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Optimization of pressurized liquid extraction and purification conditions for gas chromatography–mass spectrometry determination of UV filters in sludge

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ABSTRACT

This work presents an effective sample preparation method for the determination of eight UV filter compounds, belonging to different chemical classes, in freeze-dried sludge samples. Pressurized liquid extraction (PLE) and gas chromatography–mass spectrometry (GC–MS) were selected as extraction and determination techniques, respectively. Normal-phase, reversed-phase and anionic exchange materials were tested as clean-up sorbents to reduce the complexity of raw PLE extracts. Under final working conditions, graphitized carbon (0.5 g) was used as in-cell purification sorbent for the retention of co-extracted pigments. Thereafter, a solid-phase extraction cartridge, containing 0.5 g of primary secondary amine (PSA) bonded silica, was employed for off-line removal of other interferences, mainly fatty acids, overlapping the chromatographic peaks of some UV filters. Extractions were performed with a n-hexane:dichloromethane (80:20, v:v) solution at 75 °C, using a single extraction cycle of 5 min at 1500 psi. Flush volume and purge time were set at 100% and 2 min, respectively. Considering 0.5 g of sample and 1 mL as the final volume of the purified extract, the developed method provided recoveries between 73% and 112%, with limits of quantification (LOQs) from 17 to 61 ng g^{-1} and a linear response range up to 10 μg g^{-1}. Total solvent consumption remained around 30 mL per sample. The analysis of non-spiked samples confirmed the sorption of significant amounts of several UV filters in sludge with average concentrations above 0.6 μg g^{-1} for 3-(4-methylbenzylidene) camphor (4-MBC), 2-ethylhexyl-p-methoxycinnamate (EHMC) and octocrylene (OC).

1. Introduction

Organic UV filters are compounds designed to absorb the ultraviolet wavelengths of solar radiation preventing photo-aging and other harmful effects in human health. The concentration of UV filters in sunscreen lotions may represent up to 10% of the product weight; moreover, they are included, at lower levels, in the formulation of many other personal care products [1,2]. The above uses contribute to the direct input of UV filters in bathing waters and their indirect release in the aquatic environment through domestic sewage water [3–7]. The activity of some UV filters as endocrine disrupters [8–10], added to their ubiquity in sewage and surface water, has awaken the concern about their potential medium-term environmental effects.

Gas and liquid chromatography–mass spectrometry techniques, combined with effective sample concentration approaches [5,11–13], have been applied to obtain an overview of UV filters occurrence in different water samples, including wastewater from sewage treatment plants (STPs). However, understanding the behaviour of UV filters in STPs requires not only measuring their concentrations in the water phase, but also determining the fraction which remains attached to sludge particles [7]. This latter information is necessary to distinguish between biodegradation and sorption processes, and to assess the risk of introducing the UV filters in the terrestrial environment through the application of sludge as fertilizer in agriculture.

From the analytical point of view, sludge is an extremely complex matrix which requires well-tuned sample preparation approaches providing a balance among efficiency, selectivity, extraction time and cost. These constraints explain the limited number of studies dealing with the analysis of UV filters in sludge versus the plethora of publications focussed on water samples. The first method for sludge was proposed by Plagellat et al. [14]. It involved three consecutive liquid–liquid extractions of fresh sludge samples (60 g), followed by dryness evaporation of the combined extract and column purification with activated silica. Solvent consumption stayed above 200 mL per sample.

Pressurized liquid extraction (PLE) is a popular sample preparation technique for solid matrices showing limited solvent consumption, excellent extraction yields and possibility to inte-

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Table 1
Abbreviations, retention times, selected ions and instrumental limits of quantification (LOQs) of the GC–MS system of target analytes.

Compound	Abbreviation	Retention time (min)	Segment	Quantification ion (*m*/*z*)	Qualification ion (*m*/*z*)	LOQs (ng mL^{-1}) (S/N 10)
2-Ethylhexyl salicylate	EHS	9.65	1	120	138	2
Homosalate	HMS	10.26, 10.40	1	120	138	4
Isoamyl-p-methoxycinnamate	IAMC	11.63[a]	2	178	161	2
2-Hydroxy-4-methoxybenzophenone	BP-3	11.63	2	227	151	6
3-(4-Methylbenzylidene) camphor	4-MBC	11.87[a]	2	254	239	3
2-Ethylhexyl-p-dimethylaminobenzoate	EHPABA	13.41	2	277	165	1
2-Ethylhexyl-p-methoxycinnamate	EHMC	13.73[a]	2	178	161	1
Octocrylene	OC	16.15	3	360	249, 232	2

[a] Retention time values for the *E* isomers.

grate extraction and purification steps. The applications of PLE to the extraction of personal care compounds from sludge have been compiled in a recent review [15]. PLE, combined with in-cell clean-up using activated silica, has been reported as a straight forward alternative for gas chromatography–mass spectrometry (GC–MS) determination of UV filters in low carbon content sediment samples [16]; however, the above strategy provided too complex extracts in the case of sludge [17]. Although, the selectivity of the extraction could be improved by enclosing the sludge sample in a non-porous polyethylene membrane bag, within the cell, the efficiency of the extraction underwent a dramatic reduction, with recoveries around or below 50% for most UV filters [17]. In addition to the above procedures, Nieto et al. [18] have developed a PLE method for the extraction of several personal care products, including three UV filters (benzophenone-3, BP-3; octocrylene, OC; and 2-ethylhexyl-p-dimethylaminobenzoate, EHPABA), from sludge samples. Analytes were recovered with methanol followed by methanol:water mixtures and on-line purified with alumina Considering a sample intake of 1 g, and 25 mL as the volume of the final extract, recoveries over 79% and low signal suppression effects (below 15%) were observed in the further LC–(ESI)-MS/MS determination.

In this study, we optimize an alternative sample preparation method for the determination of eight UV filters, belonging to different chemical classes, in freeze-dried sludge samples. PLE was selected as extraction technique due to its high automation capabilities. Purification conditions were optimized in order (1) to reduce the content of interferences (coloured matter and fatty acids) in the final extract and (2) to maintain the consumption of organic solvents and the complexity of the method at acceptable levels. GC–MS was considered as determination technique on the basis of the poor detection limits reported for salicylate type UV filters using LC–(ESI)-MS systems [19]. Finally, the applicability of the method was demonstrated with sludge samples from urban STPs.

2. Experimental

2.1. Solvents, standards and sorbents

N-hexane, isooctane, acetone, dichloromethane and ethyl ether (trace analysis grade) and HPLC-grade methanol were supplied by Merck (Darmstadt, Germany). The list of UV filters included in this study is compiled in Table 1. Standards of target analytes were acquired from Aldrich (Milwaukee, WI, USA) and Merck, except isoamyl-p-methoxycinnamate (IAMC), which was kindly provided by Dr. R. Rodil (University of Santiago de Compostela, Spain). Individual solutions of each species (ca. 1000 μg mL^{-1}) were prepared in methanol. Further dilutions and mixtures of them were dissolved in acetone (when used to prepare the spiked sludge samples employed during optimization and validation of sample preparation conditions) and in isooctane (case of calibration standards).

Alumina, Florisil and silica solid-phase extraction (SPE) cartridges (0.5 g) were acquired from Waters (Milford, MA, USA). Cartridges containing 0.5 g of silica bonded to ethylenediamine-N-propyl groups (PSA sorbent) and 0.25 g of graphitized carbon were purchased from Supelco (Bellefonte, PA, USA). Both sorbents, in the bulk format, were also obtained from Supelco. Diatomaceous earth was provided by Aldrich.

2.2. Samples

Optimization of sample preparation (extraction and purification) conditions was performed with a freeze-dried pooled matrix of primary and biological sludge, fortified with 5 μg g^{-1} of each UV filter. The total carbon (TC) content of the pooled matrix was 33%. The spiking procedure consisted of the addition of a measured volume of a standard in acetone to an accurately weighed fraction of sludge. The resulting slurry was protected from light, homogenized periodically and kept in a hood until complete elimination of the acetone. The recoveries of the method were evaluated with individual samples of primary and biological sludge fortified at different concentrations. All spiked samples were aged for a minimum of 2 weeks before extraction. The optimized method was applied to grab samples of non-digested sludge (primary, secondary and mixtures of both) from several urban STPs located in the Northwest of Spain. Some samples were received as wet sludge (ca. 3–4% of dry matter) and freeze-dried after reception. Others were already lyophilized in the STPs.

2.3. Sample preparation

Extractions were performed with a pressurized liquid extractor, ASE 200 Dionex (Sunnyvale, CA, USA), furnished with 11 mL stainless-steel cells. A cellulose filter, followed by a glass fibre one, was placed on the bottom of each cell. Under final working conditions, cells were filled (bottom to top) with 1 g of diatomaceous earth, 0.5 g of graphitized carbon, 0.5 g of diatomaceous earth and 0.5 g of sludge, previously homogenized with 2 g of diatomaceous earth. Analytes were extracted with n-hexane:dichloromethane (80:20), at 75 °C, considering a single static extraction cycle of 5 min with the cell pressurized at 1500 psi. The flush volume was 100% and the purge time 2 min.

PLE extracts were evaporated, ca. 1 mL, and additionally purified with a PSA cartridge (0.5 g) previously conditioned with n-hexane:ether (1:1) and n-hexane (5 mL each). After loading the concentrated extract, the sorbent was rinsed with n-hexane (1 mL). Analytes were further recovered with 5 mL of n-hexane:ether (1:1). Thereafter, 1 mL of isooctane was added as a keeper to the purified extract, which was evaporated and adjusted to a final volume of 1 mL with the same solvent.