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Determination of pesticides in river water using rotating disk sorptive extraction and gas chromatography–mass spectrometry

Ady Giordano, Pablo Richter*, Inés Ahumada

Departamento de Química Inorgánica y Analítica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile

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ABSTRACT

The rotating disk sorptive extraction (RDSE) technique was applied to the determination of pesticides in aqueous samples. Pesticides of different polarities were considered in this study: chlorpyrifos, diazinon, fenvalarate, cyhalothrin, cypermethrin, lindane and malathion. The sorptive/desorptive behavior of the pesticides was studied using a rotating disk containing a polydimethylsiloxane (PDMS) phase on one of its surfaces. The analyte polarity was a significant factor in the extraction time; shorter extraction times were required for the more apolar pesticides. The optimum variables for the extraction of all analytes were: extraction time of 3 h, sample volume of 25 mL, rotational velocity of the disk 1250 rpm, desorption time of 30 min using methanol. For pesticides with values of Log K_{ow} > 4, the extraction time can be reduced to 30 min for a quantitative extraction. Under these conditions, recoveries between 76% and 101% were obtained for the target pesticides, and the repeatability of the methodology, expressed as relative standard deviation, was determined to be between 10% and 20%. Additionally, the limits of detection of the analytes were lower than 3.1 $\mu g\,L^{-1}$. The extraction method developed using the RDSE was compared to a stir bar sorptive extraction (SBSE) under the same conditions. It can be observed that the extraction using the rotating disk offers higher recoveries because of its higher PDMS volume and its higher surface area to volume ratio that allows for improved mass transfer.

1. Introduction

There are many pesticides available for commercial use and although they provide many benefits, especially in agriculture, they are toxic to human beings. In some cases, for instance organochlorine pesticides, these compounds bio-accumulate and become persistent in the environment. Therefore, the development of analytical methodologies for the determination of different pesticides in both aqueous and solid matrices is necessary. In traditional analytical methods, the sophistication of the analytical instruments contrasts with sample preparation techniques based on a liquid–liquid extraction (LLE). The use of LLEs has decreased significantly during the last years because it requires a considerable amount of organic solvent, which opposites the trend of green analytical chemistry.

With the purpose of avoiding or minimizing the use of organic solvents while increasing the method extraction efficiency, a series of more green strategies have been recently developed. Among them, the solid phase microextraction (SPME) stands out for its vast analytical applicability in current techniques [1–3]. Similarly, the stir bar sorptive extraction (SBSE) method, which possesses a similar fundamental principle as SPME, uses a larger amount of polydimethylsiloxane (PDMS) as the stationary phase, which results in improving the recovery of analytes of higher polarity [4]. However, the SBSE has the following drawbacks: (a) increasing the rotational velocity of the sorptive bar may cause physical damage in the PDMS phase due to its direct contact with the bottom of the sample vial during the extraction [5]; (b) stir bars offer a low PDMS area-to-volume ratio affecting the analyte mass transfer to the PDMS phase [6], and (c) the high cost of acquisition of the stir bars because they cannot be made easily in the laboratory. The novel technique proposed by our group consists of extracting low-polarity pollutants onto a rotating Teflon disk coated with a PDMS film on one of its surfaces [7], which is applied for the first time in this study to the extraction of pesticides of different polarities in water samples. We refer to this procedure as a rotating-disk sorptive extraction (RDSE). The disk configuration is very easy to make in the laboratory, and this configuration allows for the immobilization of a larger exposed surface area of PDMS than the stir bar used in SBSE. Additionally, there is no contact between the extraction phase and the container while the disk rotates, and the disk can be stirred at higher velocities without damaging the phase, thus facilitating analyte mass transfer to the PDMS surface.

* Corresponding author. Tel.: +56 2 9782804; fax: +56 2 9782809.
E-mail address: prichter@ciq.uchile.cl (P. Richter).

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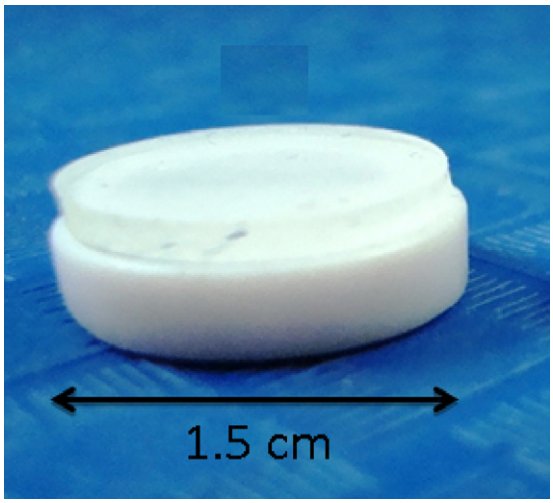

Fig. 1. Rotating disk made of Teflon containing PDMS on the surface and a miniature magnetic stirring bar inserted.

2. Experimental

2.1. Reagents

Pesticide standards of chlorpyrifos, diazinon, fenvalarate, cyhalothrin, and cypermethrin were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Lindane and malathion standards were obtained from Accustandard, Inc. (New Haven, CT, USA). Methanol, sodium chloride, and magnesium sulphate heptahydrate were purchased from Merck (Darmstadt, Germany). Hydroxy-terminated polydimethylsiloxane (PDMS-OH), methyltrimethoxysilane (MTMOS), poly(methylhydrosiloxane) (PMHS), and trifluoroacetic acid (TFA) were used in the synthesis of the PDMS phase and were purchased from Sigma–Aldrich (Milwaukee, WI, USA). 2,4,6-Tribromoanisol (TBA) was obtained from Sigma-Aldrich and used as an internal standard. The water used was Nano-pure water from a Barnstead water system (Dubuque, IA, USA).

Nitrogen 5.0 and helium 5.0 were purchased from AGA (Santiago, Chile) and used for final extract evaporation and as the chromatographic carrier gas, respectively.

2.2. Rotating disk sorptive extraction

The extraction device (Fig. 1) consists of a Teflon disk embedded with a miniature magnetic stirring bar [7] purchased from VWR International, Inc. (Tualatin, OR, USA). On one of the surfaces of the disk, a film of PDMS has been fixed with silicone. The disk is driven using a common laboratory magnetic stirrer, and in this experiment, a Mag-Mix unit from Precision Scientific (Chicago, IL, USA) was used. Teflon for the disks was purchased from Plastigen S.A. (Santiago, Chile).

The synthesis of PDMS used for the extraction was performed according to the method described by Liu et al. [8]. In this synthetic route, 200 mg of PDMS–OH was dissolved in 300 μL of methylene chloride and subsequently 100 μL of MTMOS and 50 mg of PMHS were added. After the PDMS–OH had completely dissolved, 80 μL of TFA (containing 5% water, v/v) was added and rapidly vortexed until the mixture became a clear solution. This solution was poured into a square cap of a plastic container and was placed into a vacuum desiccator for 12 h for PDMS gelation. The thickness of the PDMS film formed may be modified depending on the cap size into which the solution has been poured. One circular part of the phase was cut using a hollow punch and fixed onto the Teflon disk with silicone. The coated disk was then placed in an aluminum oven at 150 °C for 1 h under a N_2 atmosphere [9]. Prior to use, the disk was stirred in methanol for 2 h to remove the PDMS detached after cutting the phase.

The studies were performed using a 1.5 cm diameter disk, which provided a surface area of 1.76 cm^2 and a calculated quantity of 350 μL of immobilized PDMS.

2.3. Extraction–elution procedure

A volume of 25 mL of a standard or water sample was poured into a beaker with the extracting device. The disk was rotated at 1250 rpm for 3 h at room temperature. After the extraction, the disk was dried using a lint-free tissue and placed into a 10 mL beaker, which contained 2 mL of methanol as a desorbing agent and was stirred for 30 min at 1250 rpm. The methanol extract was then evaporated under a N_2 stream to 1 mL and spiked with 20 μg L^{-1} of TBA as an internal standard prior to injection.

The study of variables was made considering a sample volume of 25 mL and concentrations of 20 μg L^{-1} of each analyte.

2.4. SBSE extraction

Stir bars (SBSE) coated with PDMS (0.5 mm film thickness, 10 mm length, 24 μL PDMS, and 0.94 cm^2 surface area) were obtained from Gerstel (Műlheim and der Ruhr, Germany) and were used to compare extraction capability.

Prior to use, the stir bars were conditioned in a vial containing 20 mL of methanol. To perform the extraction, the same procedure for rotating disk was followed for both the extraction and elution of analytes. Between each extraction, the bar was cleaned with an additional 20.0 mL of methanol for 30 min.

2.5. Chromatographic determination

Quantification of analytes was performed using a Hewlett–Packard gas chromatograph, model 5890 series II (Palo Alto, CA, USA), coupled to a mass-selective detector Fisons Instruments model MD800 (Manchester, UK). One microliter of sample extract was injected into the column with an injector temperature of 200 °C and a solvent delay of 4 min. The initial column temperature was 100 °C (5 min) and increased at a rate of 8 °C min^{-1} until 300 °C (11 min) was reached. Helium was used as the carrier gas with a constant flow rate of 1 mL min^{-1}.

Quantification was performed in SIM mode. The ions (*m/z*) monitored were: **181** and 183 for lindane, **137** and 152 diazinon, **173** and 127 for malathion, **97** and 197 for chlorpyrifos, **181** and 197 for cyhalothrin, **163** and 209 for cypermethrin, and **125** and 167 fenvalerate. The ions marked in bold correspond to the target ions of the analytes.

2.6. Determination of pesticides in real samples

The method was applied to the determination of pesticides in river water samples. Samples were obtained from the Itata River (VIII region of Chile) on different dates. The samples were subjected to the extraction/desorption procedure using the optimum conditions as described previously. Subsequently, another portion of these samples was enriched with analytes at a concentration of 20 μg L^{-1} to determine the recovery of each analyte in a real sample matrix.

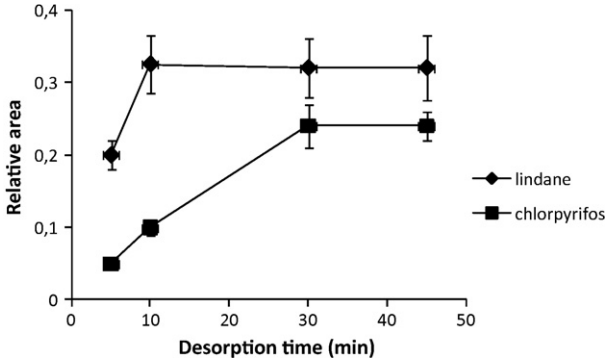

Fig. 2. Effect of the desorption time using methanol on the analytical response.

3. Results and discussion

3.1. Study of desorption using methanol

The desorption of the analytes from the PDMS phase was performed in methanol because previous studies have shown few undesired interactions when this solvent is used and no swelling of the polymer was observed [10]. Desorption conditions, such as the methanol volume and desorption time, were determined. The effect of the methanol volume used for desorption on the analyte recoveries was studied between 2 and 10 mL at 30 min employing a rotating disk velocity of 1250 rpm. The concentration of the analytes desorbed remained constant as the volume of methanol was increased. Consequently, a volume of 2 mL of methanol was selected for further studies.

Desorption time was also evaluated for representative analytes (Fig. 2). It was established that at 30 min, most pesticides have reached equilibrium between the two phases. Therefore, 30 min was adopted to diminish the total time of analysis and to not expand the desorptive stage.

3.2. Influence of the rotational velocity of the disk on analyte response

The efficiency of mass transport of the extraction using the RDSE was determined in the rotational velocity studies. In the case presented in Fig. 3, it can be observed that an improvement in the chromatographic area of the pesticides was observed with an increase in rotational velocity. This would indicate that increasing the rotational velocity of the disk would cause the mass transport of analytes to increase and consequently, the partition equilibrium is reached faster. The integrity of the polymeric phase of the disk can be maintained at higher rotational conditions, and because this

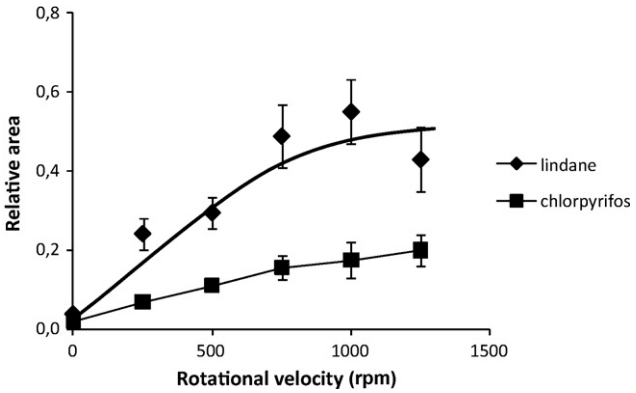

Fig. 3. Effect of the rotational velocity of the disk on the response.

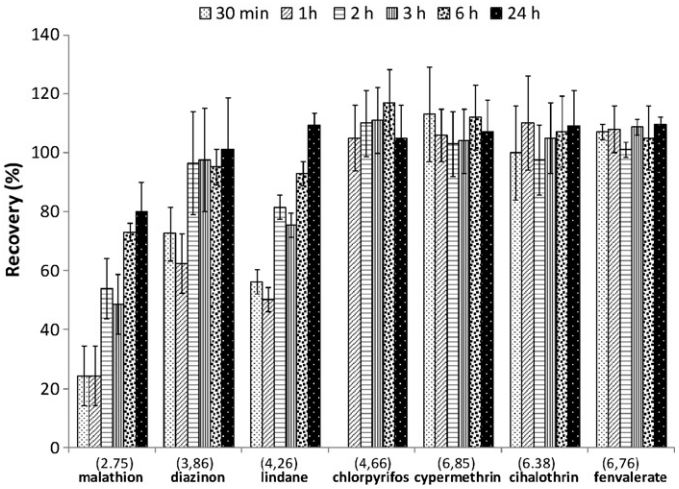

Fig. 4. Extraction time profiles for the target analytes. Values in parenthesis correspond to the Log K_{ow} of each analyte.

decreases the time for equilibrium to be reached, all experiments were performed at 1250 rpm. Unfortunately, we do not possess, for this study, a magnetic stirring unit that can operate at higher rotational velocities.

3.3. Influence of extraction time

The effect of the extraction time on the analytical response of each analyte extracted using the RDSE is shown in Fig. 4. The impact of the extraction time is significant only for the most polar pesticides, i.e., pesticides with value of Log $K_{ow} < 4$. For highly apolar pesticides (Log $K_{ow} > 4$), because PDMS is an apolar phase, equilibrium is reached faster and, therefore, 30 min is sufficient for a quantitative extraction. On the other hand, the high polarity of malathion hinders its quantitative recovery even when a 24 h extraction was employed. Finally, 3 h of extraction time was selected because most of the analytes presented quantitative recoveries.

3.4. Influence of the "salting out" effect

The low polarity of PDMS impedes a high extraction efficiency of polar analytes. In the SPME, different phases are chosen depending on the analyte polarity [11]. In some cases, a salting out effect favors the extraction of polar analytes, which is achieved by adding high salt concentrations to the sample [8,12]. Some authors have established this technique to work in a dual mode, which means extracting apolar compounds without the use of salt additives, and polar compounds using salt additives [13,14].

We study the incorporation of inert salts (NaCl, and $MgSO_4{\cdot}7H_2O$). For the incorporation of sodium chloride, the most widely used in the literature, an increase between 10% and 30% can be observed in the total recoveries for the higher polarity pesticides (Log $K_{ow} < 4$); however, quantitative values could not be reached. Also, a decrease was observed, up to a 10%, in the recovery of pesticides with lower polarity (Log $K_{ow} > 4$). Similar results were obtained with a divalent salt such as magnesium sulphate heptahydrate.

3.5. Determination of the analytical features

Calibration curves were built for each pesticide, in a concentration range between 1 and 10 $\mu g\,L^{-1}$. Table 1 summarizes the results obtained for the calculation of the LOQ and LOD of the different

Table 1
Analytical parameters of the target pesticides.

Compound	Calibration curve	Correlation coefficient	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)	%RSD ($n=6$)
Malathion	$y = 2.82E7x + 1.90E7$	0.9925	0.10	0.32	11.8
Diazinon	$y = 62.06E6x + 1.62E6$	0.9871	0.40	1.30	20.6
Lindane	$y = 4.96E6x + 3.35E6$	0.9925	0.48	1.61	16.9
Chlorpyrifos	$y = 1.05E7x + 5.69E6$	0.9976	0.06	0.21	19.2
Cihalothrin	$y = 8.07E8x + 5.56E8$	0.9991	0.03	0.10	17.6
Cypermethrin	$y = 7.84E8x + 6.93E8$	0.9983	0.03	0.10	17.0
Fenvalerate	$y = 1.80E8x + 3.14E8$	0.9891	0.01	0.03	13.0

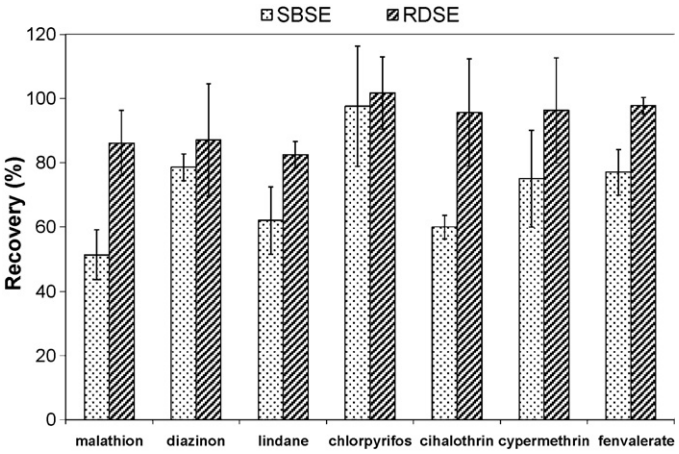

Fig. 5. Results from the comparative study of the SBSE and RDSE extractions.

pesticides. The correlation coefficient can be observed, which accounts for the linearity of the method for the target analytes. However, for most pesticides, we did not obtain values higher than 0.99. This would be the result of the reproducibility of the method, which is between 10% and 20% and would affect the values obtained.

The detection limits obtained are higher than those reported by different authors using the SBSE, and were values between 0.06 and 100 $ng\,L^{-1}$ depending on the analyte extracted [15]. This difference can be attributed to the use of thermal desorption in the SBSE method instead of solvent desorption, which lowers the detection limits and quantification. Additionally, when analyzed on the chromatograph and subsequently detected, a greater quantity of analytes in a sample, which increases the preconcentration factor in relation to the preconcentration factor of only 25 achieved using the rotating disk extraction with solvent desorption. A further study using a thermal desorption system coupled with GC–MS will be conducted elsewhere.

Evaluation of the reproducibility of the extraction method was achieved by completing six extractions under the same conditions, and the results can be observed in Fig. 5. This study reflects method reproducibility between 10% and 20% for the studied analytes. These values are comparable to those obtained using a SBSE, which repeatability is usually reported in the literature as <16% [15]. However, these values may be improved by optimizing the complete extraction method because the evaporation to obtain a higher preconcentration factor results in the manipulation of samples during the extraction.

3.6. Comparison with SBSE

A comparison of the extraction efficiency was made between RDSE and SBSE, under the same extraction conditions. The results can be observed in Fig. 5. In addition to the recovery values, similarities can be observed between the reproducibility of both methods. It is important to emphasize that under similar extraction conditions, a better recovery is obtained using the rotating disk. This is the result of the greater incorporation of PDMS to the disk than the bar, which would improve the extraction by modification of the phase ratio (β) if recovery is considered as [4]:

$$\text{Recovery} = \frac{K_{ow}/\beta}{1 + K_{ow}/\beta}$$

On the other hand, the higher surface area to volume ratio of PDMS provided by the RDSE allows for improved mass transfer, as described previously for the SPME according to the following equation:

$$\frac{dn}{dt} = \left(\frac{DA}{\delta}\right) C$$

where n is the analyte extracted mass over the extraction time t, A is the PDMS phase surface area, δ is the stagnant layer thickness, and C and D are the analyte concentration and diffusion coefficient in the sample solution, respectively [16].

These equations explain the better performance shown by the RSDE method in comparison to SBSE because there is an increase of twice the area and fourteen times the volume of PDMS when using the rotating disk method.

3.7. Determination of pesticides in real samples

The extraction method was applied to water samples from the Itata River, which were obtained on different dates. The results can be observed in Table 2.

For the pesticides malathion, diazinon, chlorpyriphos, and cyhalothrin, sample concentrations were found to be below the

Table 2
Concentration and recovery of pesticides in samples collected on different dates from the Itata River (Year 2009).

Compound	Concentration ($\mu g\,L^{-1} \pm SD$)						Recovery (% ± SD)
	June 16	June 24	July 1	July 9	July 22	July 27	
Malathion	ND	ND	ND	ND	ND	ND	76 ± 14
Diazinon	ND	1.4 ± 0.1	ND	ND	ND	ND	66 ± 16
Lindane	3.9 ± 0.2	1.8 ± 0.2	1.6 ± 0.2	ND	ND	ND	84 ± 6
Chlorpyrifos	3.8 ± 0.6	ND	ND	ND	ND	ND	87 ± 9
Cihalothrin	6.0 ± 0.5	ND	ND	ND	6.7 ± 0.1	ND	95 ± 11
Cypermethrin	27 ± 5	27 ± 2	13 ± 3	7 ± 3	6.7 ± 0.1	13 ± 5	101 ± 6
Fenvalerate	65 ± 4	20 ± 1	30 ± 7	5 ± 1	ND	ND	91 ± 10

LOD of the method. For the pesticides lindane, cypermethrin, and fenvalerate, their presence can be observed in most of the samples at concentrations above the maximum allowed by some regulation agencies (i.e., chlorpyrifos and lindane). According to the EPA, chlorpyrifos and lindane have environmental quality standards of 0.03 and 0.002 $\mu g\,L^{-1}$, respectively [17], while the maximum admissible pesticide concentration in drinking water established by the European Union is 0.1 $\mu g\,L^{-1}$ [18].

The recoveries of the different analytes, in real water samples enriched with a 20 $\mu g\,L^{-1}$ concentration of pesticides, are in accordance with those obtained during optimization of the method, and are shown in Table 2.

The proposed method could be also applied to other aqueous samples such as juice or wine. Additionally, the proposed method could be applied to fruit and vegetables, with previous sample preparation stages, as an alternative to the ethyl acetate liquid extraction, which is a technique that demands long extraction times and large solvent volumes [19]. This possibility will be assessed elsewhere.

4. Conclusion

The application of the technique RDSE for the determination of pesticides in water samples was established. Variables such as rotational velocity of the disk, extraction time, salt addition, and solvent desorption conditions were studied to select the optimum conditions.

The optimum conditions allowed determination of low-polarity pesticides with recoveries above 80% with method repeatability lower than 20%.

A comparison with the SBSE technique was performed. Under the same working conditions, better recoveries were obtained using the rotating disk extraction in comparison to those obtained using the SBSE method.

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