



Gas chromatography–tandem mass spectrometry with atmospheric pressure chemical ionization for fluorotelomer alcohols and perfluorinated sulfonamides determination



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ABSTRACT

Ionization and in source-fragmentation behavior of four fluorotelomer alcohols (FTOH) (4:2 FTOH, 6:2 FTOH, 8:2 FTOH and 10:2 FTOH) and four N-alkyl fluorooctane sulfonamides/-ethanols (N-MeFOSA, N-EtFOSA, N-MeFOSE and N-EtFOSE) by APCI has been studied and compared with the traditionally used EI and CI. Protonated molecule was the base peak of the APCI spectrum in all cases giving the possibility of selecting it as a precursor ion for MS/MS experiments. Following, CID fragmentation showed common product ions for all FOSAs/FOSEs (C₄F₇ and C₃F₅). Nevertheless, the different functionality gave characteristic pattern fragmentations. For instance, FTOHs mainly loss H₂O + HF, FOSAs showed the losses of SO₂ and HF while FOSEs showed the losses of H₂O and SO₂. Linearity, repeatability and LODs have been studied obtaining instrumental LODs between 1 and 5 fg. Finally, application to river water and influent and effluent waste water samples has been carried out in order to investigate the improvements in detection capabilities of this new source in comparison with the traditionally used EI/CI sources. Matrix effects in APCI have been evaluated in terms of signal enhancement/suppression when comparing standards in solvent and matrix. No matrix effects were observed and concentrations found in samples were in the range of 1–100 pg L⁻¹ far below the LODs achieved with methods previously reported. Unknown related perfluoroalkyl substances, as methyl-sulfone and methyl-sulfoxide analogues for FTOHs, were also discovered and tentatively identified.

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1. Introduction

Perfluorinated alkyl substances (PFAS) are a class of chemicals used in a range of applications due to their water and stain-resistant properties. They have been produced in high volumes for several decades and combine bioaccumulative potential, toxic effect and extreme persistence [1]. As a consequence of their use for more than 60 years, residues of PFAS are widely spread in the environment [2,3]. Some of these compounds can bioaccumulate and biomagnify in the food chain [4–6], and have been detected in humans [7,8]. The ubiquitous presence of these PFAS in the general population, their long half-lives, and increasing evidence of potential adverse health effects, is of concern. Among these ubiquitously

found anthropogenic chemicals are perfluoroalkane sulfonates and perfluorocarboxylates with 4–15 carbon atoms in chain length. The most widely investigated compounds of these groups are the C₈-chemicals perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) [9]. They have been used for over 50 years in the production of consumer products including carpet and upholstery stain-protectants, food-contact paper coating, nonstick cookware, waterproofing sprays, and windshield wash [10].

Due to their non-volatile and lower water-soluble properties of PFOA/PFOS, two different theories are their concerning transportations pathways. Either the moderately water-soluble compounds including shorter-chain perfluorocarboxylates could be transported directly by sea currents or by means of sea-spray. Alternatively, a suite of volatile, neutral precursors could undergo long-range atmospheric transport and be degraded in situ to form persistent PFOA and PFOS [11]. Possible atmospheric precursors include a number of fluorotelomer alcohols (FTOHs) as well as N-alkylated fluorooctane sulfonamides and sulfonamidoethanols

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(FOSAs/FOSEs). The second hypothesis is strongly supported by the number of smog chamber degradation experiments, and by the determination of neutral PFAS at ground level at the North American troposphere [9].

Analytical methods for neutral PFAS (volatile FTOHs and FOSAs/FOSEs) in environmental and indoor air include mainly gas chromatography coupled to mass spectrometry with chemical ionization (GC/CI-MS) usually in positive mode (PCI) because it produced the molecular ion $[M+H]^+$, and one or two characteristic fragment ions for all FTOHs and FOSEs with the exception of FOSAs for which only one ion could be detected in PCI [9]. Therefore, confirmation of FOSAs in samples is always performed in negative ion chemical ionization (NICI) mode, wherein three fragments can be monitored [12]. In contrast, electronic ionization (EI) is not frequently used because of the low intensity of the molecular ions and the lack of specific fragments. As an alternative to GC/MS methods, the analysis of neutral PFAS by LC/MS was also reported [13,14]. However, in LC/MS methods the co-analysis of nonionic and ionic PFAS is impeded by ionization suppression of FTOHs caused by the buffered mobile phases needed for the chromatographic separation of ionic PFAS [14].

The recently revived atmospheric pressure chemical ionization (APCI) source has been satisfactorily applied for GC-amenable compounds such as pesticides, PAHs, PCBs and, very recently, PBDEs, dioxins and dioxin-like PCBs [15–18]. The soft ionization generated by this source promotes the formation of the molecular ion and/or the protonated/deprotonated molecule (quasi-molecular ions) as the base peak of the spectrum in most cases, with low fragmentation degree, if we compare against the high fragmentation generally observed by EI. This allows the selection of $([M+H]^+ \text{ or } M^{+\bullet})$ as a precursor ion for the SRM transitions which turns into a sensitive and specific analyte detection and identification. Moreover, this source has also been revealed more universal than the traditional CI source, which is not as universal as EI and requires various injections of the sample to cover a wider range of analytes being rarely used in multiresidue methods [19].

In the present work the potential of atmospheric pressure chemical ionization (APCI) combined with GC-MS/MS with triple quadrupole analyzer has been investigated for the sensitive determination of FTOHs and FOSAs/FOSEs in surface water. GC-(APCI)QTOF MS has been also explored for the investigation of new related PFAS. Up to our knowledge this is the first study of this APCI source applied to FTOHs and FOSAs/FOSEs analysis.

2. Experimental

2.1. Reagents and standards

The fluorotelomer alcohols (FTOHs): 4:2 FTOH was purchased from Fluorochem Ltd. (Derbyshire, UK), while 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were supplied from Alfa Aesar GmbH & Co KG (Karlsruhe, Germany) with purity higher than 96%. Individual standard solutions of the perfluoroalkyl sulfonamides at a concentration of 50 mg L^{-1} in methanol of N-MeFOSE, N-EtFOSE and N-MeFOSA were supplied by Wellington Laboratories Inc. (Guelph, Ontario, Canada), while N-EtFOSA was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) (Table 1S). Individual stock standard solutions of each pure standards and the internal standard of 1000 mg L^{-1} were prepared in ethyl acetate from their respective pure standards. An intermediate standard mixture of all compounds (1 ng mL^{-1}) were obtained by dilution of the stock standard solutions in ethyl acetate and stored at 0°C .

Ethyl acetate and methanol of residue analysis grade were obtained from Sigma-Aldrich (Steinheim, Germany). In addition, ultra-pure water was obtained from a Milli-Q system coupled to an Elix 3 (Millipore, Bedford, MA, USA). Helium of high purity

($\geq 99.98\%$) was purchased from Abelló Linde, S.A. (The Linde Group, Spain). All glassware was treated with chromosulphuric acid, rinsed consecutively with Milli-Q water and acetone, and heated to 400°C before use.

2.2. Samples

Three water samples were collected in the Llobregat River (Barcelona, NE Spain) at the lower section. This river run through very densely populated and industrialized areas, receiving extensive urban and industrial waste water discharges from more than 3 million inhabitants. Sampling sites in the Llobregat River were located downstream of the towns of Sant Feliu de Llobregat, Sant Boi de Llobregat and el Prat de Llobregat (a total of 3 water samples). Additionally, 6 samples were also taken, 3 influent (at three different sampling times) and 3 effluent (at three different sampling times) wastewater samples of the San Feliu de Llobregat wastewater treatment plant (WWTP). Glass bottles (1000 mL) fitted with black Viton septa were filled with water without headspace and stored in the dark at 4°C before being analyzed. Field blanks consisting of 1000 mL of natural mineral water were prepared at the same sampling points and they were analyzed along with the water samples.

2.3. Sample treatment

The target compounds were extracted from water samples using solid-phase extraction (SPE) technique. The SPE procedure was carried out as follows: a volume of 1000 mL of centrifuged (if needed) water samples were passed through an Oasis HLB[®] cartridge (500 mg, 6 mL) (Waters, Milford, MA, USA) at a flow-rate of 10 mL min^{-1} using a Visiprep System (Supelco, Bellefonte, PA, US). Before use, SPE cartridges were conditioned with 20 mL methanol and 20 mL Milli-Q water and dried under a gentle nitrogen stream during 15 min. After sample extraction, the cartridges were washed with 10 mL of a 5:95 mixture of MeOH/Milli-Q water and dried for 30 min. The analytes were eluted with 4 mL ethyl acetate. The extract was then evaporated under a gentle nitrogen stream at 25°C down to 500 μL and it was transferred to a 1 mL-conic vial. Then, the extract was evaporated until 20 μL and the extract volume was adjusted to 50 μL with ethyl acetate. Finally, 2 μL of the extract was injected into the GC-MS(/MS) systems. The suitability of the method was further evaluated with a blank river water sample spiked with all the compounds at two concentration levels (1 ng L^{-1} and 10 ng L^{-1}) using Oasis HLB. Recoveries of all the compounds ranged from 80% to 97% with a relative standard deviation (RSD %) lower than 10%.

2.4. Instrumentation

2.4.1. GC-(APCI) MS/MS

Data were acquired using a GC system (Agilent 7890A, Palo Alto, CA, USA) equipped with an autosampler (Agilent 7693) and coupled to a triple quadrupole (QqQ) mass spectrometer (Xevo TQ-S, Waters Corporation, Manchester, UK), operating in APCI mode. A TraceGold[™] TG-WaxMS fused-silica capillary column (100% polyethylene glycol) of $30 \text{ m} \times 0.25 \text{ mm}$ I.D. and a film thickness of 0.25 μm (Thermo Scientific, USA), was used for GC separation of target compounds. The injector was operated in pulsed splitless mode (30 psi), injecting 2 μL at 250°C . The oven temperature was programmed as follows: 60°C (2 min); $10^\circ\text{C min}^{-1}$ to 200°C ; $25^\circ\text{C min}^{-1}$ to 240°C (2 min). Helium was used as carrier gas at a constant flow mode (1.4 mL min^{-1}). In the SRM method, automatic dwell time (values ranging from 9 to 46 ms) was applied in order to obtain 15 points per peak. The interface temperature was set to 240°C using N_2 as auxiliary gas at 250 L h^{-1} , a make-up gas at

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