Application of surfactant-templated ordered mesoporous material as sorbent in micro-solid phase extraction followed by liquid chromatography–triple quadrupole mass spectrometry for determination of perfluorinated carboxylic acids in aqueous media

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ABSTRACT

In the present study, micro-solid phase extraction (μ-SPE) followed by liquid chromatography–triple tandem mass spectrometery (LC–MS/MS) was developed for the determination of perfluorocarboxylic acids (PFCAs) at trace levels in water samples. The μ-SPE device comprised of a porous polypropylene membrane bag containing 5 mg sorbent. The membrane bag acted as a clean-up filter and prevented matrix compounds from interfering with the extraction process. Analysis was carried out by LC–MS/MS in negative electrospray ionization mode. MS/MS parameters were optimized for multiple reaction monitoring. Calcined and non-calcined MCM-41, as silica-ordered mesoporous materials, were used as sorbents in μ-SPE for the extraction of five PFCAs—perfluoropentanoic acid (PFPA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), and perfluorodecanoic acid (PFDA)—from aqueous media. The performances of these two sorbents were compared with other sorbents such as octadecylsilane (C18) modified silica, HayeSep-A, HayeSep-B, and Porapak-R. It was found that non-calcined MCM-41 showed better extraction performance for the analytes considered. Parameters influencing extraction efficiency, such as desorption time, extraction time, desorption solvent, and salt concentration, were investigated. The effect of the matrix on MS signals (suppression or enhancement) was also evaluated. Only minor effects on ionization efficiencies were observed. The developed method proved to be convenient and offered good sensitivity and reproducibility. The limits of detection ranged from 0.02 to 0.08 ng L^{-1}, with a relative standard deviations between 1.9 and 10.5. It was successfully applied to the extraction of PFCAs in river and rain water samples. As expected from the ubiquitous nature of PFCAs, contamination at low levels was detected for some analytes in the samples (with the highest concentration recorded for PFOA). Satisfactory relative recoveries ranging between 64% and 127% at spiking levels of 10 ng L^{-1} of each analyte were obtained.

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1. Introduction

Perfluorinated compounds (PFCs) are anthropogenic chemicals, which have been used in a wide range of products over the past 6 decades. In PFCs, aliphatic hydrogen atoms of hydrocarbon chains are replaced by fluorine atoms leading to compounds with unique physicochemical properties, including water and oil repellency, unusual thermal and chemical stability, and unusual surfactant properties. These properties make them very useful substances for a wide range of industrial applications such as in paper packaging, as surface protectors and stain repellents, fire-fighting foam, and emulsifiers for the production of fluoropolymers [1–3].

Despite their favorable properties in manufacturing, and as finished products, some of these compounds exhibit characteristics of persistent organic pollutants, as defined by the United Nations Environment Program's Stockholm Convention [4]. Most of them are toxic, extremely resistant to degradation, and bioaccumulative in biological tissues with an extended half-life [5–7]. Nongovernmental organizations as well as national and international authorities have undertaken many efforts to put pressure on

the industry to limit the production and usage of some of the most harmful PFCs. This has already led to a decreasing production and use of the chemicals in the recent years [8]. However these substances are ubiquitous and persistent, and are still widely prevalent in many environmental and biological media such as surface waters, aquatic environments, sediments, soils, human blood, and biota [9–12]. Much effort has been made to develop methods for the detection and determination of PFCs in different media; however, there are many comprehensive publications, which in particular, evaluated the analytical challenges in the analysis of PFCs [8,13]. These challenges and uncertainties have been identified in detail and must be considered by researchers in analytical studies related to PFCs. Matrix effects have been considered as one of the most important sources of uncertainties in quantitative analysis of PFCs. These can have suppressive and/or enhancing effect on the results, particularly when mass spectrometric detection is used [14].

Given that several practical suggestions have been made and evaluated to overcome matrix effects, no unique or universal strategy or solution concerning this phenomenon has been established [8]. However, it has been confirmed that sample preparation is the key step for minimizing the presence of interfering compounds in complex matrices before analysis.

PFCs are usually found at trace levels in environmental water samples, which necessitate the extraction and pre-concentration step before analysis. Solid phase extraction (SPE), with different sorbent types such as reversed phase [15], hydrophilic–lipophilic-balanced (HLB), polymers polymeric reversed phase, and weak anion exchange (WAX) phases [16–18], is a common extraction method in the determination of PFCs in environmental samples.

In 2006, an extraction and pre-concentration technique termed as micro-solid phase extraction (μ-SPE), based on the packing of sorbent material in a sealed porous polypropylene membrane envelope (bag), was reported by our group, and it has been used successfully for the extraction of various target analytes without additional sample clean-up [19]. Extraction and concentration of the analyte in one single step and easy manipulation are some of the significant benefits of μ-SPE. In μ-SPE, the bag can be quickly isolated from the sample after extraction by using a pair of tweezers. The μ-SPE is relatively inexpensive and uses only a few milligrams of sorbent. This homemade strategy does not need any expensive commercial accessories, making it very affordable for any laboratory. It has an additional practical advantage that it does not face some of the difficulties commonly encountered with other sorption-based methods including high back pressure required when the samples are passed through the SPE cartridge; blockage of the SPE column, need for frits to confine the sorbent in conventional SPE; relatively longer sample loading time in SPE (either by gravity flow or pressure/vacuum-assisted flow); isolation and collection of sorbent, as in dispersive solid phase extraction, need for evaporation or solvent exchange (which leads to analyte loss); and fragility of the extraction device as in solid phase micro-extraction (SPME). From a performance point of view, the protective role of the membrane prevents interferences in the extraction, thereby leading to minimization, if not removal of matrix effects. This in particular makes μ-SPE very useful for the analysis of analytes from complex matrices such as aqueous samples, food products, and biological tissues [20–25]. Considering all these advantages of μ-SPE over other sorbent-based methods, μ-SPE was our preferred choice of extraction procedure in this study.

The kind of sorbent used in μ-SPE is an important factor, which influences greatly the extraction of the analytes from the matrix because there occurs a dynamic partitioning of analytes between the sorbent material and the matrix. High adsorption capacity, acceptable selectivity, good stability and durability, and desirable adsorption kinetics are some of the characteristics of an ideal sorbent. These features are dependent on some properties of sorbent such as the pore size and pore size distribution, specific surface area, as well as the surface chemistry of the sorbent. Current commercial sorbents may not have all of these properties. Thus, the above requirements provide the impetus for ongoing studies on the development, design, synthesis, and applications of new materials.

In this direction, in the current study, for the first time we aimed to investigate the applicability of the ordered mesoporous material as a sorbent in μ-SPE. Many studies have focused on the use of ordered mesoporous silicates as sorbents [26–28]. MCM-41 is a well-known member of the mesoporous molecular sieve M41S family, which is largely used in shape-selective catalysis, selective adsorption and separation processes, and chemical sensors. A narrow pore size distribution, high surface area, and high pore volume are some of the properties of this material that makes it a desirable sorbent. MCM-41 is synthesized via a liquid-crystal templating mechanism [29]. During synthesis, the silicate material forms inorganic walls between ordered surfactant micelles. After polymerization of the silica, the surfactant template is removed either through chemical or thermal treatment (calcination process), which induces high porosity. Indeed, MCM-41 type materials are prepared using the S^+I^- pathway, in which strong electrostatic interactions exist between rod-like micelles of surfactants (S^+) and anionic silicate species (I^-) as inorganic network [30]. Previous studies indicated that even these surfactant-containing mesoporous silica, synthesized in alkaline conditions can ideally function as sorbent [31–33]. Thus, MCM-41 containing cationic surfactant may result in high extraction efficiency for pre-concentration and extraction of PFCs from water. The objective of the present study was to evaluate the feasibility of the μ-SPE technique using ordered mesoporous silica as sorbents, for the liquid chromatography–triple quadrupole mass spectrometery (LC–MS/MS) analysis of perfluorinated carboxylic acids (PFCAs)—as one of the major and most persistent groups of PFCs [34]. Most research on PFCs has been focused on perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). PFOS and PFOA are listed in the Annex B of the Stockholm Convention on Persistent Organic Pollutants [35]. However, temporal trends have seen decreases in the serum levels of both compounds in the United States, Sweden, Norway, and Japan since 2000 [36–40]. In contrast, PFCAs—especially those with longer carbon chains than PFOA (C_9–C_{14})—have continued to increase in human serum in East Asia and Sweden [39,40], and have been detected in human breast milk [36]. The same observation has been made regarding the monitoring of PFCAs and PFOS in aquatic ecosystems in wide geographic locations [41]. Several in vitro studies have also suggested that long-chain PFCAs are biologically more toxic than PFOA [42,43]. In 2012, considering all the necessities for PFCAs monitoring, the European Commission recommendation 2010/161/EU document invited member states to monitor and study other similar PFOA compounds with different chain lengths [44]. For these reasons, we decided to focus on PFCAs in this work.

To the best of our knowledge this was the first time mesoporous material was used as sorbent in μ-SPE and their adsorption potential with the PFCAs was investigated. MCM-41 and non-calcined MCM-41 (denoted as CTAB-MCM-41) were evaluated for their adsorptive performance. Various parameters affecting the μ-SPE, including the effect of desorption solvent, extraction time, salt concentration, and desorption time, were investigated. The performances of different commercial sorbents were compared. Under the optimized conditions, the proposed method was applied to the analysis of real world samples, including rain water and river water.