Journal of Chromatography B, 897 (2012) 32–36

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography B

journal homepage: www.elsevier.com/locate/chromb

Determination of imidacloprid in rice by molecularly imprinted-matrix solid-phase dispersion with liquid chromatography tandem mass spectrometry

Ligang Chen, Bin Li*

Department of Chemistry, College of Science, Northeast Forestry University, 26 Hexing Road, Harbin 150040, China

ARTICLE INFO

Article history:
Received 24 February 2012
Accepted 4 April 2012
Available online 12 April 2012

Keywords:
Matrix solid-phase dispersion
Molecularly imprinted polymer
Liquid chromatography–tandem mass spectrometry
Imidacloprid
Rice

ABSTRACT

A new method based on matrix solid-phase dispersion (MSPD) coupled with liquid chromatography tandem mass spectrometry has been developed for the determination of imidacloprid in rice. The molecularly imprinted polymers were synthesized and applied as the dispersant of MSPD for selective extraction of imidacloprid from rice, while interferences originated from sample matrices were eliminated simultaneously. The satisfactory recovery of imidacloprid was obtained by the optimized extraction conditions: 1:2 as the ratio of sample to MIPs; 8 min as the dispersion time; 20% aqueous methanol as washing solvent and methanol as elution solvent. Under the optimal conditions, the linearity of imidacloprid in rice sample was achieved in the range of 10–1000 ng/g, and limit of detection was 2.4 ng/g. The relative standard deviations of intra- and inter-day tests ranging from 4.5% to 5.9% and from 4.8% to 7.1% are obtained, respectively. The proposed method was applied to the determination of imidacloprid in eight rice samples with recoveries in the range of 83.8–92.5%.

1. Introduction

Imidacloprid [1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine] (Fig. 1) is a systemic nitroguanidine insecticide that belongs to the neonicotinoid family [1]. Because of the extensive application of imidacloprid in agriculture to control insect pests, such as Colorado potato beetles, aphids, termites and thrips [2], its residue may occur in foods, including grains, fruits and vegetables, and therefore, pose a potential hazard for consumers [3]. In order to guarantee consumer safety, the maximum residue limit (MRL) of imidacloprid in rice established by China is 50 ng/g [4]. It is imperative to develop a reliable analytical method for analyzing imidacloprid in food samples.

The most frequently reported method for determination of imidacloprid is based on liquid chromatography (LC) coupled with UV [5,6], diode array detector [7,8] or mass spectrometry (MS) [9,10]. Before LC analysis, sample preparation plays an essential role in the analysis of imidacloprid. The traditional method is liquid–liquid extraction (LLE) [7]. However, this technique is time consuming, laborious, and requires large volumes of organic solvent. Solid phase extraction (SPE) was also used for cleanup and preconcentration of imidacloprid in complex samples [1]. Compared with LLE, SPE usually has the advantages of simplicity, speed, and less consumption of organic solvents [11]. However, solvent extraction must be used before SPE when analyzing solid samples.

In recent years, a promising technique, in witch extraction and clean-up are performed in one step, matrix solid-phase dispersion (MSPD) was obtained extensive application [12,13]. It involves direct mechanical blending of sample with a solid support, and subsequent elution of the analytes with solvent. The technique could save analysis time and organic solvent employed. However, because the common dispersant in MSPD (C18, C8, silica, florisil, etc.) usually lack selectivity, and are easily subjected to interference by non-target substances with similar characteristics [14–16], so further improving the selectivity of MSPD is still a strategy to be mentioned.

Molecularly imprinted polymers (MIPs) are crosslinked polymers with specific binding sites for a particular analyte. These binding sites are tailor-made in situ by the copolymerization of crosslinking monomers and functional monomers in the presence of the print molecule, called the template. After polymerization, the template is removed from the polymer. This leaves recognition sites that, in terms of size, shape and functionality, are complementary to the print molecule. So, ideally, the resulting MIPs selectively rebinds the template in preference to other related structures [17]. The synthesis technique is simple, cheap and the polymers obtained exhibit high selectivity, excellent mechanical strength, and durability to heat, acid and base conditions. These properties allow MIPs to be used in various fields, such as chromatographic separation, SPE, chemical sensors and catalysis [18–21].

* Corresponding author. Tel.: +86 451 82190679 8244.
E-mail addresses: ligangchen2010@yahoo.cn (L. Chen), libinzh62@163.com (B. Li).

1570-0232/$ – see front matter © 2012 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.jchromb.2012.04.004

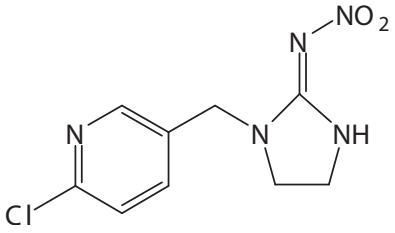

Fig. 1. The structure of imidacloprid.

If the MIPs used as MSPD sorbent, the resulting extraction method (MIP-MSPD), will not only have fast extraction characteristic, but also have selectivity for the guest molecule [22]. In this paper, the MIP-MSPD method was used for fast and selective extraction of imidacloprid from rice. The parameters affecting the performance of MSPD were evaluated in order to achieve optimal recovery and reduce non-specific interactions. The imidacloprid extracted from rice was determined by LC–MS/MS. Under the optimal conditions, good recovery and precision with low detection limit were obtained.

2. Materials and methods

2.1. Reagents and samples

The standard of imidacloprid was purchased from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Ethylene glycol dimethacrylate (EGDMA) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Methacrylic acid (MAA) and azobisisbutyronitrile (AIBN) were obtained from Guangfu (Tianjin, China). Chromatographic grade acetonitrile was obtained from Fisher (Pittsburgh, PA, USA). Methanol and acetic acid were purchased from Kermel Chemical Reagent (Tianjin, China). The water used was purified with a Milli-Q water purification system from Millipore (Billerica, MA, USA).

The stock solution of imidacloprid (1.0 mg/mL) was prepared in methanol and stored in a refrigerator at 4 °C and found to be stable for one month. The working solution was prepared daily by diluting the stock solution with water or chromatographic mobile phase.

Rice samples were randomly obtained from the local market in Harbin (China). Two kinds of rice samples, round shaped rice and long rice were analyzed in this study. The samples were stored at room temperature in the dark. One sample was checked to be free of imidacloprid, and it was used as blank rice for calibration and validation purposes.

2.2. Preparation of MIPs

For preparation of the MIPs, 1 mmol imidacloprid was dissolved in 5 mL of acetonitrile. Then 4.0 mmol MAA was added and incubated for 1 h. The cross-linker, EGDMA (20.0 mmol), and the initiator AIBN (0.05 g) were then added. The solution was degassed with nitrogen for 5 min under sonication. Then, the tube was sealed and polymerization took place at 60 °C in water bath for 24 h. The obtained polymer was ground and sieved. In order to extract the template, the polymer was subjected to Soxhlet extraction with methanol:acetic acid (9:1, v/v), until no imidacloprid could be detected by LC analysis. Finally, the polymer was dried in an oven overnight, and stored at room temperature. The non-imprinted polymers (NIPs) were prepared and processed similarly as above, except that the template molecule imidacloprid was not added.

2.3. MIP-MSPD procedure

The rice sample (0.5 g) was placed into a glass mortar and gently blended with 1 g of MIPs for 8 min using a pestle, to obtain homogeneous mixture. The homogenized sample was loaded into a cartridge. The cartridge was rinsed with 5.0 mL 20% methanol aqueous solution and then eluted with 8.0 mL methanol at the flow rate of 1.0 mL/min. The eluent was evaporated to dryness under nitrogen gas at 40 °C, and the residue was reconstituted with 1.0 mL of LC mobile phase for further LC–MS/MS analysis.

2.4. LC–MS/MS analysis

An Agilent 1100 liquid chromatograph (Palo Alto, CA, USA) consisting of a solvent degassing unit, a quaternary pump, an autosampler and a thermostatted column compartment was coupled to a MS system. Separation of the imidacloprid was achieved on a Hypersil ODS column (250 mm × 4.6 mm I.D., 5 μm) which was obtained from Elite (Dalian, China). The mobile phase was a mixture of 0.1% acetic acid aqueous solution and acetonitrile (75:25, v/v). The flow rate of the mobile phase was 1 mL/min. The column temperature was kept at 25 °C and the injection volume was 10 μL.

An API 3000 triple quadrupole mass spectrometer (Applied Biosystems, Concord, ON, Canada) equipped with electrospray ionization (ESI) source was used. Analyst 1.4.2 software (Applied Biosystems) was used for the control of equipment, data acquisition, and analysis. The ESI–MS/MS detection was performed in positive ion mode. The source dependent parameters were optimized by introducing the analyte into the mass spectrometer through direct infusion via a syringe pump (Harvard Apparatus, Holliston, MA, USA) at a flow rate of 10 μL min^{-1}. The instrument was operated with the ion spray voltage set at 4500 V and the heater gas temperature at 480 °C. Additionally, we used a nebulizer gas of 21 psi, a heater gas of 24 psi, a curtain gas of 20 psi, and a collision gas of 6 psi. All gases used were nitrogen. The declustering potential and collision energy were 62 and 22 V, respectively. The dwell time for each transition was 200 ms. The data acquisition was performed in the multiple reaction monitoring (MRM) mode.

All extraction and chromatographic analysis were performed three times.

3. Results and discussion

3.1. MS detection

The most sensitive transition in MRM mode was selected for quantification in the screening method. A minimum of three identification points are required to meet the identification performance criteria defined by the EU Commission for quantitative mass spectrometric detection. Using LC–MS/MS to monitor one precursor ion and two daughter ions 'earns' four identification points (1 for the parent ion and 1.5 for each daughter ion) and therefore fulfils these criteria. The fragment at m/z 256.1 corresponding to $[M+H]^+$ was selected as precursor ion. After fragmentation, imidacloprid exhibited the product ions at m/z 209.3 and 175.2 corresponding to $[M+H-HNO_2]^+$, $[M+H-NO_2-Cl]^+$. These transitions were used for the identification of imidacloprid. The ion transition m/z 256.1 → 209.3 was used for quantification of imidacloprid.

3.2. Binding study

The binding experiment was carried out by adding 20.0 mg MIPs or NIPs in a glass tube containing 2.0 mL of imidacloprid stock solution with concentrations varying from 0.05 to 0.5 mmol/L. The solution was incubated for 24 h at room temperature to obtain the maximum binding of imidacloprid to polymers, and then the

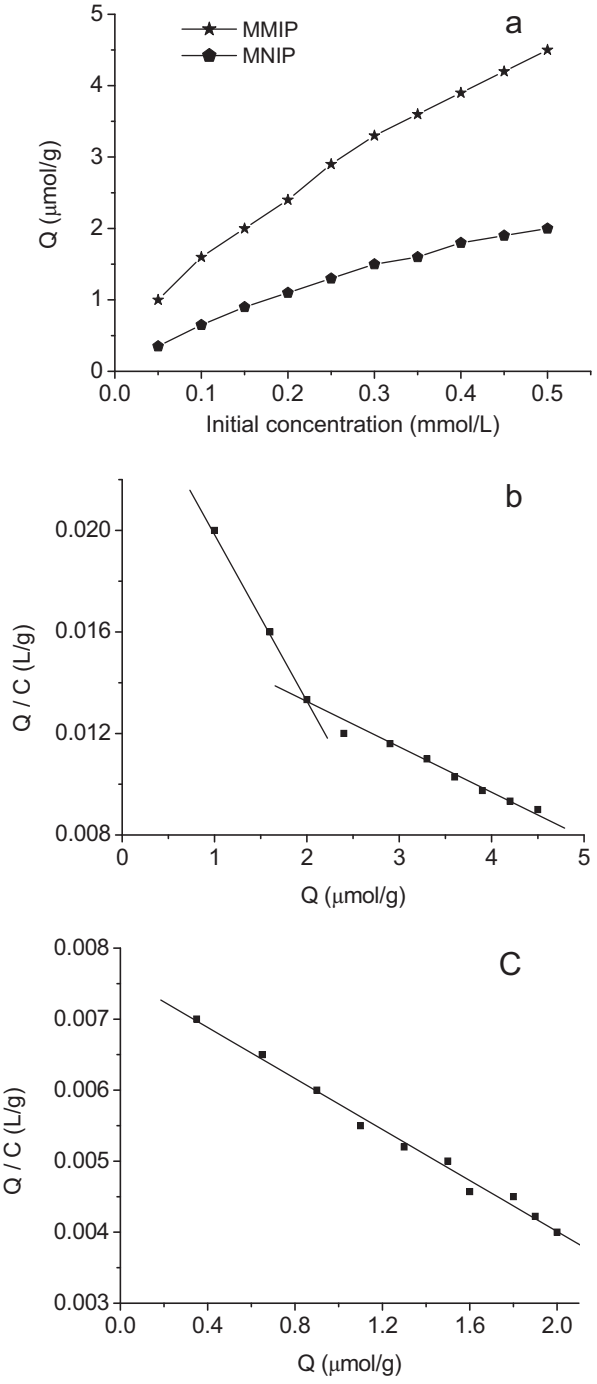

Fig. 2. Binding isotherms (a) and Scatchard plot analysis of the binding of imidacloprid onto the MIPs (b) and NIPs (c).

suspension was separated and analyzed by HPLC. The amount of imidacloprid bound to the polymers was obtained by subtracting the free concentration from initial concentration of imidacloprid added to the mixture.

As can be seen from Fig. 2a, the amount of imidacloprid bound to the MIPs and NIPs at equilibrium increased with the increasing of initial concentration of imidacloprid. However, the amount of imidacloprid bound to the MIPs was higher than that bound to the NIPs. This suggests that the imprinted cavities of the MIPs may cause the high affinity binding of the template to the polymer.

The Scatchard plot is a graphical method of analyzing equilibrium ligand binding data. It is used to determine the number of ligand-binding sites on a receptor, whether these sites show cooperative interactions, whether more than one class of site exists, and the respective affinities of each site. The experimental parameters used for a Scatchard plot are the free ligand concentration and the average number of ligand molecules bound to a receptor, at a particular ligand concentration at equilibrium. In recent years, the Scatchard plot was widely used for evaluating the interaction between template molecules and MIPs [23,24].

To estimate the binding properties of the MIPs and NIPs, static adsorption experiments were employed and the data were further processed with Scatchard analysis according to the equation:

$$\frac{Q}{C} = \frac{Q_{max} - Q}{K_d}$$

where Q is the amount of imidacloprid bound to the polymers at equilibrium; C is the free imidacloprid concentration at equilibrium; K_d is the dissociation constant and Q_{max} is the apparent maximum binding amount. The values of K_d and Q_{max} can be calculated from the slope and intercept of the linear line plotted in Q/C versus Q.

The scatchard analysis was applied by replotting the binding isotherm in the format of Q/C versus Q. As can be seen from Fig. 2b, the Scatchard plot for MIPs was not a single linear curve, and consisted of two linear parts with different slopes. It suggests that there exist two classes of heterogeneous binding sites in respect to the affinity for imidacloprid in MIPs. The linear regression equation for the left part of the curve in the Fig. 2b was $Q/C = -0.00667Q + 0.02667$. The K_d and Q_{max} were calculated to be 149.9 μmol/L and 4.0 μmol/g of dry polymer, respectively. The linear regression equation for the right part of this curve was $Q/C = -0.00168Q + 0.0164$. The K_d and Q_{max} were calculated to be 595.2 μmol/L and 9.8 μmol/g of dry polymer, respectively. The binding of imidacloprid to the NIPs was also analyzed by Scatchard method (Fig. 2c). It revealed homogeneous binding sites with K_d and Q_{max} values of 555.6 μmol/L and 4.2 μmol/g, respectively.

3.3. Optimization of the MSPD procedure

In the previous studies, many applications of MSPD have been developed by using octadecylsiloxane [25], silica gel [26], graphitic fiber [27], Florisil [28] or alumina [29] as dispersant for analysis of fish, milk, urine, plant, egg and hair samples. In addition, alumina has been used as MSPD dispersant for extraction of pesticides, such as organophosphorus insecticides (malathion and parathion-methyl) and an organochlorine pesticide (β-endosulfan) [30], and eight pesticides (penoxsulam, tricyclazole, propanil, azoxystrobin, molinate, profoxydim, cyhalofop-butyl, deltamethrin) and 3,4-dichloroaniline, the main metabolite of propanil [31] from rice.

However, due to the fact that these sorbents are usually nonselective, further purification of the extracts is often still required to remove co-extracts before further analysis [32]. In this paper, the MIP was used as dispersant for selective extraction of imidacloprid from rice. Other parameters affecting the performance of the MSPD, such as the best ratio of sample to MIPs, dispersion time, washing and elution solvents were investigated. When one parameter was changed, the other parameters were fixed at their optimal values.

In MSPD, a critical parameter is the ratio between matrix and dispersing material. The ratio (sample:sorbent) normally used in different studies ranges from 1:1 to 1:4 [33]. The best ratio guarantees that the sample is totally homogenized and dispersed in the sorbent. In this study, ratios of 1:1, 1:2, 1:3 and 1:4 (sample: MIP) were evaluated, using 0.5 g of sample (Fig. 1′a in supplementary material). Ratios 1:2, 1:3 and 1:4 presented better recovery. In this work, 1.0 g MIP was chosen because it saves material.

In the dispersion procedure, the sample needs to be completely dispersed in the sorbent [34]. However, the homogenization

process of the sample with the sorbent is laborious. The dispersion times of 2, 4, 6, 8 and 10 min were evaluated (Fig. 1′b in supplementary material). Eight minutes were used in this study, because the satisfactory recovery was obtained with saving time.

In order to reduce the non-specific adsorption and improve the selective binding of the imidacloprid, it is necessary to apply a wash step prior to elution of the target analyte [35]. Different percent of methanol aqueous solutions were used as the washing solutions. There was almost no difference in the imidacloprid recoveries for MIPs and NIPs after washing when the percent of methanol in the washing solutions were in the range of 5–10% (Fig. 1′c in supplementary material). With increased methanol in the washing solution, the recovery of imidacloprid decreased precipitously in the NIPs cartridge. When washing with 20% methanol, the recovery of imidacloprid in the NIPs cartridge was reduced to 42.7%, while the recovery with MIPs was 89.5%, indicating stronger retention of imidacloprid by the MIPs than the NIPs. In this study, 20% aqueous methanol was used as washing solvent.

Different elution solutions, 80% aqueous methanol, methanol and 1.0% acetic acid methanol solution were evaluated in order to get the highest imidacloprid recovery. The volume was 8 mL, and the flow rate was set at 1.0 mL/min. The satisfactory recoveries of imidacloprid (86.0–92.4%) were obtained by the three elution solutions. In the study, methanol was selected, because its composition was simple and it also facilitated subsequent evaporation.

3.4. Matrix effect

Many investigations into analytical troubleshooting encountered with LC–MS/MS detection have focused on the problems which arise due to matrix effect, and in particular ion suppression. The phenomenon of ion suppression results in reduction of signal intensity and consequently inferior performance of the analytical method with regard to sensitivity, precision and accuracy. The cause of ion suppression is a change in the spray droplet solution properties in the MS ion source. This is due to co-extracted non-volatile or less volatile interferences. It was demonstrated that matrix effect could be minimized or eliminated by adopting selective extraction methods [36].

In order to validate the selectivity of MIP, C18 was also used as the dispersant of MSPD for extraction of imidacloprid from rice. The extraction conditions was optimized for obtaining the satisfactory

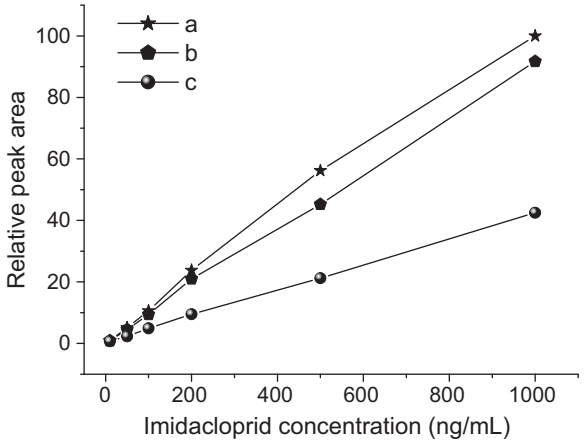

Fig. 3. The investigation of matrix effect by comparison of peak areas obtained by determining imidacloprid which were dissolved in LC mobile phase (a) or blank rice sample extracts after cleanup by MSPD with MIPs (b) or C18 (c) sorbent.

imidacloprid recovery and reducing the amount of co-extractives when using C18 as sorbent, for example: 1:2 as the ratio of sample to C18 (0.5 g rice sample and 1.0 g C18); 7 min as the dispersion time; 6 mL 10% aqueous methanol as washing solvent and 8 mL methanol as elution solvent.

The peak areas obtained by determining imidacloprid which were dissolved in LC mobile phase or blank rice sample extracts after clean-up by MSPD with MIPs or C18 sorbent were compared in order to investigate the matrix effect. As can be seen from Fig. 3, significant ion suppression was observed for the imidacloprid when the sample was cleaned-up by MSPD with C18 as sorbent. In contrast, slight ion suppression was observed for the imidacloprid when the sample was cleaned-up by MSPD with MIP as sorbent. It proved that the selectivity of the MIP-MSPD method is satisfactory.

3.5. Analytical performance

The specificity of the method was checked by analyzing different blank rice samples. No interfering peaks and false positive results were observed in the blank chromatograms (Fig. 4), which indicated that the selectivity of the method is good.

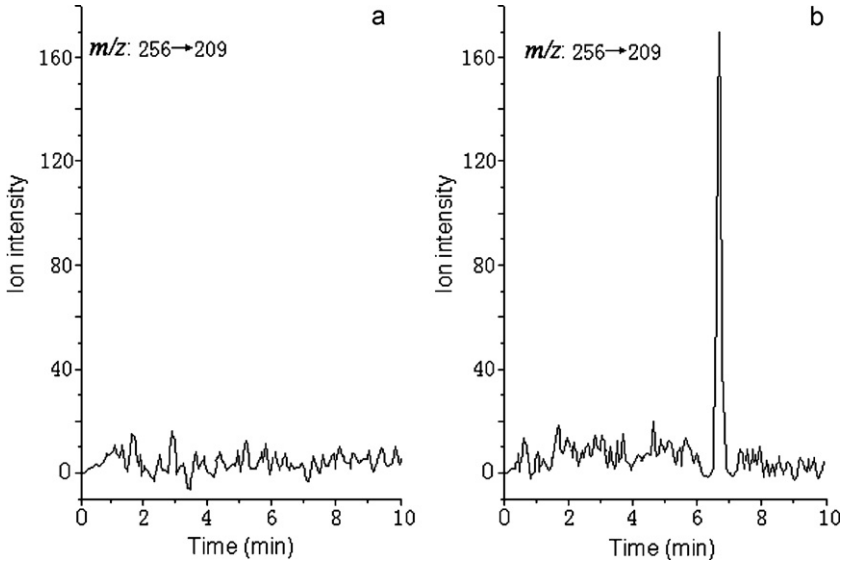

Fig. 4. LC–MS/MS extracted ion chromatograms obtained by the analysis of the blank (a) and spiked rice sample (b), the spiking level for imidacloprid is 8.0 ng/g.

Table 1
Analytical performance of the method.

Linearity range	LOD	LOQ	Intra-day precision (RSD, $n = 6$)	Inter-day precision (RSD, $n = 6$)	Recovery
10–1000 ng/g	2.4 ng/g	8.0 ng/g	4.5–5.9%	4.8–7.1%	85.2–91.5%

The analytical performance parameters of the method are shown in Table 1. The linearity of imidacloprid which was investigated by analyzing spiked rice sample was achieved in the range of 10–1000 ng/g with correlation coefficient of 0.997. Limit of detection (LOD) and limit of quantification (LOQ), defined as the concentration corresponding to a signal equal to three and ten times the standard deviation of the blank, were 2.4 and 8.0 ng/g, respectively. These values were lower than the MRL established by China (50 ng/g).

Precision was evaluated by measuring relative standard deviations (RSDs) of intra- and inter-day tests. The intra-day precision was performed by analyzing spiked rice sample six times in 1 day at three different fortified concentrations of 10, 100 and 500 ng/g. The inter-day precision was performed over 6 days by analyzing spiked rice sample at three different fortified concentrations of 10, 100 and 500 ng/g. RSDs of intra- and inter-day tests ranging from 4.5% to 5.9% and from 4.8% to 7.1% were obtained, respectively. In all three fortified levels, recoveries of the imidacloprid were in the range of 85.2–91.5%.

In order to validate the feasibility of the method to analyze imidacloprid, the proposed method was applied for analyzing eight rice samples obtained from different market. In these samples, four samples are round shaped rice and four samples are long rice. No imidacloprid residue at detectable levels was found in these samples. The recovery study was then carried out by spiking rice samples with the imidacloprid standard at level of 200 ng/g. The imidacloprid recoveries obtained for different rice samples are not very significantly different and all in the range of 83.8–92.5%.

4. Conclusions

In conclusion, we have developed a novel MIP-MSPD–LC–MS/MS method for the selective extraction, separation and determination of imidacloprid in rice. This method combines efficient enrichment and eliminating impurities for MIP-MSPD procedure, highly effective separation for LC analytical method, and high sensitivity for MS detection. The extraction and clean-up of analyte were carried out in a single step without additional purification. The simple and rapid extraction method provides good repeatability and reproducibility range, high extraction efficiency and short time compared to other methods. Therefore, the proposed analytical protocol is a promising trend that could be exploited in complex sample analysis.

Acknowledgements

This work was supported by the Fundamental Research Funds for the Central Universities (No. DL10DB01) and the Postdoctoral Science Foundation of China (No. 20110491016).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jchromb.2012.04.004.

References

[1] A.S. Carretero, C. Cruces-Blanco, S.P. Duran, A.F. Gutierrez, J. Chromatogr. A 1003 (2003) 189.
[2] H.J. Kim, S. Liu, Y.S. Keum, Q.X. Li, J. Agric. Food Chem. 51 (2003) 1823.
[3] E. Watanabe, K. Baba, H. Eun, S. Miyake, Food Chem. 102 (2007) 745.
[4] NY 1500.5.1-2007, Maximum Residue Limits for Pesticides in Farm Products, Ministry of Agriculture of the People's Republic of China, Beijing, China, 2007.
[5] S. Baskaran, R.S. Kookana, R. Naidu, J. Chromatogr. A 787 (1997) 271.
[6] Y. Ishii, I. Kobori, Y. Araki, S. Kurogochi, K. Iwaya, S. Kagabu, J. Agric. Food Chem. 42 (1994) 2917.
[7] M. Gupta, A. Sharma, A. Shanker, Food Chem. 106 (2008) 158.
[8] H. Obana, M. Okihashi, S. Hori, J. Agric. Food Chem. 50 (2002) 4464.
[9] S.C. Utture, K. Banerjee, S.S. Kolekar, S. Dasgupta, D.P. Oulkar, S.H. Patil, S.S. Wagh, P.G. Adsule, M.A. Anuse, Food Chem. 131 (2012) 787.
[10] T. Ding, D. Jacobs, B.K. Lavine, Microchem. J. 99 (2011) 535.
[11] J. Tang, M. Zhang, G. Cheng, Y. Lu, J. Liq. Chromatogr. Related Technol. 32 (2009) 59.
[12] A. Gaujaca, A. Aquinod, S. Navickiened, J. Bittencourt de Andradea, J. Chromatogr. B 881–882 (2012) 107.
[13] M. Michel, B. Buszewski, J. Chromatogr. B 800 (2004) 309.
[14] E.M. Kristenson, L. Ramos, U.A.T. Brinkman, Trends Anal. Chem. 25 (2006) 96.
[15] B. Morzycka, J. Chromatogr. A 982 (2002) 267.
[16] M. García, I. Rodríguez, R. Cela, Anal. Chim. Acta 590 (2007) 17.
[17] J. Xie, L. Chen, C. Li, X. Xu, J. Chromatogr. B 788 (2003) 233.
[18] J. Haginaka, J. Chromatogr. B 866 (2008) 3.
[19] A.R. Khorrami, S. Mehrseresht, J. Chromatogr. B 867 (2008) 264.
[20] N. Kirsch, J.P. Hart, D.J. Bird, R.W. Luxton, D.V. Mccalley, Analyst 126 (2001) 1936.
[21] P. Pasetto, S.C. Maddock, M. Resmini, Anal. Chim. Acta 542 (2005) 66.
[22] F. Qiao, H. Yan, J. Chromatogr. B 879 (2011) 3551.
[23] J. He, R. Lv, J. Zhu, K. Lu, Anal. Chim. Acta 661 (2010) 215.
[24] X. Shi, Y. Meng, J. Liu, A. Sun, D. Li, C. Yao, Y. Lu, J. Chen, J. Chromatogr. B 879 (2011) 1071.
[25] L. Pensado, M.C. Casais, M.C. Mejuto, R. Cela, J. Chromatogr. A 1077 (2005) 103.
[26] Q.H. Zou, Y. Liu, M.X. Xie, J. Han, L. Zhang, Anal. Chim. Acta 551 (2005) 184.
[27] C. Blasco, G. Font, Y. Pico, J. Chromatogr. A 1028 (2004) 267.
[28] V.I. Valsamaki, V.I. Boti, V.A. Sakkas, T.A. Albanis, Anal. Chim. Acta 573–574 (2006) 195.
[29] M. Míguez-Framil, A. Moreda-Pineiro, P. Bermejo-Barrera, I. Álvarez-Freire, M.J. Tabernero, M.A. Bermejo, J. Chromatogr. A 1217 (2010) 6342.
[30] H.S. Dórea, L.L. Sobrinho, J. Braz. Chem. Soc. 15 (2004) 690.
[31] E.D. Tsochatzis, U. Menkissoglu-Spiroudi, D.G. Karpouzas, R. Tzimou-Tsitouridou, Anal. Bioanal. Chem. 397 (2010) 2181.
[32] H. Yan, F. Qiao, K.H. Row, Anal. Chem. 79 (2007) 8242.
[33] S.A. Barker, J. Biochem. Biophys. Methods 70 (2007) 151.
[34] S.A. Rodrigues, S.S. Caldas, E.G. Primel, Anal. Chim. Acta 678 (2010) 82.
[35] X. Shi, A. Wu, S. Zheng, R. Li, D. Zhang, J. Chromatogr. B 850 (2007) 24.
[36] C. Li, Z. Wang, X. Cao, R.C. Beier, S. Zhang, S. Ding, X. Li, J. Shen, J. Chromatogr. A 1209 (2008) 1.