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Rapid analysis of 4-nonylphenol by solid phase microextraction in water samples

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ABSTRACT

Alquilphenols are considered to be endocrine disruptors and are mainly found as 4-nonylphenol (4-NP) in ecosystems. A chromatographic analytical method was developed using solid phase microextraction (SPME) combined with gas chromatography-mass spectrometry (GC-MS) for the extraction and quantification of 4-NP in sources of water in Mexico to establish environmental concentrations. A derivatization process with *N*-Methylbis(trifluoroacetamide) (MBTFA) was carried out in order to increase sensitivity in the method. The method was validated with a correlation coefficient above 0.99, and a limit of detection and quantification of $0.01 \mu\text{g L}^{-1}$ and $0.15 \mu\text{g L}^{-1}$ respectively, which were determined by a linear curve at low 4-NP concentrations. After demonstrating the feasibility of the method, an analysis in water samples was performed. Eighty-three percent of samples had detectable concentrations of 4-NP with a maximum concentration of $12.61 \mu\text{g L}^{-1}$, $12.2 \mu\text{g L}^{-1}$ and $6.08 \mu\text{g L}^{-1}$ in recreational water, wastewater discharges and drinking water respectively. Sixty-five percent of the samples presented concentrations above the limit established by the European Union ($2 \mu\text{g L}^{-1}$) and 17% above the limit by the Environmental Protection Agency ($6.6 \mu\text{g L}^{-1}$). Although the number of samples is not representative for the assessment of the real-world scenario, our data presents a general overview of the exposure levels and possible environmental and health risks. Continuous monitoring and regulation of this pollutant in Mexico is important in order to prevent exposure and thus, ecological and adverse health effects.

1. Introduction

Alquilphenol ethoxylates (APE) are non ionic surfactants widely used in detergents, plastic additives, emulsifiers, pesticides, among others. The APE most used is the nonylphenol ethoxylate (NPE), its use represents up to 80% of the total production [1]. The main characteristic of this compound is that is capable of generating micelles in solution. The amphiphilic structure of the surfactant molecule, which has a polar (hydrophilic) and a non polar (hydrophobic) end, is the cause for this activity. These chemicals are disposed directly into municipal and industrial wastewater discharges. In environmental conditions, NPE are degraded by microorganisms or ultraviolet light by transforming them into nonylphenol (NP) including the 4-nonylphenol (4-NP) [2].

4-NP is one of the most found organic pollutant in wastewater, effluents, rivers, drinking water, sediments and soil [3–7]. Several authors have reported that 4-NP possesses endocrine disruption activity

and is highly toxic to aquatic and terrestrial organisms because of its ability to mimic the female hormone 17β -estradiol [8]. Previous studies have shown a decrease in the gonadosomatic index in red seabream and black rockfish associated with the exposure of $50 \mu\text{g L}^{-1}$ of 4-NP [9]. Also, Japanese quail exposed to 4-NP presented a decrease in male spermatogenesis as well as pathologic injuries in male gonads [10]. The Water Framework Directive of the European Union has listed NP as a priority pollutant and allows a maximum concentration in water of $2 \mu\text{g L}^{-1}$ [11], while the Water Quality Criteria for the aquatic organisms protection of the Environmental Protection Agency (EPA) establishes $6.6 \mu\text{g L}^{-1}$ as the maximum concentration permitted [12]. Regulations in Mexico and Latin America that restrict the levels of NP in water are null. In addition, information on the presence of this pollutant in surface and treated waters do not exist. A study in Texcoco, which is a wastewater receptor of Mexico City, presented levels of 4-NP from 0.93 to $7.3 \mu\text{g L}^{-1}$ [13]. In addition, agricultural irrigation water used

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in Tula Valley in Hidalgo presented concentrations from 1.98 up to 7.3 $\mu\text{g L}^{-1}$. Moreover, studies in drinking water of the Cutzamala system, which supplies 60% of water consumption in Mexico City, has registered concentrations of 0.089–0.655 $\mu\text{g L}^{-1}$ [14]. Therefore, it is important to establish monitoring strategies in water in order to contribute to the generation of regulations in this respect, due to the toxicity associated to 4-NP and the wide use of NPE in Mexico.

An appropriate analytical method is necessary to quantificate 4-NP in different sources of water to be able to draw conclusions about the disposition and the possible threat and negative impacts that its use represents [15]. Some of the most used methods for the analysis of alquilphenol (AP) are liquid chromatography (LC), mass spectrometry (MS) or tandem mass spectrometry (MS/MS) [16]. NP extraction in water samples is commonly performed by liquid-liquid extraction (LLE) [17,18] nevertheless, its popularity has fallen because of the high consumption of time and solvents. To this extent, solid phase extraction (SPE) is primarily used for the extraction and pre-concentration of NP from several environmental matrices [19–21]. Although, compared to LLE, SPE reduces extraction time and solvent consumption, new analytical techniques that minimize costs, extraction time, organic solvents, quantity of sample and with high sensitivity, are being explored [22,23]. Pawliszyn reported solid phase microextraction (SPME) as a simple, rapid extraction method [24]. SPME employs an automatic device which contains a thin polymeric coating that is adapted to a microsyringe. There are two types of SPME: i) direct immersion (DI) and ii) headspace (HS). DI is mainly used to extract NP due to its non-volatile nature; however, HS has also been used combined with a derivatization process [25]. Derivative formation increases volatility, decreases polarity in organic compounds and improves the thermal stability of analytes. This causes a lower detection limit and/or better selectivity [26]. The aim of our study was to develop and validate an analytical method for the quantification of 4-NP in water samples using SPME with GC-MS with a previous derivatization process. Subsequently, an evaluation of 4-NP in different sources of water in Mexico was performed to demonstrate the effectiveness of the method as a monitoring technique of this contaminant in multiple scenarios.

2. Methods

2.1. Materials and reagents

Stock standard solution of 4-NP (1000 $\mu\text{g L}^{-1}$) was prepared in acetone and stored in the dark at -40°C until its further analysis. Standard working solution was prepared right before its use.

A 0.1 M hydrochloric acid (HCl) (JT Baker, Edo. Mexico) solution, sodium chloride (NaCl) (JT Baker, Edo. Mexico), Milli-Q deionized water (18.3 M Ω , Millipore) and *N*-Methyl-bis(trifluoroacetamide) (MBTFA) $\geq 97.0\%$ GC (Sigma Aldrich, Edo. Mexico) were used for derivatization process. Supelco supplied (Edo. Mexico) SPME fibers PDMS (100 μm polydimethylsiloxane); PA (85 μm polyacrylate) and DVB/CAR/PDMS (50/30 μm stableflex divinylbenzene/carboxen/polydimethylsiloxane) were tested for its performance. All three fibers were conditioned before use as manufacturer's instructions.

Samples and calibration curves were analyzed in a gas chromatograph (GC) (Agilent 6890) coupled to a mass spectrometry detector (MS) (Agilent 5975) in electron impact ionization mode (EI). The injection port was operated in splitless mode with a 0.75 mm liner without glass wool. Injection port temperature was 230 $^\circ\text{C}$; helium used as carrier gas at a pressure of 36 psi with a constant flow of 1 mL min^{-1} . The chromatographic separation was carried through a HP 5MS (60 m \times 0.25 mm \times 0.25 μm) column (Agilent). Setting of the oven was as follows: 90 $^\circ\text{C}$ (2 min), 180 $^\circ\text{C}$ (30 $^\circ\text{C min}^{-1}$), 200 $^\circ\text{C}$ (1 $^\circ\text{C min}^{-1}$), 230 $^\circ\text{C}$ (30 $^\circ\text{C min}^{-1}$) and held for 5 min with a run time of 31 min. The tune parameters were: emission: 34.6; energy: 69.9; repeller: 26.6 and, EMVolts: 1341. SCAN mode (50–500 m/z) was employed in order to identify the compound, identification and quantification ions were

selected for SIM mode. The identified fragment ions were 203/316 m/z . Results were obtained and processed using Chemstation Software (Agilent).

2.2. Analytical procedure

The 4-NP quantification was performed with slight modifications of the methodology described by Basher & Lee [27]. For the calibration curves 1 mL of Milli-Q water was fortified with 4-NP using independent concentrations ranging from 0.5 $\mu\text{g L}^{-1}$ up to 50 $\mu\text{g L}^{-1}$ in amber glass vials. Sodium chloride (NaCl, 3%) and 0.1 M HCl (20 μL) were used to enhance ionic strength and to adjust pH, respectively. Standard working solutions were prepared right before its use. After sample extraction a derivatization process was carried out in order to improve volatility and sensitivity. This process consists on exposing the fiber to the headspace above a solution of acetone (1 mL) with MBTFA (100 μL) at 60 $^\circ\text{C}$ for 10 min magnetically stirred at 600 rpm.

2.3. Establishing optimal conditions

Some parameters related with the adsorption of the analytes in the fiber were optimized to enhance the developed method: i) fiber coating, ii) temperature, iii) performance time and iv) ionic strength. For the optimization of the SPME procedure 1 mL of Milli-Q water was prepared fortifying with 1000 $\mu\text{g L}^{-1}$ of 4-NP. NaCl and HCl (0.1 M) were added to adjust pH in an amber glass vial with magnetic agitation. Afterwards, the fiber was exposed to the headspace above the solution. Three types of fibers were evaluated for nonpolar, semipolar and polar compounds (PDMS, 100 μm , DVB/CAR/PDMS 50/30 μm , PA 85 μm). Assays were performed in triplicate to evaluate temperature (60, 80, 100 $^\circ\text{C}$), extraction time (5, 10, 20, 30, 40 and 60 min) and ionic strength (0, 3, 7%); averages are reported.

2.4. Statistical analysis

A multivariate two way ANOVA analysis was carried out to establish significant differences between the three fibers used considering two parameters: i) performance time (5, 10, 20, 30, 40 and 60 min) and ii) temperature (60, 80, 100 $^\circ\text{C}$). Determinations were performed in triplicate at a concentration of 1000 $\mu\text{g L}^{-1}$ of 4-NP. The data distribution was evaluated using the Shapiro-Wilk test. Descriptive statistics parameters were calculated (mean, standard deviation, median, minimum and maximum). Differences between 4-NP concentrations reported in each scenario were established by the Kruskal Wallis test with a post hoc Dunn analysis using the statistic software GraphPad Prism 5.0 $^\circ$.

2.5. Analytical Technique Validation

The validation of the method was performed based on the Guide for the Validation of Analytical Methods for the Determination of Organic Compounds at Trace Levels AOAC/FAO/IAEA/IUPAC [28] considering the following parameters, limit of detection (LOD), limit of quantification (LOQ), linearity (r), sensitivity, percentage of recovery and precision (repeatability and reproducibility), evaluating different concentrations in triplicate on the same day, and in duplicate five different days. LOD and LOQ were calculated using results obtained from five calibration curves determined in a concentration range of 0.5–50 $\mu\text{g L}^{-1}$. The linearity expressed by the correlation coefficient (r) and the sensitivity determined by the slope of the working range curve (LOQ–50 $\mu\text{g L}^{-1}$) were obtained from the average of five curves obtained during three days.

2.6. Monitoring of 4-NP in water sources

A total of 29 samples were collected, from which 10 were of recreational use, 14 of wastewater discharges and 5 of drinking water.

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