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Matrix solid-phase dispersion coupled with magnetic ionic liquid dispersive liquid–liquid microextraction for the determination of triazine herbicides in oilseeds

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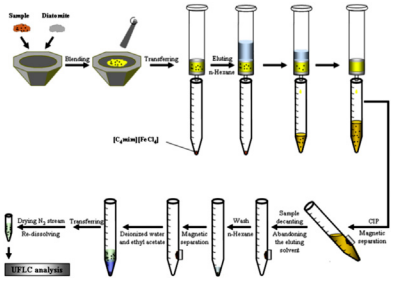
HIGHLIGHTS

- Magnetic ionic liquid was first used as a microextraction solvent for fatty solid samples.
- Magnetic separation of the ionic liquid met the requirement of rapid analysis.
- The performances achieved by the present method were acceptable.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel method was developed for the determination of six triazine herbicides from oilseeds by matrix solid-phase dispersion combined with magnetic ionic liquid dispersive liquid–liquid microextraction (MSPD-MIL-DLLME), followed by ultrafast liquid chromatography with ultraviolet detection (UFLC-UV). The MIL, 1-butyl-3-methylimidazolium tetrachloroferrate ([C_4mim][$FeCl_4$]), was used as the microextraction solvent to simplify the extraction procedure by magnetic separation. The effects of several important experimental parameters, including type of dispersant, ratio of sample to dispersant, type and volume of collected elution solvent, type and volume of MIL, were investigated. Using the present method, UFLC-UV gave the limits of detection (LODs) of 1.20–2.72 ng g^{-1} and the limits of quantification (LOQs) of 3.99–9.06 ng g^{-1} for triazine herbicides. The recoveries were ranged from 82.9 to 113.7% and the relative standard deviations (RSDs) were equal or lower than 7.7%. The present method is easy-to-use and effective for extraction of triazine herbicides from oilseeds and shows the potentials of practical applications in the treatment of the fatty solid samples.

1. Introduction

Oilseeds, which refer to the seeds of vegetables and grains containing high oil contents, are conventional sources for edible oils. In order to improve the yield and quality of oilseeds, herbicides are widely used to control the growth of weeds in farmland [1,2]. Studies have concluded that triazine herbicides represent potentials for toxic effects on human health, including birth defects, cancers and interruption of hormone functions [3]. Therefore, the herbicide residues in agricultural products and foods become a serious concern [4,5]. In European Union (EU), maximum residue limits (MRLs) of common triazine herbicides in oilseeds are in the

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range of 0.05–0.10 mg kg^{-1} (Commission Directive 2008/149/EC).

During the analyses of herbicide residues at trace level in oilseeds, the fat co-extractives, which are due to the large amounts of fat in oilseeds, is not beneficial to the extraction efficiency and analytical performance of the target analytes [6]. So the developments of techniques for effective extraction and cleanup of trace herbicide residues in fatty matrices are necessary.

Generally, solvent-based extraction methods, such as liquid–solid extraction (LSE) [6–8], microwave-assisted extraction (MAE) [9] and focused microwave-assisted Soxhlet extraction (FMASE) [10] are the main methods for extracting analytes from fatty solid samples. However, most of these traditional solvent-based extraction methods usually require large amount of toxic organic solvents and are time-consuming. The sorbent-based extraction techniques with low solvent consumption, including solid-phase extraction (SPE) [9,10] and dispersive solid-phase extraction (dSPE) [8], are usually employed for the cleanup of interference substances in the extracts obtained by the above traditional solvent-based methods. Based on the combination of solvent-based extraction and dSPE cleanup, the quick, easy, cheap, effective, rugged, and safe (QuEChERS) method was developed and applied to the treatment of fatty samples [6,11,12]. The common sorbents used in QuEChERS include florisil [9,10], primary secondary amine (PSA), C18 and graphitized carbon black (GCB) [6,11,12].

In recent years, matrix solid-phase dispersion (MSPD) was developed for the treatment of solid or semisolid samples by disrupting and dispersing the matrix in a solid phase sorbent [13,14]. Compared with other solvent-based extraction methods, the main advantages of MSPD include simplicity, efficiency, and low consumption of toxic solvents [15,16]. As an alternative to conventional liquid–liquid extraction, dispersive liquid–liquid microextraction (DLLME), in which microliter volumes of extraction solvent is used, has attracted much attention because of its relatively high extraction efficiency [17]. There are many reports about the extraction of analytes by DLLME in aqueous solutions [18–20], while applications of DLLME in fatty matrices are limited [21].

Ionic liquids (ILs) are well-known organic molten salts with low melting points produced from the combinations of organic cations and various anions [22,23]. ILs exhibit unique physicochemical properties, such as high chemical and thermal stabilities, low to negligible vapor pressures, wide ranges of viscosities, and lower toxicity than some organic solvents [24]. These properties make ILs useful in sample preparation techniques, especially in DLLME [17,19,24]. Recently, a class of novel magnetic ionic liquids (MILs) has been developed, which can favorably combine the above excellent properties of ILs with magnetic property [25–27]. These properties give MILs more advantages and potential application prospects than conventional solvents in separation processes. The magnetic property of MILs with metal-containing anions, which was not known until the paramagnetic behavior of 1-butyl-3-methylimidazolium tetrachloroferrate ($[C_4mim][FeCl_4]$) was found [28], makes the magnetic isolation of MILs from matrices possible. However, most MILs are miscible with water or polar solvents for the existence of protonated cations and the hydrophilic tetrachloro- or tetrabromoferrate (III) anions, which severely limit their applications in aqueous solutions. On the contrary, MILs are generally immiscible with hydrophobic solvents [29]. In our previous work, a MIL, 1-hexyl-3-methylimidazolium ($[C_6mim][FeCl_4]$), was used as a microextraction solvent in DLLME for liquid fatty samples dispersed in n-hexane [30]. It will also be interesting to use MILs in the extraction of analytes from solid fatty samples.

In this study, a novel MSPD-MIL-DLLME method was developed and applied to the extraction of six triazine herbicides from oilseeds. In order to speed up the magnetic separation of MIL after DLLME, carbonyl iron powder (CIP) was used to form a combination of CIP and MIL (CIP-MIL). By using this method, the elution and cleanup can be accomplished in one step. Several experimental conditions, including type of dispersant, ratio of sample to dispersant, type and volume of collected elution solvent, type and volume of MIL, were investigated and optimized. The triazine herbicides in final extracts were separated and determined by ultrafast liquid chromatography with ultraviolet detection (UFLC-UV).

2. Experimental

2.1. Chemicals and reagents

Six triazine herbicides, including desmetryn, secbumeton, terbumeton, terbutryn, dimethametryn and dipropetryn, were purchased from Chinese National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). The chemical structures of these triazine herbicides are shown in Fig. 1. Stock solutions of each triazine herbicide were prepared in acetonitrile at the concentration of 500 μg mL^{-1} and stored at 4 °C. Working and mixed working solutions were prepared by diluting the stock solutions with acetonitrile.

Chromatographic grade acetonitrile was purchased from Fisher Scientific Company (UK). $[C_4mim][FeCl_4]$ and $[C_6mim][FeCl_4]$ were purchased from Chengjie Chemical Co. LtD (Shanghai, China). Silica gel (200–300 mesh), neutral alumina (200–300 mesh), florisil (60–100 mesh), quartz sand (25–50 mesh) and diatomite (200–300 mesh) were obtained from Chinese Medical and Biological Products Institute (Beijing, China). CIP (3.5 μm) was purchased from Jilin Jien Nickel Industry (Panshi, China). PSA (50 μm), C18 (50 μm) and GCB (50 μm) were purchased from Bonna-Agela Technologies (Beijing, China). All other reagents were of analytical grade and purchased from Beijing Chemical Factory (Beijing, China). Deionized water was obtained with a Milli-Q water purification system (Millipore, USA).

2.2. Instruments

Ultrafast liquid chromatographic analyses were carried out on a LC-20ADXR liquid chromatograph (Shimadzu, Japan) with two LC-20AD pumps, a SIL-20A autosampler, and a SPD-20A UV/VIS detector. All separations were performed using a VP-ODS column (150 mm × 4.6 mm, 4.6 μm particle size, Shimadzu, Japan).

2.3. Samples

Seven oilseed samples, including three soybean samples (sample 1–3), two peanut samples (sample 4–5) and two sunflower seed samples (sample 6–7), were purchased from local markets (Changchun, China). The samples were triturated with a pulverizer, passed through a 40 mesh stainless steel sieve and stored at 4 °C. The spiked samples were prepared by spiking the mixed working solutions into samples and stored for 24 h in the dark. Except for the experiments mentioned in Section 3.2.4, all other experiments were carried out with sample 1.

2.4. Extraction procedure

2.4.1. MSPD-MIL-DLLME

1.0 g of sample and 0.5 g of diatomite were placed in an agate mortar and thoroughly blended using a pestle for 5 min to obtain a homogeneous mixture. A glass column (2 cm internal diameter and 10 cm length) was packed from bottom to top with a layer of absorbent cotton, 0.3 g of diatomite, the homogeneous sample-sorbent mixture, and a second layer of absorbent cotton. The