

Ionic Liquid-Based Dispersive Liquid-Liquid Microextraction Coupled with High Performance Liquid Chromatography for the Determination of Spirotetramat in Water Samples

Fatemeh Nourpish¹, Ali Asghar Amiri², Ali Sheibani*¹, Masoud Reza Shishehbore¹

1. Department of Chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran

2. Department of Chemistry, Shiraz Branch, Islamic Azad University, Shiraz, Iran

Received: 5 January 2020

Accepted: 30 March 2020

DOI: 10.30473/ijac.2020.52320.1168

Abstract

In this study, a simple and sensitive method was developed for pre-concentration of spirotetramat (SPT) using the ionic liquid-based dispersive liquid-liquid microextraction. After extracting of SPT into 1-butyl-3-methylimidazolium hexafluorophosphate (ionic liquid), the insecticide was injected into HPLC system for determining. Under the optimum conditions, the developed method provided a linearity in the range of 0.05–2.0 $\mu\text{g mL}^{-1}$ with $R^2 = 0.9987$, and also enrichment factor was 250. The detection limit and relative standard deviation of the developed method were 0.01 $\mu\text{g mL}^{-1}$ and 2.7%, respectively. The proposed method was successfully applied to the pre-concentration and determination of SPT in spiked water samples with mean recoveries 94.0–96.0%.

Keywords

Spirotetramat; Ionic Liquid; Dispersive Liquid-Liquid Microextraction; HPLC; Water Sample.

1. INTRODUCTION

Spirotetramat (SPT) [cis-3-(2,5 dimethylphenyl)-8-methoxy-2-oxo-1-azaspiro[4.5]dec-3-en-4-yl ethyl carbonate] is a novel keto-enol and an effective tetramic acid-based insecticide [1, 2], that can be used in agricultural products and various pest insects containing pyrethroids, organophosphates, neonicotinoids, insect growth regulators, and carbamates [3-5]. Selectively, action of SPT is in the insect nervous system by inhibiting nicotinic acetylcholine receptors [6]. Also, when SPT operates as lipid biosynthesis inhibitors, it can be decreased fecundity and fertility until ingested orally by immature life stage forms of sucking pests [7] and leading to death of juvenile insects such as whiteflies, aphids, psyllids, and scales within 2 to 10 days after application [8]. Application of SPT is identified with active over a broad temperature range, has excellent photostability and good residual activity and does not harm crops [7]. The outcomes are given that SPT has highly favorable toxicological and ecotoxicological profile [1]. Additionally, SPT is included in the description for implement and risk evaluation purposes in primary crops. Therefore, it is still necessary that sensitive and selective methods to be developed for the extraction and determination of SPT.

Ionic liquids (ILs) are salts composed of organic cations and various anions with the melting point lower than 100 °C. The application of ILs in

analytical chemistry, especially to separation fields, is valuable because these solvents have properties including negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water and organic solvents, as well as good extractability for various organic compounds. ILs have been used as environmentally friendly solvents for green chemistry, and they are good substitutes for volatile and flammable organic solvents [9]. The water miscibility of IL ions can be ordered. The select of anion has the greatest effect on controlling hydrophobicity [10]. Extra types of reactions have been done in ILs [11]. The earliest reports on ILs were the evaluation of the anions properties of hexafluorophosphate ($[\text{PF}_6]^-$), tetrafluoroborate ($[\text{BF}_4]^-$) [12], haloaluminate ($[\text{AlCl}_4]^-$) [13], bis(trifluoromethanesulfonyl) imide ($[\text{NTf}_2]^-$) and perfluoroalkylphosphate ($[\text{FAP}]^-$) [14]. It has been demonstrated that 1-alkyl-3-methylimidazolium cation based on ($[\text{PF}_6]^-$) and ($[\text{BF}_4]^-$) exhibits similar properties which are often still absorb moisture that caused to change the physical and chemical properties of the liquids [10, 15], while ($[\text{AlCl}_4]^-$) is sensitive to moisture and ($[\text{NTf}_2]^-$) or ($[\text{FAP}]^-$) less moisture sensitive than the others [16]. Carda-Broch et. al. demonstrated that 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM] $[\text{PF}_6]$ is a typical example of a room temperature IL forming a biphasic liquid system with water

*Corresponding Author: sheibani@iauyazd.ac.ir or alisheibani@ymail.com

[17]. The unique properties of [BMIM][PF₆] was reported by using in a wide range of stoichiometric, as well as catalytic reactions [18]. Furthermore, imidazolium salts of [PF₆]⁻ or [BF₄]⁻ are suited for liquid-liquid extraction and microextraction processes [19, 20].

Dispersive liquid-liquid microextraction (DLLME) is a novel technique for extraction of analytes from aqueous solutions. Assadi et. al. demonstrated that DLLME is a fast and simple pre-concentration/microextraction technique for analysis of various samples [21-23]. Recently, Pastor-Belda et. al. evaluated pesticides in soils by DLLME coupled with liquid chromatography and tandem mass spectrometry [24]. The combination of IL with DLLME provides the additional advantages of producing directly the analysis extracts by HPLC while avoiding the use of toxic chlorinated solvents [25-27]. According to the performed studies, HPLC can be more practical interest for determination of SPT [28-33]. As a result, following this strategy; a new method using DLLME technique combined with HPLC was developed for pre-concentration and determination of SPT, in present work. Herein, [BMIM][PF₆] played the role of an extracting solvent for the pre-concentration and extraction of SPT from aqueous solutions and then, SPT containing IL was injected into HPLC system for measurement. Finally, the developed sample preparation technique was applied for a selective pre-concentration/extraction of SPT from agricultural water samples. The novelty of the present research deals with the analysis of SPT in water samples with significant advantages such as extraction time, enrichment factor, volume of used IL (<80 µL), and fast determination by HPLC. The developed microextraction procedure was also simpler than conventional extraction techniques.

2. EXPERIMENTAL

2.1. HPLC apparatus and conditions

The HPLC system (Waters model 600E, U.S.A) used equipped with a helium degassing facility, auto-injector (Rheodyne model, 7125i U.S.A) with 10-µL loop, µBondapak C₁₈ column (Waters, Ireland) [300 × 3.9 mm id, 5.0 µm particle size] and UV-Vis (2487 waters) detector. The mobile phase consisted of 45:55 (%v/v) acetonitrile in water was used in this study. The prepared mobile phase was filtered using PTFE membrane filter and Supor-450 (Model Waters Corporation, U.S.A). It was pumped isocratically at a flow rate of 1.0 mL min⁻¹. The detector was utilized at 240 nm. Samples were injected via a model Millex-LCR (Ireland) syringe loading sample injector (0.45 µm).

2.2. Materials and reagents

SPT (95%) was obtained from Aldrich (Steinheim, Germany). Standard stock solution of SPT (10 µg mL⁻¹) was prepared by dissolving appropriate amount of SPT in mixture (45:55 %v/v) of acetonitrile and water as solvent. Acetonitrile and methanol solvents with HPLC grade were purchased from Merck. [BMIM][PF₆] was supplied from Aldrich. All materials used were of analytical-reagent grade and also the deionized water was used throughout the experiments. Agricultural water samples were collected from the local area of firoozabad of Iran.

2.3. DLLME procedure

A 10.0 mL of deionized water containing 1 µg mL⁻¹ SPT (pH 8.0) was placed in a glass test tube with conical bottom. 1.5 mL acetone (as disperser solvent) containing 80 µL [BMIM][PF₆] (as extracting solvent) was injected quickly using a syringe into a sample solution. A cloudy solution was rapidly formed that must be stable for a few min. After centrifugation at 4000 rpm for 10 min, the IL-rich phase was sedimented at the test tube. Then, the upper aqueous phase was removed with a syringe and IL phase was separated and dissolved in 0.2 mL of acetonitrile. Finally, the obtained mixture was injected into the HPLC system for SPT measurement.

3. RESULT AND DISCUSSION

3.1. HPLC Optimization

Due to the chemically structure of SPT particularly regarding its aromatic, chromatography column and analysis conditions should be investigated and optimized even though its retention and separation is possible with reverse phase column. The separation yield was depended on the ability of a column to separate the SPT. Intensity of SPT transitions at tested µBondapak C₁₈ column was higher than Nova-Pak C₁₈, Symmetry C₁₈, Finepak SIL C₁₈, Reprosil C₁₈ and Zorbax: Eclipse XDB (data not shown). Thus, the µBondapak C₁₈ column was used to obtain the better separation. The typical chromatogram of SPT in agriculture water as a real sample (before and after spiking) using µBondapak C₁₈ column was shown in Fig. 1. Modification of the mobile phase delivered to the column and its proportion were found to be the most important factor. In proposed method, various mobile phase compositions (acetonitrile-water and methanol-water) were investigated and evaluated. Finally, SPT was well separated using acetonitrile-water consisted of 45:55 (%v/v) in a flow rate 1.0 mL min⁻¹.

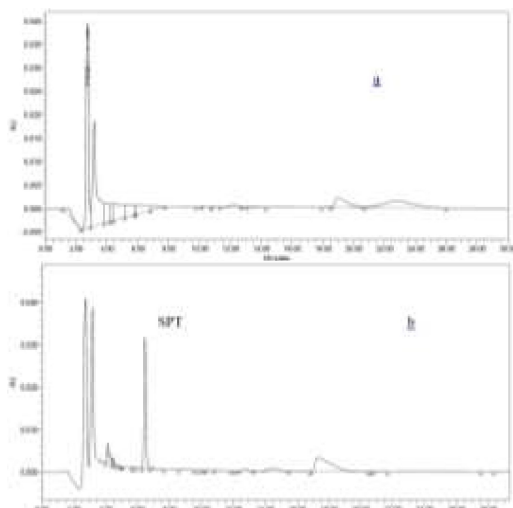


Fig. 1. Chromatogram of SPT in agriculture water as a real sample, before (a) and after (b) spiking.

3.2. Optimization of the experimental parameters for DLLME

The factors influencing the microextraction efficiency of SPT including: extraction and disperser solvent (type and volume), extraction and centrifugation time, pH and the diluent solvent volume were studied, and the optimized experimental conditions were established.

3.2.1. Effect of the disperser solvent (type and volume)

The disperser solvent should be miscible in both water sample and extraction solvent. It also has to disperse the extraction solvent in water sample. These are important characteristics for choosing the dispersive solvent. Furthermore, the combination of dispersive and extraction solvent has a key role on DLLME technique.

Acetone, acetonitrile and methanol have been applied in the most reported procedures of DLLME for different analytes. In this study, results showed that acetone was the best disperser solvent in developing the DLLME for SPT from water samples.

Optimization of volume of the dispersing solvent performed in further step. This factor can affect on formation of dispersion process. In the following, various volumes of acetone (0.5, 1.0, 1.5, 2.0 and 2.5 mL) containing extracting solvent (80 μ L) were added to aqueous sample. Then, DLLME and determining with HPLC system were made. The results showed significant dependence of extraction on the dispersing solvent volume. The best extraction efficiency (recovery) was obtained for 1.5 mL of acetone. The weak recoveries for lower dispersing solvent volumes can be related to form of unstable dispersion. Increasing solubility of [BMIM][PF₆] as the extracting solvent in high volumes (>1.5

mL) of acetone lead to reduce the recovery results. Therefore, 1.5 mL was selected as the optimum volume of acetone for obtaining the best extraction recovery.

3.2.2. Extraction time

Extraction time is an effective factor for obtaining a complete and fast extraction. Herein, extraction time is defined as the time interval between the injection of the mixture of disperser solvent and extraction solvent into the aqueous solution and starting to centrifuge. Short extraction time is a significant advantage of DLLME technique. Fig. 2 showed the effect of extraction time over the range of 1–5 min in the recovery results. It is seen that transfer of SPT from aqueous phase into IL phase reached equilibrium state quickly after 4 min, and then were constant. This time was short and also enough for rapid and complete extraction by IL-DLLME. Accordingly, extraction time 4-5 min was used for further experiments.

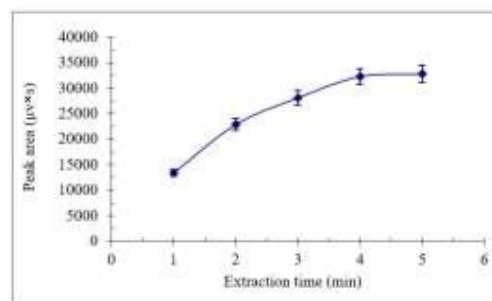


Fig. 2. Effect of extraction time on extraction recovery of SPT.

3.2.3. Centrifugation time

After optimizing the extraction time, the centrifugation time was examined in the range of 2–12 min at 4000 rpm. During this process, [BMIM][PF₆] was deposited at the bottom of conical test tube. The extraction efficiency increased up to 10 min and then, the sedimented phase had not obviously increasing. Hence, for saving time of extraction process; 10 min was selected as the optimum centrifugation time.

3.2.3. Volume of [BMIM][PF₆] (extraction solvent)

The extracting solvents must have low solubility in water and potential for extracting analytes. [BMIM][PF₆] has been used as an extracting solvent in extraction process. Capability, water-immiscibility, hydrophobicity and viscosity are the main advantages of it for separation and pre-concentration purposes [19, 20]. The volume of [BMIM][PF₆] as the extracting solvent (similar to the volume of dispersion solvent) is another important factor that should be optimized. Various volumes of [BMIM][PF₆] including: 20.0, 50.0, 80.0, 110.0, 140.0 μ L of IL were

added into 10.0 mL of sample solutions for the extraction of SPT, according to the general procedure and optimized conditions that were obtained in previous steps. The dependence curve (Fig. 3) with maximum recovery at 80 μL proved the effect of extracting solvent volume on the recovery of SPT. In smaller volumes than 80.0 μL , analyte transfer into extracting solvent was not complete and since the larger volumes did not lead to more extraction; therefore, 80.0 μL of [BMIM][PF₆] was used in further experiments. The low volume of extraction solvent in the present work is an advantage that can increase the enrichment factor.

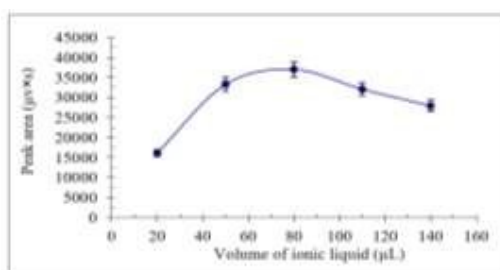


Fig. 3. Effect of [BMIM][PF₆] volume on extraction recovery of SPT.

3.2.4. pH of the SPT solution

The optimum pH of SPT solution for the DLLME procedure is based on the chemical nature of the analyte. Since SPT is a basic compound, the better recovery was expected at basic pH, at which it is non-ionized. The effect of pH was studied in range of 4–10 which exposed to the extraction procedure at the same conditions. According to the obtained results which illustrated in Fig. 4, the highest SPT extraction efficiency to interact and transfer to [BMIM][PF₆] phase was observed at pH 8.0. The low extraction recoveries were probably due to formation a ionized compound because of the reaction of proton with pair electrons on SPT (in the acidic pHs) and also the degradation of formed micelle (in the basic pHs). Therefore, further studies were performed at pH 8.0.

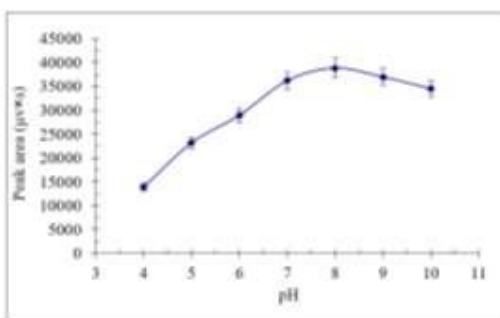


Fig. 4. Effect of pH on extraction recovery of SPT.

3.2.5. Effect of the volume of diluent solvent

The main criterion for selection of the diluent solvent is compatibility with mobile phase for injection into HPLC system and to obtain the symmetric peaks. Different volumes of acetonitrile (0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 mL) containing IL-rich of SPT was injected into HPLC system. According to the obtained results, the maximum extraction efficiency (near to 100%) was achieved at 0.2 mL of acetonitrile. Due to dilution, the extraction efficiency of developed method for SPT analysis decreased in the higher volumes of 0.2 mL. Therefore, this volume was selected as the optimum value of diluent solvent and also to reduce cost.

3.3. Analytical performance of the proposed method

For validating of the proposed method: linearity, accuracy, precision and limit of detection were determined. Under the optimized conditions, the calibration curve was drawn for extracting different concentrations of SPT (0.05–2.0 $\mu\text{g mL}^{-1}$) from aqueous solutions into [BMIM][PF₆] and injecting the SPT-containing IL into HPLC system. The linear relationship between SPT concentration and peak area ($Y = 43786 X + 2198.1$; $X = \text{SPT concentration as } \mu\text{g mL}^{-1}$) is revealed whose correlation coefficient (R^2) is 0.9987. In order to calculate the enrichment factor and extraction recovery (%), equations (1) and (2) were used:

$$EF = \frac{C_{sed}}{C_0} \quad (1)$$

where EF , C_{sed} and C_0 are the enrichment factor, the analyte concentration in sediment and aqueous samples (initial), respectively. C_{sed} was calculated from the calibration curve of insecticide standard solution in the applicable concentration range.

$$R\% = \frac{C_{sed} V_{sed}}{C_0 V_{aq}} \times 100 = EF \times \frac{V_{sed}}{V_{aq}} \times 100 \quad (2)$$

where $R\%$, V_{sed} , V_{aq} , are the extraction recovery (%), the volume of the sediment phase and the volume of aqueous sample, respectively.

The enrichment factor was calculated based on the equation (1) that was found to be 250. The limit of detection (LOD) defined as $3S_b/m$ (S_b is the standard deviation of the blank and m is the slope of the calibration curve) that was calculated to be $0.01 \mu\text{g mL}^{-1}$. The precision of method was reported as relative standard deviation (RSD%), 5 replicate determinations of retention time and the peak area were calculated and found to be 1.3 and 2.7%, respectively.

3.4. Measurement of SPT in real samples

The accuracy and applicability of proposed method were evaluated to determine SPT in

agricultural water. Water samples spiked with SPT at concentration levels of 0.5 and 1.0 $\mu\text{g mL}^{-1}$ were analyzed using the presented method for analyte extraction and determination. For each sample, analysis was repeated for five times. The results were averaged and reported as mean \pm standard deviations (SD). Recovery values were calculated and listed in Table 1. Results indicated that proposed IL-DLLME-HPLC for the pre-concentration and quantification of SPT in tested water samples were satisfactory (within 94.0–96.0%).

Table 1. Analysis of SPT in a water sample using the IL-DLLME-HPLC proposed method.

Sample	Added ($\mu\text{g mL}^{-1}$)	Found (%) ($\mu\text{g mL}^{-1}$)	Recovery (%)
	0	-	-
Agricultural water (well)	0.50	0.47 ± 0.03	94.0
	1.00	0.96 ± 0.05	96.0

Mean \pm standard deviation (n=3)

In addition, the accuracy and precision of the proposed method were compared with to those of other published methods used for the SPT analysis in different samples (Table 2). According to this Table, the proposed method presented the satisfactory results that are better or comparable to other reported methods [8, 29, 32-34]. The method can be easily adopted for analysis of spirotetramat in other matrices for pesticide residue analysis.

4. CONCLUSION

This paper describes a new method for pre-concentration/extraction and quantification of SPT. To achieve the goal of this work, an integrative and multidisciplinary approach has been successfully applied involving: using IL as extracting solvent at DLLME (sample preparation) and the development of HPLC for

analyte determining. The LOD and other aspects of method performance were good. Regarding the obtained results, the developed method in this work could be considered as an alternative for the analysis of water samples for SPT.

ACKNOWLEDGEMENTS

The authors are thankful to the Islamic Azad University, Yazd branch for the support of this work.

REFERENCES

- [1] E. Brück, A. Elbert, R. Fischer, S. Krueger, J. Kühnhold, A.M. Klueken, R. Nauen, J.F. Niebes, U. Reckman, J.J. Schnorbach, R. Steffens and X. van Waetermeulen, Movento®, an innovative ambimobile insecticide for sucking insect pest control in agriculture: biological profile and field performance, *Crop. Prot.* 28 (2009) 838–844.
- [2] S. Vemuri, C. Rao and S. Swarupa, Dissipation of spirotetramat and imidacloprid in grapes and soil, *J. Multi. Eng. Sci. Technol.* 1 (2014) 319-324.
- [3] S.Wang, Y. Zhang, X. Yang, W. Xie and Q. Wu, Resistance Monitoring for eight Insecticides on the sweetpotato whitefly (Hemiptera: Aleyrodidae) in China, *J. Econ. Entomol.* 110 (2017) 660-666.
- [4] M. Ahmad, M.I. Arif and M. Naveed, Dynamics of resistance to organophosphate and carbamate insecticides in the cotton whitefly *Bemisia tabaci* (Hemiptera: Aleyrodidae) from Pakistan, *J. Pest. Sci.* 83 (2010) 409-420.
- [5] Y. Gong, X. Shi, N. Desneux and X. Gao, Effects of spirotetramat treatments on fecundity and carboxylesterase expression of *Aphis gossypii* Glover, *Ecotoxicology* 25 (2016) 655-663.

Table 2. Comparison of accuracy and precision of the proposed IL-DLLME-HPLC method with other presented methods for SPT determination in different samples.

Method	Recovery (%)	RSD (%)	Sample	Ref.
HPLC	84.6-98.9	< 5.5	Vegetables	8
^a LLE	90.5-97.2	< 3.4	Soil	
^b LC/MS	82.0-110.0	< 14.0	Fruits and vegetables	29
^c QUEChERS				
^d HPLC (QUEChERS)	72.7-86.8	< 9.0	Mango	32
	74.8-86.9	< 7.7	Cabbage	
LC/MS (QUEChERS)	91.0-110.0	< 11.0	Pistachio	33
LC-MS/MS (QuEChERS- ^e SPE)	81.0-103.0	< 7.9	Spinacia oleracea L., soil and water	34
^f IL-DLLME-HPLC	94.0-96.0	2.7	Agricultural water	This work

^a Liquid liquid extraction. ^b Liquid chromatography/Mass spectrometry. ^c Quick, Easy, Cheap, Effective, Rugged, and Safe. ^d High performance liquid chromatography. ^e Solid phase extraction. ^f Ionic liquid-dispersive liquid liquid microextraction.

- [6] A. Elbert, U. Ebbinghaus-Kintscher, C. Erdelen, R. Nauen and H. Schnorbach, The biological profile of thiacloprid—a new chloronicotinyl insecticide, *Pflanzen-Nachricht Bayer* 54 (2001)185-208.
- [7] R. Nauen, U. Reckmann, J. Thomzik and W. Thielert, Biological profile of spirotetramat (Movento®)—a new two-way systemic (ambimobile) insecticide against sucking pest species, *Bayer Crop. Sci. J.* 61 (2008) 245-278.
- [8] B. Singh, K. Mandal, S.K. Sahoo, U. Bhardwaj and R.S. Battu, Development and validation of an HPLC method for determination of spirotetramat and spirotetramat cis enol in various vegetables and soil, *J. AOAC Inter.* 96 (2013) 670-675.
- [9] J. Liu, J.A. Jonsson and G. Jiang, Application of ionic liquids in analytical chemistry, *TrAC- Trends Anal. Chem.* 24 (2005) 20-27.
- [10] R. Sheldon, Catalytic reactions in ionic liquids, *Chem. Commun.* 23 (2001) 2399-2407.
- [11] P. Bonhote, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, Hydrophobic, highly conductive ambient-temperature molten salts, *Inorg. Chem.* 35 (1996) 1168-78.
- [12] P. Wasserscheid and W. Keim, Ionic liquids—new “solutions” for transition metal catalysis, *Angew. Chem. Int. Edit.* 39 (2000) 3772-3789.
- [13] J.S. Wilkes, J.A. Levisky, R.A. Wilson and C.L. Hussey, Dialkylimidazolium chloroaluminate melts: a new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis, *Inorg. Chem.* 21 (1982) 1263-1264.
- [14] A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J.H. Davis and R.D. Rogers, Task-specific ionic liquids for the extraction of metal ions from aqueous solutions, *Chem. Commun.* 1 (2001) 135-136.
- [15] P.Y. Chen and I.W. Sun, Electrochemical study of copper in a basic 1-ethyl-3-methylimidazolium tetrafluoroborate room temperature molten salt, *Electrochim. Acta* 45(3) (1999) 441-450.
- [16] L. Barrosse-Antle, A. Bond, R. Compton, A. O'Mahony, E. Rogers and D. Silvester, Voltammetry in room temperature ionic liquids: comparisons and contrasts with conventional electrochemical solvents, *Asian J. Chem.* 5 (2010) 202-30.
- [17] S. Carda-Broch, A. Berthod and D. Armstrong, Solvent properties of the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid, *Anal. Bioanal. Chem.* 375 (2003) 191-199.
- [18] T. Welton, Room-temperature ionic liquids: Solvents for synthesis and catalysis, *Chem. Rev.* 99(8) (1999) 2071-2084.
- [19] L. He, X. Luo, X. Jiang and L. Qu, A new 1, 3-dibutylimidazolium hexafluorophosphate ionic liquid-based dispersive liquid–liquid microextraction to determine organophosphorus pesticides in water and fruit samples by high-performance liquid chromatography, *J. Chromatogr. A* 1217 (2010) 5013-5020.
- [20] S. Li, S. Cai, W. Hu, H. Chen and H. Liu, Ionic liquid-based ultrasound-assisted dispersive liquid–liquid microextraction combined with electrothermal atomic absorption spectrometry for a sensitive determination of cadmium in water samples, *Spectrochim. Acta B* 64 (2009) 666-671.
- [21] M. Rezaee, Y. Assadi, M.R.M. Hosseini, E. Aghaee, F. Ahmadi and S. Berijani, Determination of organic compounds in water using dispersive liquid–liquid microextraction, *J. Chromatogr. A* 1116 (2006) 1-9.
- [22] S. Berijani, Y. Assadi, M. Anbia, M.R.M. Hosseini and E. Aghaee, Dispersive liquid–liquid microextraction combined with gas chromatography–flame photometric detection: Very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water, *J. Chromatogr. A* 1123 (2006) 1-9.
- [23] R.R. Kozani, Y. Assadi, F. Shemirani, M.R.M. Hosseini and M.R. Jamali, Part-per-trillion determination of chlorobenzenes in water using dispersive liquid–liquid microextraction combined gas chromatography–electron capture detection, *Talanta* 72 (2007) 387-393.
- [24] M. Pastor-Belda, I. Garrido, N. Campillo, P. Vinas, P. Hellín, P. Flores and J. Fenoll, Dispersive liquid–liquid microextraction for the determination of new generation pesticides in soils by liquid chromatography and tandem mass spectrometry, *J. Chromatogr. A* 1394 (2015) 1-8.
- [25] M.T. Pena, M.C. Casais, M.C. Mejuto and R. Cela, Development of an ionic liquid based dispersive liquid–liquid microextraction method for the analysis of polycyclic aromatic hydrocarbons in water samples, *J. Chromatogr. A* 1216 (2009) 6356-6364.
- [26] M. Asensio-Ramos, J. Hernández-Borges, T.M. Borges-Miquel and M.Á. Rodríguez-

- Delgado, Ionic liquid-dispersive liquid-liquid microextraction for the simultaneous determination of pesticides and metabolites in soils using high-performance liquid chromatography and fluorescence detection, *J.Chromatogr. A* 1218 (2011) 4808-4816.
- [27] M.J. Trujillo-Rodríguez, P. Rocio-Bautista, V. Pino and A.M. Afonso, Ionic liquids in dispersive liquid-liquid microextraction, *TrAC- Trend Anal. Chem.* 51 (2013) 87-106.
- [28] S. Mohapatra, M. Deepa, S. Lekha, B. Nethravathi, B. Radhika and S. Gourishanker, Residue dynamics of spirotetramat and imidacloprid in/on mango and soil, *Bull. Environ. Contam. Toxicol.* 89 (2012) 862-867.
- [29] Y. Zhu, X. Liu, J. Xu, F. Dong, X. Liang, M. Li, L. Duan and Y. Zheng, Simultaneous determination of spirotetramat and its four metabolites in fruits and vegetables using a modified quick, easy, cheap, effective, rugged, and safe method and liquid chromatography/tandem mass spectrometry, *J. Chromatogr. A* 1299 (2013) 71-77.
- [30] E. Watanabe, Y. Kobara and Y. Yogo, Rapid and simple analysis of pesticides persisting on green pepper surfaces swabbing with solvent-moistened cotton, *J. Agr. Food Chem.* 60 (2012) 9000-9005.
- [31] P. Jovanov, V. Guzsvány, M. Franko, S. Lazić, M. Sakač, I. Milovanović and N. Nedeljković, Development of multiresidue DLLME and QuEChERS based LC-MS/MS method for determination of selected neonicotinoid insecticides in honey liqueur, *Food Res. Int.* 55 (2014) 11-19.
- [32] S. Mohapatra, M. Deepa and G. Jagadish, An efficient analytical method for analysis of spirotetramat and its metabolite spirotetramat-enol by HPLC, *Bull. Environ. Contam. Toxicol.* 88 (2012) 124-128.
- [33] M. Faraji, R. Noorbakhsh, H. Shafieyan and M. Ramezani, Determination of acetamiprid, imidacloprid, and spirotetramat and their relevant metabolites in pistachio using modified QuEChERS combined with liquid chromatography-tandem mass spectrometry, *Food Chem.* 240 (2018) 634-641.
- [34] M. Zhiyuan, R. Li, S. Yueyi, X. Zhiying and C. Xiaojun, Simultaneous determination of spirotetramat and its four metabolites in *Spinacia oleracea* L., soil and water using liquid chromatography-tandem mass spectrometry, *Chinese J. Pestic. Sci.* 19 (2017) 482-490.

میکرواستخراج مایع - مایع پخشی بر پایه مایعات یونی جفت شده با کروماتوگرافی مایع با کارایی بالا برای اندازه‌گیری اسپروترامات در نمونه‌های آبی

فاطمه نورپیشه^۱، علی اصغر امیری^۲، علی شبانی^{۱*}، مسعودرضا شیشه‌بر^۱

۱. گروه شیمی، دانشگاه آزاد اسلامی یزد، یزد، ایران

۲. گروه شیمی، دانشگاه آزاد اسلامی شیراز، شیراز، ایران

تاریخ دریافت: ۱۵ دی ۱۳۹۸ تاریخ پذیرش: ۱۱ فروردین ۱۳۹۹

چکیده

در این مطالعه، یک روش ساده و حساس برای پیش تغلیظ و اندازه‌گیری اسپروترامات (سم) با استفاده از تکنیک میکرواستخراج مایع-مایع پخشی جفت شده با کروماتوگرافی مایع با عملکرد بالا توسعه داده شده است. پس از استخراج اسپروترامات با مایع یونی ۱-بوتیل-۳-متیل ایمیدازولیوم هگزاfluوروفسفات، این سم از محلول جدا شده و به دستگاه کروماتوگرافی جهت اندازه‌گیری تزریق می‌شود. در شرایط بهینه، یک گستره خطی در محدوده ۰/۰۵ تا ۲ میکروگرم بر میلی لیتر حاصل شد ($R^2 = ۰/۹۹۸۷$) و همچنین فاکتور تغلیظ ۲۵۰ بود. حدتشخیص و انحراف استاندارد نسبی به ترتیب ۰/۰۱ و ۲/۷ میکروگرم بر میلی لیتر بدست آمد. روش پیشنهادی برای پیش تغلیظ و اندازه‌گیری اسپروترامات در نمونه‌های آبی تزریق شده بطور موفقیت آمیزی بکار گرفته شد که متوسط بازیابی ها بین ۹۴ تا ۹۶ درصد شد.

واژه‌های کلیدی

اسپروترامات؛ مایع یونی؛ میکرواستخراج مایع مایع پخشی؛ کروماتوگرافی مایع با عملکرد بالا؛ نمونه آبی.