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Original scientific paper

Determination of multi-class herbicides in soil by liquid–solid extraction coupled with headspace solid phase microextraction method

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Abstract: Described is a method for simultaneous determination of five herbicides (metribuzin, acetochlor, clomazone, oxyfluorfen and dimethenamid) belonging to different pesticide groups in soil samples. Developed headspace solid phase microextraction method (HS-SPME) in combination with liquid––solid sample preparation was optimized and applied for the analysis of agricultural samples. Optimization of microextraction conditions, such as temperature, extraction time and sodium chloride content was performed using 100 μm polydimethyl-siloxane (PDMS) fiber. The extraction efficiencies of methanol, methanol:acetone and methanol:acetone:hexane in 1:1 and 2:2:1 volume ratios, respectively, and the optimal number of extraction steps during the sample preparation, were tested as well. Gas chromatography–mass spectrometry was used for detection and quantification, obtaining relative standard deviation (*RSD*) below 13 %, and recovery values higher than 83 % for multiple analyses of soil samples fortified at 30 μg kg^{-1} of each herbicide. Limits of detection (*LOD*) were less than 1.2 μg kg^{-1} for all the studied herbicides.

Keywords: pesticides; soil matrix; multiresidue method; gas chromatography mass spectrometry.

INTRODUCTION

In modern agricultural production, the use of herbicides for weed control is necessary and essential. United States Environmental Protection Agency (EPA) indicated that in 2006 and 2007 the worldwide pesticide usage was approximately 5.2 billion pounds, of which herbicides constituted the majority at 40 %.[1]

Usually, crops are showing larger sensitivity to weeds at the beginning of the growing period, due to their slower growth and lower density during that stage.

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Therefore, application of herbicides is required. Various pre-emergence weed control herbicides can be applied to different crops, including widely used: dimethenamid (used in corn, soybeans, sunflower, sugar beet and potatoes), acetochlor (in corn, sunflower, soybeans and potatoes), metribuzin (in soybeans, potatoes, tomatoes and peppers), clomazone (in soybeans, tobacco and rapeseed) and oxyfluorfen (in sunflower).

Soil-applied pre-emergence residual herbicides, especially those used prior to sowing, are usually incorporated into the soil. Slow degradation of pesticides in the environment and extensive or inappropriate usage by farmers could lead to soil contamination. Due to the outstanding concern for human health, and considering the manner and amount of herbicide application, programs monitoring soil contamination by agrochemicals have been established throughout the world, as well in Serbia.

Since the herbicides are a very heterogeneous group of chemicals with different physicochemical properties, the current trend in residue analysis of these compounds is developing multi-residual methods that would provide for simultaneous determination of large number of compounds. In addition, these methods should overcome the drawbacks of the traditional approaches, which are laborious, time consuming, expensive, require large amounts of organic solvents and usually involve many steps, leading to loss of analyte quantity. Solid phase microextraction (SPME), as a technique that combines extraction, purification and concentration processes into a single step, is an example of such development.

Until recently, most of the SPME applications for determination of herbicide residues in soil were based on preparation of soil mixtures with distilled water and subsequent immersion of the SPME fiber in thus prepared slurry (DM-SPME)[2–6] or its exposing to a gas phase above the slurry (HS-SPME)[7–9]. Some researchers have suggested that combination of liquid–solid (L–S) soil preparation followed by DM-SPME determination of herbicides in obtained extracts is the most reliable soil SPME method.[10–15] However, previous studies based on a combination of L–S extraction and HS-SPME determination of herbicides in soil samples were done only with triazines (simazine, atrazine and prometryn)[16,17] and mixture of the two pyridazinones (chloridazon and fluorochloridone) and pendimethalin as dinitroaniline herbicide.[18] In those studies, methanol–acetone combination was used for the extraction of pesticides from the soil matrix.

Regarding determination of herbicides belonging to various pesticide groups, there are no published methods based on a combination of L–S procedure followed by simultaneous HS-SPME herbicides determination. Therefore, the aim of this study was to develop a rapid and simple HS-SPME method combined with L–S sample preparation for simultaneous determination of five compounds (metribuzin, acetochlor, clomazone, oxyfluorfen and dimethenamid) having distinct chemical structures and belonging to different herbicide groups. Microext-

raction temperature, time and NaCl content, main parameters affecting SPME, were tested and optimized using a 100 μm long PDMS fiber. The extraction efficiencies of pure methanol, methanol:acetone and methanol:acetone:hexane mixtures (1:1 and 2:2:1 volume ratios, respectively) were optimized, as well as the optimal number of extraction steps within sample preparation stage. The proposed method was applied in the analysis of selected agricultural soil samples.

EXPERIMENTAL

Reagents and materials

The herbicides chosen for this study were: metribuzin, acetochlor, clomazone, oxyfluorfen and dimethenamid (Dr Ehrenstorfer, Germany, Table I). Standard stock solutions containing 1 g dm^{-3} of each herbicide were prepared in acetone (J. T. Baker, Holland), and stored at –18 °C. Standard working mixed solutions were prepared weekly by diluting the individual stock solutions with acetone and stored at 4 °C. Sodium chloride of 99.5 % purity was purchased from Merck (Germany) and methanol from J. T. Baker (Holland).

TABLE I. Physicochemical properties of herbicides studied;[19,20] M_r, molecular weight; S_w, water solubility; log K_{ow}, partition coefficient between *n*-octanol and water; *H*, Henry's constant

Herbicide	Chemical class	M_r / g mol^{-1}	S_w / mg dm^{-3}	log K_{ow}	*H* / Pa m^3 mol^{-1}
Metribuzin	Triazinone	214.3	1050	1.6	1×10^{-5}
Acetochlor	Chloroacetamide	269.8	223	4.14	0.383
Clomazone	Isoxayolidinone	239.7	1100	2.5	4.19×10^{-3}
Oxyfluorfen	Diphenyl ether	361.7	0.116	4.47	9.40×10^{-2}
Dimethenamid	Chloroacetamide	275.8	1200	2.15	8.32×10^{-3}

PDMS fibers (Supelco, USA), 100 μm long, were used for SPME measurements. Extraction, along with constant mixing was performed in 4 cm^3 vials (Supelco, USA).

An uncontaminated soil sample originating from region of the town of Kikinda (Serbia) was used in the study. The main physicochemical properties of the soil were: pH (in H_2O) 8.39, organic matter content, 3.17 %, sand content, 73.96 %, silt content, 22.60 % and clay content, 3.44 % (all as mass %). The soil was air-dried and sieved (2 mm pores) before use.

Polypropylene centrifuge tubes with caps (50 cm^3, Sarstedt, Germany), filter papers 1PS, 150 mm diameter (Watman, UK) and a centrifuge (UZ 4, Slovenia) were used in the soil preparation procedure.

Instrumentation

A gas chromatograph–mass spectrometer (GC–MS), model CP-3800/Saturn 2200 (Varian, Australia) was used for separation and detection. Column VF-5ms having dimensions 30 m×0.25 mm×0.25 μm by Varian was used. The thermal desorption of analytes from PDMS fiber was performed for 7 min at injector temperature of 270 °C. The GC was programmed as follows: initial temperature was 120 °C, followed by increase to 170 °C at 8 °C min^{-1} rate, kept constant for 4.5 min, increased to 280 °C at 9 °C min^{-1} rate and kept at the same temperature for 5.5 min. Helium was used as a carrier gas and its flow rate was 1.1 mL min^{-1}.

The ion trap mass spectrometer operated in the electron impact/selected ion monitoring (EI/SIM) mode. The ion trap and transferline temperatures were set to 220 °C and 250 °C, respectively. One specific herbicide ion was selected for detection and quantification, while

the second one was used for confirmation. The ions inspected were as follows: 198 (215) for metribuzin, 223 (146) for acetochlor, 204 (125) for clomazone, 252 (317) for oxyfluorfen and 154 (230) for dimethenamid.

Optimization of HS–SPME analysis

HS–SPME conditions, such as temperature, extraction time and NaCl content were tested and optimized using 100 μm PDMS fiber. Optimization was done using 2.5 cm^3 of aqueous solution containing 25 μg dm^{-3} of each herbicide. Desorption parameters (temperature and time) for this study were initially selected according to previous research.[13]

Optimization of soil sample preparation

The efficiency of the HS-SPME method, optimized for aqueous solutions, was tested using analysis of soil samples. For that part of the study, 10 g of sub-samples were placed in the polypropylene centrifuge tubes and fortified to concentration of 30 μg kg^{-1} for each herbicide using 1 mg dm^{-3} mixed standard solution. The spiked samples were homogenized for 15 min using a rotary stirrer and left to rest for 24 hours prior to further analysis. The extraction efficiencies of the pure methanol, methanol:acetone (1:1 volume ratio) and methanol:acetone:hexane (2:2:1 volume ratio) mixtures and the optimal number of extraction steps were determined by the following procedure: soil samples were extracted by dissolving in 15 cm^3 of solvent for 30 min using a rotary stirrer and then centrifuged for 15 min at 4000 rpm. The extract was filtered and evaporated to dryness at 35 °C using a rotary evaporator. The residues were redissolved in 1 cm^3 of acetone, and 0.2 cm^3 of those solutions were diluted with water to 10 cm^3 for HS-SPME measurements.

RESULTS AND DİSCUSSİON

HS-SPME optimization

Selected 100 μm PDMS fiber for SPME measurements in this multiresidue herbicides analysis, as well as the desorption time of 7 min and 270 °C desorption temperature as optimal conditions for the used fiber, were chosen according to the results presented in detail in previous study.[13] Optimal microextraction temperature, NaCl content and microextraction time, as experimental parameters affecting HS-SPME measurements, were optimized by a well-structured step-by-step approach, using spiked water samples.

Microextraction temperature

It is well known that the increase of microextraction temperature leads to increase of analyte vapor pressure, resulting in improvement of HS-SPME efficiency.[21,22] Therefore, the temperature effect in the range of 23–90 °C on the HS--SPME efficiency was analyzed. The obtained extraction-temperature profiles for each of the herbicide studied are shown in Fig. 1. The results presented, clearly indicate that the temperature increase leads to the enhancement of the overall sorbed mass on the fiber, while other experimental conditions were kept constant. This effect could be explained by the increase of analyte vapor pressure, *i.e.*, higher concentration in the gas phase. However, for temperatures above 75 °C for oxyfluorfen, further increase in temperature results in a reduction of herbicide

amount sorbed on the fiber (Fig. 1). Explanation for such a behaviour lies in the exothermic nature of the sorption process (enhanced analyte desorption from the fiber at high temperatures) and in the very low solubility of the oxyfluorfen in water (weak solvent–analyte interactions cannot be further weakened by the temperature increase).

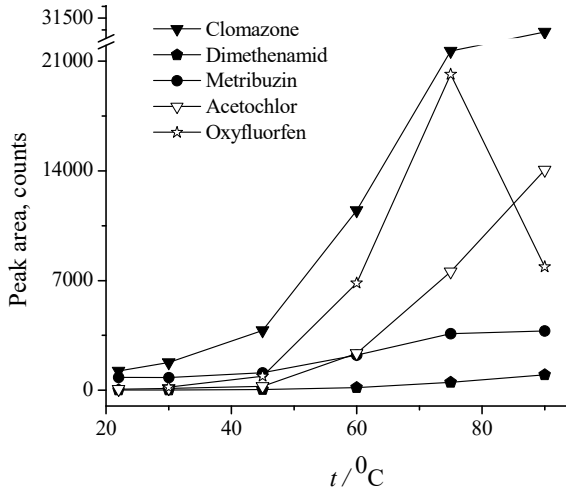

Fig. 1. HS-SPME temperature profiles for herbicides studied.

Since satisfactory sensitivity for each of the individual compounds studied was obtained at 75 °C, this temperature was chosen as optimal for the mixture of herbicides tested.

Effect of ionic strength

As previously reported, an addition of salt to the sample could decrease the solubility of some analytes in the aqueous solution, stimulating their movement into the gas phase and consequently to the fiber coating.[22] This is especially pronounced in the case of hydrophobic compounds that have low affinity for the PDMS fibers. Therefore, the ionic strength was a well studied experimental parameter influencing the HS-SPME measurements. Ionic strength was adjusted by adding different amounts of NaCl to the standard herbicide aqueous solutions (0, 25, 50, 100, 150, 200, 250 and 300 g dm^{-3}).

As shown in Fig. 2, the obtained results indicate that the ionic strength increases the SPME efficiency for all the herbicides studied. Also, it is evident that for the most hydrophobic herbicide studied (oxyfluorfen) the enhancement of mass sorbed on the fiber at higher NaCl concentrations is significantly less pronounced. A possible explanation for this behaviour of oxyfluorfen could be the presence of a strong competition between this analyte and the more polar ones for PDMS fiber sorption that finally results in a minor increase in its extraction efficacy.

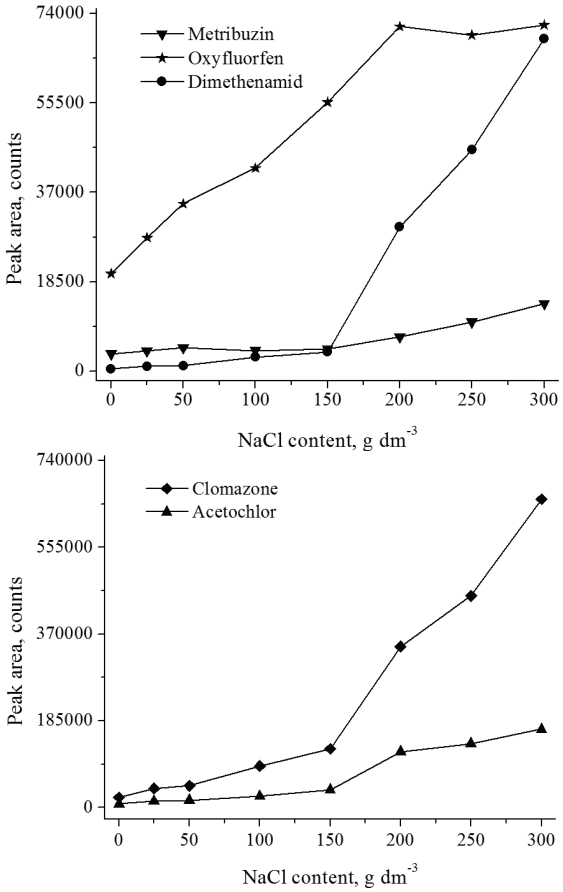

Fig. 2. Effect of ionic strength on the analytical signal for studied herbicides.

Finally, based on the results obtained for all the herbicides studied, NaCl concentration of 300 g dm^{-3} was chosen for further work.

Microextraction time

Some theoretical models proposed for explanation of the HS-SPME process recommended shortening duration time of the analysis by indicating that quantification is possible before a sorption equilibrium could be reached.[21,23] Although microextraction using equilibrium time is advised, for practical reasons an efficient half-hour microextraction (enough to provide sufficient analytical sensitivity for all the compounds studied and in accordance with the chromatographic run time of 28.47 min), was compared only to 20 min procedure. The results obtained (Fig. 3) indicate that the time period of 30 min was a better choice for all the herbicides studied, and therefore it was chosen for further work.

Overall, considering the results obtained for all the parameters optimized for HS-SPME determination of studied herbicides, the following SPME conditions

were found to be the most efficient: temperature of 75 °C, 300 g dm^{-3} NaCl content and 30 min extraction time.

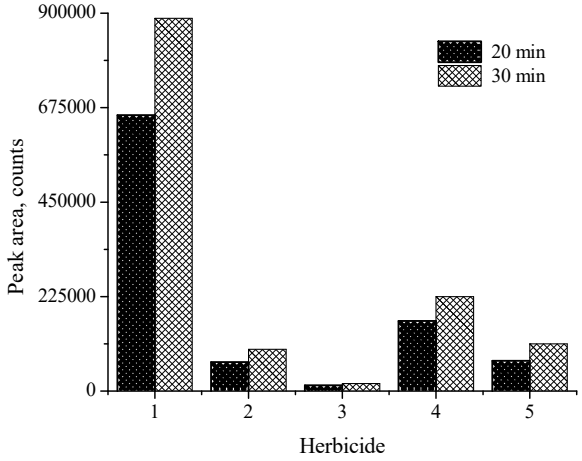

Fig. 3. Effect of microextraction time on HS-SPME determination of clomazone (1), dimethenamid (2), metribuzin (3), acetochlor (4) and oxyfluorfen (5).

Soil extraction optimization

Optimized HS-SPME method was tested by analyzing soil samples. Literature reports on the analysis of herbicide residues from soil samples, using DM-SPME of a soil organic extract obtained by L–S extraction of previously diluted samples is a more efficient method than direct immersion of the SPME fiber in the slurry of soil sample and water.[10–15] Previous study, based on the combination of conventional L–S procedure followed by DM-SPME determination of the selected herbicides, showed that among different solvents tested (water, hexane, acetonitrile, acetone and methanol), two successive extractions with methanol (Met) as the extraction solvent seemed to be the optimal sample preparation choice.[13] In the same study, somewhat lower recovery obtained for oxyfluorfen (62.82 %) was explained by insufficient power of methanol as an extraction solvent in the sample preparation step and/or the strong influence of soil matrix on this herbicide.

Considering the obtained results and aiming for an improvement of the sample preparation step, the extraction efficiency of methanol was compared to the efficiencies obtained by combining it with solvents of different polarity (methanol:acetone (Met:Ac) and methanol:acetone:hexane (Met:Ac:Hex) and employing a single extraction procedure as described in Experimental – *Optimization of soil sample preparation section*. The results (Table II) show that both solvent mixtures considerably amended the sample preparation step. The highest recoveries for majority of the tested herbicides were obtained after extraction with Met:Ac, therefore this solvent mixture was selected for future experiments.

TABLE II. Dependence of liquid-solid (LS) extraction efficiency on type of organic solvent (Met: methanol, Ac: acetone, Hex: hexane) and number of extraction steps (I-IV), using the most efficient solvent (Met:Ac)

Herbicide	Met I	Met:Ac I	Met:Ac:Hex I	Met:Ac II	Met:Ac III	Met:Ac IV
Metribuzin	98.41	99.33	99.02	102.94	101.62	102.09
Acetochlor	91.39	94.68	95.24	98.61	98.86	96.02
Clomazone	80.13	87.76	81.32	91.65	91.03	89.78
Oxyfluorfen	59.36	79.68	65.78	84.26	81.38	82.69
Dimethenamid	71.31	80.22	75.64	83.91	83.06	83.11

After selection of extraction solvent, the next step was to determine the optimal number of extraction steps. For that purpose, the extraction of spiked soil samples with methanol-acetone mixture was repeated up to four times using the same procedure. The results presented in Table II show that, for majority of the herbicides studied, the best recovery was achieved after two extraction steps.

According to the results obtained in those two sets of experiments, two successive extractions with Met:Ac as the extraction solvent were chosen as the optimal sample preparation procedure.

As clearly indicated in Fig. 4, the additional SPME step in our sample preparation method has real advantages as shown by comparative chromatograms obtained by direct injection (Fig. 4C) of the extract (after liquid-solid extraction) and after additional HS-SPME purification and concentration (Fig. 4A) of the same extract. The chromatogram obtained after DM-SPME of the selected herbicides in soil extract is presented in Fig. 4B, too. The choice of experimental conditions for DM-SPME determination was based on our previous investigation.[13] Evidently, compared to L–S method (Fig. 4C), both additional SPME steps (HS--SPME (Fig. 4A) and DM-SPME (Fig. 4B)) provide higher sensitivity in determination of all herbicides, and HS-SPME approach is slightly better. Since the SPME fiber was not in direct contact with unwanted impurities (compounds that were co-extracted from the soil matrix during LS sample preparation) for HS-SPME application, but was for DM-SPME application, the obtained results were expected.

Validation of the proposed method

The most important analytical parameters, such as linearity, limit of detection (*LOD*), precision and confidence of the presented method were determined for the optimized LS extraction procedure followed by HS-SPME measurement.

Concentration, ranging from 2 to 600 μg kg^{-1} was used for linearity testing of the developed method. The obtained arrangements and correlation coefficients (R) for all the herbicides under study are presented in Table III. The acquired correlation coefficients exceeded 0.99 for all the compounds tested, indicating good linearity.

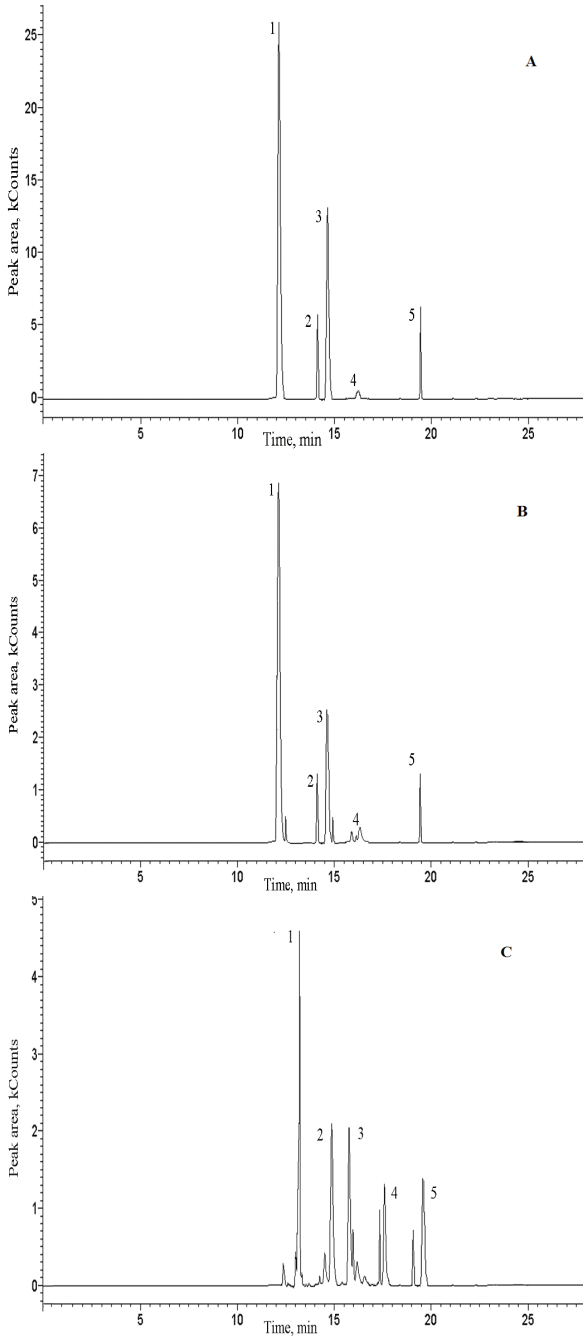

Fig. 4. GC–MS chromatograms of soil sample fortified at 30 μg kg^{-1} level of each herbicide (clomazone (1), dimethenamid (2), acetochlor (3), metribuzin (4) and oxyfluorfen (5)), obtained by applying: A) L–S–HS-SPME method, B) L–S–DM-SPME method and C) L–S method (direct injection without additional SPME step).

The limit of detection (*LOD*) was determined as $3.29 \times s_B$ (where s_B is the blank standard deviation), according to IUPAC recommendations.[24] Obtained *LOD* for all the herbicides studied were less than 1.2 μg kg^{-1} (Table III).

TABLE III. Analytical characteristics of the proposed LS–HS-SPME method for all the herbicides studied; *R,* correlation coefficient; *LOD*, limit of detection; *RSD*, relative standard deviation; Linearity range: 2–600 μg kg^{-1}

Herbicide	*R*	*LOD* / μg kg^{-1}	*RSD* / %	Recovery, %
Metribuzin	0.995	1.16	8.1	102.94
Acetochlor	0.992	0.34	12.1	98.61
Clomazone	0.996	0.10	6.3	91.65
Oxyfluorfen	0.993	0.59	3.8	84.26
Dimethenamid	0.998	0.87	10.2	83.91

Confidence and precision of the method were determined by performing four consecutive measurements of the soil samples fortified at 30 μg kg^{-1} level. *RSD* and recovery values are presented in Table III. As shown, *RSD* for all herbicides were below 13 %. As *RSD* below 20 % are considered acceptable in trace analysis,[25] the proposed method can be satisfactory in terms of precision. For all the herbicides studied, the recovery values were above 83 %, indicating that the proposed method could be used for efficient determination of the selected herbicides from complex matrix samples such as soil.

Application of the L–S–HS-SPME method

L–S–HS-SPME method proposed in this study, as well as L–S–DM-SPME method proposed in our previous study,[13] were used for analysis of twelve soil samples from Belgrade agricultural area. Quantification was done using spiked soil samples that were used in the optimization procedure. The obtained results showed that with the exception of acetochlor, detected in only one sample (concentration of 13.0 μg kg^{-1} determined using L–S–HS-SPME and 13.2 μg kg^{-1} by L–S–DM-SPME method), all the other herbicides remained below detection limits.

The effectiveness of both L–S–HS-SPME and L–S–DM-SPME methods for routine analysis of real samples were confirmed by excellent agreement with the obtained results. However, as soil represents extremely complex matrix, it seems that HS-SPME approach is more appropriate for herbicide residue analysis, considering that in this method the fiber is not in direct contact with the sample, which enables an extension of its lifespan and reduces the matrix effects. Acceptable precision and results repeatability obtained with the same SPME fiber during experiments presented in this paper showed that a single PDMS fiber could be utilized for more than 130 measurements. On the other hand, our previous studies showed that the same PDMS fiber could be used for fewer injections (about 70–80 times) when DM-SPME mode was used for determination of pesticides in the soil matrix.[13]

CONCLUSION

The multi-residue method based on a combination of liquid–solid sample preparation followed by HS-SPME herbicide determination was used for the simultaneous determination of five herbicides belonging to different pesticide groups. Investigation and optimization of microextraction conditions, such as temperature, extraction time and NaCl content was performed using 100 μm polydimethyl–siloxane (PDMS) fiber. During the optimization, the extraction efficiencies of several solvents and the optimal number of extraction steps for sample preparation were tested as well. Results indicated that two successive extractions with mixture of methanol:acetone (1:1 volume ratio) as the extraction solvent could be used as optimal sample preparation procedure. Subsequently for the HS-SPME method, temperature of 75 °C, 300 g dm^{-3} NaCl content and 30 min microextraction time could be set as microextraction conditions to yield most effective analysis.

Comparing the results obtained by application of the developed HS-SPME method and those published for application of DM-SPME method for the same set of herbicides and soils under study, we inferred that both methods are suitable for the routine determination of selected herbicides in the soil samples. However, since the proposed HS-SPME mode secures an extended fiber lifetime, compared to the DM-SPME mode, it could be more appropriate for analyzing complex soil matrix.

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ИЗВОД

МЕТОДА МИКРОЕКСТРАКЦИЈА У ЧВРСТОЈ ФАЗИ–УЗОРКОВАЊЕ ИЗ ГАСОВИТЕ ФАЗЕ У ОДРЕЂИВАЊУ ХЕРБИЦИДА ИЗ РАЗЛИЧИТИХ ХЕМИЈСКИХ ГРУПА У УЗОРЦИМА ЗЕМЉИШТА

РАДА ЂУРОВИЋ-ПЕЈЧЕВ[1], ТИЈАНА ЂОРЂЕВИЋ[1] и ВОЈИСЛАВА БУРСИЋ[2]

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У раду је представљена метода за истовремено одређивање пет хербицида (метрибузин, ацетохлор, кломазон, оксифлуорфен и диметенамид) у земљишту, који на основу своје структуре припадају различитим хемијским групама пестицида. Предложена метода микроекстракција у чврстој фази-узорковање из гасовите фазе (HS-SPME) у комбинацији са течно–чврстом припремом узорака земљишта (L–S) је оптимизована и примењена за анализу реалних узорака пољопривредног земљишта. Ортимизовање микроекстракционих услова, као што су температура, екстракционо време и садржај натријум-хлорида је извршена употребом 100 μm полидиметил-силоксанског (PDMS) влакна. Испитиване су такође екстракционе ефикасности различитих растварача (метанол, метанол:ацетон и метанол:ацетон:хексан у запреминским односима 1:1 и 2:2:1, редом), као и оптималан број екстракционих корака у току припреме узорака земљишта. Дет-

екција и квантификација испитиваних хербицида су извршени методом гасно–масене спектрометрије (GC–MS). Вредности релативних стандардних девијација и приноса одређивања хербицида у узорцима земљишта обогаћеним до концентрација од 30 μg kg^{-1} сваког једињења су биле испод 13 %, односно изнад 83 %, редом, док су границе детекције биле ниже од 1,2 μg kg^{-1}.

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