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INNOVACIONES EN SISTEMAS DE TOMA DE MUESTRAS AMBIENTALES QUE EMPLEEN NUEVAS FASES SORBENTES PARA LA PRECONCENTRACIÓN DE CONTAMINANTES

INNOVATIONS IN ENVIRONMENTAL SAMPLING DEVICES THAT USE NEW SORPTIVE PHASES FOR THE PRECONCENTRATION OF POLLUTANTS

Tesis Doctoral

Francisco Antonio Casado Carmona

Córdoba, 2022

TITULO: *Innovaciones en sistemas de toma de muestras ambientales que empleen nuevas fases sorbentes para la preconcentración de contaminantes*

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Trabajo presentado para aspirar al Grado de Doctor en Ciencias

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CERTIFICAN:

Que la Tesis Doctoral **"INNOVACIONES EN SISTEMAS DE TOMA DE MUESTRAS AMBIENTALES QUE EMPLEEN NUEVAS FASES SORBENTES PARA LA PRECONCENTRACIÓN DE CONTAMINANTES"** ha sido desarrollada en los laboratorios del Departamento de Química Analítica de la Universidad de Córdoba (España), y que, a nuestro juicio, reúne todos los requisitos exigidos a este tipo de trabajo.

Que Francisco Antonio Casado Carmona es el primer autor de todos los trabajos científicos presentados en esta Tesis Doctoral. De acuerdo con la normativa de esta Universidad y los acuerdos internos del Grupo de Investigación, el primer autor es el responsable de la realización del trabajo experimental y de la producción del manuscrito. Además, ha participado activamente en las reuniones periódicas con los directores para evaluar y discutir los resultados obtenidos durante la Tesis Doctoral.

Y para que conste y surta los efectos pertinentes, expiden el presente certificado en la ciudad de Córdoba, a 17 de enero de 2022.

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TÍTULO DE LA TESIS: INNOVACIONES EN SISTEMAS DE TOMA DE MUESTRAS AMBIENTALES QUE EMPLEEN NUEVAS FASES SORBENTES PARA LA PRECONCENTRACIÓN DE CONTAMINANTES

DOCTORANDO: Francisco Antonio Casado Carmona

INFORME RAZONADO DE LOS DIRECTORES DE LA TESIS

Francisco Antonio Casado Carmona es Licenciado en Ciencias Químicas por la Universidad de Córdoba. Se incorporó al grupo de investigación en los últimos cursos de sus estudios como alumno colaborador. Obtuvo el título de Máster en Química Fina en el curso académico 2014/15 y a partir de ese momento se dedicó intensamente al trabajo experimental apoyado por una beca de formación de personal investigador. Este periodo formativo le ha permitido la realización de la tesis doctoral, cuya Memoria se presenta para su defensa como compendio de publicaciones.

La Tesis Doctoral aborda el diseño, optimización y aplicación de dispositivos de muestreo en compartimentos ambientales. Para ello se han seleccionado agua y aire como objetos de estudio y la incorporación de nuevas fases sorbentes en los dispositivos para la preconcentración de contaminantes. El trabajo experimental se ha dividido en dos bloques atendiendo a los dos grupos de muestras que se han abordado a lo largo del trabajo experimental realizado. El primero de ellos se centra en las muestras de agua (piscina, arroyo, pozo) y el segundo aborda el muestreo en aire.

Además de la familiarización con procedimientos de síntesis de distintos materiales: nanopartículas, composites, el doctorando ha tenido la oportunidad de formarse en distintas técnicas de caracterización de nuevos materiales, tecnologías simples para la automatización de sistemas como Arduino, así como iniciar su formación en transferencia de conocimiento. En este sentido, se pueden destacar como relevantes las dos patentes que se presentan como resultados de la Tesis Doctoral, así como la posibilidad de incrementar el nivel de madurez tecnológica para facilitar su transferencia al sector productivo.

Durante los cuatro años de desarrollo de la Tesis Doctoral, ha estado implicado en un elevado número de colaboraciones con otros grupos de investigación, así como en la supervisión del trabajo de investigadores internacionales que realizaron estancias en el grupo de investigación.

Como consecuencia de la investigación realizada, se han publicado cuatro artículos científicos, diez comunicaciones a congresos nacionales e internacionales y un capítulo de libro (en vías de publicación). Es destacable el reconocimiento que ha recibido en su participación en esas reuniones científicas, que se han materializado en tres premios y/o distinciones. Adicionalmente a estos, se han publicado cinco artículos relacionados con la Tesis Doctoral

Durante este periodo formativo, además de las destrezas correspondientes al trabajo experimental, ha desarrollado destrezas personales relacionadas con la capacidad de trabajo en grupo. Ha demostrado una notable capacidad de colaboración, y una gran disponibilidad para ayudar a los compañeros a resolver los problemas asociados al trabajo diario en el laboratorio. Es una persona responsable y comprometida con las responsabilidades asignadas por sus directores.

El doctorando ha colaborado en la impartición de clases prácticas en el Grado de Química y Ciencias Ambientales durante tres cursos académicos. Ha participado en la dirección de dos TFGs del Grado de Química y uno del Grado de Ciencias Ambientales, lo que le ha permitido iniciarse en las tareas de dirección de investigación en estudiantes en formación. Su participación en actividades de divulgación ha sido notable, tal como se puede acreditar en el anexo correspondiente de esta Memoria.

Finalmente, consideramos que la tesis doctoral cumple con los requisitos de originalidad, innovación y calidad exigibles a este tipo de trabajo.

Por todo ello, se autoriza la presentación de la tesis doctoral.

Córdoba, 17 de enero de 2022

Firma de los directores

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INFORME DE FACTORES DE IMPACTO

La tabla siguiente contiene los factores de impacto y el cuartil, obtenidos del Journal Citation Reports, en el que se encuentran las publicaciones derivadas de la presente Tesis Doctoral. Todas ellas referidas al área de Química Analítica.

Revista	Año	Factor de impacto	Cuartil
Journal of Chromatography A	2019	4,049	1
Talanta	2021	6,057 (2020)	1
Analytica Chimica Acta	2022	6,558 (2020)	1

El doctorando también figura como primer firmante de un capítulo de libro (Green Approaches for Chemical Analysis, ed. Elsevier).

Asimismo, en la siguiente tabla se muestran los datos de factores de impacto y cuartil, obtenidos del Journal Citation Reports, para las publicaciones relacionadas con la Tesis Doctoral.

Revista	Año	Factor de impacto	Cuartil (Área)
Microchemical Journal	2016	3,034	1 (Química Analítica)
Applied Catalysis B: Environmental	2020	19,503	1 (Ingeniería Ambiental) D1
Spectrochimica Acta Part B	2019	3,086	1 (Espectroscopía)
Nanomaterials	2020	5,076	1 (Física Aplicada)
Current Opinions in Environmental Science and Health	2022	9,4**	1 (Medicine (Public Health)) D1

** Para los datos de 2021 y 2022 se usaron los valores indexados en Journal Citation Reports de 2020.*

*** Para este dato se usaron los valores indexados en Scopus de 2020.*

Agradezco al Ministerio de Educación, Cultura y Deporte la concesión de una ayuda de Formación del Profesorado Universitario (FPU) (Ref. FPU16-06069) que ha hecho posible la realización de la presente Tesis Doctoral.

“Do. Or do not. There is no try”

Yoda (The Empire Strikes Back)

ÍNDICE

OBJETO

AIM

La obtención de información analítica de los compartimentos ambientales conlleva necesariamente la consideración de una etapa de muestreo y de tratamiento de muestra. El impacto que ambas tienen en la calidad de los resultados es alto porque la primera de ellas afecta a la representatividad de los mismos, mientras que la segunda se relaciona con propiedades analíticas básicas del proceso de medida como son la sensibilidad, la selectividad o la precisión.

El muestreo ambiental tiene unas connotaciones particulares debido fundamentalmente a la gran diferencia que suele existir entre el tamaño/volumen del compartimento ambiental (aire, agua, suelo) sobre el que se quiere obtener la información, y el tamaño/volumen de la alícuota que debe analizarse en el laboratorio. El diseño apropiado del plan de muestreo permite también soslayar o considerar (dependiendo del tipo de información requerida) aspectos relacionados con la heterogeneidad tanto espacial como temporal de la presencia/concentración de los analitos en la muestra.

La determinación de los compuestos de interés en muestras ambientales presenta también unas características distintas al resto de matrices y que deriva de la elevada variedad de compuestos diana y su baja concentración, así como la legislación cada vez restrictiva respecto a los valores límite tolerados para minimizar su impacto negativo sobre los seres vivos.

Finalmente, hay que considerar también en este ámbito la importancia de mantener la integridad de la muestra en su transporte al laboratorio. Esta etapa, además del coste asociado al elevado número de muestras y tamaño/volumen de las mismas, puede conllevar una fuente de error adicional derivado de la pérdida o degradación de los analitos.

La investigación en el ámbito del análisis ambiental tiene como objetivo minimizar las limitaciones anteriormente expuestas. La estrategia más eficiente hace uso de sistemas de muestreo que puedan integrar la etapa de extracción de los analitos de interés. En este sentido, resulta fundamental la contribución de las técnicas de microextracción. Esta versión miniaturizada de las técnicas de extracción líquido-líquido y de la extracción en fase sólida contribuye además a la minimización del impacto ambiental del tratamiento de muestra y por tanto, al desarrollo de los principios de la Química Analítica Verde. Los materiales nanoestructurados son un pilar fundamental en estos desarrollos ya que sus excepcionales propiedades sorbentes permiten mejorar la eficacia de los procesos de extracción. Por otra parte, las propiedades magnéticas que algunos de ellos presentan, también contribuyen a la mejora de los diseños experimentales o a las propuestas de nuevos dispositivos. Finalmente, y en línea con la reducción del impacto ambiental, el empleo de materiales de origen natural que se puedan emplear como soporte (papel) o precursores de materiales sorbentes (algodón para obtener fibras de carbono) debe considerarse también en el diseño de los sistemas de muestreo.

Los nuevos muestreadores constituyen alternativas rápidas y fáciles de aplicar que disminuyen la intervención humana y aúnan las etapas de muestreo y preconcentración en una sola etapa. De esta forma, sólo es necesario transportar al laboratorio el material sorbente en el que están retenidos los analitos. Además de evitar el transporte de elevados volúmenes de muestra al laboratorio, aumenta la estabilidad de los analitos al eliminar la presencia de la matriz durante el transporte y almacenamiento.

Por todo lo anteriormente expuesto, se puede identificar que el objetivo genérico de la presente Tesis Doctoral es el diseño de dispositivos de muestreo que integren la preconcentración de los analitos de interés. Para alcanzar este objetivo genérico se han definido los siguientes objetivos específicos:

- Diseño de nuevos prototipos que integren el muestreo y la preconcentración de los analitos de interés. Se han diseñado dos dispositivos para su aplicación en el muestreo en aguas, que se recogen en el Bloque II, y otro muestreador aplicado a la toma de muestras de aire, que se describe en el Bloque III de la presente Tesis Doctoral.

- Uso de membranas poliméricas y fases afines como sorbentes. A lo largo de las diferentes propuestas, se han empleado diversos materiales sorbentes como son las membranas poliméricas, tanto comerciales (empleadas en el Capítulo 2) como modificadas (empleadas en los Capítulos 3 y 4). Por otro lado, en el Capítulo 4 se describe el uso de un polímero particulado (HLB) como sorbente.

- Preparación de membranas poliméricas y su modificación para proveerles funcionalidades especiales. El Capítulo 3 describe la preparación de una membrana magnética soportada sobre papel cuya fase sorbente activa es el nylon-6. Además, en el Capítulo 4 se propone una membrana magnética modificada con HLB, que proporciona capacidad sorbente a una cinta magnética comercial.

- Preparación de fases sorbentes basadas en materiales celulósicos. Se ha preparado un material sorbente que emplea como soporte un material celulósico (Capítulo 3).
- Aplicación de estas estrategias para la resolución de problemas analíticos en el ámbito medioambiental y de atmósfera de trabajo. Este objetivo de carácter transversal se ha abordado en las diferentes metodologías de trabajo propuestas a lo largo de la presente Memoria.

Obtaining analytical information from environmental compartments requires both sampling and sample treatment steps. These steps have a high impact on the quality of the final results. The sampling stage affects the representativeness of the results, while the sample treatment affects to the basic analytical properties of the measurement process such as sensitivity, selectivity or precision.

Environmental sampling has a series of particularities mainly due to the differences between the size/volume of the environmental compartment (air, water, soil), and the aliquot submitted to the analysis in the laboratory. The appropriate design of the sampling protocol also allows to avoid or take into consideration (depending on the type of information required) those aspects related to the spatial and temporal heterogeneity of the analytes in the sample.

The determination of the target compounds in environmental samples also presents different characteristics from the rest of the matrices related to the high variety of compounds and their low concentration, as well as the increasingly restrictive legislation in terms of tolerated limit values to minimize their negative impact on living organisms.

Finally, the importance of maintaining the integrity of the sample during the transportation process to the laboratory must also be considered. This stage may have an economic impact due to the large number of samples and the high size/volume of these, in addition to the error associated to the loss or degradation of the analytes.

The main focus of the research in this field is related to the minimization of the aforementioned limitations. The most efficient strategy makes use of sampling systems that integrates the extraction stage of the analytes of interest. In this sense, the contribution of microextraction techniques is essential. This miniaturized version of liquid-liquid extraction and solid-phase extraction techniques also contributes to minimizing the environmental impact of sample treatment and therefore to the development of the principles of Green Analytical Chemistry. In this sense nanomaterials are crucial in these proposals due to their exceptional sorbent properties that allow an improvement of the extraction process efficiency. Additionally, the magnetic properties which some of them present also contribute to the enhancement of experimental designs or proposals for new devices. Finally, to reduce the environmental impact, the use of materials of natural origin that can be used as supports (cellulose) or precursors of sorbent materials (cotton to obtain carbon fibers) should also be considered in the design of the sampling devices.

The new samplers are quick and easy-to-apply alternatives that reduce human intervention and combine the sampling and preconcentration stage. In this way, it is only necessary to transport to the laboratory the sorbent material where the analytes have been isolated. Furthermore, the use of those materials improves the extraction capacity of the sampling devices, and the stability of the analytes during its transport to the laboratory.

For all the above, it can be identified that the generic objective of this Doctoral Thesis is the design of sampling devices that integrate the preconcentration of the target analytes. To achieve this generic objective, the following specific objectives have been defined:

- The design of new prototypes that integrate the sampling and preconcentration of target compounds. Two devices have been designed for their application in water sampling, which are presented in Block II, and another one applied to air sampling, which is described in Block III of this Doctoral Thesis.

- The use of polymeric membranes and related phases as sorbents. Throughout the different proposals, various sorbent materials have been used, such as polymeric membranes, both commercial (used in Chapter 2) and modified (used in Chapters 3 and 4). On the other hand, Chapter 4 describes the use of a particulate polymer (HLB) as a sorbent.

- The preparation of polymeric membranes and modification with special functionalities. Chapter 3 describes the preparation of a magnetic paper-based membrane whose active sorbent phase is nylon-6. In addition, in Chapter 4 an HLB modified magnetic membrane is proposed, which provides sorbent capacity to a commercial magnetic tape.

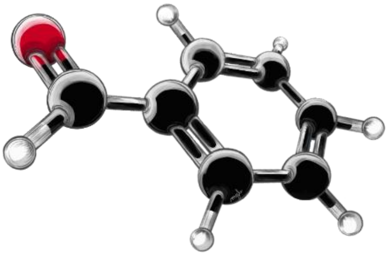
- The preparation of sorbent phases based on cellulosic materials. A sorbent material has been prepared using a cellulosic material as support (Chapter 3).

- The application of these strategies to solve analytical problems in the environment and work atmosphere. This cross-cutting objective has been addressed in the different work methodologies proposed throughout this Doctoral Thesis.


PROBLEMÁTICA DE LAS MUESTRAS AMBIENTALES
Heterogeneidad espacial y temporal
Tamaño muestra
Elevado número de analitos a bajas concentraciones
SOLUCIÓN APLICADA EN ANÁLISIS AMBIENTAL
Integración de las Etapas de Muestreo y Preconcentración
DISEÑO DE NUEVOS DISPOSITIVOS DE MUESTREO
PROPUESTAS DE LA PRESENTE TESIS DOCTORAL
Muestras de Agua
Dispositivo
Material Sorbente
Problema Analítico
Unidad Magnética
Taladro
Motor/ Arduino
DISPOSITIVO PATENTADO
Nylon Comercial
Membrana de Papel Magnética con Nylon
Cinta Magnética con HLB
Benzofenonas en piscinas
Parabenos y triclosán en piscinas
Triazinas en arroyos y pozos
Muestras de Aire
Dispositivo
Unidad
Material Sorbente
Problema Analítico
Ventilador
Ventilador
Fabric Phase (CW20M)
Volátiles en laboratorios
DISPOSITIVO PATENTADO

BLOQUE I

INTRODUCCIÓN



El muestreo se define como el proceso por el cual se toma una porción representativa del sistema u objeto en estudio, siendo dicha alícuota la que se someterá finalmente al proceso analítico. La representatividad de los resultados obtenidos se sustenta por tanto en la realización de un buen muestreo. Sin embargo, asegurar esta propiedad analítica suprema no es fácil puesto que son muchos los factores que condicionan el muestreo como son: la elevada diferencia que puede existir entre el tamaño del sistema objeto de análisis y la alícuota que se debe analizar; la heterogeneidad de la distribución espacial y temporal de los analitos, así como la baja concentración a la que estos suelen encontrarse. Esto se complica si se considera también la variedad de combinaciones muestra-analito que se puede encontrar y la necesidad de adaptar los procesos de muestreo a cada situación específica. Si bien la toma de muestra es compleja en cualquier campo, esto se acrecienta en análisis ambiental, debido a las características intrínsecas de los compartimentos ambientales (agua, aire, suelo).

1. Problemática del análisis ambiental

La primera dificultad a la que hay que hacer frente en el análisis ambiental es la heterogeneidad espacial y temporal de los sistemas ambientales. Así pues, se puede tener en cuenta heterogeneidad desde el punto de vista espacial, es decir, la concentración de los analitos varía en el espacio y no es la misma en todos los puntos. Por otro lado, hay que considerar la heterogeneidad temporal, ya que los sistemas ambientales están sometidas a un cambio continuo a lo largo del tiempo. Finalmente, también es crucial considerar las dos a la vez, ya que en cualquier compartimento ambiental dinámico ambas coexisten y por tanto no se pueden entender por separado. Con el fin de tener en cuenta la heterogeneidad de estas muestras es vital elaborar un plan de muestreo que contemple dichos factores, e identifique con claridad el lugar y lapso temporal en el que se toma dicha muestra.

En segundo lugar, hay que considerar la diferencia en tamaño entre el sistema objeto de estudio y la muestra que se va a analizar. Esto puede requerir que la muestra bruta, la que se toma directamente del sistema, deba ser sometida a distintos pasos/procesos de reducción de tamaño en los que puede quedar comprometida la representatividad.

Por otra parte, es también relevante la baja concentración a la que se encuentran los analitos y la posible interferencia que en su determinación pueden tener los componentes de la matriz de la muestra. Esto hace necesario que, para adaptar las concentraciones de los compuestos a la sensibilidad experimental y adecuar la selectividad deban considerarse sistemáticamente técnicas de tratamiento de la muestra. Así pues, la técnica de tratamiento de muestra empleada supondrá un proceso de *clean-up*, que eliminará los problemas asociados al efecto matriz, y por tanto mejorará la selectividad, y por otro lado mejorará la sensibilidad del método por medio de la preconcentración de los analitos. Si bien es cierto que no siempre tienen por que cumplir todos los objetivos al mismo tiempo, ya que en ocasiones la eliminación de las interferencias dependiendo de la técnica instrumental empleada puede mejorar la sensibilidad del método de forma indirecta, tal es el caso de la eliminación de la supresión iónica en análisis directo por espectrometría de masas [1].

2. Problemas asociados al transporte de la muestra

Todos estos factores afectarán a la calidad de los resultados, pero no serán los únicos, ya que la etapa de transporte de la muestra al laboratorio también tendrá implicaciones en los mismos [2]. Los factores que pueden afectar a la concentración de los analitos durante la etapa de transporte se pueden clasificar en dos grupos: factores fisicoquímicos y biológicos [3,4].

Los factores fisicoquímicos comprenden todos los procesos y las reacciones que sufran los analitos con la matriz de la muestra, con el contenedor u otros factores externos, y que interfieren en la determinación posterior de los mismos.

Entre los problemas más comunes asociados al transporte de la muestra se encuentra la adsorción de los analitos a las paredes del contenedor. Por tanto, la elección del material del contenedor es de suma importancia. Cuando se pretende determinar analitos orgánicos se prefieren contenedores de vidrio que son inertes y no porosos. De este modo se evitan pérdidas por adsorción o por difusión a través de las paredes. Por otro lado, para la determinación de especies inorgánicas se suele emplear recipientes de plástico.

A estos factores hay que añadir la reactividad de los analitos. Las reacciones de fotodegradación se pueden minimizar usando recipientes opacos. El control de la temperatura durante el transporte y almacenamiento juega un papel esencial para reducir la velocidad de las reacciones indeseadas y para minimizar la pérdida de los analitos por volatilización. La refrigeración de la muestra es también importante para reducir la actividad microbiana que puede provocar una variación de la concentración de los analitos. Esta actividad puede reducir o aumenta la concentración de los analitos según sean sustratos o productos del metabolismo microbiano. En este caso, la refrigeración de la muestra puede complementarse con otras medidas como la adición de conservantes, la acidificación de la muestra o su filtración.

3. Dispositivos de muestreo

Atendiendo a toda esta problemática, la tendencia actual es la de aunar en una sola etapa el muestreo y la extracción de los compuestos de interés. Para ello se emplean dispositivos que emplean de fases sorbentes más eficientes que las convencionales. Esta aproximación simplifica la logística ya que no es necesario transportar la muestra sino la fase sorbente con los analitos retenidos. Además, los analitos suelen ser más estables cuando se encuentran retenidos en una fase sorbente, ya que se minimizan las pérdidas por reactividad y volatilidad.

Estos dispositivos de muestreo se han propuesto, tanto para muestras de agua, como de aire. Su empleo en procesos de extracción *on-site* exige a los mismos unos requisitos que si bien no son de obligado cumplimiento sí son deseables. En primer lugar, deben ser miniaturizados y portátiles [5]. El empleo de dispositivos miniaturizados enlaza con una de las tendencias clave de los procesos analíticos como es la reducción de las dimensiones de las herramientas analíticas. Por otro lado, los dispositivos empleados deben ser fáciles de usar, cumpliendo por tanto con otra de las tendencias de la Química Analítica, la simplificación. A todo esto, hay que sumar un consumo reducido tanto de energía, como de reactivos y disolventes, en línea con los objetivos del desarrollo sostenible; impulsados por las Naciones Unidas [6].

Las dos modalidades de muestreo *on-site* que se pueden identificar son procesos de muestreo activo o procesos de muestreo pasivo [5]. La diferencia entre dichas modalidades reside en cómo se lleva a cabo el proceso de toma de muestra, y su selección dependerá del tipo de información necesaria. En el caso del muestreo activo, se fuerza la interacción entre la fase extractante y la muestra, ya sea favoreciendo el contacto entre las mismas o forzando el paso de la muestra a través de la fase sorbente. Los procesos de muestreo activo son especialmente adecuados para conocer valores puntuales de la concentración de los compuestos de interés. Además, son procesos rápidos, y por ende la frecuencia de muestreo es alta. Así pues, tienen especial importancia para la monitorización de vertidos entre otros. Por el contrario, en los procesos de muestreo pasivo, la fase sorbente se introduce o se expone al sistema objeto de estudio sin emplear ningún tipo de fuerza externa que favorezca el contacto entre la muestra y el sorbente. Son procesos más lentos, basados en la difusión pasiva de los analitos, y proporcionan los valores medios de concentración de los analitos durante el periodo de muestreo.

Independientemente de la modalidad de muestreo, ambas coinciden en el empleo de técnicas de extracción miniaturizadas. Las técnicas de microextracción en las que se basan estos dispositivos son fundamentalmente la microextracción en fase líquida (*liquid phase microextraction* (LPME)) [7,8] y la microextracción en fase sólida (*solid phase microextraction* (SPME)) [9]. De hecho, la SPME en sus diferentes modalidades se convierte en la técnica de referencia en el campo de los dispositivos de muestreo *on-site* debido a su simplicidad, carácter miniaturizado y fácil acoplamiento con técnicas instrumentales [10–12].

Si bien las técnicas de microextracción se desarrollaran en detalle en el **Capítulo 1**, se comentarán aquí los fundamentos teóricos de la SPME, así como los factores a tener en cuenta para la aplicación de esta técnica en muestreo *on-site*. La SPME es una técnica de microextracción descrita por primera vez a principios de los años noventa por el grupo de investigación de profesor Pawliszyn de la Universidad de Waterloo (Canadá). Se describe como una técnica de extracción no exhaustiva, aunque esto no limita su potencial de aplicación. La primera modalidad descrita, y la que hoy día se conoce formalmente como SPME, emplea una fibra como material sorbente [13,14].

En la SPME clásica, la fibra se sumerge en la muestra o se expone a su espacio de cabeza para retener los analitos. A diferencia de la SPE, el proceso de elución de los analitos no tiene por qué ser químico, sino que se puede acoplar directamente con el sistema instrumental. En este caso, lo habitual sería la desorción térmica en el inyector del cromatógrafo de gases para la determinación de compuestos volátiles o semivolatiles.

Si bien la SPME es una técnica que revolucionó los procesos de análisis, hay que tener en cuenta que no es una técnica exhaustiva en la que se suele trabajar en el rango dinámico. El tiempo requerido para alcanzar el equilibrio del proceso de reparto ($t_{95\%}$), se muestra en la Ecuación 1:

$$t_{95\%} = 3\frac{\delta K_{ps}(b-a)^2}{2D_s} \quad \textit{Ecuación 1}$$

donde δ es el espesor de la capa límite de difusión, K_{ps} es la constante que rige el equilibrio de distribución del analito entre la fase sorbente y la muestra, *(b-a)* representa el espesor de la fase extractante y, por último, D_s se define como la constante de difusión de los analitos.

La cantidad de analito que se retiene en la fase sorbente cuando se alcanza el equilibrio (n_{eq}), se define en la Ecuación 2 como:

$$n_{eq} = \frac{K_{ps}V_eV_s}{K_{ps}V_e+V_s}C_s \quad \textit{Ecuación 2}$$

donde V_e el volumen de fase extractante, V_s el volumen de muestra y finalmente C_s la concentración inicial del analito en la muestra [15]. La aplicación de esta ecuación se puede extender a todas las técnicas de microextracción en fase sólida, hagan o no uso de la fibra.

A continuación, se discutirán las innovaciones más relevantes en el ámbito de los sistemas de muestreo activo que integren la etapa de extracción. Estos desarrollos se han dividido en función del estado de agregación de la muestra (líquida o gaseosa). En todos los casos se ha seleccionado la SPME o µSPE como técnica de extracción.

3.1. Dispositivos de muestreo activo para el análisis de muestras líquidas

En el muestreo activo, el contacto íntimo entre la muestra y la fase sorbente es esencial para garantizar un aislamiento efectivo y rápido de los analitos de interés. Este contacto puede favorecerse forzando el paso de la muestra a través del medio de extracción o agitando la muestra de forma eficiente durante la extracción.

En 2009, Quin *et al.* en 2009, propusieron un dispositivo que basado en la técnica de microextracción en película delgada (*thin film microextraction*, TFME) permitía la integración del muestreo y la extracción en una única etapa. En esta aproximación, la fase sorbente plana se acoplaba mediante un eje a un taladro portátil. Esta configuración permitía agitar la fase sorbente directamente en el sistema ambiental objeto de estudio (Figura 1) [16]. El acoplamiento de la fase sorbente a taladros comerciales se ha extendido a otras técnicas de microextracción. Mao *et al.* han empleado una barra agitadora como las empleadas en la técnica *stir sorptive phase* [17] mientras que Roldán-Pijuán *et al.* han sugerido el uso de discos de borosilicato modificados con nanomateriales como medio de extracción [18].

Fig. 1. Muestreador *on*-site propuesto por Quin *et al.* basado en el empleo de TFME. Reproducida con permiso de la referencia [16]. Copyright 2009 Elsevier B.V.

Los dispositivos descritos se aplican de forma manual y solo pueden desplegarse en localizaciones de fácil acceso. El uso de drones, propuesto por Grandy *et al.*, permite el muestreo en zonas menos accesibles. Los autores han propuesto un dron aéreo modificado con flotadores de poliestireno para permitir que se pose sobre el agua. La fase sorbente plana se ancla a un juego de pesas que permiten desplegarla durante el muestreo y quede sumergida en la masa de agua (Figura 2). Aunque este dispositivo se basa en la difusión pasiva de los analitos, permite obtener información química puntual sobre el sistema ambiental [19].

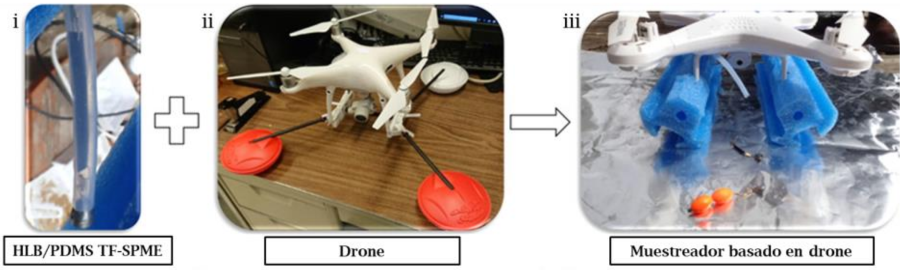


Fig. 2. Muestreador *on*-site basado en el empleo de un drone para el muestreo de aguas propuesto por Grandy *et al.* (i) Unidad de extracción, *Hydophilic-Lypofilic Blance,* HLB/Polidimetilsiloxano, PDMS. (ii) Drone empleado para portar la unidad de extracción. (iii) Muestreador basado en el empleo del drone. Adapatada con permiso de la referencia [19]. Copyright 2020 American Chemical Society.

A su vez, en este proceso evolutivo, en los dispositivos de muestreo han surgido otros que pueden utilizarse tanto de forma estática como dinámica [20].

3.2. Dispositivos de muestreo para el análisis de muestras gaseosas

El muestreo en fase gaseosa supone un reto aún mayor en comparación con la toma de muestras líquidas, debido a la dificultad adicional para obtener estándares de concentración conocida de los analitos. En este campo, los dispositivos desarrollados no son tan numerosos como en el anterior. Las innovaciones surgidas en este campo derivan de la necesidad de abaratar costes en el diseño de los sistemas.

En 2017 Alcudia-León *et al.* diseñaron una nueva unidad de muestreo para el análisis de volátiles, empleando una bomba de aspiración de aire como sistema de propulsión de la muestra. La nueva unidad de extracción estaba compuesta por unas piezas de latón (Figura 3), en la que se introducía la fase sorbente, en este caso *Fabric Phases* (FPs). Esta unidad aportaba una novedad en su diseño y es que, tras el proceso de muestreo, se podía introducir directamente en un módulo de espacio de cabeza para el análisis final de los volátiles mediante cromatografía de gases acoplada a espectrometría de masas [21].

Fig. 3. Unidad de muestreo de aire propuesta por Alcudia-León *et al.* (i) Unidad de muestreo empleada en la etapa de toma de muestra. (ii) Unidad de muestreo preparada para la etapa de análisis. Adaptada con permiso de la referencia [21]. Copyright 2017 Elsevier B.V.

Ruiz-Jimenez *et al.* han propuesto un nuevo dispositivo de muestreo que podría aplicarse tanto en la modalidad de muestreo pasivo como en la de muestreo activo. Como cuerpo central del dispositivo de muestreo emplearon un dron (Figura 4), al cual se le acopló en la base una pequeña caja que permitía controlar de forma remota la modalidad de muestreo mediante una placa RaspBerry Pi. Además, en la misma se incluyeron las válvulas necesarias, así como las conducciones y la bomba de aspiración de aire para hacer llegar la muestra al receptáculo donde se lleva a cabo el proceso de extracción [22].

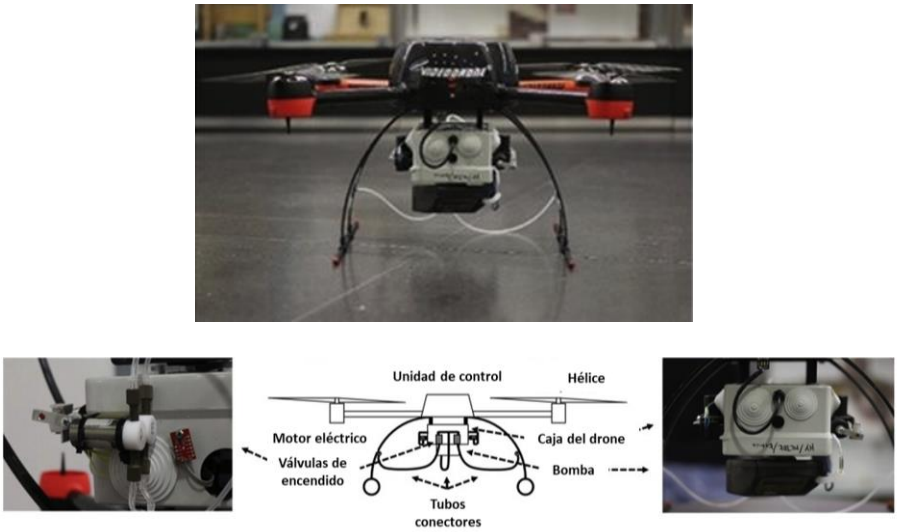


Fig. 4. Muestreador basado en el empleo de un drone para la toma de muestras de aire propuesto por Ruíz-Jimenez *et al.* Adaptada de la referencia [22] bajo licencia Creative Commons (https://creativecommons.org/licenses/by/4.0/).

4. Contaminantes orgánicos emergentes

Se define como contaminante emergente a todo aquel compuesto que, aunque su presencia en el medio ambiente no sea nueva, sí lo es la preocupación suscitada por el mismo [23,24]. Es decir, se puede definir como contaminante emergente todo compuesto químico, biológico, o material particulado, entre otros, que tengan un efecto dañino para el medio ambiente y los seres vivos. La presencia de estos compuestos en compartimentos ambientales puede tener origen natural o pueden deberse a la actividad humana [25]. En el contexto de la presente Tesis Doctoral, son especialmente importantes los contaminantes orgánicos emergentes, que engloban a una gran variedad de familias. En esta sección se han destacado algunas de ellas como los conservantes o los filtros solares empleados en la industria cosmética, los empleados como agentes plastificantes en la industria, los pesticidas y herbicidas usados en agricultura, y las hormonas de origen vegetal. La característica común de todos estos compuestos es que se pueden englobar dentro de los que se conocen como disruptores del sistema endocrino [26]. Además, hay que destacar que los problemas causados por estos disruptores del sistema endocrino no solo afectan al ser humano, sino también a los ecosistemas en los que se encuentren.

4.1. Filtros solares

Los filtros solares son compuestos empleados por la industria cosmética para impedir que la radiación ultravioleta cause daños en la piel. Para esta finalidad, se emplean compuestos de diversas familias como son las benzofenonas, los p-aminobenzoatos, salicilatos y cinamatos, entre otros [27]. La creciente demanda en el empleo de estos productos ha causado un aumento en la concentración de los mismos en el medio ambiente y esto ha motivado que sean considerados contaminantes emergentes.

De estas familias, cabe destacar las benzofenonas (Figura 5), un grupo de doce cetonas aromáticas y sus derivados, las cuales, gracias a los anillos aromáticos presentes en su estructura, son capaces de absorber la radiación solar [28]. Si bien a bajas concentraciones no suponen ningún problema, elevadas concentraciones tienen efectos perniciosos en el sistema endocrino, que derivan en efectos carcinogénicos y mutagénicos [29]. Aunque se degradan con el tiempo, hay que destacar que en ocasiones los metabolitos de estas son más peligrosos que los compuestos originales [30].

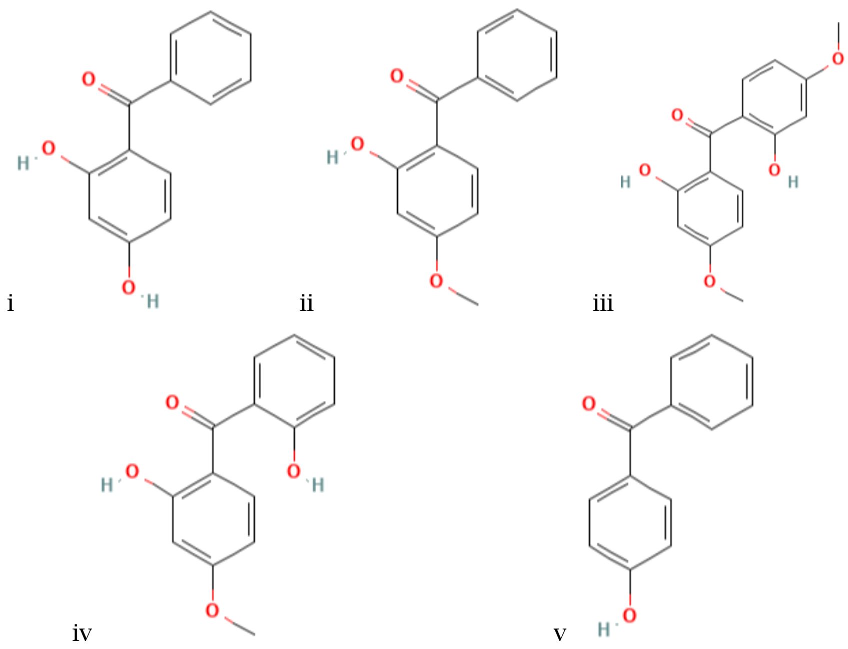


Fig. 5. Estructura de las benzofenonas empleados en la Tesis Doctoral. (i) Benzofenona 1. (ii) Benzofenona 3. (iii) Benzofenona 6. (iv) Benzofenona 8. (v) 4-Hidroxibenzofenona. Estructuras obtenidas de PubChem (https://pubchem.ncbi.nlm.nih.gov).

4.2. Conservantes

Los conservantes son un conjunto de compuestos empleados en la industria alimentaria y cosmética con el fin de evitar que el producto comercial se degrade, o sus propiedades químicas y organolépticas se vean alteradas [26,31]. Dentro de los compuestos empleados como conservantes en la industria cabe destacar los empleados como fungicidas, que evitan la aparición y proliferación de hongos.

En este grupo de fungicidas se encuentran los parabenos (derivados del ácido *p*-hidroxibenzóico) [32,33] y el triclosán [34] (Figura 6). Estos compuestos, en principio, tienen propiedades beneficiosas y se pueden encontrar en algunas plantas, si bien en los últimos años su empleo se ha visto reducido debido a sus efectos nocivos en la salud humana. Entre los problemas más destacables para la salud está su influencia en la proliferación de tumores.

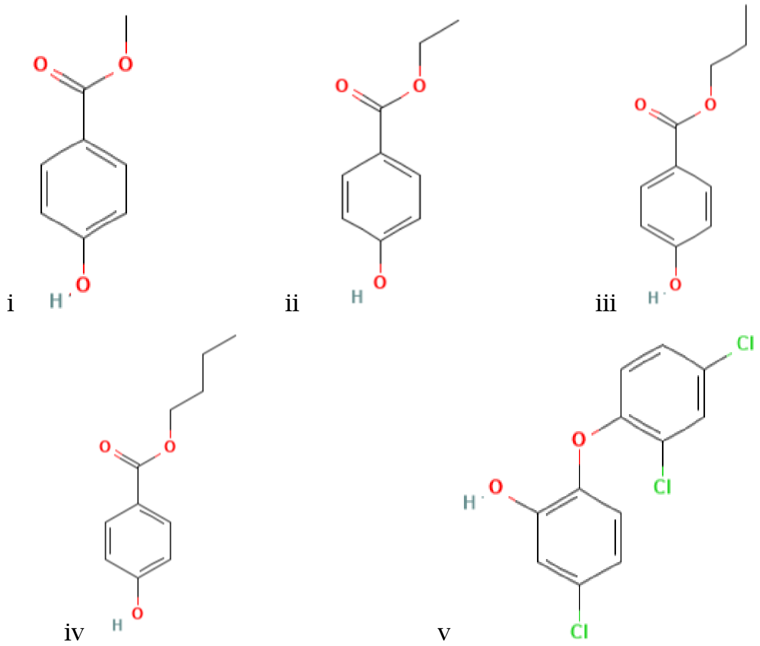


Fig. 6. Estructura de los conservantes empleados en la Tesis Doctoral. (i) Metilparabeno. (ii) Etilparabeno. (iii) Propilparabeno. (iv) Butilparabeno. (v) Triclosán. Estructuras obtenidas de PubChem (https://pubchem.ncbi.nlm.nih.gov).

4.3. Plaguicidas/Herbicidas

Los plaguicidas son sustancias que tienen como objetivo prevenir, destruir, repeler o controlar una plaga. Dentro de esta clasificación se encuentran los herbicidas, cuyo uso para inhibir el crecimiento de plantas no deseadas en tierras de cultivo está muy extendido. De todas las familias de herbicidas, destacan las triazinas [35]. Dos de los compuestos más utilizados son la atrazina y simazina (Figura 7), que forman parte de las cloroatrazinas. Por tanto, la legislación ha fijado la concentración máxima admisible en aguas superficiales en 0,6 y 1 µg/L, y en aguas no superficiales en 2 y 4 µg/L para atrazina y simazina respectivamente [36].

Su amplio uso en la agricultura hace que sean un problema en el medio ambiente. Este se ve acrecentado en el caso de la fauna, ya que, aunque no se ha demostrado que dichos compuestos sean dañinos para los seres humanos, si lo son para esta. Entre los problemas asociados a estos compuestos están los efectos cancerígenos y mutagénicos, problemas cutáneos y transtornos metabólicos [37].

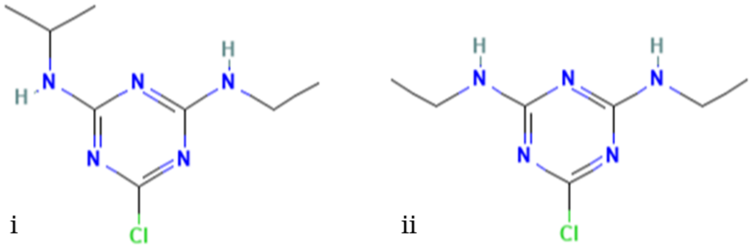


Fig. 7. Estructura de las triazinas empleadas en la Tesis Doctoral. (i) Atrazina. (ii) Simazina. Estructuras obtenidas de PubChem (https://pubchem.ncbi.nlm.nih.gov).

5. Integración de la etapa de muestreo y de extracción: el potencial de las fases sorbentes planas

En el campo de la determinación de los contaminantes orgánicos emergentes es también importante el empleo de nuevos materiales que presenten una mayor eficacia en la preconcentración de los analitos que los sorbentes convencionales. De todos los formatos disponibles para la determinación de estos compuestos, cabe resaltar el empleo de fases sorbentes planas. El uso de este formato da lugar al desarrollo de las técnicas de extracción en membrana (*membrane extraction* (ME)) [38], las cuales se caracterizan por la facilidad para la integración de las etapas de muestreo y extracción. La gran variedad de materiales que se pueden emplear para la fabricación de estas membranas hace que se puedan abordar diferentes problemas analíticos.

Las membranas descritas en la bibliografía se pueden dividir en dos grandes grupos, membranas poliméricas comerciales y membranas poliméricas modificadas.

En la bibliografía se pueden encontrar numerosos métodos para la preparación de este tipo de materiales, destacando los métodos de *electrospinning, dip-coating*, *spin-coating* o polimerización sol-gel, entre otros.

El método de *electrospinning* consiste en la preparación de la membrana polimérica a partir de una disolución del polímero cargada, la cual se coloca en una jeringa y se dispensa lentamente sobre una superficie plana bajo un campo eléctrico de dirección controlada. De este modo, las fibras del polímero se depositan dando lugar a una fina capa polimérica [39].

El método de *dip-coating* es de los métodos más simples para la preparación de este tipo de materiales sorbentes. Este método consiste en la preparación de una disolución del polímero (disolución precursora), en la cual se sumergirá un soporte plano que será la base de la membrana. En esa etapa de inmersión, el polímero impregnará el soporte. Para obtener una película de material polimérico, se puede optar por la evaporación del disolvente, o bien por cambios en el medio que promuevan la precipitación del mismo sobre el soporte [40,41].

La preparación de membranas por polimerización sol-gel es un proceso algo más complejo que requiere de una serie de reacciones de policondensación de los monómeros que compondrán la red polimérica. Para ello, se hidrolizan los monómeros dando lugar a una suspensión coloidal (sol). Tras esto, la suspensión se mezcla con agua o etanol, promoviendo las reacciones de policondensación que generarán la fase sorbente (gel) [42].

5.1. Membranas poliméricas comerciales

Las membranas poliméricas que se pueden adquirir en el mercado son numerosas y tienen diferentes utilidades, desde su empleo como filtros hasta el uso como material sorbente, que es el más importante en el marco de esta Tesis Doctoral. La membrana comercial más empleada en técnicas de microextracción es la de polipropileno, y se emplea tanto en técnicas de microextracción en fase líquida en la modalidad de fibra hueca [43,44], como en metodologías basadas en el empleo de electro-membranas [45,46]. No obstante, si bien las membranas de polipropileno son las más empleadas, en la actualidad también se ha descrito el empleo de membranas de fluoruro de polivinilideno (PVDF) [47,48].

5.2. Membranas modificadas

Las membranas modificadas tienen especial relevancia pues permiten tener a disposición un amplio catálogo de materiales para su empleo, cada uno de ellos con las propiedades adecuadas y características necesarias para la resolución del problema analítico de interés.

Si se clasifican en función del soporte empleado, podemos diferenciar entre membranas de poliestirero modificadas, membranas de inclusión polimérica, membranas de agarosa en gel, *Fabric Phases* (FPs) y membranas basadas en papel. De todas ellas, en esta Tesis Doctoral tienen especial interés las FPs y las membranas basadas en papel.

5.2.1. *Fabric Phases*

El empleo de este tipo de material se describió por primera vez en 2014 por Kabir y Furton como membranas que se soportaban sobre un sólido de alta porosidad (celulosa o fibra de vidrio), el cual se recubría poliméricamente por medio de la tecnología sol-gel. Esto permite obtener fases sorbentes planas de diversa naturaleza en función del recubrimiento polimérico realizado [49].

La técnica de extracción asociada a su uso, *fabric phase sorptive extraction* (FPSE), se basa en el empleo de estas fases sorbentes en extracción. Aunque tienen propiedades físicas similares a las membranas, la interacción con los analitos es diferente. En esta modalidad de extracción, la interacción de la membrana con los compuestos de interés está gobernada por fuerzas electrostáticas.

Entre las ventajas relacionadas con el empleo de este tipo de materiales se encuentra su versatilidad ya que pueden ser empleadas para extraer muestras líquidas y gases [50,51].

En lo que respecta a la aplicabilidad de estas membranas en técnicas de extracción, se han desarrollado numerosas aplicaciones. La primera de estas aplicaciones demostró su potencial en la determinación de estrógenos en muestras líquidas (agua y orina) por inmersión directa de la FP en la muestra. La transferencia de los analitos se favorecía por la agitación de la muestra [52].

En el campo del análisis ambiental, Roldán-Pijuán *et al.* propusieron una unidad de agitación integrada que adaptaba la técnica de extracción con membrana agitada (*stir membrane extraction,* SME) [53]. El problema analítico seleccionado fue la determinación de triazinas en muestras de agua [51].

Otras aplicaciones ambientales se han centrado en la determinación de hormonas sexuales [52,54], derivados fenólicos [55,56], metales [57,58], conservantes cosméticos [59,60], fármacos y productos cosméticos [61,62], y drogas [63,64], entre otros [65].

Además de las aplicaciones ya citadas, estos materiales también se han empleado para el análisis de muestras de aire. Una de estas aplicaciones fue descrita en 2017 por Alcudia-León *et al.*, quienes emplearon FPs para el control temprano de la *Tuta absoluta* (plaga que afecta al tomate) mediante la monitorización de sus feromonas sexuales [21].

Para finalizar, es importante resaltar que estos materiales no solo tienen un amplio campo de aplicabilidad en análisis ambiental, sino que también hay numerosos desarrollos en bioanálisis, que vienen impulsados por la selectividad de estos, así como por la posibilidad de aplicación directa sobre la muestra [66].

5.2.2. Membranas de papel modificado

El papel es un biopolímero plano producido por el empaquetamiento de las fibras de celulosa [67], siendo uno de los más abundantes en la naturaleza. Su empleo en técnicas de extracción no es nuevo [68], aunque recientemente se ha visto incrementado su uso. La alta disponibilidad de este material, además de su fácil acceso debido a su bajo coste, lo hacen un soporte ideal para la preparación de fases sorbentes. La geometría de la fase extractante puede además adaptarse a la de la unidad de extracción de forma muy sencilla, ya que pueden recortarse en las dimensiones requeridas. A estas características hay que añadir la facilidad de modificación, ya que debido a su composición química exhibe gran cantidad de grupos hidroxilo en superficie.

Las propiedades químicas de este material no solo lo convierten en un soporte ideal para la preparación de fases sorbentes, sino que también permiten su uso como sorbente sin modificar. Meng *et al.* han propuesto su empleo en microextracción en fase sólida para la determinación de 8-hydroxy-2'-deoxyguanosine en muestras de orina. En esta aplicación tres fragmentos de papel de filtro sin tratar se introducción en la muestra, la cual se agita para favorecer la interacción entre el sorbente y el analito. Este interacciona por medio de puentes de hidrógeno con los grupos superficiales de la celulosa. Tras esto, los fragmentos de papel se secan y se someten a un proceso de elución química con un buffer que contiene el agente derivatizante [69]. También en esta línea, Díaz-Liñán *et al.* han descrito una aplicación en la que emplean papel de filtro sin modificar para la determinación de aminas biogénicas en muestras de cerveza. En esta aplicación se demuestra el potencial de este material como sorbente ya que los grupos hidroxilo de la superficie interaccionan con los grupos amino de las aminas formando puentes de hidrógeno que permiten la extracción de las mismas. De un modo similar, los autores introducían un fragmento de papel de filtro en la muestra previamente desgasificada, la cual se agita durante 45 min. Transcurrido ese tiempo el fragmento de papel se lavaba con agua y se llevaba a cabo la elución de los analitos. Para la elución de los analitos emplearon una mezcla metanol/agua (60/40) que contenía un 0.1% de ácido fórmico (que facilitaba la ruptura de la interacción entre el sorbente y los analitos). El eluido se analizaba finalmente por inyección directa en espectrometría de masas en tándem. De esta forma se desarrollaba un método rápido para la resolución del problema analítico propuesto [70].

Además de las aplicaciones descritas previamente, Benedé *et al.* también han demostrado el potencial de la celulosa sin modificar como fase sorbente. En esta aplicación, los autores preparan una membrana de papel modificado con nailon-6 para la extracción de antibióticos en muestras de saliva. No obstante, aunque la fase sorbente estaba compuesta por nailon-6, los autores demuestran que en el caso de algunos de estos analitos (amoxicilina y ampicilina) el nailon-6 no proporciona capacidad de extracción, sino que es el papel sin modificar el que lo hace. Esto es debido a las interacciones electrostáticas que se producen entre estos analitos y los grupos superficiales de la celulosa, lo que permitía la extracción de los mismos por el papel sin modificar, pero no empleando nailon-6 puro como sorbente [71].

Por otra parte, la modificación del papel para la preparación de materiales sorbentes se puede llevar a cabo atendiendo a dos estrategias: la deposición física de la fase extractante sobre el papel y la unión covalente de la misma.

- **Deposición física**

Las aplicaciones descritas de fases sorbentes con papel modificado por el proceso de deposición física son numerosas. En particular, la deposición de la fase sorbente se puede llevar a cabo por la metodología de *dip-coating.* Siguiendo este proceso, en 2017 Ríos-Gómez *et al.* describieron una fase sorbente basada en papel de filtro, común en el laboratorio analítico, recubierto con poliestireno como fase extractante. Para la preparación de este sorbente, el poliestireno se solubilizó en cloroformo, el cual se dejó evaporar tras la inmersión del papel en la disolución precursora. Dicho material se empleó con muy buenos resultados para la extracción de metadona en muestras de orina. Para dicho fin, un fragmento de la fase sorbente preparada se introdujo en una punta de pipeta, empleando una micropipeta como sistema de extracción [41].

Posteriormente, Diaz-Liñan *et al.* describieron la preparación de otro material sorbente, sumergiendo el papel en una disolución que contenía los precursores necesarios para la preparación de un polímero de impresión molecular (*moleculary imprinted polymer,* MIP). Entre las ventajas de este procedimiento cabe destacar su simplicidad, ya que no fue necesario incluir ninguna etapa de polimerización. Este material se empleó en la extracción de quinina en bebidas refrescantes. Con este fin el sorbente se introdujo en la muestra previamente desgasificada, y se agitó para favorecer el proceso de retención de la quinina. Finalmente, una vez retenido el analito, el soporte se introdujo en un receptáculo fabricado en el laboratorio, que permitía el acoplamiento directo con un detector fluorimétrico. De este modo, los autores consiguieron un método selectivo, sencillo y rápido para la resolución del problema propuesto [72]. Siguiendo lo anteriormente descrito Diaz-Liñan *et al.* también prepararon otro MIP empleado en la determinación de ketoprofeno. La preparación del nuevo sorbente se realizó en dos etapas. Por un lado, prepararon las nanoflores de plata y por otro funcionalizaron con plata la superficie del papel. Una vez preparados estos dos materiales anclaron las nanoflores a la superficie. Este nuevo material era compatible con espectroscopía Raman aprovechando las características de las partículas de plata y espectrometría de masas en la modalidad de *paper-spray.* [73].

Si bien todas las aplicaciones de materiales preparados por *dip-coating* que se han descrito emplean como fase sorbente polímeros insolubles en fase acuosa, esta no es la única posibilidad. Estos materiales también se pueden preparar empleando polímeros solubles en agua, como los líquidos iónicos poliméricos [74], o bien empleando dispersiones de partículas [75], obteniendo de este modo papeles modificados con nanopartiículas.

Finalmente, como combinación de los dos tipos de fases sorbentes anteriores, surgen los papeles modificados con *nanocomposites*, es decir, sorbentes que combinan en su estructura polímero y nanomateriales. Estos materiales exhiben sinérgicamente las propiedades de los dos componentes que los forman. El polímero aportará estabilidad mecánica y capacidad sorbente, mientras que el nanomaterial además de poder aportar capacidad sorbente y porosidad al entramado polimérico, puede contribuir con alguna otra propiedad beneficiosa, como, por ejemplo, aportando magnetismo. Así pues, para la preparación de estos en la disolución precursora del polímero, se dispersa el nanomaterial seleccionado, el cual quedará atrapado en el entramado polimérico al depositarse sobre el papel. Entre las aportaciones a este tipo de materiales se pueden destacar las realizadas por Ayazi *et al.*, los cuales prepararon membranas en las que dopaban una poliamida con diferentes materiales como óxido de zinc [76] y óxido de grafeno [77].

- **Modificación covalente**

La modificación covalente es la otra posibilidad para la preparar fases sorbentes empleando papel como soporte. En esta modalidad se aprovechan los grupos funcionales de la superficie del papel para realizar el anclaje de la fase extractante. De este modo, se consiguen fases sorbentes con base papel más estables que las obtenidas por deposición física, sobre todo en el caso de las preparadas con polímeros solubles en agua. Aunque sus propiedades mecánicas son mejores que las preparadas por deposición física, tienen como punto débil que el proceso de preparación no es tan simple.

Una de las primeras modificaciones covalentes propuestas la llevaron a cabo Saraji *et al.,* quienes modificaron la superficie del papel con isocianatos mediante la reacción de estos con los grupos hidroxilo de la celulosa. Una vez acondicionado, el material se introducía en la muestra anclándolo al tapón de un vial, que se agitaba por un tiempo definido. Los analitos se retienen por interacciones π-π entre los analitos y el fenil isocianato de la superficie del sorbente. El material preparado se empleó para extracción de estrógenos de muestras de agua [78].

Aunque en el caso del análisis ambiental no se han descrito muchas aplicaciones que emplean este tipo de sorbentes, si se han desarrollado más aplicaciones en otros campos. Se han descrito modificaciones con diisocianatos [79], silano [80], polidopamina [81], aptámeros [82], o enzimas [83], entre otras.

* * *

En la presente Tesis Doctoral, se ha abordado la integración de la etapa de muestreo y extracción de los analitos en ámbito del análisis ambiental. Con este fin, se han diseñado diferentes dispositivos cuya finalidad es integrar la etapa de muestreo con la extracción de los analitos en la misma unidad. Estos se han aplicado en dos compartimentos ambientales diferentes, como son agua y aire. Atendiendo a estas dos matrices, los distintos prototipos se han agrupado en dos bloques diferentes.

En el primero de estos bloques, se presentan los sistemas de muestreo basados en una unidad magnética para su empleo en sistemas agitados y su aplicación en el análisis de muestras de agua. A dicha unidad se le ha conferido agitación con dos sistemas diferentes: a) con un taladro portátil, y b) con un pequeño motor eléctrico.

En el segundo bloque se recoge el dispositivo diseñado para el muestreo de aire, pudiendo ser aplicado tanto para análisis de muestras de aire ambiental como en atmósferas de trabajo. El dispositivo diseñado se basó en el empleo de un ventilador de ordenador como elemento central de la unidad de muestreo, en cuyas aspas se situó la fase sorbente. Al ponerlo en funcionamiento, se favorecía el paso de la muestra sobre el medio de extracción.

En los siguientes bloques de esta memoria se presentarán las distintas aportaciones que han resultado de la investigación desarrollada durante la Tesis Doctoral. Se incluye un bloque de Resultados y Discusión en el que se realiza un estudio comparativo de las distintas unidades y la evolución derivada de las limitaciones observadas en el prototipo inicial en el caso de los muestreadores de aguas.

Para finalizar, se expondrán las conclusiones más relevantes y líneas de desarrollo futuro del trabajo realizado.

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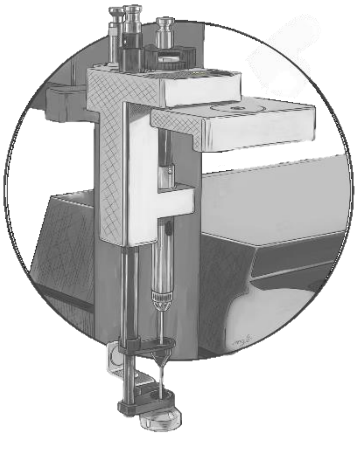
BLOQUE II

TÉCNICAS DE TRATAMIENTO DE MUESTRA EN ANÁLISIS AMBIENTAL



La implementación de métodos de análisis más respetuosos con el medio ambiente es cada día más una realidad en todo laboratorio de análisis, y en los procesos de análisis ambiental, no iba a ser diferente. Esta tendencia se focaliza normalmente en la etapa de tratamiento de muestra, centrándose en la reducción de consumo de reactivos y disolventes orgánicos, así como en la minimización de la producción de residuos. Por tanto, siguiendo esta tendencia, las técnicas clásicas de tratamiento de muestra, y especialmente las de extracción, se han visto superadas por sus versiones miniaturizadas, tanto en fase líquida como en fase sólida, que se soportan en los principios de la Química Analítica Verde [1].

En el caso de muestras líquidas y gaseosas, la técnica de extracción más empleada es la microextracción en fase sólida en cualquiera de sus formatos. No obstante, también se aplican otras modalidades como la microextracción en fase líquida. La ventaja de la microextracción en fase sólida frente a otras modalidades reside en sus características intrínsecas: simplicidad, facilidad de uso y versatilidad para su acoplamiento con técnicas instrumentales [2].

En el caso de las muestras sólidas el proceso se complica algo más, siendo necesario en este caso una extracción previa para compatibilizar la muestra con la técnica instrumental. En este caso, la microextracción en fase líquida es la técnica de referencia aunque puede verse sustituida por las técnicas de espacio de cabeza cuando los analitos son compuestos volátiles [3].

En el **Capítulo 1** de la memoria de la presente Tesis Doctoral, se recogen las técnicas empleadas para el tratamiento de las distintas matrices ambientales objeto de estudio, todas ellas con un enfoque respetuoso con el medio ambiente. Se inicia este capítulo con una contextualización de las técnicas clásicas de extracción en sus diferentes modalidades, para continuar con las versiones de estas que las han sustituido. Para finalizar, se muestra el potencial de las técnicas descritas en análisis ambiental.

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CAPÍTULO 1

GREEN SAMPLE PREPARATION IN ENVIRONMENTAL ANALYSIS

ELSEVIER

Green Approaches
for
Chemical Analysis
2022

Green Sample Preparation techniques in environmental analysis

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The need for the analysis of environmental samples: air, water and soils arose from the crucial importance that these compartments have for the development of living beings. The presence of contaminants will jeopardize the normal growth of plants, animals, and humans. On most occasions, the human activity is responsible for the contaminants that finally reach the environment. In parallel, it should be taken into consideration that the methodologies proposed for the determination of environmental parameters must be eco-friendly to not add more pollution and contribute to the depletion of the natural resources. This chapter presents an overview of the analytical methodologies that have been proposed for the analysis of water, air and soil in which the green rating prevails. On most cases, miniaturized extraction techniques and the use of less contaminant solvents have been highlighted. Moreover, the devices proposed for the simultaneous sampling and extraction have been emphasized.

Keywords: Miniaturized extraction techniques, Solid phase microextraction, Liquid phase microextraction, Dispersive microextraction techniques, Water, Air, Soil.

BLOQUE III

SISTEMAS INTEGRADOS DE MUESTREO/EXTRACCIÓN EN ANÁLISIS DE MUESTRAS LÍQUIDAS

Con el fin de evitar el transporte de elevados volúmenes de muestra hasta el laboratorio, es relevante la integración de las etapas de toma de muestra y extracción. Esta integración supone el empleo de un material sorbente en el que los analitos sean estables y, por tanto, no haya pérdidas/deterioro de estos durante el tiempo de transporte y almacenaje.

En este punto resultan de gran interés las fases sorbentes planas, las cuales presentan ciertas ventajas en el campo de muestreo ambiental. Por un lado, tiene una elevada capacidad sorbente, relacionada con la alta relación superficie/volumen de muestra [1]. Por otro lado, una vez retenido el analito, son fácilmente transportables al laboratorio en bolsas, sobres o embalajes de reducidas dimensiones. A esto hay que sumarle la facilidad para su acoplamiento a dispositivos de muestreo con agitación integrada, lo que supone un avance respecto a los materiales sorbentes particulados.

Estos dispositivos de muestreo con agitación integrada favorecen la interacción entre la matriz de la muestra y la fase sorbente. Esta interacción elimina los problemas de difusión a la fase sorbente, favoreciendo por tanto la extracción de los compuestos de interés desde la matriz de la muestra [2]. A esta ventaja hay que sumar el potencial de estos dispositivos para su aplicación en muestreo *on-site*, reduciendo así las etapas de tratamiento de muestra y, por tanto, mejorando la calidad de los resultados.

En este Bloque de la presente Tesis Doctoral se recogen las mejoras implementadas a una unidad agitada para la toma de muestras de aguas. En los distintos capítulos que componen el bloque, se exponen las diferentes mejoras con respecto a la unidad de extracción inicial, además de las mejoras debidas al empleo de diferentes fases sorbentes poliméricas con geometría plana. En este sentido, se comienza por el empleo de una membrana comercial (**Capítulo 2**), pasando por una fase sorbente en base papel que emplease el mismo polímero (**Capítulo 3**), para finalizar en el **Capítulo 4** con el empleo de una fase magnética que emplea el material sorbente de referencia en el muestreo ambiental (HLB).

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CAPÍTULO 2

PORTABLE STIR MEMBRANE DEVICE FOR ON-SITE ENVIRONMENTAL SAMPLING AND EXTRACTION

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Portable stir membrane device for on-site environmental sampling and extraction

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A portable device that integrates sampling and extraction is proposed in this work. The unit is fabricated using commercial and standardized elements which guarantees the construction reproducibility. Also, it is simple to be mounted and on-site deployed making possible the multi-site sampling. The device uses a commercial nylon membrane as extraction phase for the isolation of the target compounds, but it can be adapted to other flat sorptive phases thus expanding the applicability. Once mounted, the unit is stirred into the sample by means of a portable drill enhancing in that way the diffusion of the target analyte towards the extraction phase. The hydrodynamic behavior and the design have been optimized and the device has been finally used for the extraction benzophenones from swimming pool samples. These endocrine disruptive compounds are determined by liquid chromatography tandem mass spectrometry (LC–MS/MS) at concentrations as low as 0.1 µg/L with precision, expressed as relative standard deviation, better than 9.9 %. The accuracy, calculated as relative recovery, was in the range from 74 to 111 % thus being considered appropriate.

Keywords: Sampler, Microextraction, Stir membrane, Benzophenone, Swimming pool.

1. Introduction

Environmental analysis is challenging due to the size of the compartments under study, the heterogeneous distribution (both temporal and geographical) of the target analytes and the low con-centration and different states (free, associated to sediments or organic matter) of the latter [1]. In this situation, the sample representativeness can be only ensured if a multiple-sampling protocol is applied. The classical analytical workflow, which is based on the transportation of the sample to the laboratory for the final analysis, is not suitable when the analytes are prone to be lost (by adsorption, volatilization, chemical or biochemical degradation). Also, the contamination risks, as well as the costs and productivity issues derived from the transportation and storage of large sample volumes, are additional disadvantages to this standard approach. In such situations, two alternative workflows, namely on-site analysis, and on-site extraction, are worthy of being evaluated [2]. On-site analysis simplifies the analytical process as the measurement is done in the sampling site. However, portable instruments usually present. lower performance (in terms of sensitivity and selectivity) than bench-top instruments and the robustness must be high enough to work in changing (sometimes extreme) environments. On-site extraction integrates the isolation of the analytes in a solid or liquid extraction phase, which can be transported and stored more easily than the sample itself. Also, the analytes are stabilized in the extraction phase reducing the negative effects mentioned above. The on-site extraction paradigm has transcended the environmental analysis sphere being extended to in-vivo extractions, which have opened a range of possibilities in clinical [3,4] and environmental [5,6] contexts.

To be on-site applied, an extraction technique should be miniaturized and portable (capacity of sampling in hard-to-reach locations), easy to handle, rapid (allowing multiple sampling) and reproducibly manufactured [7]. Although classic extraction techniques have been used in this context, microextraction alternatives fit better with the mentioned criteria.

Liquid phase microextraction (LPME) uses a liquid extraction phase for the isolation of the target analytes. In this sense, Larsson et al. proposed a time-integrating sampler for the on-site extraction of triazine herbicides and their degradation products. The sampler is completely portable and autonomous as it is operated by a 12 V battery, which is rechargeable by a solar panel [8]. The same group has evaluated the potential of hollow fiber LPME for the on-site extraction of non-steroidal anti-inflammatory drugs from waters [9]. Although the number of reported LPME-samplers is scarce, some techniques could be easily adapted to be on-site applied. Dispersive liquid-liquid extraction (DLLME), based on the efficient dispersion of the extracting solvent into the sample, can be highlighted among them thanks to its simplicity and rapidity. The dispersion and recovery of the solvent, which require special apparatus to be developed (like vortexes, ultrasound probes, or centrifuges), may limit its on-site application. However, the use of switchable solvents [10,11] and effervescence reaction [12–14] simplify the procedure opening the door to the on-site application of DLLME.

Solid phase microextraction [15] (SPME) is the technique of reference for on-site extraction considering its simplicity, miniaturized character, and easy deployment [16–20]. It can operate under passive and active sampling modes [7], and it can also be applied in environmental air monitoring [21]. Other techniques based on solid extraction phases, like in-syringe solid phase extraction [22,23], tip extraction [24] and purge and trap [25], have also been reported in this context with success.

The integration of the stirring and extraction elements is the same device boosts the diffusion of the target analytes from the bulk sample to the sorptive phase [26]. This is especially interesting to design portable samplers that can be directly introduced into the system under study (river, lake, etc.) thus simplifying the analytical procedure. This integration was already implemented at the beginning of thin film microextraction (TFME) technique, and it has been considered in other developments. In this sense, Mao et al. attached a polydimethylsiloxane rod to an electric stirrer to design a portable sampler [27]. This idea has been extended by using magnetic polymeric monolith integrated into a battery operated micromotor [28]. Our group suggested the use of borosilicate disks modified with nanoparticles to fabricate a portable sampler for environmental analysis [29].

In this article, a new portable stir membrane device that integrates sampling and extraction is presented. An electric drill, as suggested by Prof. Pawliszyn group for the design of on-site samplers [30–32], is used to stir the extraction device. In this case, in order to assess the reproducibility on the fabrication of the device, commercial elements rather than lab-made ones have been used.

This strategy, already reported by other researchers in similar and different contexts [33–35], makes the transferability of the idea between laboratories easier. Also, the new device can theoretically be used with any flat sorptive phase. The design of the device has been optimized to promote the mass transference from the bulk samples to the sorptive phase (a commercial nylon membrane). The device has been practically applied to the on-site extraction of several benzophenones from swimming pool samples as proof-of-concept problem.

2. Experimental

2.1. Reagents and samples

All the reagents were of analytical grade or better. Unless otherwise specified, they were purchased from Sigma Aldrich (Madrid, Spain). Stock standard solutions of each analyte (benzophenone-1, benzophenone-3, benzophenone-6, benzophenone-8 and 4-hydroxybenzophenone) and internal standard (ozybenzone-(phenyl-d5)) were prepared in methanol at a concentration of 1000 mg/L and stored at 4◦C in the dark. Working standards were prepared daily by rigorous dilution of the stock in Milli-Q water (Millipore Corp., Madrid, Spain) or methanol as required. Methanol was also employed as eluent in the microextraction procedure. Acetonitrile, ammonium formate and Milli-Q water were employed as components of the chromatographic mobile phase. Nylon filtration membranes (47 mm ID, 0.45 μm pore size) were acquired from Thermo Scientific (Madrid, Spain) and used with-out previous conditioning. The membranes were only cut to be adjusted to the proposed device where a circular section of 18 mm in diameter is exposed to the sample. The thickness of the membranes was measured by scanning electron microscopy (SEM) and it resulted to be 66 ± 8 m. SEM micrographs were taken using a JEOL JSM 7800F microscope at the Central Service for Research Support (SCAI) of the University of Córdoba. The nominal resolution was 0.8 nm at 15 kV. The membranes were coated with gold before the micrographs acquisition. Samples were taken from a private swimming pool, and they were processed as it will be described further on.

2.2. Portable stir membrane device

A NdFeB countersunk pot magnet (Supermagnete, Gottmadingen, Germany) with a magnetic force of 88.3 N (upper panel of Fig. 1A) is the core of the extraction device. Thanks to the magnet geometry (lower panel of Fig. 1A), a countersunk screw can be easily introduced through the magnet (Fig. 1B) and fastened with a nut. The screw, whose length can be selected considering the sampling site, is attached to a wireless electric drill that allows the stirring of the extraction device. The membrane is magnetically attached to the device using a metallic washer making the attachment/detachment of the sorptive phase very easy (Fig. 1C). This aspect is essential for the replacement of the membrane after sampling in a specific location.

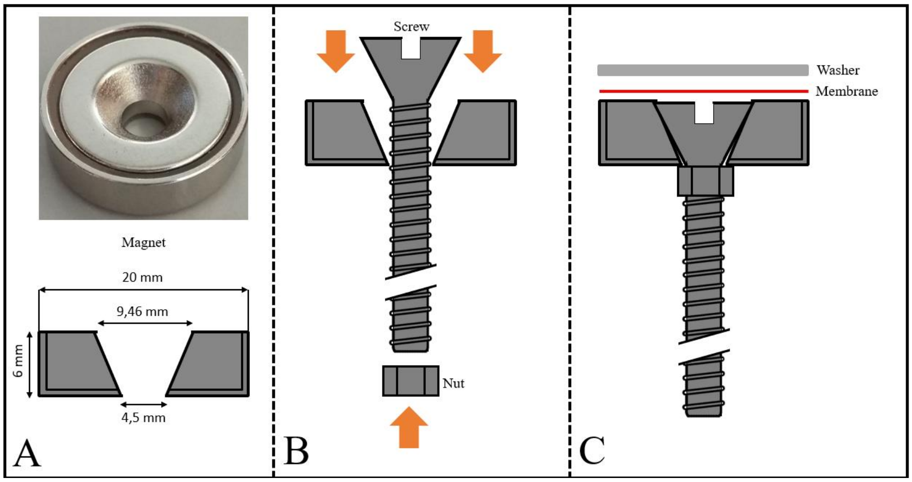

Fig. 1. (A) Picture (upper panel) and lateral view diagram (lower panel) of the magnet; (B) Attachment of the screw to the unit; (C) Attachment of the membrane using a metallic washer.

2.3. Sampling/extraction protocol

For calibration, 2 L of aqueous standards, containing the analytes at a defined concentration, is taken in a beaker and the internal standard is added at a final concentration of 5 µg/L. The portable stir membrane device is subsequently immersed in the sample and stirred for 10 min to isolate the target compounds. After the extraction, the membrane is dried with a paper tissue and introduced in an eppendorf for storage (in the dark and 4 °C) until their final analysis. As the volume of sample is a critical factor, it must be controlled. The on-site extraction is performed in collected samples. For this purpose, 2 L of sample is collected in a beaker and the internal standard is subsequently added at a final concentration of 5 µg/L. The extraction is done under the same conditions employed for the calibration standards. The membrane is finally dried, stored in an eppendorf and transported to the laboratory.

For the analyte's detection and quantitation, the membranes are eluted with 1 mL of methanol under vortex stirring for 15 min. The eluent is evaporated to dryness in a Concentrator Plus (Eppendorf AG, Hamburg, Germany) and the residue is redissolved in 100 µL of methanol for further preconcentration. Finally, 5 µL of the extract is analyzed by LC–MS/MS.

2.4. LC–MS/MS analysis

Liquid chromatographic analyses were carried out on an Agilent1260 Infinity HPLC system (Agilent, Palo Alto, CA, USA) equipped with a binary high-pressure pump for mobile phase delivery and an autosampler. Chromatographic separation was performed on an Eclipse XDB-C18 (4.6 mm x 150 mm, 5 m) column from Agilent, using 0.1 % ammonium formate aqueous solution and acetonitrile as mobile phase components in a 25/75 (v/v) ratio. A guard column (0.2 µm filter, 2.1 mm), also from Agilent, was used to preserve the integrity of the analytical column. The injection volume was 5 µL, and the flow rate was maintained at 0.5 mL/min.

Quantification was performed on Agilent 6420 Triple Quadrupole MS with electrospray source using Agilent MassHunter Software (Version B.06.00) for qualitative and quantitative analyses. The mass spectrometer settings were fixed to improve the multiple reaction monitoring (MRM) signals. The flow rate and the temperature of the drying gas (N_2) were 9 L/min and 350 °C, respectively. The nebulizer pressure was 30 psi, and the capillary voltage was kept to 3000 V in positive mode. The MS parameters for the analytes and the internal standard are specified in Table S1(supplementary material).

3. Results and discussion

3.1. Design and operating optimization of the portable stir membrane device

Thin film microextraction evolved from the traditional SPME fiber geometry to a device with larger surface area-to-volume ratio [36]. This apparently simple change produces a dramatic enhancement of the extraction kinetics (as the coating thickness remains thin) and the sorption capacity (as larger volume of extractive phase is exposed to the sample). TFME has demonstrated a great potential for the development of faster and sensitive methods [37] in fields as different as bioanalytical [38,39] and environmental analysis [40,41].

Membrane-based TFME uses a flat sorptive phase which conveniently attached to a stainless-steel rod can be easily deployed, in a flag shape, into the sample or the system under study. Although commercial membranes can be used in this technique, other material like fabric-phases [42,43], lab-made electrospun membranes [44] or even paper-based sorptive phases [45] can be potentially used making the application scope wider.

In the initial developments of TFME, Pawliszyn et al. realized that the integration of the stirring and extraction elements in the same device would open the door to the development of TFME environmental samplers. Although other techniques like stir membrane [46] or rotating disk extraction [47] have also the potential for on-site extraction, this capacity has not been evaluated or reported. Inspired by the previous developments in the field, this article presents and evaluates a new stir membrane sampler. User friendliness (easy mounting and demounting of the device), fabrication reproducibility (the unit is based on commercial and standardized elements) and enhanced membrane-protection during the extraction have been the main design criteria.

The hydrodynamic behavior of the sampler was initially evaluated using sand as a tracer. For this purpose, the sampler was introduced and stirred in a beaker containing 2 L of water and sand. As it can be observed in Movie 1 (supplementary material) the sand remained in the bottom of the beaker after 40 s thus indicating a low stirring capacity. To increase the stirring power, two lab-made (based on already commercial products) blades were attached to the unit. As it can be watched in Movie 2 (supplementary material) the blades modify the hydrodynamic behavior thus allowing to move the sand from the bottom of the beaker. Figure S1 (supplementary material) shows the original and modified sampler as well as the initial and final photograms of movies 1 and 2, clearly showing the stirring capacity.

The membrane is attached to the magnet by a simple metallic washer making the mounting and demounting of the device very easy. The attachment is robust enough during sampling and thus the membrane is always exposed to the sample in the same way. If it is compared with the flag configuration, the new device gives higher protection to the membrane at the expense of lower exposure. In the initial configuration, the membrane is directly attached to the magnet with the washer (Fig. 2Ai). When all the elements are combined (Fig. 2Aii), the membrane is separated from the bulk sample by a stagnant layer whose thickness corresponds to the washer height (2 mm). This layer makes the diffusion of the analytes to the membrane very slow, thus affecting the extraction of the targets. In fact, no extraction was observed under these conditions for short extraction times. To avoid this limitation, a septum (with a thickness slightly higher than the washer height) was introduced as an element, and it was located between the membrane and the magnet (Figure 2Bi). When the modified unit is mounted (Fig. 2Bii) the septum displaces the membrane over the washer exposing the sorptive phase to the sample. In such conditions, the analytes were detected in the eluate after the extraction.

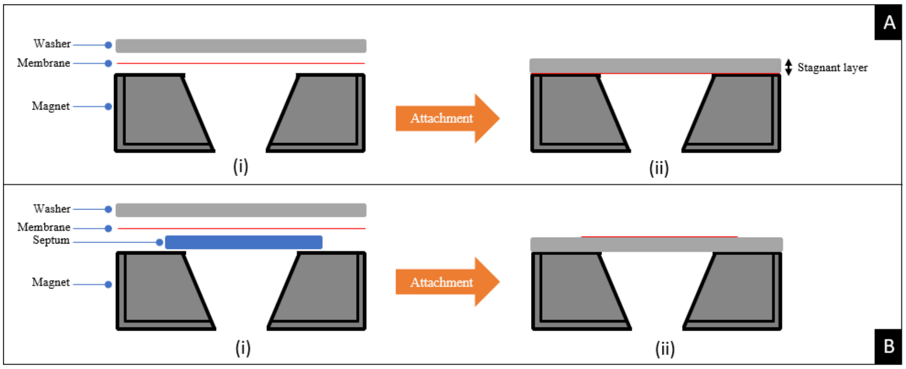

Fig. 2. Diagrams of the (A) initial sampler and (B) the septum-modified one. The elements (i) and the final disposition of the device (ii) when it is attached is also shown.

The effect of the sample volume on the extraction efficiency defines the sampling strategy. According to the SPME theory [48], when the sample volume is much higher than the sorptive one the amount of analyte extracted at equilibrium is directly proportional to the distribution coefficient, the volume of sorptive phase and the concentration of the analyte. In such conditions, the extracted amount is independent of the sample volume, and the sampler can be directly immersed in the system under study to get the isolation of the analytes. Fig. 3 shows how the peak area varies with the sample volume in the range from 250 mL to 5 L. The signal increases up to 2 L, and a slight increase is observed for 5 L.

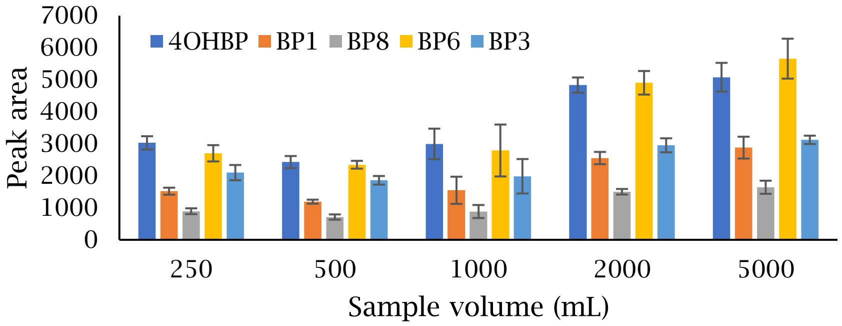

Fig. 3. Evolution of the peak area with the sample volume. The analytes: 4-hydroxybenzophenone (4OHBP), benzophenone-1 (BP1), benzophenone-8 (BP8), benzophenone-6 (BP6) and benzophenone-3 (BP3).

Although these results may enable us to introduce the device directly into the system under study, thus integrating the sampling and extraction, both processes were decoupled to enhance the precision. For this purpose, 2 L of the sample was taken in a beaker, and the internal standard was subsequently added to correct potential irreproducibility during the extraction. 2 L was selected as the optimum volume, although 5 L provided slightly better results, since the lower the sample the lower the internal standard consumption. Other variables affecting the extraction are briefly discussed in the supplementary information.

3.2. On-site extraction of benzophenones in swimming pools and their subsequent determination by LC–MS/MS

Benzophenones are usually employed as UV-filters in many cosmetic products and therefore they can be presented in aquatic environments such as seawater or swimming pools. There is evidence about the potential interference of these compounds with the human endocrine system [49,50], and therefore, their monitoring is necessary to study the toxicological exposure.

Under the selected experimental conditions for the proposed on-site extraction, the analytical method was evaluated in terms of linearity, sensitivity, precision, and accuracy. A calibration model was built using aqueous standards (submitted to the extraction and analysis procedure) containing the analytes at seven concentration levels. The linearity (R > 0.997 for all the analytes) was maintained up to 50 µg/L. The LODs, calculated for a signal to noise ratio of 3, were 0.1 µg/L for all the analytes while the precision, calculated an intermediate level (5 µg/L) and expressed as relative standard deviation (RSD), was better than 9.9 %. The enrichment factors were in the range from 8.9 to 20.8. These data can be contextualized in the light of the recent literature dealing with the determination of endocrine disruptive compounds in water by LC–MS/MS. The application of exhaustive extractions, like SPE on-line coupled to the chromatograph, provides LODs in the very low ng/L range [51]. Reported microextraction techniques provided slightly higher LODs (but lower than 10 ng/L) although in some cases large extraction times (2 h) are proposed [52] or dispersive protocols with ad-hoc synthesized materials are needed [53]. In this article, a commercial membrane is used as the main objective is to present the potential of the device. Nylon was selected as material since it can interact with the tar-get analytes via dispersion forces (thanks to the polymeric chain) and H-bonding (thanks to the amide group). These interactions are enough to isolate the target in this proof-of-concept approach. However, other materials (for example, including aromatic moieties) are worthy of being checked if the sensitivity is intended to be boosted.

The accuracy of the proposed method was corroborated by the analysis of blank samples (previously analyzed and not presenting signals for any of the analytes) spiked at 10 µg/L. The results, which varied between 74 ± 7 % (for benzophenone 1) and 111 ± 8 % (for benzophenone 3) were acceptable. All the analytical figures are summarized in Table 1.

Table 1. Analytical figures of merit obtained for the determination of the target analytes by the combination of the portable stir membrane device with LC-MS/MS.

Analyte	LOD (µg/L)	Linear range (µg/L)	Linearity (R^2)	Intra-day precision (% RSD, n = 5)	Accuracy (% RR)	FF
Benzophenone-1	0.1	0.3-50	0.997	9.9	74 ± 7	18.8
Benzophenone-3			0.998	7.6	111 ± 8	13.5
Benzophenone-6			0.998	4.1	102 ± 4	20.8
Benzophenone-8			0.998	9.6	99 ± 9	16.6
4-hydroxybenzophenone			0.998	8.2	90 ± 7	8.9

LOD, limit of detection; RSD, relative standard deviation; RR, relative recovery at 5 µg/L; EF, enrichment factor.

The method was finally applied to the determination of the benzophenones in swimming pool water samples where these analytes are expected to be found. As it is indicated, four samples were analyzed in triplicate, providing positive results (Table 2). Only in two cases, the concentrations of the analytes were lower than the limit of quantification (0.3 µg/L). It should be highlighted that these concentrations correspond to the free analytes into the samples as no digestion is performed to release the analytes from a potential interaction with the organic matter.

Table 2. Analysis of real swimming pool samples. The results as expressed as mean concentration (in µg/L) ± standard deviation.

Sample	BP1	BP3	BP6	BP8	4OHBP
Swimming pool 1	-	0.42 ± 0.03	1.05 ± 0.03	Detected	0.70 ± 0.03
Swimming pool 2	Detected	0.61 ± 0.05	2.7 ± 0.3	1.14 ± 0.09	1.56 ± 0.07
Swimming pool 3	-	1.6 ± 0.1	1.6 ± 0.2	0.81 ± 0.07	0.36 ± 0.02
Swimming pool 4	0.52 ± 0.05	-	1.8 ± 0.2	0.39 ± 0.03	1.25 ± 0.05

The analytes: benzophenone-1 (BP1), benzophenone-3 (BP3), benzophenone-6 (BP6), benzophenone-8 (BP8) and 4-hydroxybenzopehnone (4OHBP).

4. Conclusions

In this article, a new device that integrates sampling and preconcentration for environmental applications is presented. The device uses a flat sorptive phase which is stirred in the sample to pro-mote the diffusion of the target compounds. The device has been designed following some driving criteria such as building reproducibility and simple deployment.

In this initial approach, a commercial membrane was selected to show the potential of the approach. Although the analytical characterization provided good results, the enrichment factors must be improved to face more sensitive determinations. This improvement would rely on the use of better extraction phases (e.g fabric phases, electrospun membranes) and the increase of the exposed membrane to the sample but avoiding an excessive exposure that may damage the flat sorptive phase.

Future studies will be focused on achieving full on-site analysis which will be made by the diffusion improvement and/or loading the internal standard in the membrane.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: https://doi.org/10.1016/j.chroma.2019.07.013.

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Supplementary data

1. Mass spectrometry parameters.

The determination of the target analytes was done by LC-MS/MS as it is described in the main text. Table S1 summarizes the multiple reaction monitoring (MRM) parameters used for the detection and quantification of the benzophenone studied in this article. The parameters for the internal standard are also shown.

Table S1. MS parameters for the target analytes and the internal standard.

Compound	Precursor ion (m/z)	Fragmentor voltage (V)	Product ion (m/z)	Collision energy (V)	Quantitation transition
Benzophenone-1	215	115	137	20	215→137
			105	20	
Benzophenone-3	229.1	125	151	20	229.1→151
			105	20	
Benzophenone-6	275	120	151	20	275→151
			95.1	45	
Benzophenone-8	244.9	110	151	20	244.9→121
			121	20	
4-Hydroxybenzophenone	199	105	121	20	199→121
			77.2	45	
Ozybenzone-(phenyl-d_5)	234	135	150.9	20	234→150.9
			110	25	

2. Original and blade-modified device

The hydrodynamic behavior of the device is critical to allow a good stirring of the sample thus increasing the mass transference of the analytes from the bulk sample to the sorptive phase. As it is indicated in the main text, the introduction of blades in the device improve this behavior. Figure S1 shows the original and modified sampler and the initial and final state of the sample before the stirring.

3. Variables study

In order to achieve the best method performance, all the variables that influence the extraction of the analytes were deeply studied. In all the cases, an aqueous standard containing the analytes at a concentration of 0.05 mg/L was used in these studies.

Different organic solvents (namely: methanol, ethanol, acetone and acetonitrile) were tested as eluents, methanol providing the best results in sensitivity terms.

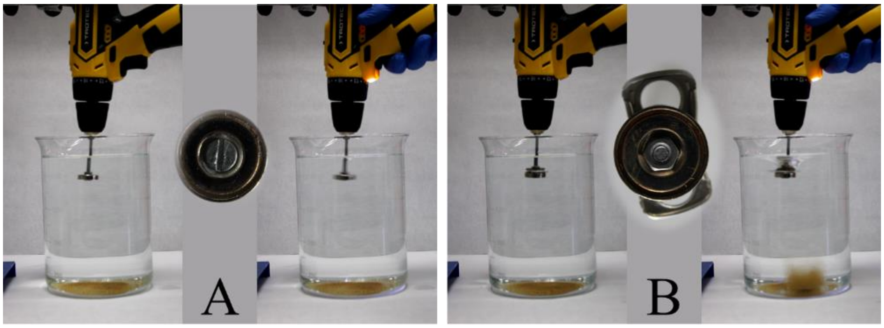

Figure S1. Pictures related to (A) the initial sampler and (B) the blades-modified one. The photograms show the beaker before being stirred (left panel) and after 40 s of stirring (right panel). The central panel shows a picture of each sampler where the position of the blades is observable.

Extraction time was evaluated in the range from 5 to 30 min. As it was expected, the analytical signal increased with the extraction time in this interval as it is shown in Figure S2. However, 10 min was selected as the optimum value as a compromise between sensitivity and sample throughput.

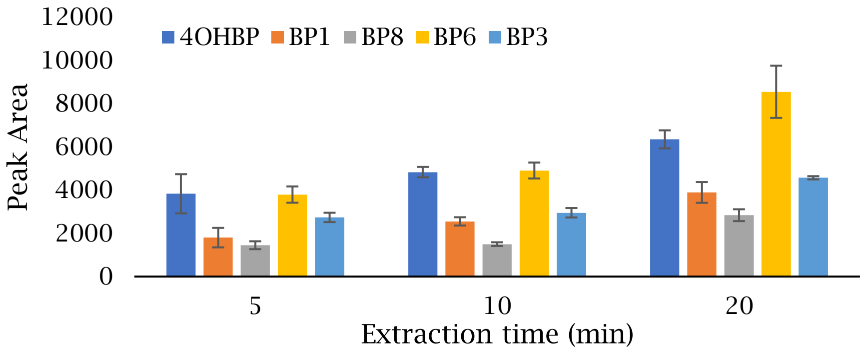

Figure S2. Effect of the extraction time on the isolation of the target compounds

Methanol volume was further studied in the interval from 0.1 mL to 2 mL. A complete elution of the analytes was achieved with 1 mL of methanol. In order to improve the sensitivity, the eluate was evaporated to dryness and redissolved in 100 µL of methanol for the subsequent chromatographic analysis.

Movie 1	Movie 2

CAPÍTULO 3

MAGNETIC PAPER-BASED SORPTIVE PHASE FOR ENHANCED MASS TRANSFERENCE IN STIR MEMBRANE ENVIRONMENTAL SAMPLERS

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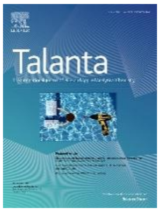

Magnetic paper-based sorptive phase for enhanced mass transference in stir membrane environmental samplers

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In this article, a magnetic paper-based sorptive phase is synthesized, which synergically combines the sorption capacity of a polyamide with the magnetic behavior of silica shielded Fe_3O_4 nanoparticles. The resulting material can be easily integrated into a drill-based environmental sampler, minimizing the diffusion boundary layer for enhanced mass transference. The new material has been evaluated for the extraction of four parabens and triclosan from swimming pool water samples. The main variables affecting the extraction have been studied in detail. The sampler is easy to transport allowing the on-site extraction of the analytes. This aspect can simplify the overall analytical procedure as only the sorptive phases, and not the samples, must be transported to the lab for the final analysis. The combination of the sampler with liquid chromatography-mass spectrometry allows determining the target analytes with limits of detection between 0.07 µg/L (butylparaben) and 0.1 µg/L (methylparaben and propylparaben). The precision, calculated at 5 µg/L, provides relative standard deviations better than 8 %. The accuracy, which was evaluated spiking a blank swimming pool water sample with the target analytes at a concentration of 0.75 µg/L, provided relative recoveries in the range from 88 to 98 %.

Keywords: Magnetic membrane, Dip-coating on-site extraction, Microextraction, Parabens, Triclosan.

1. Introduction

Environmental monitoring is crucial to assess the quality of natural waters, considered by the European Union as a heritage to be protected [1]. The size of the environmental systems and the heterogeneous distribution of the contaminants make multisampling (at different sites and times) necessary to guarantee the representativeness of the analytical information [2,3]. In most cases, the targets' concentration goes below the sensitivity levels of the instrumental technique, and their extraction and preconcentration become mandatory [4]. In contrast to the classical approach, where the sample is transported to the laboratory for its final analysis, the design of samplers that integrate the isolation of the compounds opens the door to the simplification of the logistics (only the extraction media and not the sample must be transported) [5]. These samplers also provide better representativeness levels, reducing the losses of the analytes during transportation and storage [6]. Although liquid-phase microextraction based samplers have been reported [7,8], solid traps increase the chemical stability of the analytes. For this reason, micro-solid phase extraction (μ-SPE) [9–14] and solid-phase microextraction (SPME) [15,16] are by far the preferred techniques for the development of these samplers.

Thin-film microextraction (TFME) is an evolution of the SPME technique that uses a layer of sorptive phase to extract the target analytes [17,18]. This new geometry enhances the mass transference thanks to a more advantageous surface to volume ratio, and it has been extensively used for environmental applications [19–21]. In 2006, Bragg et al. reported the first TFME environmental sampler [22], which was based on a thin layer of polydimethylsiloxane that is immersed into the environmental compartment for the passive sampling of the target analytes. This approach can be easily adapted to the active sampling mode if the sorptive phase is integrated into a drill for stirring [23,24].

In the last years, very innovative TFME environmental samplers have been reported. Magi et al. described the integration of TFME blades in a laboratory stirrer for the extraction of emerging contaminants in drinking water [25]. Prof Pawliszyn group has proposed different alternatives, including robust samplers [26], able to stabilize the isolated compounds for more than 10 days with negligible losses, and drone-based samplers capable of sampling in remote and difficult to access sites [27].

The design of new planar sorptive phases is crucial in TFME to increase the extraction capacity and, therefore, the sensitivity of the determinations. Commercial polymeric membranes [28], lab-made membranes fabricated by electrospinning [29] or spin coating [30], and fabric phases [31] are interesting materials in this concern. Paper-based sorptive phases prepared by the dip-coating technique emerge as a straightforward alternative to the previous procedures [32]. It is based on the direct immersion of a paper substrate into a polymeric solution [33,34] or dispersion [35,36] and the subsequent elimination of the solvent to create a thin coating over the paper surface. If a more controlled coating is intended to be obtained, a drop-casting approach where the precursor solution is directly deposited over the paper is also possible [37,38]. The resulting phases can be ad-hoc designed depending on the target analytes in a given analytical application.

In 2019, our research group proposed a water sampler based on the integration of commercial polymeric membranes in an electric drill [28]. In this new contribution, a magnetic paper is proposed as the sorptive phase to enhance the mass transference due to the minimization of the diffusion boundary layer. The sorptive phase is synthesized by the dip-coating of a filter paper into a dispersion containing solubilized nylon 6 in formic acid and dispersed magnetic nanoparticles. Therefore, the material combines the extraction performance of the polymer and the magnetic behavior of the nanoparticles, which make easier the deployment of the sampler and enhance the mass transference. The membrane's composition and the optimum extraction conditions have been studied using four parabens and triclosan as model compounds. These analytes are common ingredients of sunscreen cosmetic products. After application on the skin surface, they can be released into the water after swimming activities. Considering their harmful character for human beings, the monitorization of their presence and potential accumulation in aqueous environmental compartments is highly desirable.

2. Experimental section

2.1. Reagents and materials

Unless otherwise specified, the reagents were provided from Sigma Aldrich (Madrid, Spain). Methanolic standards of each analyte (methylparaben, ethylparaben, propylparaben, butylparaben, and triclosan) and the internal standard (triclosan-d_3, TRC Canada, Toronto, Canada) were made at a concentration of 1 g/L. Working solutions were obtained by the dilution of the stock solutions in ultrapure water (Millipore Corp., Madrid, Spain) or methanol, depending on their final use.

Several reagents were needed for the preparation of the magnetic membranes. Filter paper (Filter-Lab ream 42 × 52 cm, density: 73 g/m^2) was used as the substrate. Ferric chloride, ferrous chloride, and ammonia were used to synthesize the magnetic nanoparticles (MNPs) core. Tetraethyl orthosilicate (TEOS) and ethanol were used for coating the MNPs with a silica shell (MNPs@SiO_2). Finally, nylon-6 and formic acid were used to prepare the polymeric solution where the silica-coated MNPs were dispersed.

2.2. LC-MS analyses

The analytes were determined by liquid chromatography on an Agilent 1260 Infinity HPLC system (Agilent, Palo Alto, CA, USA) using an Eclipse XDB-C18 (4.6 mm× 150 mm, 5 µm) column. The mobile phase consisted of a 0.2 % (v/v) ammonia aqueous solution and methanol mixture in a 20/80 (v/v) ratio. A guard column (0.2 µm filter, 2.1 mm) was employed to avoid damages to the analytical column. The flow rate was fixed at 0.3 mL/min and 5 µL of the standards or extracts were injected in each run.

An Agilent 6420 ESI-Triple Quadrupole MS was used for the identification and quantification of the compounds. The analyzer worked under the multiple reaction monitoring (MRM) mode. Nitrogen was used a drying gas (9 L/min and 250 °C). The nebulizer pressure was 30 psi, and the capillary voltage was kept to 4 kV in negative mode. The MS parameters are listed in Table S1 (supplementary material).

2.3. Synthesis of the magnetic paper-based sorptive phase (MPSP)

The synthesis comprises several consecutive steps. First, silica-coated MNPs (MNPs@SiO_2) were synthesized following the procedure described elsewhere [39]. The magnetic core was synthesized by a coprecipitation method. Initially, $FeCl_3·6H_2O$ (24 g) and $FeCl_2·4H_2O$ (9.8 g) were mixed and dissolved in water (100 mL), and ammonia (50 mL) was added to induce the precipitation of the MNPs. After that, the MNPs were coated with a silica shell by using a sol-gel approach. For this purpose, MNPs (1 g) was dispersed in a ethanol:water mixture

(25:2) containing TEOS (2 mL), and the dispersion was maintained for 12 h under continuous stirring. The resulting MNPs were collected with a magnet, washed with water, and dried for further use. 600 mg of the MNPs@SiO_2 were dispersed in 10 mL of a 3 % (w/v) nylon-6 solution in formic acid using ultrasounds. Square segments of filter paper (2.5 × 2.5 cm) were dipped three times into the dispersion. After each dipping, the paper strips were immersed in water to induce the precipitation of the polymer (nylon is soluble in formic acid but insoluble in water) which is physically deposited over the paper surface. The MNPs@SiO_2 were entrapped into the polymeric network, thus providing magnetic character to the membrane. The MPSPs were finally cut into circles (20 mm in diameter) to be used in the sampler. The membranes are stable for at least 2 months.

MPSPs were chemically and physically characterized by infrared spectroscopy (IR) and scanning electronic microscopy (SEM). The instruments and measurement parameters are included in the supplementary information.

2.4. Portable stir membrane device

The extraction device (Fig. 1) is similar to that previously described [28], although it presents some modifications. A NdFeB countersunk pot magnet (Supermagnete, Gottmadingen, Germany) is the central element and the place where the MPSPs are magnetically attached. A screw is used as the stirring shaft of the device. One of the screw ends is fastened to the magnet using a nut, and the other end is fixed to a wireless electric drill. An improved blade is also included and closed with a nut to promote mass transference.

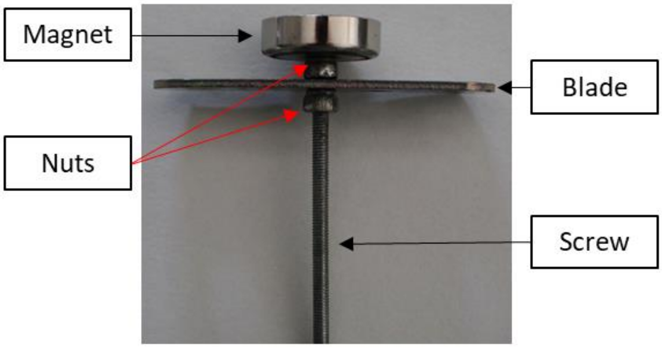

Fig. 1. Picture of the extraction device where the main elements are labeled. For details, see the text.

2.5. Sampling/extraction protocol

In the first step, MPSP is pre-loaded with the IS. For this purpose, the sampling device with a clean MPSP attached is immersed into 2 L of an aqueous solution containing the IS (5 µg/L) where it is stirred for 5 min. This loading time provides a IS measurable signal that responds to the changes in the extraction conditions. After the IS loading, the MPSP is dried and stored (in the dark and 4 °C) in a hermetic plastic bag until being used. The IS loading protocol varies slightly for calibration and on-site sampling. In the first case, the IS solution is prepared in Milli-Q water similarly to the calibration standards. For on-site sampling, the IS solution is prepared in Milli-Q water at the same pH and conductivity of the system to be analyzed. Therefore, these parameters must be previously measured. For the calibration, the sampling device with the pre-loaded MPSP is immersed in 2 L of an aqueous standard containing the five target compounds and stirred for 10 min. Then, the magnetic membrane is detached, dried, and stored. The analytes are finally eluted in 1 mL of methanol under vortex stirring (10 min), and 5 µL of the eluate is chromatographically analyzed.

On-site sampling is developed by the direct immersion of the device into 2 L of the environmental water, which is previously taken from the swimming pool, where it is stirred for 10 min. After that, the membrane is detached, dried with a paper tissue, stored, and transported to the laboratory for the final analysis.

3. Results and discussion

In our previously reported stir membrane sampler [28], the membrane was fixed to the device using an iron washer. However, this washer generates a 2 mm stagnant boundary layer between the membrane and the bulk sample, thus restricting the mass transference and reducing the extraction kinetics. In this new research, a magnetic paper- based sorptive phase is synthesized to overcome this limitation since the MPSP can be directly fixed to the device. Also, the process becomes easier, avoiding excessive manipulation of the sorptive phase.

The MPSPs were synthesized by dip-coating a segment of filter paper in a formic solution of nylon 6 where magnetic nanoparticles were dispersed. MPSP spectrum (Fig. 2) shows a band at 1600 cm^{-1} assigned to the stretch of carboxylic moieties, and another one at 1500 cm^{-1} attributed to N–H stretch [40]. Both bands are ascribed to the polymer. Furthermore, characteristics bands of cellulose can be observed at 1000 cm^{-1} (COC stretch) and 3500 cm^{-1} (OH stretch) [33]. The absorption bands from the magnetic nanoparticles are not easily observable due to the prevalence of the cellulose background, which absorbs in the same region [39]. For comparative purposes, the spectra of nylon-6, magnetic nanoparticles, and raw paper are included in Figure S1 (supplementary material).

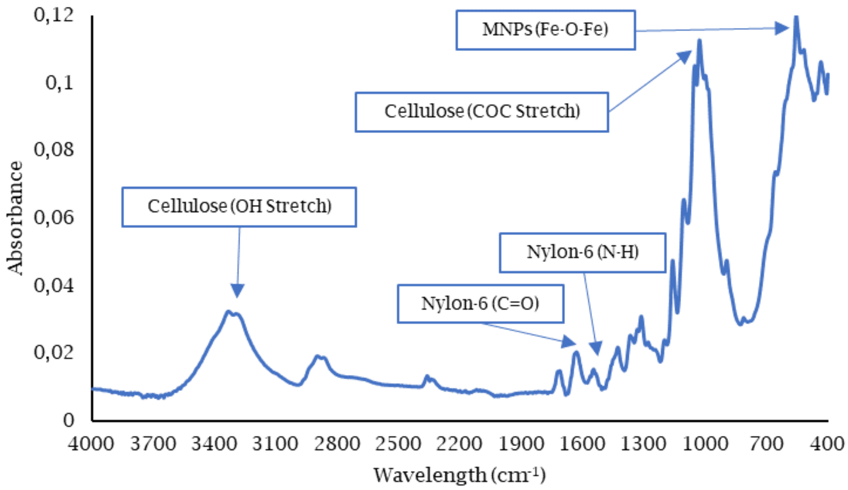

Fig. 2. Infrared spectrum of the magnetic paper-based sorptive phase. The spectra of the individual components (paper, MNPs and nylon 6) are presented in the supplementary information (Figure S1) for comparative purposes.

MPSPs present a characteristic brown color (Fig. 3a) due to the presence of the magnetic nanoparticles. The MPSPs were further studied by SEM to determine their morphology, using EDX to identify the presence of the nanoparticles. As is shown in Fig. 3b, the MPSP consists of a cellulose fiber mat containing some depositions of the magnetic polyamide composite, which are more easily observed at higher magnification (Fig. 3c). These nanocomposite deposits are similar to those previously reported by our group for magnetic polyamide composites [41]. The EDX analysis demonstrated the presence of Fe (Fig. 3d), coming from the core of the magnetic nanoparticles. A more detailed image presenting the distribution of C, O, Fe and Si, is included in the supplementary material (Figure S2). Although SEM images suggest a microscopical heterogeneity of the coating, MPSP are macroscopically homogeneous (Fig. 3a).

The size of the MPSP (circles of 20 mm in diameter) and the use of an IS minimize the effect of the microscopical heterogeneity on the analytical performance of the method.

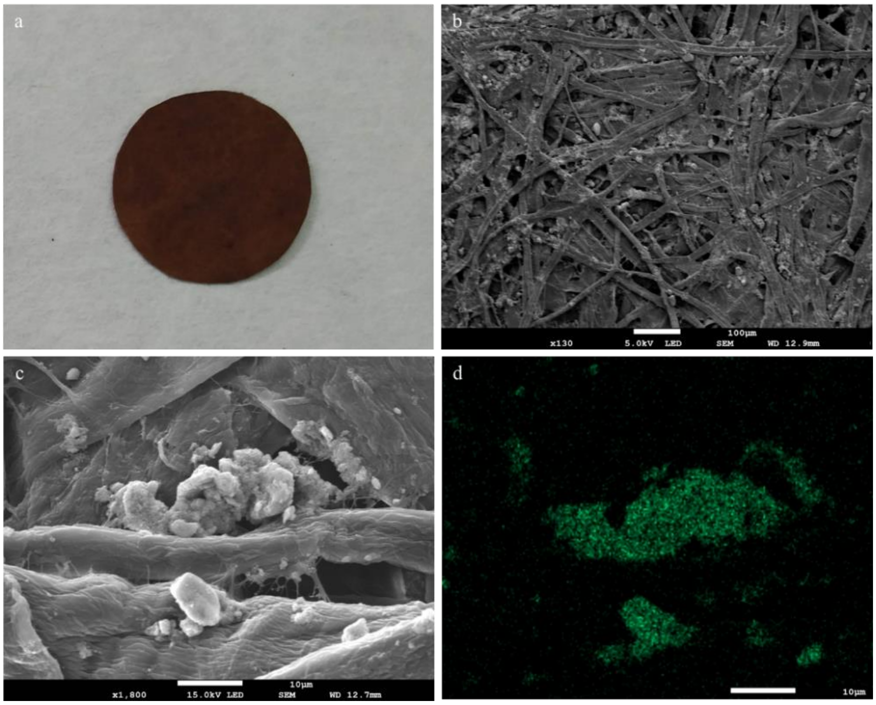

Fig. 3. Characterization of the magnetic paper-based sorptive phase. (a) picture of the sorptive phase; (b) SEM micrograph (magnification x130) of the sorptive phase where the cellulose fibers and the nanocomposite deposits are observable; (c) SEM micrograph (magnification x1800) of the sorptive phase where a close view of the nanocomposite deposits is presented; (d) EDX analysis

Once the MPSPs were synthesized, and before the optimization, the performance of different extraction devices was compared to demonstrate the initial hypothesis. The results can be seen in Fig. 4. The previously reported device (denoted as PRD in Fig. 4 and represented in Fig. 4i) provided the lower signals. A first prototype (denoted as FP in Fig. 4 and represented in Fig. 4ii), where the washer was eliminated, provided a clear improvement of the signal (by a factor of 1.3–1.9, depending on the analyte) due to the elimination of the stagnant boundary layer. Finally, a new device (denoted as ND and shown in Fig. 4iii) was designed, including an improved stirring blade for a better mass transference.

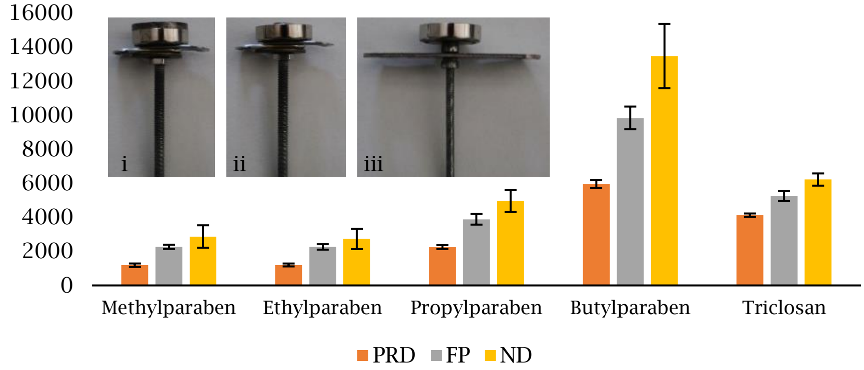

Fig. 4. Initial comparison of the performance of different sampling devices. The results are presented as bars, while a picture of each device is included for a better explanation. (i) PRD: Previously reported device, (ii) FP: First prototype, (iii) ND: New device.

3.1. Optimization of the MPSP synthesis

MPSP synthesis was optimized considering two main variables, namely: the type of polymer and the number of dips. Considering the structure of the analytes and our previous experience, two polymers (nylon-6 and polystyrene) were initially studied. MPSPs were synthesized using two consecutive dips into a solution containing the polymer and the same amount of magnetic nanoparticles. The polymer concentration in the precursor solution was fixed to the 3 % w/v using formic acid and chloroform as the solvent for nylon-6 and polystyrene solubilization, respectively. The results demonstrated that the nylon-6 MPSP provides better extraction results than polystyrene MPSP, as the analytical signals were 2.3–4.7 better depending on the analyte. H-bonding (between amide groups) and hydrophobic forces (between the hydrocarbon chains) are the main interactions behind the stacking of the polyamide chains. Therefore, polyamides can isolate compounds based on these interactions. The analytes present H-bond donors (-OH) and acceptors (C=O, -O-) in their structures, and they also can interact with the polymeric backbone by hydrophobic interactions. A combination of these interaction is responsible for the efficient extraction of the target analytes.

Once nylon-6 was selected as extractant polymer, the dipping number was evaluated in the range 1–5. As it is shown in Fig. 5, the analytical signal increases up to 3 dips, remaining constant or slightly decreasing for higher dips depending on the analyte. This behavior can be ascribed to the coating process. At lower dips, the intricated superficial area of the cellulose fibers is fully exploited, but at higher dips these fibers can be completed covered, making the surface smother. This smoothing reduces the effective contact surface. According to the results, 3 dips were selected as the optimum value.

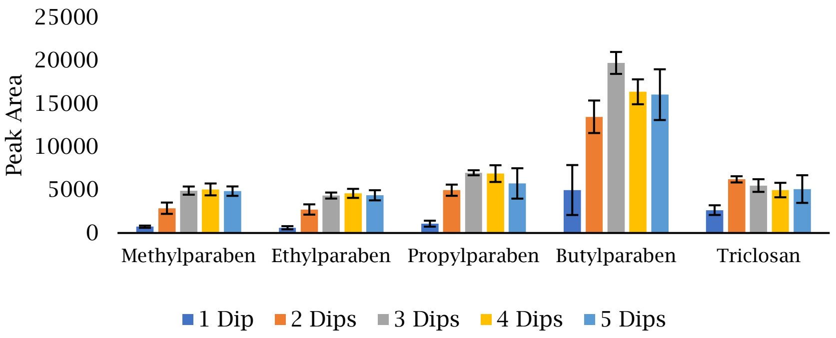

Fig. 5. Effect of the number of dips on the extraction performance of the sorptive phase.

3.2. Optimization of the extraction

The influence of the sample volume on the extraction performance is crucial to define the application strategy of the sampler. If there is a strong dependence of the analytical signal with the sample volume, the sampler can only be applied on-site, dividing into different and consecutive steps the sampling and extraction. If this influence is not significant, the sampler can be on-site applied, combining sampling and extraction in the same step. The influence of the sample volume in the peak area is shown in Fig. 6. As can be seen, the signal increases but remains almost constant for high sample volumes. In this region, the signal is only dependent on the analyte concentration, opening the door to the direct immersion of the sampler into the environmental system. However, further studies should be developed at higher sample volumes sampling and extraction are split in separate steps, 2 L was selected as working volume.

Finally, the sampling/extraction time was studied in the range from 5 to 20 min. Figure S3 indicates that 20 min provides better results. However, 10 min was finally selected as extraction time to make sampling faster and increase the sample throughput.

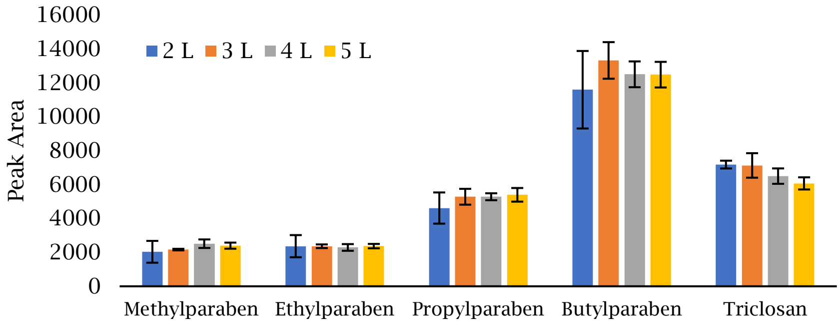

Fig. 6. Effect of the sample volume on the extraction of the target analytes.

3.3. Analytical characterization of the method and application to samples

The analytical characterization of the method is presented in Table 1. The calibration curves for the target analytes were constructed at 6 different levels of concentration. Although the data for the 4 lower concentration levels fit well to a linear model, the curve starts to flatten at higher concentration. This fact can be ascribed to the reduction of sorptive sites in the membrane when the concentration of the target analytes is increased (especially if the high sampling volume is considered). For this reason, a double logarithm model, which is presented in Figure S4, was selected, representing the logarithm of the analyte/internal standard ratio against the logarithm of the concentration.

Table 1. Analytical figures of merit of the proposed method for determining parabens and triclosan in swimming pool water samples.

Analyte	LOD (µg/L)	LOQ (µg/L)	R^2	RSD intraday, n =5 (%)	Accuracy (% relative recovery)
Methylparaben	0.1	0.3	0.994	8.0	97 ± 8
Ethylparaben	0.08	0.26	0.992	7.3	94 ± 7
Propylparaben	0.1	0.3	0.991	6.7	98 ± 6
Butylparaben	0.07	0.23	0.996	4.9	88 ± 4
Triclosan	0.09	0.3	0.988	6.9	94 ± 6

The limits of detection (LOD) and quantification (LOQ) were calculated for a signal to noise ratio of 3 and 10, respectively. The LODs values range from

0.07 µg/L (butylparaben) to 0.1 µg/L (methylparaben and propylparaben). The precision was calculated for 5 independent extractions at 5 µg/L, resulting in relative standard deviations better than 8%.

The accuracy was evaluated by spiking a blank swimming pool sample with the target analytes at 0.75 µg/L providing values in the interval from 88 to 98%. For this study, the pH and I of the sample was preliminary measured and the IS was preloaded in the MPSP using an aqueous standard with the same parameters.

Several samples were analyzed by the proposed method, only one of them resulting positive. In this sample, the presence (below the LOQ) of methylparaben and propylparaben was identified. The MRM chromatogram for the positive sample and the standards is shown in Figure S5.

The analytical figures of merit of the proposed method were compared with other approaches previously reported in the literature (Table 2) [42-59] Although it does not provide the best sensitivity level, the proposed method is simple, consumes fewer reagents (some GC-MS approaches require a derivatization) and solvents (SPE requires conditioning and elution solvent in the large mL range), and presents a very good precision. In terms of relative recoveries, it competes with the most accurate methods. However, the main relevant feature of the proposed method is its on-site applicability. This aspect simplifies the whole analytical procedure as only the sorbents, and not the samples, are transported to the laboratory for their final analysis.

4. Conclusions

The complexity of environmental analysis requires robust and efficient samplers just to be able to obtain representative samples while reaching the sensitivity levels required. Also, the portability of the device and simplification of the samples' delivery to the laboratory, preserving their integrity is also needed. The sampler device presented in this research fulfills all these requirements, being the simplicity, low-cost, and robustness its main favorable features. Also, the MSPS can be tailored to the specific family of compounds to be determined by the proper selection of the polymeric phase. The sampler has improved the limitations presented by previous prototypes by including additional elements that facilitate the mass transference of the analytes from the matrix to the sorbent phase. The geometry of paper-based membranes can be easily adapted to other sampler devices.

Table 2. Comparison of the present work with other counterpart reported to solve the same analytical problem.

Reference	Analytes	Matrix	Extraction	Instrument	Sample volume (mL)	LOD (ng/L)	RSD (%)	Accuracy (%)
[42]	MPb, EPb, PPb, BPb and TCS	Tap, river and well waters	RDSE, deriv	GC-MS	20	40-110	<12	-
[43]	EPb, BPb and TCS	Tap, municipal, ground and sewage waters	FPSE	GC-MS	10	8-21	<4.1	94.26-98.89
[44]	MPb, EPb, PPb, BPb and TCS	River water	SPE	UPLC-MS/MS	1000	0.009-0.03	-	94-103
[45]	EPb, PPb and TCS	Lake and river waters	SPE	HPLC-MS/MS	500	8000-30300	<33.67	54.49-92.25
[46]	MPb, EPb, PPb, and TCS	River and waste waters	SPE	UPLC-MS/MS	1000 (river water), 20 (influent) 500 (efluent)	0.17-45	<20.3	82.5-113
[47]	MPb, EPb, PPb and TCS	River water	SPE, deriv	GC-MS/MS	1000	0.9-14	<4.6	56.8-113.5
[48]	BPb and TCS	Sea water	LOV-µSPE	HPLC-MS/MS	5	0.5-0.6	<5.8	97-107
[49]	MPb, EPb, PPb and BPb	Sea and swimming pool waters	MNP-µSPE, deriv	GC-MS	30	23.2–86.1	<7.1	96-106
[50]	MPb, EPb, PPb, BPb and TCS	Waste, river, and swimming pool waters	SPME, in situ deriv	GC-MS/MS	10	<17	<12	>82
[51]	TCS	Tap, lake and river waters	DLLME-SFO	HPLC-UV	5	100	4.1	84-116
[51]	TCS	Tap, lake and river waters	DLLME-SFO	LC-MS/MS	5	2	6.2	
[52]	MPb, EPb, PPb, BPb and TCS	Tap, well, pond, swimming pool, river and waste waters	SPE, deriv	GC-MS	100	0.01-0.08	<6.9	90-101

Table 2 continue. Comparison of the present work with other counterpart reported to solve the same analytical problem.

Reference	Analytes	Matrix	Extraction	Instrument	Sample volume (mL)	LOD (ng/L)	RSD (%)	Accuracy (%)
[53]	TCS	Tap and surface waters	HF-LPME, deriv	GC-MS	15	20	6.9	83.6-114.1
[54]	TCS	Tap and waste waters	IL-DLLME	HPLC-MS/MS	5	580	8.8	70-103
[55]	MPb, EPb, PPb and BPb	River water	SPE, deriv	GC-MS	1000	0.8-4.2	11	89-104
[56]	TCS	Surface and waste waters	SPE, deriv	GC-MS	100	0.4	2-6	95
[57]	TCS	Surface waters	SPE	HPLC-DAD	1000	40	<2	97
[58]	MPb, EPb, PPb and BPb	Tiver, reservoir and sea waters	HF-LPME	HPLC-UV	3.5	20-270	<17	
[59]	TCS	River and waste waters	SPME	HPLC-UV	10	1	7	91-105
This work	MPb, EPb, PPb, BPb and TCS	Swimming pool water	SME	HPLC-MS/MS	2000	70-100	<8	88-98

Analytes: Methylparaben (MPb), Ethylparaben (EPb), Propylparaben (PPb), Butylparaben (BPb) and triclosan (TCS).
Extraction: Rotating disk sorptive extraction (RDSE); Fabric phase sorptive extraction (FPSE); Solid phase extraction (SPE); Lab-on-valve micro-solid phase extraction (LOV-µSPE); Magnetic micro-solid phase extraction (MNP-µSPE); Solid phase microextraction (SPME); Dispersive liquid-liquid microextraction by solidification floating organic drop (DLLME-SFO); Hollow fiber liquid phase microextraction (HF-LPME); Ionic liquid based dispersive liquid-liquid microextraction (IL-DLLME); Stir membrane extraction (SME); derivatization (deriv).
Instruments: Gas chromatography (GC), liquid chromatography (LC); ultra-performance liquid chromatography (UPLC); Mass spectrometry (MS); UV detection (UV); Diode array detector (DAD).
LOD, limit of detection.
RSD, relative standard deviation.

Credit author statement

F. A. Casado Carmona, conceptualization, investigation, data treatment. R. Lucena, conceptualization; project organization, funding acquisition, writing - review & editing. S. Cárdenas, supervision, funding acquisition, writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2021.122217.

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Supplementary data

1. Mass spectrometry parameters

The determination of the analytes was carried out by LC-MS/MS as it was described in the main text. The following table (Table S1) shows the multiple reaction monitoring (MRM) parameters used for the detection and determination of the parabens and triclosan. Furthermore, in Table S1 it could be seen the parameters for the internal standard.

Table S1. Mass spectrometry parameters for parabens, triclosan, and internal standard.

Compound	Precursor ion (m/z)	Fragmentor voltage (V)	Product ion (m/z)	Collision energy (V)	Quantitation transition
Methylparaben	151	96	136 92.1	14 22	151→92.1
Ethylparaben	165.1	96	137 92.1	14 22	165.1→92.1
Propylparaben	179.1	114	136 92.1	14 26	179.1→92.1
Butylparaben	193	115	136 92.1	15 25	193→92.1
Triclosan	286.8	85	35.2	5	286.8→35.2
Triclosan-d_3	289.9	90	35.1	8	289.9→35.1

2. Infrared spectroscopy

Infrared were obtained in a Bruker Tensor37 FT-IR spectrometer, equipped with a diamond ATR cell with a circular surface of 3 mm diameter and three internal reflections. A Deuterated Triglycine Sulfate (DTGS) detector was used for spectra acquisition between 4000 and 400 cm^{-1} at a 4 cm^{-1} resolution with 64 coadded scans each. Data collection was made using OPUS software (Bruker, Ettligen, Germany). The spectra of raw paper, nylon 6 and MNPs are shown in Figure S1.

3. SEM/EDX study

Scanning electronic microscopy (SEM) micrographs were obtained using a JEOL JSM 7800F microscope at the Central Service for Research Support (SCAI) of the University of Córdoba. Figure S2 shows a micrograph of the magnetic membrane and the distribution of C, O, Fe and Si measured by EDX.

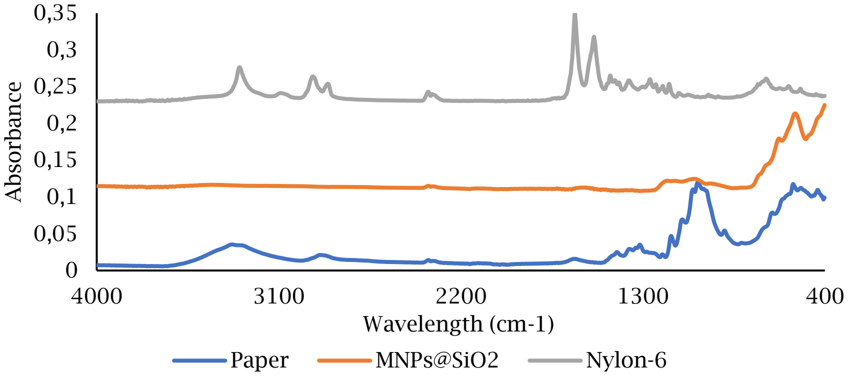

Figure S1. Normalized spectra of raw paper, silica coated magnetic nanoparticles and nylon6. The spectrum of the resulting composite is presented in the main text (Figure 2).

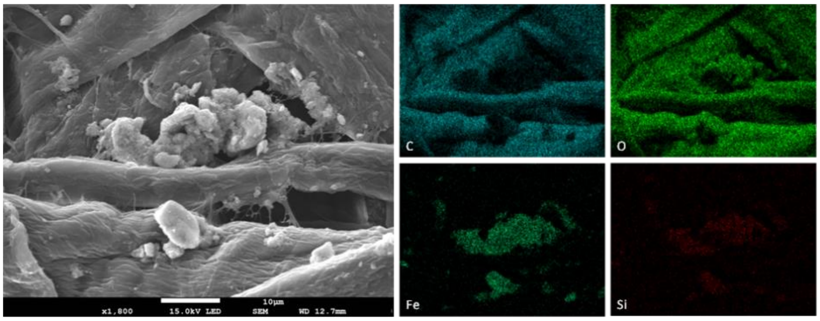

Figure S2. SEM micrograph (left panel) and C, O, Fe and Si distributions (right panels) measured by EDX.

4. Effect of sampling time

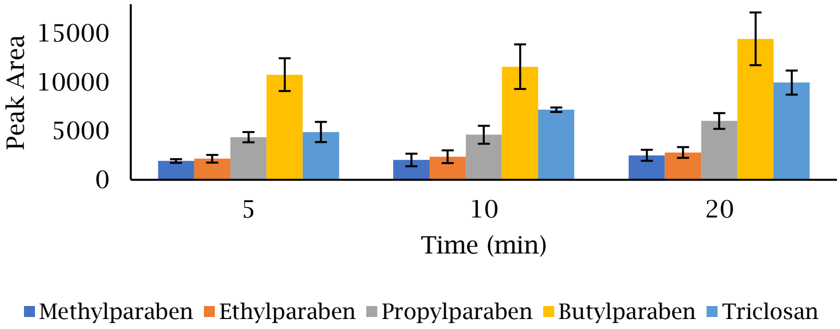

Figure S3. Effect of the sampling time on the extraction of the target analytes.

5. Calibration models

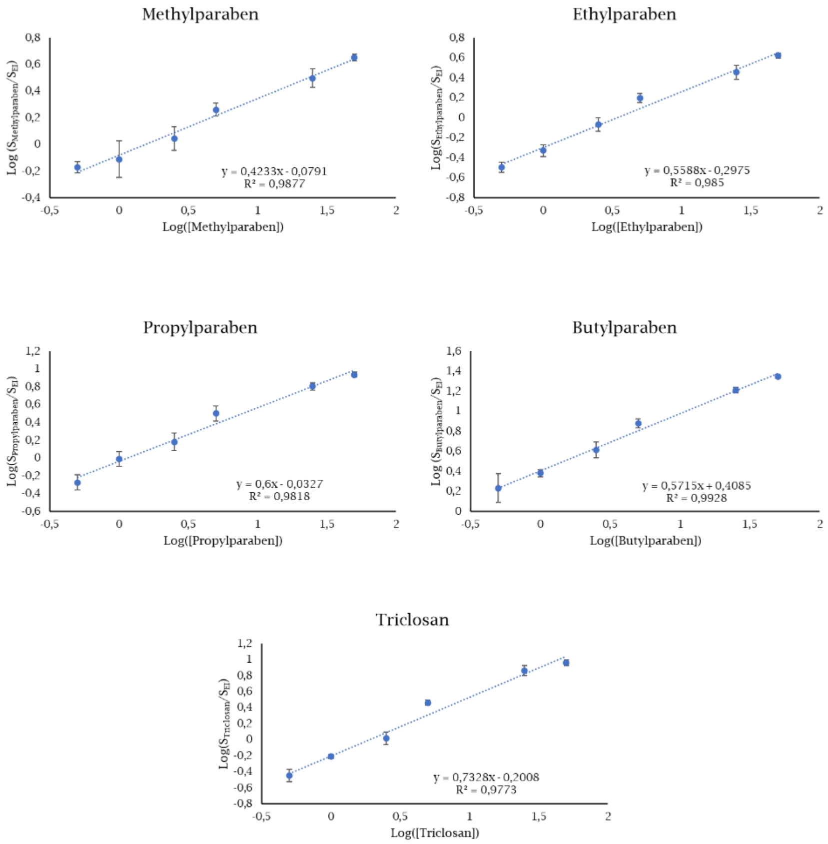

Figure S4. Calibration models for the target analytes.

6. Determination of target analytes in real samples

Table S2. Determination of parabens and triclosan in swimming pool samples.

Sample	MPb	EPb	PPb	BPb	TCS
Swimming pool 1	-	-	-	-	-
Swimming pool 2	Detected	-	Detected	-	-
Swimming pool 3	-	-	-	-	-

Methylparaben (MPb), Ethylparaben (EPb), Propylparaben (PPb), Butylparaben (BPb) and triclosan (TCS).

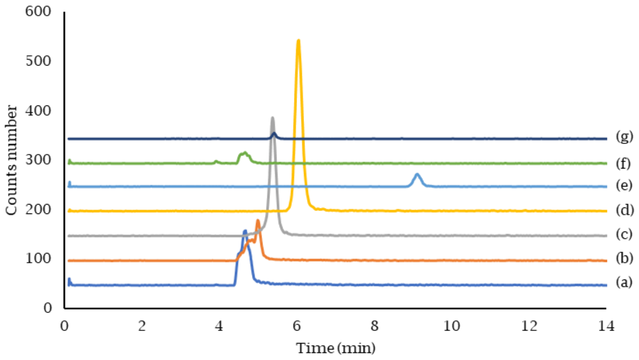

Figure S5. MRM chromatograms obtained for standards (a-e) and the positive samples (f-g). (a,f) Methylparaben transition; (b) ethylparaben transition; (c,g) propylparaben transition;(d) butylparaben transition; and (e) triclosan transition.

CAPÍTULO 4

PORTABLE STIRRING DEVICE FOR THE ON-SITE EXTRACTION OF ENVIRONMENTAL WATERS USING MAGNETIC HYDROPHILIC-LIPOPHILIC BALANCE TAPE

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Portable stirring device for the on-site extraction of environmental waters using magnetic hydrophilic-lipophilic balance tape

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The spatial heterogeneity of environmental systems makes sampling at multiple locations crucial to provide complete and representative information. The on-site application of an extraction technique simplifies the sampling logistics, increasing sample integrity during transportation and storage. This article presents a portable, simple, and low-cost device capable of performing the simultaneous on-site extraction of several environmental water samples. The device consists of a small electric motor integrated into the plastic cap of a conventional glass bottle and operated with a portable battery. The electric motor provides stirring to a novel magnetic sorptive phase based on the deposition of hydrophilic-lipophilic balance (HLB) particles over a magnetic tape. The use of open technology makes the device globally affordable. In this first approach, the isolation and preconcentration of atrazine and simazine have been selected as proof of concept. Using an internal standard made unnecessary the adjustment of the ionic strength before the extraction, thus simplifying the analytical procedure. Under the optimum conditions and using direct infusion mass spectrometry as the instrumental technique, detection limits as low as 15 ng/L were obtained. The precision calculated at three different levels was better than 8.3 %. The accuracy, calculated with spiked samples, indicates the applicability of the approach for environmental water analysis.

Keywords: On-site extraction, Portable, Environmental waters, Magnetic sorptive phases, Simazine, Atrazine.

1. Introduction

On-site extraction techniques face two main challenges found in environmental analysis (viz. the heterogeneous distribution of the pollutants and their low concentration in environmental compartments), minimizing their effects on the analytical results [1]. On-site extraction simplifies the logistics since only the sorptive phases and not the whole samples are transported to the laboratory. Also, they protect the sample integrity, reducing cross-contamination and analytes losses during transportation and storage [2]. To be on-site applied, an extraction procedure should be miniaturized, portable, easy to handle, simple (low requirements of energy, reagents, and apparatus), rapid (when short-term information is required), and reproducible manufactured. Microextraction techniques fulfill most of these criteria [3,4]. Although liquid-phase microextraction techniques have been on-site applied in environmental analysis [5,6], the use of solid traps is preferred as they increase the stability of the analytes reducing losses by evaporation, diffusion, or reactivity.

In most techniques, the amount of extracted analyte depends directly on the sample volume. Splitting sampling and extraction into consecutive but different steps [7,8] or using special portable devices [9–12] (syringes, pumps) to control the volume during the extraction, are the two main strategies in this scenario. However, under defined circumstances [13], the extraction yield in solid-phase microextraction (SPME) is independent of the sample volume allowing the integration of sampling and extraction in a sole step [14]. The versatility and small size of SPME sorptive phases have allowed the design of drone-based samplers in environmental analysis. Grandy et al. recently proposed a cheap aerial drone modified with a polystyrene foam base for better buoyancy. The drone transported a thin film sorptive phase, consisting of hydrophilic-lipophilic balance (HLB) particles, deployed by an elegant design of floaters and sinkers [15].

United Nations has defined Clean Water as one of the primary goals to be globally achieved by 2030 [16]. Global analytical strategies necessarily rely on the use of affordable (simple and low cost) devices. The use of open technologies like 3D-printing [17–19], microcontrollers (Arduino, Raspberry) [20–23], drone-based [15,24,25], portable [26] and cell phone-based [27–31] platforms is a revolutionary approach for the democratization [32,33] of our discipline. It is also in line with a socially responsible view of science [34,35]. In on-site extraction procedures, sample stirring is essential to promote the diffusion of the analytes towards the sorptive phase. However, these devices are usually cost-driving elements. Although portable magnetic plates are commercially available, they have been scarcely used in on-site extractions. Portable stirrers [36,37] and drills [14,38–40] have been preferred to design on-site devices. In most cases, the stirring element is integrated with the sorptive phase for a more compact design. The price of the stirrers and drills does not afford to build several devices making multisampling more complicated.

In this article, a simple and cheap (less than 1$) device is proposed as an affordable alternative to the reported approaches. The device consists of a small electric motor integrated into the plastic cap of a conventional glass bottle and operated with a portable battery. The electric motor provides stirring to a novel magnetic sorptive phase based on the deposition of HLB particles over a magnetic tape. The low cost of the glass bottles, which have been reported as extraction vessels in on-site extractions [41], maintains the cost effectiveness of the approach. The determination of atrazine and simazine has been selected as proof-of-concept due to their global use as pesticides, especially in developing countries. Both compounds belong to the triazine family, which is considered as potential human carcinogens. Also, simazine and related compounds presents hormone disrupting effects [42].

2. Experimental section

2.1. Chemicals

The reagents, including the analytes and the internal standard (IS), were provided by Sigma Aldrich (Madrid, Spain). Methanolic stock solutions of the analytes (atrazine and simazine) and the internal standard (atrazine-d5) were made at a concentration of 1 g/L and stored in the fridge. Working solutions were built by diluting the stocks in Milli-Q water (Millipore Corp., Madrid, Spain) or methanol, depending on the final use.

Hydrophilic-lipophilic balance (HLB) sorbent (50–70 µm of particle size, 80–200 Å of pore size) was used to extract the target analytes. The sorbent was purchased from Sigma Aldrich. A glass bottle was used as the extraction vessel. Commercial bottles, like those used to market 2.5 L of solvents, were selected for simplicity and availability. These bottles have a maximum storage volume of 2.88 L.

Environmental waters were sampled at five different locations (two creeks and three wells), and they were processed as it is described further on.

2.2. Instrumentation

Direct infusion mass spectrometry analyses were performed on an Agilent 1260 Infinity liquid chromatography (LC) system (Agilent, Palo Alto, CA, USA). A guard column (0.2 µm filter, 2.1 mm) was used to protect the mass spectrometry (MS) source from potential particles. 5 µL of the standards or the sample extracts were directly injected in the carrier (0.1% of formic acid in Milli-Q water), maintaining the flow rate at 0.2 mL/min. An Agilent 6420 Triple Quadrupole MS with an electrospray source was used for the determination of the target compounds. The instrumental parameters are summarized in Table S1.

Scanning electronic microscopy (SEM) studies were developed in a JEOL JSM 7800F microscope at the Central Service for Research Support of the University of Córdoba.

2.3. Preparation of the magnetic hydrophilic-lipophilic balance tape

Self-adhesive ferrous tape (13 × 10 mm) (Supermagnete, Gottmadingen, Germany) was used for supporting the extractant material (Fig. 1a). The tape was covered with a double side adhesive tape (Milan, Mont-Ras, Spain) (Fig. 1b) to make its surface stickier. The modified tape was then introduced and shaken in a vial containing HLB particles. 3 mg of HLB was adhered to the sticky surface (Fig. 1c). Finally, the resulting magnetic HLB sorptive phase was shaken outside the vial to remove HLB excess. The color of the tape changes from black (Fig. 1b) to grey blue (Fig. 1c) due to the efficient attachment of the HLB particles (white powder over a black substrate).

Due to the low price of the phases, new sorptive phases were used for each extraction. This approach also avoids cross-contamination between samples.

2.4. Portable extraction device

The device (patent pending), which can be seen in Fig. 2a, was designed as follows. A small electric motor (DollaTek, Hong Kong, China), which operates in

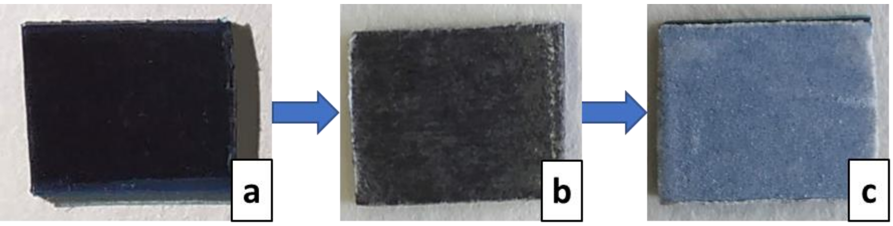

Fig. 1. a) Ferrous tape self-adhesive used as support. b) Ferrous tape self-adhesive covered with double side adhesive tape. c) Magnetic HLB sorptive phase.

the range from 3 to 6 V, was integrated into a glass bottle's cap (Fig. 2b). The electric motor was attached to a NdFeB countersunk pot magnet (Supermagnete, Gottmadingen, Germany) by means of a 10 cm in length screw using a nut (Fig. 2c). A small blade is also added for better agitation. The HLB sorptive phase is magnetically fixed to the countersunk pot magnet. Finally, this extraction device is introduced on a glass bottle containing the sample to isolate the analytes (Fig. 2d). The electric motor, which is powered with a portable supply (5 V), provides stirring to the sorptive phase, improving the mass transference of the analyte.

Fig. S1 shows how the screw is attached to the small electric motor.

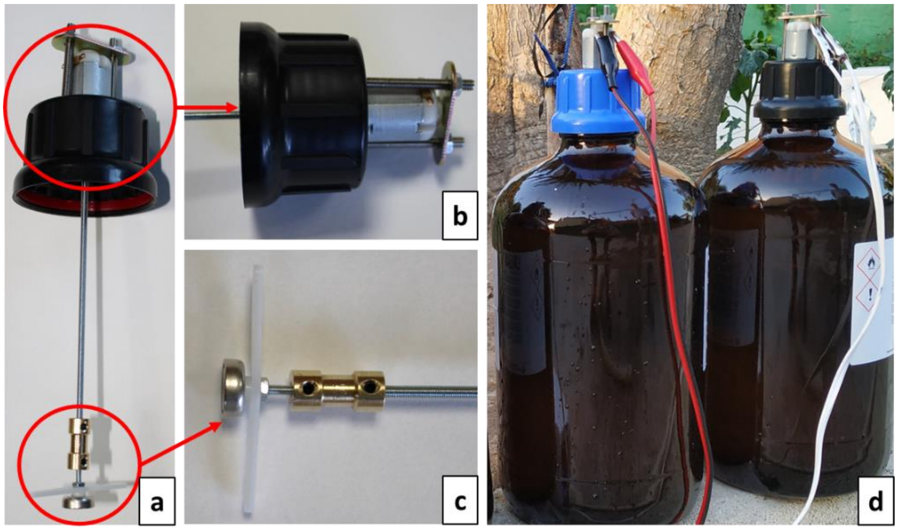

Fig. 2. a) Extraction device. b) Coupling of the electric motor with the cap. c) Core of the extraction device. d) Extraction device during sampling procedure.

2.5. Analytical procedure

For calibration purposes, the extraction device is submerged in 2.5 L of an aqueous standard containing the analytes at a defined concentration and the IS at 0.5 µg/L. Then, the extraction device is switched on for 30 min to isolate the analytes and the IS. After this step, the sorptive phase is detached, dried using a tissue, and stored until its analysis. Before MS analysis, the sorptive phase is eluted using 500 µL of methanol under mechanical stirring for 10 min, and 5 µL of the eluate is directly infused in the MS. The solvent type and volume were selected according to our recent experience. Methanol is compatible with the direct infusion MS and the volume is enough to completely cover the tape during the elution.

For on-site extraction, 2.5 L of the environmental water is sampled, introduced in the glass bottle and spiked with the IS (final concentration of 0.5 µg/L). After that, the extraction device is introduced into the sample and activated for 30 min. The adjustment of the pH, ionic strength, and temperature of the sample is not required before the extraction. Finally, the sorptive phase is recovered, dried using a tissue, and stored in an airtight plastic bag until its final analysis in the laboratory. Once in the laboratory, the sorptive phases are stored in the fridge or immediately eluted for analysis.

3. Results and discussion

In 2019, our group reported a portable stir membrane device for onsite sampling and extraction [39]. The prototype used a countersunk pot magnet, connected to a portable drill for stirring, as the central element. The sorptive phase, a commercial nylon membrane, was fastened to the magnet with a metallic ring. The ring played an essential role, but it created an almost stagnant layer over the membrane, limiting the diffusion of the analytes to the sorptive phase. To avoid this limitation, we have recently proposed using magnetic paper-based sorptive phases in this device [40]. As the metallic ring is no longer needed to attach the sorptive phase (it is magnetically fixed), the diffusion of the analytes is improved. The two prototypes present two main challenges. On the one hand, the price of the electric drill (ca. 40 $) makes the simultaneous extraction of multiple samples unaffordable. On the other hand, both used nylon which is not the standard sorptive phase in environmental analysis. The prototype presented in this article goes further as it uses a small electric motor (ca. 0.8 $) to design each extraction unit reducing the cost 50 times. Also, it uses HLB particles as actual sorbent. HLB is extensively applied in environmental water analysis [43] thanks to its wide polarity window.

The use of particulate sorbents in a flat support is not an easy task. Most times, it has been accomplished using a chemical binder that mechanically stabilizes the particles, maintaining them exposed to the sample. Here, we propose the use of self-adhesive ferrous tape as a valuable alternative. Its magnetic core should allow an easy attachment to the magnet, while the adhesive surface should retain the HLB particles during the extraction. Although the first premise was confirmed, the adhesive capacity was deficient. For making the surface of the tape stickier, double-sided adhesive tape was used to cover the magnetic tape. A SEM micrograph of the modified magnetic tape coated with HLB particles is shown in Fig. 3. The average particle size, 58.8 µm, matches with the data of the supplier. The presence of the HLB particles increased the analytical signal 5 and 10 times for atrazine and simazine, respectively compared to the sticky tape.

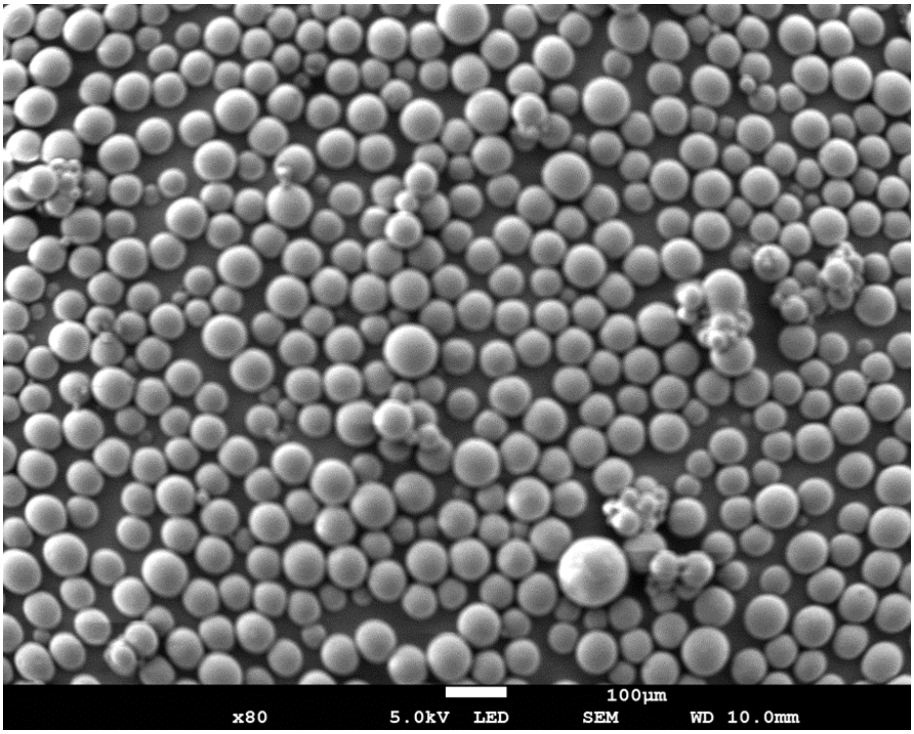

Fig. 3. SEM micrograph of the extractant phase.

This work aims to develop a portable, easy to handle, and cheap device to be on-site applied. For this reason, its integration in the cap of a standard glass bottle was considered. The concept is flexible enough to be adapted to other containers. According to the theory, the analytical signal would increase with the sample volume as the total amount of analyte would be higher. However, we avoid exploiting the maximum capacity of the bottle (2.88 L) to minimize sample projections during the stirring. For this reason, 2.5 L was selected as initial threshold.

Once the container is selected, the length of the screw remains the primary variable of design. This length defines the immersion depth of the device and affects its stirring ability. The length was studied in the range from 8 to 12 cm. Shorter lengths do not guarantee the appropriate immersion of the device, while longer lengths induce an excessive axis pitch, thus affecting the integrity and durability of the electric motors. The results, shown in Fig. S2, indicated that 10 cm provided the best results.

3.1. Study of the extraction workflow

The expeditiousness of an extraction technique is relevant to provide a high sample throughput. The extraction time was studied in the interval 5–60 min using 2.5 L of aqueous standards containing the analytes at 5 μg/L. As is shown in Fig. 4, the highest signals are obtained for 60 min. However, 30 min was selected since it permits double the sampling rate also providing a better precision.

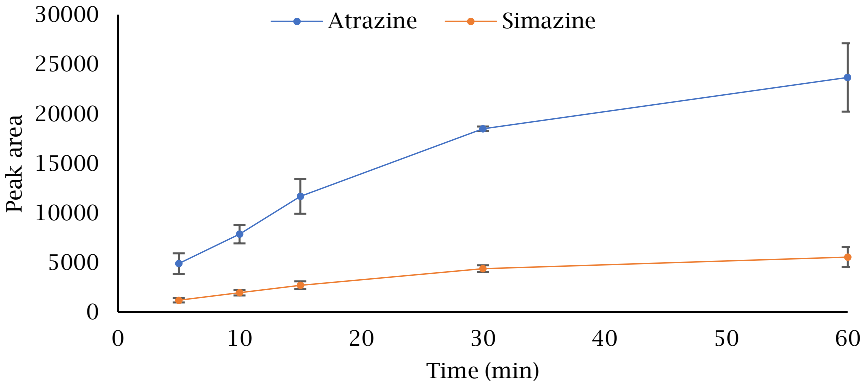

Fig. 3. Time extraction profile of atrazine and simazine.

The simplicity, understood as the reduction of steps number, is relevant in on-site approaches. The effect of the sample volume was studied in the interval 2.25–2.75 L to evaluate if an accurate sample volume would be required. As expected, the signal varies in the interval, and they cannot be corrected using the IS. Therefore, an accurate volume of 2.5 L is recommended to avoid a negative effect on the precision.

The adjustment of the pH and ionic strength and the water temperature are key factors in on-site extractions. The pH is different for each environmental water. Seawater pH is commonly in the 7.5–8.5 interval depending on the salinity [44]. Natural waters typically present a pH in the 6–8 interval. In particular, the reported values for the Guadalquivir river basin are in the range from 7.7 to 8.2 [45]. The polarity of the analytes (log K_{ow}) is not affected by the pH in the interval 5–11 since the analytes in this range remain neutral (see Fig. S3). The log K_{ow} in this interval for atrazine and simazine are 2.2 and 1.78, respectively. Therefore, the pH adjustment is not mandatory, thus simplifying the extraction procedure. However, the sample pH measurement with an indicator paper is highly recommended to assess this point.

The ionic strength can affect the extraction rate. According to US Environmental Protection Agency, the conductivity of rivers in the US ranges from 50 to 1500 μmhos/cm [46]. The conductivity was studied in a wide interval (0.75–2460 μΩ/cm) using 2.5 L of aqueous standards containing the analytes and the IS at 5 μg/L. As is shown in Fig. 5i, the absolute signal of the analytes is affected by the sample conductivity. However, the IS (Fig. 5ii) corrects this effect. This fact permits simplifying the workflow, making the ionic strength adjustment not necessary.

Analyte extraction is an exothermic process, and it is affected by the sample temperature. This fact is especially pertinent in on-site extraction, where the temperature cannot be easily controlled. The temperature was evaluated at 6.2, 17.8, and 26 °C. The absolute signal for the analytes varied slightly with the temperature (the relative standard deviation considering the triplicate at the 3 levels was 19.7 % and 16 %, for atrazine and simazine, respectively). However, the internal standard corrects the influence reducing the variability to 3.9 % (atrazine) and 2.5 % (simazine).

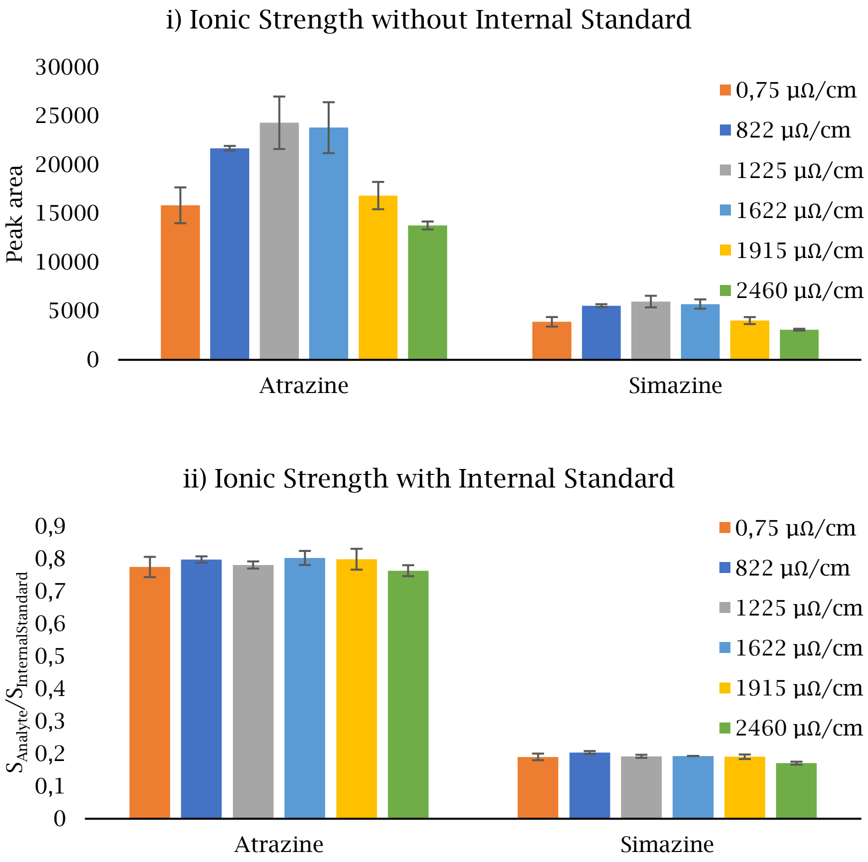

Fig. 5. i) Effect of the conductivity on the absolute signal (peak area) of the analytes. ii) Internal standard's normalization in the effect of the ionic strength on the sampling procedure.

3.2. Stability of the analytes during the storage

In on-site environmental extractions, different locations are sampled every day, and the resulting sorptive phases are transported to the laboratory, where they are stored until their analysis. The stability of the analytes during the storage is crucial to guarantee the representativeness of the results. For this reason, 24 independent sorptive phases were prepared and incubated with aqueous standards containing the analytes and the IS. After the extractions, which were performed on the same day, the sorptive phases were dried with a tissue. Three phases were immediately eluted and analyzed, while the rest were stored in the fridge. Every two days, three phases were taken from the fridge, eluted, and analyzed. Fig. 6 shows the evolution of the normalized signals for both analytes during 16 consecutive days. The results show that the compounds are stable during the interval studied. Normalized signals, instead of absolute signals, were used to correct the inter-day irreproducibility of the ESI source.

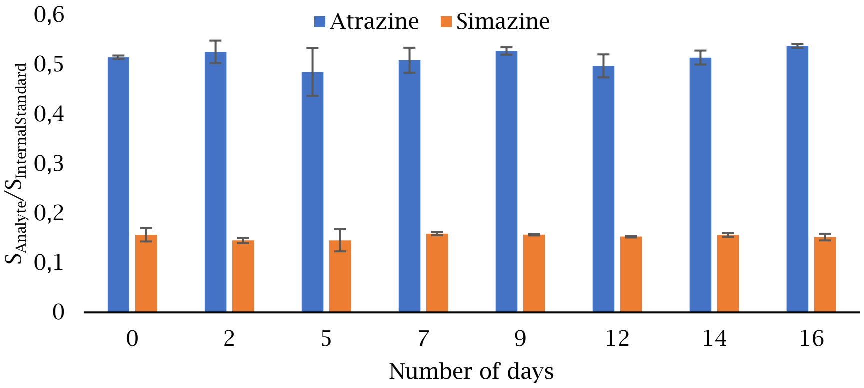

Fig. 6. Evaluation of the stability of the analytes in the extractant phase.

3.3. Analytical features and application to samples

Working under the optimum conditions, the proposed method was evaluated in terms of linearity, sensitivity, precision, and accuracy. The analytical figures are summarized in Table 1. The calibration models (Fig. S4) were constructed by processing in triplicate aqueous solutions containing the analytes at defined concentrations and maintaining the concentration of IS fixed at 0.5 µg/L. The limit of quantification (LOQ), defined for a signal-to-noise ratio of 10, was 50 ng/L for both analytes. Linearity (R2 > 0.9995) was maintained between the LOQ and 25000 ng/L. The precision was calculated at three concentration levels (50, 500 and 10000 ng/L), for 5 independent extractions at each concentration level. The values of the precision expressed as relative standard deviation (RSD) were always lower than 8.3 %. Finally, the accuracy was evaluated by spiking a blank creek sample at three different concentration levels. These results were in the range from 70 to 121 %. The proposed method was used for the on-site extraction of five creek and well samples, only two resulting positive for simazine. The concentrations found in the positive samples are presented in Table S2. Fig. S5 shows the chronogram for a creek sample.

Table 2 compares the performance of the proposed method with other reported for the same analytical problem [47–54]. The sensitivity levels are overpassed by those approaches using an exhaustive extraction (solid phase extraction, SPE) or an enhanced analyte-sorbent interaction (dispersive SPE). The precision and accuracy data are competitive with their counterparts. The main advantages of the proposed alternative rely on eco-friendly character (low consumption of reagents and solvents), its on-site application, and the high sample throughput that the direct infusion MS provides.

Table 1. Analytical figures of merit of the proposed method for the determination of triazines in environmental water samples.

Analyte	LOD (ng/L)	LOQ (ng/L)	R^2	Linear range (ng/L)
Atrazine	15	50	0.9995	LOQ - 25000
Simazine	15	50	0.9996	LOQ - 25000

Analyte	RSD intra-day, n=5 (%)			Accuracy (% Relative Recovery)		
	50 ng/L	500 ng/L	10000 ng/L	50 ng/L	500 ng/L	10000 ng/L
Atrazine	5.9	3.8	2.9	110 ± 6	90 ± 3	71 ± 3
Simazine	8.3	5.1	2.8	121 ± 10	99 ± 5	70 ± 2

4. Conclusions

The integration of sampling and analyte extraction in a single device is one of the most relevant trends in environmental analytical chemistry. Among the advantages this approach provides, the enhancement of the representativeness of the results can be highlighted. The analytical chemist can define the number of sampling locations according to the information needs. On the other hand, a high simplification of the whole analytical process is achieved as the number of steps is reduced. The present approach brings together these two advantages by using a sorbents phase commonly employed in environmental analysis. In addition to its portable character, the sampler is cheap, built from commercial elements, which ensures reproducibility in its construction. It is perfectly adaptable to the sample volume that will eventually be needed to reach the sensitivity levels required. For the present approach, the sample treatment does not require any pH, ionic strength, or temperature adjustment. Specifically important is the independence from the ionic strength as its effect is compensated by the internal standard. The sensitivity of the method allows the determination of simazine and atrazine in environmental waters, as is demons-

Table 2. Comparison of the proposed method with other alternatives reported in the literature.

Analytes	Matrix	Pretreatment	Equipment	Sorbent (Amount (mg))	Sample volume (mL)	LOD (ng/L)	RSD (%)	Accuracy (%)	Reference
Atrazine	Tap, river and lake waters	SPME	DART-MS	MIL (1)	50	50	<9.3	99.7-109.6	47
Atrazine	Sea water	IT-SPME	NanoLC-DAD	c-SWNTs, c-MWNTs (-)	4	25	-	-	48
Atrazine and simazine	Sea water	SPE	UPLC-MS/MS	HLB (500)	1000	<0.05	<7	103-109	49
Atrazine and simazine	River water	D-µSPE	LC-MS/MS	MWNTs@Fe_3O_4@MIR (50)	20	29-43	<9	89-98	50
Atrazine	Surface water	D-MSPE	LC-UV	IL-MG (1000)	50	120	<4.8	99.8-100.7	51
Atrazine and simazine	Lake and river waters	D-µSPE	LC-MS/MS	Fe_3O_4@SiO_2@MIPs (100)	500	0.07-0.08	<6.2	86.1-93.2	52
Atrazine and simazine	Farmland, lake, and river waters	IT-SPME	LC-DAD	ME-MB (-)	0.9	74-79	<9.3	81.7-119	53
Atrazine	Rain, river and tap waters	D-MSPE	GC-MS	Magnetic nanocomposite (25)	50	1-5	<14	99-100	54
Atrazine and simazine	Creek and well waters	TFME	DI-MS/MS	HLB (3)	On-site (2500)	15	<8.3	70-121	This work

SPME, solid phase microextraction; IT, in tube; SPE, solid phase extraction; D-, dispersive; µSPE, micro solid phase extraction; MSPE, magnetic solid phase extraction; TFME, thin film microextraction; DART, direct analysis in real time; MS, mass spectrometry; LC, liquid chromatography; DAD, diode array detector; UPLC, ultrahigh pressure liquid chromatography; UV, ultraviolet detection; GC, gas chromatography; DI, direct infusion; MIL, metal organic framework; c-SWNTs, single-walled carbon nanotubes; c-MWNTs, multi-walled carbon nanotubes; HLB, hydrophilic-lipophilic balance; MWNTs@Fe3O4@MIR, magnetic multi-walled carbon nanotubes imprinting resin; IL-MG, ionic liquid-magnetic graphene; Fe3O4@SiO2@MIPs; magnetic molecularly imprinted polymer; ME-MB, magnetism-enhanced monolith-based.

trated by the two positive samples found. The stability of the analytes into the sorptive phase is also an advantage of the proposed configuration. The device presented in this article can be adapted to multiple environmental analytical problems just by considering the nature of the target analytes and selecting the most appropriate sorbent for their isolation.

The current version of the device does not permit the control or adjustment of the stirring rate. Although this rate directly influences the mass transference, using an IS corrects the effect in the calibration model. However, this aspect will be the focus of further research.

Credit authorship contribution statement

Francisco Antonio Casado-Carmona: development of the prototype, investigation, data treatment, writing. Juan Manuel Jiménez-Soto: design of the first prototype. Rafael Lucena: conceptualization, project organization, writing - review & editing. Soledad Cárdenas: supervision, funding acquisition, writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aca.2021.339186.

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Supplementary data

1. Mass spectrometry parameters

The determination of the analytes, which is described in the main text, was carried out by LC-MS/MS. The following table (Table S1) shows the multiple reaction monitoring (MRM) parameters used for the detection and determination of the triazines and the internal standard.

Table S1. Mass spectrometry parameters for triazine and internal standard.

Compound	Precursor ion (m/z)	Fragmentor voltage (V)	Product ion (m/z)	Collision energy (V)	Identification transition	Quantitation transition
Atrazine	216.1	110	174 104	18 34	216.1→104	216.1→174
Simazine	202.1	130	132 104	18 30	202.1→104	202.1→132
Atrazine-d_5	221.1	132	179 69.2	18 30	221.1→69.2	221.1→179

2. Attachment of the engine with the screw

Figure S1. Detail of the attachment of the engine with the screw.

3. Design of the extraction device

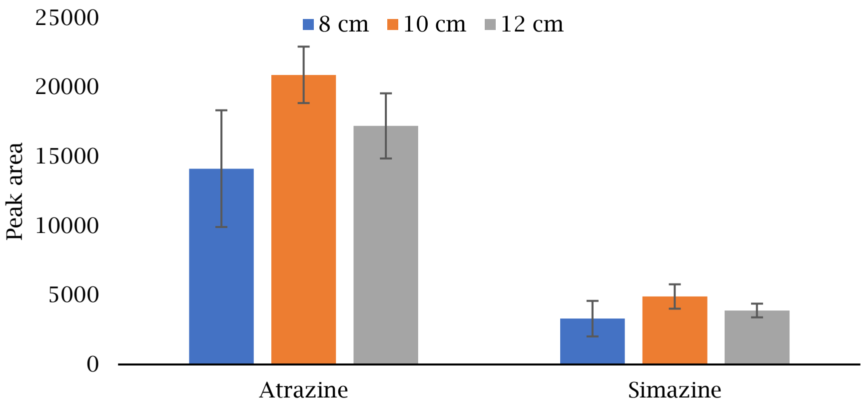


Figure S2. Evaluation of the screw's length in the design of the extraction device.

4. Influence of the pH in analyte's charge.

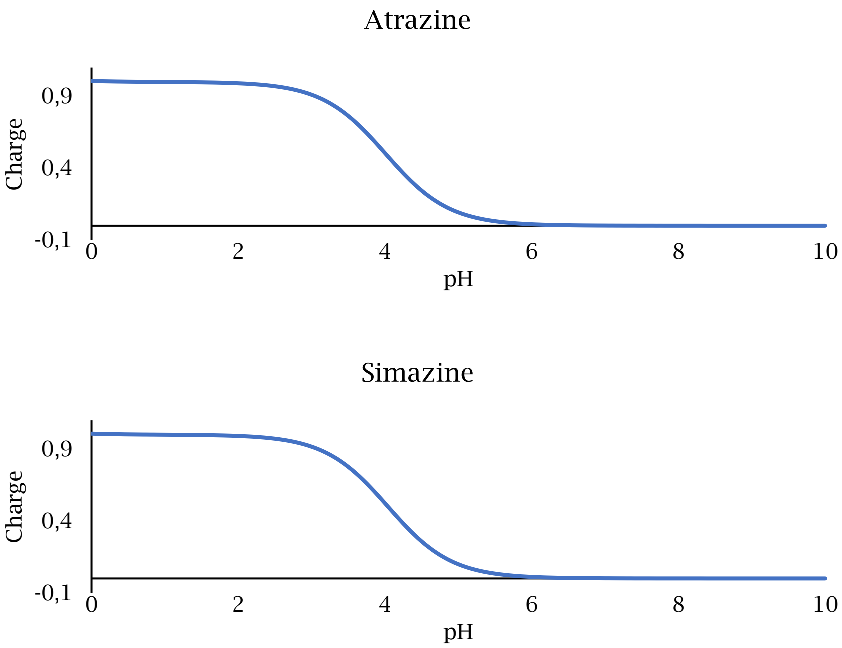
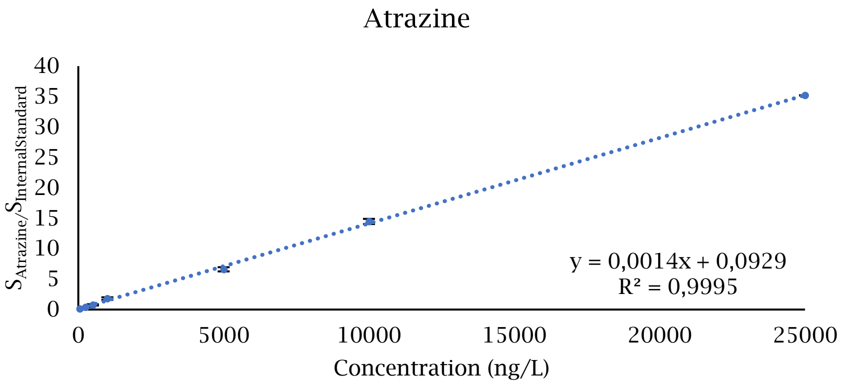


Figure S3. Influence of the pH in the charge of the target analytes. Data obtained from ChemAxom.

5. Calibration models



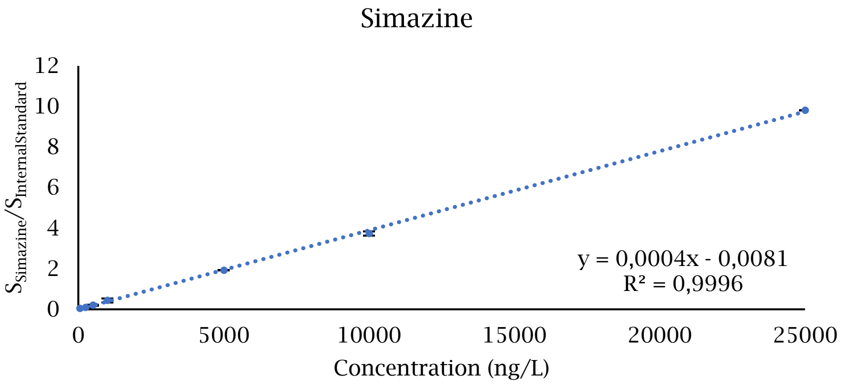
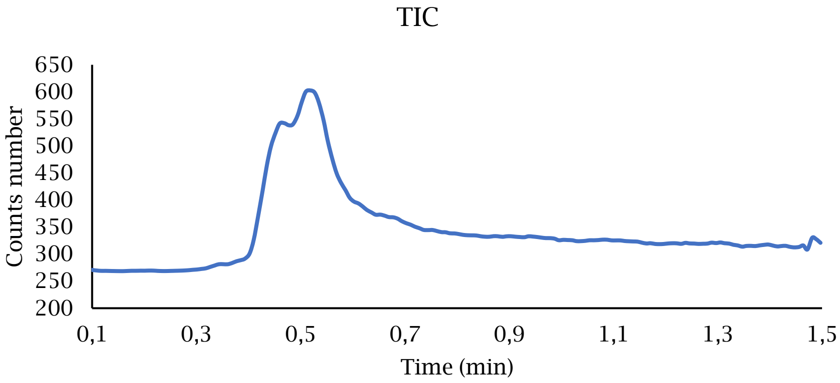


Figure S4. Calibration models for the target analytes.

6. Determination of target analytes in real samples

Table S2. Determination of parabens and triclosan in swimming pool samples.

Sample	Atrazine (ng/L)	Simazine (ng/L)
Creek 1	Non detected	Non detected
Creek 2	Non detected	105 ± 9
Well 1	Non detected	68 ± 6
Well 2	Non detected	Non detected
Well 3	Non detected	Non detected



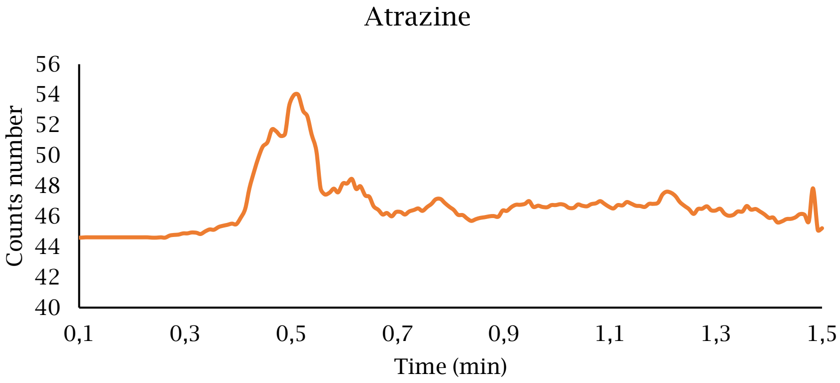


Figure S5. Chronograms of creek 2 sample.

BLOQUE IV

SISTEMAS INTEGRADOS DE MUESTREO/EXTRACCIÓN EN ANÁLISIS DE MUESTRAS GASEOSAS

La actividad humana, y las emisiones que esta produce a la atmósfera ha generado un aumento en las enfermedades respiratorias severas [1] motivado por la disminución de la calidad del aire debía a dicha actividad. Existe una amplia variedad de alternativas disponibles para medir la calidad del aire con el objetivo de planificar actuaciones para disminuir el riego de esas enfermedades. Sin embargo, en la mayoría de los casos, el coste asociado es elevado. El incremento del precio de estas unidades de muestreo viene determinado por dos factores. En primer lugar, los costes de producción asociados, y en segundo lugar, la complejidad de las estaciones de muestreo implica la contratación de personal especializado.

Con el fin de abaratar costes de producción y de mano de obra, los esfuerzos se centran en el diseño de nuevos dispositivos de toma de muestra que permitan minimizar el impacto de ambos factores. Estos nuevos dispositivos de muestreo se soportan en el uso de tecnologías de bajo coste, asequibles, de fácil manejo y puesta en marcha, consiguiendo así abaratar el proceso de análisis de las muestras de aire. A esto se suma su carácter potencialmente portátil que aporta valor añadido a los mismos.

Además, estos nuevos dispositivos se pueden soportar, al igual que sus homólogos para muestreo de aguas, en el empleo de fases sorbentes planas. Entre las distintas alternativas, es destacable el empleo de las *Fabric Phase*s como sorbente [2]. Su potencial como fase sorbente se complementa con la facilidad para el análisis final debido a la posibilidad de acoplamiento de estas con técnicas como espacio de cabeza o desorción térmica acopladas con cromatografía de gases.

En el **Capítulo 5** de la presente Tesis Doctoral se demuestra el potencial de un dispositivo de toma de muestra de aire basado en el uso de un ventilador de ordenador cuyo papel es favorecer el contacto del material sorbente con la muestra de aire. Para ello, se situaron fragmentos de *Fabric Phases*, sobre las aspas del ventilador.

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CAPÍTULO 5

FAN-BASED DEVICE FOR INTEGRATED AIR SAMPLING AND MICROEXTRACTION

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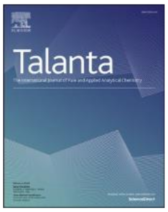

Fan-based device for integrated air sampling and microextraction

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In this article, a new air sampler based on a conventional computer fan is presented and evaluated. The fan has a double role as it acts as the air pumping system and supports the sorptive phases, which are located on its blades. The compact design and the reduced energy consumption (it can operate with a standard cell phone charger) confers high portability to the device. Also, a simple alternative integrated into the fan is proposed for using an internal standard during the sampling, thus increasing the precision of the measurements. In this first communication, sol-gel Carbowax 20 M coated fabric phases are used as sorptive membranes thanks to their planar geometry, mechanical and thermal stability, and their versatility covering different interaction chemistries. After sampling, the fabric phases are placed in a headspace vial, which is finally analyzed by gas chromatography-mass spectrometry. The sampler has been characterized for the extraction of selected volatile organic compounds (chloroform, benzaldehyde, toluene, and cyclohexane) from air and its versatility has also been evaluated by the identification of semi-volatile compounds in working place (toluene and xylene in laboratory residue storage room) and biogenic volatile compounds in natural samples (terpenes in fresh pine needles and orange peel samples).

Keywords: Air sampler**,** Fabric phases, Portable device**,** In-site extraction, Volatile organic compounds, Semi-volatile organic compounds, Biogenic volatile organic compounds.

1. Introduction

The determination of volatile and semi-volatile substances in outdoor [1] and indoor [2] air is a very relevant analytical problem of environmental and safety (human exposure to hazardous substances) concerns. Environmental analysis is especially challenging due to the vast volume of the compartments, their heterogeneous distribution (both spatial and temporal), and the typical low concentration of the target compounds to be monitored [3]. These issues make multisampling (at different locations and times) necessary to get representative information about the system under study [4]. The classical workflow, consisting of sampling and sample transportation to the laboratory for final analysis, has been surpassed for on-site approaches. On-site measurement is the ideal strategy [5,6], but it requires portable instruments, which are not always affordable and present lower performance than benchtop instruments [7]. An alternative approach consists of the on-site integration of sampling and isolation of the analytes in an extraction phase, which is further transported to the laboratory for the final instrumental analysis [8]. This type of sampling has a very positive effect on representativeness as the analytes are more stable in the extraction phases than in the original samples, where losses (e.g., sorption in the container's walls or evaporation) and contamination with external sources may occur [9]. Interestingly, Gallego et al. have recently proposed combining the two later approaches using a gas sensor as a trigger for the activation of a multi-sorbent sampler, thus allowing to respond to episodic odor events [10].

The design of samplers that integrate the isolation of the target analytes from water [11,12] and air [13] has been a hot topic in environmental analytical chemistry during the last decade. Depending on their operating principles, these devices can be divided into passive or active samplers [14,15]. Air passive samplers are designed in such a way that air flows freely, and the analytes diffuse to the extraction phase according to Fick's first law of diffusion. These samplers are cheap, and they do not require any external energy source, which makes them suitable alternatives for sampling in remote regions. Interestingly, biota can be used as natural passive samplers to monitor organic pollutants [16–19]. Passive sampling provides an average concentration during large periods from days [1] to even months [20]. By contrast, active samplers use an air pumping element to force the flow of the air samples through the extraction phase. This design allows for processing larger volumes, thus providing better sensitivity. Active sampling provides a snapshot at a defined short sampling time. Solid-phase microextraction (SPME) is the reference technique in environmental sampling/preconcentration strategies due to its simplicity and miniaturized character that simplifies the overall analytical process (e.g., easier transportation of the extraction phases in on-site applications) [21]. These positive features, which have also permitted their use in aerial drones for sampling [12,22] are complemented by a high versatility, which can be considered at three different levels, namely available sorptive phases, extraction phases geometry, and sampling approaches. SPME sorptive phases cover a wide range of analyte polarities and volatilities. Polydimethylsiloxane (PDMS) is the best option for semi volatile and highly non-polar compounds [23], while polyethylene glycol is more appropriate for polar substances [24]. Also, the sorption capacity of PDMS can be tuned by its combination with other polymers [25]. The design of new sorptive phases based on novel polymers [26], nanocomposites [27], and nanoporous materials [28] will increase the flexibility of the technique to solve different analytical problems. The original fiber-based SPME has been complemented in the last decade with other geometries and formats. On the one hand, the surface area of the sorptive phase has a definite impact on the extraction kinetics. Ramsey et al. proposed the so-called high surface area SPME, which consists of a large coated helical wire which is confined in a glass tube where the air sample flow through aided by a pump [29]. The temperature of the wire can be controlled to achieve the thermal desorption of the analytes permitting their injection in the gas chromatograph [30]. This sorptive area can also be boosted using planar phases in the so-called thin-film microextraction (TFME) [31,32]. On the other hand, the sorptive phase volume affects sensitivity. In this context, SPME arrows can provide better detection limits [33], and they have been proposed for the field measurements of biogenic volatile organic compounds in the air [34]. The last versatility level of the SPME-based techniques is related to the sampling strategy. If in fiber SPME is commonly used for passive [35] and dynamic sampling [36,37], needle trap devices (NTD) are generally used for active and exhaustive sampling [38–41], although they can be easily adapted to passive sampling if required [42].

In this article, a new dynamic air sampler is presented. The device consists of a computer fan, in whose blades the sorptive phases are located. As far as we know, fans have been proposed in air samplers as external pumping systems to make the air flows through the sorptive phase [31,43] and to homogenize the gaseous standards in dedicated chambers [44]. The new device integrates the pumping and the sorptive elements resulting in a compact and easy to transport sampler that opens the door for on-site applications. The geometry of the blades is more compatible with planar sorptive phases, and therefore, in its present form, the device can be classified as a TFME sampler. Fabric phases (FPs) obtained by the sol-gel modification of inert supports (e.g., cellulose, fiberglass) with different polymers [45] have been proved as excellent sorptive phases for both liquid [46–49] and air [32] samples. They are also easy to handle and locate in the blades. Additionally, the thermal stability of those FPs built-in fiberglass allows the thermal desorption of the target analytes. In this article, the main variables affecting the new design are considered using selected volatile organic compounds (VOCs) as model analytes. The main findings are discussed, making emphasis on the versatility and potential of the sampler.

2. Experimental section

2.1. Reagents and samples

All the reagents were of analytical grade, and unless otherwise specified, they were supplied by Sigma-Aldrich (Madrid, Spain). Benzaldehyde, chloroform, cyclohexane, n-hexane, octane, toluene, and p-xylene were selected as model volatile organic compounds. For the preparation of the gaseous standards, individual vials containing each analyte were prepared and processed, as will be further explained. Bromoform was used as the internal standard.

The retention of the volatile organic compounds from air standards/ samples was done by a sol-gel Carbowax 20 M coated FP, which was synthesized over a fiberglass substrate. The fabrics were synthesized as described elsewhere [48].

2.2. Fan-based air sampler

A computer fan (Microser Computers, Córdoba, Spain) operated by a voltage adjustable power supply unit (Nimo Electronic, Antlec S.L, Córdoba, Spain) is the core of the proposed sampler (Patent P202030192). Pre-cut pieces of FPs (15 × 10 mm) were attached to the fan blades using double side adhesive tape (Milan, Mont-Ras, Spain), as it is shown in Fig. 1A. A polypropylene SPE frit, which is used to support the internal standard during sampling, is located in the front section of the fan, as it is also shown. A volume of 5 µL of the internal standard is deposited with a micropipette into the frit immediately before the extraction. A fresh frit is used for each extraction.

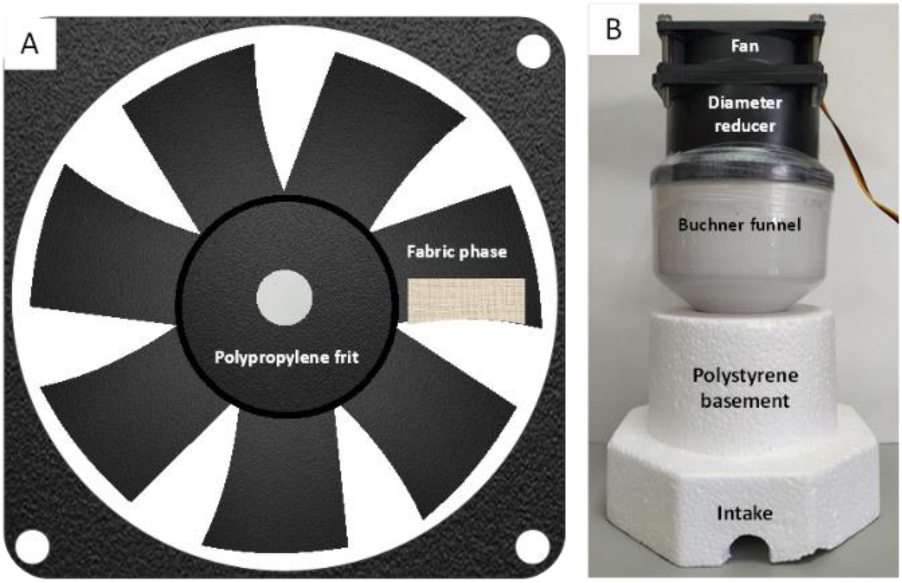

Fig. 1. A) Location of the polypropylene frit (where the internal standard is deposited) and the fabric phase in the fan; B) Manifold proposed for the generation of the gaseous standards coupled to the fan-based sampler (for details read text).

A special lab-made manifold, which is presented in Fig. 1B, was designed for studying the effect of the analyte's concentration on the analytical signal. A porcelain Büchner funnel is used as the standard generation chamber. For this purpose, different vials (empty volume 5.2 mL) containing 5 mL of the individual model analytes are located in the Büchner porous plate (Fig. S1). The fan is tightly attached to the upper section of the Büchner by a diameter reducer, and finally, the system is located in an expanded polystyrene base for better stability. The base presents built-in intakes to permit the airflow through the system. When the fan is switched on, an air stream is aspirated from the bottom of the platform. This stream subsequently passes through the Büchner stem and the small chamber where the vials are located. In this small chamber, the air stream drags the analyte vapor to the fan, and the analytes are finally retained according to their sorptive affinity in the FPs. After the sampling, the FPs are transferred in individual 10 mL HS vials for further analysis.

2.3. Headspace-gas chromatography-mass spectrometry analysis

Chromatographic analyses were carried out on an HP6890 gas chromatograph coupled with an HP5973 mass spectrometer from Agilent (Palo Alto, CA, USA). The instrument was equipped with an MPS2 headspace autosampler (Gerstel, Mülhein and der Ruhr, Germany).

For HS-GC-MS the vials containing the FPs are incubated at 100 °C for 30 min under mechanical stirring. After this incubation, 2 mL of the headspace are automatically aspirated by the autosampler using a gas-tight syringe, which is maintained at 150 °C to avoid analyte condensation.

For the evaluation of the sampler performance, the model analytes are separated in a HP-5MS column (30 m × 0.25 mm I.D. × 0.25 μm film thickness) using Helium (6.0 grade purity, Air Liquid, Seville, Spain) at a flow rate of 1 mL/min as the carrier gas. The column temperature program was as follow: 40 °C for 1 min; raised to 80 °C at 5 °C/min and finally increased to 200 °C at 50 °C/min, maintaining this temperature for 3 min. The injector was set at 180 °C, and a split mode injection (split ratio 1:10) was selected. Electron impact ionization (70 eV) was used for the ionization and fragmentation of the analytes. The analyzer swept *m/ z* values from 45 to 300. The MS source and quadrupole temperatures were 230 °C and 150 °C, respectively. The identification of the target compounds was made according to the retention time and MS spectra. Peak areas were used for quantitative purposes. A typical chromatogram obtained for the analysis of the FPs after the extraction of a gaseous standard containing the analytes is presented in Fig. S2. For comparative purposes, an analysis of the double-side adhesive tape, used for fixing the FPs to the fan blades, is also included.

As will further be explained in the results section, a dedicated chromatographic separation was used for studying the versatility of the sampler.

3. Results and discussion

3.1. Location of fabric phase

The study of the hydrodynamic airflow through the fan-blades is essential for the selection of the best location for the FPs. This appropriate selection would improve the mass transference from the air to the extraction phase, thus enhancing the sensitivity. For this purpose, a special manifold, which is depicted in Fig. 2A, was designed. It consisted of an airbrush, previously loaded with a white acrylic paint, which is orthogonally arranged to the fan. Both elements, the airbrush and the fan, were simultaneously switched on for 2 min. A part of the paint spray was aspirated, passing through the blades and impacting them. The visual inspection of the fan blades revealed the position where these impacts took place (Fig. 2B), which was finally selected as the optimum location for the FPs. Movie 1, attached as supplementary information, shows how this study was carried out.

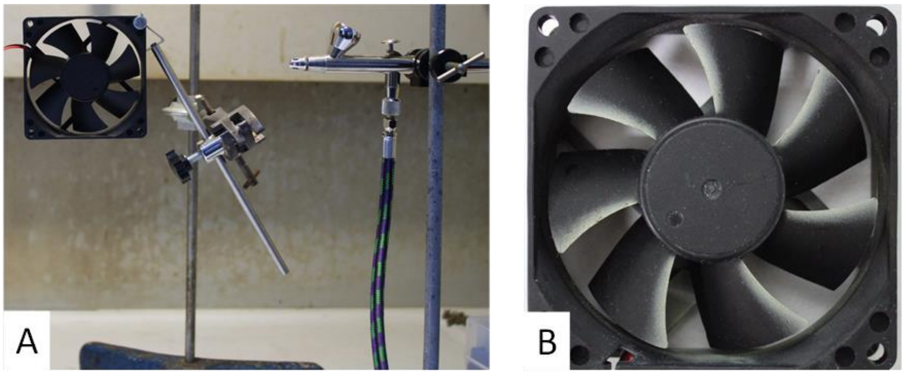

Fig. 2. A) Manifold proposed for the evaluation of the better place to locate the fabric; B) Picture of the fan after the study where the white acrylic paint deposition is visible.

3.2. Air flow optimization

Airflow is a critical parameter in sampling. In this case, the air aspirated by the fan depends on the operating voltage since it defines the blade's speed. Two different voltages were evaluated, namely 12 V and 5 V. 12 V is the standard operating voltage for this type of fan, but portable 5 V-sources are easily available (they are used in cell phone chargers), and they could open the door to on-site sampling approaches. The flow rates were measured with a commercial anemometer. Fig. 3 shows how the flow rate varies with the operating time (this parameter is an equivalent concept to the sampling time) at the two mentioned voltages. The flow rate obtained for 12 V (832 ± 34 L/min) was higher than that provided at 5 V (297 ± 11 L/min). Both flow rate values were calculated considering all the data, that is, three replicates at all the different times (n = 21). The relative standard deviation of the flow rates was 9.12 % and 3.83 % for 12 V and 5 V, respectively. These values are even better (negligible standard deviation) if the initial value is not considered, which indicates that a warm-up period is necessary as specified by the manufacturer. Interestingly, the flow rate is not affected by the location of the fabrics in the blades.

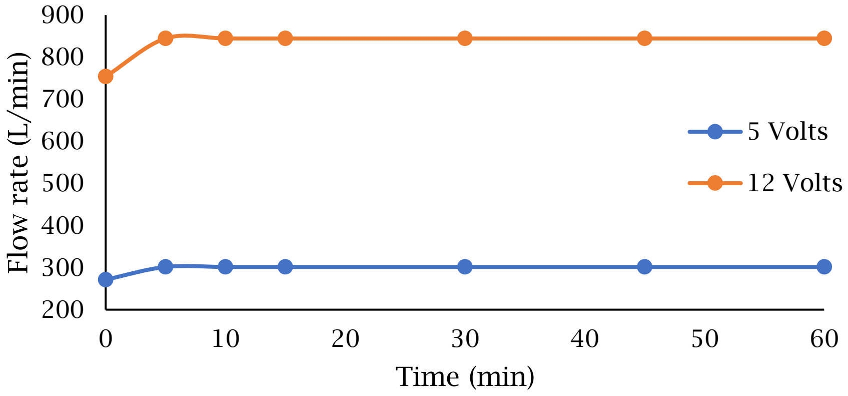

Fig. 3. Variation of the air flow rates with the operation time of the fan. Values were obtained at two different voltages. The error bars are represented, although the good precision avoids their easy observation.

3.3. Effect of flow rate

The effect of the flow rate on the analytical signals was then evaluated. Sol-gel Carbowax 20 M based FPs were selected for the isolation of the model analytes according to previous results [50]. Although they can be obtained both over fiberglass and cellulose substrates, fiberglass was selected due to its better thermal stability. Also, the mechanical endurance of the fiberglass makes it easier to hold the fabric in the blades. Fig. 4 shows the results which were obtained sampling the same air-volume (ca. 8140 L) at the different voltages (flow rates). A detail of the less intense peaks is shown in Fig. S3 (supplementary material). The results showed that the flow rate has a clear effect on the extraction of the analytes. The lower flow rate provided better results for all the analytes, thus indicating the relevance of the residence time on the extraction of the analytes. This behavior is typical in dynamic extractions. For further studies, 5 V was selected as the operating voltage. This selection is advantageous, as a simple cell phone charger or a power bank can be used. This aspect makes the fan-based sample portable and applicable for in-situ analysis.

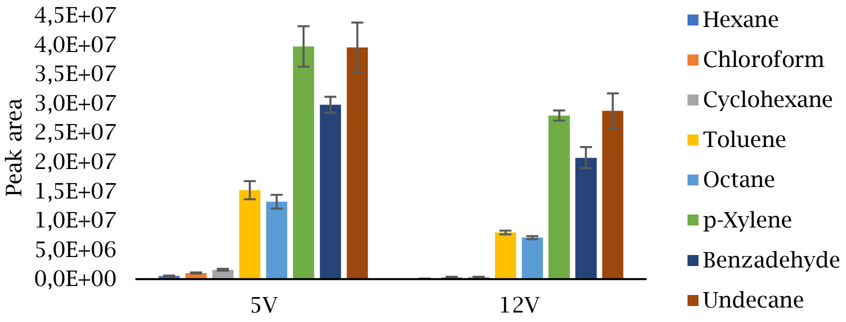

Fig. 4. Effect of the operating voltage on the extraction of the target compounds. A detail of the less intense peaks is included in the supplementary material.

3.4. Sampling time

The sampling time was evaluated within a wide interval, from 15 to 210 min. The results, which are presented in Fig. 5, show an increase of the analytical signal up to 30 min. Then, the signal decreases and remains almost constant for larger times. Initially, this behavior was ascribed to the warming of the fan motor. A continuous increase in the blades' temperature due to the motor operation was hypothesized. However, the temperature of the blades was measured over time, and a negligible variation (the values were in the interval 18.3–18.5 °C) was observed. Finally, this effect was ascribed to the different evaporation rates of the standards in the proposed system. At the beginning of the assays, the vial is completely full (the level of the standards is closer to the vial upper part), making the evaporation rate higher. At longer extraction times, the volume of the vial decreases, resulting in a slower transference of the analytes to the gaseous phase.

For further analysis, 30 min was selected as the working sampling time.

3.5. Concentration profile

Exhaustive samplers present quantitative extraction recoveries, and their calibration can be easily done by the direct or indirect [51] spiking of blank samplers with a known amount of the target analyte. However, an external calibration with gaseous standards is necessary for non-exhaustive samplers since their recoveries are not quantitative and depend on the target analyte. Although gaseous standards can be prepared using commercial generators

[52,53], several alternatives have been reported and discussed in the literature [54]. Most of them rely on the controlled evaporation of the analyte, which can be achieved using permeation tubes [55], purging a liquid standard with a carrier gas [32] or injecting the standard in a gas stream [56]. In some approaches, a controlled temperature chamber is used to homogenize the gaseous standard increasing its volume to mimic the conditions found in environmental air analysis [27]. In this article, a dedicated device is designed for the standard generation as it was previously explained. The analytes are introduced into different vials, and each one is weighted before and after the sampling time. The concentration is calculated according to the next formula $C = \Delta m/Ft$ where Δm, F and t are the evaporated amount of analyte, the airflow rate, and the sampling time, respectively. The concentration of the gaseous standard can be changed just by increasing the number of vials of each analyte. For example, for the first concentration level, one vial per analyte is introduced in the device, while for the second concentration level, two vials per analyte are introduced, and so on.

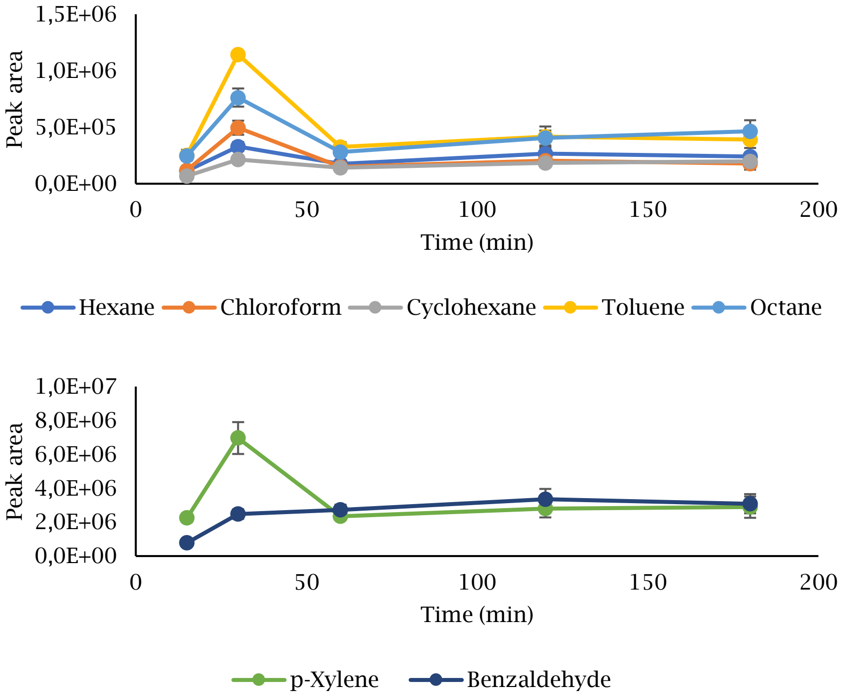

Fig. 5. Effect of the sampling time on the extraction of the target analytes.

Non-exhaustive devices are sensitive to different variables that can critically affect the precision of the measurements. The so-called in-fiber calibration solves this reproducibility issue by loading the sorptive phase with an internal standard that is desorbed during the sampling [57]. The amount of internal standards loaded in the sorptive phase is critical, and several approaches have been proposed to its accurate control [58,59]. In this article, the internal standard is deposited over a blank polypropylene frit that is located in the frontal section of the fan. The internal standard is desorbed from the frit during the sampling time. Although deuterated compounds of the target analytes would be preferred for better performance, in this preliminary approach, a single compound (bromoform) is evaluated a model internal standard.

Due to the geometry of the standards generation device, the maximum number of vials that can be included at the same time is limited. For this reason, the concentration profile was built for four different analytes, namely: chloroform, benzaldehyde, toluene, and cyclohexane that covers a wide range of polarities and interactions with the FPs. The profiles are presented in Fig. 6. Although the manifold offers clear advantages (simplicity, low cost), it also gives some shortcomings that must be indicated.

The concentration of each gaseous standard is accurate since the amount of analyte is gravimetrically measured, and the flow rate is instrumentally obtained. However, the preparation of a standard with an intentional and specific concentration is sometimes difficult as it depends on the vial location inside the chamber and how the air flows around the vial. For this reason, the concentration profile for toluene and cyclohexane only contains four points, although enough to study the influence of the concentration on the signal.

The generation of low concentration standards is limited by the evaporation rate of the analytes and the geometry of the vial. For example, the lower concentrations represented in Fig. 6 showed signal-to-noise ratios (considering the raw signal before dividing it by the internal standard area) in the interval from 656.3 (for chloroform) to 36080 (for benzaldehyde). Therefore, the limits of detection are lower in some order of magnitude from the concentrations evaluated.

The target compounds, chloroform excepted, presented a linear increase of the signal with the concentration with R2 in the range from 0.974 (benzaldehyde) to 0.999 (cyclohexane). Chloroform showed a logarithmic profile, which can be ascribed to the higher concentration of this analyte (ascribed to its higher volatility) on the gaseous standard, as it can be observed in the X-axis of Fig. 6.

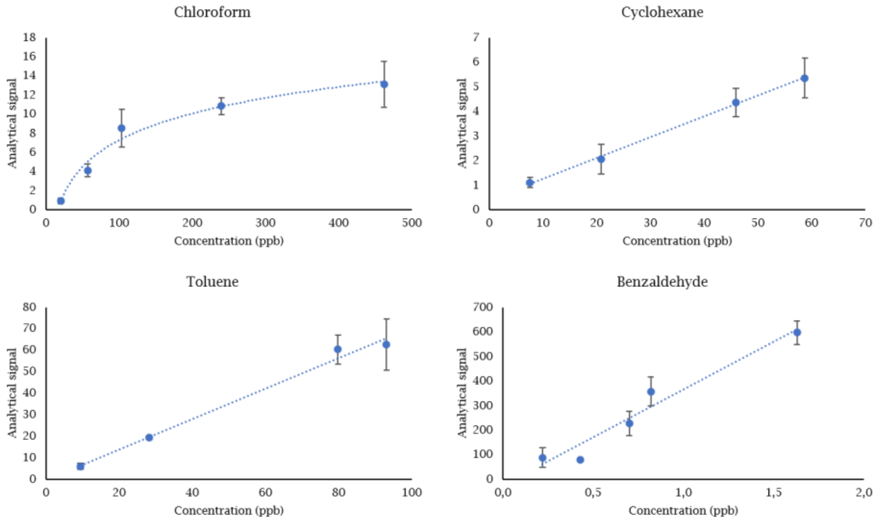

Fig. 6. Concentration profiles for four model analytes.

The device was finally used for sampling the laboratory air. Fortunately, most of the samples were negative, indicating a low exposure of the researchers to these compounds. Only the sample acquired in the room where all our reagents are stored demonstrated the presence of toluene and xylene. The signals correspond to concentrations below the range studied in the concentration profile. This analysis allowed us to implement security measures to avoid future exposure to these substances.

3.6. Versatility of the fan sampler

Once the potential of the fan sampler on the extraction of the model volatile compounds from the air was evaluated, its performance for the isolation of unknown volatile and biogenic volatile compounds was studied. For this purpose, two solid samples (fresh pine needles and orange peel) were individually introduced in the Büchner funnel, and the fan was switched on for 30 min. In such conditions, the air flows around the solid sample driving the biogenic volatile compounds to the fabrics located in the blade. The FPs were analyzed in the same headspace conditions reported before, although the chromatographic run was modified, introducing a slower temperature ramp (1 °C/min from 40 to 200 °C) to permit a better separation of the unknown compounds. The compounds were identified using their retention indexes, calculated using a mixture of linear hydrocarbons as described elsewhere [60], and their MS spectra (compared with the NIST database) [61]. Representative chromatograms for both samples are included in the supplementary material (Figs. S4–S14). Table 1 summarizes all the analytes that were satisfactorily identified by their MS spectra (the comparison of the obtained spectra with the reference ones are included in the supplementary material). The experimental retention index (RI), the tabulated one (RI^{o}) and the error (expressed as 100 (RI-RI^{o})/RI^{o}) is presented for better understanding. These compounds have been previously reported for pine needles [62] and orange peel [63] samples. Apart from the compounds presented in this table, many other terpenes (according to the fragmentation pattern) were present in the samples, although they were not identified as some chromatographic peaks are not completely resolved, being overlapped spectra of several compounds.

Table 1. Identification of semi volatile compounds in solid samples.

Sample	Compound	Experimental Retention Index (RI)	Tabulated Retention Index (RI^{o})[a]	Error (%)
Pine	Tricyclene	925	923	0.2
	β-Pinene	970	964	0.6
	β-Myrcene	991	991	0
Orange	Tricyclene	925	923	0.2
	β-Pinene	970	964	0.6
	Octanal	1004	1001	0.3
	Limonene	1030	1029	0.1
	(Z)-β-Ocimene	1042	1039	0.3
	Trans-β-Ocimene	1052	1050	0.2

[a] The tabulated retention indexes were obtained for a HP-5MS column from the NIST chembook.

4. Conclusions

In this article, a novel air sampler is presented and evaluated to extract model volatile organic compounds. The sampler consists of a computer fan that integrates the air pumping element and the sorptive phases. The price of the fan is two orders of magnitude cheaper than an aspirating air pump. Thanks to its compact design, it can be easily transported to the field, opening the door for on-site sampling approaches. The design and the key variables affecting its performance have been considered. In this research, a simple approach to easily integrate the internal standard in the sampler for better precision is also proposed. As it has been outlined, the sampler can also be used for the extraction of biogenic-volatile compounds from solid samples.

Although further research will be focused on the application of the air sampler in environmental analysis considering this environment in the broadest sense of the term (outdoor and indoor air, especially at the workplace), the sampler will also be developed from the design point of view. In this sense, the cooling of the sorptive phases during the extraction, which has been deeply studied by Prof. Pawliszyn's group [64–66], will be one of the next objectives to increase the retention of the analytes into the sorptive phases.

Also, the fan design would allow to deploy several sorptive phases simultaneously. Therefore, if sorptive phases of different polarities are used, a wider variety of substances can be extracted and detected if present.

Credit author statament

F. A. Casado Carmona: Investigation, data treatment. G. Lasarte- Aragonés: Data curation, visualization of data, writing – first draft. A. Kabir: Resources (fabric phases), writing – review & editing. K.G. Furton: Resources (fabric phases). R. Lucena: Conceptualization; project administration, writing – first draft &review & editing. S. Cárdenas, Supervision, funding acquisition, writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2021.122290.

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Supplementary data

1. Vials location during the calibration process

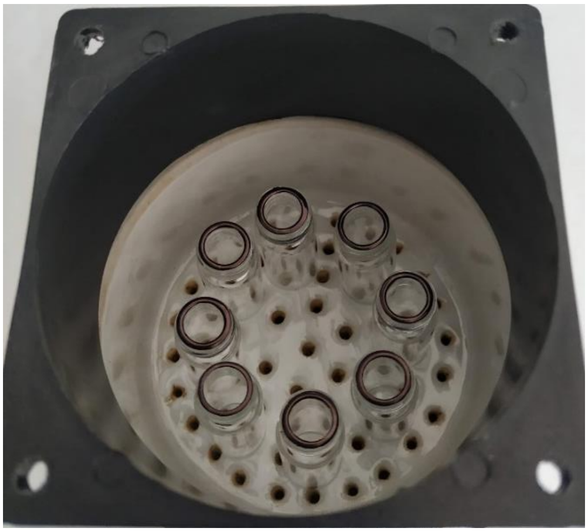


Figure S1. Vials location in the manifold proposed for the generation of gaseous standards. Up to 8 vials can be placed without interfering the normal air flow.

2. Background of the double-side adhesive tape on the chromatogram

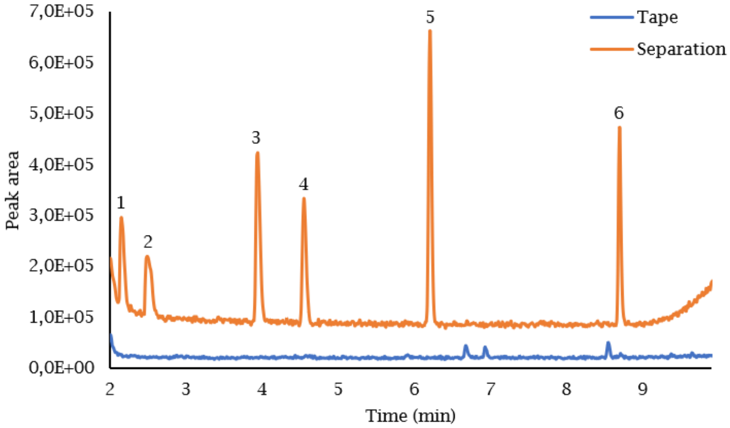


Figure S2. Chromatograms obtained for the analysis of a FP previously used for the extraction of a gaseous standard (orange line) and for the analysis of a blank double double-side adhesive tape (blue line). The analytes: 1) Chloroform; 2) cyclohexane; 3) toluene; 4) octane; 5) p-xylene; 6) benzaldehyde.

3. Effect of the flow rate on the extraction of hexane, chloroform and cyclohexane

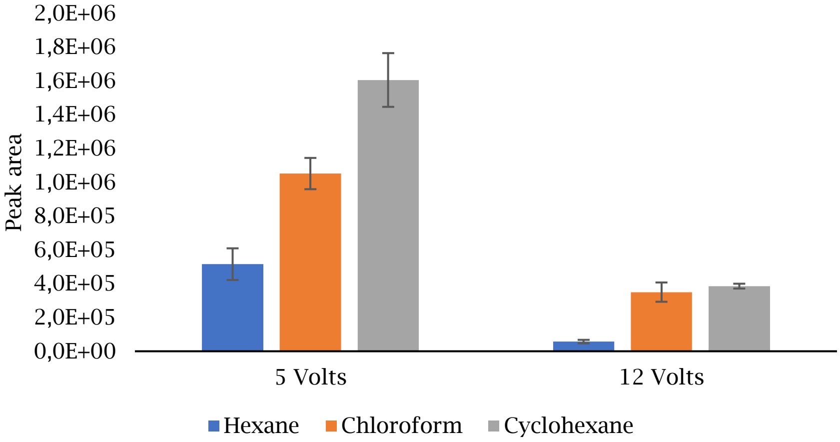


Figure S3. Detail of the effect of the flow rate on the extraction of the less intense peaks of Figure 4.

4. Analysis of pine needles samples and MS spectra of the identified compounds

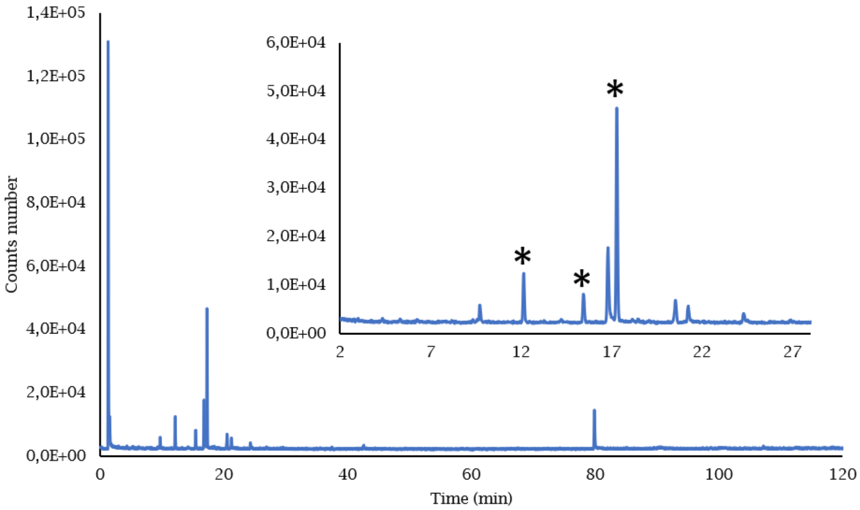


Figure S4. Chromatogram obtained for the analysis of pine leaves. The identified peaks are indicated with an asterisk. An inset of the chromatographic run between 2-30 min is includes for a better observation of the identified peaks.

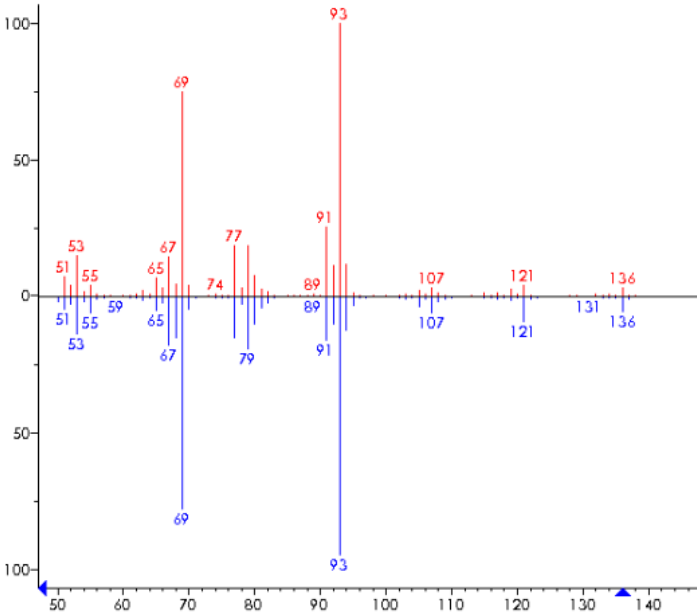


Figure S5. Spectrum of the unknown compound at a retention time of 12.16 min (red) and NIST database spectrum for tricyclene (blue).

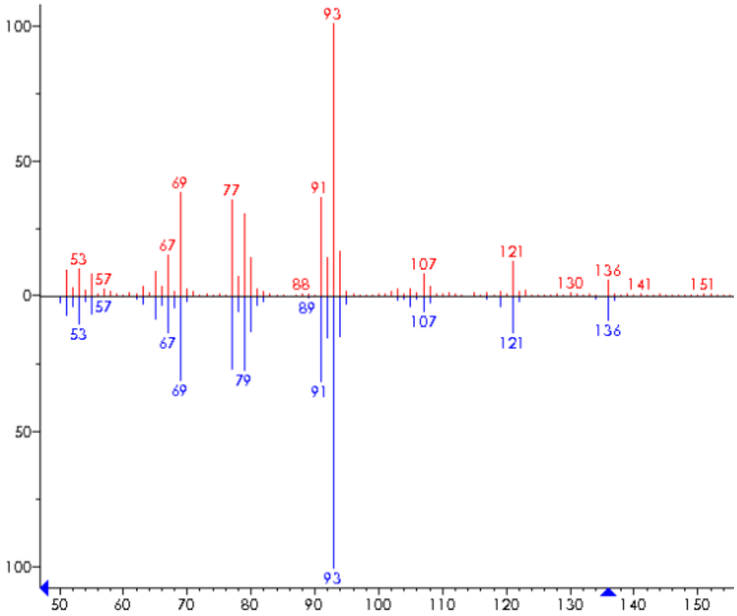


Figure S6. Spectrum of the unknown compound at a retention time of 15.46 min (red) and NIST database spectrum for β-pinene.

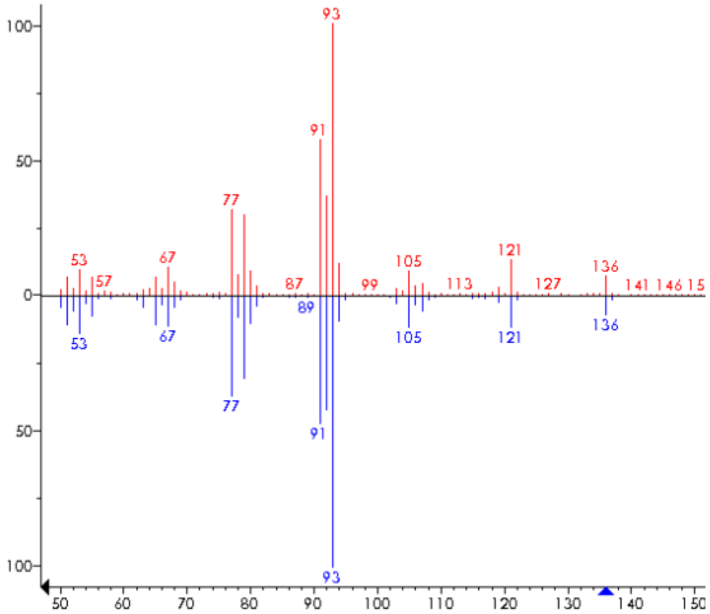


Figure S7. Spectrum of the unknown compound at a retention time of 17.32 min (red) and NIST database spectrum for β-myrcene.

5. Analysis of orange peel samples and MS spectra of the identified compounds

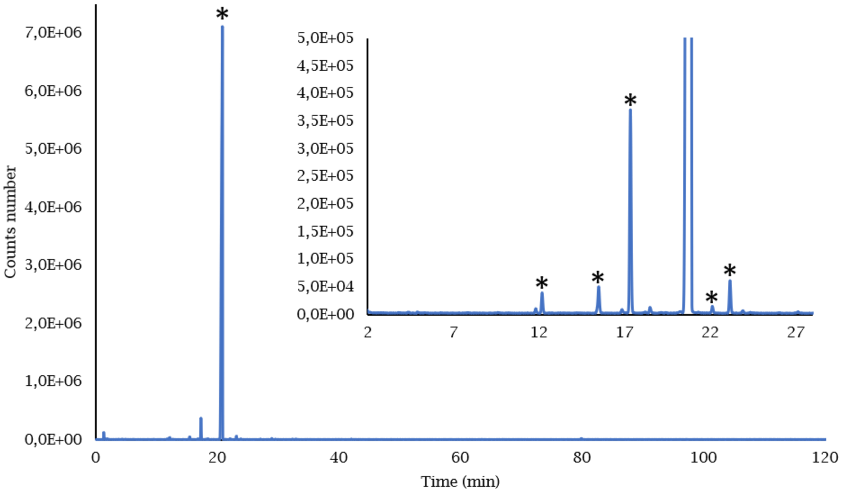


Figure S8. Chromatogram obtained for the analysis of orange peel. The identified peaks are indicated with an asterisk. An inset of the chromatographic run between 2-30 min is includes for a better observation of the identified peaks.

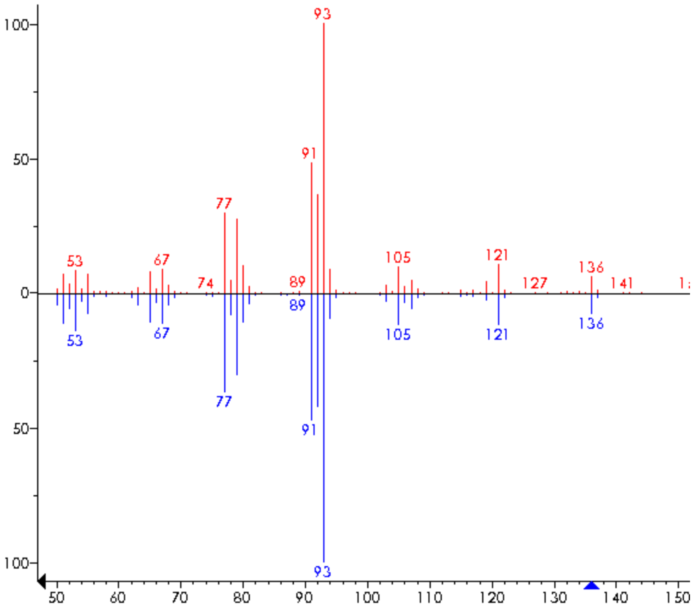


Figure S9. Spectrum of the unknown compound at a retention time of 12.16 min (red) and NIST database spectrum for tricyclene (blue).

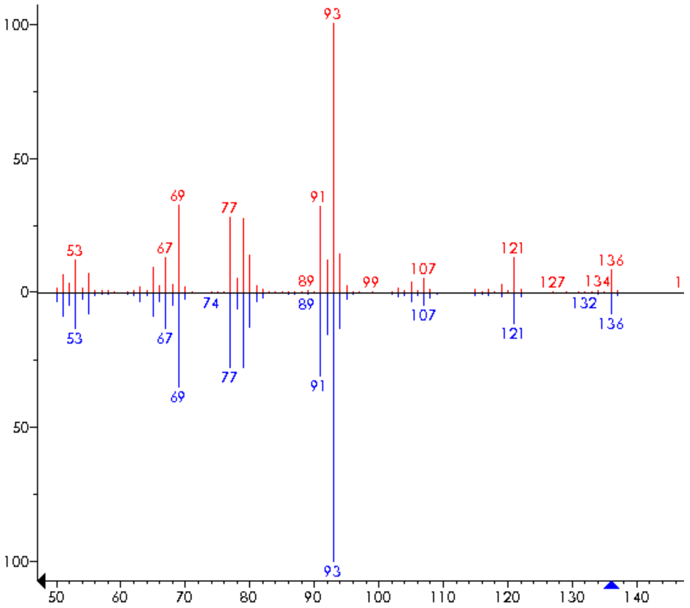


Figure S10. Spectrum of the unknown compound at a retention time of 15.46 min (red) and NIST database spectrum for β-pinene.

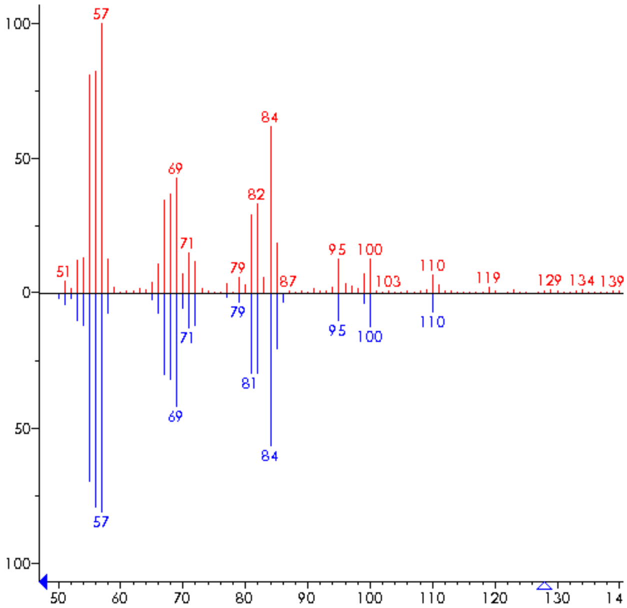


Figure S11. Spectrum of the unknown compound at a retention time of 18.46 min (red) and NIST database spectrum for octanal.

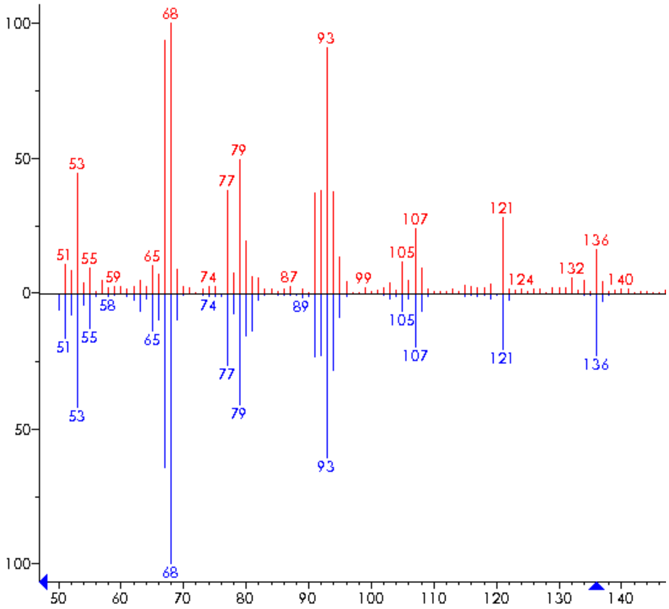


Figure S12. Spectrum of the unknown compound at a retention time of 20.84 min (red) and NIST database spectrum for limonene.

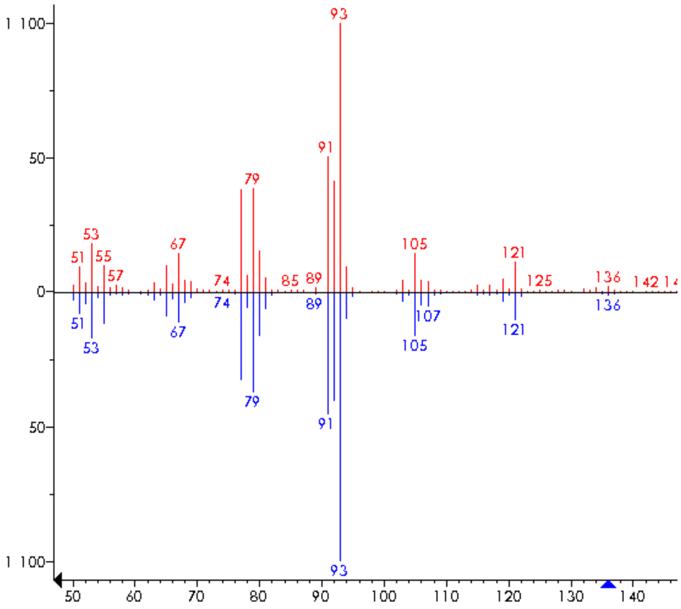
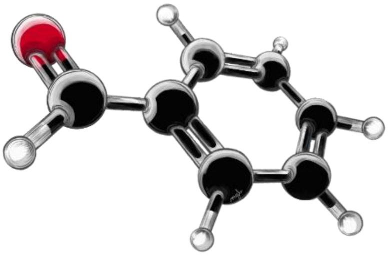


Figure S13. Spectrum of the unknown compound at a retention time of 22.1 min (red) and NIST database spectrum for (Z)-β-Ocimene.

Movie 1

BLOQUE V

RESULTADOS Y DISCUSIÓN



A continuación, se presenta la discusión de los resultados más relevantes de los trabajos experimentales desarrollados en la presente Tesis Doctoral. El objetivo genérico de la misma es el diseño de dispositivos de muestreo que integren la preconcentración de los analitos de interés. Para abordar dicho objetivo, la investigación se dividió en dos líneas de trabajo bien definidas. Por un lado, el diseño de dispositivos para la toma de muestras de agua y, por otro, su aplicación en la toma de muestras de aire. Como punto en común de las dos líneas de trabajo, se han desarrollado diseños que permitieran realizar la extracción *on-site* soportados en el empleo de tecnologías baratas y sostenibles con el medio ambiente, los cuales, además, proporcionen información analítica de calidad. Esto hace que la investigación desarrollada esté en línea con los principios de la Química Analítica Blanca [1].

La presente sección se ha organizado manteniendo los dos bloques anteriores. Se abordará en primer lugar el desarrollo y mejora de prototipos para el muestreo de aguas.

1. Innovaciones en el diseño de sistemas que integren la toma de muestra y extracción de analitos de muestras de agua

Las innovaciones en esta línea de trabajo se centraron en el desarrollo de un prototipo con agitación integrada para su aplicación en la extracción *on-site*. Esta configuración, además de mantener la homogeneidad en la muestra, favorece la interacción entre los analitos y el sorbente. Esta agitación mejora la cinética de los procesos de extracción, ya que facilita la difusión de los compuestos de interés desde la matriz de la muestra hasta la fase extractante.

En todos los diseños de esta sección se empleó una unidad de extracción magnética, la cual soporta la fase sorbente (Figura 1). La unidad de extracción propuesta estaba compuesta por un imán circular horadado, que se unió al dispositivo de agitación mediante el empleo de un tornillo de longitud variable.

En el prototipo inicial (**Capítulo** 2), se empleó un taladro de batería para agitar la unidad de extracción. Además, para mejorar la agitación y crear un régimen turbulento en la muestra, se añadieron unas pequeñas aspas a la unidad de extracción descrita.

En el primer desarrollo de este dispositivo de muestreo/extracción se empleó como fase extractante una membrana de nailon-6 comercial. Al no presentar

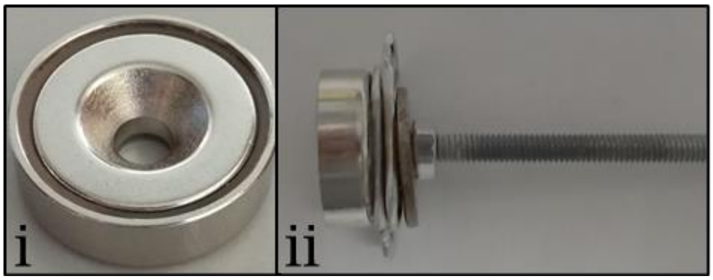


Fig. 1. Primer diseño de la unidad de extracción magnética empleada en el **Bloque III**. (i) Imán horadado empleado como núcleo de la unidad de extracción. (ii) Primer prototipo de la unidad de extracción con aspas empleado en el **Capítulo 2**.

propiedades magnéticas, el anclaje del sorbente a la unidad de extracción se realizó por medio de una arandela metálica. El empleo de esta arandela metálica no permitía que el material sorbente quedase completamente expuesto a la muestra, lo que creaba una pequeña capa de difusión limitada, y por tanto no permitía el aislamiento de los analitos presentes en la muestra.

Este problema se soslayó inicialmente introduciendo entre la fase sorbente y la unidad de extracción un septum polimérico que aumentase la exposición del extractante a la matriz de la muestra (Figura 2). De esta forma, se consiguieron eliminar los problemas en la difusión de los analitos para que pudiesen extraerse en la membrana de nailon-6.

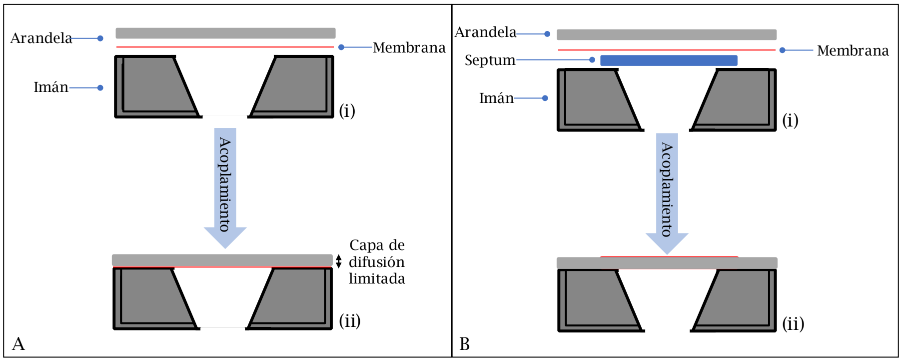


Fig. 2. A) Anclaje de la membrana en la unidad inicial. B) Anclaje de la membrana en la unidad de extracción finalmente propuesta.

No obstante, la solución anteriormente propuesta no se podía aceptar como definitiva, ya que el empleo del septum implicaba una excesiva manipulación de la fase sorbente por parte del operador. Por tanto, en el **Capítulo 3**, se propuso un avance que aportaría un cambio significativo al dispositivo propuesto.

En primer lugar, se sintetizó una nueva fase sorbente polimérica. Esta nueva fase sorbente comparte semejanzas con la comercial, pero también existen elementos que la diferencian y que, además, suponen una mejora significativa. La nueva fase sorbente está soportada sobre papel, material de origen natural que proporcionaba una mayor superficie al soporte debido a las fibras de celulosa y, por tanto, mejoraba las propiedades sorbentes de la membrana. A esto hay que añadir que este soporte es barato y reciclable, lo que hace que el material sea respetuoso con el medio ambiente, además de estar en línea con los principios de la Química Analítica Blanca. Otro elemento diferenciador de esta fase sorbente es la presencia de las nanopartículas magnéticas en su composición, las cuales conferían magnetismo al material a la vez que contribuían a la porosidad. Como fase polimérica y, por tanto, responsable de la extracción, se seleccionó el nailon-6, mismo material empleado en el diseño del muestreador del **Capítulo 2**.

El material descrito se preparó mediante un proceso de *dip-coating.* Para ello, el papel empleado como soporte se sumergió en la disolución precursora (nailon-6 en ácido fórmico) con las nanopartículas magnéticas dispersas. Como se ha descrito anteriormente, estas nanopartículas son las que confieren magnetismo a la membrana, permitiendo así el anclaje directo de esta a la unidad de extracción. De esta forma, se conseguía además eliminar la arandela metálica, y por tanto se soslayaban los problemas relacionados con la transferencia de los analitos desde la matriz de la muestra a la fase sorbente.

Además de la mejora de la fase sorbente, en este dispositivo también se incluyeron aspas de mayor tamaño (Figura 3) para una mejor agitación de la muestra y, por tanto, para favorecer la cinética del proceso de extracción.

En la Figura 4, se comparan los resultados obtenidos al incorporar esta nueva fase sorbente en tres unidades diferentes. La primera de ellas fue el prototipo inicial propuesto en el **Capítulo 2**, incluyendo la arandela para anclar la fase sorbente. En segundo lugar, se empleó la misma unidad, pero en este caso sin arandela. Finalmente se utilizó la nueva unidad con agitación mejorada. Al comparar las dos primeras unidades, se demuestra que el empleo de la nueva

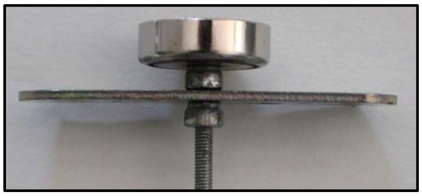


Fig. 3. Unidad de extracción magnética con aspas de mayor tamaño (**Capítulo 3**).

fase sorbente elimina los problemas relacionados con la capa de difusión limitada creada por la arandela. Por tanto, se puede concluir que el empleo de una fase sorbente magnética soslaya los problemas de difusión de esta unidad. Finalmente, comparando los resultados obtenidos para las dos unidades en las que la fase sorbente estaba totalmente expuesta, se demuestra que la mejora de la agitación derivada del empleo de unas aspas de mayor tamaño aumentó la capacidad de extracción del dispositivo propuesto.

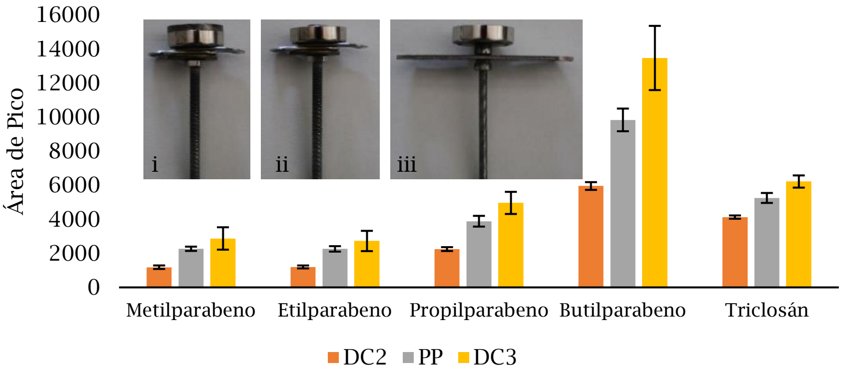


Fig. 4. Comparación inicial del rendimiento de extracción de diferentes dispositivos de muestreo. Los resultados se presentan como barras, mientras que se incluye una imagen de cada dispositivo para facilitar la interpretación. (i) DC2: Dispositivo capítulo 2, (ii) PP: Primer prototipo, (iii) DC3: Dispositivo capítulo 3.

A la vista de estos resultados, se puede concluir que el empleo de una fase sorbente magnética elimina los problemas de difusión de esta unidad. Así pues, se continuó avanzando en esta línea de investigación con ese objetivo, es decir, la propuesta de nuevas fases sorbentes planas con carácter magnético.

De esta forma, en el **Capítulo 4** se sintetizó una nueva fase sorbente magnética plana. En esta ocasión, la fase extractante se sustituyó por partículas

Hydrophilic-Lypophilic Balance, las cuales se soportaron sobre una cinta magnética recubierta con cinta adhesiva. En comparación con el proceso de síntesis del anterior sorbente magnético, este es más rápido y sencillo de preparar, además de ser un proceso de preparación más respetuoso con el medio ambiente ya que se elimina el uso de disolventes. La Figura 5 recoge la evolución de las fases sorbentes empleadas en el desarrollo del **Bloque III** de la Tesis Doctoral.

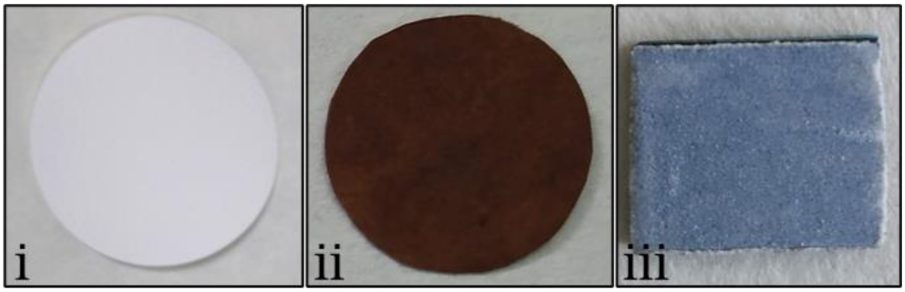


Fig. 5. Fases sorbentes empleadas en los diferentes desarrollos del **Bloque III**. (i) Membrana de nailon comercial (**Capítulo 2**). (ii) Membrana magnética de nailon con base papel **(Capítulo 3**). (iii) Fase sorbente magnética conteniendo partículas *Hydrophilic-Lypophilic Balance* (**Capítulo 4**).

Además de la preparación de una nueva fase sorbente magnética que es el punto en común del **Capítulo 4** con el anterior, se introdujo otra novedad en el dispositivo de muestreo. En este caso, un pequeño motor eléctrico acoplado a un tapón (Fig. 6ii) sustituyó al taladro de batería como sistema de agitación (Fig. 6i). El empleo de este motor abarata el coste del muestreador 50 veces. En este sentido, se pueden preparar un mayor número de dispositivos por el mismo precio y, por tanto, realizar un mayor número de extracciones de forma simultánea incrementando así la frecuencia de muestreo. Además, como recipiente para la extracción se reutilizaba una botella de disolventes comercial.

2. Determinación de contaminantes en muestras de agua

Los diferentes prototipos de muestreo/extracción de agua se emplearon para la determinación de varias familias de contaminantes emergentes en muestras de agua de distinta naturaleza. En esta sección, se discutirán los resultados más relevantes obtenidos de la aplicación del dispositivo propuesto a la resolución de tres problemas diferentes. Para poder exponer los resultados de forma más

Fig. 6. **D**ispositivos para proveer agitación en los muestreadores diseñados. (i) Taladro de batería empleado en los **Capítulos 2 y 3**. (ii) Pequeño motor eléctrico empleado en el **Capítulo 4**.

clara, este apartado se ha dividido en tres epígrafes, que coinciden con cada uno de los capítulos que componen el **Bloque III** de la Tesis Doctoral.

a. Determinación de benzofenonas en muestras de agua de piscina

El primer prototipo diseñado en el **Bloque III** se aplicó a la determinación de benzofenonas en muestras de agua de piscina (**Capítulo 2**). Para poder desarrollar el método final, se evaluaron diferentes variables cruciales para el proceso de muestreo/extracción. Una de las variables con mayor interés en esta sección es el estudio de la influencia del volumen de muestra en la señal analítica. Para evaluar este parámetro, se tuvo en cuenta la ecuación que rige el equilibrio en la microextracción en película delgada (*thin film microextraction,* TFME) (Ecuación 1):

$$n_{eq} = \frac{K_{es}V_eV_s}{K_{es}V_e+V_s}C_s \quad \textit{Ecuación 1}$$

donde n_{eq} es la masa total de analito extraída en el equilibrio, K_{es} define la constante de distribución del analito entre la matriz de la muestra y la fase sorbente, V_e el volumen de fase extractante, V_s el volumen de muestra y finalmente C_s la concentración inicial del analito en la muestra.

Así pues, si el volumen de muestra es muy grande en relación al de la fase extractante, se puede deducir que la masa de analito extraída es independiente del volumen de muestra y, por tanto, sólo depende de la concentración inicial de analito en la muestra. Por ende, si se cumple esta premisa, el dispositivo se podría aplicar en procesos de extracción *in-site*.

No obstante, al estudiar esta variable, no se pudo demostrar completamente que se cumpliese la premisa anteriormente expuesta, por lo cual el dispositivo de extracción no podría aplicarse en procesos de muestreo *in-site*. Por tanto, la estrategia que se debía seguir era la de un proceso de muestreo/extracción *on-site,* ya que como muestra la Figura 7, al aumentar el volumen de muestra, la señal analítica seguía aumentando.

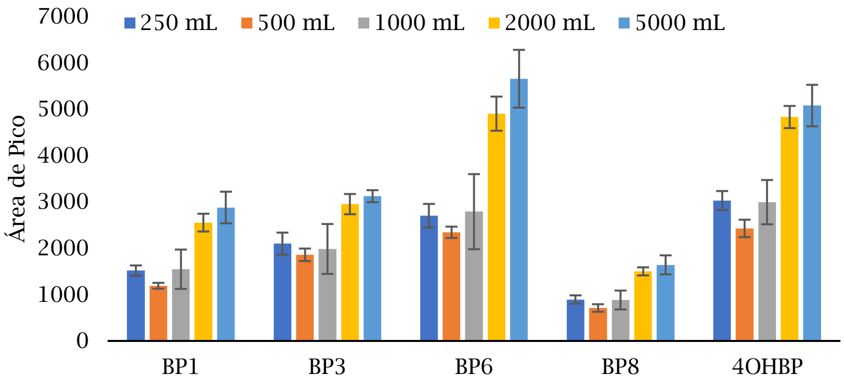


Fig. 7. Influencia del volumen de muestra en la capacidad de extracción.
BP1: Benzofenona 1, BP3: Benzofenona 3, BP6: Benzofenona 6, BP8: Benzofenona 8, 4OHBP: 4-Hidroxibenzofenona.

Sin embargo, aunque el proceso no puede ser aplicado en muestreo/extracción *in-site*, su empleo en procesos *on-site* sigue siendo ventajoso, ya que elimina la etapa de transporte de la muestra hasta el laboratorio, implicando sólo el transporte de la membrana en la que se encuentran retenidos los analitos.

b. Determinación de parabenos y triclosán en muestras de agua de piscina

En el **Capítulo 3** de la Tesis Doctoral, se aplicó el dispositivo de extracción para la determinación de parabenos y triclosán en muestras de agua de piscina. En el desarrollo del método propuesto, se evaluó tanto el proceso de síntesis del sorbente, como las variables involucradas en el proceso de muestreo/extracción. En esta sección se discuten los resultados en dos apartados diferenciados.

i. Síntesis del sorbente

La capacidad sorbente del material es un parámetro crucial en el proceso de extracción, ya que determina la sensibilidad del método propuesto. Por eso, el proceso de síntesis de la nueva membrana magnética con papel como soporte se optimizó con objeto de maximizar su capacidad sorbente.

La nueva membrana magnética soportada sobre papel se preparó mediante el método de *dip-coating*. Esta estrategia de síntesis se seleccionó debido a la simplicidad del proceso, así como a su mayor reproducibilidad.

Como variables del proceso de síntesis, por un lado, se evaluó el material polimérico que actuaría como fase extractante en el proceso de muestreo/extracción y, por otro, se estudió el número de inmersiones en la disolución precursora durante el proceso de *dip-coating*.

Atendiendo a la composición polimérica del material sorbente preparado, se concluye que tanto el poliestireno como el nailon-6 pueden emplearse como fase extractante para la resolución del problema analítico propuesto (Figura 8). Finalmente, y para aumentar la sensibilidad del proceso, se seleccionó en esta aplicación nailon-6 como fase extractante ya que demostró una mayor capacidad de extracción.

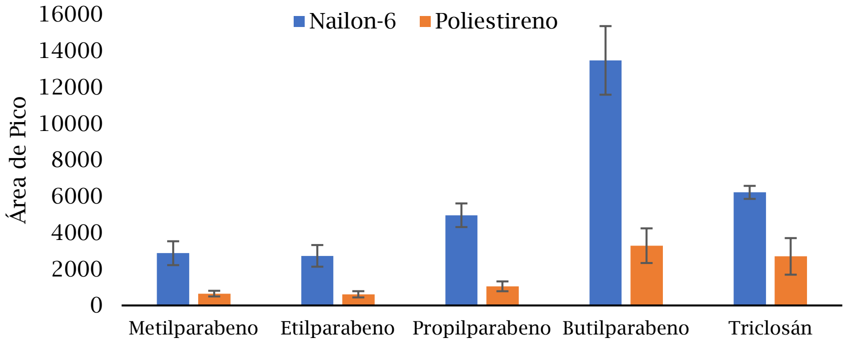


Fig. 8. Selección de la fase extractante empleada en la membrana magnética soportada sobre papel.

Cabe reseñar que en el proceso de preparación de las membranas de nailon-6 se añade una etapa más al proceso de síntesis, como es la inmersión de la membrana en agua tras sumergirla en la disolución precursora (nailon-6 en ácido fórmico). Este cambio de medio provoca la precipitación del nailon-6, insoluble en fase acuosa. En el caso de las membranas de poliestireno, este paso no es necesario ya que el sólido se genera tras la evaporación del cloroformo, disolvente que se emplea para solubilizar el polímero.

Una vez se seleccionó el nailon-6 como fase extractante, se evaluó el número de inmersiones en la disolución precursora. En la Figura 9 se puede observar que, si bien la señal aumenta hasta 3 inmersiones, una vez se supera ese número, la capacidad extractante del material preparado no aumentaba y, en algunos casos, incluso disminuía. Este efecto observado se debe a una menor porosidad del material como consecuencia del número de capas superpuestas. Además, si bien un número mayor de inmersiones aumenta la cantidad de fase extractante, esto también puede afectar a la cinética de extracción. Para explicar esto, es necesario recurrir de nuevo a las ecuaciones teóricas de la SPME, en este caso a la que define el tiempo necesario para alcanzar el equilibrio (t_e):

$$t_e = \frac{3\delta(b-a)}{D_s} \quad \textit{Ecuación 2}$$

donde δ es el espesor de la capa límite de difusión, *(b-a)* representa el espesor de la fase extractante y, por último, D_s se define como la constante de difusión de los analitos desde la matriz de la muestra. Así al aumentar el espesor de la fase extractante, aumentará el tiempo necesario para alcanzar el equilibrio, es decir, afectará a la cinética del proceso de extracción haciendo que este sea más lento y, por tanto, la capacidad sorbente del material a igualdad de tiempo de extracción se vea mermada.

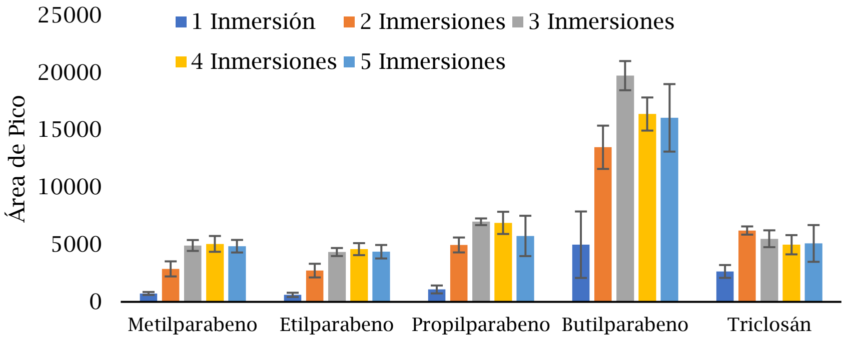


Fig. 9. Influencia del número de inmersiones en la capacidad de extracción de la fase sorbente.

ii. Variables del proceso de muestreo/extracción

En este capítulo y, como ocurrió en el **Capítulo 2**, una de las variables más importantes del proceso de muestreo/extracción fue el volumen de muestra. En este caso, las conclusiones que se extraen de este estudio son diferentes a las obtenidas en el prototipo anterior.

En la Figura 10, se observa cómo al aumentar el volumen de muestra, se alcanza un valor a partir del cual no se aprecia una diferencia sensible en la señal analítica. Esto puede explicarse en base a la Ecuación 1. En este caso, y debido al empleo de una fase sorbente diferente a la empleada en el **Capítulo 2,** un aumento en el volumen de muestra no produce cambios sensibles en la señal, es decir, la señal analítica solo depende de la concentración de analito presente en la muestra. Esto implica que el dispositivo con la nueva fase sorbente podría emplearse en procesos de extracción *in-site*.

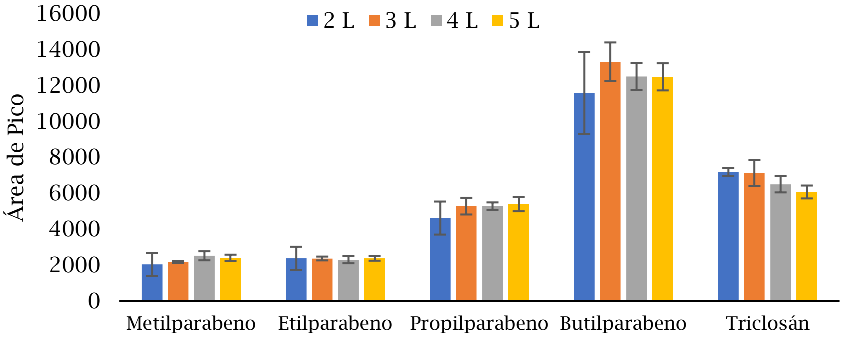


Fig. 10. Influencia del volumen de muestra en la capacidad de extracción de la membrana magnética soportada sobre papel.

c. Determinación de triazinas en muestras de agua de arroyo y pozo

En el **Capítulo 4**, se recoge la última aplicación desarrollada en la evolución del dispositivo de muestreo/extracción para muestras de agua. En primer lugar, se preparó una fase sorbente magnética que utiliza HLB el material más empleado en los procesos de análisis ambiental. En segundo lugar, se sustituye el sistema de agitación por otro más económico.

En la optimización del método para la determinación de triazinas en estas muestras de agua, se evaluaron las diferentes variables que afectaban al proceso de muestreo/extracción. En este caso, la variable que mayor interés tiene es la influencia de la fuerza iónica. El volumen de muestra queda relegado a un segundo plano, ya que este va a venir determinado por el del recipiente empleado para llevar a cabo el proceso de extracción.

En la Figura 11i se observa cómo la fuerza iónica de la muestra afecta al proceso de extracción. El intervalo estudiado es el esperable en aguas naturales [2]. No obstante, con vistas a no tener que ajustar este parámetro en las muestras, se incluyó en este estudio un estándar interno (EI) de manera que se pudiera evaluar si su presencia podía normalizar el efecto de la fuerza iónica de la muestra en la extracción de los analitos. En la Figura 11ii, se observa cómo la

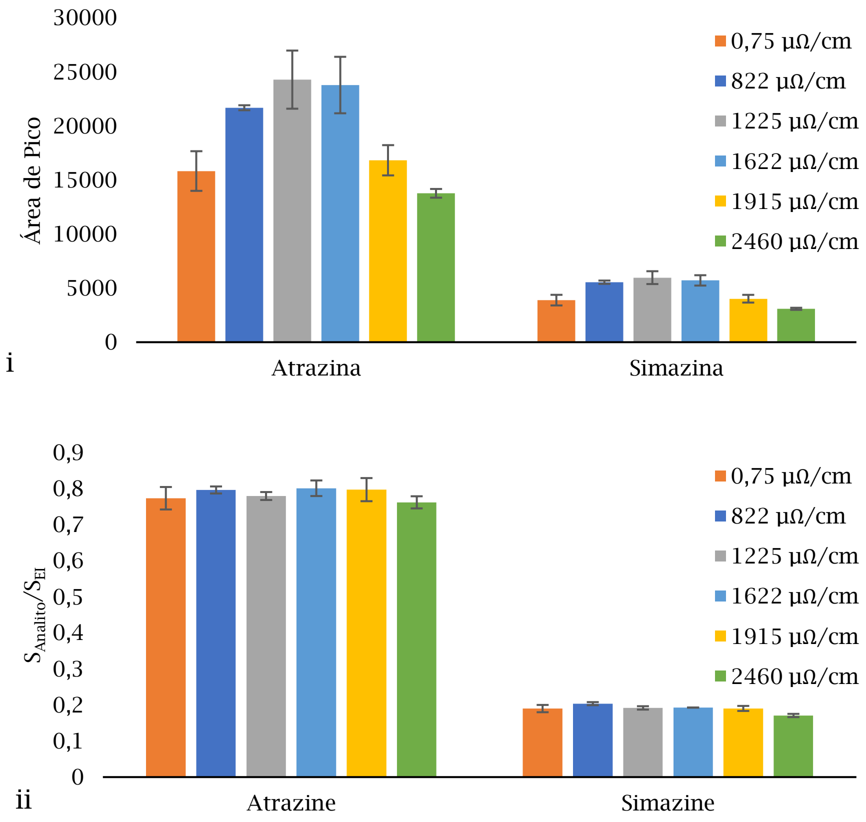


Fig. 11. Influencia de la fuerza iónica en el proceso de muestreo/extracción. (i) Sin adición de estándar interno. (ii) Adicionando estándar interno.

señal relativa (área del analito/área del EI) permanecía constante y, por tanto, no era necesario controlar la fuerza iónica. Esto se traduce en una simplificación del proceso de muestreo/extracción, así como en una reducción en el consumo de reactivos.

Una vez evaluada la influencia de las diferentes variables implicadas en el proceso de extracción, también se estudió la estabilidad de los analitos en el nuevo material sorbente. A la vista de los resultados recogidos en la Figura 12, se pudo concluir que los analitos eran estables en el material sorbente al menos 16 días, consiguiendo así demostrar que no habría problemas de degradación/pérdida de analito en el proceso de transporte y almacenaje.

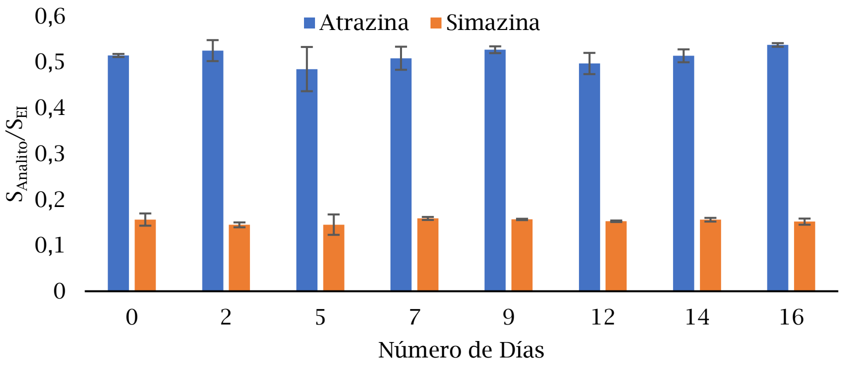


Fig. 12. Estudio de estabilidad de los analitos en la fase extractante.

3. Aplicabilidad de los métodos propuestos para muestreo/extracción en muestras de agua

En este apartado, se discutirán y evaluarán las fortalezas y debilidades de los diferentes métodos desarrollados para la determinación de las familias de contaminantes incluidas en esta Memoria. Para ello, se va a realizar un estudio comparativo en términos de sensibilidad (LOD), precisión (RSD) y exactitud (expresada como recuperación relativa) de los diferentes métodos con otros descritos en la bibliografía. También se tendrán en cuenta otras propiedades analíticas, así como el potencial de los distintos métodos para la integración en metodologías *on-site*.

a. Determinación de benzofenonas

En el **Capítulo 2**, se demostró la aplicabilidad del dispositivo de muestreo/extracción diseñado para la determinación de benzofenonas en muestras de agua. En la Tabla 1, se compara el método propuesto con los métodos descritos en la bibliografía empleando los parámetros indicados anteriormente [3–12].

Se puede observar que el método propuesto no es de los más sensibles de la bibliografía aun siendo la espectrometría de masas la técnica empleada para la detección de los analitos, si bien puede competir con los de espectrometría masas en tándem que, aunque no mejora la sensibilidad del método, si aporta selectividad al mismo. Sin embargo, los límites de detección obtenidos con la metodología propuesta son comparables o mejores a los que determinan un número similar de benzofenonas.

En relación con la precisión y exactitud del método, en la Tabla 1 se puede observar que es un método preciso y exacto, lo que demuestra su aplicabilidad para el problema analítico propuesto.

Por otro lado, comparando los volúmenes de muestra empelados en los diferentes métodos, el método propuesto permite procesar los volúmenes de muestra más elevados sin necesidad de transportarlos al laboratorio. La aplicación *on-site* de la alternativa desarrollada en esta Tesis Doctoral es su ventaja más interesante ya que, aunque el método [9] puede procesar hasta 1 L de muestra con mejor sensibilidad, requiere del transporte de la misma al laboratorio. A esto hay que sumar que el tiempo de procesamiento de la muestra en el caso de la propuesta del **Capítulo 2** es menor, 10 min frente a los 500 min necesarios en el caso del método [9].

Comparando la técnica instrumental empleada para la separación/detección de los analitos, la metodología propuesta puede minimizar las posibles interferencias en la determinación instrumental dada la selectividad que proporciona la espectrometría de masas en tándem.

Además, si se compara la metodología propuesta en [3], ya que es la única que integra las etapas de muestreo y extracción, la propuesta del **Capítulo 2** tiene mejores límites de detección, y mayor precisión, incluso determinando un número mayor de benzofenonas.

Tabla 1. Comparativa del método desarrollado para la determinación de benzofenonas con otros métodos de la bibliografía.

Analitos	Tipo de agua	Técnica de tratamiento de muestra	Instrumentación	Volumen de muestra (mL)	LOD (ng/L)	Precisión (%)	Exactitud (%)	Referencia
BP1, BP3, BP6, BP8, 4-OHBP	-	D-µSPE	UPLC-DAD	40	500-3000	< 4.9	84-105	[1]
BP1, BP3	Lago	IL-DLLME	UPLC-UV	30	16-20	< 4.8	70.5-91.3	[2]
BP3	Piscina	SPMD- Muestreador pasivo	LC-DAD	100	200	< 19	74.9-94.6	[3]
4OHBP	Superficial y residuales	SPE	LC-MS/MS	200/100	1.11/2.22	< 13.5	84/82	[4]
BP1, BP3, 4OHBP	Arroyo, grifo y mar	MR-SHS-HLLME	LC-UV	8	700-800	< 7.9	80-103	[5]
BP3	Lago, mar, piscina y río	FPSE	GC-MS/MS	500	4.5	< 12	88-94	[6]
BP1, BP3	Piscina, pozo y río	AA-LLME	LC-UV	5	45-160	< 3.7	89.1-104.8	[7]
BP3	Residuales	µ-ABS	LC-DAD	10	240	< 7.3	117	[8]
BP1, BP3, 4-OHBP	Residuales	SPE	LC-MS/MS	1000	30-60	-	97-103	[9]
BP3	-	MEPS	GC-MS	0.2	1.8-3.2	< 15.5	90-106	[10]
BP1, BP3, BP6, BP8, 4-OHBP	Piscina	SME	LC-MS/MS	2000 (*On-site*)	100	< 9.9	74-111	**Capítulo** 2

IL-DLLME: microextracción líquido-líquido en fase dispersiva empleando líquidos iónicos. SPMD: Dispositivo de membrana semipermeable. MR-SHS-HLLME: Microextracción líquido-líquido homogénea con disolventes de hidrofobicidad conmutable recuperados magnéticamente. AA-LLME: microextracción líquido-líquido asistida con aire. µ-ABS: sistema acuoso bifásico miniaturizado.

Por otro lado, la comparación con otros métodos descritos que determinan un número similar de benzofenonas tal es el caso de [1], la metodología propuesta en esta Tesis Doctoral es más simple, ya que no requiere derivatización para la etapa de detección de los analitos. Además, permite procesar un volumen de muestra mayor que el de la técnica dispersiva, mejorando la sensibilidad.

Finalmente, en el apartado del tratamiento de muestra, la metodología propuesta destaca, ya que es de las más sencillas y rápidas de aplicar. Además, la minimización del uso de disolventes, así como la reducción de la manipulación en esta etapa, la hace de las más seguras desde el punto de vista del operador y del medio ambiente.

b. Determinación de parabenos y triclosán

En esta sección, se evalúa el potencial de la nueva membrana magnética soportada sobre papel para la determinación de conservantes empleados en la industria cosmética descrito en el **Capítulo 3.** Para ello, en la Tabla 2 [13–20] se compara la metodología propuesta con otras para el mismo fin descritas en los últimos años.

Se observa que la metodología propuesta no es la más sensible de las descritas en la bibliografía, si bien los límites de detección alcanzados permiten resolver el problema analítico propuesto.

En lo que se refiere a precisión y exactitud, la metodología propuesta se puede considerar de las más precisas descritas en este campo. Además, la exactitud del método también compite con la de los demás descritos, lo que soporta el potencial del material descrito para la resolución del problema analítico seleccionado.

Si se compara el volumen de muestra, el método propuesto en esta Memoria es el que permite trabajar un volumen de muestra más elevado sin necesidad de transportar la muestra al laboratorio, ya que los analitos se aíslan en la etapa de muestreo/extracción y se pueden transportar hasta el laboratorio retenidos en el material sorbente. El potencial para la aplicación *on-site* lo convierte en uno de los más competitivos para la determinación de los analitos seleccionados, proporcionando mejores valores de precisión que técnicas exhaustivas como las descritas en [13,15]. Además, la rapidez del método lo coloca por delante de estas propuestas que implican el empleo de la SPE, donde

Tabla 2. Comparativa del método desarrollado para la determinación de parabenos y triclosán con otros métodos de la bibliografía.

Analitos	Tipo de agua	Técnica de tratamiento de muestra	Instrumentación	Volumen de muestra (mL)	LOD (ng/L)	Precisión (%)	Exactitud (%)	Referencia
MPb, EPb, PPb, BPb and TCS	Grifo, pozo y río	RDSE, deriv	GC-MS	20	40-110	<12	-	[11]
EPb, BPb and TCS	Cloacal, grifo, municipal y subterránea	FPSE	GC-MS	10	8-21	<4.1	94.26-98.89	[12]
MPb, EPb, PPb, BPb and TCS	Río	SPE	UPLC-MS/MS	1000	0.009-0.03	-	94-103	[13]
EPb, PPb and TCS	Lago y río	SPE	HPLC-MS/MS	500	8000-30300	<33.67	54.49-92.25	[14]
MPb, EPb, PPb, and TCS	Residual y río	SPE	UPLC-MS/MS	1000 Sin fil río, 20 diluidos a 500 y 500 sin fil del eflu	0.17-45	<20.3	82.5-113	[15]
MPb, EPb, PPb, and TCS	Río	SPE, deriv	GC-MS/MS	1000	0.9-14	<4.6	56.8-113.5	[16]
MPb, EPb, PPb and BPb	Superficial	UASS-DLLME	GC-MS/MS	10	1-5	<11	79-101	[17]
BPb and TCS	Mar	LOV-µSPE	HPLC-MS/MS	5	0.5-0.6	<5.8	97-107	[18]
MPb, EPb, PPb, BPb and TCS	Piscina	SME	HPLC-MS/MS	2000 (*On-site*)	70-100	<8	88-98	**Capítulo 3**

los tiempos de retención de los analitos pueden llegar a los 100 min como en [15].

Desde el punto de vista de la etapa de tratamiento de muestra, la aplicación *on-site* del método propuesto reduce las etapas de este proceso. Además, hace que el método descrito sea sencillo y respetuoso con el medio ambiente ya que, a diferencia con otros de los descritos, reduce el consumo de reactivos al eliminar etapas de derivatización (como ocurre en las metodologías que emplean GC-MS).

Por otro lado, al realizar la comparativa con métodologías similares, tal es el caso de [11], la propuesta del **Capítulo 3** la aventaja en varios aspectos, como son la eliminación de una etapa de derivatización, que hace que el proceso sea más simple. Además, presenta límites de detección comparables con una mejor precisión. A esto hay que añadir que la velocidad de muestreo es mayor que en [11], que requiere 60 min para la etapa de retención frente a los 10 min del método desarrollado en esta Tesis Doctoral que, además, permite la aplicación *on-site*.

c. Determinación de triazinas

Finalmente, sintetizó un nuevo material magnético con partículas *hydrophilic-lipophilic balance* (HLB) para su incorporación en el dispositivo de muestreo/extracción en agua. En el **Capítulo 4**, se evaluó su potencial para la determinación de triazinas. En la Tabla 3, se presenta un estudio comparativo de la metodología propuesta con otras descritas en la bibliografía para la resolución de dicho problema analítico [21–28].

Atendiendo a la sensibilidad del método, se puede concluir que la metodología propuesta compite con las más sensibles de la bibliografía.

Desde el punto de vista de la precisión y la exactitud de los resultados, esta metodología es de las más precisas descritas en los últimos años. Además, atendiendo a la exactitud del método, es lo suficientemente exacta como para ser aplicada a la resolución del problema propuesto.

Por otro lado, desde el punto de vista del volumen de muestra procesado, es el método que permite procesar volúmenes de muestra más altos. Lo que sumado a la aplicación *on-site*, la coloca como la metodología con mayor potencial de las

Tabla 3. Comparativa del método desarrollado para la determinación de atrazina y simazina con otros métodos de la bibliografía.

Analitos	Tipo de agua	Técnica de tratamiento de muestra	Instrumentación	Volumen de muestra (mL)	LOD (ng/L)	Precisión (%)	Exactitud (%)	Referencia
Atrazina	Grifo, lago y río	SPME	DART-MS	50	50	<9.3	99.7-109.6	[19]
Atrazina	Mar	IT-SPME	NanoLC-DAD	4	25	-	-	[20]
Atrazina y simazina	Mar	SPE	UPLC-MS/MS	1000	<0.05	<7	103-109	[21]
Atrazina y simazina	Río	D-µSPE	HPLC-MS/MS	20	29-43	<9	89-98	[22]
Atrazina	Superficial	D-MSPE	HPLC-UV	50	120	<4.8	99.8-100.7	[23]
Atrazina y simazina	Lago y río	D-µSPE	HPLC-MS/MS	500	0.07-0.08	<6.2	86.1-93.2	[24]
Atrazina y simazina	Cultivo, lago y río	IT-SPME	HPLC-DAD	0.9	74-79	<9.3	81.7-119	[25]
Atrazina	Grifo, lluvia y río	D-MSPE	GC-MS	50	1-5	<14	99-100	[26]
Atrazina y simazina	Arroyo y pozo	SME	DI-MS/MS	2500 (*On-site*)	15	<8.3	70-121	**Capítulo 4**

descritas, ya que evita el transporte de la muestra al laboratorio. Consiguiendo así, una vez más, uno de los objetivos de la Tesis Doctoral.

A lo anteriormente descrito, hay que añadir el reducido tiempo de análisis instrumental ya que al realizarse por infusión directa en espectrometría de masas, se elimina la etapa de separación cromatográfica.

En comparación con las técnicas dispersivas [22-24,26], presenta una sensibilidad intermedia, permitiendo procesar en todos los casos volúmenes de muestra más elevados. Además, la precisión de metodología del **Capítulo 4** es comparable con la de este tipo de técnicas de tratamiento de muestra. Además, es más sencilla de aplicar que cualquiera de las técnicas dispersivas, necesita menos manipulación de la muestra por parte del operador y tiene el potencial de la aplicación *on-site*.

4. Innovaciones en el diseño de sistemas que integren la toma de muestra y extracción de analitos en muestras de aire

En la línea de muestreo de aire se propuso un dispositivo dinámico y de bajo coste para la extracción de volátiles. El prototipo diseñado (Figura 13) estaba compuesto por un ventilador, que favorecía el paso de la muestra hacia la fase sorbente situadas en las aspas del mismo (Figura 13i). El ventilador funcionaba mediante el cable de un cargador convencional de un teléfono móvil. En el dispositivo se incluyó una frita de polipropileno (Figura 13ii) sobre la que se podía adicionar un estándar interno, el cual se emplearía en la cuantificación de

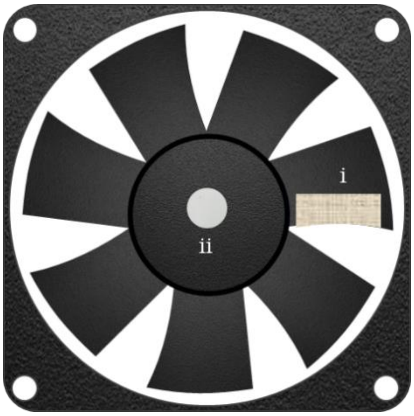


Fig. 13. Dispositivo para la toma de muestras de aire. (i) *Fabric Phase* empleada como fase sorbente. (ii) Frita de polipropileno para añadir el estándar interno.

de los volátiles para normalizar la señal analítica. El diseño propuesto es fácil de aplicar y tiene ventajas frente a los convencionales que se comentarán al final del apartado.

Para su puesta a punto, se evaluaron en primer lugar las variables hidrodinámicas y, a continuación, las relacionadas con el proceso de extracción. Por tanto, se discutirán los resultados más relevantes del desarrollo del prototipo en dos apartados diferenciados.

a. Estudio de las variables hidrodinámicas

Para la puesta a punto del dispositivo de muestreo, se estudiaron diferentes variables hidrodinámicas como son la identificación de la zona de máximo contacto de la muestra con el dispositivo para poder seleccionar la mejor localización de la fase sorbente y el caudal en función del voltaje aplicado al dispositivo.

Para el estudio de la primera variable, se utilizó un aerógrafo situado de forma ortogonal respecto al ventilador, tal como se muestra en la Figura 14a. Al ser la dirección de propagación del spray perpendicular a la de aspiración del ventilador, las zonas de las aspas que quedasen marcadas por la pintura corresponderían al paso de muestra debido a la aspiración del ventilador y no consecuencia de la impulsión de la pintura por el aire comprimido del aerógrafo. Como puede verse en la Figura 14b, sólo una parte de las aspas del

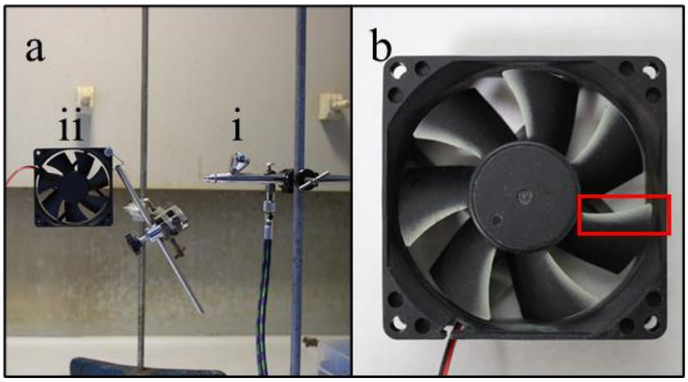


Fig. 14. Montaje empleado para el estudio de la zona de mayor contacto dispositivo/muestra. (ai) Aerógrafo. (aii) Ventilador empleado como dispositivo de muestreo. (b) Dispositivo tras la experiencia realizada donde se aprecia la zona de mayor interacción entre este y la muestra.

ventilador quedó marcada preferentemente por la pintura, indicando la zona de mayor contacto de las aspas con el aire que pasa a través del ventilador y, por tanto, el lugar óptimo para fijar la fase sorbente. Con esta disposición se maximiza el contacto de la muestra con el medio de extracción, y por tanto la retención de los analitos en el dispositivo de muestreo.

Una vez seleccionada la localización de la fase extractante, se evaluó el caudal de aspiración del ventilador. Esta variable está directamente relacionada con el volumen de muestra. Para llevar a cabo este estudio, se modificó el voltaje del dispositivo de muestreo, ya que un mayor voltaje implica una mayor velocidad de giro del ventilador y, por tanto, un caudal de aspiración más elevado. El voltaje se controló con una fuente de alimentación de voltaje variable, pero no se estudiaron voltajes inferiores a 5 V, voltaje basal de funcionamiento. Para la medida del caudal del dispositivo, se empleó un anemómetro que permitió establecer una relación lineal entre el caudal y el voltaje aplicado (Figura 15).

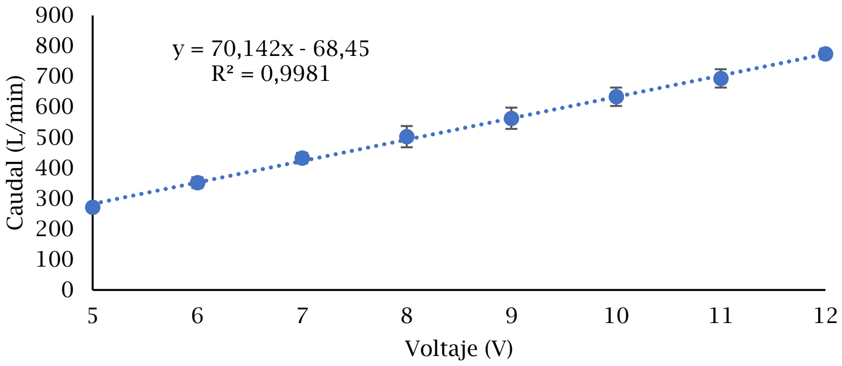


Fig. 15. Modelo de calibración empleado para determinar el caudal del dispositivo de muestreo en función del voltaje.

A continuación, se estudió la estabilidad del caudal con el tiempo. El objetivo de este estudio era evaluar si el caudal se mantenía constante y permitía, por tanto, calcular de forma reproducible el volumen de muestra que pasaba a través del sistema de muestreo, y por tanto emplearlo con fines cuantitativos. Para ello, se seleccionaron dos valores 5 V (voltaje de salida de los USB y cargadores portátiles de los Smartphones) y 12 V (voltaje de trabajo del ventilador cuando se emplea como disipador de calor en los ordenadores). En la Figura 16, se muestran los resultados obtenidos, donde puede verse que tras un corto periodo inicial de aproximadamente 5 min, el caudal de aspiración se mantiene constante.

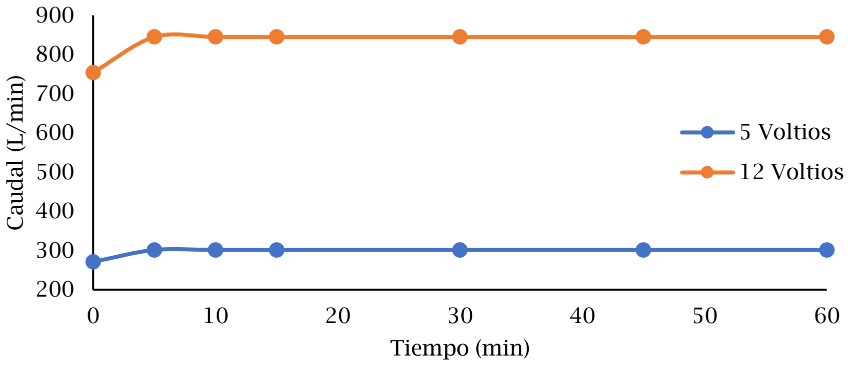


Fig. 16. Influencia del tiempo en el caudal del muestreador.

b. Estudio de las variables que afectan al proceso de extracción

Una vez evaluadas las variables hidrodinámicas del dispositivo de muestreo, se estudiaron las variables que afectaban al proceso de extracción. Se estudió en primer lugar el volumen de muestra, empleando para ello los dos valores de voltaje anteriormente estudiados en función del tiempo. En la Figura 17, se observa que 5 V proporcionó los mejores resultados de extracción, cuando inicialmente cabría esperar que 12 V proporcionase señales mayores para los

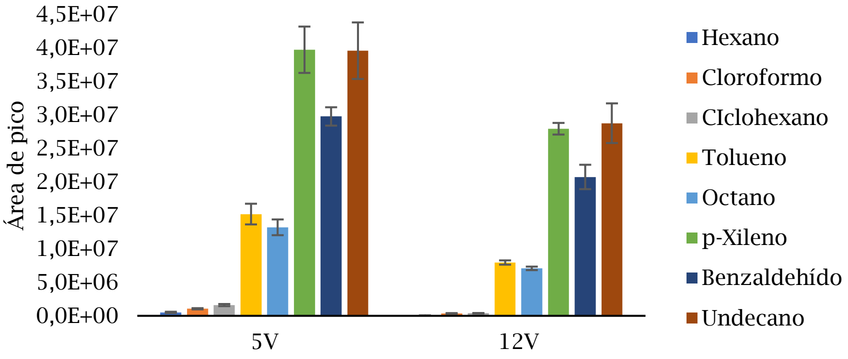


Fig. 15. Modelo de calibración empleado para fijar el caudal del dispositivo de muestreo en función del voltaje.

analitos, ya que el volumen de aire que pasó a través del muestreador también lo era. Sin embargo, si bien un aumento de voltaje aumenta el volumen de aire muestreado, también implica que el tiempo de interacción entre la muestra y la fase sorbente se reduce al incrementarse la velocidad a la que pasa a través del muestreador, lo que reduce la eficacia de la etapa de retención de los analitos. Por tanto, resulta más conveniente el empleo del voltaje más bajo para maximizar el rendimiento del muestreador.

5. Aplicabilidad del dispositivo de muestreo/extracción para la toma de muestras de aire

Una vez estudiadas las variables más importantes del dispositivo de muestreo/extracción, se evaluó su potencial para la cuantificación de compuestos volátiles en aire, así como para la identificación del perfil de volátiles de productos naturales. Se empleó como fase sorbente en ambos casos Carbowax 20M. Las *Fabric Phases* de Carbowax 20M, de 1 x 1,5 cm se colocaron en tres de las aspas del ventilador en la posición óptima seleccionada anteriormente.

a. Determinación de compuestos volátiles en aire

El principal problema de la determinación de compuestos volátiles en aire es la preparación de los estándares para poder establecer la correspondiente relación entre la concentración del analito en la muestra y la señal analítica obtenida tras el análisis instrumental. En este caso, se propuso un sistema que permitía generar los estándares gaseosos de forma muy sencilla (Figura 16), ya que la concentración se calculó por diferencia de pesada. Para ello se colocaron en un embudo buchner viales (5 mL) individuales con compuestos de cuatro familias diferentes de disolventes orgánicos (benzaldehído, ciclohexano, cloroformo y tolueno). La elección de dichos analitos se basó en una selección de compuestos de familias diferentes de los empleados en la optimización del tiempo de muestreo. A dicho embudo se adaptó el dispositivo de muestreo, permitiendo la entrada de aire por la parte inferior, consiguiendo así que al aspirar el muestreador arrastrase los volátiles hacia el mismo. Por otro lado, con el fin de normalizar la señal, se añadieron 5 µL de bromoformo, compuesto empleado como estándar interno, a la frita de polipropileno que se encontraba en el centro del muestreador. De esta manera, se incorporaba a la corriente de aire que pasaba a través del muestreador de forma controlada y se quedaba retenido sobre la fase sorbente junto con los analitos.

Fig. 16. Sistema empleado para la generación de estándares.

Para demostrar el potencial en análisis cuantitativo, se construyeron los modelos de calibración para los diferentes compuestos colocados en viales individuales, incrementando el número de viales dentro del sistema para aumentar la concentración de analito. La única limitación que podía tener el sistema era conseguir estándares de concentraciones bajas para los analitos seleccionados, pues el valor más bajo depende de la velocidad de evaporación de los mismos. Sin embargo, se lograron construir modelos de calibración en el rango de los microlitros. En la Tabla 4 se recogen los datos para los modelos de calibración construidos, datos en base a los cuales se concluyó que el dispositivo tenía potencial para la cuantificación de compuestos volátiles en aire. A la vista de los datos de la Tabla 4, se puede apreciar que todos los modelos de calibración siguen una tendencia lineal, excepto el cloroformo. En este caso, su mayor volatilidad y, por tanto, el intervalo de calibración más amplio, hace que la tendencia sea logarítmica. Por otro lado, cabe destacar que la sensibilidad del método (pendiente del modelo de calibración) para el benzaldehído es más elevada que para el resto de los analitos. Esto no se debe a la volatilidad del mismo, pues es el compuesto es el que tiene una temperatura de ebullición (178,1 °C) más elevada de los seleccionados. Sin embargo, si bien no es el más volátil si es el que mayor afinidad tiene con la *Fabric Phase* y, por tanto, se retiene mejor sobre ella.

Tabla 4. Modelos de calibración para los volátiles cuantificados

Analito	Curva de calibración	R^2	Intervalo de concentración (µg/L)
Cloroformo	$y = 4{,}0104\ln(x) - 11{,}18$	0,9784	20,1 – 462,05
Ciclohexano	$y = 0{,}0847x + 0{,}4081$	0,9984	7,58 – 58,74
Tolueno	$y = 0{,}7095x - 0{,}2532$	0,9892	9,44 – 93,05
Benzaldehído	$y = 388{,}77x - 25{,}06$	0,9505	0,22 – 1,63

b. Análisis no dirigido del perfil de volátiles

Como complemento al análisis cuantitativo, se quiso evaluar el potencial del sistema de muestreo para llevar a cabo un análisis no dirigido. Esto es interesante si se quiere emplear el dispositivo para llevar a cabo estudios de calidad del aire y/o la identificación temprana de compuestos que puedan ser indicativos de un problema de contaminación ambiental. Para el desarrollo de esta aproximación, se seleccionaron unas condiciones controladas de análisis. Así, se emplearon así muestras naturales con un perfil más o menos complejo de compuestos volátiles, de manera que se pudiera establecer si el sistema de muestreo era capaz de arrastrarlo hasta la fase sorbente, pudiendo ser determinados posteriormente mediante la técnica instrumental (cromatografía de gases acoplada espectrometría de masas). Para ello, se seleccionaron dos muestras sólidas (agujas de pino y cáscara de naranja) que se situaron en mismo dispositivo empleado para la generación de los estándares gaseosos. El análisis de la fase sorbente (Carbowax 20M) transcurridos 30 min de muestreo se resume en la Tabla 5. Para llevar a cabo la identificación, se empleó la base de datos del NIST [29], asignándose así los compuestos identificados en la fase sorbente. Además, se comparan los índices de retención de los semivolatiles identificados en las diferentes muestras, con los índices de retención descritos en la bibliografía para los mismos compuestos [30].

De la identificación realizada se concluye que el dispositivo tiene potencial para el aislamiento y posterior identificación de compuestos semivolatiles presentes en productos naturales mediante un análisis no dirigido.

Tabla 5. Identificación de compuestos semivolatiles en muestras sólidas.

Muestra	Compuesto	Índice de retención experimental (RI)	Índice de retención tabulado (RI°)	Error (%)
Pino	Tricicleno	925	923	0,2
	β-pineno	970	964	0,6
	β-mirceno	991	991	0
Naranja	Tricicleno	925	923	0,2
	β-pineno	970	964	0,6
	Octanal	1004	1001	0,3
	Limoneno	1030	1029	0,1
	(Z)-beta-Ocimeno	1042	1039	0,3
	trans-β-Ocimeno	1052	1050	0,2

6. Perspectivas futuras

Una vez expuestos los resultados más relevantes de la investigación realizada durante la presente Tesis Doctoral, resulta interesante abordar las posibilidades de desarrollos en un futuro próximo. Así pues, a continuación, se hará una reflexión de las posibles perspectivas de avance de las líneas de investigación desarrolladas en la presente Memoria.

a. Dispositivos para análisis de muestras de agua

Una vez diseñado un dispositivo que cumple con los principios fundamentales de la Química Analítica Blanca, las posibilidades de este se pueden concretar en varios puntos que se enumeran a continuación:

- Automatización total del sistema de muestreo. Este proceso de automatización pasa por el empleo de la tecnología Arduino con el que controlar el encendido y apagado del motor, así cómo controlar la velocidad de rotación del motor.

- Incorporación de sensores para la monitorización de parámetros como el pH, la fuerza iónica y la temperatura, todo ello basado en la tecnología Arduino.

- Evaluación del cambio de geometría de la unidad de extracción, para así aumentar la superficie activa de la fase sorbente y, por tanto, los factores de enriquecimiento de los procesos de muestreo/extracción aplicados.

b. Dispositivos para análisis de muestras de aire

Las perspectivas futuras de este dispositivo son las siguientes:

- Automatización de la unidad de muestreo/extracción, consiguiendo un dispositivo de toma de muestra totalmente automatizado, fácil de emplear y barato puesto que se basará en la tecnología Arduino.
- Evaluación del potencial de nuevas fases sorbentes no comerciales para extender la aplicación del dispositivo a la resolución de nuevos problemas analíticos.
- Evaluación del potencial del dispositivo para el muestreo de material particulado en aire.

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CONCLUSIONES

CONCLUSIONS

El trabajo de investigación llevado a cabo en la presente Tesis Doctoral se ha focalizado en la innovación en sistemas de toma de muestra ambiental mediante el empleo de nuevas fases sorbentes. Los dispositivos desarrollados aúnan en una sola etapa el muestreo y el aislamiento de los analitos, simplificando el proceso analítico. Además, estos dispositivos están en línea con los principios de la Química Analítica Blanca. Por un lado, se ha considerado el desarrollo de dispositivos baratos y sostenibles con el medio ambiente, mediante el empleo de las nuevas tecnologías. Por otro lado, se ha contemplado sistemáticamente la evaluación de propiedades analíticas tan relevantes como la sensibilidad, reproducibilidad y robustez.

Tras la discusión realizada en el apartado anterior de esta Memoria, se exponen a continuación las conclusiones más relevantes que se pueden extraer de las metodologías desarrolladas en la presente Tesis Doctoral.

1. Análisis de muestras de agua

Se ha diseñado una unidad agitada para el muestreo/extracción de contaminantes presentes en muestras de agua. Durante el desarrollo de la Tesis Doctoral se fueron añadiendo diferentes mejoras al prototipo inicial, así como incorporando cambios en la fase sorbente empleada.

a. Dispositivos

La configuración inicial se basó en una unidad de extracción magnética agitada que actuaba como soporte de la fase sorbente. Como sistema de agitación se empleó un taladro portátil, al cual se unía la unidad mediante un eje. La unidad de extracción propuesta era ideal para el empleo de fases sorbentes planas.

Los problemas de difusión de los analitos hasta la muestra se solventaron inicialmente con el empleo de un septum polimérico que facilitaba una mayor exposición de la fase sorbente a la muestra. Además, para favorecer la cinética de la extracción, se le añadieron unas pequeñas aspas para mejorar la agitación de la muestra. Posteriormente se aumentó el tamaño de las aspas para incrementar aún más la extracción.

Finalmente, se mejoró el sistema de agitación sustituyendo el taladro por un pequeño motor eléctrico acoplado al tapón de una botella de vidrio. Si bien la agitación no se veía mejorada con respecto a la propuesta inicial, en este nuevo diseño se redujo el coste 50 veces. Además, la reutilización de las botellas de vidrio como recipientes de extracción lo hacen un sistema sostenible con el medio ambiente.

b. Fases sorbentes

La primera fase sorbente empleada fue una membrana de nylon-6 comercial. Para unirse a la unidad de extracción, necesitaba de una arandela metálica. Sin embargo, su empleo creaba una capa de difusión limitada, siendo este el punto débil del dispositivo.

Estos problemas de difusión se pudieron soslayar con el empleo de una membrana de nylon-6 magnética en base papel incluyendo nanopartículas magnéticas en la síntesis. La presencia del material nanoestructurado permitió, por un lado, aumentar la porosidad de la fase sorbente, y por otro su anclaje sobre la unidad de extracción sin necesidad de un elemento externo.

Puesto que el magnetismo de las fases sorbentes mejoró la difusión de los analitos, se propuso una nueva fase sorbente magnética, basada en partículas de *Hydrophilic-Lipophilic Balance* (HLB), material ampliamente usado en análisis ambiental. Para la preparación de esta fase sorbente se empleó como soporte una cinta autoadhesiva magnética que se recubrió con cinta de doble cara para que su superficie fuese más adherente y permitir así que las partículas HLB quedasen fijadas sobre la cinta magnética. De esta manera, se obtuvo una fase sorbente plana, magnética basada en un sorbente comercial. Entre sus ventajas se pueden citar: su fácil preparación, elevada reproducibilidad, bajo coste y ausencia de disolvente en su preparación.

c. Analitos y muestras

Los diseños desarrollados en la presente Tesis Doctoral se aplicaron a la determinación de disruptores del sistema endocrino, presentes en muestras de agua de diferente naturaleza. Esto ha demostrado la versatilidad de la propuesta para la resolución de diferentes problemas ambientales:

- La determinación de benzofenonas (filtros solares) en muestras de agua de piscina.
- La extracción de conservantes empleados en la industria cosmética, como son los parabenos y el triclosán en muestras de agua de piscina.

- La determinación de herbicidas (triazinas) en aguas naturales (arroyo y pozo).

2. Análisis de muestras de aire

Se ha diseñado un sistema de muestreo/extracción para la determinación de compuestos volátiles en muestras de aire. Además, se ha realizado una aproximación cualitativa para la identificación de compuestos semivolátiles en muestras de origen vegetal.

a. Dispositivo

El dispositivo propuesto se basa en el uso de un ventilador de ordenador para aspirar la muestra y hacerla pasar sobre la fase sorbente fijada sobre las aspas de este mediante cinta adhesiva. El empleo del ventilador como dispositivo de muestreo permite tener un sistema de toma de muestra de aire de bajo coste, ya que reduce el precio de los sistemas convencionales en aproximadamente 200 veces. Por otra parte, el empleo de la cinta adhesiva como sistema para anclar la fase sorbente confiere simplicidad al diseño, además de permitir el empleo de fases sorbentes planas en este dispositivo.

Se ha caracterizado completamente el dispositivo en términos hidrodinámicos con vistas a establecer las condiciones óptimas de trabajo.

b. Fase sorbente

Las *Fabric Phases* son materiales sorbentes con unas propiedades muy adecuadas para el muestreo de aire. Las diversas combinaciones posibles tanto desde el punto de vista del soporte como de la fase extractante aumentan su potencial. Específicamente el empleo de *Fabric Phases* preparadas en fibra de vidrio permiten su empleo directamente en equipos de desorción térmica.

c. Analitos y muestras

Se ha demostrado el potencial del dispositivo tanto para la extracción de compuestos volátiles como semivolatiles.

Por un lado, se aplicó a la cuantificación de disolventes orgánicos de uso común en laboratorios. En este caso, los estándares gaseosos se generaron de forma sencilla, lo que permitió la construcción de los correspondientes modelos de calibración para la cuantificación de los analitos modelo.

Por otro lado, se llevaron a cabo pruebas preliminares para la identificación de compuestos presentes en muestras sólidas, consiguiendo así identificar la presencia de compuestos de la familia de los terpenos, característicos de muchos aromas naturales. De este modo, se sentaban las bases para el empleo del dispositivo en análisis no supervisado.

3. Transferencia de conocimiento

La investigación recogida en esta Memoria tiene un elevado potencial de transferencia al sector productivo.

- Se han patentado dos de los dispositivos desarrollados en el marco de esta Tesis Doctoral.
- La versión más eficiente del dispositivo para análisis de agua se ha empleado para el inicio de las actividades previstas en el marco del proyecto PY20_00461: "Soportes planos para la extracción de alteradores endocrinos de muestras ambientales: de la extracción in-situ a los muestreadores biomiméticos". En el marco de este proyecto está también previstas la protección de los prototipos bajo patente.
- El sistema de análisis de aire ha servido de base para la solicitud del proyecto Prueba de Concepto "Muestreadores de aire basados en ventiladores" recientemente concedido. Entre los objetivos de este se encuentra la mejora de la propuesta inicial, así como la extensión al análisis de material particulado.

The research work carried out in this Doctoral Thesis has been focused on the innovation in environmental sampling devices through new sorptive phases. The devices try to combine the sampling and isolation of analytes in a single stage, thus simplifying the analytical process. Moreover, these devices are in line with the principles of White Analytical Chemistry. On the one hand, the development of inexpensive and environmentally sustainable devices, supported by new technologies, has been considered. On the other hand, the evaluation of relevant analytical properties such as sensitivity, reproducibility, and robustness has been systematically considered.

Following the discussion in the previous section of this Report, the most relevant conclusions that can be drawn from the methodologies developed in this Doctoral Thesis are presented below.

1. Analysis of water samples

A stirring unit has been designed for the sampling/extraction of pollutants present in water samples. During the development of the Doctoral Thesis, different improvements were implemented to the initial prototype, including the proposal of new sorptive phases.

a. Devices

The initial configuration was based on a stirred magnetic extraction unit that supported the sorbent phase. A portable drill was used as the agitation system, to which the unit was attached using an axis. The proposed extraction unit was ideal for the use of planar sorbent phases.

The problems of diffusion of the analytes to the sample were primarily solved using a polymeric septum that exposes the sorptive phase to the sample. In addition, to enhance the extraction kinetics, small blades were added to improve sample agitation. Moreover, the size of the blades was increased to further extraction enhancement.

Finally, the agitation system was improved by replacing the wireless drill with a small electric motor attached to the cap of a glass bottle. Although the agitation was not improved over the initial proposal, the cost was reduced 50-fold in this new design. In addition, the reuse of glass bottles as extraction containers makes it an environmentally sustainable system.

b. Sorptive phases

The first sorptive phase employed was a commercial nylon-6 membrane. The attachment to the extraction unit was achieved using a metal washer. However, its use creates a stagnant diffusion layer, which was the weak point of the device.

These diffusion problems could be avoided by using a paper-based magnetic nylon-6 membrane incorporating magnetic nanoparticles during the synthesis process. The presence of the nanomaterial, on the one hand, increases the porosity of the sorbent phase and, on the other hand, facilitates its attachment to the extraction unit without needing an external element.

Due to the improvement in the analyte diffusion associated with magnetic sorptive phases, a new magnetic sorbent phase was proposed. This sorptive phase was based on Hydrophilic-Lipophilic Balance (HLB) particles, well-known used in environmental analysis. To prepare this sorptive phase, a magnetic self-adhesive tape was used as a support, which was coated with double-sided tape to make its surface stickier, thus allowing HLB particles to be fixed on the magnetic tape. In this way, a planar magnetic sorptive phase based on a commercial sorbent was prepared. The main advantages are its easy preparation, high reproducibility, low cost, and solvent-free preparation.

c. Analytes and samples

The devices developed in this Doctoral Thesis were applied to determine endocrine-disrupting compounds present in water samples of different origins. This aspect has demonstrated the versatility of the design for the resolution of different environmental problems:

- The determination of benzophenones (sunscreens) in swimming pool water samples.
- The extraction of preservatives used in the cosmetic industry, such as parabens and triclosan from swimming pool water samples.
- Determination of herbicides (triazines) in natural waters (streams and wells).

2. Analysis of air samples

A sampling/extraction device has been designed to determine volatile compounds in air samples. In addition, a qualitative approach for the identification of semi-volatile compounds in samples of plant origin has been carried out.

a. Device

The proposed device uses a computer fan to aspirate the sample and make it pass over the sorptive phase, which is fixed on the blades by adhesive tape. Using a fan as a sampling device is considered a low-cost air sampling system since its price is approximately 200 times lower than the market-available systems. On the other hand, using the adhesive tape to attach the sorbent phase is simple. This strategy also allows the use of planar sorptive phases efficiently.

The device was fully characterized by its hydrodynamic behavior to establish the optimum operating conditions.

b. Sorptive phase

Fabric Phases are sorbent materials with very suitable properties for air sampling. The variety of possible combinations for both the support and the extractant phase increases their potential. Specifically, the use of Fabric Phases prepared on glass fiber enables its use with thermal desorption equipment.

c. Analytes and samples

The potential of the device has been demonstrated for the extraction of volatile and semi-volatile compounds.

On the one hand, it was applied to quantifying organic solvents commonly used in laboratories. In this case, the gaseous standards were generated in a simple way, allowing the construction of the corresponding calibration models to quantify the model analytes.

On the other hand, preliminary tests were carried out to identify compounds present in solid samples. Compounds of the terpene family, characteristic of many natural aromas, were identified. This aspect establishes the foundations for using the device in unsupervised analysis.

3. Knowledge transfer

The research reported in this Doctoral Thesis has a high potential to be transferred to the productive sector.

- Two of the devices developed within the framework of this Doctoral Thesis have been patented.
- The most efficient version of the device for water analysis has been used to start the activities planned in the project PY20_00461: " Soportes planos para la extracción de alteradores endocrinos de muestras ambientales: de la extracción in-situ a los muestreadores biomiméticos ". This project also provides for patent protection of the prototypes.
- The air analysis system has served as the basis for the application of a recently awarded Proof of Concept project " Muestreadores de aire basados en ventiladores". The improvement of the initial proposal, and its extension to the analysis of the particulate matter, are the main project goals.

ANEXOS

ANEXO A

PUBLICACIONES CIENTÍFICAS DERIVADAS DE LA TESIS DOCTORAL

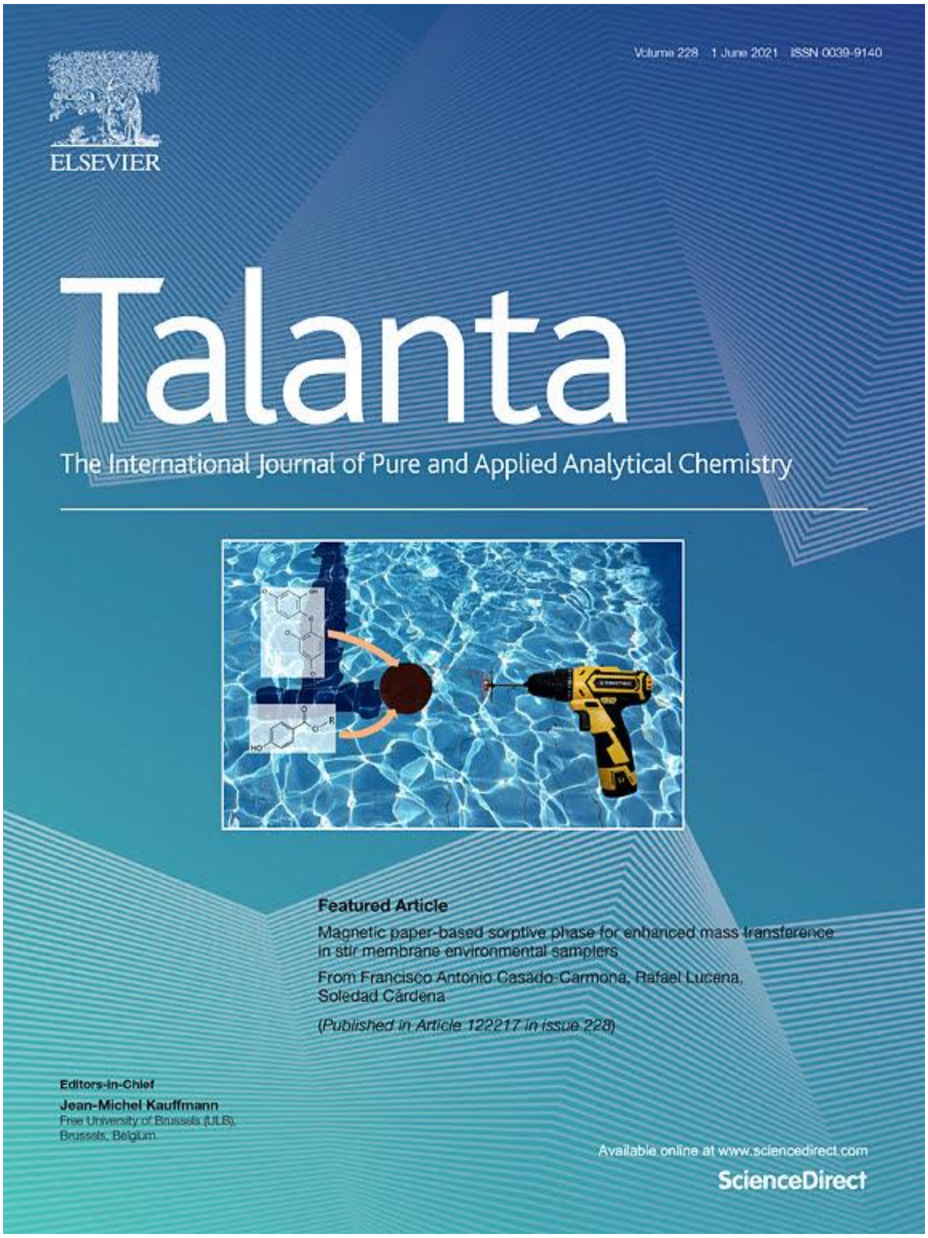
1. Portable stir membrane device for on-site environmental sampling and extraction.
F.A. Casado-Carmona, M.C. Alcudia-León, R. Lucena, S. Cárdenas
Journal of Chromatography A, 1606 (2019) 360359.

2. Magnetic paper-based sorptive phase for enhanced mass transference in stir membrane environmental samplers.
F.A. Casado-Carmona, R. Lucena, S. Cárdenas
Talanta, 228 (2021) 122217.
Portada del volumen 228 de la revista Talanta.
Volumen especial "Magnetic Nanomaterials in Analytical Chemistry" Editado por Antonio Canals, Mazaher Ahmadi.

3. Fan-based device for integrated air sampling and microextraction.
F.A. Casado-Carmona, G. Lasarte-Aragonés, A. Kabir, K.G. Furton, R. Lucena, S. Cárdenas
Talanta, 230 (2021) 122290.

4. Portable stirring device for the on-site extraction of environmental waters using magnetic hydrophilic-lipophilic balance tape.
F.A. Casado-Carmona, J.M. Jiménez-Soto, R. Lucena, S. Cárdenas
Analytica Chimica Acta, 1189 (2022) 339186.

5. Green Sample Preparation techniques in environmental analysis.
F.A. Casado-Carmona, G. Lasarte-Aragonés, R. Lucena, S. Cárdenas
Green Approaches for Chemical Analysis, 9780128222348 (2022).



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Featured Article

Magnetic paper-based sorptive phase for enhanced mass transference
in stir membrane environmental samplers

From Francisco Antonio Casado-Carmona, Rafael Lucena,
Soledad Cárdena

(*Published in Article 122217 in issue 228*)

Editors-in-Chief

Jean-Michel Kauffmann
Free University of Brussels (ULB),
Brussels, Belgium

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ScienceDirect

ANEXO B

TRANSFERENCIA DE RESULTADOS DE LA INVESTIGACIÓN

Patentes

1. Dispositivo y procedimiento de muestreo y monitorización de componentes volátiles en aire.

S. Cárdenas, R. Lucena, M.C. Alcudia-León, G. Lasarte-Aragonés, F.A. Casado-Carmona

Nº solicitud: P202030192. Fecha: 06/03/2020.

2. Sistema multi-estación para muestreo ambiental que integra el aislamiento del analito.

S. Cárdenas, R. Lucena, F.A. Casado-Carmona, J.M. Jiménez-Soto

Nº solicitud: P202131000. Fecha: 25/10/2021.

Proyectos I+D+i Pruebas de Concepto

1. Muestreadores de Aire Basados en Ventiladores.

PDC2021-120900-I00. Ministerio de Ciencia e Innovación IP: R. Lucena y S. Cárdenas. (Universidad de Córdoba). 2021-2023. 74.750,00 EUR.

Participación: Investigador

ANEXO C

PUBLICACIONES CIENTÍFICAS RELACIONADAS CON LA TESIS DOCTORAL

1. Magnetic nanoparticles coated with ionic liquid for the extraction of endocrine disrupting compounds from waters.

F.A. Casado-Carmona, M.C. Alcudia-León, R. Lucena, S. Cárdenas, M. Valcárcel

Microchemical Journal, 128 (2016) 347-353.

Publicación derivada del Trabajo Fin de Máster (TFM).

2. Paramagnetic ionic liquid-coated SiO_2@Fe_3O_4 nanoparticles—The next generation of magnetically recoverable nanocatalysts applied in the glycolysis of PET.

I. Cano, C. Martin, J.A. Fernandes, R.W. Lodge, J. Dupont, F.A. Casado-Carmona, R. Lucena, S. Cárdenas, V. Sans, I. de Pedro

Applied Catalysis B: Environmental, 260 (2020) 118110.

3. Ultra-trace tellurium preconcentration and speciation analysis in environmental samples with a novel magnetic polymeric ionic liquid nanocomposite and magnetic dispersive micro-solid phase extraction with flow-injection hydride generation atomic fluorescence spectrometry detection.

M. Llaver, F.A. Casado-Carmona, R. Lucena, S. Cárdenas, R.G. Wuilloud

Spectrochimica Acta Part B, 162 (2020) 105705.

4. Magnetic graphene oxide composite for the microextraction and determination of benzophenones in water samples.

A. Medina, F.A. Casado-Carmona, A.I. López-Lorente, S. Cárdenas

Nanomaterials, 10 (2016) 168.

Volumen especial “Development of Nanomaterials for Applications in Trace Analysis” Editado por Kerstin Leopold.

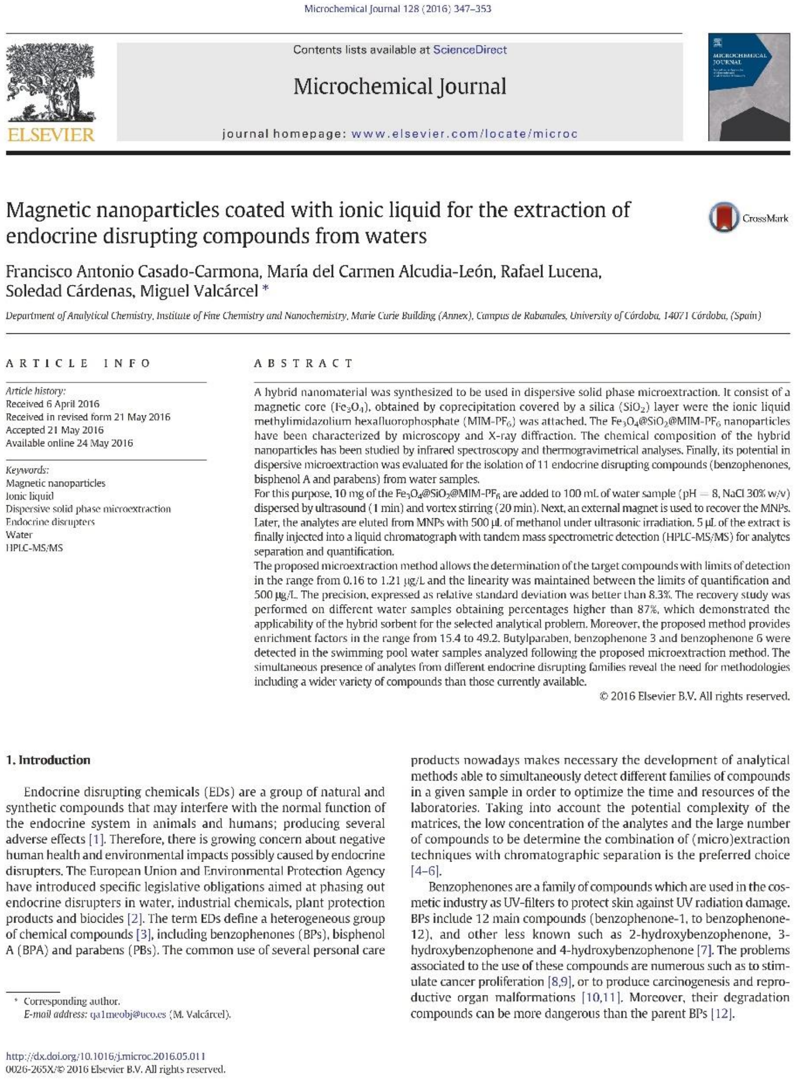
Publicación derivada de la tutorización del Trabajo Fin de Grado (TFG) QM-16-26-QAM del estudiante Alejandro Medina Jaraba.

5. Polymeric nanocomposites as sorbents in environmental water analysis, a close view to the synthesis and potential applications.

J. Millán-Santiago, F.A. Casado-Carmona, R. Lucena, S. Cárdenas

Current Opinion in Environmental Science & Health, 25 (2022) 100320.

Volumen especial “Environmental Technologies: Nanomaterials as Materials for Extraction, Sensing, and Detection of Environmental Contaminants” Editado por Muhammad Sajid.



Microchemical Journal 128 (2016) 347–353

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Magnetic nanoparticles coated with ionic liquid for the extraction of endocrine disrupting compounds from waters

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Endocrine disrupters
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HPLC-MS/MS

ABSTRACT

A hybrid nanomaterial was synthesized to be used in dispersive solid phase microextraction. It consist of a magnetic core (Fe_3O_4), obtained by coprecipitation covered by a silica (SiO_2) layer were the ionic liquid methylimidazolium hexafluorophosphate (MIM-PF_6) was attached. The Fe_3O_4@SiO_2@MIM-PF_6 nanoparticles have been characterized by microscopy and X-ray diffraction. The chemical composition of the hybrid nanoparticles has been studied by infrared spectroscopy and thermogravimetrical analyses. Finally, its potential in dispersive microextraction was evaluated for the isolation of 11 endocrine disrupting compounds (benzophenones, bisphenol A and parabens) from water samples.

For this purpose, 10 mg of the Fe_3O_4@SiO_2@MIM-PF_6 are added to 100 mL of water sample (pH = 8, NaCl 30% w/v) dispersed by ultrasound (1 min) and vortex stirring (20 min). Next, an external magnet is used to recover the MNPs. Later, the analytes are eluted from MNPs with 500 µL of methanol under ultrasonic irradiation. 5 µL of the extract is finally injected into a liquid chromatograph with tandem mass spectrometric detection (HPLC-MS/MS) for analytes separation and quantification.

The proposed microextraction method allows the determination of the target compounds with limits of detection in the range from 0.16 to 1.21 µg/L and the linearity was maintained between the limits of quantification and 500 µg/L. The precision, expressed as relative standard deviation was better than 8.3%. The recovery study was performed on different water samples obtaining percentages higher than 87%, which demonstrated the applicability of the hybrid sorbent for the selected analytical problem. Moreover, the proposed method provides enrichment factors in the range from 15.4 to 49.2. Butylparaben, benzophenone 3 and benzophenone 6 were detected in the swimming pool water samples analyzed following the proposed microextraction method. The simultaneous presence of analytes from different endocrine disrupting families reveal the need for methodologies including a wider variety of compounds than those currently available.

1. Introduction

Endocrine disrupting chemicals (EDs) are a group of natural and synthetic compounds that may interfere with the normal function of the endocrine system in animals and humans; producing several adverse effects [1]. Therefore, there is growing concern about negative human health and environmental impacts possibly caused by endocrine disrupters. The European Union and Environmental Protection Agency have introduced specific legislative obligations aimed at phasing out endocrine disrupters in water, industrial chemicals, plant protection products and biocides [2]. The term EDs define a heterogeneous group of chemical compounds [3], including benzophenones (BPs), bisphenol A (BPA) and parabens (PBs). The common use of several personal care products nowadays makes necessary the development of analytical methods able to simultaneously detect different families of compounds in a given sample in order to optimize the time and resources of the laboratories. Taking into account the potential complexity of the matrices, the low concentration of the analytes and the large number of compounds to be determine the combination of (micro)extraction techniques with chromatographic separation is the preferred choice [4–6].

Benzophenones are a family of compounds which are used in the cosmetic industry as UV-filters to protect skin against UV radiation damage. BPs include 12 main compounds (benzophenone-1, to benzophenone-12), and other less known such as 2-hydroxybenzophenone, 3-hydroxybenzophenone and 4-hydroxybenzophenone [7]. The problems associated to the use of these compounds are numerous such as to stimulate cancer proliferation [8,9], or to produce carcinogenesis and reproductive organ malformations [10,11]. Moreover, their degradation compounds can be more dangerous than the parent BPs [12].

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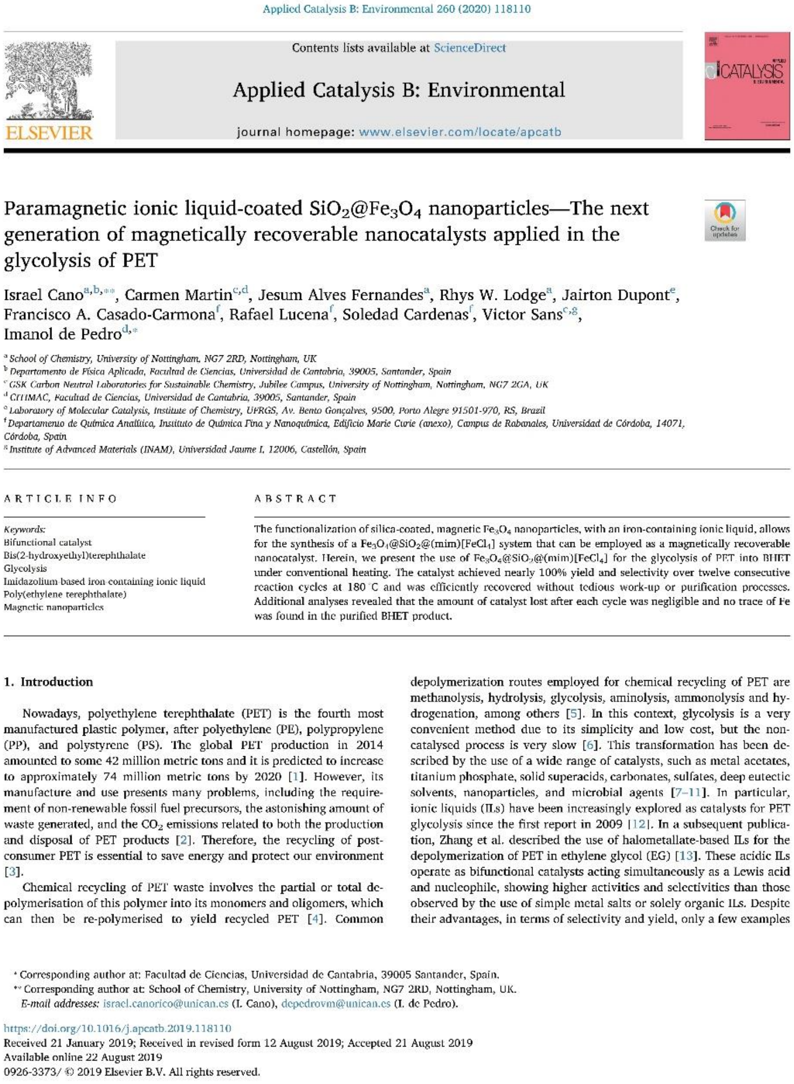

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Paramagnetic ionic liquid-coated $SiO_2@Fe_3O_4$ nanoparticles—The next generation of magnetically recoverable nanocatalysts applied in the glycolysis of PET

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ABSTRACT

The functionalization of silica-coated, magnetic Fe_3O_4 nanoparticles, with an iron-containing ionic liquid, allows for the synthesis of a $Fe_3O_4@SiO_2@(mim)[FeCl_4]$ system that can be employed as a magnetically recoverable nanocatalyst. Herein, we present the use of $Fe_3O_4@SiO_2@(mim)[FeCl_4]$ for the glycolysis of PET into BHET under conventional heating. The catalyst achieved nearly 100% yield and selectivity over twelve consecutive reaction cycles at 180 °C and was efficiently recovered without tedious work-up or purification processes. Additional analyses revealed that the amount of catalyst lost after each cycle was negligible and no trace of Fe was found in the purified BHET product.

1. Introduction

Nowadays, polyethylene terephthalate (PET) is the fourth most manufactured plastic polymer, after polyethylene (PE), polypropylene (PP), and polystyrene (PS). The global PET production in 2014 amounted to some 42 million metric tons and it is predicted to increase to approximately 74 million metric tons by 2020 [1]. However, its manufacture and use presents many problems, including the requirement of non-renewable fossil fuel precursors, the astonishing amount of waste generated, and the CO_2 emissions related to both the production and disposal of PET products [2]. Therefore, the recycling of post-consumer PET is essential to save energy and protect our environment [3].

Chemical recycling of PET waste involves the partial or total depolymerisation of this polymer into its monomers and oligomers, which can then be re-polymerised to yield recycled PET [4]. Common depolymerization routes employed for chemical recycling of PET are methanolysis, hydrolysis, glycolysis, aminolysis, ammonolysis and hydrogenation, among others [5]. In this context, glycolysis is a very convenient method due to its simplicity and low cost, but the non-catalysed process is very slow [6]. This transformation has been described by the use of a wide range of catalysts, such as metal acetates, titanium phosphate, solid superacids, carbonates, sulfates, deep eutectic solvents, nanoparticles, and microbial agents [7–11]. In particular, ionic liquids (ILs) have been increasingly explored as catalysts for PET glycolysis since the first report in 2009 [12]. In a subsequent publication, Zhang et al. described the use of halometallate-based ILs for the depolymerization of PET in ethylene glycol (EG) [13]. These acidic ILs operate as bifunctional catalysts acting simultaneously as a Lewis acid and nucleophile, showing higher activities and selectivities than those observed by the use of simple metal salts or solely organic ILs. Despite their advantages, in terms of selectivity and yield, only a few examples

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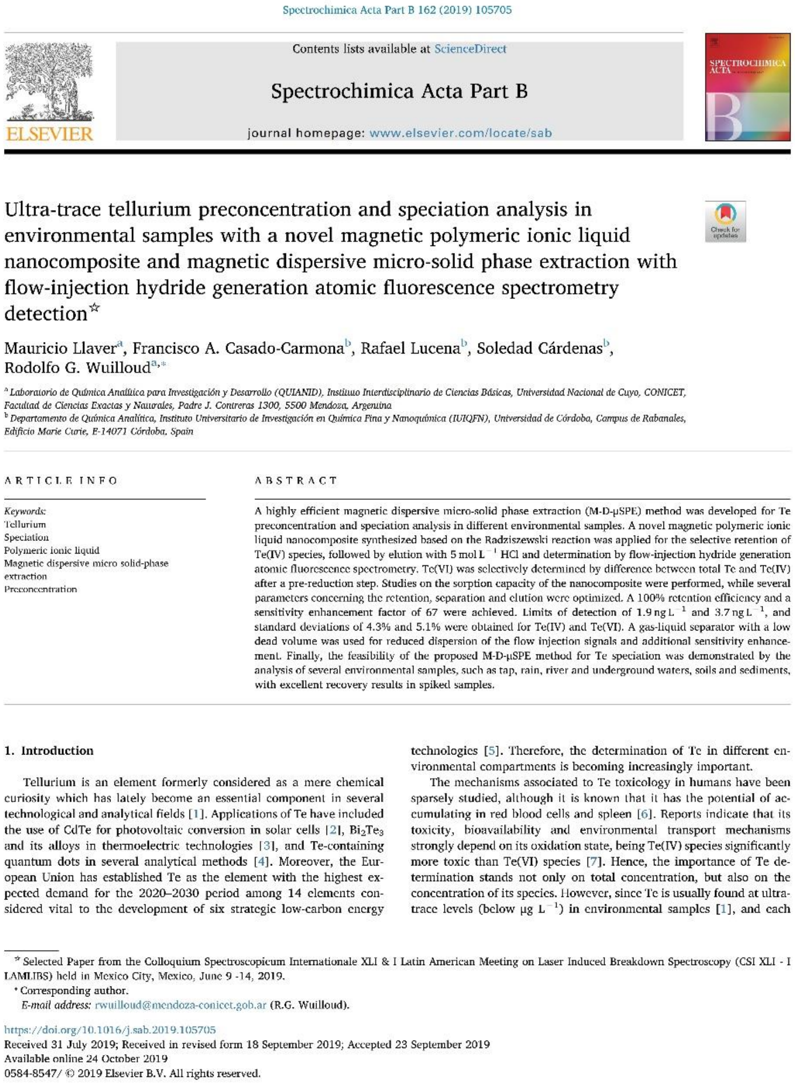
Anexo C



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journal homepage: www.elsevier.com/locate/sab

Ultra-trace tellurium preconcentration and speciation analysis in environmental samples with a novel magnetic polymeric ionic liquid nanocomposite and magnetic dispersive micro-solid phase extraction with flow-injection hydride generation atomic fluorescence spectrometry detection[☆]

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ARTICLE INFO

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Preconcentration

ABSTRACT

A highly efficient magnetic dispersive micro-solid phase extraction (M-D-μSPE) method was developed for Te preconcentration and speciation analysis in different environmental samples. A novel magnetic polymeric ionic liquid nanocomposite synthesized based on the Radziszewski reaction was applied for the selective retention of Te(IV) species, followed by elution with 5 mol L^{-1} HCl and determination by flow-injection hydride generation atomic fluorescence spectrometry. Te(VI) was selectively determined by difference between total Te and Te(IV) after a pre-reduction step. Studies on the sorption capacity of the nanocomposite were performed, while several parameters concerning the retention, separation and elution were optimized. A 100% retention efficiency and a sensitivity enhancement factor of 67 were achieved. Limits of detection of 1.9 ng L^{-1} and 3.7 ng L^{-1}, and standard deviations of 4.3% and 5.1% were obtained for Te(IV) and Te(VI). A gas-liquid separator with a low dead volume was used for reduced dispersion of the flow injection signals and additional sensitivity enhancement. Finally, the feasibility of the proposed M-D-μSPE method for Te speciation was demonstrated by the analysis of several environmental samples, such as tap, rain, river and underground waters, soils and sediments, with excellent recovery results in spiked samples.

1. Introduction

Tellurium is an element formerly considered as a mere chemical curiosity which has lately become an essential component in several technological and analytical fields [1]. Applications of Te have included the use of CdTe for photovoltaic conversion in solar cells [2], Bi_2Te_3 and its alloys in thermoelectric technologies [3], and Te-containing quantum dots in several analytical methods [4]. Moreover, the European Union has established Te as the element with the highest expected demand for the 2020–2030 period among 14 elements considered vital to the development of six strategic low-carbon energy technologies [5]. Therefore, the determination of Te in different environmental compartments is becoming increasingly important.

The mechanisms associated to Te toxicology in humans have been sparsely studied, although it is known that it has the potential of accumulating in red blood cells and spleen [6]. Reports indicate that its toxicity, bioavailability and environmental transport mechanisms strongly depend on its oxidation state, being Te(IV) species significantly more toxic than Te(VI) species [7]. Hence, the importance of Te determination stands not only on total concentration, but also on the concentration of its species. However, since Te is usually found at ultra-trace levels (below μg L^{-1}) in environmental samples [1], and each

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nanomaterials

MDPI

Article

Magnetic Graphene Oxide Composite for the Microextraction and Determination of Benzophenones in Water Samples

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Abstract: Magnetite nanoparticles (Fe_3O_4) functionalized with graphene oxide (GO) have been synthesized through a silanization process of the magnetic nanoparticles with tetraethyl orthosilicate and (3-aminopropyl)triethoxysilane and further coupling of GO. The synthesized nanomaterials have been characterized by several techniques, such as transmission electron microscopy (TEM), and infrared and Raman spectroscopy, which enabled the evaluation of the different steps of the functionalization process. The hybrid nanomaterial has been employed for the extraction of five benzophenones (benzophenone-1, benzophenone-3, 4-hydroxybenzophenone, benzophenone-6 and benzophenone-8) in aqueous samples by dispersive micro-solid phase extraction, combining the magnetic properties of magnetite nanoparticles with the excellent sorption capacity of graphene oxide via hydrophobic interactions with the analytes. The subsequent separation and quantification of the analytes was performed by liquid chromatography with tandem mass spectrometric detection, achieving limits of detection (LODs) in the range 2.5 to 8.2 $\mu g \cdot L^{-1}$, with relative standard deviations ranging from 1.3–9.8% and relative recovering in the range 86 to 105%. Positive swimming pool water samples analysed following the developed method revealed the presence of benzophenones in from 14.3 to 39 $\mu g \cdot L^{-1}$.

Keywords: dispersive micro-solid phase microextraction; benzophenones; magnetic nanoparticles; graphene oxide; swimming pool water

1. Introduction

Graphene and its derived materials are attracting great attention in the last years in many fields such as electrochemistry, energy storage, membranes for gas transport or water treatment, and microextraction techniques, among others [1–3]. Their outstanding properties, such as high specific surface area and the presence of a delocalized π–π system, which provides good affinity towards aromatic compounds, have boosted their application in the microextraction context. However, its broadband application is hindered by the tendency of carbon nanomaterials to aggregation, which has been overcome by the use of the graphene derivative graphene oxide (GO). Graphene can be easily oxidized to GO, which possesses rich oxygen functional groups, such as hydroxyl, epoxy, and carboxyl, and shows good dispersibility in water. GO has been employed in solid phase microextraction (SPME) mainly incorporated to composite materials, e.g., with cross-linked polyoxyethylene as fiber coating material [4], incorporated poly acrylamide-ethylene glycol dimethacrylate monolithic fiber [5], packed in-tube solid phase microextraction supporting GO on

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Polymeric nanocomposites as sorbents in environmental water analysis, a close view to the synthesis and potential applications

Jaime Millán-Santiago, Francisco Antonio Casado-Carmona,
Rafael Lucena and Soledad Cárdenas

Abstract

Polymeric nanocomposites have been extensively used as sorbents to extract pollutants from environmental waters before their final instrumental analysis. These materials are highly versatile and can be adapted to a given analytical problem by selecting the polymer/nanomaterial combination adequately. The adaptability of the materials is strengthened by their easy preparation in the laboratory and the different formats (particles, membranes, monoliths, or fibers) in which they can be obtained. This article delivers a general overview of the potential of polymeric nanocomposites, emphasizing the practical aspects (synthesis and microextraction techniques). It aims to inspire researchers by showing the almost endless possibilities of these materials in sample preparation and the main trends in the near future.

Addresses

Affordable and Sustainable Sample Preparation (AS_2P) Research Group, Departamento de Química Analítica, Instituto Universitario de Investigación en Química Fina y Nanoquímica (IUNAN), Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie (anexo), Córdoba, España

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Edited by **Muhammad Sajid**

For a complete overview see the Issue and the Editorial

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Keywords

Polymeric nanocomposites, Sorptive phases, Nanoparticles, Microextraction.

Introduction

Green Analytical Chemistry (GAC) identifies the sample preparation as a step with a potential environmental impact owing to the resources (reagents, solvents, and energy) it requires [1]. However, the direct analysis of environmental waters is usually impeded by the complexity of the matrices and the low concentration of the target compounds, which usually falls below the sensitivity levels of the instruments. The isolation and preconcentration of the target pollutants before their analysis overcome these two limitations and reduce the exposure of the instrument to excessive soiling. Combining an efficient extraction technique and a sensitive instrument also allows responding to the increasingly restrictive environmental policies. The White Analytical Chemistry concept tries to frame the GAC, recalling that obtaining useful chemical information is the main aim of Analytical Chemistry [2]. Sample preparation is allowed in the scenario defined by GAC and White Analytical Chemistry because it is essential to solving many analytical problems.

Sorbent-based extraction is widely used in environmental water analysis owing to its high capacity and versatility (widely availability of commercial sorbents). In the last decades, the increasing environmental awareness of analytical scientists has driven the miniaturization of sorbent-based extraction, giving rise to two different groups of techniques: solid-phase microextraction (SPME) [3,4]; and micro-solid phase extraction (µ-SPE) [5,6]. Reducing the amount of sorbent challenges the capacity, and the design of very efficient material results key in this context. Polymeric phases have been extensively used as sorbents thanks to their high capacity, chemical and thermal stability, and versatility in interaction chemistries with the target analytes. Nanomaterials (NMs) emerged in the last decade as powerful sorbents thanks primarily to their high surface-to-volume ratio that accelerates the mass transference in the extraction [7,8]. Polymeric nanocomposites (PNCs) mix a polymer (or several polymers) with a nanostructured solid providing a distinct material that shares the properties of the individual ingredients [9]. For clarity, in this article, the term nanocomposite (NC) will be limited to those materials obtained by combining two or more NMs in the absence of a polymer.

The extraction selectivity of the PNCs is a relevant issue that will depend on the type of analysis. For nontargeted analysis, PNCs that extract compounds in a

ANEXO D

ACTIVIDADES DE DIVULGACIÓN CIENTÍFICA

1. Participación en el "Paseo por la Ciencia"

Ediciones 2016, 2017, 2018 y 2019.

Entidad organizadora: Asociación Profesorado de Córdoba por la Cultura Científica (APCCC).

2. Participación en "Actividades de difusión de las líneas de investigación e infraestructuras (laboratorios e instrumentación científica) del Departamento de Química Analítica, dirigidas a estudiantes de centros de enseñanza secundaria". Del Programa "ORIENTAUCO" y del "Plan Integral de Difusión de la Facultad de Ciencias y el programa PACE de la Universidad de Córdoba".

Ediciones 2015/16, 2016/17, 2017/18 y 2018/19.

Entidad organizadora: Facultad de Ciencias (Universidad de Córdoba) y Universidad de Córdoba.

3. Participación en "Ingenios en Ruta"

Taller: Química Analítica: Extraer o no extraer, he ahí la cuestión.

Edición 2018.

Entidad organizadora: Universidad de Córdoba.

4. Participación en "III Jornadas de divulgación científica #divulgA3. Más allá de los papers"

Edición 2015.

Entidad organizadora: Universidad de Córdoba.

5. Participación en "La Noche Europea de los Investigadores"

Ediciones 2016, 2017 y 2018.

Entidad organizadora: Fundación Descubre.

6. Participación en "II Campus de Investigación de la Universidad de Córdoba"

Taller: ¿Cuánta cafeína consumimos? Determinación de cafeína y alcaloides en bebidas.

Entidad organizadora: Universidad de Córdoba.

7. Entrevista realizada para la página de Facebook Camina Leiva-Nuestra Voz

En relación con la presente Tesis Doctoral tras la publicación en la revista Talanta del artículo titulado: “Magnetic paper-based sorptive phase for enhanced mass transference in stir membrane environmental samplers”

ANEXO E

PRESENTACIÓN DE COMUNICACIONES EN CONGRESOS

1. Póster

Autores: Casado-Carmona, F.A.; Alcudia-León, M.C.; Lucena, R.; Cárdenas, S.; Valcárcel, M.

Título: **Ionic liquid coated magnetic nanoparticles for the extraction of endocrine disrupting compounds from waters.**

Congreso: XVI Latin-American Congress on Chromatography & 9th National Meeting on Chromatography. Lisboa (Portugal), Enero 2016.

2. Comunicación Flash

Autores: Casado-Carmona, F.A.

Título: **Nanopartículas magnéticas recubiertas con líquido iónico para la determinación de disruptores del sistema endocrino en aguas.**

Congreso: V Congreso Científico de Investigadores en Formación de la Universidad de Córdoba. Córdoba (España), Diciembre 2016.

3. Póster

Autores: Casado-Carmona, F.A.; Alcudia-León, M.C.; Lucena, R.; Cárdenas, S.; Valcárcel, M.

Título: **Extracción de disruptores endocrinos mediante nanopartículas magnéticas recubiertas con líquido iónico.**

Congreso: NANOUCO VI: Encuentro sobre Nanociencia y Nanotecnología de Investigadores Andaluces. Córdoba (España), Enero 2017.

4. Póster

Autores: Casado-Carmona, F.A.; Medina Jaraba, A.; López-Lorente, Á.I.; Cárdenas, S.

Título: **Nanopartículas magnéticas recubiertas con óxido de grafeno para la extracción de benzofenonas.**

Congreso: NANOUCO VII: Encuentro sobre Nanociencia y Nanotecnología de Investigadores Andaluces. Córdoba (España), Enero 2019.

5. Comunicación Flash

Autores: Casado-Carmona, F.A.

Título: **Muestreo y preconcentración on-line de benzofenonas en muestras de agua.**

Congreso: VII Congreso Científico de Investigadores en Formación de la Universidad de Córdoba. Córdoba (España), Febrero 2017.

6. Comunicación Flash

Autores: Casado-Carmona, F.A.; Lasarte-Aragonés, G.; Lucena, R.; Cárdenas, S.

Título: **Potential of air sampling device based on a computer fan for the isolation of volatile organic compounds and nanoparticles.**

Congreso: 4th International Caparica Christmas Conference on Sample Treatment 2020. Caparica (Portugal), Diciembre 2020.

7. Póster

Autores: Casado-Carmona, F.A.; Lucena, R.; Cárdenas, S.

Título: **Magnetic paper sorptive phase for the extraction of parabens and triclosan from swimming pool waters.**

Congreso: 1st European Sample Preparation e-Conference. Marzo 2021.

Premio al mejor póster en la categoría "New Materials"

8. Póster

Autores: Casado-Carmona, F.A.; Lasarte-Aragonés, G.; Kabir, A.; Furton, K.G.; Lucena, R.; Cárdenas, S.

Título: **Computer fan's potential in air sampling.**

Congreso: XXIII International Symposium on Advances in Extraction Technologies (ExTech). Alicante (España), Julio 2021.

Premio al mejor póster.

9. Comunicación Oral

Autores: Lucena, R.; Casado-Carmona, F.A.; Cárdenas, S.

Título: **In-situ extraction approaches for enviromental waters analysis.**

Congreso: XXIII International Symposium on Advances in Extraction Technologies (ExTech). Alicante (España), Julio 2021.

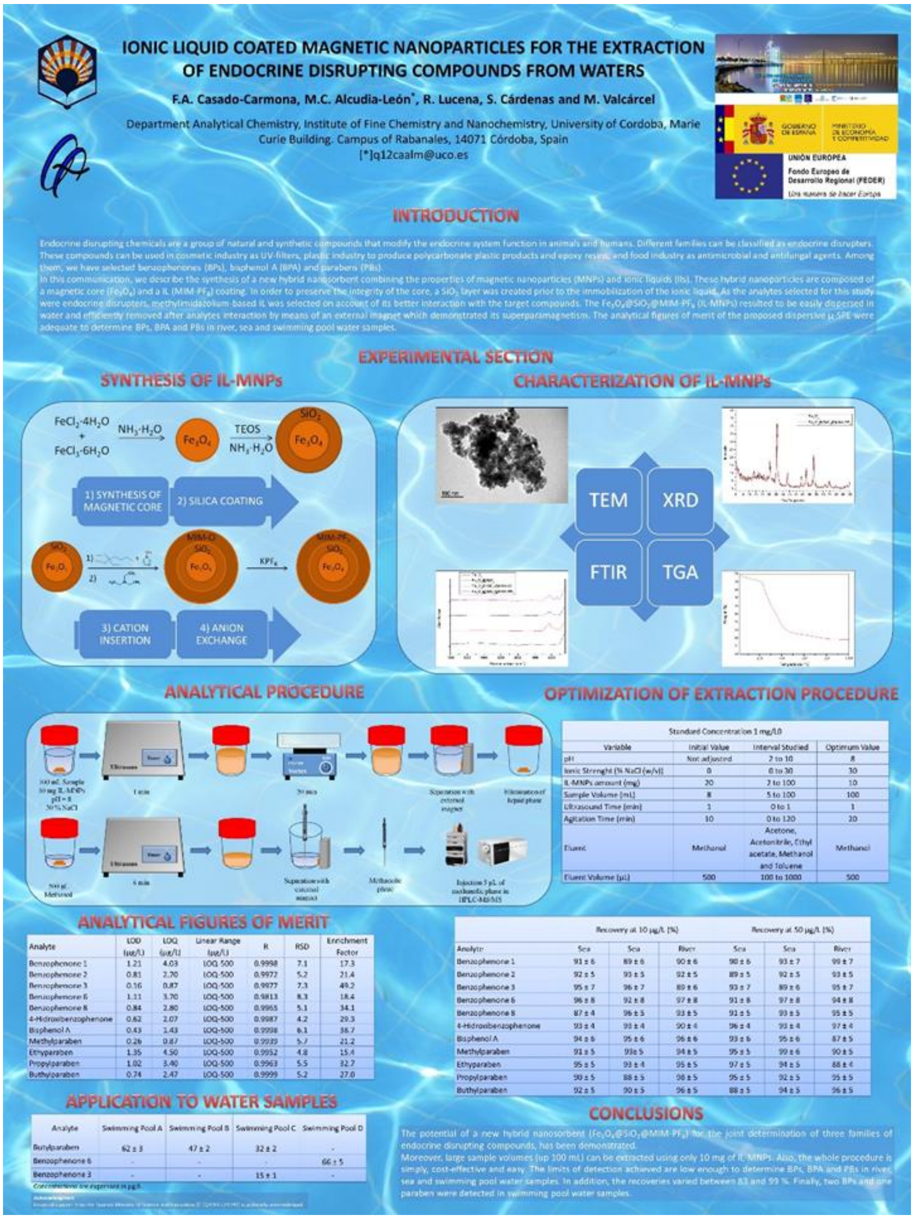
10. Comunicación Flash

Autores: Casado-Carmona, F.A.; Lucena, R.; Cárdenas, S.

Título: **Magnetic paper-based sorptive phase for environmental analysis.**

Congreso: 5th International Caparica Christmas Conference on Sample Treatment 2021. Caparica (Portugal), Noviembre 2021.

Premio al mejor Shotgun póster.



IONIC LIQUID COATED MAGNETIC NANOPARTICLES FOR THE EXTRACTION OF ENDOCRINE DISRUPTING COMPOUNDS FROM WATERS

F.A. Casado-Carmona, M.C. Alcudia-León[*], R. Lucena, S. Cárdenas and M. Valcárcel

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MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD
UNIÓN EUROPEA
Fondo Europeo de Desarrollo Regional (FEDER)
Una manera de hacer Europa

INTRODUCTION

Endocrine disrupting chemicals are a group of natural and synthetic compounds that modify the endocrine system function in animals and humans. Different families can be classified as endocrine disrupters. These compounds can be used in cosmetic industry as UV-filters, plastic industry to produce polycarbonate plastic products and epoxy resins, and food industry as antimicrobial and antifungal agents. Among them, we have selected benzophenones (BPs), bisphenol A (BPA) and parabens (PBs).
In this communication, we describe the synthesis of a new hybrid nanosorbent combining the properties of magnetic nanoparticles (MNPs) and ionic liquids (ILs). These hybrid nanoparticles are composed of a magnetic core (Fe$_3$O$_4$) and a IL (MIM-PF$_6$) coating. In order to preserve the integrity of the core, a SiO$_2$ layer was created prior to the immobilization of the ionic liquid. As the analytes selected for this study were endocrine disrupters, methylimidazolium-based IL was selected on account of its better interaction with the target compounds. The Fe$_3$O$_4$@SiO$_2$@MIM-PF$_6$ (IL-MNPs) resulted to be easily dispersed in water and efficiently removed after analytes interaction by means of an external magnet which demonstrated its superparamagnetism. The analytical figures of merit of the proposed dispersive µ-SPE were adequate to determine BPs, BPA and PBs in river, sea and swimming pool water samples.

EXPERIMENTAL SECTION

SYNTHESIS OF IL-MNPs

CHARACTERIZATION OF IL-MNPs

ANALYTICAL PROCEDURE

OPTIMIZATION OF EXTRACTION PROCEDURE

Standard Concentration 1 mg/L0			
Variable	Initial Value	Interval Studied	Optimum Value
pH	Not adjusted	2 to 10	8
Ionic Strenght (% NaCl (w/v))	0	0 to 30	30
IL-MNPs amount (mg)	20	2 to 100	10
Sample Volume (mL)	8	5 to 100	100
Ultrasound Time (min)	1	0 to 1	1
Agitation Time (min)	10	0 to 120	20
Eluent	Methanol	Acetone, Acetonitrile, Ethyl acetate, Methanol and Toluene	Methanol
Eluent Volume (µL)	500	100 to 1000	500

ANALYTICAL FIGURES OF MERIT

Analyte	LOD (µg/L)	LOQ (µg/L)	Linear Range (µg/L)	R	RSD	Enrichment Factor
Benzophenone 1	1.21	4.03	LOQ-500	0.9998	7.1	17.3
Benzophenone 2	0.81	2.70	LOQ-500	0.9972	5.2	21.4
Benzophenone 3	0.16	0.87	LOQ-500	0.9977	7.3	49.2
Benzophenone 6	1.11	3.70	LOQ-500	0.9813	8.3	18.4
Benzophenone 8	0.84	2.80	LOQ-500	0.9965	5.1	34.1
4-Hidroxibenzophenone	0.62	2.07	LOQ-500	0.9987	4.2	29.3
Bisphenol A	0.43	1.43	LOQ-500	0.9998	6.1	38.7
Methylparaben	0.26	0.87	LOQ-500	0.9939	5.7	21.2
Ethyparaben	1.35	4.50	LOQ-500	0.9952	4.8	15.4
Propylparaben	1.02	3.40	LOQ-500	0.9963	5.5	32.7
Buthylparaben	0.74	2.47	LOQ-500	0.9999	5.2	27.0

	Recovery at 10 µg/L (%)			Recovery at 50 µg/L (%)		
Analyte	Sea	Sea	River	Sea	Sea	River
Benzophenone 1	91 ± 6	89 ± 6	90 ± 6	90 ± 6	93 ± 7	99 ± 7
Benzophenone 2	92 ± 5	93 ± 5	92 ± 5	89 ± 5	92 ± 5	93 ± 5
Benzophenone 3	95 ± 7	96 ± 7	89 ± 6	93 ± 7	89 ± 6	95 ± 7
Benzophenone 6	96 ± 8	92 ± 8	97 ± 8	91 ± 8	97 ± 8	94 ± 8
Benzophenone 8	87 ± 4	96 ± 5	93 ± 5	91 ± 5	93 ± 5	95 ± 5
4-Hidroxibenzophenone	93 ± 4	93 ± 4	90 ± 4	96 ± 4	93 ± 4	97 ± 4
Bisphenol A	94 ± 6	95 ± 6	96 ± 6	93 ± 6	95 ± 6	87 ± 5
Methylparaben	91 ± 5	93± 5	94 ± 5	95 ± 5	99 ± 6	90 ± 5
Ethyparaben	95 ± 5	93 ± 4	95 ± 5	97 ± 5	94 ± 5	88 ± 4
Propylparaben	90 ± 5	88 ± 5	98 ± 5	95 ± 5	92 ± 5	95 ± 5
Buthylparaben	92 ± 5	90 ± 5	96 ± 5	88 ± 5	94 ± 5	96 ± 5

APPLICATION TO WATER SAMPLES

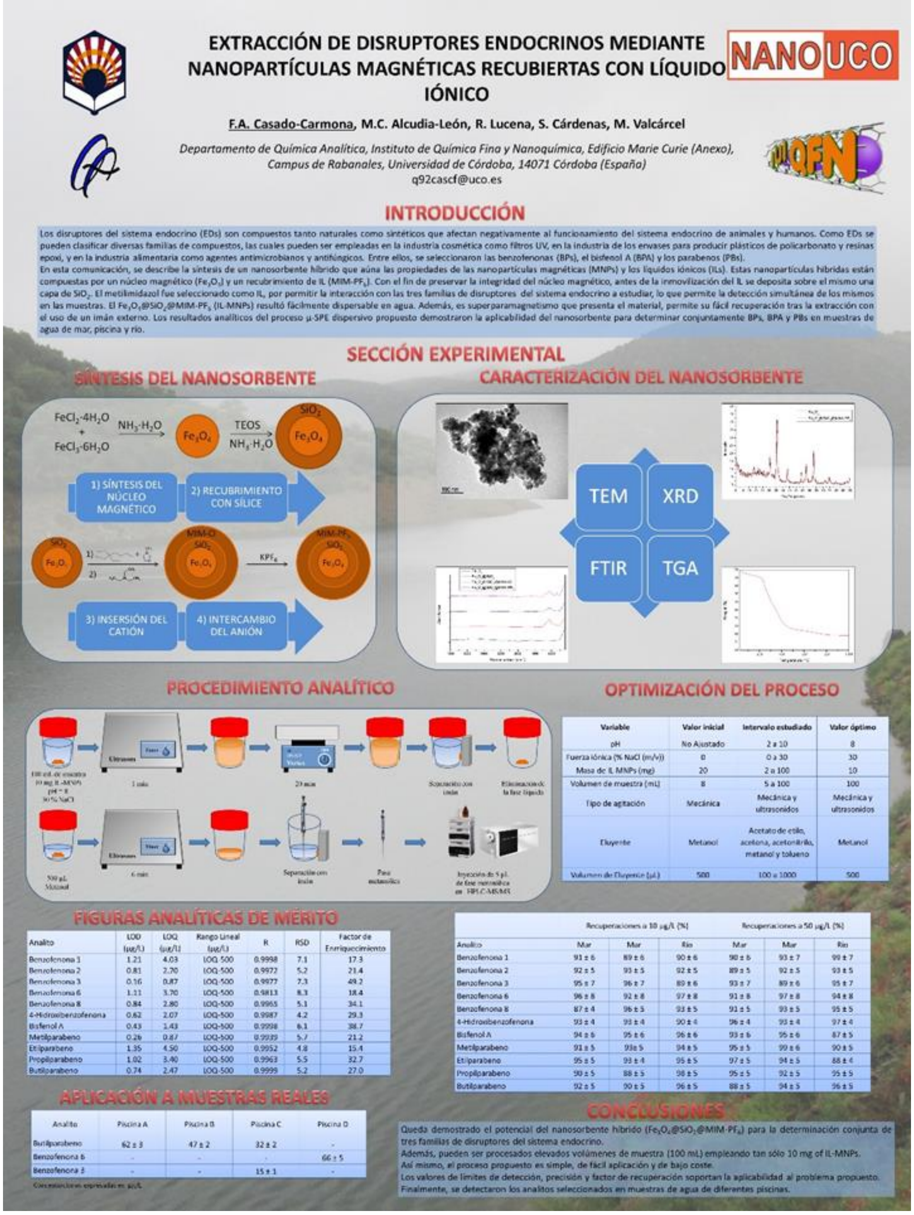
Analyte	Swimming Pool A	Swimming Pool B	Swimming Pool C	Swimming Pool D
Butylparaben	62 ± 3	47 ± 2	32 ± 2	-
Benzophenone 6	-	-	-	66 ± 5
Benzophenone 3	-	-	15 ± 1	-

Concentrations are expressed in µg/l

Acknowledgment
[illegible]

CONCLUSIONS

The potential of a new hybrid nanosorbent (Fe$_3$O$_4$@SiO$_2$@MIM-PF$_6$) for the joint determination of three families of endocrine disrupting compounds, has been demonstrated.
Moreover, large sample volumes (up 100 mL) can be extracted using only 10 mg of IL-MNPs. Also, the whole procedure is simply, cost-effective and easy. The limits of detection achieved are low enough to determine BPs, BPA and PBs in river, sea and swimming pool water samples. In addition, the recoveries varied between 83 and 99 %. Finally, two BPs and one paraben were detected in swimming pool water samples.



EXTRACCIÓN DE DISRUPTORES ENDOCRINOS MEDIANTE NANOPARTÍCULAS MAGNÉTICAS RECUBIERTAS CON LÍQUIDO IÓNICO

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INTRODUCCIÓN

Los disruptores del sistema endocrino (EDs) son compuestos tanto naturales como sintéticos que afectan negativamente al funcionamiento del sistema endocrino de animales y humanos. Como EDs se pueden clasificar diversas familias de compuestos, las cuales pueden ser empleadas en la industria cosmética como filtros UV, en la industria de los envases para producir plásticos de policarbonato y resinas epoxi, y en la industria alimentaria como agentes antimicrobianos y antifúngicos. Entre ellos, se seleccionaron las benzofenonas (BPs), el bisfenol A (BPA) y los parabenos (PBs).

En esta comunicación, se describe la síntesis de un nanosorbente híbrido que aúna las propiedades de las nanopartículas magnéticas (MNPs) y los líquidos iónicos (ILs). Estas nanopartículas híbridas están compuestas por un núcleo magnético (Fe_3O_4) y un recubrimiento de IL (MIM-PF$_6$). Con el fin de preservar la integridad del núcleo magnético, antes de la inmovilización del IL se deposita sobre el mismo una capa de SiO_2. El metilimidazol fue seleccionado como IL, por permitir la interacción con las tres familias de disruptores del sistema endocrino a estudiar, lo que permite la detección simultánea de los mismos en las muestras. El Fe_3O_4@SiO_2@MIM-PF$_6$ (IL-MNPs) resultó fácilmente dispersable en agua. Además, es superparamagnetismo que presenta el material, permite su fácil recuperación tras la extracción con el uso de un imán externo. Los resultados analíticos del proceso µ-SPE dispersivo propuesto demostraron la aplicabilidad del nanosorbente para determinar conjuntamente BPs, BPA y PBs en muestras de agua de mar, piscina y río.

SECCIÓN EXPERIMENTAL

SÍNTESIS DEL NANOSORBENTE

1) SÍNTESIS DEL NÚCLEO MAGNÉTICO
2) RECUBRIMIENTO CON SÍLICE
3) INSERCIÓN DEL CATIÓN
4) INTERCAMBIO DEL ANIÓN

CARACTERIZACIÓN DEL NANOSORBENTE

TEM
XRD
FTIR
TGA

PROCEDIMIENTO ANALÍTICO

OPTIMIZACIÓN DEL PROCESO

Variable	Valor inicial	Intervalo estudiado	Valor óptimo
pH	No Ajustado	2 a 10	8
Fuerza iónica (% NaCl (m/v))	0	0 a 30	30
Masa de IL MNPs (mg)	20	2 a 100	10
Volumen de muestra (mL)	8	5 a 100	100
Tipo de agitación	Mecánica	Mecánica y ultrasonidos	Mecánica y ultrasonidos
Eluyente	Metanol	Acetato de etilo, acetona, acetonitrilo, metanol y tolueno	Metanol
Volumen de Eluyente (µL)	500	100 a 1000	500

FIGURAS ANALÍTICAS DE MÉRITO

Analito	LOD (µg/L)	LOQ (µg/L)	Rango Lineal (µg/L)	R	RSD	Factor de Enriquecimiento
Benzofenona 1	1.21	4.03	LOQ-500	0.9998	7.1	17.3
Benzofenona 2	0.81	2.70	LOQ-500	0.9972	5.2	21.4
Benzofenona 3	0.16	0.87	LOQ-500	0.9977	7.3	49.2
Benzofenona 6	1.11	3.70	LOQ-500	0.9813	8.3	18.4
Benzofenona 8	0.84	2.80	LOQ-500	0.9965	5.1	34.1
4-Hidroxibenzofenona	0.62	2.07	LOQ-500	0.9987	4.2	29.3
Bisfenol A	0.43	1.43	LOQ-500	0.9998	6.1	38.7
Metilparabeno	0.26	0.87	LOQ-500	0.9939	5.7	21.2
Etilparabeno	1.35	4.50	LOQ-500	0.9952	4.8	15.4
Propilparabeno	1.02	3.40	LOQ-500	0.9963	5.5	32.7
Butilparabeno	0.74	2.47	LOQ-500	0.9999	5.2	27.0

	Recuperaciones a 10 µg/L (%)			Recuperaciones a 50 µg/L (%)		
Analito	Mar	Mar	Río	Mar	Mar	Río
Benzofenona 1	91 ± 6	89 ± 6	90 ± 6	90 ± 6	93 ± 7	99 ± 7
Benzofenona 2	92 ± 5	93 ± 5	92 ± 5	89 ± 5	92 ± 5	93 ± 5
Benzofenona 3	95 ± 7	96 ± 7	89 ± 6	93 ± 7	89 ± 6	95 ± 7
Benzofenona 6	96 ± 8	92 ± 8	97 ± 8	91 ± 8	97 ± 8	94 ± 8
Benzofenona 8	87 ± 4	96 ± 5	93 ± 5	91 ± 5	93 ± 5	95 ± 5
4-Hidroxibenzofenona	93 ± 4	93 ± 4	90 ± 4	96 ± 4	93 ± 4	97 ± 4
Bisfenol A	94 ± 6	95 ± 6	96 ± 6	93 ± 6	95 ± 6	87 ± 5
Metilparabeno	91 ± 5	93± 5	94 ± 5	95 ± 5	99 ± 6	90 ± 5
Etilparabeno	95 ± 5	93 ± 4	95 ± 5	97 ± 5	94 ± 5	88 ± 4
Propilparabeno	90 ± 5	88 ± 5	98 ± 5	95 ± 5	92 ± 5	95 ± 5
Butilparabeno	92 ± 5	90 ± 5	96 ± 5	88 ± 5	94 ± 5	96 ± 5

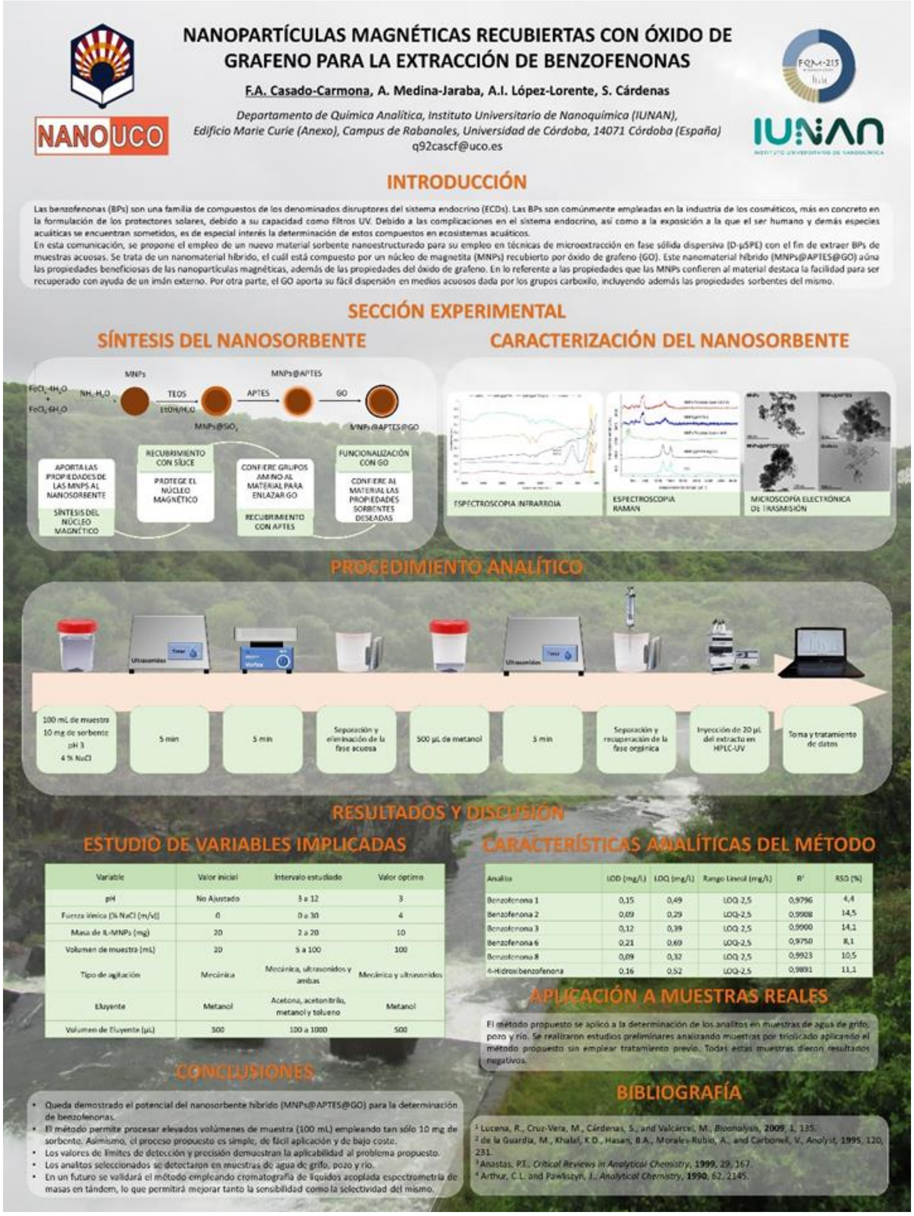
APLICACIÓN A MUESTRAS REALES

Analito	Piscina A	Piscina B	Piscina C	Piscina D
Butilparabeno	62 ± 3	47 ± 2	32 ± 2	-
Benzofenona 6	-	-	-	66 ± 5
Benzofenona 3	-	-	15 ± 1	-

Concentraciones expresadas en µg/L.

CONCLUSIONES

Queda demostrado el potencial del nanosorbente híbrido (Fe_3O_4@SiO_2@MIM-PF$_6$) para la determinación conjunta de tres familias de disruptores del sistema endocrino.
Además, pueden ser procesados elevados volúmenes de muestra (100 mL) empleando tan sólo 10 mg of IL-MNPs.
Así mismo, el proceso propuesto es simple, de fácil aplicación y de bajo coste.
Los valores de límites de detección, precisión y factor de recuperación soportan la aplicabilidad al problema propuesto.
Finalmente, se detectaron los analitos seleccionados en muestras de agua de diferentes piscinas.



NANOPARTÍCULAS MAGNÉTICAS RECUBIERTAS CON ÓXIDO DE GRAFENO PARA LA EXTRACCIÓN DE BENZOFENONAS

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INTRODUCCIÓN

Las benzofenonas (BPs) son una familia de compuestos de los denominados disruptores del sistema endocrino (ECDs). Las BPs son comúnmente empleadas en la industria de los cosméticos, más en concreto en la formulación de los protectores solares, debido a su capacidad como filtros UV. Debido a las complicaciones en el sistema endocrino, así como a la exposición a la que el ser humano y demás especies acuáticas se encuentran sometidos, es de especial interés la determinación de estos compuestos en ecosistemas acuáticos.

En esta comunicación, se propone el empleo de un nuevo material sorbente nanoestructurado para su empleo en técnicas de microextracción en fase sólida dispersiva (D-µSPE) con el fin de extraer BPs de muestras acuosas. Se trata de un nanomaterial híbrido, el cuál está compuesto por un núcleo de magnetita (MNPs) recubierto por óxido de grafeno (GO). Este nanomaterial híbrido (MNPs@APTES@GO) aúna las propiedades beneficiosas de las nanopartículas magnéticas, además de las propiedades del óxido de grafeno. En lo referente a las propiedades que las MNPs confieren al material destaca la facilidad para ser recuperado con ayuda de un imán externo. Por otra parte, el GO aporta su fácil dispersión en medios acuosos dada por los grupos carboxilo, incluyendo además las propiedades sorbentes del mismo.

SECCIÓN EXPERIMENTAL

SÍNTESIS DEL NANOSORBENTE

SÍNTESIS DEL NÚCLEO MAGNÉTICO: APORTA LAS PROPIEDADES DE LAS MNPS AL NANOSORBENTE

RECUBRIMIENTO CON SÍLICE: PROTEGE EL NÚCLEO MAGNÉTICO

RECUBRIMIENTO CON APTES: CONFIERE GRUPOS AMINO AL MATERIAL PARA ENLAZAR GO

FUNCIONALIZACIÓN CON GO: CONFIERE AL MATERIAL LAS PROPIEDADES SORBENTES DESEADAS

CARACTERIZACIÓN DEL NANOSORBENTE

ESPECTROSCOPIA INFRARROJA

ESPECTROSCOPIA RAMAN

MICROSCOPÍA ELECTRÓNICA DE TRASMISIÓN

PROCEDIMIENTO ANALÍTICO

- 100 mL de muestra
10 mg de sorbente
pH 3
4 % NaCl
- 5 min
- 5 min
- Separación y eliminación de la fase acuosa
- 500 µL de metanol
- 5 min
- Separación y recuperación de la fase orgánica
- Inyección de 20 µL del extracto en HPLC-UV
- Toma y tratamiento de datos

RESULTADOS Y DISCUSIÓN

ESTUDIO DE VARIABLES IMPLICADAS

Variable	Valor inicial	Intervalo estudiado	Valor optimo
pH	No Ajustado	3 a 12	3
Fuerza iónica (% NaCl (m/v))	0	0 a 30	4
Masa de IL-MNPs (mg)	20	2 a 20	10
Volumen de muestra (mL)	20	5 a 100	100
Tipo de agitación	Mecánica	Mecánica, ultrasonidos y ambas	Mecánica y ultrasonidos
Eluyente	Metanol	Acetona, acetonitrilo, metanol y tolueno	Metanol
Volumen de Eluyente (µL)	500	100 a 1000	500

CARACTERÍSTICAS ANALÍTICAS DEL MÉTODO

Analito	LOD (mg/L)	LOQ (mg/L)	Rango Lineal (mg/L)	R²	RSD (%)
Benzofenona 1	0,15	0,49	LOQ-2,5	0,9796	4,4
Benzofenona 2	0,09	0,29	LOQ-2,5	0,9908	14,5
Benzofenona 3	0,12	0,39	LOQ-2,5	0,9900	14,1
Benzofenona 6	0,21	0,69	LOQ-2,5	0,9750	8,1
Benzofenona 8	0,09	0,32	LOQ-2,5	0,9923	10,5
4-Hidroxibenzofenona	0,16	0,52	LOQ-2,5	0,9891	11,1

APLICACIÓN A MUESTRAS REALES

El método propuesto se aplicó a la determinación de los analitos en muestras de agua de grifo, pozo y río. Se realizaron estudios preliminares analizando muestras por triplicado aplicando el método propuesto sin emplear tratamiento previo. Todas estas muestras dieron resultados negativos.

CONCLUSIONES

- Queda demostrado el potencial del nanosorbente híbrido (MNPs@APTES@GO) para la determinación de benzofenonas.
- El método permite procesar elevados volúmenes de muestra (100 mL) empleando tan sólo 10 mg de sorbente. Asimismo, el proceso propuesto es simple, de fácil aplicación y de bajo coste.
- Los valores de límites de detección y precisión demuestran la aplicabilidad al problema propuesto.
- Los analitos seleccionados se detectaron en muestras de agua de grifo, pozo y río.
- En un futuro se validará el método empleando cromatografía de líquidos acoplada espectrometría de masas en tándem, lo que permitirá mejorar tanto la sensibilidad como la selectividad del mismo.

BIBLIOGRAFÍA

[1] Lucena, R., Cruz-Vera, M., Cárdenas, S., and Valcárcel, M., *Bioanalysis*, **2009**, 1, 135.
[2] de la Guardia, M., Khalaf, K.D., Hasan, B.A., Morales-Rubio, A., and Carbonell, V., *Analyst*, **1995**, 120, 231.
[3] Anastas, P.T., *Critical Reviews in Analytical Chemistry*, **1999**, 29, 167.
[4] Arthur, C.L. and Pawliszyn, J., *Analytical Chemistry*, **1990**, 62, 2145.

Magnetic Paper Sorptive Phase for the Extraction of Parabens and Triclosan from Swimming Pool Waters

F.A. Casado-Carmona, R. Lucena, and S. Cárdenas.
Departamento de Química Analítica, Instituto Universitario Nanoquímica (IUNAN), Universidad de Córdoba,
Campus de Rabanales, Edificio Marie Curie, E-14071, Córdoba, Spain

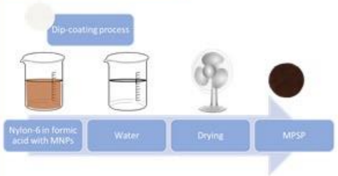
INTRODUCTION

The analysis of environmental waters is challenging due to the high volume of the systems (e.g., lake, river, sea) and the complexity of the sample matrix, where the analytes are at low concentration levels. For that reason, the design of new sampling devices that integrate the preconcentration of target analytes is important. Furthermore, this isolation prevents the analytes degradation until sample processing. Those devices are mainly supported in microextraction techniques, solid-phase microextraction being the most used technique.

In this research work, a new magnetic sorbent was synthesized to improve the mass transference in a previously reported stir membrane sampling device. Magnetic paper sorptive phase (MPSP) was synthetized by dip-coating method, and combines synergically the properties of nylon-6, magnetic nanoparticles, and paper as support. Magnetic nanoparticles promote the attachment to the extraction device, which is easy to employ and portable. The potential of the new material was evaluated in the determination of parabens and triclosan in swimming pool samples. Finally, to enhance the selectivity of the determination, mass spectrometry was used as instrumental technique. The limits of detection of the proposed method were in the range of 0.07 μg/L (butylparaben) to 0.1 μg/L (methylparaben and propylparaben). The precision at 5 μg/L in terms of relative standard deviation was always better than 8 %. And the accuracy of the proposed method was evaluated by spiking of blank samples, and the relative recoveries were in the range of 88-98 %.

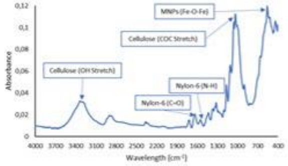
EXPERIMENTAL SECTION

Synthesis of MPSP

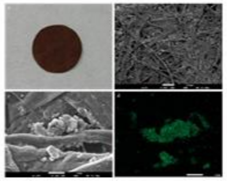


The dip-coating process was repeated three times. After the last cycle, MPSP can be stored at least for two months.

Characterization of MPSP



FTIR



SEM-EDX

Sampling/extraction procedure

The internal standard used in this analytical procedure was pre-loaded before each extraction using a solution standard with similar values of pH and ionic strength than the sample.

RESULTS AND DISCUSION

Optimization of extraction procedure

Variable	Initial value	Study range	Selected value
Polymer	Not adjusted	Nylon-6 and polystyrene	Nylon-6
Dips number	2	1 - 5	3
Extraction time (min)	10	5 - 20	10

Analytical figures of merit

Analyte	LOD (μg/L)	LOQ (μg/L)	R^2	RSD intra-day, n=5 (%)	Accuracy (% relative recovery)
Methylparaben	0.1	0.3	0.994	8.0	97 ± 8
Ethylparaben	0.08	0.26	0.992	7.3	94 ± 7
Propylparaben	0.1	0.3	0.991	6.7	98 ± 6
Butylparaben	0.07	0.23	0.996	4.9	88 ± 4
Triclosan	0.09	0.3	0.988	6.9	94 ± 6

Application to real samples

The optimized extraction process was applied for the determination of the target analytes in swimming pool samples, but only methylparaben and propylparaben were detected in one sample.

CONCLUSIONS

- A new magnetic paper-based sorptive phase was synthetized.
- The MPSP combines synergically the properties of the paper, magnetic nanoparticles and nylon-6.
- The use of the new material enhanced the transference of the analytes to the sorbent.
- The extraction procedure could be applied in in-site sampling process.
- The procedure can be applied to the proposed analytical problem.

Acknowledgments

Financial support from the Spanish Ministry of Economy and Competitiveness (CTQ2017-83175R) is gratefully acknowledged. F.A. Casado-Carmona expresses his gratitude for the predoctoral contract (ref. FPU16/06069) from the Spanish Ministry of Education, Culture and Sport.

P17. Computer fan's potential in air sampling

F.A. Casado-Carmona[1], G. Lasarte-Aragonés[1], A. Kabir[2], K.G. Furton[2], R. Lucena[1], and S. Cárdenas[1]
[1]*Affordable and Sustainable Sample Preparation (AS_2P) research group, Departamento de Química Analítica, Instituto Universitario de Investigación en Química Fina y Nanoquímica IUNAN, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E 14071, Córdoba, Spain*
[2]*Department of Chemistry and Biochemistry, International Forensic Research Institute, Florida International University, 11200 SW 8th St., Miami, FL, 33199, USA*

ExTech XXIII

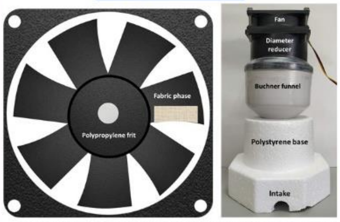
INTRODUCTION

The analysis of environmental air is challenging due to the vast volume of this compartment, its heterogenous distribution (both spatial and temporal) and the usual low concentration of the target compounds intended to be monitored. For those reasons, effective analysis should preferably integrate sampling and preconcentration on a single step which can be developed in an active (forced flow though of the sample) and passive sampling approaches. In this context, solid phase microextraction has been extensively applied to the analysis of volatile organic compounds in air.

In this research work an active sampling device (Patent pending) which is based on micro-solid phase extraction was designed and evaluated. The invention consists of a computer fan where the trap (the extraction media used for the isolation of the targets) is attached to the blades.

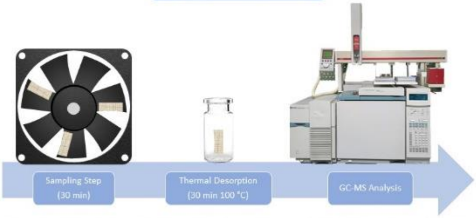
EXPERIMENTAL SECTION

Sampling extraction device



A scheme of the sampling/extraction device is presented on the left. On the right panel, the manifold proposed for the generation of the gaseous standards is shown.

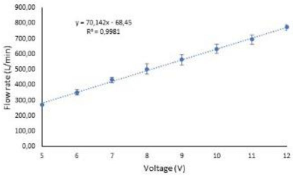
Sampling extraction procedure

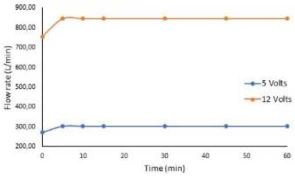


The internal standard used in this analytical procedure was loaded in the polypropylene frit. Thermal desorption process was carried out by means headspace using an autosampler.

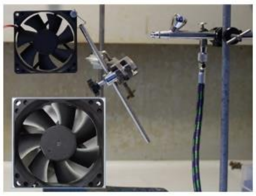
RESULTS AND DISCUSION

Flow rate evaluation

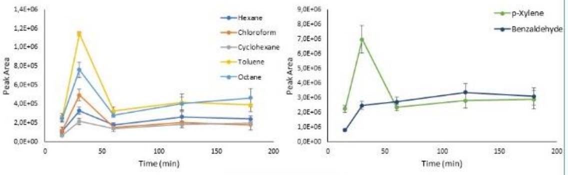




Sorbent location



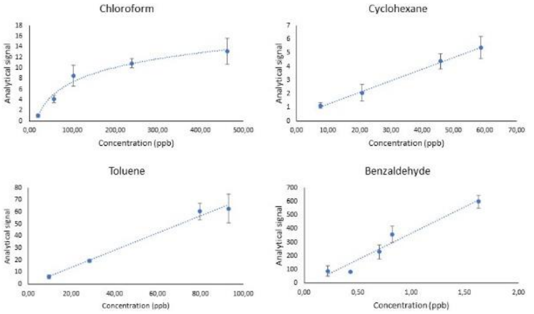
Extraction time



Analyte	Calibration Curve	R^2
Chloroform	$y = 4{,}0104\ln(x) - 11{,}18$	0,9784
Cyclohexane	$y = 0{,}0847x + 0{,}4081$	0,9984
Toluene	$y = 0{,}7095x - 0{,}2532$	0,9892
Benzaldehyde	$y = 388{,}77x - 25{,}06$	0,9505

y: analytical signal; x: analyte's concentration

Concentration profile



The concentration calibration models were constructed for different families of volatile organic compounds.

Versatility of the fan sampler

In order to demonstrate de versatility of the fan sampler, two solid samples (fresh pine needles and orange peel) were analyzed using the design previously described. Different biogenic volatile compounds were detected and identified in these samples

Sample	Compound
Pine	Tricyclene β-pinene β-myrcene
Orange	Tricyclene β-pinene Octanal Limonene (Z)-beta-Ocimene trans-β-Ocimene

CONCLUSIONS

- A novel air sampler is presented.
- The new air sampler is cheaper than the conventional ones.
- Easy to transport and to be used.
- The internal standard is integrated in the sampler.
- It can be used for the extraction of biogenic organic compounds.

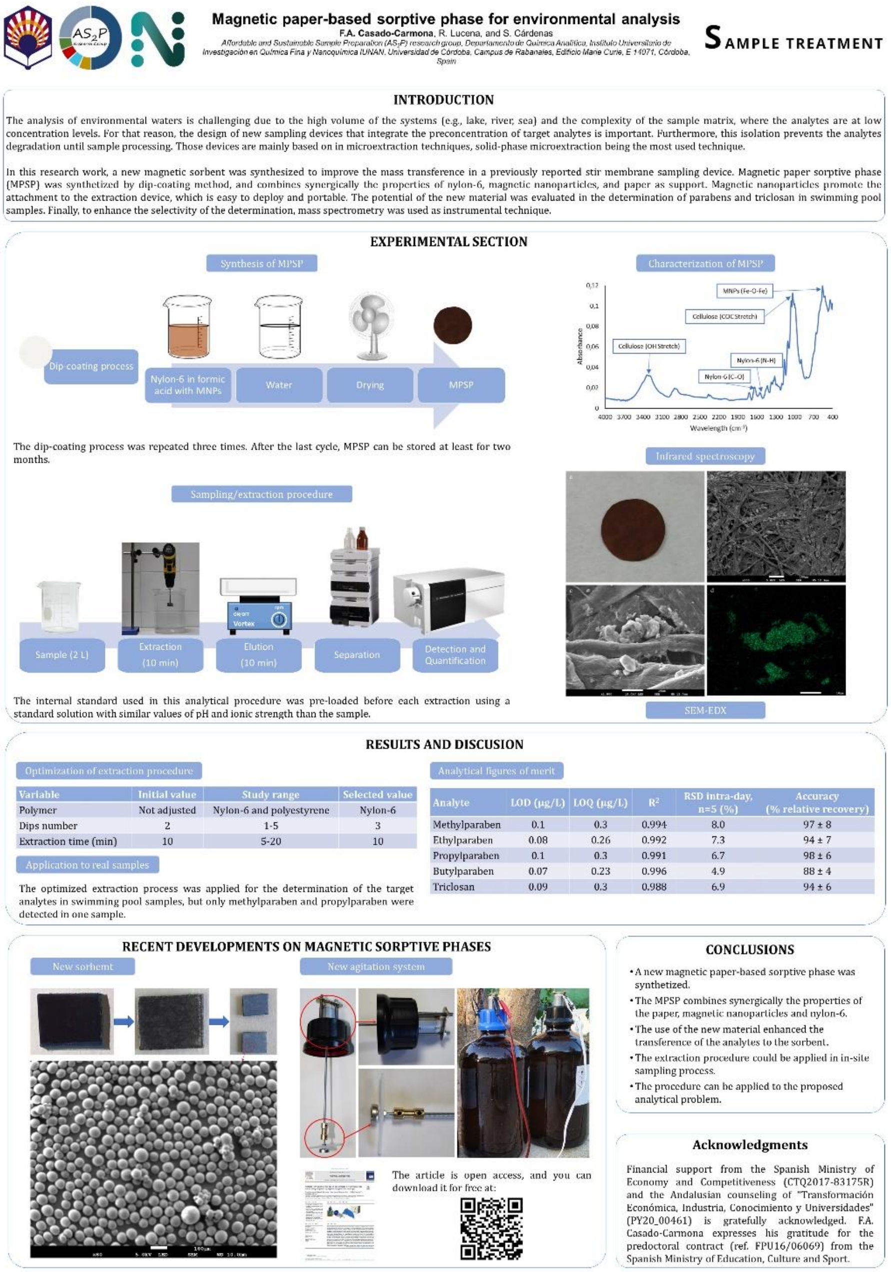
FUTURE RESEARCH

- Application of the device in environmental analysis.
- Application of the air sampler in workplace ambient.
- The use of other sorptive phases, with different geometries.
- The simultaneous use of different sorptive phases.

Acknowledgments

Financial support from the Spanish Ministry of Economy and Competitiveness (CTQ2017-83175R) is gratefully acknowledged.

F.A. Casado-Carmona expresses his gratitude for the predoctoral contract (ref. FPU16/06069) from the Spanish Ministry of Education, Culture and Sport.



Magnetic paper-based sorptive phase for environmental analysis

F.A. Casado-Carmona, R. Lucena, and S. Cárdenas

Affordable and Sustainable Sample Preparation (AS$_2$P) research group, Departamento de Química Analítica, Instituto Universitario de Investigación en Química Fina y Nanoquímica IUNAN, Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E 14071, Córdoba, Spain

SAMPLE TREATMENT

INTRODUCTION

The analysis of environmental waters is challenging due to the high volume of the systems (e.g., lake, river, sea) and the complexity of the sample matrix, where the analytes are at low concentration levels. For that reason, the design of new sampling devices that integrate the preconcentration of target analytes is important. Furthermore, this isolation prevents the analytes degradation until sample processing. Those devices are mainly based on in microextraction techniques, solid-phase microextraction being the most used technique.

In this research work, a new magnetic sorbent was synthesized to improve the mass transference in a previously reported stir membrane sampling device. Magnetic paper sorptive phase (MPSP) was synthetized by dip-coating method, and combines synergically the properties of nylon-6, magnetic nanoparticles, and paper as support. Magnetic nanoparticles promote the attachment to the extraction device, which is easy to deploy and portable. The potential of the new material was evaluated in the determination of parabens and triclosan in swimming pool samples. Finally, to enhance the selectivity of the determination, mass spectrometry was used as instrumental technique.

EXPERIMENTAL SECTION

Synthesis of MPSP

The dip-coating process was repeated three times. After the last cycle, MPSP can be stored at least for two months.

Sampling/extraction procedure

The internal standard used in this analytical procedure was pre-loaded before each extraction using a standard solution with similar values of pH and ionic strength than the sample.

Characterization of MPSP

Infrared spectroscopy

SEM-EDX

RESULTS AND DISCUSION

Optimization of extraction procedure

Variable	Initial value	Study range	Selected value
Polymer	Not adjusted	Nylon-6 and polyestyrene	Nylon-6
Dips number	2	1-5	3
Extraction time (min)	10	5-20	10

Application to real samples

The optimized extraction process was applied for the determination of the target analytes in swimming pool samples, but only methylparaben and propylparaben were detected in one sample.

Analytical figures of merit

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Butylparaben	0.07	0.23	0.996	4.9	88 ± 4
Triclosan	0.09	0.3	0.988	6.9	94 ± 6

RECENT DEVELOPMENTS ON MAGNETIC SORPTIVE PHASES

New sorbent

New agitation system

The article is open access, and you can download it for free at:

CONCLUSIONS

- A new magnetic paper-based sorptive phase was synthetized.
- The MPSP combines synergically the properties of the paper, magnetic nanoparticles and nylon-6.
- The use of the new material enhanced the transference of the analytes to the sorbent.
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Acknowledgments

Financial support from the Spanish Ministry of Economy and Competitiveness (CTQ2017-83175R) and the Andalusian counseling of "Transformación Económica, Industria, Conocimiento y Universidades" (PY20_00461) is gratefully acknowledged. F.A. Casado-Carmona expresses his gratitude for the predoctoral contract (ref. FPU16/06069) from the Spanish Ministry of Education, Culture and Sport.

ANEXO F

RECONOCIMIENTOS A LAS COMUNICACIONES EN CONGRESOS

1. Póster

Autores: Casado-Carmona, F.A.; Lucena, R.; Cárdenas, S.

Título: **Magnetic Paper Sorptive Phase for the Extraction of Parabens and Triclosan from Swimming Pool Waters.**

Congreso: 1st European Sample Preparation e-Conference. Marzo 2021.

Premio al mejor póster en la categoría "New Materials"

2. Póster

Autores: Casado-Carmona, F.A.; Lasarte-Aragonés, G.; Kabir, A.; Furton, K.G.; Lucena, R.; Cárdenas, S.

Título: **Computer fan's potential in air sampling.**

Congreso: XXIII International Symposium on Advances in Extraction Technologies (ExTech). Alicante (España), Julio 2021.

Premio al mejor póster.

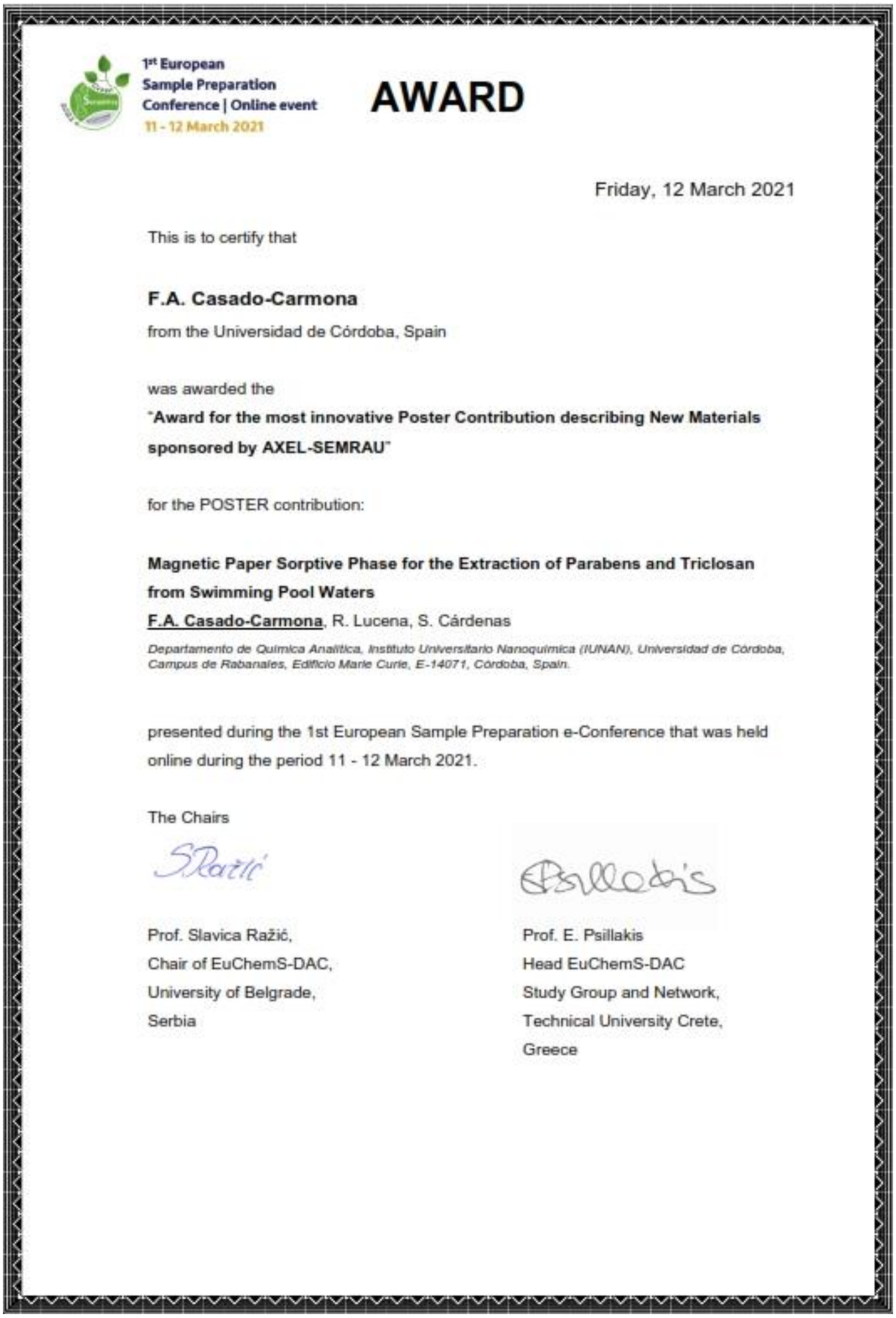
3. Comunicación Flash

Autores: Casado-Carmona, F.A.; Lucena, R.; Cárdenas, S.

Título: **Magnetic paper-based sorptive phase for environmental analysis.**

Congreso: 5th International Caparica Christmas Conference on Sample Treatment 2021. Caparica (Portugal), Noviembre 2021.

Premio al mejor Shotgun póster.



1st European
Sample Preparation
Conference | Online event
11 - 12 March 2021

AWARD

Friday, 12 March 2021

This is to certify that

F.A. Casado-Carmona

from the Universidad de Córdoba, Spain

was awarded the

"Award for the most innovative Poster Contribution describing New Materials sponsored by AXEL-SEMRAU"

for the POSTER contribution:

Magnetic Paper Sorptive Phase for the Extraction of Parabens and Triclosan from Swimming Pool Waters

F.A. Casado-Carmona, R. Lucena, S. Cárdenas

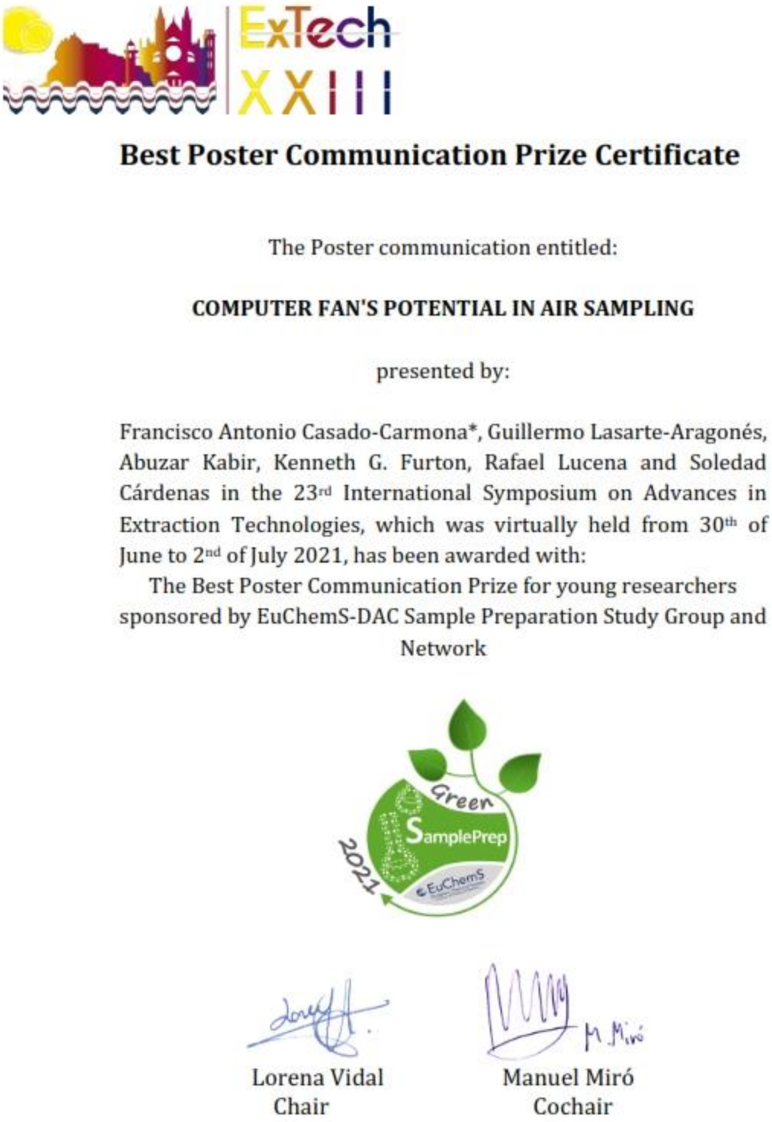
Departamento de Química Analítica, Instituto Universitario Nanoquímica (IUNAN), Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E-14071, Córdoba, Spain.

presented during the 1st European Sample Preparation e-Conference that was held online during the period 11 - 12 March 2021.

The Chairs

Prof. Slavica Ražić,
Chair of EuChemS-DAC,
University of Belgrade,
Serbia

Prof. E. Psillakis
Head EuChemS-DAC
Study Group and Network,
Technical University Crete,
Greece



Best Poster Communication Prize Certificate

The Poster communication entitled:

COMPUTER FAN'S POTENTIAL IN AIR SAMPLING

presented by:

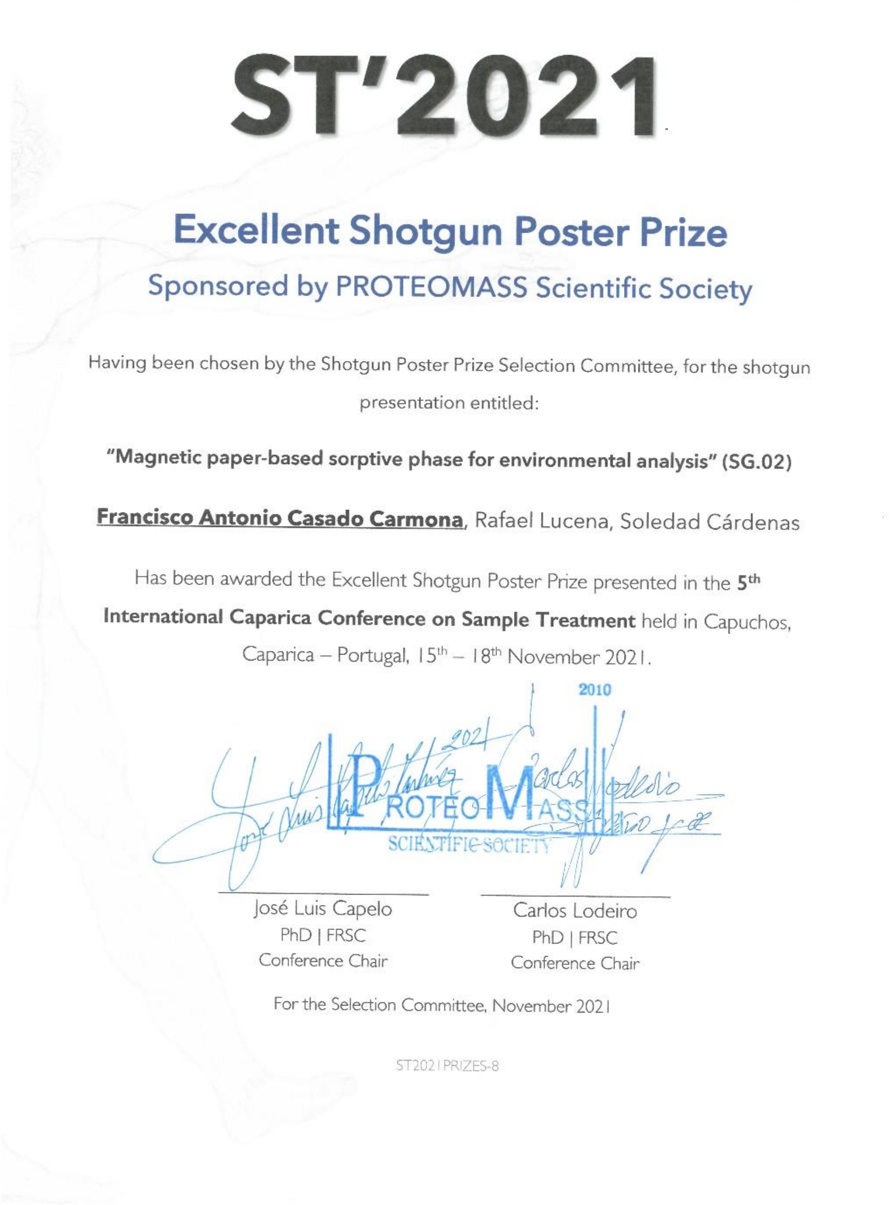
Francisco Antonio Casado-Carmona*, Guillermo Lasarte-Aragonés, Abuzar Kabir, Kenneth G. Furton, Rafael Lucena and Soledad Cárdenas in the 23rd International Symposium on Advances in Extraction Technologies, which was virtually held from 30th of June to 2nd of July 2021, has been awarded with:

The Best Poster Communication Prize for young researchers sponsored by EuChemS-DAC Sample Preparation Study Group and Network

M. Miró

Lorena Vidal
Chair

Manuel Miró
Cochair



ST'2021

Excellent Shotgun Poster Prize

Sponsored by PROTEOMASS Scientific Society

Having been chosen by the Shotgun Poster Prize Selection Committee, for the shotgun presentation entitled:

"Magnetic paper-based sorptive phase for environmental analysis" (SG.02)

Francisco Antonio Casado Carmona, Rafael Lucena, Soledad Cárdenas

Has been awarded the Excellent Shotgun Poster Prize presented in the **5th International Caparica Conference on Sample Treatment** held in Capuchos, Caparica – Portugal, 15th – 18th November 2021.

2010

José Luis Capelo
PhD | FRSC
Conference Chair

Carlos Lodeiro
PhD | FRSC
Conference Chair

For the Selection Committee, November 2021

ST2021PRIZES-8

ANEXO G

ACTIVIDADES RELACIONADAS CON LA DOCENCIA

1. **Dirección de trabajo fin de grado (TFG)**

Autora: Mónica Sánchez Parra

Título: **Detección temprana de la presencia de la polilla de la vid mediante la determinación de feromonas en el fruto.**

Código: QM-16-26-QAM, Grado en Química, Curso 2016/17

2. **Dirección de trabajo fin de grado (TFG)**

Autor: Alejandro Medina Jaraba

Título: **Síntesis y caracterización de nanopartículas magnéticas modificadas superficialmente para la extracción de contaminantes.**

Código: QM-17-16-QAM, Grado en Química, Curso 2017/18

3. **Dirección de trabajo fin de grado (TFG)**

Autor: Celia Cruz López

Título: **Integración de muestreo y tratamiento de muestra en análisis ambiental.**

Código: CA19-31-QAN, Grado en Ciencias Ambientales, Curso 2019/20

4. **Participación en proyectos de innovación docente**

Título: **Integración transversal de diversas asignaturas y titulaciones mediante el aprendizaje basado en fenómenos y la virtualización de procesos.**

Código: 2020-2-2002, Curso 2020/21

DEPARTAMENTO DE QUÍMICA ANALÍTICA
Edificio Marie Curie (Anexo)
Campus Universitario de Rabanales
Facultad de Ciencias. Universidad de Córdoba
14071 Córdoba (Spain)
Tfno: 34 957 218614 Fax: 34 957 218614

Don/Doña Francisco Antonio Casado Carmona, adscrito/a al Departamento de Química Analítica como investigador y doctorando del grupo FQM-215, ha colaborado con el/los Prof(s) María del Carmen Alcudia León en la tutorización del Trabajo Fin de Grado cuyos datos se refieren más abajo.

Alumno:	Mónica Sánchez Parra		
Título del TFG:	Detección Temprana de la Presencia de la Polilla de la Vid mediante la Determinación de Feromonas en el Fruto. (QM16-26-QAN).		
Grado:	Química		
Tutor/es	María del Carmen Alcudia León		
Fecha de defensa:	21/07/2017	Créditos de la asignatura TFG:	15 créditos

Y para que conste y surta los efectos oportunos, firman el presente en Córdoba, a 26 de septiembre de 2017

Tutor del TFG

Alcudia

Fdo: María del Carmen Alcudia León

El Director del Departamento

Fdo: Manuel Silva Rodríguez

V°B°

El Decano

Fdo.: Dr. Manuel Blázquez Ruiz

DEPARTAMENTO DE QUÍMICA ANALÍTICA
Edificio Marie Curie (Anexo)
Campus Universitario de Rabanales
Facultad de Ciencias. Universidad de Córdoba
14071 Córdoba (Spain)
Tfno: 34 957 218614 Fax: 34 957 218614

Don Francisco Antonio Casado Carmona, adscrito al Departamento de Química Analítica como contratado FPU del grupo FQM-215, ha colaborado con la Prof. Ángela I. López Lorente en la tutorización del Trabajo Fin de Grado cuyos datos se refieren más abajo.

Alumno:	Alejandro Medina Jaraba		
Título del TFG:	Síntesis y caracterización de nanopartículas magnéticas modificadas superficialmente para la extracción de contaminantes. (QM17-16-QAN).		
Grado:	Grado en Química		
Tutor/es	Ángela I. López Lorente		
Fecha de defensa:	11/07/2018	Créditos de la asignatura TFG:	15 créditos

Y para que conste y surta los efectos oportunos, firman el presente en Córdoba, a 16 de julio de 2018

Tutor del TFG

Fdo: Ángela I. López Lorente

El Director del Departamento

Fdo: Manuel Silva Rodríguez

VºBº

La Decana

María de la Paz Aguilar Caballos

Facultad de Ciencias

MARTA ROSEL PÉREZ MORALES, SECRETARIA DE LA FACULTAD DE CIENCIAS DE LA UNIVERSIDAD DE CÓRDOBA,

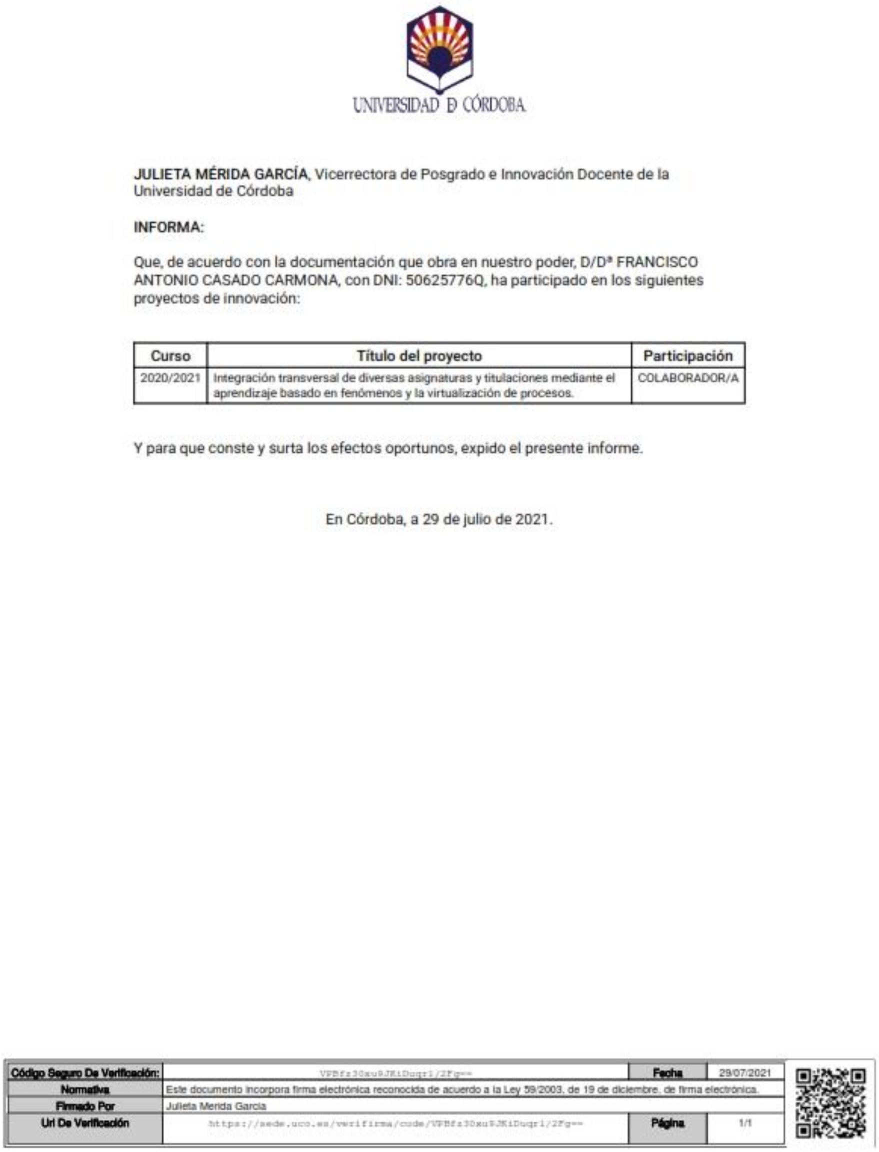
CERTIFICA:

Que **D. FRANCISCO ANTONIO CASADO CARMONA,** con D.N.I.: 50625776Q, ha sido tutor del siguiente Trabajo de Fin de Grado:

- CA19-31-QAN "INTEGRACIÓN DE MUESTREO Y TRATAMIENTO DE MUESTRA EN ANÁLISIS AMBIENTAL". Defendido en la convocatoria de julio del curso 2019/2020, obtuvo la calificación de 9,2 Sobresaliente.

Y para que conste y surta los efectos oportunos, firmo el presente en Córdoba, a 22 de octubre de 2021.

Código Seguro De Verificación:	BBfvUsvANSMYiyARvYAduw==	**Fecha**	22/10/2021
Normativa	Este documento incorpora firma electrónica reconocida de acuerdo a la Ley 59/2003, de 19 de diciembre, de firma electrónica.		
Firmado Por	Marta Rosel Pérez Morales		
Url De Verificación	https://sede.uco.es/verifirma/code/BBfvUsvANSMYiyARvYAduw==	**Página**	1/1



UNIVERSIDAD DE CÓRDOBA

JULIETA MÉRIDA GARCÍA, Vicerrectora de Posgrado e Innovación Docente de la Universidad de Córdoba

INFORMA:

Que, de acuerdo con la documentación que obra en nuestro poder, D/Dª FRANCISCO ANTONIO CASADO CARMONA, con DNI: 50625776Q, ha participado en los siguientes proyectos de innovación:

Curso	Título del proyecto	Participación
2020/2021	Integración transversal de diversas asignaturas y titulaciones mediante el aprendizaje basado en fenómenos y la virtualización de procesos.	COLABORADOR/A

Y para que conste y surta los efectos oportunos, expido el presente informe.

En Córdoba, a 29 de julio de 2021.

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Normativa	Este documento incorpora firma electrónica reconocida de acuerdo a la Ley 59/2003, de 19 de diciembre, de firma electrónica.		
Firmado Por	Julieta Merida Garcia		
Url De Verificación	https://sede.uco.es/verifirma/code/VPBfz30xu9JKiDuqrl/2Fg==	**Página**	1/1