



Applicability of the direct injection liquid chromatographic tandem mass spectrometric analytical approach to the sub-ng L⁻¹ determination of perfluoro-alkyl acids in waste, surface, ground and drinking water samples



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ABSTRACT

The applicability of a direct injection UHPLC-MS/MS method for the analysis of several perfluoroalkyl acids (PFAAs) in a wide range of water matrices was investigated. The method is based on the direct injection of 100 μ L of centrifuged water sample, without any other sample treatment. Very good method detection limits (0.014–0.44 ng L⁻¹) and excellent intra and inter-day precision (RSD% values in the range 1.8–4.4% and 2.7–5.7%, respectively) were achieved, with a total analysis time of 20 min per sample. A high number of samples – i.e. 8 drinking waters (DW), 12 ground waters (GW), 13 surface waters (SW), 8 influents and 11 effluents of wastewater treatment plants (WWTP_{IN} and WWTP_{OUT}) were processed and the extent of matrix effect (ME) was calculated, highlighting the strong prevalence of |ME| < 20%. The occurrence of |ME| > 50% was occasionally observed only for perfluorooctanesulphonic and perfluorodecanoic acids. Linear discriminant analysis highlighted the great contribution of the sample origin (i.e. DW, GW, SW, WWTP_{IN} and WWTP_{OUT}) to the ME. Partial least square regression (PLS) and leave-one-out cross-validation were performed in order to interpret and predict the signal suppression or enhancement phenomena as a function of physicochemical parameters of water samples (i.e. conductivity, hardness and chemical oxygen demand) and background chromatographic area. The PLS approach resulted only in an approximate screening, due to the low prediction power of the PLS models. However, for most analytes in most samples, the fitted and cross-validated values were such as to correctly distinguish between |ME| higher than 20% or below this limit. PFAAs in the aforementioned water samples were quantified by means of the standard addition method, highlighting their occurrence mainly in WWTP influents and effluents, at concentrations as high as one hundred of μ g L⁻¹.

1. Introduction

Perfluoro-alkyl acids (PFAAs) are a class of compounds having a CF₃-(CF₂)_n-R structure, where R is a carboxylic or a sulfonic or a phosphonic group, and “n” ranges mostly between 2 and 10. PFAAs are characterized by high resistance to physical, chemical and biological degradation and have been widely employed since the 1950s in a wide range of industrial and commercial applications, as well as in fluoropolymer production, giving rise to a widespread contamination of environmental matrices. More in detail, PFAAs have been determined

in wastewater [1–3], surface water [4–6] and drinking water [7]. Moreover, PFAAs have been detected in remote areas like open oceans [8] and Arctic [9,10].

Among PFAAs, perfluorooctanesulphonic acid (PFOS) and perfluorooctanoic acid (PFOA) have been the most industrially employed until 2006, when some regulatory restrictions have been promulgated both in Europe and United States [11,12]. Furthermore, in 2013 PFOS has been included in the list of priority hazardous substances, within the Directive 2013/39/EU [13], whereas PFOA has been included in the candidate list of Substances of Very High Concern because of its

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carcinogenic, mutagenic or toxic for reproduction effects as well as persistent, bioaccumulative and toxic properties [14].

For PFOS an annual average environmental quality standard (EQS) and a maximum allowable concentration (MAC) of 0.65 ng L^{-1} and $36 \text{ } \mu\text{g L}^{-1}$ have been respectively established for inland waters by the European Community (EC) [13]. As regards drinking water, Provisional Health Advisories of $0.4 \text{ } \mu\text{g L}^{-1}$ and $0.2 \text{ } \mu\text{g L}^{-1}$ have been proposed by the Environmental Protection Agency of United States (USEPA) for PFOA and PFOS, respectively [15]. For these compounds concentration limits in drinking water of $0.5 \text{ } \mu\text{g L}^{-1}$ (PFOA) and $0.03 \text{ } \mu\text{g L}^{-1}$ (PFOS) have been recommended by the Italian Health Institute, on the basis of maximum tolerable daily intake (TDI) data reported by the European Food Safety Authority [16]. Conversely, to the best of our knowledge, no limits have been established for the presence of PFAAs in groundwater.

Several analytical methods for the determination of PFAAs in water media at trace level have been published, mostly employing solid-phase extraction (SPE) and liquid chromatography (LC) coupled with tandem mass spectrometry (MS/MS) [1,17–19].

However, physicochemical properties (i.e. solubility/lipophilicity and acidity) of these molecules greatly vary depending on the chain length and the acidic group present in the molecule, thus making challenging the recovery of all analytes during extraction and clean-up processes. Furthermore, special care should be taken during sample manipulation, treatment and analysis, since, as demonstrated by various inter-laboratory studies, there is an actual risk of contamination during the whole analytical process, owing to the presence of fluorinated polymers in commonly used laboratory materials and equipment [20].

In order to minimize sample manipulation and treatment, as well as to increase the analytical throughput, several on-line SPE-LC-MS/MS methods have been developed for PFAAs determination in water samples [21–24].

The direct injection (DI) approach is the best choice to overcome any contamination of the sample due to its manipulation and treatment, as well as to ensure a high analytical throughput. However, this approach may suffer a lower sensitivity, compared to SPE-based methods. Moreover, when the DI approach is used, matrix effect (ME) may significantly affect the precision and/or the sensitivity of the method, owing to the absence of extraction and clean-up steps. Several applications of the DI technique have been reported in literature for the determination of different classes of organic micro-pollutants in water samples [3,20,25–28]. Furthermore, the DI approach is also included in official methods for the analysis of selected organic contaminants in drinking water [29,30], where ME is usually less important than in freshwater or wastewater [31–34]. Nevertheless, to the best of our knowledge, only two papers have been published to date concerning the application of DI-LC-MS/MS to PFAA analysis [3,20]. Furdui et al. evaluated ME for DI-LC-MS/MS analysis of C7–C12 perfluoro-carboxylic acids (PFCAs), C6 and C8 perfluoro-sulfonic acids (PFSAs) and C8 perfluoro-sulfonamide in lake water and effluent wastewater, highlighting in all real samples a suppressive ME [3]. Conversely, on a larger group of PFAAs, including also C4–C6 PFACs and C4 PFSA, Wolf and Reagen evidenced the absence of ME in various synthetic and real drinking water samples, as well as in groundwater, cooling-water and effluent wastewater samples [20]. It should be however noted that in both studies ME was not systematically investigated, and the applicability of the DI-LC-MS/MS approach to a wide range of aqueous matrices, including those characterized by a strong matrix component (e.g. wastewaters and environmental waters), still remains worth to be further investigated. In this regard, it should be remarked that the analysis of PFAAs in aqueous samples provides a realistic picture of their presence in the whole environmental compartment (i.e. water with sediments and particulate matter), since these analytes are almost completely partitioned in the dissolved phase [8].

According to the considerations reported above, the aim of this

work was to evaluate the feasibility of using the DI-LC-MS/MS analytical approach for the determination of PFCAs and PFSAs in a very wide range of water samples (i.e. drinking water, groundwater, river water, lake water and wastewater). For each sample ME was investigated by the standard addition method and tentatively interpreted as a function of a set of physicochemical parameters of water samples (i.e. conductivity, hardness, and organic carbon content), as well as chromatographic outputs.

Moreover, since water samples herein analysed were collected in zones never investigated before for PFAA occurrence (i.e. various rural, urban and industrial districts of Tuscany, Italy), this study provides for the first time information regarding the contamination by PFAAs of these areas.

2. Material and methods

2.1. Standards and reagents

Perfluorobutanesulphonic acid (PFBS, CAS no. 375-73-5), perfluoropentanoic acid (PFPeA, CAS no. 2706-90-3), perfluorohexanoic acid (PFHxA, CAS no. 307-24-4), perfluorohexanesulphonic acid (PFHxS, CAS no. 355-46-4), perfluoroheptanoic acid (PFHpA, CAS no. 375-85-9), perfluorooctanoic acid (PFOA, CAS no. 335-67-1), perfluoro-*n*-(1,2,3,4- $^{13}\text{C}_4$)octanoic acid (MPFOA), perfluoroactanesulphonic acid (PFOS, CAS no. 1763-23-1), and perfluoro-1-(1,2,3,4- $^{13}\text{C}_4$) octanesulphonate (MPFOS), perfluorononanoic acid (PFNA, CAS no. 375-95-1), perfluorodecanoic acid (PFDA, CAS no. 335-76-2), methanol stock solutions ($50 \text{ } \mu\text{g mL}^{-1}$) were purchased by Wellington Laboratories Inc. (Guelph, ON, Canada).

Water and methanol (LC-MS grade) were obtained from Carlo Erba (Milan, Italy).

Ammonium acetate (Sigma-Aldrich, St. Louis, MO, USA) 1 M solution was freshly prepared in water LC-MS grade.

2.2. UHPLC-MS/MS analysis

Ultra-high performance liquid chromatographic (UHPLC) analyses were performed on a Shimadzu (Kyoto, Japan) chromatographic system consisting of a low pressure gradient quaternary pump Nexera $\times 2$ LC-30AD, a DGU-20A 5R degassing unit, a SIL-30AC autosampler equipped with a 100 μL loop, a CTO/20AC thermostatted column compartment and a CBM-20A module controller. A delay column (C_{18} , $100 \times 4.6 \text{ mm}$) was installed between the mixer and the sample injector, in order to separate the impurity PFAAs originating from the LC system from the analyte PFAAs of the sample.

Chromatographic separation was obtained with a Waters ACQUITY UPLC BEH C_{18} column ($100 \times 2.1 \text{ mm}$, particle size $1.7 \text{ } \mu\text{m}$) equipped with a guard column (Waters, Milford, MA, USA), thermostatted at $50 \text{ } ^\circ\text{C}$, employing a mixture of 95% water 5% methanol solution of 2 mM ammonium acetate (solvent A) and a methanol solution of 2 mM ammonium acetate (solvent B) at a flow rate of 0.5 mL min^{-1} . All glassware was thoroughly rinsed with methanol before use. The eluents were freshly prepared by adding a suitable aliquot of 1 M ammonium acetate solution filtered on $0.2 \text{ } \mu\text{m}$ polyethersulfone filters. The chromatographic gradient was the following: 25% B for 2 min, from 25% to 90% in 6 min, 90% for 5 min, from 100% to 25% in 0.5 min and final hold for 6.5 min for system re-equilibration. Total analysis time was 20 mins. The injection volume used was set to $100 \text{ } \mu\text{L}$. Fig. S1 of the Supplementary material section illustrates a reconstructed DI-LC-MS/MS chromatogram of the quantifier and qualifier transitions of target PFAAs obtained by injecting $100 \text{ } \mu\text{L}$ of a standard mixture in Milli-Q water at the concentration of 5 ng L^{-1} each.

In order to minimize MS source contamination, the first 2 min and the last 8 min of the chromatographic run have been diverted to waste by means of a two-position six-port valve installed before the mass spectrometer.

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