



Magnetic ionic liquid-based dispersive liquid–liquid microextraction for the determination of triazine herbicides in vegetable oils by liquid chromatography



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ABSTRACT

Magnetic ionic liquid-based dispersive liquid–liquid microextraction (MIL-based DLLME) was developed for extracting triazine herbicides from vegetable oils. The MIL, 1-hexyl-3-methylimidazolium tetrachloroferrate ($[\text{C}_6\text{mim}][\text{FeCl}_4]$), was used as the microextraction solvent. The magnetic separation time was shortened by simply mixing carbonyl iron powder with the MIL in the sample after DLLME. The effects of several important experimental parameters, including the amount of MIL, the time of ultrasonic extraction, the type and the volume of cleanup solvent were investigated. The MIL-based DLLME coupled with liquid chromatography gave the limits of detection of $1.31\text{--}1.49\text{ ng mL}^{-1}$ and limits of quantification of $4.33\text{--}4.91\text{ ng mL}^{-1}$ for triazine herbicides. When the present method was applied to the analysis of vegetable oil samples, the obtained recoveries were in the range of 81.8–114.2% and the relative standard deviations were lower than 7.7%. Compared with existing methods, the performances achieved by the present method were acceptable.

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1. Introduction

Triazine herbicides are a class of pre- and post-emergent broadleaf herbicides with similar chemical structure that inhibit the growth of weeds through disruption of photosynthesis pathways [1]. These herbicides, such as atrazine, cyanazine, and desmetryn, are used widely for maize, sorghum, citrus orchards, and grapes [2]. Because of the prolonged and widespread use, the residues of the herbicides have been found in a lot of agriculture products [3,4]. The study has indicated that some triazine herbicides are suspected to cause cancers, birth defects, and interruption of hormone functions [5]. Consequently, there is a growing need to monitor triazine herbicides in agriculture products.

Vegetable oils which are mainly composed of triglycerides, are commonly extracted from plant seeds, i.e., the oilseeds, such as the seeds of soybean, maize, and sunflower. Pesticide residues in these seeds may be transferred to vegetable oils during the oil extraction process. Maximum residue limits (MRLs) in the range of $0.05\text{--}0.1\text{ mg kg}^{-1}$ for the residues of some triazine herbicides in oilseeds are established by the European Union (Commission Directive 2008/149/EC), while the MRLs for triazine herbicide

residues in vegetable oils have not been established. Therefore, a sensitive and accurate method for determination of triazine herbicides in vegetable oils is particularly important to guarantee public health and safety. To the best of our knowledge, the available literatures on determination of triazine herbicides in vegetable oils are very limited [6,7].

Extraction and cleanup are the most challenging parts for determination of pesticide residues in food stuffs, especially in vegetable oils with inherent complex fatty matrices [8]. Additionally, the low concentrations of pesticide residues in oil samples also make the direct determining of them difficult by chromatographic methods, such as liquid chromatography (LC) or gas chromatography (GC) [9]. Therefore, there is a need to employ exhaustive sample preparation technique for the extraction and preconcentration of the residues from oil samples before determination. Various sample preparation techniques, such as liquid–liquid extraction (LLE) [6–8,10,11] and low-temperature fat precipitation (LTFP) [12,13], have been widely applied to the extraction and preconcentration of target analytes from fatty samples. However, traditional LLE need time-consuming operating procedure and large amount of organic solvents, and LTFP usually takes a long time to precipitate fats in samples. Other preparation techniques, including solid-phase extraction (SPE) [8,10,13], matrix solid-phase dispersion (MSPD) [7,9], and dispersive solid-phase extraction (dSPE) [11] were commonly coupled with the above-mentioned

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techniques and applied for the clean-up. In recent years, research efforts on sample preparation techniques have been directed toward simplifying the extraction procedure, saving operating time and reducing the consumption of organic solvents.

Since dispersive liquid–liquid microextraction (DLLME) was proposed by Assadi and coworkers [14], this method has attracted much attention owing to its significant advantages including small solvent usage of microliter volumes, rapidity and high enrichment factor. DLLME is a promising alternative to the classic LLE and has been widely applied to the extraction of target analytes in water-soluble samples [15–17], while there are only a couple of reports about the application of DLLME in the sample preparation of fat-soluble vegetable oils [18,19].

Ionic liquids (ILs) are a class of organic salts with low melting points [20]. The unique properties of ILs, including negligible vapor pressure, good chemical and thermal stability, excellent solubility for both organic and inorganic compounds, and environmental friendliness [21,22], make them promising extraction solvents used in separation [16,17,23]. The combinations of different organic cations with various organic or inorganic anions leads to a large amount of ILs with numerous possible applications, and ILs with special properties can also be designed through proper chemical modifications [24].

Nowadays, developments and applications of magnetizable ILs become a new field and a hotspot of research in sample preparation techniques [25–28]. Generally, ILs were bonded or immobilized on the surface of magnetic supports to form solid materials and used as magnetic adsorbents in magnetic solid-phase extraction [25–27], while only few publications reported on the metal-containing ILs, which incorporated the metal in the ILs to introduce magnetic property [28]. Recently, a novel class of magnetic ionic liquids (MILs) with single-component was discovered, of which the magnetic property is no longer introduced as external magnetic supports, but provided by complex ions of metals [26,29,30]. The first example of MILs is 1-butyl-3-methylimidazolium tetrachloroferrate ($[\text{C}_4\text{mim}][\text{FeCl}_4]$). Although the compound has been known for some time [31], its magnetic behavior was not described until 2004 [32]. These MILs are basically based on the anions containing high-spin d^5 iron (III), which were in the forms of tetrachloro- or tetrabromoferrate (III), with varieties of counter cations. Because of their high single-ion magnetic moments, MILs show a good response to an external magnetic field [28], and are very interesting to be employed as novel extraction solvents to take the place of routine nonmagnetic ILs of DLLME. The MILs can be uniformly dispersed in sample solutions through ultrasound irradiation and can be isolated from the solutions by means of an external magnetic field. However, to our knowledge, there is only one report about the application of MILs on separation of target analytes, in which the MIL was used for solvent extraction of phenolic compounds from aqueous solution [33]. Because MILs contain polar functional groups, such as protonated primary amines and esters, as well as the hydrophilic tetrachloroferrate (III) anions, most MILs are miscible with water or other polar solvents after vigorous shaking, which restrict their applications of separation and concentration of analytes dissolved in water. In contrast, they are immiscible with hydrophobic solvents such as carbon tetrachloride and *n*-hexane [26]. Herein, MILs are promising microextraction solvents of DLLME for vegetable oils.

In this study, 1-hexyl-3-methylimidazolium tetrachloroferrate ($[\text{C}_6\text{mim}][\text{FeCl}_4]$) was selected as the microextraction solvent of the MIL-based DLLME for extracting triazine herbicides from vegetable oils, including two soybean oils, three maize oils and two sunflower seed oils. In addition, carbonyl iron powder (CIP) was added to shorten magnetic separation time after DLLME, which can be magnetically attracted by the MIL to form a combination of CIP and MIL (CIP-MIL). Several important experimental

parameters, such as the amount of MIL, the time of ultrasound extraction, the type and the volume of cleanup solvent, were optimized. Under the optimized conditions, the present method was successfully applied to the analysis of real vegetable oil samples

2. Experimental

2.1. Chemicals and reagents

Chromatographic grade acetonitrile was purchased from Fisher Scientific Company (UK). $[\text{C}_6\text{mim}][\text{FeCl}_4]$ (>99%) was purchased from Chengjie Chemical Co. LTD (Shanghai, China). CIP with average particle size less than $4.30\ \mu\text{m}$ (Purity > 97.8%) was purchased from Jilin Jien Nickel Industry (Panshi, China). Padding materials of primary secondary amine (PSA, $50\ \mu\text{m}$), C18 ($50\ \mu\text{m}$) and graphitized carbon black (GCB) were purchased from Bonna-Agela Technologies. 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, New York, USA).

Standards of cyanazine, desmetryn, secbumeton, terbutryn, dimethametryn and dipropetryn were obtained from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). The chemical structures of these herbicides are shown in Fig. 1. Stock solutions were prepared by dissolving each substance in chromatographic grade acetonitrile at a concentration of $400\ \mu\text{g mL}^{-1}$ and stored at 4°C in darkness. Mixed working solutions at desirable concentrations were prepared by mixing the stock solutions followed by diluting with chromatographic grade acetonitrile.

2.2. Instruments

LC analyses were performed using a LC-20ADXR liquid chromatograph (Shimadzu, Japan) with two pumps (LC-20AD), an autosampler (SIL-20A), a column oven (CTO-20A) and a UV–vis detector (SPD-20A). Chromatographic separation of the analytes were carried out using a shim-pack VP-ODS column ($150\ \text{mm} \times 4.6\ \text{mm}$, $4.6\ \mu\text{m}$ particle size). Relevant data acquisition and processing were accomplished with Shimadzu LC solution software.

The KQ-100 ultrasonic cleaner was purchased from Kunshan Ultrasonic Instrument Co., Ltd. (Kunshan, China). The frequency and output power of the ultrasonic cleaner are 40 kHz and 100 W, respectively.

2.3. Samples

The vegetable oil samples were purchased from local supermarkets. Seven vegetable oil samples, including 2 soybean oil (sample 1, 2), 3 maize oils (sample 3–5) and 2 sunflower seed oil (sample 6, 7) were analyzed. The samples used for recovery and precision studies were previously analyzed. The experimental results showed that there was no peak at the retention positions of the analytes in the chromatograms obtained with the sample extracts. The target pesticides in the samples were undetectable. Spiked samples containing triazine herbicides were prepared by spiking the mixed working standard solutions into samples. After being well mixed, the samples were equilibrated for 1 h in the dark at room temperature. All the experiments were carried out with sample 1 except for those mentioned in Section 3.2.4 in which all samples (sample 1–7) were used.

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