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Headspace ionic liquid-based microdrop liquid-phase microextraction followed by microdrop thermal desorption-gas chromatographic analysis

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ABSTRACT

Headspace microdrop liquid-phase microextraction (LPME) using ionic liquids as extracting solvents, followed by gas chromatography–electron capture detection was successfully developed to determine organochlorine pesticides in soil samples. A feature of the developed procedure is the simple handling of the ionic liquid extract in a normal, unmodified gas chromatograph injection port such that no special provision was needed to ensure that the ionic liquid did not contaminate it. This was achieved by only exposing the ionic liquid extract in the injection port while it was still attached to the syringe needle tip (i.e. mirroring the extraction configuration) to permit volatilization of the analytes, instead of injecting the extract. In this way, the spent ionic liquid could be recovered from the injection port, obviating the need to clean the port. Four 1-butyl-3-methylimidazolium-based ionic liquids were investigated, and 1-butyl-3-methylimidazolium hexafluorophosphate was finally selected as the most suitable extracting solvent. Parameters that affect the extraction and determination of the organochlorine pesticides were studied. Under the optimal conditions, the proposed method produced good linearity over a concentration range of 5–250 ng/g. Limits of detection ranging from 0.25 to 0.5 ng/g were achieved.

1. Introduction

Headspace microextraction techniques provide the possibility of determination of volatile and semivolatile compounds in soil samples or other complex matrices [1]. Headspace solid-phase microextraction (SPME), in which a sorbent-coated rod is exposed to the headspace of sample solution, have been applied to determine pesticides [2–4], chlorinated benzenes [5], polycyclic aromatic hydrocarbons (PAHs) [6,7] and other volatile or semivolatile organic compounds [8–13]. In the past few years, alternatives to SPME such as headspace microdrop liquid-phase microextraction (LPME), or single-drop microextraction, in which a drop of a relatively high boiling organic solvent is exposed to the headspace of a sample matrix to extract organic compounds, has been applied to environmental analysis [14–17]. Since solvent and a microsyringe only are involved, headspace LPME has the advantages of low cost and easy operation without any sample carryover [18]. There are some requirements in choosing a solvent for this procedure. Firstly, it should have a low vapor pressure so that it will not evaporate during the extraction procedure. In addition, the solvent peak produced by the extraction solvents should not interfere with the chromatographic analysis of the target analytes [15].

Room temperature ionic liquids have recently emerged as alternatives to organic solvents in LPME [19,20]. They are usually composed of large asymmetric organic cations and inorganic or organic anions. In contrast to inorganic salts like sodium chloride, ionic liquids exhibit significantly lower melting temperatures. Ionic liquids show good thermal stability and high densities, thus hastening phase separation in liquid–liquid partition [21,22]. Because of their thermal stability, ionic liquids are good alternatives to conventional organic solvents when headspace microdrop LPME is applied to different environmental samples, in which heat is usually applied to accelerate extraction efficiency [23–26]. They have negligible vapor pressure, which reduces the possibility of generating potentially toxic vapors as in the case of organic solvents. Ionic liquids are able to dissolve a lot of organic compounds [27,28]. Importantly, ionic liquids are commonly regarded as “designer solvents”. This term highlights the possibility to fine tune their physical and chemical properties to suit the requirement of a particular chemical, or extraction procedure [29]. By varying the length and branching of the alkyl chain and the anionic component, properties such as melting point, viscosity, density and hydrophobicity can be changed. By such variation, the number of ionic liquids is estimated to be of the order of 1 billion [30]. Thus, the choice of ionic liquids is virtually limitless. In LPME applications, however, the direct injection of an ionic liquid extract into the injection port of a gas chromatograph poses a problem since it has such low volatility and results in the contamination of the port. Very recently,

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some approaches have been developed [31–33] to prevent contamination of the GC injection port, including a specific custom-made interface [31,32] or a modification of the injection liner that allowed the ionic liquid extract to be exposed only in the port (no injection is involved) [33].

In the present study, headspace microdrop LPME using an ionic liquid as extracting solvent followed by gas chromatography–electron capture detection (GC–ECD) was developed. The simple approach did not require any specially fabricated interface or modification of the injection port or injection liner to prevent contamination by the ionic liquid. In this procedure, the latter extract was simply exposed, while still attached to the syringe needle tip, in the injection port for analyte "desorption," in a manner identical to the headspace LPME process. The procedure was evaluated for the determination of organochlorine pesticides (OCPs) in soil. OCPs are examples of some of the most persistent and harmful organic pollutants present in the environment [34], and are thus of important interest in environmental analysis.

Table 1
Physical properties of organochlorine pesticides.

Analyte	CAS	log K_{ow}	Henry's law constant (Pa m^3/mol)
BHC	319-84-6	3.80	1.22
Heptachlor	76-44-8	6.10	29.4
Aldrin	309-00-2	6.50	4.4
Endosulfan (I)	959-98-8	3.83	0.71
Dieldrin	60-57-1	5.40	1.00

2. Experimental

2.1. Standards and reagents

The pesticides α-hexachlorocyclohexane (BHC), heptachlor, aldrin, endosulfan (I) and dieldrin were purchased from Polyscience (Niles, IL, USA). The structures of these pesticides are shown in Fig. 1. Their physical properties are listed in Table 1. Liquid chromatography-grade methanol was purchased from Fisher Sci-

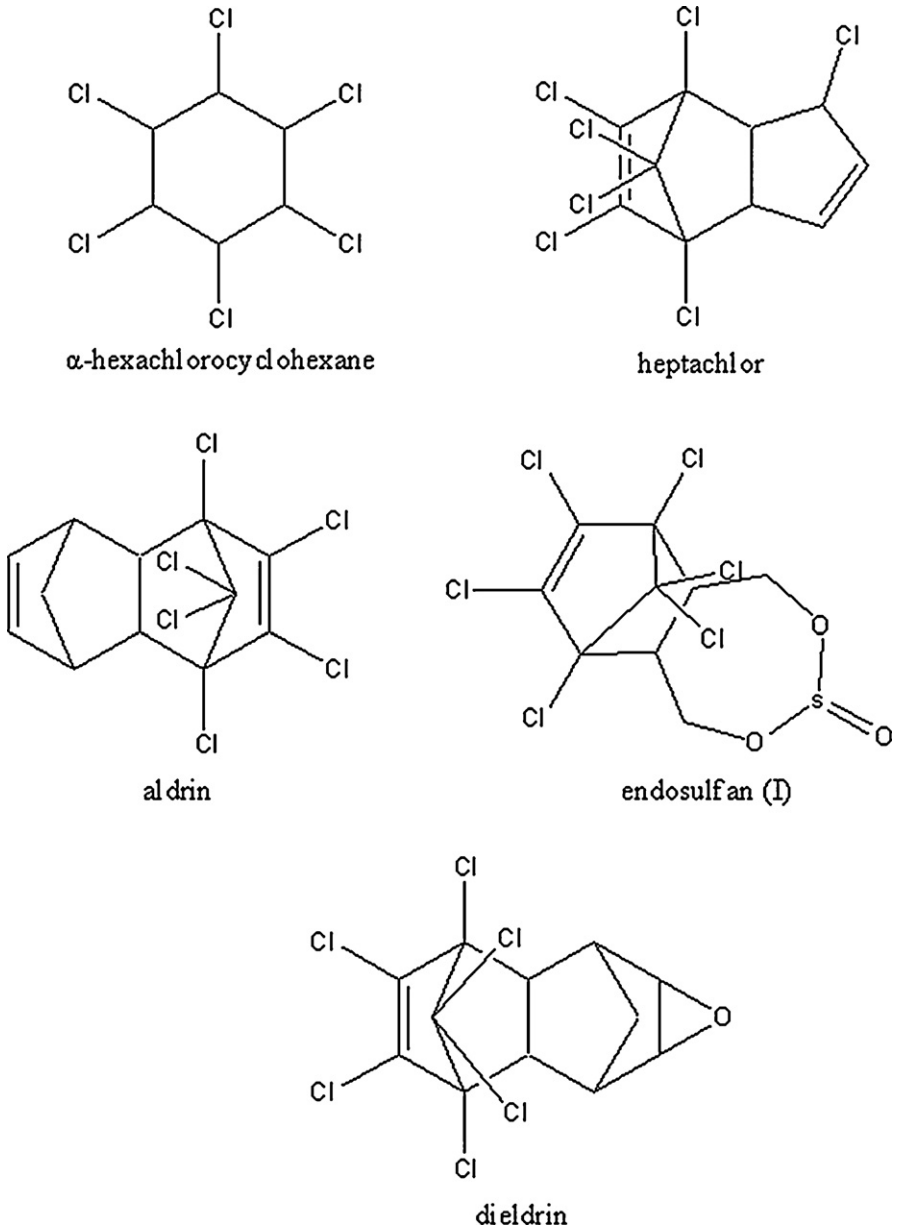

Fig. 1. Structures of OCPs considered.

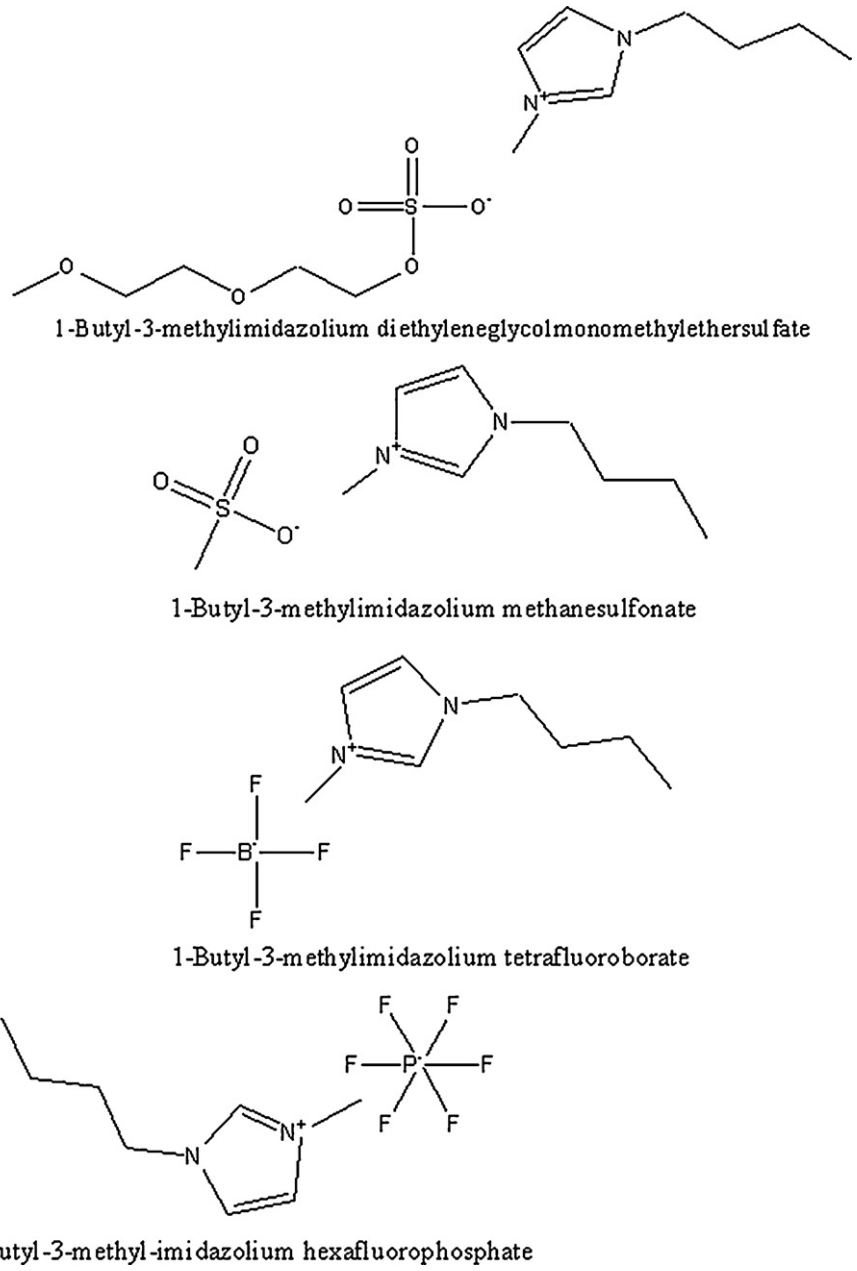

Fig. 2. Structures of the ionic liquids considered.

entific (Fair Lawn, NJ, USA). Purified water was obtained from a Nanopure system (Barnstead, IA, USA). A standard stock solution mixture containing 10 μg/mL of each of the OCPs was prepared in methanol. The solution was stored in the refrigerator until needed. A fresh working solution containing 1 μg/mL of each analyte, whenever needed, was prepared by dilution from the stock solution with methanol.

The ionic liquids considered in this work were 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) (purchased from Merck, Darmstadt, Germany), and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]), 1-butyl-3-methylimidazolium diethyleneglycol monomethylethersulfate ([BMIM][$MEDGSO_4$]), and 1-butyl-3-methylimidazolium methylsulfate ([BMIM][$MeSO_4$]) which were bought from Strem Chemicals (Newburyport, MA, USA). The structures of these ionic liquids are shown in Fig. 2.

Acid-washed sea sand supplied by Goodrich Chemical Enterprise (Avon Lake, OH, USA) was used for optimization of the LPME method. Freshly spiked soil sample were prepared by adding an appropriate volume of the working solution to the soil sample. The spiked soil was homogenized by shaking carefully using a Vortex-Genie®2 (model G-560E, Scientific Industries, Inc., Bohemia, NY, USA). The spiked soil sample was air-dried overnight and extracted directly thereafter. Natural soil samples were collected from sites near a highway and air-dried, ground and sieved through a 60-mesh sieve. It was stored for 2 months before processing.

2.2. Headspace LPME

A 10-μL microsyringe, with a 22° bevel-tipped needle (Model MS-GF10, ITO Corp., Fuji, Japan) was used for LPME. The extraction and thermal desorption setup are illustrated in Fig. 3. Briefly,

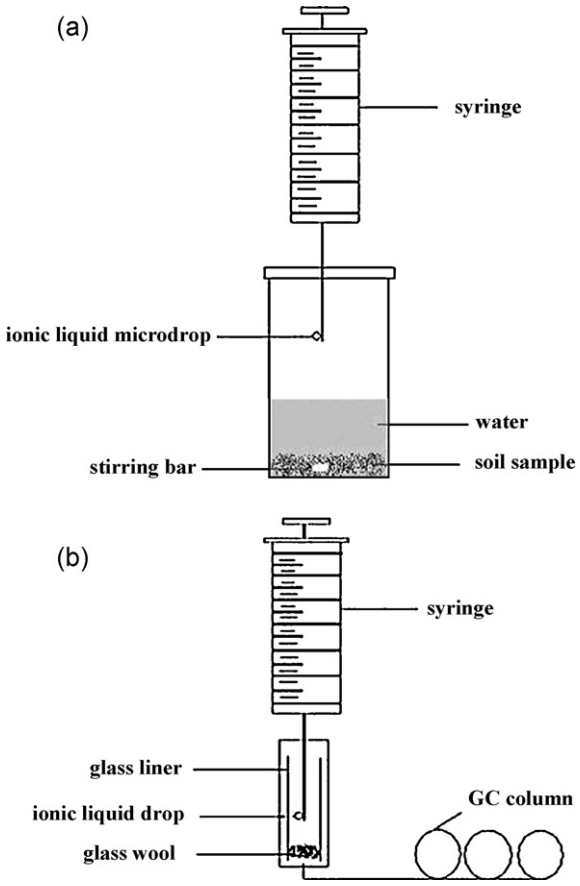

Fig. 3. Schematics of headspace ionic liquid-based LPME. (a) Extraction setup; (b) Thermal desorption. Figures are not to scale.

an aliquot (1 μL) of ionic liquid was withdrawn into the syringe. A 2-g sandy soil sample and a specified volume of water were placed in a 10 mL flat-bottomed sample vial. The syringe needle was inserted through the sample vial septum and exposed to the sample headspace. The syringe was held at a fixed position by a clamp. The syringe plunger was then depressed to expose the ionic liquid microdrop. After a 40-min extraction, the microdrop was retracted into the syringe. The syringe was then removed from the sample vial. The GC injection port with a liner (4-mm internal diameter, Agilent Technologies, Inc., Santa Clara, CA, USA) filled with glass wool, was used as the thermal desorption unit for the ionic liquid extract. Ionic liquids are thermally stable solvents and it was found that they can adhere to the syringe tip relatively strongly due to their high viscosity. The needle was inserted into the GC injection port and held at a certain position such that its tip was not in contact with the glass wool (this position was determined in preliminary experiments). The syringe plunger was slowly depressed so as to expose only (and not inject) the ionic liquid microdrop to duplicate the setting as for the extraction. After several minutes, the spent ionic liquid microdrop was recovered by withdrawing it back into the syringe. The ionic liquid drop was discarded after thermal desorption to prevent potential carryover effects.

2.3. Chromatographic conditions

Chromatographic analysis was performed on Hewlett-Packard (Avondale, PA, USA) 5890 GC system equipped with a ^{63}Ni ECD. A DB-5 30 m × 0.32 mm I.D. capillary column (J&W Scientific, Folsom, CA, USA) was used. Helium was used as carrier gas with

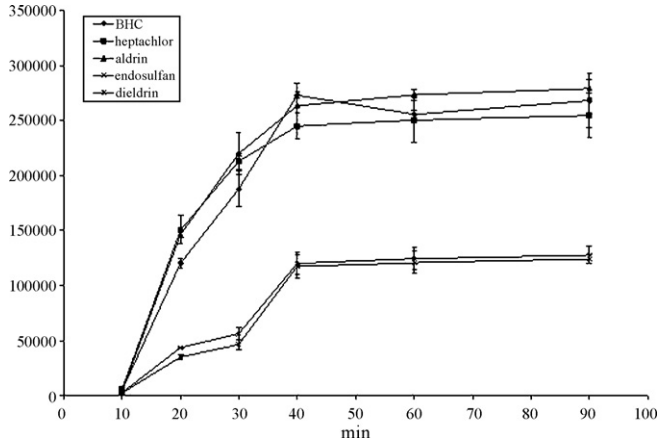

Fig. 4. Extraction profile (sample concentration 12.5 ng/g of each analyte) using [BMIM][PF_6] as extracting solvent. Extraction was conducted at 65 °C, with 1 mL of water added to 2 g of spiked soil sample.

constant flow rate 1.5 cm/s. The injector was maintained at 260 °C and splitless injection mode was used. The GC oven temperature was operated with the following temperature program: 60 °C for 6 min, an increase in temperature to 150 °C, at a rate of 20 °C/min. This temperature was held for 3 min and then further increased at a rate of 15 °C/min to 260 °C. The final temperature was maintained for 2 min.

3. Results and discussion

3.1. Selection of ionic liquids and stability of the extraction system

The four ionic liquids ([BMIM][PF_6], [BMIM][BF_4], [BMIM][$MEDGSO_4$] and [BMIM][$MeSO_4$]), based on the same cation butyl imidazole, were chosen to be evaluated for their suitability for the extraction of OCPs, as 1,3-dialkylimidazolium-based ionic liquids are the largest group of ionic liquids currently available [27]. Initial experimental results show that for most target compounds, [BMIM][PF_6] gave a better extraction efficiency, a finding that is fortuitous, for reasons discussed in the following paragraph. Moreover, ionic liquids based on 1,3-dialkylimidazolium cations are generally preferred since they are thermally more stable than the quaternary ammonium cations [35]. That they are commercially available means that they are also more easily accessible to most laboratories.

The stability of the extraction system was preliminarily evaluated separately for the 4 ionic liquids as extracting solvent. Although LPME could be carried out with all of them, the degree of successful and efficient extraction exhibited some variation. For water-soluble ionic liquids like [BMIM][BF4] and [BMIM][MeSO4], the microdrop tended to detach from the tip of the syringe needle, possibly because they were affected by the moisture in the headspace during the extraction (see below). [BMIM][$MEDGSO_4$] is reactive with air and it was found that its microdrop was also not stable during extraction. [BMIM][PF_6] is insoluble in water and unreactive with air, and was the only solvent found to be stable during extraction. This ionic liquid was subsequently used for all experiments.

3.2. Extraction time

A series of extraction times was investigated to study the extraction process by extracting 2 g of a spiked soil sample (containing 12.5 ng/g of each analyte) with an addition of 1 mL water (extraction temperature: 65 °C (see below)). As shown in Fig. 4, the amount

Table 2
Effect of amount of water added on extraction efficiency (soil sample was spiked at a level of 12.5 ng/g of each analyte).

Analyte	GC relative response			
	0 mL	1 mL	2 mL	5 mL
BHC	100	214	85	52
Heptachlor	100	264	161	140
Aldrin	100	287	156	137
Endosulfan (I)	100	672	491	204
Dieldrin	100	591	545	242

of the analytes extracted increased significantly with increasing extraction time from 10 to 40 min. After 40 min, the extraction time curve maintained a flat profile indicating that equilibrium had been reached.

Ionic liquids, are high boiling point solvents, and [BMIM][PF_6] is no exception. They generally exhibited no adverse effects at the extraction temperature of 65 °C, even after 90 min of extraction.

3.3. Effect of the addition of water

Water is usually added to increase the extraction efficiency in the headspace microextraction of semivolatile compounds in soil samples [2,36]. The presence of water facilitates the release of such compounds from the soil sample. However, too much water was unfavorable, since the analytes might remain in the aqueous phase rather than partition to the headspace [2]. In addition, it has been found that water vapor in the headspace could interfere with extraction [36], as referred to above. In the present case, the effect of the amount of water added was investigated, by considering a 2-g sandy soil sample. As shown in Table 2, addition of 1 mL of water gave better extraction efficiency compared to a "dry" soil extraction. On the other hand, too much water led to a decrease in extraction efficiency. Compared to headspace SPME and determination of OCPs in soil samples [2], less water needs be added to enhance extraction efficiency. Thus it can be surmised that in headspace ionic liquid-based LPME the effect of water vapor on the reduction of the extraction efficiency is greater than that in headspace SPME. One possible reason is that ionic liquids are polar compounds and despite being water-insoluble may be affected by the moisture content in the headspace.

3.4. Effect of extraction temperature

Extraction temperature plays a key role in the headspace microextraction technique. By increasing the sampling temperature, the diffusion coefficients as well as the Henry's law constants of the analytes are increased. Thus, the analytes can be more easily released from the soil matrix and subsequently distributed to the headspace. In addition, in headspace ionic liquid-based LPME, by increasing the sampling temperature, the viscosity of the extracting ionic liquid can be significantly decreased [37], which is favorable for mass transfer of analytes into the ionic liquid microdrop. However, a high sampling temperature is not favorable for headspace microextraction since the partition coefficients of the analytes between the microdrop and headspace are decreased.

Table 3
Effect of sampling temperature on extraction efficiency (soil sample was spiked at a level of 12.5 ng/g of each analyte).

	GC relative response					
	25 °C	40 °C	Analyte	65 °C	75 °C	85 °C
BHC	100	240	340	561	415	368
Heptachlor	100	114	143	181	160	121
Aldrin	100	118	149	195	162	136
Endosulfan (I)	100	166	304	601	568	511
Dieldrin	100	200	381	510	410	370

Table 4
Effect of thermal desorption time on extraction efficiency (soil sample was spiked at a level of 12.5 ng/g of each analyte).

Analyte	GC relative response				
	0.5 min	1.0 min	3 min	5 min	10 min
BHC	100	112	138	153	163
Heptachlor	100	125	156	199	208
Aldrin	100	116	142	166	172
Endosulfan (I)	100	139	183	275	303
Dieldrin	100	150	198	274	302

A series of sampling temperatures was investigated to determine their effect on the extraction. As shown in Table 3, for all the 5 analytes, chromatographic peak areas continued to increase with the rise in temperature until 65 °C. Beyond this temperature, the peak responses of the analytes started to decline. Thus, 65 °C represented the optimum extraction temperature.

3.5. Effect of the thermal desorption

Thermal desorption within the GC injection port is a complicated process. Parameters affecting the thermal desorption performance include injection port temperature, carrier gas flow rate, the viscosity of ionic liquid, the size and shape of the drop and thermal desorption time. In line with most microextraction studies, in the present study, only the effect of thermal desorption time was investigated. As shown in Table 4, the analytical signal did not increase significantly when the thermal desorption time was >5 min. Thus, it may be concluded that most of the analytes had been "desorbed" from the extracting ionic liquid to the column within 5 min.

3.6. Features of the method

The method evaluation data are summarized in Table 5. A series of spiked soil samples were used to investigate headspace ionic liquid-based LPME with respect to repeatability and limits of detection (LODs). By plotting GC peak areas vs. concentration of analytes in the spiked soil sample, calibration curves were generated to evaluate the linearity of the method. Squared regression coefficients (r^2) ranging from 0.952 to 0.993 were obtained. The RSDs was from 8.86% to 15.3%. The LODs, based on a signal to noise ratios of 3, range from 0.1 to 0.5 ng/g. Fig. 5 shows, respectively, the GC traces of (a) "neat" (pure) ionic liquid (representing a blank sample), (b) unspiked soil extract after headspace ionic liquid-based LPME

Table 5
Features of headspace ionic liquid-based LPME.

Analytes	RSD (%) (n = 6)	Linearity range (ng/g)	r^2	Real sample RSD (%) (n = 3)	LODs (ng/g)
BHC	8.92	5–250	0.968	7.28	0.2
Heptachlor	10.63	5–250	0.993	7.47	0.1
Aldrin	8.86	5–250	0.993	9.04	0.1
Endosulfan (I)	14.51	5–250	0.974	11.54	0.5
Dieldrin	15.30	5–250	0.952	11.66	0.5

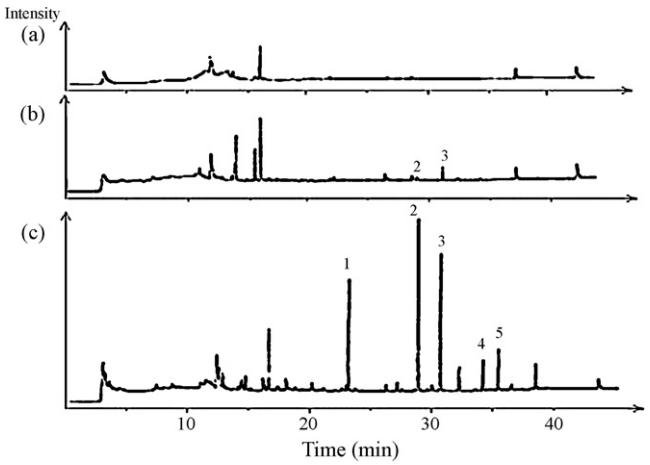

Fig. 5. Chromatograms of (a) "neat" ionic liquid; (b) unspiked soil sample extract after headspace ionic liquid-based LPME; (c) spiked and aged soil extract after headspace ionic liquid-based LPME. Peak identities: (1) BHC, (2) heptachlor, (3) aldrin, (4) endosulfan (I), (5) dieldrin.

(showing the presence of two OCPs), and (c) spiked and aged soil extract after headspace ionic liquid-based LPME. (The soil was aged by being placed in an open-air environment for a period of time after standard spiking to better represent a naturally contaminated sample.) Two pesticides (heptachlor and aldrin) were detected in the soil samples, at concentrations of 0.21 and 0.97 ng/g, respectively. The precision of determination of the real sample ranged from 7.28% to 11.66%.

4. Summary

Headspace ionic liquid-based microdrop LPME with GC–ECD analysis was developed, in an approach that involved the exposure only (without injection) of the analyte-enriched ionic liquid extract, in the injection port, to avoid contamination of the port. The ionic liquid could subsequently be withdrawn and recovered from the GC. This procedure is much convenient and simple than existing means of GC analysis involving the use of ionic liquids, in which special handling or dedicated devices are used to prevent contamination, and thus avoid frequent cleaning, of the injection port. Whether ionic liquids will eventually be considered as superior solvents for microextraction applications remains to be seen. The work described in this study at least permits the convenient evaluation of these liquids as extracting solvents for this purpose, using a conventional and unmodified GC injector port.

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