59%, with RSD of 1.03–7.54% and LOD of 0.10–1.38 μg L^{-1}. The proposed method was compared with other methods for the determination of triazole fungicides in environmental samples in terms of organic solvents used, extraction time, linearity range, and LOD, and was found to be superior due to the use of an environmentally friendly solvent, lower LOD, and wide linearity range [176].

Farajzadeh et al. [177] developed a DLLME method based on solidification of floating IL for the determination of four carbamate pesticides (carbofuran, carbaryl, methiocarb, and thiodicarb) in seven fruit juice and vegetable samples. The IL was prepared by mixing 10 mmol of diisobutyl amine (1.69 mL) with 10 mmol of stearic acid (2.56 g) at room temperature in a test tube. The mixture was vortexed for 10 min, and the clear solution formed was used as extraction solvent. It was considered an IL liquid because the product formed had a lower melting point than the starting materials, and the melting point was also lower than room temperature. The fruit juice samples were filtered and diluted with HPLC-grade water at a ratio of 1:3, while the vegetable samples were washed and immersed in distilled water for 5 min and then dried overnight at room temperature. After drying, the sample was crushed to produce a juice, and 50 mL of the juice was centrifuged for 10 min. The clear supernatant was then diluted with HPLC-grade water at a ratio of 1:5. A 5-mL aliquot of the fruit juice samples was spiked with 20 ng mL^{-1} of each pesticide in a 12.5-mL glass centrifuge tube and then placed in a water bath at 45 °C for 3 min. Next, 60 μL of the prepared IL (diisobutyl ammonium stearate) dissolved in 0.75 mL of acetonitrile was rapidly dispersed into the spiked sample and the mixture was centrifuged for 4 min. After centrifugation, the tube was placed in a water bath for 2 min at 10 °C, leading to solidification of the IL. The solidified IL was removed and dissolved in 20 μL of methanol, and 10 μL was then injected into an HPLC system. The method validated using optimized conditions gave linearity ranging from 1.09 to 2000 ng mL^{-1}, with $r^2 > 0.99$. The average recovery ranged from 88 to 99% and RSD from 1 to 7%, with LOD of 0.32–0.51 ng mL^{-1}. The method was compared with other microextraction methods (DLLME and SPME) for the extraction of carbaryl pesticides in fruit and vegetable samples and was found to be superior in terms of linearity range, extraction time, LOD, and RSD.

An environmentally friendly analytical method was developed for the analysis of aryloxyphenoxypropionate herbicides (clodinafop-propargyl, haloxyfop-R-methyl, fenoxaprop-P-ethyl, and diclofop-methyl) in vegetable (tomato, onion) samples using IL-based air-assisted liquid-liquid microextraction (AA-LLME) [178].

A 250-g portion of vegetable sample washed with tap water and deionized water was crushed to produce a juice. The juice was centrifuged for 5 min, and the supernatant of the tomato juice was used without dilution, while that of the onion was diluted with deionized water at a ratio of 1:10. A 5-mL aliquot of the sample solution was spiked with 250 ng mL^{-1} of each analyte in a 10-mL glass centrifuge tube containing 0.125 g of NaCl. Then, 44 μL of IL [$C_6MIM(PF_6)$] was placed at the bottom of the tube and was aspirated five times. The mixture was then centrifuged for 4 min, leading to the sedimentation of the IL. The sedimented IL (10 μL) was withdrawn and injected into an HPLC system. The method validation estimated under optimized conditions gave linearity in the range of 0.52–5000 ng mL^{-1}, with a correlation coefficient greater than 0.997. The recovery ranged from 72 to 97% (RSD = 2–8), and LOD ranged from 0.16 to 0.31 ng mL^{-1}. The method was compared with other microextraction techniques including SDME, LLME, and DLLME for the analysis of target analytes in fruit and vegetable samples, and was found to yield a wider linear range and lower LOD and RSD.

A vortex-assisted surfactant-enhanced emulsification microextraction (VA-SEME) technique, referred to as binary-based IL-assisted surfactant-enhanced emulsification microextraction (BS-ILASEME), was successfully applied for the determination of four fungicides (pyrimethanil, fludioxonil, cyprodynil, pyraclostrobin) in apple juice and apple vinegar samples. A 5-mL aliquot of the sample containing 0.06 g mL^{-1} of NaCl was transferred into a 15-mL screw-cap conical-bottom glass tube and the pH adjusted to 7. A 100-μL aliquot of extraction solvent (mixture of amyl acetate and [$C_6MIM(PF_6)$]) and 15 μL of 5 mmol L^{-1} Tween 20 (emulsifier) were added to the sample solution, and the solution was shaken on a vortex agitator for 15 s and then centrifuged for 5 min at 3800 rpm. The sedimented binary solvent was removed by syringe needle and redissolved in 50 μL of methanol to reduce the impact of trace water. The mixture was then transferred into a 200-μL glass insert tube inserted into a 1-mL autosampler vial, and 20 μL was

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injected into an HPLC system for analysis. Factors affecting extraction efficiency including extraction solvent, volume of binary solvent, sample pH, type and concentration of emulsifier, vortex time, and salt addition were carefully optimized using a univariate design, and the optimized conditions were used for method validation. The method yielded linearity ranging from 5 to 2000 μg L^{-1} ($r^2 > 0.996$), with relative recovery of 51.9–107.8% (RSD = 1.7–11.9) and LOD of 0.5 to 1.5 μg L^{-1}. The proposed method was compared with other microextraction techniques including DLLME, SD-UA-SEME, and SD-DLLME based on LOQ and extraction time, and was found to give lower LOD and shorter extraction time, while retaining the advantage of using green IL and low-toxicity organic solvents [179].

A method was developed for the determination of six benzoylurea herbicides (diflubenzuron, triflumuron, flufenoxuron, and lufenuron and diafenthiuron) and four pyrethroid pesticides (transfluthrin, fenpropathrin, γ-cyhalothrin, and deltamethrin) in fruit juices using ultrasound-assisted hybrid IL-DLLME (UA-HIL-DLLME). The extraction solvent comprised a mixture of 1-octyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [C_8DMIM(NTf_6)] and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [C_6MIM(NTf_6)] (45:9 v/v). An 8-mL aliquot of homogeneous aqueous sample spiked with 50 μg L^{-1} of target analytes was transferred into a 10-mL PTFE tube, followed by rapid injection of 54 μL of the mixture of extraction solvents dissolved in 240 μL of acetonitrile. The mixture was ultrasonically treated for 8 min to form a cloudy solution and centrifuged for 5 min at 4000 rpm. The upper aqueous phase was carefully removed with a syringe, and the IL phase was dissolved in 60 μL of acetonitrile, and 10 μL of the solution was injected into an HPLC system for analysis. The importance of factors affecting extraction efficiency (volume of IL, centrifugation time, ionic strength, volume of dispersion solvent, and ultrasonication time) were screened using a PBD, while the main effect of the factors was determined using one-way analysis of variance (ANOVA). The volume of mixed IL, volume of dispersion solvent, and ultrasonication time were found to have a significant ($p < 0.05$) influence on extraction efficiency and were optimized using a central composite design (CCD). The method validated using the multivariate design-optimized conditions gave linearity of 2.5–500 μg L^{-1}, with a correlation coefficient greater than 0.996 and LOD from 0.19 to 0.69 μg L^{-1}. The recovery ranged from 75.48 to 177.88%, with an EF of 133–157, showing little or no matrix effect. A comparison of the method with other microextraction techniques for the analysis of target analytes showed that the proposed method gave comparable or better recovery of the target analyte. The use of the log *P* values of the target analytes served as a reference value when the extraction solvent separated the target analytes from the matrix based on equilibrium theory [180].

A microwave-assisted DLLME method was proposed for the determination of triazine herbicides (desmetryn, atrazine, ametryn, propazine, terbuthylazine, prometryne, and dimethametryn) in fruit juice samples using IL as the extractant solvent. A 5-mL aliquot of juice sample was transferred into a centrifuge tube, followed by the addition of 60 μL of extractant solvent [C_6MIM(PF_6)] and 80 μL of dispersive solvent [C_6MIM(BF_6)], and the mixture was shaken for 5 min. The mixture was then microwaved for 90 s at 180 W, after which 0.10 g of [NH_4(PF_6)] was added, followed by manual shaking for 1 min and centrifugation. The supernatant was discarded, and the sedimented IL phase was withdrawn with a syringe needle and transferred into a 1-mL PTFE tube and diluted with acetonitrile. The solution was then filtered and the filtrate injected into an HPLC system. The method was validated using a carefully optimized univariate design. The linearity ranged from 5 to 250 μg L^{-1}, with a correlation coefficient greater than 0.998. The LOD ranged from 1.01 to 1.52 μg L^{-1}, while the relative recovery ranged from 82.4 to 104.1%, with RSD of 1.8–5.6%. The proposed method was compared with other DLLME methods, and the results showed that while there was no significant difference in the recovery obtained in comparison with other methods, the advantage of the proposed method lay in the fact that it made use of microliter volume of an environmentally friendly IL solvent [181].

The use of IL in DLLME in combination with ultrasound was tested for the determination of thiabendazole in fruit and vegetable samples. Before analysis, the fruit and vegetable samples were carefully washed with ultrapure water and then homogenized. A 10-g portion of each homogenized sample was transferred into a 50-mL centrifuge tube followed by the addition of 10 mL of acetonitrile, and the tube was shaken vigorously by hand. This was followed by the addition of 2 g of NaCl and 4 g of $MgSO_4$ and vigorous shaking again. The mixture was then centrifuged for 5 min at 5000 rpm, and a 5-mL aliquot of the acetonitrile phase was transferred into a 15-mL centrifuge tube and spiked with standard calibration solution and 450 μL of 5 mg L^{-1} Cu(II) solution, 15 mg of [C_4MIM(PF_6)], and 300 μL of acetonitrile. The final volume was completed with 15 mL of water, and the tube was placed in an ultrasonic bath for 10 min at 40 °C, followed by centrifugation at 3500 rpm for 2 min. The lower IL phase was removed and diluted to 400 μL with methanol, and was subjected to spectrophotometric determination at 340 nm. Validation of the proposed method was conducted under the optimal extraction conditions, which yielded linearity of 0.8–250 μg L^{-1} ($r^2 > 0.997$), with LOD of 0.24 μg L^{-1} and relative recovery of 91–95.6% (RSD = 4.8–6.5). The use of spectrophotometry provided the advantages of simplicity, speed, low cost, ease of use, and ready availability when compared with chromatographic methods [182].

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Table 2 Applications of ILs in microextraction techniques

Analyte	Matrix	ME technique	IL used	Relative Recovery (RSD) (%)	Linearity	LOD	Analytical method	r^2	References
8 MCPs	Banana	DLLME	[$C_6MIM(PF_6)$]	53–97 (2.7–8.7)	0.010–6.83 μg kg^{-1}	0.32–4.66 μg kg^{-1}	HPLC–DAD	≥ 0.994	[145]
8 MCPs	Table grape, plum	DLLME	[$C_6MIM(PF_6)$]	64–105 (1.4–9.1)	0.01–6.83 μg kg^{-1}	0.651–6.33 μg kg^{-1}	HPLC–DAD	≥ 0.995	[146]
4 OPPs	Pear	DLLME	[$BBIM(PF_6)$]	78.60–86.80 (1.1–2.7)	5–1000 ng mL^{-1}	0.01–0.05 ng ml^{-1}	HPLC–UV	≥ 0.998	[152]
7 CPs	Watermelon, apple, cantaloupe, orange, strawberry	LLME	[$C_4MIM(PF_6)$]	81–118 (4–10.2)	0.01–8 μg mL^{-1}	0.002–0.040 μg mL^{-1}	HPLC–UV	> 0.990	[148]
6 OPPs	Apple, pear	DLLME	[$C_6MIM(PF_6)$]	69.80–109.10 (2.3–5.7)	2–100 μg kg^{-1}	0.061–0.73 μg kg^{-1}	HPLC–UV	≥ 0.995	[149]
7 PPs	Cabbage, cucumber	SPME	[$ViHDIM(PF_6)$]	67.40–93.52 (3.61–13.76)	0.10–100 μg L^{-1}	0.21–0.49 μg kg^{-1}	GC–ECD	> 0.990	[153]
5 APs	Grape, apple, pear juices	DLLME	[$C_6MIM(NTf_2)$]	87–99.60 (1.2–5.3)	0.5–500 ng mL^{-1}	0.05–0.53 ng mL^{-1}	HPLC–UV	≥ 0.995	[154]
3 APs	Grape, peach, orange juices	TEME	[$C_6MIM(NTf_2)$]	91.90–103.70 (2.0–4.8)	0.1–600 ng L^{-1}	21.1–61.4 ng L^{-1}	HPLC–UV	NR	[155]
3 PPs	Tomato	DLLME	[$C_4MIM(PF_6)$]	83.90–96.70 (1.7–4.5)	0.05–1.5 μg kg^{-1}	8.1–14.3 μg kg^{-1}	HPLC–UV	> 0.999	[156]
7 BUIs	Apple, pear, grape, peach juices	ILSFOD-LLME	[$P_{14,6,6,6}(PF_6)$]	75.6–113.9 (0.1–7.3)	0.5–500 ng mL^{-1}	0.03–0.28 ng mL^{-1}	HPLC–UV	≥ 0.996	[157]
4 THs	Garlic, sprouts, strawberry, cabbage, cucumber, cherry tomato, cole, tomato	SPME	[ViBIM(TfO)]	71.50–96.90 (4.1–9.9)	25–5000 μg kg^{-1}	3.3–13 μg kg^{-1}	GC–FID	≥ 0.994	[158]
3 FRs	Apple, grape juices	MSUSAEME	[$C_2MIM(NTf_2)$]	61.40–86 (1.8–9.7)	5–400 μg L^{-1}	0.4–1.6 μg L^{-1}	HPLC–UV	≥ 0.998	[159]
5 MCPs	Grape	SPME	[$C_{12}MIMBr$]	88.70–101.70 (7.1–17.8)	0.01–30 μg kg^{-1}	0.002–0.667 ng mL^{-1}	GC–ECD	≥ 0.987	[160]
6 TFs	Pear, apple, grape	QuEChERS–DLLME	[$C_6MIM(PF_6)$]	63.80–119.10 (1.1–12.6)	10–10,000 μg L^{-1}	3.4–26.8 μg kg^{-1}	HPLC–PDA	≥ 0.997	[161]
5 MCPs	Tomato	SPME	[$C_4MPy(BF_4)$]	NR (1.2–4.6)	60–1000 μg kg^{-1}	20–90 μg kg^{-1}	GC–FID	≥ 0.987	[162]

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Table 2 (continued)

Analyte	Matrix	ME technique	IL used	Relative Recovery (RSD) (%)	Linearity	LOD	Analytical method	r^2	References
5 FRs	Apple, grape, pear juices	AA–LLME	$[C_6MIM(NTf_6)]$	74.90–115.40 (1.2–10.1)	5–400 μg L^{-1}	0.4–1.8 μg L^{-1}	HPLC–UV	≥ 0.998	[163]
4 OPPs	Apple, mango, cherry juices	SPME	$[C_{16}MIM(NTf_6)]$	54–109 (2–21)	0.01–10 ng L^{-1}	0.57–4.13 ng L^{-1}	GC–FPD	> 0.999	[164]
8 MCPs	Jackfruit, strawberry, cucumber, pear, carrot	QuEChERS–DLLME	$[C_6MIM(PF_6)]$	89–138 (0–18)	5–300 μg kg^{-1}	0.01–0.39 μg kg^{-1}	LC–MS	≥ 0.990	[165]
8 MCPs	Banana, cabbage, onion, tomato, orange	QuEChERS–DLLME	$[C_6MIM(PF_6)]$	82–137 (0–19)	5–400 μg kg^{-1}	0.02–0.32 μg kg^{-1}	LC–MS	≥ 0.996	[167]
7 FRs	Apple, grape juices	DLLME	$[C_6MIM(PF_6)]$	65.40–93.10 (2.2–11.6)	0.02–2 mg L^{-1}	3.1–10.2 μg L^{-1}	HPLC–DAD	> 0.990	[168]
3 PPS	Apple, peach, grape	MA-DLLME	$[N_{88881}(NTf_2)]$	40–125 (NR)	n. r	NR	HPLC–DAD	NR	[169]
2 BUIs	Grape, pear	QuEChERS–DLLME	$[C_6MIM(PF_6)]$	98.60–109.30 (0.6–5.2)	0.01–0.5 μg mL^{-1}	5 μg kg^{-1}	HPLC–DAD	> 0.999	[170]
4 NIs	Watermelon, apple, grape, orange	VA-LLME	$[C_6MIM(PF_6)]$	92–108 (1.3–6.9)	2–1000 ng mL^{-1}	0.25–0.30 ng mL^{-1}	HPLC–UV	> 0.999	[171]
8 OPPs	Apple, peach juices	SPME	$[ESC_4APIM(PF_6)]$	76.10–121.30(0.5–6.1)	1–500 μg mL^{-1}	0.11–0.29	GC–ECD	≥ 0.993	[173]
6 TFs	Peach, apple, orange juices	VA-DLLME	$[C_6MIM(PF_6)]$	71–104.50 (1.4–11.8)	10–15,000 μg L^{-1}	0.4–6.7 μg L^{-1}	HPLC–PDA	≥ 0.997	[174]
3 NIs	Sour cherry, apple, strawberry, tomato, lettuce, cucumber	DLLME	$[C_6MIM(PF_6)]$	66–84 (4–9)	0.41–5000 ng L^{-1}	0.12–0.33 ng L^{-1}	HPLC–DAD	≥ 0.998	[175]
4 TFs	Apple, grape, peach	UA-SSIL-DLLME	$[(P_{4448}(PF_6)]$	75.41–108.59 (1.03–7.54)	5–500 μg L^{-1}	0.10–1.38 μg L^{-1}	HPLC–UV	> 0.999	[176]

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Table 2 (continued)

Analyte	Matrix	ME technique	IL used	Relative Recovery (RSD) (%)	Linearity	LOD	Analytical method	r^2	References
4 CPs	Grape, apricot, apple, tomato, sugar beet, potato, zucchini	SFIL-DLLME	$[C_4Am(C_{18}H_{39})]$	86–99 (1–7)	1.09–2000 ng mL^{-1}	0.32–0.51 ng mL^{-1}	HPLC–DAD	> 0.997	[177]
4 OCPs	Tomato, onion	AA-LLME	$[C_6MIM(PF_6)]$	72–97 (2–8)	0.52–5000	0.16–0.31	HPLC–DAD	> 0.997	[178]
4 FRs	Apple juice, apple vinegar	VA-SEME	$[C_6MIM(PF_6)]$	51.90–107.80	5–200 µg L^{-1}	0.9–1.5 µg L^{-1}	HPLC–UV	> 0.996	[179]
6 BUIs, 4PPs	Pear, orange, peach juices, fruit blend	UA-DLLME	$[C_8DMIM(NTf_6)]$/ $[C_6MIM(NTf_6)]$	75.18–117.88 (1.24–2.64)	2.5–500 µg L^{-1}	0.19–0.69 µg L^{-1}	HPLC–UV	> 0.996	[180]
7 THs	Apple, grape, strawberry, blueberry juices	MA-DLLME	$[C_6MIM(PF_6)]$	82.40–104.10 (1.8–5.6)	2.5–500 µg L^{-1}	1.01–1.52 µg L^{-1}	HPLC–DAD	> 0.998	[181]
TBZ	Mushroom, cherry, tomato, green pepper, corn, carrot, grape, apple, banana, orange, lemon, apricot	LPME	$[C_4MIM(PF_6)]$	91.00–95.60 (4.8–6.5)	0.8–250 µg L^{-1}	0.24 µg L^{-1}	UV-Vis	≥ 0.997	[182]

ME technique microextraction technique, *IL solvent* ionic liquid solvent, *RSD* relative standard deviation, *LOD* limit of detection, *Ref* reference, *MCPs* multi-class pesticides, *OPPs* organophosphorus pesticides, *APs* acaricide pesticides, *PPs* pyrethroid pesticides, *BUIs* benzoylurea insecticides, *NIs* neonicotinoid insecticides, *THs* triazine herbicides, *CPs* carbamate pesticides, *TFs* triazole fungicides, *FRs* fungicide residues, *DLLME* dispersive liquid-liquid microextraction, *TEME* totally organic solvent-free emulsification microextraction, *LLME* liquid–liquid microextraction, *ILSFOD* ionic liquid-solidification of floating organic droplets, *SPME* solid phase microextraction, *QuEChERS* quick, easy, cheap, effective, rugged, *AA* air-assisted, *MA* microwave-assisted, *UA* ultrasound-assisted, *SSIL* solidification of sediment ionic liquid, *SFIL* solidification of floating ionic liquid, *MSUSAEME* manual-shaking-enhanced ultrasound-assisted emulsification microextraction, *SEME* surfactant-enhanced emulsification microextraction, *HPLC* high-performance liquid chromatography, *UV* ultraviolet, *DAD* diode array detector, *GC* gas chromatography, *FID* flame ionization detector, *PDA* photodiode array detector, *FPD* flame photometric detector, *ECD* electron capture detector, *LC–MS* liquid chromatography–mass spectrometry, *UV-Vis* ultraviolet-visible spectrophotometer, *NR* Not Reported

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Environmental Effects and Safety Concerns

The use of ILs as environmentally friendly solvents is based on their negligible vapor pressure [183], which reduces the risk of air pollution. Despite their numerous uses and wide-ranging applications, however, there has been cause for concern regarding their level of toxicity in the environment. A number of studies examining such effects over their entire life cycle [184] have found them to be probable pollutants in soil or water, which poses environmental risks [184–186]. The toxicity of ILs is measured based on their interaction with cellular membranes [48]. Imidazolium-based ILs have been found to be nontoxic toward marine and freshwater fish according to the Fish and Wildlife Service Acute Toxicity Rating Scale [187], while pyridinium-based ILs are more toxic [188].

It has also been observed that the toxicity of ILs is affected mainly by the cations, structural modification, and the side chain length [48, 185]. The environmental fate of ILs also depends on other environmental factors such as dissolved organic matter and salinity [48, 189, 190]. The study of the toxicity mechanisms of ILs has shown that their level of toxicity depends on their chemical structure, and that they can be even more toxic than organic solvents [191–193], with toxicity varying considerably across their types, test conditions, and morphology of test organisms [48, 183]. Therefore, it is important to understand the chemical structure of ILs in order to determine their level of toxicity [194], as environmentally benign ILs can be synthesized using proper combinations of anions and cations [48]. It has been suggested that there is an urgent need to establish a comprehensive database of the chemical structures and toxicity of ILs, as well as establishing guidance and legislation governing their synthesis [184, 185].

Conclusion

ILs have been used for a wide range of applications, in particular as an extractant in sample preparation. They are mainly used in DLLME, LLME, SPME, and QuEChERS coupled with ultrasound-, vortex-, and air-assisted extraction. It has also been observed (Table 2) that imidazolium anion in combination with hexafluorophosphate anion are the most widely used ILs for the analysis of a wide variety of pesticides in different fruit and vegetable samples. This may reflect the fact that studies have shown low toxicity for imidazolium-based ILs. In addition, their ease of synthesis, the ability to modify their surface properties, and their efficiency in extraction procedures has led to increasing demand for their use. The establishment of a database of ILs will enable researchers to determine the available routes and different combinations of anions and cations that can be employed for the synthesis of environmentally friendly and less toxic ILs.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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