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Directly suspended–solidified floating organic droplets for the determination of fungicides in water and honey samples

Songqing Li, Xiaoling Yang, Lu Hu, Xiangqian Cui, Sanbing Zhang, Runhua Lu, Wenfeng Zhou, and Haixiang Gao*

A directly suspended–solidified floating organic droplet microextraction (DS–SFO) method was developed for the preconcentration of four fungicides (i.e., chlorothalonil, triadimefon, cyprodinil, and trifloxystrobin) from water and honey samples prior to HPLC-DAD detection. In this technique, no special devices or supporting materials are required. The extraction phase can be easily collected via solidification of the microdroplet after the desired extraction time. The experimental parameters affecting the extraction efficiency were investigated and optimized, which resulted in optimal conditions of a 20-µL microdroplet of 1-dodecanol as the organic extractant, 3 mL of water or diluted honey sample without salt addition, and 90 min of stirring at 900 rpm and 30 °C. Under the optimized conditions, the proposed method achieved high extraction recoveries of 80% to 93% and 70% to 83% for water and honey samples, respectively. The limits of detection (LOD) of the method were in the range of 0.20–1.95 ng mL\(^{-1}\) for water samples and 1.14–11.06 ng g\(^{-1}\) for honey samples. The relative standard deviations (RSD) were <9.2% for both samples. Good linearities (r > 0.9980) over the calibration range of 5–1000 ng mL\(^{-1}\) were obtained. This method allowed the use of green solvents, a minimal usage of organic solvents, simple device and extraction processes, and high-throughput operations. Finally, the proposed method was successfully applied to the determination of fungicides in real water and honey samples.

Introduction

Chlorothalonil, triadimefon, cyprodinil, and trifloxystrobin are broad-spectrum fungicides widely used in agricultural activities. The fungicides can enter water systems and agricultural products through different routes [1–3]. When fungicides enter water systems and edible agricultural products, not only aquatic organisms but also to humans are threatened. For this reason, it is necessary to develop methods for residue analysis of fungicides in water and food samples.

A challenge for fungicide determination is that there are usually low concentration levels of fungicides in the environment or food matrices. It is necessary to develop sample enrichment methods that allow for the accurate and sensitive analysis of fungicides in water and food samples. [4–6] In recent years, some efforts have focused on the development of miniaturized, efficient, and economical sample preparation methods. Liquid-phase microextraction (LPME) was developed as a solvent-minimizing pretreatment procedure that is inexpensive, simple to use, and requires very little exposure to toxic organic solvents. LPME achieves relatively high analyte enrichment factors due to its very high sample-to-solvent ratio and thus it allows for the determination of the analytes at the low concentrated levels [5, 7]. Different innovative approaches based on LPME have recently emerged. These innovations can be classified into two categories according to the extraction method. In the first type, a small amount of extractant is dispersed into the matrix to extract the analytes, and the extractant is then separated from the matrix using centrifugation or other methods. Dispersive liquid–liquid microextraction (DLLME) [8] and ultrasound assisted emulsification microextraction (USAEME) [9] belong to this type.

In conventional DLLME or USAEME, the extractant needs a density higher than water for the simple separation of the extraction phase using centrifugation. However, most solvents that have a density higher than water are hazardous, such as chlorinated solvents including chlorobenzene, chloroform and carbon tetrachloride [10, 11]. For this reason, solvents with a density lower than water that are more environmentally friendly
than those used in conventional DLLME and USAEME were identified and used in some new microextraction [12–14]. In these microextraction, special home-made devices with narrow neck tubes or syringes are required to facilitate the collection of the extraction phase because the shape of the extraction phase floats on the aqueous matrix are usually amorphous, which restricts the application of the technique.

For the easy collection of low density extractants, a second type of LPME could be more suitable. In the second type, specific devices or materials are often required to hold the extractant, such as microsyringe needles or a hollow fiber in singe-drop microextraction (SDME) [15, 16] and hollow fiber liquid-phase microextraction (HF-LPME) [17]. The extractants continue aggregating throughout the extraction process. Because the shape and state of the extraction phase do not change during the extraction, easy extractant collection can be realized in this type of LPME.

Directly suspended droplet microextraction (DSDME) is a special method in the second type of LPME [18]. In this method, a free microdroplet of solvent is suspended under the surface of an aqueous sample while being agitated by a stirring bar placed on the bottom of the sample cell. Under the proper conditions, the microdroplet can be suspended in the top-center position of the sample solution and will not break up even in the absence of any support from the microsyringe needle, polymer rod or other supporting materials, such as hollow fibers. Conversely, the movement of the microdroplet is affected by the flow field, which promotes mass transfer inside the microdroplet. Moreover, the extractant used in DSDME can be extended to high melting point solvents (solids at room temperature), such as 1-bromohexadecane and 1-dodecanol. After the extraction, solidification of the floating organic solvent (SFO) can be accomplished by lowering the temperature of the system [19]. The complete collection of a solid floating droplet is much more accurate and easier than that of a liquid droplet because, in the collection of liquid extracts, some aqueous samples are easily drawn into the microsyringe with the extractant, which introduces a large negative influence on the precision of the methods. Therefore, in general, the directly suspended–solidified floating organic droplet microextraction (DS–SFO) technique has the following advantages compared with other LPME techniques: (1) green solvents with densities lower than water are used to lower the health risk to the operators and make the technique more environmentally friendly; (2) the extractant maintains a microdroplet throughout the extraction process and can be solidified after the extraction, which makes the extraction phase easy to collect; (3) no special devices are needed, and the operation is very simple, which allows the high-throughput technique to be automated. The technique can be extended to many applications in the analysis of a wide range of pollutants or other analytes.

To the best of our knowledge, the DS–SFO technique has not yet been combined with high-performance liquid chromatography (HPLC) analysis. In this study, a novel method, DS–SFO–HPLC-DAD, is developed and applied for the determination of four fungicides in honey and water samples. Based on a stable, single-drop system, no specific holder, such as the needle tip of a microsyringe or a hollow fiber, is required to support the organic droplet. The extraction parameters, including the volume of the extractant, extraction temperature, extraction time, stirring rate and salt addition, were evaluated and optimized. The proposed method is proven to be an easy, simple, inexpensive, and efficient microextraction technique that has great potential in many applications in the future.

**Experimental**

**Materials and methods**

**REAGENTS**

Chlorothalonil, triadimefon, cyprodinil, and trifloxystrobin were obtained from the Agricultural Environmental Protection Institution (Tianjin, China). 1-Dodecanol was purchased from Ouche Technology Co. Ltd. HPLC-grade methanol and acetonitrile were purchased from Dickma Technologies, Inc. (California, USA). Sodium chloride (analytical grade) was purchased from Beijing Chemical Reagent Company. Tributyl(dodecyl)phosphonium bis(trifluoromethylsulfonyl)amide (P4,4,4,12 NTf2) was purchased from the Center for Green Chemistry and Catalysis, LIPC, CAS (Lanzhou, China).

Stock solutions of the fungicides (1 mg mL−1) were prepared in HPLC-grade methanol and were stored in a refrigerator. Mixed standard solutions were also prepared in methanol. Fresh working standard solutions were prepared daily by diluting the mixed standard solutions to different concentrations using either ultrapure water or the diluted honey solutions.

**PREPARATION OF HONEY AND WATER SAMPLES**

Honey samples

Honey samples from different producing areas (i.e., Fangshan, Beijing; Fuzhou, Jiangxi; Fengxian, Shanghai; Jiamusi, Heilongjiang, and Chengde, Hebei) were purchased from local supermarkets to evaluate the proposed method. Each honey sample (1.5 g) was mixed with 10.5 g deionized water, vortexed and ultrasonicated to a homogeneous solution, and filtered through a 0.22-μm mixed cellulose membrane (Agela, USA). The prepared samples were stored in darkness at 4 °C.

Water samples

The lake water used in this work was collected from Longtan Lake in Beijing, China; paddy field water was collected from Jiangsu Province, China; tap water was collected from the laboratory. The water samples were collected in glass bottles and stored in a refrigerator, protected from light, and filtered through a 0.22-μm membrane before use. All of the samples were stored in the dark at 4 °C.

**INSTRUMENTATION**

A ZNCL-DS Intelligent Multi-point heater/magnetic stirrer (Henan, China) was used to stir the solutions and control the temperature of the samples. Chromatographic analysis was carried out using an Agilent 1100 HPLC system equipped with
a diode array detection (DAD) system. (California, USA). The injection volume was 10 µL in all cases. Separation of the fungicides was carried out on an Agilent Eclipse Plus C18 column (5 µm, 4.6 mm × 250 mm) using acetonitrile:water (65:35, v/v) as the mobile phase with flow rate of 1 mL min⁻¹. The absorbance wavelengths were set to 200, 225, 254 and 270 nm and scanned from 190 to 400 nm.

**Calculation of enrichment factor, extraction recovery and relative recovery**

The enrichment factor (EF) and extraction recovery (ER%) were used to evaluate the extraction efficiency under different conditions and to determine the optimized extraction procedure. EF<sub>real</sub> is defined as the ratio of the concentration of the analyte in the extraction phase to the concentration in the initial sample solutions before dilution, and EF<sub>dil</sub> is the concentration ratio between the diluted extraction phase (extractant volume diluted to 30 µL) and the initial sample solutions. The equations for EFs and ER% are shown in Eqs. 1 to 4:

\[
EF_{\text{real}} = \frac{C_{\text{real}}}{C_0}
\]

(1)

where \(C_{\text{real}}\) and \(C_0\) are the analyte concentration in the extractant phase before dilution and the initial analyte concentration in the aqueous sample, respectively.

\[
EF_{\text{dil}} = \frac{C_{\text{dil}}}{C_0}
\]

(2)

where \(C_{\text{dil}}\) is the analyte concentration in the diluted extractant phase.

ER% is computed as follows:

\[
ER\% = \frac{C_{\text{dil}} \cdot V_{\text{dil}}}{C_0 \cdot V_0} \times 100 = \frac{V_{\text{dil}}}{V_0} \times 100
\]

(3)

where \(V_{\text{dil}}\) is the volume of the diluted extraction phase, which is equal to 30 µL in the present study; \(V_0\) is the volume of the sample solutions, which is equal to 3000 µL. Therefore, the calculation of ER% can be expressed as:

\[
ER\% = \frac{C_{\text{dil}} \cdot V_{\text{dil}}}{C_0 \cdot V_0} \times 100 = \frac{EF_{\text{dil}} \cdot 30}{3000} \times 100 = EF_{\text{dil}}
\]

(4)

The relative recovery (RR%) was used in the analysis of real water and honey samples. RR was obtained as Eqs. 5:

\[
RR\% = \frac{C_{\text{found}} - C_{\text{real}}}{C_{\text{added}}} \times 100
\]

(5)

where \(C_{\text{found}}\), \(C_{\text{real}}\), and \(C_{\text{added}}\) are the concentration of fungicide after addition of known amount of standard in the real sample, the concentration of analyte in real sample and the concentration of known amount of standard which was spiked to the real sample, respectively.

**Results and discussion**

**Easy collection of the extraction phase after solidification**

The SFO technique is used not only in the second type but also in first type of LPME [20–24]. Methodologies such as DLLME-SFO and USAEME-SFO have been developed and applied to the determination of different target analytes [20–23]. Centrifugation is often required to separate the extraction phase and matrix in these methods. However, according to our experience, the shape of the solidified extraction phase is difficult to control under the following conditions: extractants with low surface tension, such as ionic liquids [25], and a complicated matrix. In the present work, a comparison between DLLME-SFO and DS–SFO was performed to evaluate the applicability of the methods. Solutions of 1-dodecanol and P<sub>4,4,4,12</sub>Tf<sub>2</sub> NTF<sub>2</sub> ionic liquid (1/1, v/v) were used as the extraction phase.

In DS–SFO, the extraction phase kept aggregating and matrix in these methods. However, according to our experience, the shape of the solidified extraction phase is difficult to control under the following conditions: extractants with low surface tension, such as ionic liquids [25], and a complicated matrix. In the present work, a comparison between DLLME-SFO and DS–SFO was performed to evaluate the applicability of the methods. Solutions of 1-dodecanol and P<sub>4,4,4,12</sub>Tf<sub>2</sub> NTF<sub>2</sub> ionic liquid (1/1, v/v) were used as the extraction phase.

In DS–SFO, the extraction phase kept aggregating during the agitation; the shape of solidified microdroplet did not change after lowering the system temperature. In DLLME-SFO, the extraction phase is dispersed into the aqueous sample, then separated from the matrix using centrifugation, and finally solidified in an ice-bath. The solidified extraction phase did not aggregate into a droplet or slice but attached to the inner wall of centrifuge tube in a ring. (see Fig. S2) Therefore, the collection of the extraction phase is much easier in DS–SFO than in DLLME-SFO. In other words, compared with methods using centrifugation, DS–SFO has advantages in a wider selection of extractants.

**Optimization of the directly suspended droplet microextraction with solidified floated organic droplet method**
SELECTION OF THE EXTRACTION SOLVENT

The selection of an appropriate extractant is important for the DS–SFO process because a suitable extractant not only contributes to high extraction efficiency but also facilitate the retrieval of the extraction phase after extraction. The extractant used in this method should fulfill certain requirements, such as a melting point near room temperature (in the range of 15–30 °C), low water solubility and low volatility (so that it is stable during the extraction and can be separated from the analyte peaks in the chromatogram) [26]. Therefore, three extraction solvents, including 1-undecanol (melting point: 13–15 °C), 1-dodecanol (melting point: 22–24 °C), and 1-bromohexadecane (melting point: 17–18 °C), were investigated. 1-Undecanol and 1-dodecanol were found to give similar extraction efficiencies for the fungicides, which were much higher than that of 1-bromohexadecane. The melting point of 1-undecanol is relatively low, which lead to rapid re-melting during collection of the extraction phase. Thus, 1-dodecanol was selected as the extraction solvent in this technique.

OPTIMIZATION OF EXTRACTION TEMPERATURE

The extraction temperature is an important factor not only affecting the state of extractant but also affecting the extraction efficiency of DS–SFO. Considering the melting point of extractant used in this method, 30, 35, 40, 45, and 50 °C were evaluated for the extraction temperature. At the same volume of extractant, EF\text{real} and ER\% had a fixed relationship expressed by $EF_{\text{real}} = 3/2 \cdot EF_{\text{rel}}$. Both of these values are proportional to the ER, so ER was monitored, and the result is shown in Fig. 2. It can be observed that for all the fungicides, the recovery decreased when the extraction temperature increased, which could be due to a reduction in the oil/water partition coefficient of the reduced at high temperatures, and the mass transfer also required a longer equilibrium time in the extractions. Therefore, a higher extraction temperature may prevent a smooth extraction, the extraction at 30 °C was proven to be the best and was used in the ensuing experiments.

OPTIMIZATION OF EXTRACTION TIME

For precision and sensitivity in the DS–SFO method, a reasonable extraction time is necessary to guarantee equilibrium between the samples and extractants [27] and appropriate recovery of the fungicides. A series of experiments were conducted and the extraction time profile was obtained by drawing the recovery versus the extraction time in the range of 30 – 120 min for each fungicide. Fig. 3 shows the influences of the extraction time on the method efficiency. By increasing the extraction time, the recovery of cyprodinil and trifloxystrobin increased monotonically; recovery of chlorothalonil and triadimefon increased from 30 to 75 min, and decreased slightly.
Fig. 3. The effects of the extraction time on the recoveries of fungicides at a spiked concentration of 100 ng mL\(^{-1}\), sample volume of 3 mL, extractant volume of 20 μL, extraction temperature at 30 °C, stirring rate of 900 rpm, and no salt addition.

Fig. 4. The effects of the stirring speed on the recoveries of fungicides at a spiked concentration of 100 ng mL\(^{-1}\), sample volume of 3 mL, extractant volume of 20 μL, extraction temperature at 30 °C, extraction time of 90 min, and no salt addition.

for longer times. Because the recovery of chlorothalonil and triadimefon were less than cyprodinil and trifloxystrobin and peak area of triadimefon is relatively low in HPLC-DAD, a 90-min exposure time was selected as a compromise and used in subsequent experiments.

Optimization of the Stirring Speed

An appropriate stirring speed is very important for effective extraction in the DS–SFO method. It not only enhances the extraction efficiency but also reduces the extraction time [28]. Based on penetration theory, the aqueous phase mass-transfer coefficient increases with increasing stirring speed [29]. In the optimization, sample solutions were continuously agitated at different stirring speeds (600, 700, 800, 900, and 1,000 rpm) using a magnetic stirrer and a 10-mm stirring bar. The recoveries of each extraction were shown in Fig. 4. All the ERs increased when the speed increased from 600 to 900 rpm; a significant decrease was observed when the stirring speed was further increased. When the stirring speed was 1,000 rpm, the organic droplet was not able to remain stably suspended under the sample surface and broke into several smaller microdrops. Stirring the sample with too high of a speed had the opposite effect on the extraction efficiency. Therefore, a stirring rate of 900 rpm was chosen for further studies.

Optimization of the Salt Addition

In organic-based ME procedures, the salting-out effect can promote the separation of the aqueous solution and organic phase by lowering the solubility of the organic solvent in water (commonly used in LLE and SPME [30, 31]). However, the results may be different in LPME. In this work, the effect of salt addition on the extraction efficiency was evaluated by increasing the NaCl ratio from 0 to 20% (w/w) in the spiked sample solutions. Fig. 5 shows that the recovery of trifloxystrobin decreased significantly, and the recovery of the other three decreased slightly after adding different concentrations of NaCl. A decrease in the extraction efficiency at higher salt concentrations can be explained by the fact that the addition of salt can restrict the transportation of the analytes to the extractant drop due to an increase of the sample viscosity. In addition, NaCl dissolved in water might have changed the physical properties of the Nernst diffusion film and reduced the diffusion rate of the target analytes into the organic solvent [32]. The extraction efficiencies of the no salt addition and 5% NaCl addition were not significantly different. Considering the low concentrations of salts in the real samples, no salt was added to the samples in all subsequent experiments.

Fig. 5. The effects of the salt addition on the recoveries of fungicides at a spiked concentration of 100 ng mL\(^{-1}\), sample volume of 3 mL, extractant volume of 20 μL, extraction temperature at 30 °C, and extraction time of 90 min.
Based on the method described above, the optimal conditions for DS–SFO were determined to be a 3-mL sample of water or diluted honey, 1-dodecanol as the organic extractant, a 20-µL microdroplet volume, an extraction temperature of 30 °C, a 90-min extraction time, a 900-rpm stirring speed, and no salt addition. The method was evaluated in terms of its linearity, limits of detection, precision, and extraction recovery under the optimized conditions. A calibration study was performed by spiking blank water and honey samples with fungicides over the concentration range of 5–1000 ng mL\(^{-1}\). The correlation coefficient (\(r\)) ranged from 0.9996–0.9999 for the water samples and from 0.9980–0.9997 for the honey samples. The extraction recovery of the fungicides ranged from 80 to 93% in the water samples and from 70 to 83% in the honey samples. Such high extraction recoveries of target analytes were first reported using DSDME approaches. The precision was obtained by performing six replicates of water and diluted honey samples at spiked levels of 100 ng mL\(^{-1}\) and 50 ng mL\(^{-1}\), respectively. The RSDs of these water samples ranged from 4.8% to 7.1%. The sensitivity was evaluated in terms of the LOD and 50 ng mL\(^{-1}\) for the honey samples. The results are shown in Table 1.

Comparison of the proposed method with other preconcentration techniques

A comparison of the proposed method with other analytical methodologies [33–38] was summarized in Table 3. It can be observed that the proposed DS–SFO method provided good analytical features in terms of linearity, LOD, and enrichment factor. Most of the results are comparable to the other reported methodologies using expensive detection instruments. For this process, hazardous chlorinated extractants and large amounts of dispersants were not required, only a small amount of green solvent was used. In addition, centrifugation or demulsification can be avoided, which leads to a very simple, low cost and efficient method. In general, DS–SFO was proven to be a reliable and extensible alternative for the determination of target analytes in different matrices.

Conclusions

In the present study, a DS–SFO method was proposed for the preconcentration of four fungicides prior to analysis by HPLC-DAD. The method not only provided high extraction recovery, a low detection limit, and good accuracy and precision but also...
Table 2. Recoveries and RSDs for the blank and spiked samples using the DS–SFO-HPLC-DAD method

<table>
<thead>
<tr>
<th>Sample Added</th>
<th>Honey sample</th>
<th>Fuzhou</th>
<th>Fengxian</th>
<th>Water sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lake</td>
</tr>
<tr>
<td>Sample</td>
<td>Added</td>
<td>RR(%)</td>
<td>RSD(%)</td>
<td></td>
</tr>
<tr>
<td>Honey sample</td>
<td>0</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>111</td>
<td>2.4</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>110</td>
<td>4.7</td>
<td>110</td>
</tr>
<tr>
<td>Fuzhou</td>
<td>0</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>97</td>
<td>2.4</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>98</td>
<td>4.5</td>
<td>94</td>
</tr>
<tr>
<td>Fengxian</td>
<td>0</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>99</td>
<td>6.3</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>104</td>
<td>4.0</td>
<td>105</td>
</tr>
<tr>
<td>Water sample</td>
<td>Lake</td>
<td>0</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>92</td>
<td>6.7</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>95</td>
<td>3.8</td>
<td>93</td>
</tr>
<tr>
<td>Paddy field</td>
<td>0</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>99</td>
<td>4.6</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>97</td>
<td>2.0</td>
<td>97</td>
</tr>
<tr>
<td>Tap</td>
<td>0</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>106</td>
<td>1.5</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>97</td>
<td>3.9</td>
<td>98</td>
</tr>
</tbody>
</table>

*a Units of the spike levels were ng mL⁻¹ for the diluted honey and water samples

*b RR is the relative recovery

*c Three replicates were performed to obtain the RSD values

Table 3. Comparison of DS–SFO with other methods for the determination of fungicides

<table>
<thead>
<tr>
<th>Fungicides</th>
<th>Method</th>
<th>Matrix</th>
<th>Extractant</th>
<th>Dispersant/ emulsifier</th>
<th>EF</th>
<th>Linear range (ng mL⁻¹)</th>
<th>LOD (ng mL⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triadimefon</td>
<td>DLLME-HPLC-DAD</td>
<td>Water</td>
<td>chloroform</td>
<td>acetoniitrile</td>
<td>157</td>
<td>30-1500</td>
<td>8.5</td>
<td>[34]</td>
</tr>
<tr>
<td>Triadimefon</td>
<td>SPE(C18)-UHPLC-ESI-MS/MS</td>
<td>Alcohol</td>
<td>methanol</td>
<td>(elution solvent)</td>
<td>-</td>
<td>1-125</td>
<td>0.06</td>
<td>[35]</td>
</tr>
<tr>
<td>Chlorothalonil</td>
<td>SD-DLLME-GC/MS</td>
<td>Water</td>
<td>n-xylene</td>
<td>acetoniitrile</td>
<td>55</td>
<td>0.2-50</td>
<td>0.013</td>
<td>[36]</td>
</tr>
<tr>
<td>Chlorothalonil</td>
<td>DLLME-GC/IT/MS</td>
<td>Honey</td>
<td>chloroform</td>
<td>acetoniitrile</td>
<td>94</td>
<td>0.1-5</td>
<td>0.02</td>
<td>[37]</td>
</tr>
<tr>
<td>Cyprodinil</td>
<td>UASEME-SFO-HPLC-DAD</td>
<td>Water</td>
<td>1-dodecanol</td>
<td>tween 80</td>
<td>-</td>
<td>5-200</td>
<td>0.4</td>
<td>[38]</td>
</tr>
<tr>
<td>Trifloxystrobin</td>
<td>UASEME-SFO-HPLC-VWD</td>
<td>Fruit juice</td>
<td>1-undecanol</td>
<td>tween 80</td>
<td>134</td>
<td>10-10000</td>
<td>4</td>
<td>[39]</td>
</tr>
<tr>
<td>Four fungicides</td>
<td>TC-DS-SFO-HPLC-DAD</td>
<td>Honey, water</td>
<td>1-dodecanol</td>
<td></td>
<td>70-93</td>
<td>5-10000</td>
<td>0.2-1.95</td>
<td>present study</td>
</tr>
</tbody>
</table>

*a Ultra performance liquid chromatography–tandem mass spectrometry (UHPLC-ESI-MS/MS)

*b Solvent-based de-emulsification dispersive liquid–liquid microextraction (SD-DLLME) combined with gas chromatography–mass spectrometry (GC/MS)

*c Gas chromatography and ion trap mass spectrometry (GC-IT/MS)

showed reliability with an analytical detection range that is well-suited for applications in water and honey samples. Compared with the conventional sample preparation methods, DS–SFO-HPLC–DAD offers many advantages, such as minimal green organic solvent consumption (which makes this method more environmentally friendly), no requirement for...
special devices and easy retrieval of the extractant (which makes this method low cost and simple). The technique may easily be converted into a high-throughput and automated operation. Therefore, DS–SFO-HPLC possesses great potential in the analysis of trace compounds in many complicated matrices.

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Notes and references