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[Hmim]PF₆ enhanced the extraction of polycyclic aromatic hydrocarbons from soil with the QuEChERS method

Qianjun Liu^{a,*}, Jiepeng Tang^a, Di Chen^a, Yangmei Zhou^a, Qintie Lin^a,
Xiaoguo Ma^a, Min Zhang^{b,**}, Huawen Hu^b

^a Guangdong Industrial Contaminated Site Remediation Technology and Equipment Engineering Research Center, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, PR China

^b School of Materials Science and Energy Engineering, Foshan University, Foshan 528000, PR China

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Abstract To detect, identify, and quantify the polycyclic aromatic hydrocarbons (PAHs) released into the environment, the PAHs need to be isolated from the soil matrix. In this work, a modified quick, easy, cheap, efficient, rugged and safe (QuEChERS) method with ionic liquid was combined with liquid chromatography to identify 16 selected PAHs in soil. Ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim]PF₆) was applied as an extractant component to enhance the process. The [Hmim]PF₆ content in acetonitrile (ACN) was optimized. The [Hmim]PF₆ modified QuEChERS method has the advantages defined by its name and a similar recovery to other extraction methods reported in the literature. Adding [Hmim]PF₆ may eliminate the co-extract proportion and achieve a more effective extraction. Compared with ACN alone, the matrix effect (ME) of ACN containing 5% [Hmim]PF₆ was reduced by approximately 35%. Additionally, the ME of using ACN containing [Hmim]PF₆ without a clean-up procedure was similar to that of using ACN followed by a clean-up procedure. The recoveries of the QuEChERS method implemented with [Hmim]PF₆ ranged from 75.19% to 100.98%. The limits of detection (LOD) and limits of quantification (LOQ) ranged from 0.86 to 4.51 µg/kg and from 2.87 to 15.13 µg/kg, respectively.

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* Corresponding author at: Guangdong University of Technology, 100 Wai Huan Xi Road, Guangzhou Higher Education Mega Center, Guangzhou, Guangdong 510006, PR China.

** Corresponding author at: Foshan University, Jiangwan 1 st Road, Chancheng, Foshan, Guangdong 528000, PR China.

E-mail addresses: lqjzhch@gdut.edu.cn (Q. Liu), zhangmin@gic.ac.cn (M. Zhang).

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants mostly derived from the processing and combustion of fossil fuels and anthropogenic activities. Due to their recalcitrance and bioaccumulation potential, PAHs do not degrade easily under natural conditions and their persistence increases with increasing molecular weight. Therefore, PAHs have received significant environmental concern (Fernández-Luqueño et al., 2016). Upon exposure to high levels of pollutant mixtures containing PAHs, occurring short-term effects include eye irritation, nausea, vomiting, diarrhoea, etc. Mixtures of PAHs are also known to cause skin irritation and inflammation. The carcinogenic and mutagenic potencies of PAHs are also an important concern (Soukariéh et al., 2018). Sixteen basic PAHs are included in the United States Environmental Protection Agency (16 US EPA PAHs) priority pollutant list (Kosnar et al., 2018). Because of the hydrophobic character of PAHs, they tend to accumulate in soils, sediments, and sewage sludge. Soil is considered to be a major reservoir of PAHs. PAHs may further accumulate in vegetables and other biota after deposition on surface soils, and then be transferred to humans via the food chain. Some PAHs may strongly sorb on soil, where they persist for a long period of time (Soukariéh et al., 2018).

To detect, identify, and quantify the PAHs released into the environment, the PAHs need to be isolated from the soil matrix. Several extraction methods have been developed (Wang et al., 2007; Camel, 2001; Page et al., 2004). In 2003, Anastassiades and Lehotay (2003) described the “quick, easy, cheap, effective, rugged and safe” (QuEChERS) method for the multiclass, multiresidue analysis of pesticides in fruits and vegetables. The original QuEChERS method (Anastassiades and Lehotay, 2003) has the following steps: (a) use acetonitrile (ACN) as the extractant; (b) add magnesium sulfate (MgSO₄) and sodium chloride (NaCl) to induce phase separation; and (c) perform clean-up and drying of the ACN phase simultaneously during dispersive solid phase extraction (d-SPE) with anhydrous MgSO₄ and the primary secondary amine (PSA). The steps of the modified method AOAC 2007.01 (Lehotay, 2007) include: (a) use ACN containing 1% (v/v) acetic acid (AcOH) as an extractant; (b) separate the phase by MgSO₄/sodium acetate (NaAc); and (c) for substrates with a fat content greater than 1%, add 50 mg of C18 solid phase adsorbent per mL of extract (if analysing compounds without planar structure, add 50 mg of graphitized carbon black (GCB) per mL of extract agent for solid phase adsorption). The ruggedness characteristics of the QuEChERS approach have been thoroughly evaluated in the original (Anastassiades and Lehotay, 2003) and subsequent publications by the original authors (Mastovska et al., 2010; Koesukwiwat et al., 2010). Compared with other extraction method (Ma et al., 2010, 2011; Song et al., 2012), the QuEChERS method has a low cost per sample, short elapse time and all the other advantages defined by its name.

The QuEChERS method is very flexible and the original method has evolved into a template for modification depending on the analyte properties, matrix composition, equipment and analytical techniques available in the lab. The template also can be achieved for many pesticides in many matrices, even if different ratios and types of sample sizes, solvents, salts

and sorbents are use (Lehotay et al., 2010). Some examples were showed in Table 1.

The matrix consists of one or more undetected components from the sample, which often significantly affects the accuracy of analytical results. Such disturbances from matrixes are called matrix effect (ME) which are likely caused by different compounds in soils such as salts, ion-pairing agents, endogenous compounds, metabolites and proteins given that soil is an extremely variable mixture of minerals, organic particles and diverse microbial communities. Furthermore, the extraction efficiency of target analytes can be affected by the sorption and limitation in analytical procedures for examining soils with high organic matter (Varona-Torres et al., 2018).

Ionic liquids (ILs) are organic salts that exist as liquids below a threshold temperature. ILs offer a highly solvating and non-coordinating medium in which a number of organic and inorganic solutes may be dissolved (Blanchard and Brennecke, 2001). ILs are considered as green solvents that are non-volatile, non-flammable, highly thermostable, relatively undemanding and inexpensive to manufacture (Ngo et al., 2000). The usable liquid range may include that used for conventional synthetic chemistry, and separation ionic liquids are considered to be ideal substitutes for traditional volatile organic solvents (Liu et al., 2005). Han et al. (2012) provided an overview of the applications of ILs in liquid phase microextraction technology. Aqueous solutions containing aggregates of the ionic liquid (IL) 1-hexadecyl-3-methylimidazolium bromide (HDMIm-Br) could be an extracting medium to extract PAHs from sediments (Pino et al., 2008).

1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim]PF₆) is one of the most stable and hydrophobic ionic liquids in ambient conditions (Martínez-Romero et al., 2017). Additionally, [Hmim]PF₆ has been applied in different separation methods, such as single-drop microextraction (SDME) (Chisvert et al., 2009), liquid-phase microextraction (LPME) (Liu et al., 2004) and ultrasound-assisted microextraction (UAME) (Zhou et al., 2009). The extracted target substance in liquid-liquid separation processes with [Hmim]PF₆ can be heavy metal ions and organic compounds (common pollutant aromatic compounds and acetone) (Vidal et al., 2010; Hirayama et al., 2005; Saïen et al., 2015).

The aim of this study was to develop and validate a [Hmim]PF₆evolved QuEChERS method for extracting 16 PAHs from soil. By comparing the recoveries and the ME of the 16 PAHs, the role of [Hmim]PF₆ in the QuEChERS extraction process was explored.

2. Materials and methods

2.1. Chemicals and reagents

The standard mixture of the sixteen PAHs (200 mg/L), dissolved in 1 mL of ACN and containing naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorine (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DBA), benzo[g,h,i]perylene (BPE), and indeno[1,2,3-cd]pyrene (IPY), was purchased from ANPEL Scientific Instrument

Table 1 Some examples of the QuEChERS method.

No	Target	Matrix	Extraction and Separation	Recovery	
1	PAHs	Animal tissues	Extraction: ACN Clean-up: PSA, C18, MgSO ₄	84–107%	Kielbasa and Buszewski (2017))
2	PCBs, PAHs, PBDES, PCDD/Fs	Biological samples	Extraction: EtOAc Clean-up: GPC, n-hexanes, DCM	~100%	Cloutier et al. (2017)
3	Drugs	Food	Extraction: ACN Clean-up: PSA, MgSO ₄ ,	90%	Schmidt and Snow (2016)
4	Pesticides, PAHs, PCBs	Honey	Extraction: ACN Clean-up: PSA	60–103%	Al-Alam et al. (2017)
5	PAHs	Food	Extraction: ACN Clean-up: PSA, C18, MgSO ₄	72–112%	Petrarca and Godoy (2018)
6	PAHs	Cachaça	Extraction: DCM Elution: EtOAc	84.8–118.2%	da Silva et al. (2019)
7	Veterinary drugs	Milk	Extraction: ACN, AcOH, Na ₂ EDTA	70–110%	Aguilera-Luiz et al. (2008)
8	PAHs	Soil	Extraction: hexane, acetone Clean-up: MgSO ₄ , PSA, C18, clinoptilolite, florisil, diatomaceous earth	70–110%	Nikolić et al. (2018)
9	PAHs	Fish	Extraction: ACN, AcOH Clean-up: MgSO ₄ , PSA, C18	63.5–110%	Ramalhosa et al. (2009)
10	PAEs	Soil	Extraction: ACN, acetone, n-hexane, DCM Clean-up: MgSO ₄ , PSA, C18	70–117.9%	Liu et al. (2018)
11	Neonicotinoid insecticide residues	Soil	Extraction: ACN, AcOH Clean-up: GCB, PSA, C18	72–104.8%	Dankyi et al. (2014)
12	Herbicides	Soil	Extraction: ACN, AcOH Clean-up: GCB	80–110%	Pang et al. (2016)
13	Chlorinated compounds	Soil	Extraction: EtOAc	62–93%	Pinto et al. (2010)
14	Pyraclostrobin	Soil	Extraction: ACN Clean-up: MgSO ₄	80.3–109.4%	Zhang et al. (2012)
15	Aromatic organochlorines	Soil	Extraction: ACN Clean-up: MgSO ₄ , PSA	60–100%	Rouviere et al. (2012)

EtOAc: ethyl acetate; GPC: Gel Permeation Chromatography; DCM: dichloromethane; Na₂EDTA: Ethylenediaminetetraacetic acid disodium salt.

(Shanghai, China). The sixteen standard stock solutions of the PAHs (2 mg/L) were obtained by 1:100 dilution with ACN.

The ionic liquid [Hmim]PF₆ (99%, 5 g) was purchased from ANPEL Scientific Instrument (Shanghai, China). HPLC-grade n-hexane and acetone were purchased from Merck (Darmstadt, Germany). HPLC-grade ACN, analytical-grade anhydrous MgSO₄ and NaCl were obtained from Aladdin Industrial Corporation (Shanghai, China). PSA (40–63 μm) and LC-C18 (40–63 μm), which were used as the clean-up materials, were purchased from ANPEL Scientific Instrument (Shanghai, China). Ultrapure water was produced in the laboratory with a Milli-Q gradient system from Millipore (Vienna, Austria).

2.2. Apparatus and conditions

All the PAHs samples were quantified using a Shimadzu LC-20AD high performance liquid chromatography (HPLC) coupled to a Shimadzu SPD-M20A diode array detector (DAD) (Shimadzu corporation, Kyoto, Japan) with a 4.6 mm × 250 mm × 5 μm C18 column (Shimadzu corporation, Kyoto, Japan). The mobile phase, which was degassed and filtered before analysis, consisted of ACN (A) and ultra-pure water (B). Flow rate of eluent was 1.0 mL/min with the

mobile phase initially consisting of 65% A and 35% B, with a linear increase to 80% A from 30.0 min to 40.0 min and to 100% A from 50.0 min to 51.0 min, finally decreased to 40% A from 54.5 min to 56 min and held for 1.0 min. The temperature of the column oven was maintained at 30 °C and the injection volume was 20 μL. Fig. 1 shows the chromatogram of 16 PAHs at the conditions above which registered in 254 nm.

The identification of sample peaks was based on the retention time of the standard peaks. The detection wavelengths were based on the maximum UV absorption wavelength of each PAHs, which were according to the Soil and sediment—Determination of polycyclic aromatic hydrocarbons—High performance liquid chromatography (HJ784-2016, China).

2.3. Sample preparation

The soil samples were collected from middle soil layers (20–60 cm depth) in an area in Guangzhou China, as far away from PAHs pollution sources as possible. Soil samples were transported and stored at 4 °C in pre-cleaned glass containers. After removing the plant tissues and silt, soil samples were dried at room temperature before being ground in a mortar and sieved.

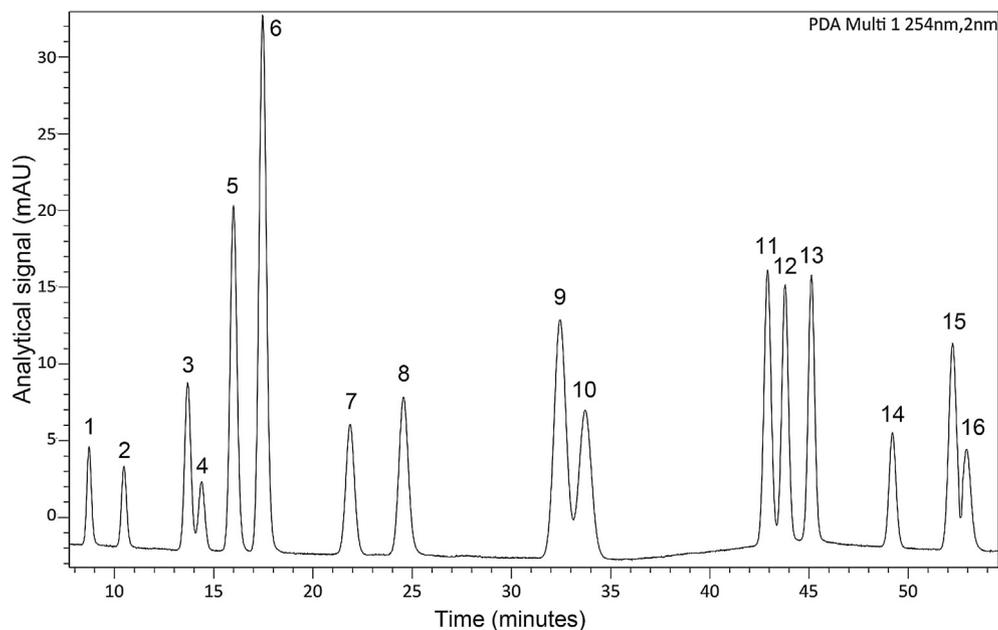


Fig. 1 The chromatogram of 16 PAHs in 254 nm. Compounds: (1) NAP; (2) ANT; (3) ANA; (4) FLU; (5) PHE; (6) ANT; (7) PLT; (8) PYR; (9) BaA; (10) CHR; (11) BbF; (12) BkF; (13) BaP; (14) DBA; (15) BPE; (16) IPY.

The soil pH was 4.42 in the soil/water suspension (1:2.5, v/v), and the organic matter content was 1.017%. Then, the soil samples were spiked with 200 µg/kg of the PAHs standards and stirred with a mechanical stirring apparatus to obtain a homogeneous sample. Samples were then left in a ventilated location to allow all the solvent to evaporate. The standards are thought to bind to the soil samples in a manner similar to natural processes.

2.4. The QuEChERS method

The modified QuEChERS procedure in this paper consisted of the following steps, which were based on the literature (Liu et al., 2018; Schenck and Hobbs, 2004). (a) Sample (5.0 g) was weighed into a 50 mL disposable polypropylene centrifuge tube, and 5 mL of ultrapure water was added. The sample was stood for 10 min. (b) Twenty millilitres of extraction solvent (ACN, n-hexane, acetone, n-hexane/acetone (1:1, v/v) or ACN containing [Hmim]PF₆ (5%, 10%, 15%)) was added, and the tube containing samples was ultrasonicated for 20 min. (c) NaCl (2.0 g) and MgSO₄ (2.0 g) were added to the centrifuge tube, and the tube was shaken vigorously by hand for 1 min and centrifuged at 4000 rpm. (d) A 10 mL aliquot of the supernatant was transferred into a 15 mL disposable polypropylene centrifuge tube. PSA (500 mg) and C18 (500 mg) were added to the tube, which was ultrasonicated for 5 min. (e) Finally, 5 mL of the supernatant was filtered with 0.22 µm organic phase membrane. The filtrate was transferred and concentrated by rotary evaporation to less than 1 mL. Three millilitres ACN was added before rotary evaporation and the solution was concentrated to less than 1 mL again. (f) The extract was transferred to an autosampler vial (CNW, Germany) and then diluted with ACN to 1.5 mL for analysis by HPLC.

2.5. Calibration curve

The matrix standard solutions (ACN, n-hexane, acetone, n-hexane/acetone (1:1, v/v) and ACN/5% [Hmim]PF₆) were prepared following the steps in Section 2.4. The concentrations of the working standards were 20.0, 50.0, 100.0, 200.0, 500.0, and 1000.0 µg/L, which were diluted from the PAHs standard stock solutions (2 mg/L) with matrix standard solutions.

2.6. Method validation

The performance of the method was validated by evaluating the parameters including recovery, relative standard deviation (RSD), the limits of detection (LOD) and the limits of quantification (LOQ). The LOD and LOQ were calculated based on the official method of the Official Analytical Chemists Association, that is, derived from the blank and quantified as the mean plus three times and ten times the field blank standard deviation (SD), respectively.

2.7. Matrix effect

To compare the ME, solutions of 1000 µg/L PAHs were prepared using five matrix standard solutions (ACN, n-hexane, acetone, n-hexane/acetone (1:1, v/v) and ACN/5% [Hmim]PF₆) and ACN pure solvent. The ME is calculated by the following formula (Matuszewskiet al., 2003):

$$ME(\%) = \frac{A_2}{A_1} \times 100\% \quad (1)$$

In the formula, ME refers to the matrix effect, A₁ refers to the peak area of PAHs in the pure solvent sample at a certain concentration, and A₂ refers to the peak area of PAHs in the matrix standard solution at the same concentration. If the

average ME exceed 20%, the ME can significantly affect the detection results, and vice versa, the influence of the ME on the analysis results can be neglected (Matuszewski et al., 2003).

3. Results and discussion

3.1. Effect of [Hmim]PF₆ on the extraction of PAHs

The extraction efficiency strongly depends on the extraction solvent, the nature of the sample, and the chemical properties of the pollutants. In this study, an extraction solvent of ACN/5% [Hmim]PF₆ was used to investigate the effects of ionic liquids on the extraction of PAHs from soil. The extraction results were compared those obtained with ACN, n-hexane, acetone and n-hexane/acetone (1:1, v/v). ACN, n-hexane and acetone are typically used for the extraction of PAHs (Liu et al., 2018; Socas-Rodríguez et al., 2017). A mixed solvent of n-hexane/acetone (1:1, v/v) was recommended for the extraction of semivolatile organics from soil by the EPA Method 3540C and 3550C. DCM can also be used as an extractant for PAHs (Albinet et al., 2013; Pena et al., 2009). However, DCM is denser than water, and after solvent delamination, the DCM was below the aqueous phase, making its removal difficult. Therefore, DCM was not suitable for the QuEChERS extraction process (Liu et al., 2018).

Table 2 shows the recoveries and the RSD of the sixteen PAHs. Using n-hexane/acetone (1:1, v/v) as an extractant has advantages in terms of both the recovery and the RSD. The extraction effect of ACN is slightly worse than that of n-hexane/acetone (1:1, v/v), but when ACN containing 5% [Hmim]PF₆ is used, the recoveries and the RSD increased to 75.19–100.98% and 0.58–6.44%, respectively. The recovery of most PAH components was increased. Eleven PAH components have higher recovery when using ACN containing 5% [Hmim]PF₆ than when using n-hexane/acetone (1:1, v/v). It appears that [Hmim]PF₆ can enhance the extraction of PAHs from soil with the QuEChERS method.

ACN containing [Hmim]PF₆ (5%, 10%, or 15%) was used as the extractant to investigate the effect of [Hmim]PF₆ content on the extraction process. The recoveries and the RSD of the sixteen PAHs are listed in Table 3. Compared with ACN, ACN containing [Hmim]PF₆ shows higher recovery and RSD. It shows that the content of [Hmim]PF₆ in the extractant has a certain influence on the extraction efficiency of a variety of PAH compounds, which may be related to the structure difference. A [Hmim]PF₆ concentration of 5% was selected considering the extraction efficiency and convenient operation.

3.2. Matrix effect

ME was originally discussed by Liang and Kebarle (1993). Because of the existence of interferences which would co-elute along with the analyte of interest in a sample compared to a pure standard solution, leading to a significant increase or decrease in the detector response (Liang and Kebarle, 1993). Hence, the evaluation of ME is required to obtain more accurate and reliable results (Annesley, 2003). The ME observed with five extract solvents were shown in Fig. 2.

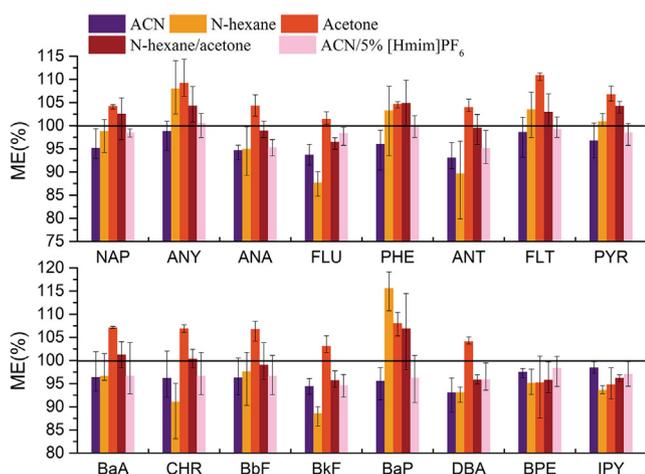
The ME of ACN, n-hexane, acetone, n-hexane/acetone (1:1, v/v) and ACN/5% [Hmim]PF₆ were 93.08–98.79%, 87.68–115.60%, 94.78–110.87%, 95.68–106.88% and 94.61–100.57%, respectively. Among these effects, the maximum ME of n-hexane and acetone reached 110% or more, and the minimum ME of n-hexane was lower than 90%. ACN, hexane/acetone (1:1, v/v) and ACN/5% [Hmim]PF₆ had ME within 90–110%. The ME of ACN/5% [Hmim]PF₆ were close to 100%. Compared with ACN, ME of ACN containing 5% [Hmim]PF₆ was reduced by approximately 35%. The results show that the ME was within the range of 85–115% for both the QuEChERS method and the [Hmim]PF₆ modified QuEChERS method for PAHs. Compared with that extracted by ACN, the chromatogram of the analyte extracted by ACN/5% [Hmim]PF₆ showed a clean baseline and narrower peaks, in consistence with references (Bi et al., 2011;

Table 2 Recovery (R) and RSD of sixteen PAHs.

PAHs	ACN		N-hexane		Acetone		N-hexane/acetone (1:1, v/v)		ACN/5% [Hmim]PF ₆	
	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	PAHs	R (%)	RSD (%)	R (%)	RSD (%)
NAP	91.47	4.41	61.39	2.75	86.87	8.43	90.27	3.29	89.64	3.42
ANY	86.41	0.98	77.55	0.64	80.24	4.58	81.84	0.21	100.09	4.32
ANA	72.48	1.51	89.71	2.31	86.01	0.34	91.18	2.30	93.06	3.47
FLU	74.12	3.26	76.42	2.60	72.34	1.59	88.51	2.35	75.19	0.73
PHE	87.99	1.19	82.87	5.47	66.92	4.58	82.82	3.16	90.35	6.44
ANT	78.32	1.38	70.71	4.21	91.12	1.31	80.95	0.68	87.59	3.22
FLT	112.69	0.28	85.16	1.62	110.58	4.69	97.02	5.22	100.97	5.05
PYR	110.29	1.10	86.13	0.69	101.38	6.04	79.45	2.64	100.98	6.35
BaA	76.10	7.54	66.17	3.18	107.54	1.83	105.39	1.07	94.96	2.62
CHR	70.26	7.85	81.67	0.65	106.05	3.34	84.37	0.73	100.94	6.15
BbF	85.89	2.30	83.63	6.45	73.72	2.98	95.51	2.61	78.75	5.77
BkF	81.08	8.00	89.31	0.21	88.89	2.09	96.45	2.42	100.11	5.25
BaP	80.52	4.80	79.51	6.59	86.10	8.22	77.38	3.01	100.68	0.58
DBA	71.84	6.87	77.23	3.95	77.72	4.25	90.33	2.80	75.79	3.94
BPE	88.92	1.66	91.73	0.65	92.05	0.55	95.76	1.09	100.22	1.63
IPY	70.00	5.81	88.30	1.68	92.88	2.93	90.48	0.90	79.81	6.40

Table 3 R and RSD of sixteen PAHs extracted by ACN/[Hmim]PF₆.

PAHs	ACN		ACN/5% [Hmim]PF ₆		ACN/10% [Hmim]PF ₆		ACN/15% [Hmim]PF ₆	
	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)
NAP	91.47	4.41	89.64	3.42	85.30	5.67	77.84	0.41
ANY	86.41	0.98	100.09	4.32	95.60	0.88	94.76	5.17
ANA	72.48	1.51	93.06	3.47	93.11	4.87	89.47	0.31
FLU	74.12	3.26	75.19	0.73	75.91	1.96	74.68	1.32
PHE	87.99	1.19	90.35	6.44	92.25	4.21	80.06	2.88
ANT	78.32	1.38	87.59	3.22	92.36	5.08	96.43	1.13
FLT	112.69	0.28	100.97	5.05	100.29	1.73	97.98	0.52
PYR	110.29	1.10	100.98	6.35	98.36	4.81	101.16	4.96
BaA	76.10	7.54	94.96	2.62	98.98	0.42	99.38	0.81
CHR	70.26	7.85	100.94	6.15	97.58	5.87	95.15	4.10
BbF	85.89	2.30	78.75	5.77	85.79	0.12	90.88	5.28
BkF	81.08	8.00	100.11	5.25	91.17	1.68	100.17	3.59
BaP	80.52	4.80	100.68	0.58	95.08	1.75	89.94	3.05
DBA	71.84	6.87	75.79	3.94	75.51	1.92	86.81	0.56
BPE	88.92	1.66	100.22	1.63	91.17	4.18	92.39	0.61
IPY	70.00	5.81	79.81	6.40	93.94	2.24	93.90	1.40

**Fig. 2** ME with five solvents.

Fernandez-Navarro et al., 2012; Ubeda-Torres et al., 2015), with a more inconspicuous impurity peak. All the results demonstrate the effectiveness of [Hmim]PF₆ in the extraction selectivity of PAHs in soil.

3.3. Clean-up procedure

Clean-up procedure in QuEChERS method can recede ME, remove the co-extractants and eliminate the interference peaks which present in the chromatograms. Some sorbents have the ability to attenuate ME, such as PSA and NH₂ have the ability to remove fatty acids, sugars, and other matrix co-extractives, GCB can remove planar molecules such as natural pigments (e.g., chlorophyll, hemoglobin, and carotenoids), C18 has extreme retentive nature for non-polar compound like fat, and strong anion exchange material (SAX) is suited for the extraction of compounds like carboxylic acids (Molina et al., 2014; Yang et al., 2015; Hercegovca et al., 2007; Wen et al.,

2014). The combined effects of ACN/5% [Hmim]PF₆ and clean-up procedure on ME were studied. Four matrix standard solutions (ACN, ACN without clean-up, ACN/5% [Hmim]PF₆ and ACN/5% [Hmim]PF₆ without clean-up) were prepared following the steps in Section 2.4. Among these solutions, the matrix standard solutions of ACN without clean-up and ACN/5% [Hmim]PF₆ without clean-up bypassed this step (d). Then formula (1) was used to calculate the ME. The ME of four matrix solutions were compared and are shown in Fig. 3.

Fig. 3 showed that the ME of ACN followed by clean-up, ACN without clean-up, ACN/5% [Hmim]PF₆ followed by clean-up and ACN/5% [Hmim]PF₆ without clean-up were 93.08–98.79%, 87.61%–106.41%, 94.61–100.57%, and 92.67–103.43%, respectively. It was evident that the most severe ME was found for ACN without clean-up. The ME of ACN/5% [Hmim]PF₆ followed by clean-up were relatively weaker than ACN followed by clean-up, while the ME of adding [Hmim]PF₆ without clean-up were similar to that of

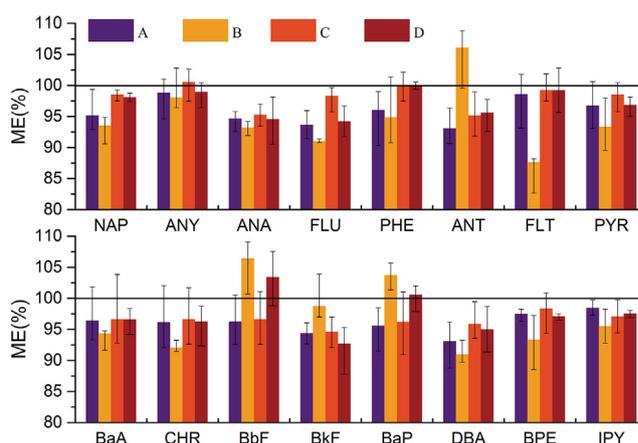
**Fig. 3** The ME of four process matrix solutions. A: ACN extraction followed by clean-up. B: ACN extraction without clean-up. C: ACN/5% [Hmim]PF₆ extraction followed by clean-up. D: ACN/5% [Hmim]PF₆ extraction without clean-up.

Table 4 Linear range, LOD, LQD and recovery of the method.

Extractant	Line range ($\mu\text{g/L}$)	Recovery (%)	LOD ($\mu\text{g/kg}$)	LQD ($\mu\text{g/kg}$)
ACN	20–1000	70.00–112.69	1.64–4.51	5.47–15.03
n-hexane	20–1000	61.39–91.73	1.37–4.45	4.57–14.83
acetone	20–1000	66.92–110.58	1.61–5.45	5.37–18.17
n-hexane/acetone	20–1000	77.38–105.39	1.42–4.55	4.73–15.17
ACN/5% [Hmim]PF ₆	20–1000	75.19–100.98	0.86–4.51	2.87–15.03

Table 5 The comparison of the proposed methods in literature.

No.	Extractant	Pretreatment Method	Instrument detection	Recovery (%)	RSD (%)	LOD ($\mu\text{g/kg}$)	Source
1	ACN/5% [Hmim]PF ₆	QuEChERS	HPLC-DAD	75.19–100.98	0.58–6.44	0.86–4.51	This work
2	DCM	UAE + SPE	HPLC-FLD	70.32–115.51	3.80–13.56	0.0015–0.2	Pan et al. (2013)
3	ACN	MAE + SPE	FI-LC- UV	98.00–99.00	2.40–4.80	2.00–40.00	Criado et al. (2004)
4	ACN	MAE + SPE	FI-LC- FD	98.00–99.00	2.50–5.40	0.30–2.00	Criado et al. (2004)
5	Hexane/acetone(1:1)	MSPD + SPE	HPLC-DAD	94.30–103.90	0.2–1.9	0.004–0.20	Pena et al. (2007)
6	Cyclohexane	UAE + SLE	HPLC-FLD	70.00–98.00	2.00–15.00	0.138–2.688	Kayali-Sayadi et al. (2000)
7	ACN/water	QuEChERS	GC-MS	80.59–109.82	0.97–18.95	0.39–1.53	Cvetkovic et al. (2016)

UAE: ultrasonic assisted extraction; SPE: solid phase extraction; FLD/FD: fluorescence detector; MAE: microwave-assisted extraction; FI: flow injection; UV: UV-vis detector; MSPD: matrix solid-phase dispersion; SLE: soil-liquid extraction; MS: mass spectrometry.

ACN followed by clean-up. These results proved that [Hmim]PF₆ has a purifying effect due to the high selectivity of [Hmim]PF₆ (Chisvert et al., 2009; Liu et al., 2004; Zhou et al., 2009; Vidal et al., 2010; Hirayama et al., 2005; Saïen et al., 2015). Since the MEs were similar, it was feasible to extract PAHs from soil by using an ACN solution with the addition of [Hmim]PF₆, thereby bypassing the clean-up step to achieve a rapid analysis.

3.4. Method validation

When the linear concentration ranges from 20 to 1000 $\mu\text{g/L}$, the ranges of correlation coefficients (R^2) and LOD for the calibration curves of the 16 PAHs extracted by the five extractants are listed in Table 4. The good linearity was found for ACN/5% [Hmim]PF₆ with R^2 ranging from 0.999 to 0.9999. The LOD and LQD ranged from 0.86 to 4.51 $\mu\text{g/kg}$ and 2.87 to 15.13 $\mu\text{g/kg}$, respectively. Compared with other four extractions, the minimum LOD and minimum LQD of ACN/5% [Hmim]PF₆ are lower by 30%. This finding means that using ACN/5% [Hmim]PF₆ as the extractant might effectively increase sensitivity. Some proposed methods reported in the literature are shown in Table 5. The 5% [Hmim]PF₆ modified QuEChERS method has a similar recovery to other extraction methods. However, the QuEChERS method requires less solvent and less extraction time. The No. 7 QuEChERS method with ACN/5% [Hmim]PF₆ as an extractant has a higher recovery and RSD than using ACN/water as an extractant. The lower LOD of observed with the No. 7 method might be related to the detection method.

4. Conclusion

A QuEChERS method that uses less solvent and less time than traditional methods was applied to extract 16 PAHs from soil. Based on the high selectivity of ILs, [Hmim]PF₆

was added to ACN to explore the effects of ILs on the extraction efficiency and the ME. The recoveries and the RSD of the sixteen PAHs in the soil were 75.19–100.98% and 0.58–6.44%, respectively. The extraction results were better than using n-hexane/acetone (1:1, v/v) which was recommended by the EPA Method 3540C and 3550C. The content of [Hmim]PF₆ in the extractant has a certain influence on the extraction efficiency of a variety of PAH compounds. The addition of [Hmim]PF₆ can effectively reduce the ME. Compared with ACN, the ME of ACN containing [Hmim]PF₆ were reduced by approximately 35%. Meanwhile, the ME of four procedures (ACN followed by clean-up, ACN without clean-up, ACN/5% [Hmim]PF₆ followed by clean-up and ACN/5% [Hmim]PF₆ without clean-up) were compared. The ME of the ACN/5% [Hmim]PF₆ without clean-up procedure were similar to that of the ACN followed by clean-up procedure, which proved that [Hmim]PF₆ has a purifying effect due to the high selectivity of [Hmim]PF₆. The QuEChERS method has the advantages of fastness, high efficiency, and high selectivity. When this method is optimized by adding [Hmim]PF₆, the extraction efficiency can be increased and the ME can be reduced significantly. [Hmim]PF₆ modified QuEChERS method may be applied for the rapid analysis of PAHs in soil samples, and field application of this method may be broadened accordingly.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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