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Room temperature imidazolium ionic liquid: A solvent for extraction of carbamates prior to liquid chromatographic analysis

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ABSTRACT

A simple and rapid method for preconcentration of carbamate insecticides, including methomyl, propoxur, carbofuran, carbaryl, isoprocarb, methiocarb and promecarb, has been developed. It was based on a liquid–liquid microextraction using a [C_4MIM][PF_6] room temperature ionic liquid as an extraction solvent prior to analysis by high performance liquid chromatography with UV detection. Experimental parameters affecting the extraction performance, such as the volumes of sample, extractant and dissolving solvent, and extraction time, were studied. Under the selected conditions, the enrichment factors in the range between 10 and 25 could be achieved with the limit of detection in the range of 2–40 $\mu g\,L^{-1}$, and with the relative standard deviations of lower than 0.6 and 10.2% for retention time and peak area, respectively. The proposed method offers advantages in reduction of the exposure danger to toxic solvents used in the conventional liquid–liquid extraction, simplicity of the extraction processes, rapidity, and sensitivity enhancement. The method was demonstrated to apply to the analysis of fruit and natural surface water samples.

1. Introduction

Carbamate insecticides are a large class of pesticides widely used in agriculture. Some carbamates are extreamly toxic to the central nervous system and are suspected carcinogens and mutagens [1]. Carbaryl, carbofuran and methiocarb are three of the most important *N*-methylcarbamate insecticides which currently constitute a class of chemicals widely used to combat a high number of pests in a great variety of crop [2]. Carbamate residues may be widely distributed in fruits, vegetables, as well as in the aqueous environmental through runoff and reaching from soil into ground and surface waters, because of their high solubility in water [3,4]. Many countries have formulated strict limit about the carbamates in various matrices. Rapid and reliable control means to ensure that the residue levels under safety band of maximum residue levels (MRLs) would require highly sensitive and selective analytical techniques for the quantification of carbamates.

Spectrophotometry [5,6] is a simple and cost-effective analytical technique for carbamate determination but does not allow a multi-component analysis, and require derivatization to improve selectivity. High performance liquid chromatograph (HPLC) coupled with a variety of detection systems, including ultraviolet [7], diode array spectrophotometry [8], fluorescence [9], and mass spectrometry [10], is the favoured technique for multi-analysis of carbamate insecticides. Although HPLC is a sensitive and selective analytical technique, but carbamates usually exhibit in very low concentrations and in complex matrices. Therefore, sample preparation is still needed.

There is an increasing demand for simple, rapid and accurate sample preparation methods for the analysis of carbamate residues in real samples. Good sample preparation should provide not only clean-up, but also preconcentration of analytes. A variety of choices have been proposed for pretreatment and/or preconcentration of carbamates in various matrices. The most popular pretreatment methods are liquid–liquid extraction (LLE) [11] and solid phase extraction (SPE) [12]. However, big disadvantages are the large quantities of solvent utilized and the multiple operation steps needed [10]. Recently, attention is being paid to the development of miniaturized, more efficient and environmentally friendly extraction techniques that could greatly reduce the toxic organic solvent consumption [3,8,13]. Cloud point extraction (CPE), or micelle-mediated extraction (MME) has been recognized as an alternative to the conventional extraction because of its performance, lower cost and less toxic because a surfactant is used as an extractant [14]. This method poses some disadvantages as extraction is time-consuming, and requires a temperature control and centrifugation for phase separation. In some cases, addition of salt is needed.

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Nowadays, the quick, easy, cheap, effective, rugged and safe (QuEChERS) method has been introduced for the analysis of pesticide residues in fruits and vegetables [15,16]. It is based on an acetonitrile extraction, addition of salts to induce partition and then clean-up by dispersive solid-phase extraction (DSPE) with sorbents, such as C_{18}, primary secondary amine (PSA) and graphitized carbon black (GCB). It provides some advantages including high recovery for wide polarity and volatility range of pesticides and the use of small amounts of organic solvent. However, one of the main drawbacks of QuEChERS methodology is the fact that there is no pesticide concentration step in the final extract [17].

In the last few years, the use of room temperature ionic liquids (RTILs) as an alternative solvent for extraction and preconcentration has attracted attention in analytical chemistry. RTILs are ionic media resulting from the combination of organic cations and various anions [18]. They have some unique properties, such as negligible vapor pressure, good solvating properties together with large spectral transparency, good thermal stability, tunable viscosity and miscibility with water and organic solvent, as well as good extractability for various organic compounds and metal ions [19]. The main types of RTILs are alkylammonium, tetraalkylammonium, tetraalkylphosphonium, 1,3-dialkylimidazolium, and *N*-alkylpyridinium salts formed with weak nucleophilic anions such as hexafluorophosphate, tetrafluoroborate and perfluoroalkylsulfonate. There are some literatures on the use of RTILs for sample preconcentration [18]. The majority of them deals with the application for atomic spectrophotometric determination of metal ions [20,21]. However, a few literatures on chromatographic application of RTILs as extractants were also reported for pesticide analysis, including the use of 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$) for extraction of multiclass pesticides [22–24], pyrethroid [25] and organophosphorus pesticides [26], and 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIM][PF_6]$) for extraction of organophosphorus [27]. All these extraction methods mentioned above were based on dispersive liquid–liquid microextraction (DLLME) which required several extraction steps including rapid injection of the mixture of extractant and disperser, and centrifugation.

The aim of the present work was to develop a simple liquid–liquid microextraction (LLME) using RTIL as extractant for preconcentration of carbamate pesticides prior to HPLC analysis. 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4MIM][PF_6]$ RTIL was selected because of its low viscosity, compared with $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$ [28], which allowed the compatibility with the liquid chromatographic system. This work also constituted the first application of $[C_4MIM][PF_6]$ RTIL as extraction solvent for carbamate pesticides. The carbamates of interest are methomyl, propoxur, carbofuran, carbaryl, isoprocarb, methiocarb and promecarb. The experimental parameters affecting the extraction efficiency and enrichment factor were investigated and the proposed method was applied to analyze surface water and fruit samples. The satisfactory recovery was achieved. In comparison with DLLME procedure, the proposed method offers advantage of extraction and preconcentration in simple step.

2. Experimental

2.1. Chemicals and reagents

Carbamate standards of highest purity were used. Isoprocarb, methomyl, carbaryl and carbofuran were obtained from Fluka (Switzerland). Promecarb and propoxur were obtained from Riedel-de Haën (Germany) and methiocarb was supplied by Supelco (USA). The stock standard solutions of each carbamate ($1000\,\mu g\,mL^{-1}$) were prepared by dissolving each carbamate standard in methanol. Working standard solutions were prepared by diluting the stock solution with water. Deionized water obtained from RiOs^{TM} Type I Simplicity 185 (Millipore Waters, USA) with the resistivity of $18.2\,M\Omega\,cm$ was used throughout the experiments. Methanol and acetonitrile (ACN) of HPLC grade were obtained from Lab-Scan Asia (Thailand). Acetic acid of analytical reagent (AR) grade was obtained from Carlo Erba (Italy). The $[C_4MIM][PF_6]$ RTIL was provided by Sigma–Aldrich (Germany).

2.2. Apparatus

Chromatographic separation was performed using a Waters Tiger LC system (Waters, Massachusetts, USA) equipped with a UV detector operated at 270 nm. An Atlantis C18 column (4.6 mm i.d. × 150 mm, 5 μm particle diameter) was used. The Clarity software was used for data acquisition. A commercial food processor (Moulinex, Ningbo Kitchen Appliance Co. Ltd., China) was used for blending and mixing the samples. Rotavapor R-200 (BÜCHI Labortechnik AG, Flawil, Switzerland) and Shaker (Vision Scientific Co. Ltd., Kyunggi-do, Korea) were also used.

2.3. Sample preparation

2.3.1. Surface waters

The natural surface water samples were taken from three different areas located near rice fields in Khon Kaen province, northeastern of Thailand, and were filtered through a Whatman No.1 filter paper before analysis.

2.3.2. Fruits

Fruit samples, including watermelon, cantaloupe, strawberry, apple and orange, were purchased from local market and supermarkets in Khon Kaen province. To prepare fruit samples, the edible parts of samples were cut into 1-cm cubes and blended in a commercial food mixer. A 25 g portion of each sample was shaken (at 200 rpm) with ACN (25 mL) for 1 h. The extract was then evaporated using rotary evaporator at 45 °C, until the volume became 2–3 mL. The residue was dissolved with deionized water to the final volume of 25.00 mL, and filtered before analysis.

2.3.3. Liquid–liquid Microextraction using room temperature ionic liquid (RTIL-LLME)

After the preparation of samples (see Sections 2.3.1 and 2.3.2), the extraction was performed by putting 3.00 mL of sample in a test tube, then with 100 μL of $[C_4MIM][PF_6]$ RTIL before shaking the test tube for 7 min. The analytes in the sample were extracted into the fine droplets of ionic liquid settled to the bottom of the test tube. The aqueous phase was removed by using a 10 mL syringe. The settled phase of 30 μL was withdrawn using a 50-μL microsyringe and then diluted with ACN (50 μL) to decrease viscosity before being injected into the HPLC system.

3. Results and discussion

3.1. Chromatographic separation of carbamate insecticides

The HPLC separation of the studied carbamates was performed on a reversed-phase system with the gradient mobile phase of ACN and 0.1% acetic acid. Gradient elution was performed at a flow rate of $1.0\,mL\,min^{-1}$ as follows: 40% ACN (0–5 min), ramped to 43% ACN (5–8 min), ramped to 45% ACN (8–10 min), ramped to 60% ACN (10–15 min), ramped to 90% ACN (15–20 min) before returning to 40% ACN (20–25 min) and holding for 5 min. Under the selected conditions, the seven carbamate pesticides of interest were separated within 20 min with the following order of elution: methomyl ($t_R = 2.827$ min), propoxur ($t_R = 8.533$ min),

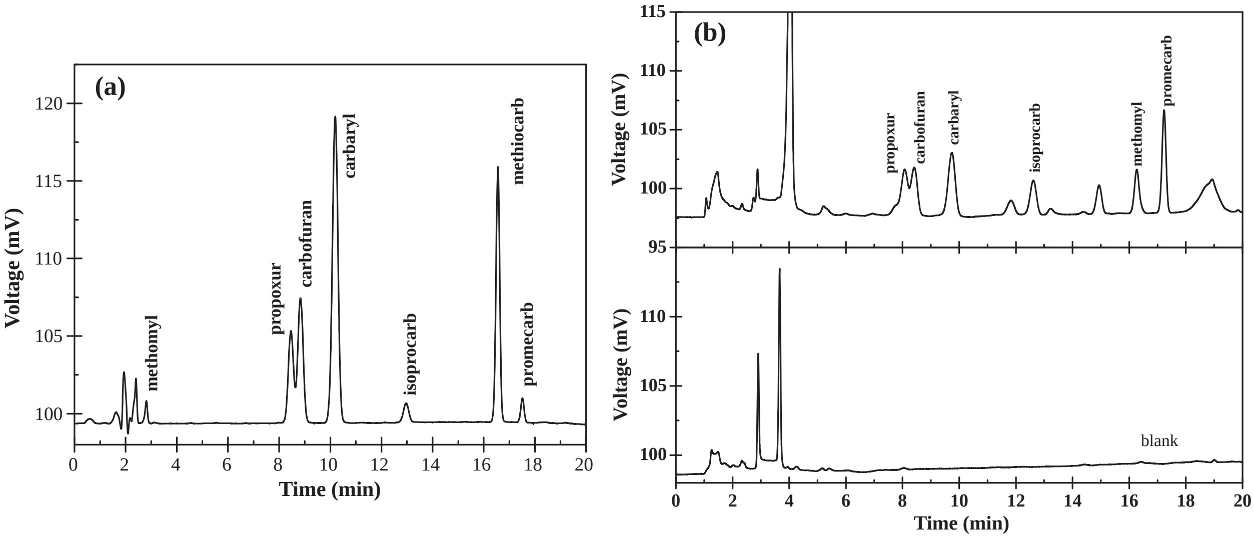

Fig. 1. Chromatograms of standard carbamates obtained by (a) direct injection without preconcentration: methomyl (15.0 μg mL^{-1}); propoxur (10.0 μg mL^{-1}); carbofuran (10.0 μg mL^{-1}); carbaryl (10.0 μg mL^{-1}); isoprocarb (15.0 μg mL^{-1}); methiocarb (10.0 μg mL^{-1}); promecarb (15.0 μg mL^{-1}) and (b) using RTIL-LLME: methomyl (4.0 μg mL^{-1}); propoxur (0.5 μg mL^{-1}); carbofuran (0.5 μg mL^{-1}); carbaryl (0.2 μg mL^{-1}); isoprocarb (2.0 μg mL^{-1}); methiocarb (1.0 μg mL^{-1}); promecarb (4.0 μg mL^{-1})

carbofuran (t_R = 8.913 min), carbaryl (t_R = 10.317 min), isoprocarb (t_R = 13.063 min), methiocarb (t_R = 16.683 min) and promecarb (t_R = 17.623 min).

A chromatogram of mixture standards is shown in Fig. 1(a).

3.2. Optimization of the RTIL-LLME conditions

In the present study, RTIL-LLME was developed for preconcentration of carbamates prior to HPLC analysis. The parameters to be studied include the volumes of sample, [C_4MIM][PF_6] RTIL and dissolving solvent (ACN) and the extraction time.

Sample volume is one of the most important parameters to be studied because it determines the enhancement factor of the method. The effect of sample volume was examined in a range of 1.00–5.00 mL, while the other experimental conditions were fixed and included the use of 100 μL [C_4MIM][PF_6], extraction time of 7 min and 50 μL ACN. The peak areas of the analytes increased with increase of the sample volume from 1.00 to 3.00 mL, and slightly decreased with further increase of sample volume to 5.00 mL. Therefore, the sample volume of 3.00 mL was chosen for further experiments.

The influence of the RTIL volume was studied in the range of 50–200 μL. Optimization of the minimal volume is required to reach a high enrichment factor. Based on this criteria, it could be stated that the [C_4MIM][PF_6] RTIL volume of 100 μL was chosen for quantitative extraction of the analytes.

Because the process of mass transfer between two phases in extraction procedure should be time-dependent, the influence of extraction time on the peak area was examined. A series of extraction times ranging from 3 to 10 min was studied while other experimental conditions were kept constant (3.00 mL of sample, 100 μL of [C_4MIM][PF_6] and 50 μL of ACN). The peak areas of most of the carbamates increased slightly with increasing the extraction time, and reached the highest at 7 min. Afterwards, the tendency of peak areas remained constant (or slightly decreased for some analytes, i.e. propoxur and methiocarb), therefore 7 min was chosen to ensure the efficient extraction.

To decrease the viscosity of the extract before injecting to the HPLC system, ACN was chosen for dissolving the analyte containing RTIL-rich phase because of its solubility property in [C_4MIM][PF_6] and the compatibility with the mobile phase being used. The ACN volume was studied in the range of 50–150 μL. It was found that the peak areas of all analytes decreased by increasing the volume ACN. Using ACN of less than 50 μL, the RTIL rich-phase could not be completely dissolved. Therefore, 50 μL of ACN was adopted for dissolving the extract before introducing into the HPLC system. The selected conditions for RTIL-LLME of carbamates were 3 mL sample, 100 μL [C_4MIM][PF_6], 7 min extraction time and 50 μL ACN.

3.3. Analytical performance

Under the above-selected conditions, the analytical performance of RTIL-LLME combined with HPLC for analysis of carbamates was evaluated. A series of experiments was

Table 1
Analytical performance of the method.

Carbamates	HPLC				RTIL-LLME-HPLC				
	Linear range (μg mL^{-1})	LOD (μg mL^{-1})	% RSD (n = 5)		Linear range (μg mL^{-1})	LOD (μg mL^{-1})	% RSD (n = 5)		EF
			t_R	Area			t_R	Area	
Methomyl (MTM)	2.0–15.0	1.00	0.32	2.52	–	–	–	–	–
Propoxur (PPX)	0.2–10.0	0.10	0.18	3.50	0.02–5.00	0.005	0.52	10.17	20
Carbofuran (CBF)	0.2–10.0	0.10	0.16	3.42	0.02–5.00	0.005	0.48	3.96	20
Carbaryl (CBR)	0.1–10.0	0.02	0.28	3.28	0.01–5.00	0.002	0.32	5.89	10
Isoprocarb (IPC)	2.0–15.0	0.50	0.40	4.10	0.04–8.00	0.02	0.62	6.56	25
Methiocarb (MTC)	0.2–15.0	0.05	0.23	1.82	0.05–8.00	0.005	0.49	8.40	10
Promecarb (PMC)	1.0–15.0	0.50	0.14	4.79	0.40–8.00	0.04	0.30	4.90	12.5

–: not determined.

Table 2
Analysis of carbamate pesticides in real samples.

Sample	Market	Amount found, $\mu g\,g^{-1}$ ($n = 3$)					
		PPX	CBF	CBR	IPC	MTC	PMC
Watermelon	Local Market	–	–	–	–	0.10 ± 0.05	0.17 ± 0.03
	Super Market I	–	–	–	1.28 ± 0.50	0.60 ± 0.20	1.34 ± 0.35
	Super Market II	0.04 ± 0.01	0.53 ± 0.20	0.06 ± 0.03	–	0.45 ± 0.25	2.61 ± 0.53
Cantaloupe1	Local Market	–	–	0.06 ± 0.02	–	0.01 ± 0.002	–
	Super Market I	–	–	–	–	0.37 ± 0.06	–
	Super Market II	–	–	–	–	0.45 ± 0.27	–
Cantaloupe2	Local Market	0.02 ± 0.01	–	0.06 ± 0.03	–	0.11 ± 0.03	0.55 ± 0.25
Strawberry	Local Market	–	–	–	–	–	–
	Super Market I	–	0.11 ± 0.05	0.02 ± 0.01	0.54 ± 0.30	0.43 ± 0.23	1.55 ± 0.37
Orange	Local Market	–	–	0.07 ± 0.02	0.18 ± 0.05	4.50 ± 1.35	–
	Super Market I	0.72 ± 0.20	0.21 ± 0.10	0.16 ± 0.05	1.50 ± 0.50	0.94 ± 03	1.81 ± 0.83
	Super Market II	0.22 ± 0.10	0.18 ± 0.07	–	0.90 ± 0.30	0.38 ± 0.13	21.25 ± 5.73
Apple	Super Market I	0.03 ± 0.01	–	–	–	0.45 ± 0.23	1.24 ± 0.45
	Super Market II	–	–	–	–	0.38 ± 0.14	1.30 ± 0.73

–: not detected.

designed for obtaining linear range, precision, limit of detection (LOD) and enrichment factor. Linearity was observed in the range of 0.01–8.00 $\mu g\,mL^{-1}$ with the correlation coefficient of greater than 0.99. The characteristic calibration data obtained are listed in Table 1. The relative standard deviation (RSD) was determined using five solutions of the carbamates (4.0 $\mu g\,mL^{-1}$ methomyl, 0.5 $\mu g\,mL^{-1}$ propoxur, 0.5 $\mu g\,mL^{-1}$ carbofuran, 0.2 $\mu g\,mL^{-1}$ carbaryl, 2.0 $\mu g\,mL^{-1}$ isoprocarb, 1.0 $\mu g\,mL^{-1}$ methiocarb and 4.0 $\mu g\,mL^{-1}$ promecarb). The RSD values of the retention times and peak areas range from 0.3 to 0.6% and 4.0 to 10.2%, respectively. The sensitivity was evaluated in term of LOD as concentration giving the signal-to-noise ratio of 3 (S/N = 3) and ranged between 0.002 and 0.040 $\mu g\,mL^{-1}$. The enhancement factors, calculated by comparing the slopes of the calibration

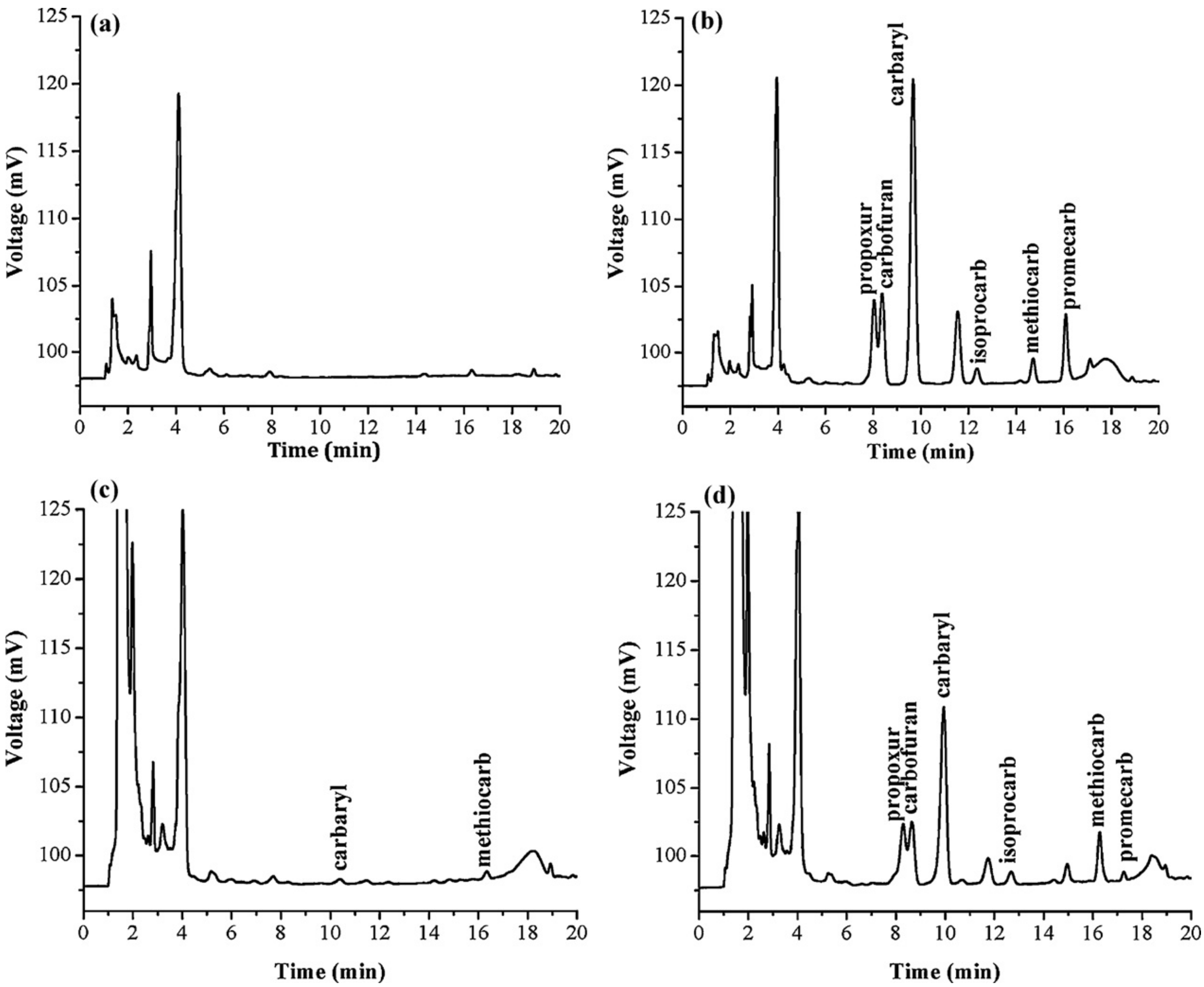

Fig. 2. Typical chromatograms of the studied samples: (a) water, (b) water spiked with 1.0 $\mu g\,mL^{-1}$ of each carbamates, (c) cantaloupe and (d) cantaloupe spiked with 1.0 $\mu g\,mL^{-1}$ of each carbamates.

Table 3
Recoveries of the studied carbamates in spiked samples.

Sample	Market	Recovery (%)					
		PPX	CBF	CBR	IPC	MTC	PMC
Water I[a]	–	90	99	102	98	98	89
Water II[a]	–	92	96	87	93	93	104
Water III[a]	–	100	95	103	100	116	94
Watermelon	Local Market[b]	115	88	81	90	93	85
	Super Market I[c]	96	100	106	92	104	101
	Super Market II[c]	96	100	103	103	93	88
Cantaloupe1	Local Market[b]	98	103	82	118	117	104
	Super Market I[c]	95	96	104	107	101	107
	Super Market II[c]	93	95	98	105	93	94
Cantaloupe2	Local Market[b]	83	99	93	101	88	86
Strawberry	Local Market[b]	93	102	82	92	103	92
	Super Market I[c]	107	103	99	101	107	82
Orange	Local Market[b]	83	98	85	107	102	110
	Super Market I[c]	89	110	106	106	99	98
	Super Market II[c]	100	99	99	98	108	97
Apple	Super Market I[c]	105	103	102	92	94	92
	Super Market II[c]	100	104	99	104	97	112

–: not determined.

[a] Spiked concentration, 1 $\mu g\,mL^{-1}$.

[b] Spiked concentration, 1 $\mu g\,g^{-1}$.

[c] Spiked concentration, 0.20 $\mu g\,g^{-1}$.

graphs with and without preconcentration, were in the range of 10–25. Unfortunately, methomyl could not be determined under the selected HPLC conditions after LLME using [C_4MIM][PF_6] RTIL because it could not be separated from the ionic liquid peak, as shown in Fig. 1(b). However, the enrichment factors as well as the LODs obtained by the present work were improved when comparing with those obtained by cloud point extraction previously reported by our group [14].

3.4. Application to real samples

The applicability of the proposed RTIL-LLME combined with HPLC method was evaluated by determination of carbamates in various samples. Application in environmental samples was demonstrated by analyzing natural surface waters, while application in food samples was studied by testing with a variety of fruits. Before analysis, samples were treated by following the procedure described in Section 2.3. The results are summarized in Table 2. It was found that no residue of the studied carbamates was observed in the water samples (data not shown). The carbamates commonly found in the studied fruit samples were carbaryl, methiocarb and promecarb. However, the amounts of carbamates found in the fruit samples were lower than the maximum residue levels (MRLs) established by Thai Agricultural Commodity and Food Standard, TACFS 9002-2008 (carbaryl, 1.0 $mg\,kg^{-1}$, 3.0 $mg\,kg^{-1}$ and 15 $mg\,kg^{-1}$ in watermelon, cantaloupe and orange, respectively; carbofuran, 0.1 $mg\,kg^{-1}$ and 0.3 $mg\,kg^{-1}$ in watermelon and cantaloupe, respectively; methomyl, 0.2 $mg\,kg^{-1}$, 0.2 $mg\,kg^{-1}$, 1.0 $mg\,kg^{-1}$ and 0.2 $mg\,kg^{-1}$ in watermelon, cantaloupe, orange and apple, respectively).

To test the accuracy and selectivity of the method, these samples were spiked with the standards of each analyte at 1.00 $\mu g\,mL^{-1}$ for water and 0.20 and 1.00 $\mu g\,g^{-1}$ for fruit samples, before analysis by whole analytical process as proposed. The recoveries were calculated, as listed in Table 3, and were in the range of 87–116% and 81–118% for surface water samples and fruit samples, respectively. Fig. 2 shows the typical chromatograms of the samples.

4. Conclusion

In the present study, a simple LLME method using [C_4MIM][PF_6] RTIL as extraction solvent was proposed for preconcentration of carbamates prior to analysis by HPLC. The method provided good precision, acceptable recovery and showed reliability with well suited analytical detection range for application in fruit samples. The proposed simple extraction procedure with a very low consumption RTIL offers an alternative green analytical method for routine analysis.

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