



Research article

Green method to determine triazine pesticides in water using Rotating Disk Sorptive Extraction (RDSE)

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ABSTRACT

The following work presents the development of the solid phase extraction technique with rotary disk (RDSE) in which the analysis for seven triazines in surface waters was first implemented. All the variables involved in extraction have been studied and optimized using a solid phase of octadecyl (C18) deposited on surface of the disk. Triazines were analyzed quantitatively by gas chromatography with simple quadruple mass detector, recoveries obtained for seven triazines were between 80% and 120%, accuracy expressed as RSD was between 3.21% and 6.34%, and detection limit of the method was between 0.020-0.056 $\mu\text{g L}^{-1}$ according to each analyte, which indicates a good reproducibility and precision of the method. Finally, the method was applied to analyze the objective compounds in water samples obtained in the Bolo River (Palmira-Colombia), in which triazines were not detected.

1. Introduction

The development of miniaturized systems represents a very important line of work within analytical chemistry. In recent years, advances in sample preparation have been directed towards the development of techniques that allow minimizing the manipulation of the sample, which require little use of organic solvents, and that incorporate the concept of green chemistry (Viapiana et al., 2013) criteria that meet the techniques based on Microextraction. Since the appearance of solid phase micro extraction (Arthur and Pawliszyn, 1990), numerous studies based on miniaturization of sample preparation have emerged, including developments such as in-tube Microextraction (Fernández et al., 2016), Sorption extraction on stir bar (SBSE) (Lei et al., 2016), Hollow-Fiber Solvent Bar Microextraction (Correa et al., 2014; Alcudia-León et al., 2011). All microextraction techniques involve the use of small amounts of sorbent phase in relation to sample size; these techniques are based on a distribution balance between the sorbent phases and the analyte matrix which in this distribution balance is governed by thermodynamic and kinetic factors. Thermodynamic factor defines the maximum amount of analytes that can be extracted using a technique, while the kinetics defines the speed at which this transfer occurs (Alcudia-León et al., 2011; Reyes-Garcés et al., 2018). There are also other methods for the determination

of contaminants present in aqueous samples as solid phase extraction (SPE), magnetic solid phase extraction (MSPE), dispersive liquid-liquid microextraction (DLLME) and solid phase microextraction (SPME) (Vieira et al., 2020). Recently, a novel Microextraction technique was developed based on a rotating disk "Rotating Disk Sorptive Extraction" (RDSE), which has shown to have a good performance, is fast, requires small volumes sample and sorbent phase is easily replaceable, allowing the use of commercial, natural sorbents or synthesized sorbents (Cañas and Richter, 2012; Fiscal-Ladino et al., 2017). Different studies have been reported for the determination of pesticides (Richter et al., 2009), Triclosan (Jachero et al., 2015), PAHs (Corrotea et al., 2014) among others. Triazines are pesticides belonging to herbicide group, used to control weed growth. Chemically they are six-member rings that contain three nitrogen atoms and one Azina. They are classified as symmetric and asymmetric triazines. In the symmetric triazines, nitrogens in the ring are distributed symmetrically, while in the non-symmetric ones there are two nitrogens in a straight position, Figure 1.

In the group of symmetric triazines are atrazine, simazine and prometryn known as chloro-atrazines, in the group of asymmetric ones. Metribuzin is found and in a third group, alachlor and metolachlor are classified as chloroacetamides. Table 1 shows the characteristics of the seven structures of triazines studied, toxicological classification

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according to WHO is shown, and who performs this classification taking into account parameters such as lethal dose 50 (LD 50) dermal or oral routes. Residuality of each of these herbicides is influenced by physico-chemical characteristics of the soil such as pH, temperature, soil type, humidity conditions, and ambient temperature. Triazines are considered toxic to aquatic life (Graymore et al., 2001; Guangying et al., 2011) and 0.1 gmL^{-1} concentrations is one inductor of hermaphroditism in frogs (Hayes et al., 2002), the Agency for the Environmental Protection of the United States determined that there is evidence of carcinogenicity of the herbicide in animals, but at the same time considers them slightly toxic to some aquatic species (USEPA, 2013). Atrazine and simazine are used in Colombia for preemergence and early post-emergence in the control of weeds in sugarcane, corn and sorghum crops (Gómez, 1995) (ICA, 2016). In sampling conducted during 2010 and 2011, concentrations of simazine and atrazine were found in the Cauca River equal to $172 \text{ }\mu\text{gL}^{-1}$ at the Puente Guayabal point and $240 \text{ }\mu\text{gL}^{-1}$ at Mediacanoa respectively (Sarría-Villa et al., 2016). In this investigation, a new application of the RDSE-based technique was developed for the determination of seven triazines formed by simazine, atrazine, metolachlor, alachlor, cyanazine, metribuzin, and prometryn in water samples by GC-MS. The classification of the seven triazines studied is shown in Table 1, as are the types of crops where they are regularly used.

2. Materials and methods

2.1. Reagents and solutions

The reagents used in this study were analytical grade. A standard solution composed of seven triazines was used: simazine (SMZ), atrazine (ATZ), metribuzin (MMZ), alachlor (AAC), prometryn (PMT), metolachlor (MTC), cyanazine (CAZ) concentration 100 mgL^{-1} of each of the analytes obtained from Sigma-Aldrich (Milwaukee, WI, USA). A standard was prepared in ultra-pure hexane (Merck) at a concentration of 10 mgL^{-1} for all analytes. They were subsequently performed. Dilutions to prepare five concentration levels between 0.3 mgL^{-1} to 3.0 mgL^{-1} using hexane as a capacity solution. Methanol and ultra-pure grade dichloromethane (purity $\geq 99.8\%$) acquired from Merck (Darmstadt, Germany), were evaluated as extraction solvents. The sorbent phase used was Cromabond C18 (Germany), with a particle size of $25 \text{ }\mu\text{m}$, and a pore size of 200 \AA . Nitrogen 5.0 was used for analyte preconcentration, carrier gas of the chromatographic system was helium 5.0; both gases were obtained from Cryogas (Medellín, Colombia).

2.2. Rotary disc extraction procedure

2.2.1. Extraction device

The device for extracting the analytes is a 1.5 cm external diameter, 2 mm deep, 1.3 internal diameter and 1.2 g of device height. Teflon disc in which a miniature magnetic stirring bar integrated that helps the extraction and elution of the analytes by constant agitation of the disc in a stirrer plate (Cañas and Richter, 2012). The upper part of the disc has a

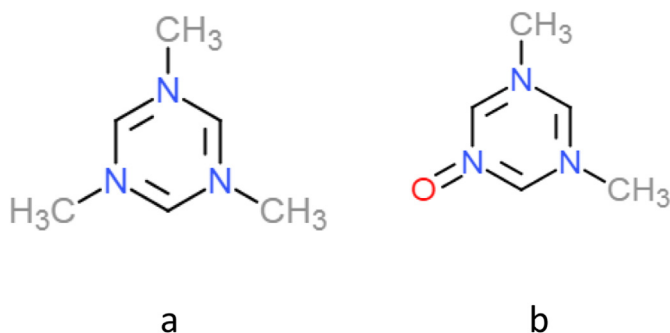


Figure 1. Structure symmetric (a) and asymmetric (b) triazines.

Table 1. Characteristics of the seven triazines compounds studied.

Trade name	Active ingredient	Toxicity classification	Crops
Triazol 80 wp	Atrazine	III	Corn, Sorghum, Sugarcane, Fruit trees, African palm.
Sencor®sc 480	Metribuzin	III	Asparagus, Potato, Tomato, Pea, Sugarcane, Chili and paprika.
Alanex	Alachlor	III	Cotton and Sorghum.
Gesard 500sc	Prometryn	III	Cotton, Corn, Celery and Pea.
Metolagan 960 sc	Metolachlor	III	Grasses, Cypresses, and Corn Leaf.
Simazine	Simazine	III	Sugarcane, Corn, Sorghum.
Bladex500wp	Cyanazine	III	Corn, Sugarcane.

Source: Breckenridge et al. (2010).

cavity that allows depositing a sorbent phase in our C18 study. Once the sorbent phase is on, it is covered with a $0.22 \text{ }\mu\text{m}$ Merck glass fiber filter and subsequently sealed with a Teflon ring as shown in Figure 2.

2.2.2. Rotary disk conditioning

For the conditioning of the disk, a 5.0 mL beaker was used so that the disk with the sorbent material C18 was completely immersed in the solvent; 2.0 mL methanol and 2.0 mL dichloromethane were used as conditioning solvents. The conditioning time was established in 5 min with each solvent at a rotation of the disk of 600 rpm, thus achieving that the absorbent material was continuously exposed to two solutions with different polarity. Finally, the disc was submitted to a rinse with 5.0 mL deionized water for 5 min in order to remove residues from the solvents (Richter et al., 2009).

2.2.3. Extraction and elution process

The extraction was carried out, introducing the rotary disk with the C18 phase activated, in 25.0 mL of sample with shaking of 1200 rpm for 60 min at room temperature. The analytes were eluted in a 5.0 mL beaker to which 2.0 mL of methanol was added by placing the disc in the opposite direction to the extraction and stirring at 600 rpm for 5 min; After this time the disk is removed and the analytes are preconcentrated with a flow of nitrogen grade 5.0 flow 1.0 mL/min and then taken to a volume of $25 \text{ }\mu\text{L}$ with Hexane, for further analysis (Richter et al., 2009).



Figure 2. Rotating disk sorbent extraction (RDSE).

2.3. Chromatographic conditions

The triazine analysis was performed on a Thermo Scientific gas chromatograph coupled to a Shimadzu QP2010 plus brand selective mass detector (Waltham, MA, USA). All separations were made with a 30 m × 0.25 mm thick RTX-5MS chromatographic column, 0.25 μm film, coated with 5% phenyl-95 methyl polysiloxane Restek brand (Bellefonte, PA, USA). The injection volume was two microliters (2 μL) of sample extract; the injector temperature was 250 °C in the "splitless" mode, according to the elution times found, a solvent delay of 5 min was established. Helium was used as a carrier gas at a constant flow of 1.0 mLmin⁻¹; the oven temperature program started at 70 °C up to 260 °C at 10°Cmin⁻¹; subsequently, the temperature was increased to 300 °C at a speed of 5°Cmin⁻¹ and was maintained for 8 min. The elution time of the solvent was 7 min, the mass spectrometer was operated with electronic impact (EI) at 70eV in SIM mode; waiting time for each of the ions was set between 15 and 30 ms for each m/z value, so that the highest number of scans per peak was obtained. MS transfer line remained at 250 °C. Table 2 shows the ions monitored for each triazine.

2.4. Statistical methodology

Within methodology developed, the best characteristic chromatographic profile of the 7 triazines and their peaks corresponding to the compounds simazine, atrazine, metribuzin, alachlor, prometryn, metolachlor, cyanazine was standardized, acceptance of the chromatographic profile was based on the capacity of resolution of the column and its chromatographic system. For the validation of the analytical methodology, calibration curves were prepared with five standard solutions with some concentrations between 0.30 μgL⁻¹ and 3.00 μgL⁻¹ for simazine, atrazine, metribuzin, alachlor, prometryn, metolachlor and cyanazine, each concentration level is prepared by diluting in Milli-Q water. Statistical criteria evaluated in the validation of the analytical technique were those recommended by the United States Pharmacopeia (USP) for the development of chromatographic methodologies. To retention time (CV%≤5%), resolution (R², R = 2), tailing factor (S ≥ 0.8 and S ≤ 2), linearity (Significance test), Precision (Hortwits theory), Repeatability (CV%≤5%), Robustness (Youden-Steiner linear combination), Accuracy (Sistematyc error≤10%), Standards recovery (70%–130%), Uncertainty (Total uncertainty combined), Sensitivity (Detection limit, Quantification limit) (US-EPA, 2018).

2.5. Collection of samples

Samples used to evaluate the proposed extraction methodology were taken in the Bolo River located in Palmira-Colombia, which was chosen because it flows through areas of great agricultural activity before it flows into the Cauca River. For sampling, a non-probabilistic sampling was carried out on trial, three simple samples were taken at three sampling points of 250 mL of tributary water 1.5 m from the shore and 0.50 m deep in the opposite direction to the current. Which were stored in amber Pyrex borosilicate glass bottles and stored at 4 °C. Water temperature at the time of sampling was 19.3 °C and a pH of 5.7. The sample

Table 2. Retention times Quantifier ion, qualifying ions for each of the analytes.

Analyte	Retention time (min)	Target ion (m/z)	Qualifying ions (m/z)
Simazine	17.60	201	186.173
Atrazine	17.80	172	174.187
Metribuzin	19.30	198	199.144
Alachlor	21.20	160	188.237
Prometryn	23.20	140	241.173
Metolachlor	24.00	162	238.240
Cyanazine	23.60	225	240.173

was taken in the dry season in the month of January 2018, the GPS point 3.499303N, -76.447152W. At the time of the study, a composite sample was obtained to have a more representative sample. Figure 3 shows a map of sampling points.

3. Results and discussion

Rotary disk extraction for aqueous samples is a preparative technique which is based on the standardization of optimal conditions that favor the partition equilibrium between the sorbent surface and the analyte matrix, the technique standardization process seeks to favor equilibrium thermodynamic. This occurs due to the interaction between the contact surface of the stationary phase and the sample, so that thermodynamic equilibrium can be reached quickly (Jachero et al., 2014). By optimizing these thermodynamic conditions, it is possible to standardize the conditions of absorption and elution of the analytes both from the sample towards the sorbent phase and from the sorbent phase towards the elution phase of the analyte, thus establishing unique extraction conditions for each one of the analytes to quantify.

3.1. Method validation

As a first step for the standardization of chromatographic conditions and in order to obtain qualitative information on analytes, injections were made in the "scan" mode using an injection volume of 1.00 μL at a concentration of 10 μg mL⁻¹ solution standard of the 7 triazine compounds. Taking into account criteria of suitability of the chromatographic system (Skoog. and Nieman, 2001) such as resolution of chromatographic peaks (R²) asymmetry factor or tailing (0.8 ≤ S ≤ 2.0), reproducibility in retention time and height of peaks. Subsequently, the creation of the Selective Ion Monitoring SIM methodology was carried out, for the development of the selective ion methodology, three fundamental factors for the choice of ions were taken into account, and these factors were: Unique ions for the compound, high molecular mass, high abundance and that were characteristic of triazines. 5 groups were created and a residence time between 15 and 30 ms was set for each of the ions, thus obtaining a number of cycles/peak between 12 and 25 so that a loss of response and quality decrease did not occur spectral. The standardized variables in SIM mode were to Group 1: Start time 3.09 min, 13 Cycles/sec, Ion: 173, 201, 215, 186, 202, 200, 203. Group 2: Start time: 19.48 min, 22 Cycles/sec, Ion: 198, 199. Group 3: Start time: 20.84, 23 Cycles/sec, Ion: 160, 188, 237, 162, 199, 241, 184, 226. Group 4: Start time: 22.36, 24 Cycles/sec, Ion: 162, 163, 238, 240. Group 5: Start time: 23.23, 22 Cycles/sec, Ion: 172, 173, 198, 225. As a criterion of correct identification and fractionation of the mass spectrometry detector, a tolerance interval of ±30% (Soboleva et al., 2004) was accepted, with respect to the proportions of abundance of absolute ions of each of the spectra obtained for each molecule "Target." The statistical criteria evaluated in the validation of the analytical technique were linearity (Statistical analysis of the correlation coefficient), precision (Horwitz coefficient of variation), repeatability (CV ≤ 5%), robustness (Youden-Steiner linear combination), accuracy (systematic error≤10%), uncertainty (Combined total uncertainty) and sensitivity (LOD and LOQ). The validation criteria were based on the BIAS% form the linear model following ICH guidelines (ICH, 2005).

3.2. Statistical results of the method by GC-MS

The results obtained for each of the statistical parameters proposed in the methodology are shown in Table 3. As one of the most important parameters can be observed, this is due to the fact that when working at concentrations at the level of trace factors commonly routine, such as the change in the use of volumetric material such as micro-pipettes, the analysis and its reproducibility can intervene significantly. Lineal range from 0.3 μg L⁻¹ to 3 μg L⁻¹ for all pesticides were obtained, with R² since 0.997 to 0.999, LOD from 0.032 μg L⁻¹ to 0.219 μg L⁻¹ and %RDS from



Figure 3. Location of sampling sites in the Bolo River. The river current goes from point 1 to point 3.

2.97% to 4.02% for all pesticides. The magnitudes of uncertainty associated with each of the processes used in the extraction with rotating disk were: Relative standard uncertainty in analyte concentration (± 0.005), relative standard uncertainty measurement sample volume (± 0.002), relative standard uncertainty preparation stock solution (± 0.116), uncertainty of analyte concentration in measurement 2.4 mgL^{-1} (± 0.560), expanded measurement uncertainty $U 1.7 \text{ mgL}^{-1}$ (± 0.396), uncertainty of analyte concentration in measurement 0.4 mgL^{-1} (± 0.093), expanded method uncertainty (± 0.233) and total combined uncertainty (± 0.117). The method was robust for all the factors tested since the values were lower than $S\sqrt{2}$ (Youden and Steiner classic scheme) except for elution time in which the difference was greater. It was verified that the best results are presented for capital letters, since the differences were less than zero. Therefore, low elution times were defined as the factor with greatest impact on quality of analytical results.

3.3. Optimization of the experimental conditions to RDSE

3.3.1. Sorbent phase evaluation

Efficiency of the proposed extraction method depends mainly on the constant distribution of analytes divided between sorbent material and sample matrix. Taking into account the chemical nature of the analytes, the efficiency of the extraction was studied using the area of the chromatographic peak. Sorbent phases C18 and a clay of Montmorillonite Sodium modified with ionic liquids were evaluated (Obando et al., 2016), showing a better performance for the extraction of triazines than the polymeric phase C18. According to the comparative results obtained in other investigations (Obando et al., 2016) for this modified clay it was decided to test the performance of the modified montmorillonite sodium clay to extract triazines, using the same procedure of extraction of the C18 polymer phase. Clearly how it can be shown in the full scan scanning chromatogram there is a retention by the clay of the compounds atrazine, alachlor, prometryn and metolachlor, one of the reasons for a low retention could be due to the medium polarity of the triazine compounds because the clay has a high polar degree as reported by the researcher Obando (Obando et al., 2016). Mean recoveries for hexachlorobenzene in water of $84 \pm 2\%$ and $85 \pm 3\%$ for the C₁₈ and PDMS have been obtained

(Cañas and Richter, 2012). Relative recoveries between 80–111% to PAHs using magnetic nanoparticles-nylon 6 composite (Reyes-Gallardo et al., 2014) and relative recoveries between 90–115% to hydrophilic organic compounds were obtained using stir bar sorptive-dispersive microextraction by magnetic nanoparticles-nylon 6 composite (Benedé et al., 2016). The over position between the chromatograms obtained can be seen in Figure 4. It should be clarified that the peaks run in “scan” were identified with the NIST 2.0 library. One of the main objectives was that the disc during shaking will not release absorbent material, an interest that was confirmed during the spectral scan in “full scan” mode in which no peaks from the polymer phase were observed.

3.3.2. pH effect

The 7 triazines studied are weak acids with Pka values between 0.64 and 4.1 with the exception of cyanazine which has a pKa value of 12.9 (Agriculture & Environment Research at the University of Hertfordshire, 2018) and according to results obtained. Figure 5 are shown at pH values between 7 and 9, recoveries of the seven analytes during the extraction process are favored, while at pH values less than 7 the extraction process is not favored, these results are structurally explained in the fact that since the seven weak acidic analytes and present in their structure polar functional groups such as amines, ethers and hydroxides, they are given a weakly polar character, which is why when they are in a neutral pH this polarity is solvated, allowing so that van der Waals interactions are greater between analytes and the octadecyl sorbent phase with apolar characteristics (Uzal-Varela, 2016). This low polarity coincides with the partition coefficient values found in the literature. Figure 5 shows results of the analytical signal obtained for pH values between 2 and 10, obtaining better analytical signals at neutrals pH values. Recoveries from 70.1 to 119.9% to pesticides as atrazine, carbaryl, carbofuran, chlorpyrifos, diazinon, simazine between others were found using pH 2 to rotating disk sorptive extraction technique (Donato et al., 2017).

3.3.3. Determination of extraction time and rotation speed of the disc

Extraction time is one of the most important factors in most extraction processes, since it influences the accuracy of the results. The equilibrium time is defined as the time after which the amount of analyte extracted

Table 3. Linearity, Correlation coefficient, Detection limit, standard deviation and repeatability of the method.

Analyte	Linear equation	R ²	Linear Range	LOD (μgL^{-1})	Extraction efficiency (%R)	Relative standard deviation	Repeatability %RSD
Simazine	$Y = 5.965 \times 10^4 - 2.8336 \times 10^3$	0.997	0.3–3.0	0.032	90–112	3.21	3.21
Atrazine	$Y = 9.3361 \times 10^4 - 7.8865 \times 10^3$	0.998	0.3–3.0	0.067	94–110	6.34	3.36
Metribuzin	$Y = 4.1652 \times 10^3 + 7.0841 \times 10^4$	0.999	0.3–3.0	0.149	87–113	4.34	3.32
Alachlor	$Y = 1.095 \times 10^4 - 8.8577 \times 10^2$	0.997	0.3–3.0	0.203	80–90	3.44	2.97
Prometryn	$Y = 1.46961 \times 10^4 - 7.212 \times 10^3$	0.998	0.3–3.0	0.191	83–98	4.12	3.23
Metolachlor	$Y = 5.597 \times 10^4 - 1.941 \times 10^3$	0.997	0.3–3.0	0.084	87–105	5.98	3.00
Cyanazine	$Y = 1.363 \times 10^4 + 1.017 \times 10^3$	0.997	0.3–3.0	0.219	92–116	4.56	4.02

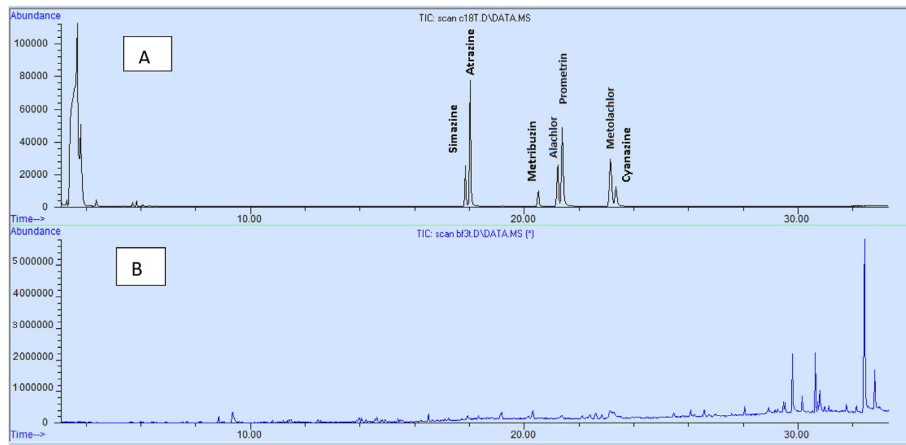


Figure 4. Total Ionic Chromatogram of triazines using C18 absorbent (A) vs modified montmorillonite clay (B).

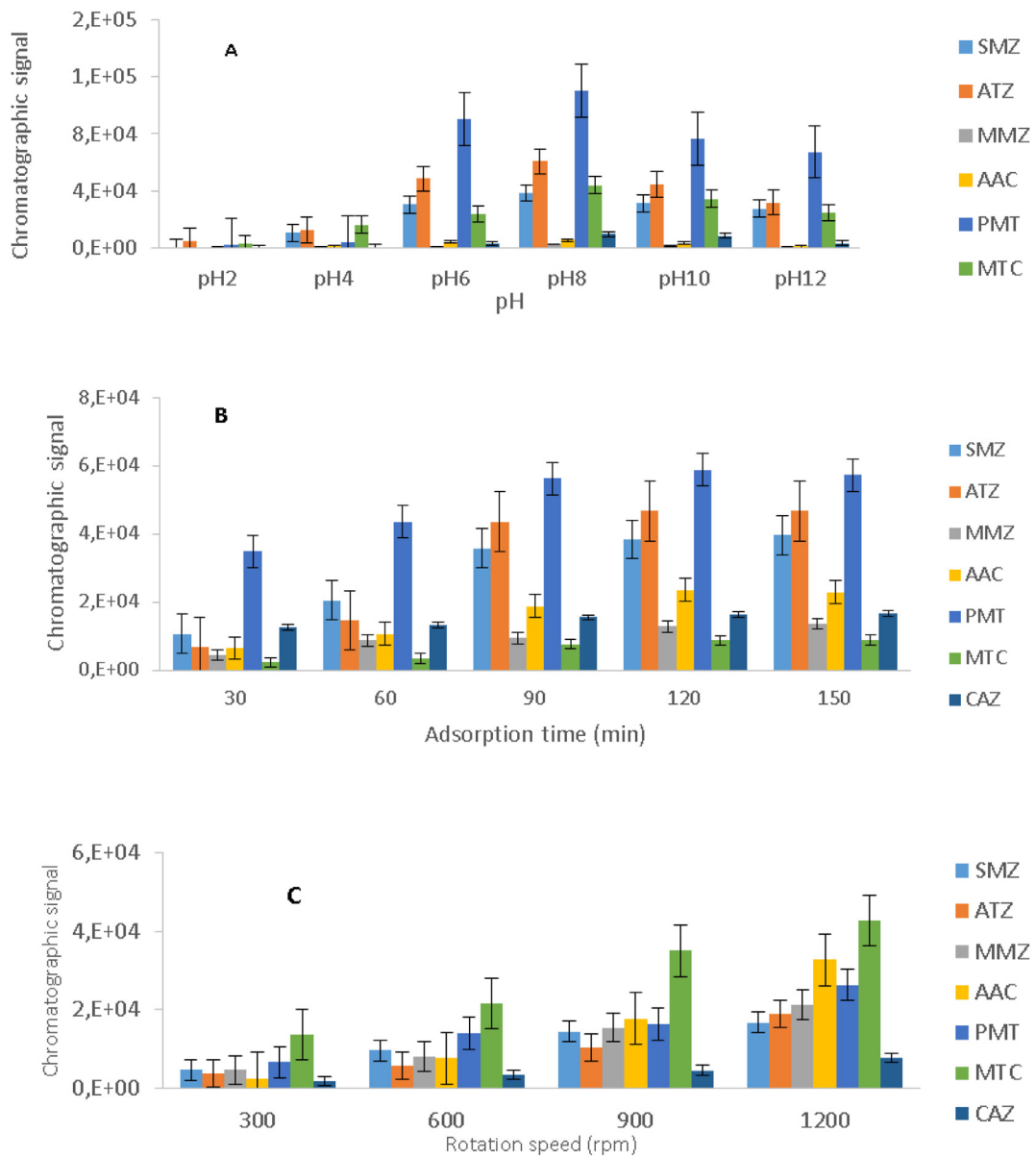


Figure 5. Influence of pH (A), adsorption time (B), rotation speed (C) in the extraction process.

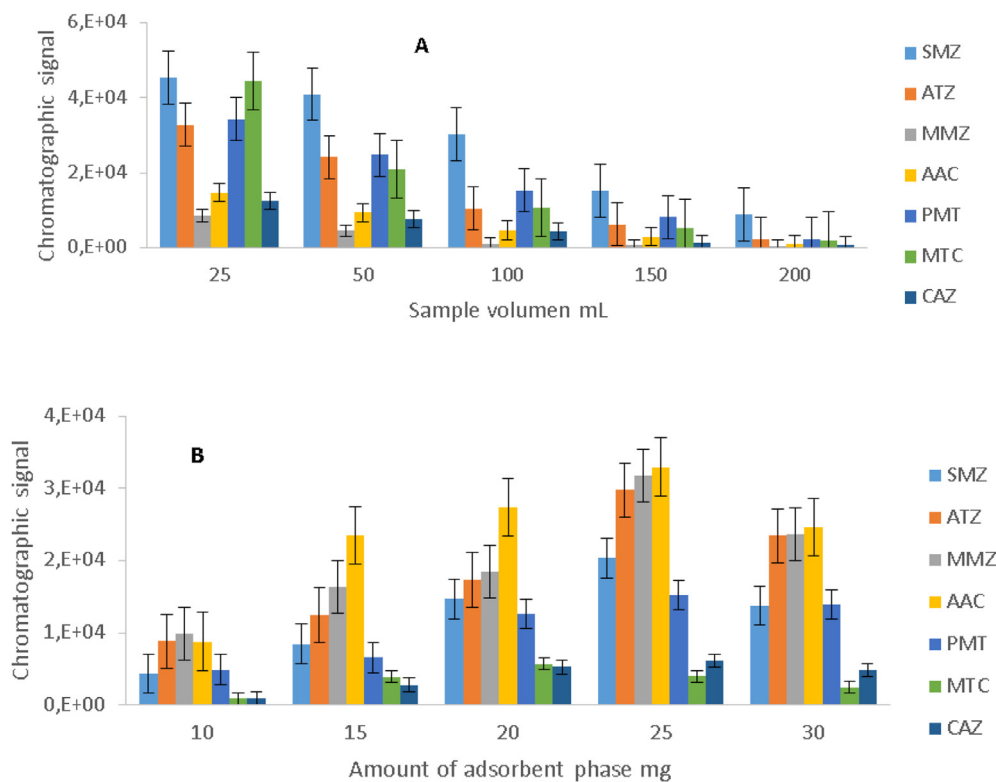


Figure 6. Decrease in the stationary water layer due to the decrease in sample volume (A), Amount of absorbing phase during the extraction process (B).

remains. The effect of the extraction time on the recovery values for the extraction of the seven triazines with rotary disk of octadecyl sorbent phase was studied in times that varied from 30 to 120 min. The efficiency of triazine extraction increases with increasing extraction time from 30 to 60 min, and then remains almost constant with a greater increase in extraction efficiency at values greater than 90 min. Therefore, the extraction time of 100 min it was selected as optimal. Extraction times between 60 min (Becerra-Herrera et al., 2015) and 90 min (Manzo et al., 2014) were reported for determination of non-steroidal anti-inflammatory drugs. Extraction time of 3 h for determination of pesticide residues in river water were determined (Giordano et al., 2011). The high extraction times show the polar trend of the seven triazines analyzed (log Kow values between 2.3 and 3.5) and their degree of interaction with the sorbent (Zhao et al., 2011). On the other hand, the efficiency of the mass transport phenomenon during the extraction process using the rotating disk was analyzed in terms of rotational speed. The study showed that the extraction is favored with the increase in rotation speed, because at high speed of rotation of the disk it causes an increase in the migration of the analytes towards sorbent phase, causing that partition equilibrium between the aqueous phase of the matrix and absorbent phase is reached faster. An advantage of the RDSE over other extraction techniques is that the absorbing phase of the disk can be maintained in higher rotation conditions, and remain unchanged by contact with the reservoir or solid matrix components (Richter et al., 2009). Figure 5 shows the influence of the pH, adsorption time and rotation speed in RSDE process.

The most adequate rotation speed during the extraction process was 1200 rpm, according to the results obtained, it can be affirmed that, the stirring speed is one of the most important factors during the extraction process using rotary disk. According to Richter, P (Richter et al., 2009) "at a higher agitation speed (turbulent flow) the thickness of the stationary layer that forms on the surface of the disk decreases, which facilitates mass transport from the solution to the extraction phase", causing the adsorption of the sorbent to the analyte to be favored. Highest rotation disk velocity (1600 rpm) conducted to the best

extraction conditions for the majority of the pesticides studied by Donato and collaborators (Donato et al., 2017). Previously reported results indicate that increased rotation also favors the transfer of the analyte from the sorbent to the solvent (Jachero et al., 2013; Manzo et al., 2015).

3.3.4. Sample volume and desorption volume

The study process of the variable sample volume resulted in values consistent with the results obtained with stirring speed, since it was observed to what extent the sample volume increased the analytical signals decreased proportionally. This is consistent with the thermodynamically predicted behavior because at higher sample volumes the thickness of the stationary layer that forms on the surface of the disk increases causing a decrease in the mechanical interaction between the disk and the stationary layer the attic mathematical model that describes said phenomenon is Eq. (1), which describes the phenomena of mass transport for SPME (Bruheim et al., 2003).

$$t_e = \frac{3 \cdot \sigma \cdot Kd \cdot pt}{D} \quad (1)$$

where σ is the thickness of the stationary layer; D is the diffusion coefficient of the solution; t_e , equilibrium time; Kd the analyte distribution coefficient between the sorbent phase and the solution and pt is thickness of the sorbent phase. Consequently, by decreasing the volume of the sample, the diameter of the stationary water layer is reduced thereby increasing the extraction and consequently the equilibrium time decreases. By having the analytes retained in the polymer phase, 2 solvents of high dielectric strength dichloromethane and methanol were added in order to cover both low and high polarities and that had a high vapor pressure so that preconcentration after elution was carried out quickly. The results obtained are shown in Figure 6 (A) where, as can be seen, the elution volumes are still governed by the thickness of the stationary layer formed during the stirring process. In this way it was concluded that extraction times with rotating disk are a function of sample volumes and stirring speed.

3.3.5. Amount of absorbing phase

Optimal amount of absorbent phase for the extraction process was studied, for this, we worked with masses of sorbent in the range of 10, 15, 20, 25 and 30 mg as a result an optimal value of 25 mg of necessary sorbent material was obtained to perform the extraction; At higher values of 30 mg, presence of polymeric material in the chromatograms from bleeding of the sorbent phase during the agitation process is noted, where an increase of baseline and appearance of anomalous peaks. Other studies have experimentally established the optimal amount of sorbent at a value of 25 mg, arguing that increasing the amount of sorbent phase tends to compress causing a limited interaction between analyte and sorbent, while at a value of 25 mg of sorbent active sites of the sorbent are more available thus allowing greater interaction and favoring extraction process (Ulisse Ulisse, 2014). As an optimal result of the absorbent amount, an optimal value of 25 mg was observed. Figure 6 shows the results obtained for optimal amount of absorbent. To pesticides extraction, the effect of different amount (10, 20, 30 and 40 mg) of Oasis® HLB in the rotating disk resulted that for 39% of the compounds the difference in the amount used was significant. Smaller amounts of sorbent permit free circulation of sorbent into the disk cavity allowing better sample circulation and interaction with analytes (Donato et al., 2017; Fiscal-Ladino et al., 2017).

3.3.6. Ionic force

Within the parameters studied, the addition of a matrix modifier was analyzed, this modifier was NaCl, the intention of adding this salt was to increase the ionic strength of the triazine solution, thus allowing the analytes to acquire a greater affinity for the sorbent phase caused by the decrease of its polarity. As a result, no significant influence was obtained in the areas obtained for the analytes, which is why it was decided to work without the addition of NaCl. Other results indicate that the extraction of compounds of high and medium polarity increases in the presence of salts due to the salting out effect (Cañas et al., 2014; Corrotea et al., 2016). The optimized values for the extraction of the seven triazines were pH: 8, Sample volume (mL): 25.0, elution volume (mL): 4.0, amount of adsorbent material (mg): 25, extraction time (min): 100, elution time (min): 5, stirring speed (rpm): 1200. The extraction efficiency was to simazine (90–112%), atrazine (94–110%), metribuzin (87–113%), alachlor (80–90%), prometryn (83–98%), metolachlor (87–105%), cyanazine (92–116%).

3.4. Determination of triazines in real samples

RDSE-based extraction method was optimized, the analytical methodology was validated and applied to evaluate the presence of triazines in water samples from the Bolo River, finding that none of the samples contained detectable amount of the target triazines. This research allowed to evaluate the solid phase extraction technique with a rotating disk which is an innovative technique with new analytes, in this case triazines in aqueous samples, which allows to work aqueous matrices with a high content of sedimentable material; which is an important aspect when carrying out environmental analyzes, since most of the analytical methods described in the literature and international standards suggest that during the water analysis the aqueous phase obtained after filtration of the water must be analyzed. Sample without taking into account the sedimentable organic matter retained in the filter (Barco-Bonilla et al., 2013), one of the main reasons why this filtration is generally recommended is due to the saturation of the filter by the amount of sediment, causing a large amount of analyte, depending on its physicochemical properties (water solubility, octanol/water partition coefficient (log K)) is not quantified. This fact makes clear the relevance of the analysis of both phases in water samples residuals and the main advantage of solid phase extraction with rotary disc for which the non-filtration of the sample does not generate interference or complications during the analysis, being at the forefront with current European methodologies, which recommend that suspended particles should be

considered within the analysis since all wastewater is considered as a solution of solids suspended in solution (Directive 2008/105/EC of the European Parliament and of the Council, 2008).

4. Conclusions

Microextraction with rotating disk in sorbent phase C18, showed to be a fast, simple method of good performance for the determination of seven triazines in water samples, simplified the process of extraction and desorption at a single step, obtaining high recoveries and showing advantages over conventional techniques for their analysis such as LLE and SPE. In addition, the discs are reusable and allow easy replacement of sorbent phases, thus allowing the potential chemical modification of the sorbent phase. GC-MS method allowed the identification and quantification of seven triazine herbicides of aqueous matrices. In the validation, recoveries were obtained for the seven triazines which were between 80% and 120%, the accuracy expressed as RSD was between 3.21% and 6.34%, and detection limit of the method was between 0.020–0.056 $\mu\text{g L}^{-1}$ according to each analyte, indicating a good reproducibility and precision of the method. The methodology developed complies with the statistical parameters required by international standards such as US-EPA and EU which establish limits of detection of 0.3 mg L^{-1} for triazine herbicides in water. After validation, the method developed was successfully applied for qualitative confirmation and quantitative detection of the seven triazines in real water samples. Analyzed samples from the Bolo River, quantities below LOD were not detected or found for the seven triazines.

Declarations

Author contribution statement

Edouard Velasco: Performed the experiments.

Jhon Ríos: Conceived and designed the experiments.

Rodrigo Sarria-Villa: Analyzed and interpreted the data; Wrote the paper.

Milton Rosero: Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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