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A sustainable on-line CapLC method for quantifying antifouling agents like irgarol-1051 and diuron in water samples: Estimation of the carbon footprint

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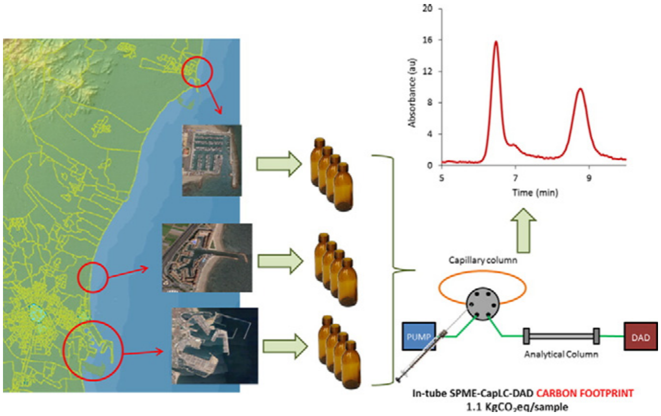
HIGHLIGHTS

- Irgarol and diuron are considered priority pollutants due to their harmful effects.
- In-tube SPME-CapLC-DAD has been proposed to determine these compounds.
- The analytical performance was satisfactory to meet the EQS (EU Commission).
- A rather small carbon footprint (1.1 $kgCO_2eq$) was estimated for the method.
- The proposed procedure is a sustainable and operational efficient methodology.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, in-tube solid phase microextraction (in-tube SPME) coupled to capillary LC (CapLC) with diode array detection has been reported, for on-line extraction and enrichment of booster biocides (irgarol-1051 and diuron) included in Water Frame Directive 2013/39/UE (WFD). The analytical performance has been successfully demonstrated. Furthermore, in the present work, the environmental friendliness of the procedure has been quantified by means of the implementation of the carbon footprint calculation of the analytical procedure and the comparison with other methodologies previously reported.

Under the optimum conditions, the method presents good linearity over the range assayed, 0.05–10 μg/L for irgarol-1051 and 0.7–10 μg/L for diuron. The LODs were 0.015 μg/L and 0.2 μg/L for irgarol-1051 and diuron, respectively. Precision was also satisfactory (relative standard deviation, RSD < 3.5%). The proposed methodology

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Abbreviations: CapLC, capillary liquid chromatography; DLL-ME-HPLC-MS/MS, dispersive liquid-liquid microextraction-high resolution liquid chromatography-mass spectrometry; EQS, environmental quality standards; GHG, greenhouse gases; HS-SPME, headspace solid phase microextraction; MAC, maximum allowable concentrations; MAE-SPE, microwave assisted solid phase microextraction; MF-LPME, microfunnel liquid phase microextraction; PDMS, polydimethylsiloxane; SBSE-(TD)-GC–MS, stir bar sorptive extraction-thermal desorption-gas chromatography–mass spectrometry; SD-SPME, single drop solid phase microextraction; SPME-CapLC-DAD, solid phase microextraction-capillary liquid chromatography-diode array detection; WFD, Water Framework Directive.

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In-tube solid phase microextraction
Screening
Water samples

was applied to monitor water samples, taking into account the EQS standards for these compounds. The carbon footprint values for the proposed procedure consolidate the operational efficiency (analytical and environmental performance) of in-tube SPME-CapLC-DAD, in general, and in particular for determining irgarol-1051 and diuron in water samples.

1. Introduction

The updates of the List of priority pollutants included in the Water Framework Directive (WFD) (European Commission, 2013) have essentially gone in two different directions: to revise the maximum permitted concentrations of some compounds in water and to include new substances considering their potential risks according for adverse effects, total production and environmental exposure levels. One of the new substances included in the list is irgarol-1051. This compound, along with diuron, has been widely employed as booster biocides in antifouling paints to prevent the fouling in surfaces submerged in water (Lam et al., 2005). However, both compounds show high harmful effects to the marine ecosystem (Lam et al., 2006). Additionally, these compounds can be degraded to different transformation products that are potential contaminants as secondary pollution (Fernandez and Gardinali, 2016; Ferrer and Barceló, 2001; Giacomazzi and Cochet, 2004).

The environmental quality standards (EQS) expressed as maximum allowable concentrations (MAC) for irgarol-1051 and diuron are 0.016 μg/L and 1.8 μg/L, respectively (European Commission, 2013). Consequently, the determination of these compounds in water involves extraction, clean-up and preconcentration before the chromatographic analysis. Solid phase extraction (SPE) coupled with HPLC-UV detection or HPLC-MS detection have been reported to determine booster biocides in environmental matrices (Kaonga et al., 2015; Maragou et al., 2011; Piedra et al., 2000; Sánchez-Rodríguez et al., 2011) Fully automated procedures such as SPE coupled on-line with LC–MS have also been investigated (Ferrer and Barceló, 1999; Gimeno et al., 2001; Singer et al., 2010). These systems showed high sensitivity, reproducibility and selectivity not only for biocides but also for multiresidue analysis. Giraldez et al. evaluated stir bar sorptive extraction (SBSE) and thermal desorption (TD)-GC–MS to determine these compounds in sea water with successful results (Giraldez et al., 2013). In addition, microwave assisted extraction followed by SPE (MAE-SPE) and combined with LC-MS/MS has also been proposed to estimate booster biocide in environmental matrices (Sánchez-Rodríguez et al., 2011).

Microextraction based techniques are other alternatives as pretreatment step to extract and preconcentrate booster biocides from environmental samples. Headspace solid phase microextraction (HS-SPME), SPME and single drop solid phase microextraction (SDSPME) were first utilized (Lambropoulou and Albanis, 2004; Lambropoulou et al., 2002, 2003). More recently, microfunnel-supported liquid-phase microextraction (MF-LPME) coupled to HPLC-UV detection has been described to determine irgarol-1051 and diuron in water samples (Saleh et al., 2014). Moreover, dispersive liquid-liquid microextraction (DLL-ME)-HPLC-MS/MS has also been proposed for these biocides (Marube et al., 2015). In all cases, these techniques are carried out in off-line mode, which yield to long analysis times, especially if the number of samples is high. Therefore, in this context, the use of on-line SPME techniques, such as in-tube solid phase microextraction (in-tube SPME), can be advantageous compared with off-line SPME modalities since it extraction, preconcentration, injection, separation and detection are carried out in a single step. Thus, analysis time is reduced and sensitivity and precision can be improved. In-tube SPME is based on the extraction and preconcentration of the analytes by adsorption or absorption in the inner surface of a capillary column, coated internally with a thin film of extractive phase, which in turn, is on-line coupled with a chromatographic system. In addition, the coupling of in-tube SPME with miniaturized chromatographic techniques has become a commonly used approach in several applications. The main goals of these couplings are the improvement of column efficiency, enhancement of the sensitivity and reduction of solvents consumption, and so it yield to an environmental friendly procedure (Gou and Pawliszyn, 2000; Moliner-Martínez et al., 2015a; Sun et al., 2015).

In the scenario of environmental friendliness, Green Analytical Chemistry (GAC) emerged in order to mitigate the negative environmental impacts of the analytical procedure (Gałuszka et al., 2013). The sustainability of an analytical method is governed by minimization of toxic solvents, reduction of wastes, employment of energy-efficient and cost-effective methodologies, but maintaining the reliability of the performance parameters, such as sensitivity, precision and accuracy (Turner, 2013). In most of the reported green analytical methodologies the greenness of the procedure is justified by the use of less hazardous solvents or reagents and the reduction of solvents, reagents and wastes. But an analytical process is comprised by different steps influencing each other and so, most of the methods requires at least one reagent, generates waste and, of course, energy is consumed depending on the instrumentation used. However, the energy consumption is neglected in the vast majority of these works. It should be noted that energy consumption is directly related with the emission of greenhouse gases (GHG). Therefore, Analytical Chemistry itself is a GHG emitter contributing to anthropogenic climate change, since these methodologies imply the use of chemicals, waste generation and use of energy depending on the instrumentation. Thus, the assessment of environmental impacts of all the analytical procedure's life, as an actual emitter, is a challenge that must be addressed in order to develop sustainable and green analytical methodologies and to reduce emissions. So, the question is if there is any parameter to quantify the environmental impact of an analytical procedure in order to categorize them as a function of their environmental performance. And the answer could be found in the carbon footprint estimation (MacCuspie et al., 2014; Schmitz et al., 2004) as a metric tool to evaluate the environmental negative impact of a methodology. It is important to remark, that the quantification of the environmental performance is a demand both for routinely analytical procedures and new developments in materials, methodologies or instrumentation.

In this work, we propose an on-line procedure to determine irgarol-1051 and diuron in water samples based on in-tube SPME-CapLC-DAD. The reliability of the proposed method has been demonstrated through the analysis of real water samples. The proposed procedure is an alternative method to determine irgarol-1051 and diuron in water samples according to water quality legislation. The operational efficiency of the proposed methodology has been successfully demonstrated not only estimating the analytical performance but also quantifying the environmental impact by means of the calculation and comparison of the carbon footprint. The main advantages are the elimination of the sample pretreatment step, minimization of analysis time and wastes, reduction of the analysis costs and so, improvement of the analytical and environmental performance. To our knowledge this work represents the first estimation of the analytical methodologies carbon footprints in order to categorize them in terms of GHG emissions.