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# Derivatization method for sensitive determination of fluorotelomer alcohols in sediment by liquid chromatography–electrospray tandem mass spectrometry

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ABSTRACT

Fluorotelomer alcohols (FTOHs) are the main precursors of environmentally ubiquitous perfluorinated acids, and determination of FTOHs at low concentrations presents significant challenges. In this study, a new liquid chromatography–electrospray mass spectrometry (LC–ESI-MS) method in conjunction with low-energy collision dissociation tandem mass spectrometry (CID-MS/MS) was developed by employing an optimized derivatization reaction with dansyl chloride (DNS) in acetonitrile under catalysis of 4-(dimethylamino)-pyridine (DMAP). The instrument detection limits (IDLs) of the newly developed method were 0.014, 0.015, 0.014, 0.0075 and 0.0093 μg/L for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:1 FTOH and 10:2 FTOH respectively, which were 7.5–241 times lower than those without derivatizaiton and 57–357 times lower than previous GC/MS method. The method was successfully applied to analyze FTOHs in sediments combined with WAX and silica cartridges cleanup. The overall method recoveries were from 67 ± 6.0% to 83 ± 9.4% with matrix effects of <15%. The limits of quantification for all FTOHs were 0.017–0.060 ng/g dry weight (dw). The method was applied to analyze six marine sediment samples from Liaodong Bay, China. All FTOHs except for 10:1 FTOH were detected, and the total concentrations of FTOHs were 0.19–0.52 ng/g dw. The developed method provides a new method to sensitively determine FTOHs in environmental matrices.

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## 1. Introduction

Perfluorinated acids (PFAs) are a class of compounds which have been widely used in the production of inks, water repellents and as coatings on paper during the past 50 years [1–3], and were found to be environmentally persistent and globally distributed in soil [4,5], water [6,7], atmosphere [8,9], foods [10], and human serum [11,12]. Two major PFAs, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been added as new persistent organic pollutants (POPs) in the Stockholm Convention in 2009 [13]. Although PFAs are often found at the highest levels in environmental monitoring compartments, fluorotelomer alcohols (FTOHs) are produced in much greater quantities and used in a wide range of products such as paints, adhesives, waxes, polishes, metals, electronics, and caulks [14]. The total production of FTOHs was estimated to be $5 \times 10^6$ kg year$^{-1}$ worldwide during the years 2000–2002 [14]. It has been proven that, during the life cycles of FTOHs, these chemicals could be transformed to PFAs under microbial biodegradation [15], oxidation in the atmosphere [16], and in vivo metabolism [17]. Therefore, it is necessary to develop a sensitive methodology for analyzing FTOHs in environmental matrices to provide direct evidence on their contributions to PFAs exposure.

Gas chromatography–mass (GC/MS) has been used as a routine method to analyze FTOHs in air samples [18–20]. However, the method suffers from low sensitivity with the instrument detection limits (IDLs) in the range of 0.8–20 μg/L [21,22]. Liquid chromatography–electrospray tandem mass spectrometry (LC–MS/MS) is an alternative method to analyze FTOHs, and it shows higher instrumental sensitivity than GC/MS when analyzing odd-chain-length FTOHs including 7:1 FTOH (IDL: 0.1 μg/L) and 10:1 FTOH (IDL: 0.02 μg/L) [23]. However, the instrumental sensitivity for analyzing even-chain-length FTOHs using LC–MS/MS was relatively low (IDLs: 1 μg/L, 3 μg/L and 30 μg/L for 6:2 FTOH, 10:2 FTOH and 4:2 FTOH, respectively) [24], which limited the application of LC–MS/MS method on the analysis of the even-chain-length FTOHs. In addition, the LC–MS/MS method with electrospray ionization cannot be used to detect FTOHs in real environmental samples due to the signal suppression caused by matrix effects.

Converting these poorly ionizable analytes into easily detectable derivatives has been reported to be useful in enhancing the

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detection sensitivity and reducing matrix effects [25]. A derivatization LC/MS methodology with high sensitivity and good linearity has been developed using dansyl chloride (DNS) as the derivatization agent [26]. DNS shows many advantages such as a short incubation step and simple reaction conditions, and has been applied for analyzing phenols [27] and amines [28] by introducing a dimethylamino moiety in the structure to improve the ionization activity in the ESI source by 10–100 fold [27]. The aim of the present work was to develop a sensitive LC–MS/MS method based on dansylation for analyzing five FTOHs, and then applied this method to determine FTOHs in marine sediment samples from Liaodong Bay.

## 2. Experimental

### 2.1. Chemicals and reagents

4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:1 FTOH and 10:2 FTOH and stable isotope-labeled standard $^{13}C_4$-8:2 FTOH were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Triethylamine, sodium carbonate, DNS and 4-(dimethylamino)-pyridine (DMAP) were obtained from Sigma–Aldrich (St. Louis, MO, USA). Oasis WAX (3 $cm^3$, 60 mg, 30 μm) and silica (6 $cm^3$, 1 g) solid-phase extraction (SPE) cartridges were purchased from Waters (Milford, MA, USA). All solvents including hexane, dichloromethane (DCM), acetone, acetonitrile (ACN) and methanol were HPLC grade and purchased from Fisher Chemicals (New Jersey, USA). Water obtained by a Milli-Q Synthesis water purification system (Millipore, Bedford, MA, USA) was used throughout the study.

### 2.2. Optimization of dansylation conditions

Each dansylation was carried out in a sealed 1.5 mL glass sample vial (Waters, Milford, MA, USA). The dansylation conditions of FTOHs were optimized by changing the solvents (acetone, methanol, ACN or DCM) under different catalysts (sodium carbonate, DMAP or triethylamine). Aliquots of a mixture of standards were dissolved in a solvent of 1 mL, and then a mixture (200 μl) of 30 mg/mL DNS and catalysts was added and shaken vigorously for 1 min. The resulting mixture was kept at 65 °C for 60 min followed by mixing with a vortex device for 30 s. The residuals were blown to dryness and then dissolved with 1 mL of ACN for UPLC–MS/MS in conjunction with low-energy collision dissociation (CID) or UPLC–ESI-QTOF-MS analysis. The reaction temperature and time were optimized by varying the DNS concentration from 0.75 to 6.0 mg/mL, and the derivatization time from 15 to 120 min. Methanol (20–100 μl) was added to the derivatization solutions to verify the influence of methanol on the dansylation efficiencies.

### 2.3. Sediment sample collection and preparation

Sediment samples were collected from Liaodong Bay in northern China in September 2009. Sediments were freeze-dried, grounded, and sieved through a 0.2 mm mesh and then stored at −20 °C until analysis. pH, salinity, and total organic carbon (TOC) of the sediment were 7.2 ± 0.3, 0.3 ± 0.06% and 0.48 ± 0.04%, respectively.

Approximately 1.0 g (dry weight) of sediment samples were added to a 15 mL polypropylene (PP) centrifuge tube, and then were spiked by 50 μl $^{13}C_4$-8:2 FTOH (2 μg/L). The samples were left to stand for 24 h at room temperature in the dark and then 4 mL of ACN was added for extraction. After shaking vigorously for 20 min, sonication for 20 min, and centrifugation at 4000 rpm for 10 min, 1 mL of the supernatant was diluted by 2.6 mL of ultrapure water and then was loaded on WAX cartridges which had been conditioned by 3 mL of ACN and 3 mL of ultrapure water. After being rinsed with 2 mL of ultrapure water and blown to dryness under gentle nitrogen flow, 1 mL of ACN was used to elute target FTOHs from the WAX cartridges. 200 μl of 30 mg/mL DNS and 30 mg/mL DMAP in DCM was then added to the eluate and shaken vigorously for 1 min. The resulting mixture was kept at 65 °C for 60 min and then transferred to a 15 mL centrifuge tube, and then 3 mL of ultrapure water and 6 mL of hexane were added. After being shaken vigorously for 10 min, the organic layer was separated by centrifugation at 4000 rpm for 10 min. The extraction was repeated and the combined extracts were loaded onto silica cartridges which had been conditioned with 8 mL DCM and 8 mL hexane. The target dansylated FTOHs were eluted with 8 mL hexane:DCM (1:1) and then blown to dryness and dissolved in 0.1 mL of ACN for UPLC–CID-MS/MS analysis.

### 2.4. UPLC–CID-MS/MS and UPLC–ESI-QTOF-MS analysis

The LC apparatus was an ACQUITY UPLCTM system (Waters, Milford, MA, USA). Separation for dansylated FTOHs was conducted using a Waters ACQUITY UPLC BEH phenyl column (1.7 μm; 2.1 mm × 100 mm). The column was maintained at 40 °C, and the flow rate and injection volume were 0.3 mL/min and 5 μL, respectively. Methanol (A) and ultrapure water containing 0.1% formic acid (B) were used as mobile phases. The initial composition of 20% A was increased to 80% in 1 min, then increased to 100% at 5 min and kept for 2 min, followed by a decrease to 10% A and held for 2 min to allow for equilibration. Mass spectrometry was performed using a Waters Micromass Quattro Premier XE triple-quadrupole instrument detector equipped with an electrospray ionization source (+ion mode) (Micromass, Manchester, UK). The optimized parameters were as follows: source temperature, 110 °C; desolvation temperature, 350 °C; capillary voltage, 3.50 kV; desolvation gas flow, 800 L/h; cone gas flow, 50 L/h; and multiplier, 650 V. Finally, the CID-MS/MS data acquisition was performed in the multiple-reaction monitoring (MRM) mode, and time-segmented scanning in four functions was used based on the chromatographic separation of target compounds to maximize the detection sensitivity. MS/MS parameters for the analytes including their precursors and product ions, cone voltage, and collision energy are summarized in Table 1. The UPLC–CID-MS/MS method for analyzing non-derivatized FTOHs in a negative ion mode has been described in our previous paper [29]. In that paper, 5 mM ethanolamine and methanol was used as mobile phases, and Waters ACQUITY UPLC BEH C18 column (1.7 μm; 2.1 mm × 100 mm) was used for separation.

UPLC–ESI-QTOF-MS for analyzing dansylated FTOHs was conducted under the same UPLC conditions as those of UPLC–CID-MS/MS as mentioned above except that the injection volume was increased to 10 μL. Mass spectrometry was performed using a Waters XEVO G2 QT operated with an electrospray ionization source in a positive ion mode. Sodium formate was used for a mass calibration check with the mass range of $m/z$ 100–1000, and leucine-enkephalin (MW = 555.62 Da) was used as a lock mass. The instrument was set to acquire over the $m/z$ range 400–800 with scan time of 0.5 s, and data were collected in centroid mode.

### 2.5. Quantitation

Identification of FTOHs was accomplished by comparing the retention time (within 2%) and the ratio (within 20%) of the two selected precursor ion-production ion transitions with those of standards. To automatically correct the losses of analytes during sample preparation and the matrix-induced change in ionization, and to compensate for variations in instrument response from injection to injection, $^{13}C_4$-8:2 FTOH was used as surrogate standard in this study.

All equipment rinses were done with ACN to avoid sample contamination, and laboratory blanks were analyzed in each batch to

**Table 1**
Analytes, surrogate standards, and selected reaction monitoring conditions by UPLC-CID-MS/MS and UPLC-QTOF-MS.

| Analyte | Transition monitored (*m/z*) | CV (V)[b] | CE (V)[c] | Measured mass[d] | Theoretical mass | Error[e] (ppm) |
|---|---|---|---|---|---|---|
| 4:2 FTOH | 498.7 → 237.3[a] | 35 | 50 | 498.0789 | 498.0785 | 0.80 |
| | 498.7 → 252.4 | | 45 | | | |
| 6:2 FTOH | 598.7 → 237.2 | 45 | 50 | 598.0724 | 598.0722 | 0.33 |
| | 598.7 → 252.4 | | 35 | | | |
| 8:2 FTOH | 698.6 → 237.2 | 60 | 50 | 698.0649 | 698.0658 | −1.3 |
| | 698.6 → 252.2 | | 50 | | | |
| 10:1 FTOH | 784.6 → 157.1 | 60 | 50 | 784.0411 | 784.0437 | −3.3 |
| | 784.6 → 171.4 | | 50 | | | |
| 10:2 FTOH | 798.6 → 237.3 | 50 | 45 | 798.0586 | 798.0594 | −1.0 |
| | 798.6 → 252.3 | | 45 | | | |
| $^{13}C_4$-8:2 FTOH | 702.6 → 237.2 | 60 | 50 | – | – | – |
| | 702.6 → 252.2 | | 50 | | | |

[a] MRM transition used for quantitation.
[b] Cone voltage.
[c] Collision energy.
[d] Measured by UPLC–QTOF-MS.
[e] The error between theoretical mass and measured mass by UPLC–QTOF-MS.

assess potential sample contamination. Since it is impossible to obtain samples free of analytes, the recoveries ($n = 3$) were calculated by subtracting the background concentrations in non-spiked samples from spiked samples at two spiked levels (low spiked level was 0.10 ng/g dw, 0.20 ng/g dw, 0.20 ng/g dw, 0.20 ng/g dw and 0.50 ng/g dw for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:1 FTOH and 10:2 FTOH, respectively; high spiked level was 1.0 ng/g dw, 2.0 ng/g dw, 2.0 ng/g dw, 2.0 ng/g dw and 5.0 ng/g dw for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:1 FTOH and 10:2 FTOH, respectively). The inter-day precision was calculated based on the means for three spiked samples (0.10 ng/g dw, 0.20 ng/g dw, 0.20 ng/g dw, 0.20 ng/g dw and 0.50 ng/g dw for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH,10:1 FTOH and 10:2 FTOH) in each of three days. The method limits of detection (LODs) and limits of quantification (LOQs) for FTOHs which can be detected in sediment were based on the peak-to-peak noise of the baseline near the analyte peak obtained by analyzing field samples and on a minimal value of signal-to-noise of 3 and 10, respectively. For 10:1 FTOH which could not be detected in samples, the method LODs and LOQs were calculated based on the signal-to-noise of 3 and 10 after adding 10:1 FTOH standard to samples at concentrations ranging from 0.005 to 1 ng/g dw. Since matrix effect is a general problem in LC–MS/MS analysis, we evaluated the extent of signal suppression or enhancement by spiking standards of dansylated FTOHs (0.10 ng/g dw for 4:2 FTOH, 0.20 ng/g dw for 6:2 FTOH, 8:2 FTOH and 10:1 FTOH, and 0.50 ng/g dw for 10:2 FTOH) into the extracts of sediment samples. The matrix effect observed for each analyte was calculated using the percentage of signal intensity in the sample matrix versus the signal of the same concentration in acetonitrile.

## 3. Results and discussion

### 3.1. Optimization of dansylation conditions

For optimizing dansylation conditions of FTOHs, solvents (acetone, methanol, ACN, or DCM), bases (sodium carbonate, DMAP, or triethylamine), incubation time (15, 30, 60, or 120 min), and DNS concentrations (0.75, 1.5, 3.0, or 6.0 mg/mL) were tested. Dansylation yielded the highest signal level for all FTOHs at 6.0 mg/ml of DNS in ACN for 60 min with catalysis by DMAP (6.0 mg/ml) (Fig. 1), and therefore these conditions were selected for the dansylation of FTOHs in the following experiments. Although dansylation in DCM also yielded relatively high signal compared to methanol and acetone, the solvent was not used since DCM is volatile during reaction at 65 °C. It was found that small volumes of methanol (50 μl) greatly decreased the sensitivities by 30–80% for all FTOHs, possibly due to the reaction of methanol with DNS, and therefore all stock solutions were diluted with ACN and all reactions had to be conducted in ACN in this study.

### 3.2. Optimization of analytical conditions

Full-scan ESI-MS analysis in the positive ion mode was performed for the determination of the produced FTOH derivatives. All protonated molecular ions $[M+H]^+$ of the dansylated FTOHs were detected in the reaction solution at the optimized cone voltage from 35 to 60 V as shown in Table 1. The accurate masses of the derivatives were confirmed by UPLC–ESI-QTOF-MS. The most probable elemental compositions of the ions were obtained with a high degree of confidence, and the relative errors between experimental and theoretical masses were within ±5 ppm (Table 1). Analysis of the product ion spectra of dansylated FTOHs indicated that the precursor ions were fragmented via two fragmentation routes. The CID-spectra of the protonated molecular ions $[M+H]^+$ obtained from dansylated FTOHs with even carbon number (Fig. 2(a)) was governed by cleavage of the C—O bond and yielded the major predominant product ions at *m/z* 252 and *m/z* 237. In addition, we also observed relatively low abundance of the product ions at *m/z* 156 and *m/z* 171 formed via the cleavage of S—C bond between S and aromatic ring. However, the CID-MS/MS spectra of the precursor ion extracted from dansylated 10:1 FTOH with odd carbon number formed only the product ions at *m/z* 156 and *m/z* 171 (Fig. 2(b)). These latter ions were similar to dansylated derivatives of chemicals with phenolic groups such as bisphenol A and hydroxylated polybrominated diphenyl ethers [27]. This may be due to the stronger bond energy of C—O bond for odd-chain-length FTOH (10:1 FTOH) than even-chain-length FTOHs under the influence of $CF_2$ group, and therefore decreasing the cleavage efficiency of C—O bond in collision cell.

Although BEH C18 column and BEH C8 column using 0.1% formic acid in water/methanol as the mobile phases achieved complete chromatographic separation of all target FTOHs derivatives, the dansylated FTOHs have strong retention on BEH C18 column or BEH C8 column and high background noise was observed. Since BEH phenyl column generated the highest signal-to-noise ratios at the same concentration with high separation efficiency, the BEH phenyl column was finally selected as the analytical column for separating dansylated FTOHs. Fig. 3 compared the UPLC–CID-MS/MS chromatograms of FTOHs with and without dansylation. It can be found that distinct peak for each target FTOH was observed at 1 μg/L for the former, while no obvious peaks for 4:2 FTOH and 6:2 FTOH

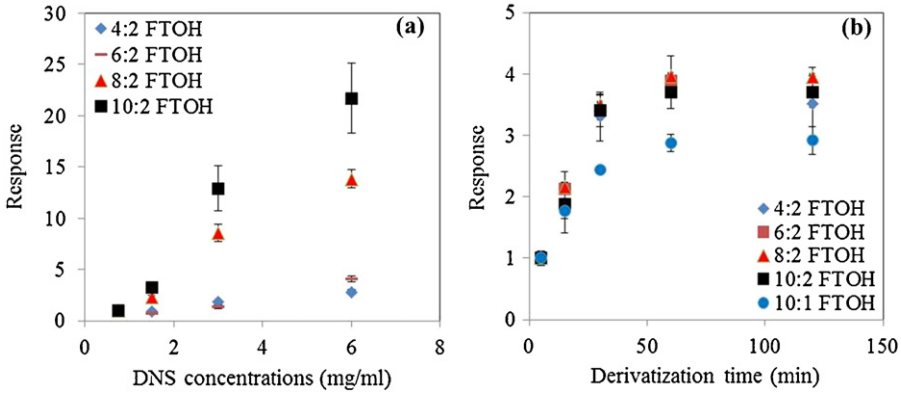


**Fig. 1.** Effects of dansyl chloride (DNS) concentrations (a) and derivatization time (b) on dansylation efficiencies of FTOHs. Dansylation was carried in acetonitrile under the catalysis of DMAP ($n = 3$). Response indicates the increased folds of signal intensity of dansylated FTOHs at each point relative to the first point.

were observed for the latter even at relatively high concentration (5 μg/L).

### 3.3. Calibration, sensitivity and precision

A series of calibration standard solutions of FTOHs were prepared for dansylation to evaluate the dynamic linear response of the analysis. Dansylation showed good linearity in the range from 0.006 to 3.125 μg/L, and the values of $r^2$ were 0.9989, 0.9991, 0.9983, 0.9996 and 0.9999 for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:1 FTOH and 10:2 FTOH, respectively. The IDLs for dansylated FTOHs using UPLC–MS/MS were defined as the concentration of analyte producing a peak with a signal-to-noise (S/N) ratio of 3. Thus, IDLs for dansylated FTOHs were estimated to be 0.014, 0.015, 0.014, 0.0075 and 0.0093 μg/L for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:1 FTOH and 10:2 FTOH, respectively (Table 2). The IDLs were 7.5–241 times lower than those (0.067–3.43 μg/L) using UPLC–CID-MS/MS without dansylation and 57–357 times lower than those using GC/MS (0.8–5 μg/L) [21]. It is interesting to find that all FTOHs derivatives showed similar sensitivities, although the sensitivities of 4:2 FTOH and 6:2 FTOH were 51 and 7 times lower than longer-chain FTOH using LC–MS/MS without derivatization. More importantly, it should be noted that the dansylated FTOHs become to be non-volatile, which provided a convenience for analyzing environmental samples since volatile loss was the main reason for low recoveries (35–55%) of FTOHs during pretreatment or cleanup procedures of samples as reported in previous study [23].

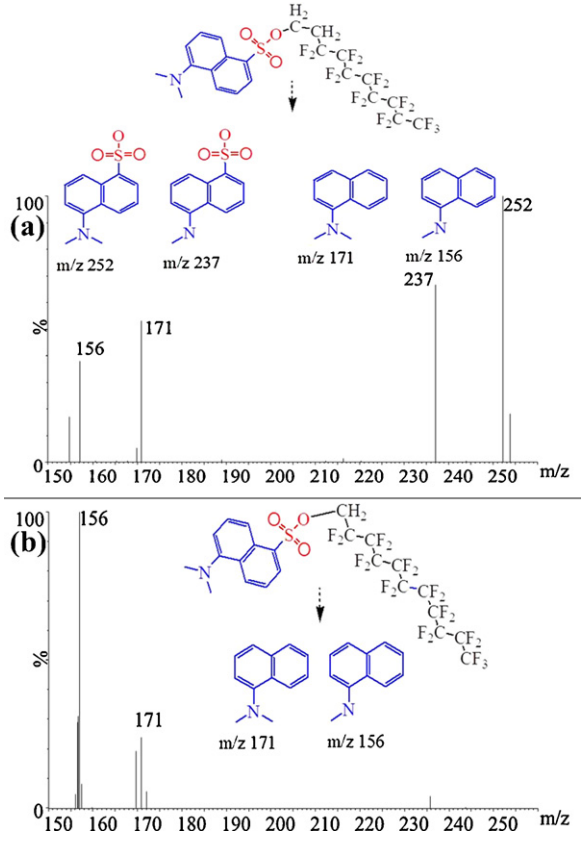


**Fig. 2.** Typical CID-MS/MS spectra of dansylated 8:2 FTOH (a) and dansylated 10:1 FTOH (b).

The repeatability of dansylation (in terms of intravial and intervial) was investigated for evaluating the precision of the method. The intravial repeatability was determined by repeated analysis ($n = 6$) of the same dansylated FTOHs (0.5 μg/L for all FTOHs). The repeatability of dansylation for intervial comparisons was determined by measuring the samples of dansylated FTOHs (0.5 μg/L for all FTOHs) incubated in different vials ($n = 6$). The relative standard derivation (RSD) for the peak intensity of each dansylated FTOH ranged from 1.0% to 3.7% for intravial RSD and from 1.9% to 4.0% for intervial RSD, indicating an acceptable precision for the developed method. To assess the stability of each dansylated derivative, the peak area of each derivative at each week was measured during the 4-week storage (at 4 °C). All dansylated compounds were stable, and the relative variation of signal intensities of all dansylated FTOHs after 4-week storage were within −16 to 11%.

### 3.4. Method performance for marine sediment samples

To apply the dansylation method for detection of FTOHs in complex sediment samples, sample preparation and cleanup before dansylation were necessary to reduce potential interferences such as amines or alcohols in sediment which would react with DNS and then decrease the dansylation efficiency. WAX-based method was used in this study for sediment samples cleanup prior to dansylation. For assessment of potential matrix effects on dansylation efficiency, extracts from sediments after WAX cartridge cleanup were spiked with standards of FTOHs (0.5 μg/L for each analyte) prior to dansylation. The results showed that the matrix effects on dansylation efficiencies after cleanup were less than 15% for all target FTOHs. It should be noted that acetonitrile was used throughout the cleanup since small amounts of methanol tended to cause decreased reaction efficiencies as mentioned above, while methanol was usually used to elute FTOHs from WAX cartridges [23]. In addition, the relatively high concentrations of DNS and DMAP used in dansylation were found to accumulate in the mass

**Table 2**
Instrument detection limits (IDLs, μg/L) of FTOHs using different analytical methods.

| Analytes | GC–MS[a] | LC–MS/MS (without dansylation) | LC–MS/MS (dansylation) | Intraval precision (%) | Intervial precision (%) |
|---|---|---|---|---|---|
| 4:2 FTOH | 2 | 3.43 | 0.014 | 2.1 | 1.9 |
| 6:2 FTOH | 5 | 0.49 | 0.015 | 1.0 | 2.3 |
| 8:2 FTOH | 2 | 0.23 | 0.014 | 1.5 | 4.0 |
| 10:1 FTOH | NA[b] | 0.067 | 0.0075 | 3.7 | 3.3 |
| 10:2 FTOH | 0.8 | 0.16 | 0.0093 | 2.2 | 2.2 |

[a] Ref. [21].
[b] Not analyzed in that study.

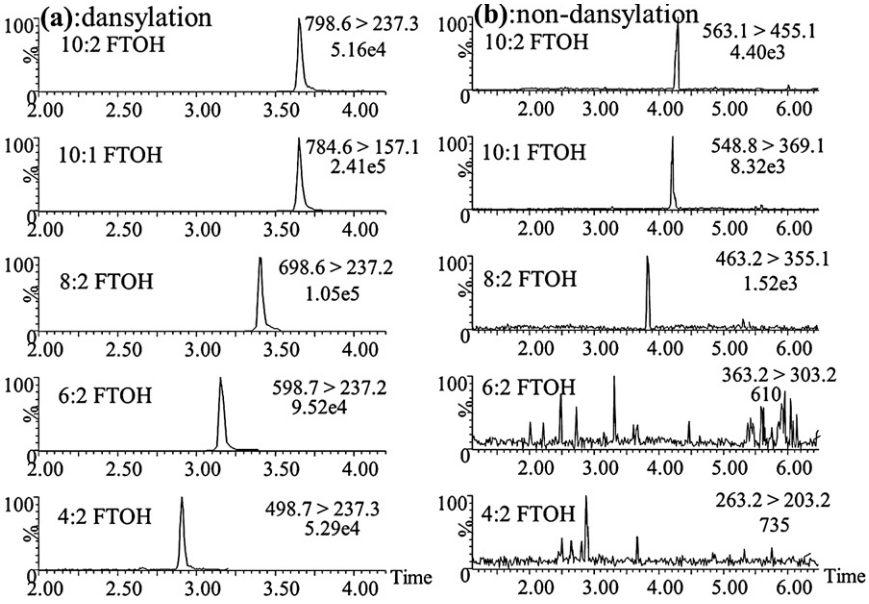


**Fig. 3.** Typical UPLC–CID-MS/MS chromatograms of FTOHs standards. (a) Concentration for each dansylated FTOH: 1 μg/L and (b) concentration for each FTOH: 5 μg/L.

spectrometry causing a significant loss of sensitivity if dansylation solutions were directly injected to instrument. Therefore, all dansylated FTOHs were extracted with hexane from water-diluted derivatization solutions and then passed through a silica cartridge for further cleanup. The overall method recoveries of FTOHs in real sediment samples for the whole procedures were evaluated at two spiked levels. The absolute recoveries of FTOHs were 83 ± 9.4%, 81 ± 9.8%, 76 ± 12%, 76 ± 5.6% and 67 ± 6.0% for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:1 FTOH and 10:2 FTOH at low spiked levels (Table 3), and the recoveries at high spiked levels were 88 ± 6.6%, 82 ± 11%, 77 ± 7.7%, 71 ± 12% and 62 ± 5.6%, respectively.

LODs, LOQs and inter-day precision of dansylated FTOHs were investigated for method validation using marine sediment samples. The LODs of dansylated FTOHs in sediment samples were determined to be 0.006, 0.006, 0.008, 0.016 and 0.0.018 ng/g dw for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:1 FTOH and 10:2 FTOH, respectively, and their LOQs were 0.017, 0.020, 0.026, 0.053 and 0.060 ng/g dw, respectively (Table 3). The LOQs were 29–93 folds lower than previously reported LOQs (0.5–5.6 ng/g dw) for the analysis of soil samples using GC/MS [30]. The inter-day precision, based on the means for three replicate spiked samples assayed in each of three days, was 2.6%, 11%, 6.1%, 6.4% and 3.5% for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:1 FTOH and 10:2 FTOH, respectively. Since matrix effect is a general problem in LC–MS/MS analysis, potential matrix effects were evaluated in this study. Less than 15% signal suppression or enhancement was observed for all target FTOHs (1.1 ± 9.7%, 9.7 ± 11%, 10 ± 5.3%, 10 ± 3.0% and 7.4 ± 3.5% for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:1 FTOH and 10:2 FTOH, respectively) when using the newly developed dansylation method combined with LC–MS/MS. This is significant since signal suppression is a major limitation for analyzing FTOHs in environmental samples upon using LC–MS/MS [31].

**Table 3**
Limits of detection (LODs, ng/g dw), limits of quantification (LOQs, ng/g dw), recoveries (%, $n = 3$) and inter-day precision (%, $n = 3$ for each batch in three days) of FTOHs in sediment.

| Analytes | LOD (ng/g dw) | LOQ (ng/g dw) | Recovery (%)[a] | Inter-day precision (%) |
|---|---|---|---|---|
| 4:2 FTOH | 0.006 | 0.017 | 83 ± 9.4 | 2.6 |
| 6:2 FTOH | 0.006 | 0.020 | 81 ± 9.8 | 11 |
| 8:2 FTOH | 0.008 | 0.026 | 76 ± 12 | 6.1 |
| 10:1 FTOH | 0.016 | 0.053 | 76 ± 5.6 | 6.4 |
| 10:2 FTOH | 0.018 | 0.060 | 67 ± 6.0 | 3.5 |
| $^{13}C_4$-8:2 FTOH | – | – | 75 ± 11 | – |

[a] The spiked level was 0.10 ng/g dw, 0.20 ng/g dw, 0.20 ng/g dw, 0.20 ng/g dw and 0.50 ng/g dw for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:1 FTOH and 10:2 FTOH, respectively.

**Table 4**
Concentrations of FTOHs (ng/g dw) in six sediment samples from Liaodong Bay.

| Analytes | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 |
|---|---|---|---|---|---|---|
| 4:2 FTOH | 0.02 | ND[a] | 0.02 | ND | ND | ND |
| 6:2 FTOH | 0.06 | 0.05 | 0.06 | 0.08 | 0.06 | 0.10 |
| 8:2 FTOH | 0.06 | 0.05 | 0.18 | 0.06 | 0.08 | 0.07 |
| 10:1 FTOH | ND | ND | ND | ND | ND | ND |
| 10:2 FTOH | 0.11 | 0.08 | 0.26 | 0.14 | 0.09 | 0.15 |
| ΣFTOHs | 0.25 | 0.19 | 0.52 | 0.28 | 0.23 | 0.32 |

[a] ND, not detected.

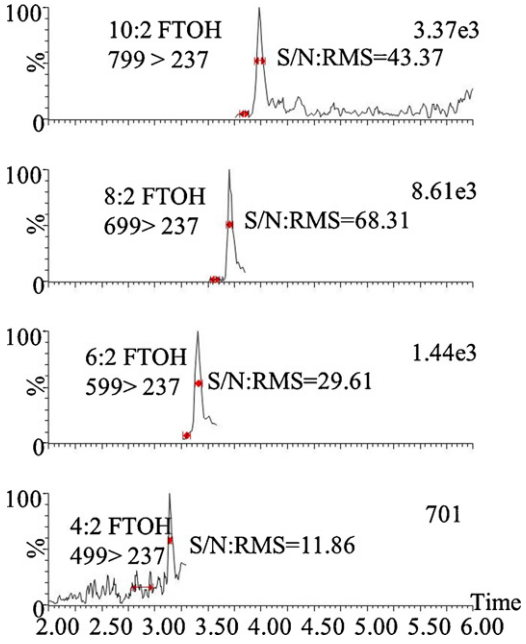


**Fig. 4.** Typical UPLC–CID-MS/MS chromatograms of detected FTOHs in a sediment sample.

### 3.5. Marine sediment samples

The method was successfully applied to analyze FTOHs in six marine sediment samples collected from Liaodong Bay, north China. All FTOHs except for 10:1 FTOH were detected in marine sediments, and Fig. 4 showed the typical chromatograms of FTOHs detected in a sediment sample. The concentrations of total FTOHs (ΣFTOHs) ranged from 0.19 to 0.52 ng/g dw (Table 4). 10:2 FTOH was the predominant FTOH in all sediment samples accounting for 39–50% of total FTOHs, followed by 8:2 FTOH with the relative contributions of 22–35%. It is interesting that the FTOHs profiles in sediments were different from those in air in which 8:2 FTOH was the predominant FTOH [9], which may be due to the greater sorption coefficients of 10:2 FTOH to soil than 8:2 FTOH [24].

## 4. Conclusions

UPLC–MS/MS combined with dansylation allowed the quantitative analysis of FTOHs with good sensitivity and reproducibility. A 7.5–241 fold enhancement of method sensitivity was achieved compared with previous method without dansylation. This paper firstly reported the quantitative determination of FTOHs in sediment samples by the developed method, and the method newly developed in this paper can be expected to be used in the investigation on the occurrence and fate of FTOHs in environment.

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