Journal of Chromatography A, 1235 (2012) 132–140

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Derivatization and liquid chromatography–UV–tandem mass spectrometric analysis of perfluorinated carboxylic acids

Jinxue Qiu, Chunmei Wu, Yingyu Fang, Cui Yang, Xiuhua Li, Xiangfan Piao, Donghao Li*

Key Laboratory of Nature Resource of the Changbai Mountain and Functional Molecular (Yanbian University), Ministry of Education, Park Road 977, Yanji City, Jilin Province, China

ARTICLE INFO

Article history:
Received 4 December 2011
Received in revised form 21 February 2012
Accepted 21 February 2012
Available online 28 February 2012

Keywords:
Derivatization
p-Bromophenacyl bromide
PFCAs
ESI-MS
Multidimensional analysis

ABSTRACT

The presence of perfluorocarboxylates (PFCAs) in the environment is of increasing concern due to their possible toxicity to humans and bioaccumulation in organisms. PFCAs are frequently found in river water, sediment and organisms and sometimes even in groundwater. In order to quantitatively determine these PFCAs, a fast derivatization coupled with a liquid chromatography–ultraviolet detector–electrospray ionization-tandem mass spectrometry (LC–UV–ESI-MS/MS) method was developed. The PFCAs were quantitatively converted to their corresponding phenacyl esters using p-bromophenacyl bromide as the derivatization reagent. Under optimized reaction conditions, the conversion yield of the PFCAs ranged from 86 to 92% with low %RSD. The typical derivatization product (p-bromophenacyl bromide perfluorooctanoate) was characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and mass spectrometry. UPLC with a BEH C18 column and CAN/H_2O (8/2, v/v) as a mobile phase were used to separate the derivatives. The analytes were completely eluted within 6 min and multidimensional detection using UV at 260 nm and ESI–MRM in the negative ion mode were carried out. Bromide isotopic characteristic fragment ions appeared in the first Q1 scans, and four daughter ions of the MRMs at m/z $[M-H-222]^-$, $[M-H-250]^-$, $[M-H-278]^-$ and $[M-H-316]^-$ were used for quantification and confirmation. The mass spectral information ensured accurate identification of the analytes even when the sample matrices were complex. The method successfully eliminated the PFCAs background problems originating from polymeric parts in liquid chromatographic systems. The LODs of the method were lower than 5 ng mL^{-1}, and the relative standard deviation (RSD%) values ranged from 5.2 to 9.8%. The method was successfully applied for the quantification of PFCAs in river water contaminated by industrial wastewater, and this indicated that the method was useful in the determination of PFCAs in environmental samples.

1. Introduction

Perfluorinated carboxylic acids (PFCAs) are a growing concern due to their global distribution, potential toxicity, physical and biological stability [1]. PFCAs are fatty acid derivatives in which all the hydrogen atoms are replaced by fluorine atoms. However, they are more thermally and chemically stable than their corresponding fatty acids [1,2]. PFCAs are both water and fat-repellent which is related to their strong polarity and high energy carbon-fluorine bonds [3], moreover, they are extraordinarily stable under hydrolysis, photolysis, and biodegradation procedures [4]. As a result of these unique properties, PFCAs are frequently employed in various industrial and commercial uses such as surfactants, paints, polishes, adhesives, food packaging, PTFE precursors, photographic, and fire-fighting foams [5,6]. Due to their widespread use, emissions of PFCAs have reached considerable levels, and an estimated 3200–7300 tons of PFCAs were released between 1951 and 2004 [7,6], and this amount will increase as PFCAs continue to be released into the environment without regulation. PFCAs have been found in various matrices [8–11], including human serum [12]. Recent findings indicate that they are biologically active and toxic [2]. Perfluorooctanoic acid (PFOA) was listed as a "likely" human carcinogen by the EPA in 2005 [13]. Therefore, the monitoring of environmental levels of PFCAs is essential.

The gas chromatography [14,15] and high-performance liquid chromatography [16–18] are usually used method in the analysis of PFCAs. Tailing peaks will result if PFCAs are directly injected into a GC system owing to their high polarity [19]. Thus, derivatization of PFCAs prior to GC analysis is essential. Many published works have suggested that PFCAs can be converted into their corresponding more volatile and less polar derivatives using various methods [15,20–22]. For example, some PFCAs with longer chains such as perfluoroheptanoic acid (PFHpA) and PFOA can be derivatized to their methyl esters and analyzed by GC/ECD [12]. To date, the most commonly used instrument for the analysis of PFCAs is HPLC–MS (MS) due to its high sensitivity and selectivity. However, there

* Corresponding author. Tel.: +86 433 2732040; fax: +86 433 2732207.
E-mail address: dhli@ybu.edu.cn (D. Li).

0021-9673/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2012.02.047

is still one obvious drawback of quantitative analysis using this method, as high background signals of the PFCAs are usually generated from the internal fluoropolymers of the HPLC system when the mobile phase flows through [23,24]. These high background values lead to errors in quantitative analysis.

The present study aimed to develop an accurate, reliable and applicable analytical method for PFCAs which would eliminate the interference caused by background signals. In a previous study, Durst et al. [25] used p-bromophenacyl bromide (BPBr) as the derivatization reagent for the analysis of fatty acid and obtained satisfactory results. BPBr is widely used in the derivatization of fatty acids due to its large molar UV absorptivity (1.82×10^6 L/mol cm) and high derivative efficiency. The procedure proposed in the present study involved the conversion of PFCAs to their corresponding esters by BPBr, and 18-crown-6 was added to catalyze the reaction. The reaction scheme can be seen in Fig. 1.

The reaction was carried out in an alkaline solution and the corresponding ester derivatives (Br-PFCAs) were easily obtained. Further qualitative and quantitative analysis of the corresponding PFCA derivatives were carried out using HPLC–UV–MS, which automatically eliminated the interferences generated by the LC system. The derivatives had high molar absorptivity as BPBr allowed low detection at subsequent UV detection. In addition, the characteristic isotope ratio of bromine contained in the derivatives ensured accurate qualitative analysis. In this study, we selected perfluorooctanoic acid (PFOA) as a model compound, then synthesized and characterized the phenacyl ester of PFOA which was used as standard, then optimized the parameters in the derivatization protocol. We verified this optimized method by analyzing five PFCAs in river water samples which evaluated its applicability and reliability.

2. Experimental

2.1. Standards, reagents and materials

Perfluorinated carboxylic acid standards: perfluoroheptanoic acid (PFHpA, 99%), perfluoro-n-octanoic acid (PFOA, 96%), perfluoro-n-nonanoic acid (PFNA, 97%), perfluorodecanoic acid (PFDA, 98%) and perfluoroundecanoic acid (PFUnA, 95%) were purchased from Sigma–Aldrich (Bellefonte, PA, USA), 18-crown-6 (99%) was also purchased Sigma–Aldrich (Bellefonte, PA, USA) and the derivatization reagent, p-bromophenacyl bromide (BPBr, ≥98.5%), was purchased from Fluka (Buchs, Switzerland). Five PFCA standard mixture stock solutions (1.0 mg mL^{-1}) were prepared by dissolving an appropriate amount of each substance in HPLC-grade acetonitrile which were immediately stored in the refrigerator for subsequent use. The p-bromophenacyl perfluorooctanoate (Br-PFOA) standard was used as the analytical standard and synthesized in our laboratory as described in Section 2.3.

Organic solvents (dichloromethane, methanol, acetonitrile and hexane) were of HPLC grade were obtained from Caledon (Georgetown, Ont., Canada), and used without further treatment. The triple distilled water used in all experiments was prepared using a Milli-Q water purification system (Millipore, Milford, MA, USA). Inorganic salts: potassium hydroxide, sodium sulfate, sodium chloride and phenolphthalein were purchased from Sanfu Chemical Reagent (Yanji, China). UPLC BEH C_{18} column (2.1 mm × 50 mm, i.d. 1.7 μm) was purchased from Waters (Shanghai, China).

2.2. Instrumentation

HPLC analyses were performed using an Agilent 1100 series (Palo Alto, CA, USA) HPLC system. The HPLC system consisted of a quaternary pump, vacuum degasser, high performance autosampler, and a controlled-temperature column compartment. An Agilent G1315A diode array detector (Palo Alto, CA, USA) and an Applied Biosystems API 2000 electrospray triple-quadrupole mass spectrometer (ESI-MS/MS) were selected. The FT-IR analysis was recorded on a Shimadzu Prestige-21 spectrometer (Shimadzu, Tokyo, Japan) with KBr pellets. ^{1}H and ^{13}C NMR spectra were respectively recorded at 300 MHz and 75 MHz using Bruker AV-300 spectrometer, $CDCl_3$ and tetramethylsilane (TMS) was used as solvent and reference, respectively.

2.3. Synthesis and characterization of p-bromophenacyl bromide perfluorooctanoate and derivatization of PFCAs

PFOA (1.242 g, 3 mmol), BPBr (0.834 g, 3 mmol) and KOH 0.168 g were dissolved in 50 mL ACN and maintained for 4 h at 70 °C in ultrasonic wave. The solution was cooled to room temperature and extracted with DCM after the addition of saturated sodium chloride aqueous solution. The organic phase was dried over anhydrous Na_2SO_4 and filtered; the filtrate was then concentrated using a rotary evaporator. The evaporated residue was cleaned up by silica column chromatography and eluted with dichloromethane. The elution was evaporated to dryness to obtain the product which was characterized by ^{1}H NMR analysis (Fig. 1) where the obtained results (δ (ppm): 7.78 (2H, d, J = 8.4 Hz), 7.69 (2H, d, J = 8.4 Hz), 5.57 (2H, s)) were in agreement with the proposed structure. Moreover the data obtained through FT-IR (Fig. S1) and ^{13}C NMR (Fig. S2) confirmed the proposed structure.

For derivatization of trace level target chemicals from river water samples, the reaction conditions were slightly modified as follows: A mixture which comprized of the PFOA standard solution (5 mL, 100 μg mL^{-1}) in ACN and two drops of phenolphthalein was neutralized to a phenolphthalein end point by the KOH/methanol solution under ultrasonification, and then the same volume of crown/MeOH was added. After 5 min under ultrasonification, 5 mL of BPBr/ACN (10 mg mL^{-1}) was added. The mixture was heated, under ultrasonic conditions, at 70 °C for 30 min. The moisture was excluded during the reaction.

2.4. Sample preparation

Samples of river water were collected from the Tumen River at a site known to be contaminated by industrial wastewater. The samples were obtained 0.5 m below the surface water using 4 L brown glass bottles. The samples were immediately acidified with 6 M HCl to prevent biodegradation.

For laboratory analysis, the water samples were first filtered through nylon membranes (47 mm in diameter, 0.45 μm, Whatman, Maidstone, England) to remove suspended particles. One liter of the water samples was loaded onto the SPE cartridge which was previously conditioned by 10 mL of methanol. The column was not allowed to dry out. 50 mL MeOH was eluted, and the eluent was collected in a 250 mL flat-bottomed flask. The eluent was concentrated using a rotary evaporator and the solvent was exchanged to 5 mL of ACN. The derivatization was carried out as described in Section 2.3. The resulting derivatized solution was subjected to a clean-up procedure which was achieved by silica column chromatography. The column contained 1 g of silica gel (deactivated with 5% H_2O) sandwiched between two 0.5 g anhydrous sodium sulfate layers in a 10 mL glass syringe. Hexane (10 mL) was eluted first and discarded, and then the analytes were eluted sequentially with a mixture of hexane and dichloromethane (5 mL, 5:1), and a mixture of hexane and dichloromethane (5 mL, 1:1). The sample was concentrated to 0.1 mL using a gentle flow of dry nitrogen, and the final volume was fixed at 1 mL, a subsample was subjected to HPLC for further analysis.

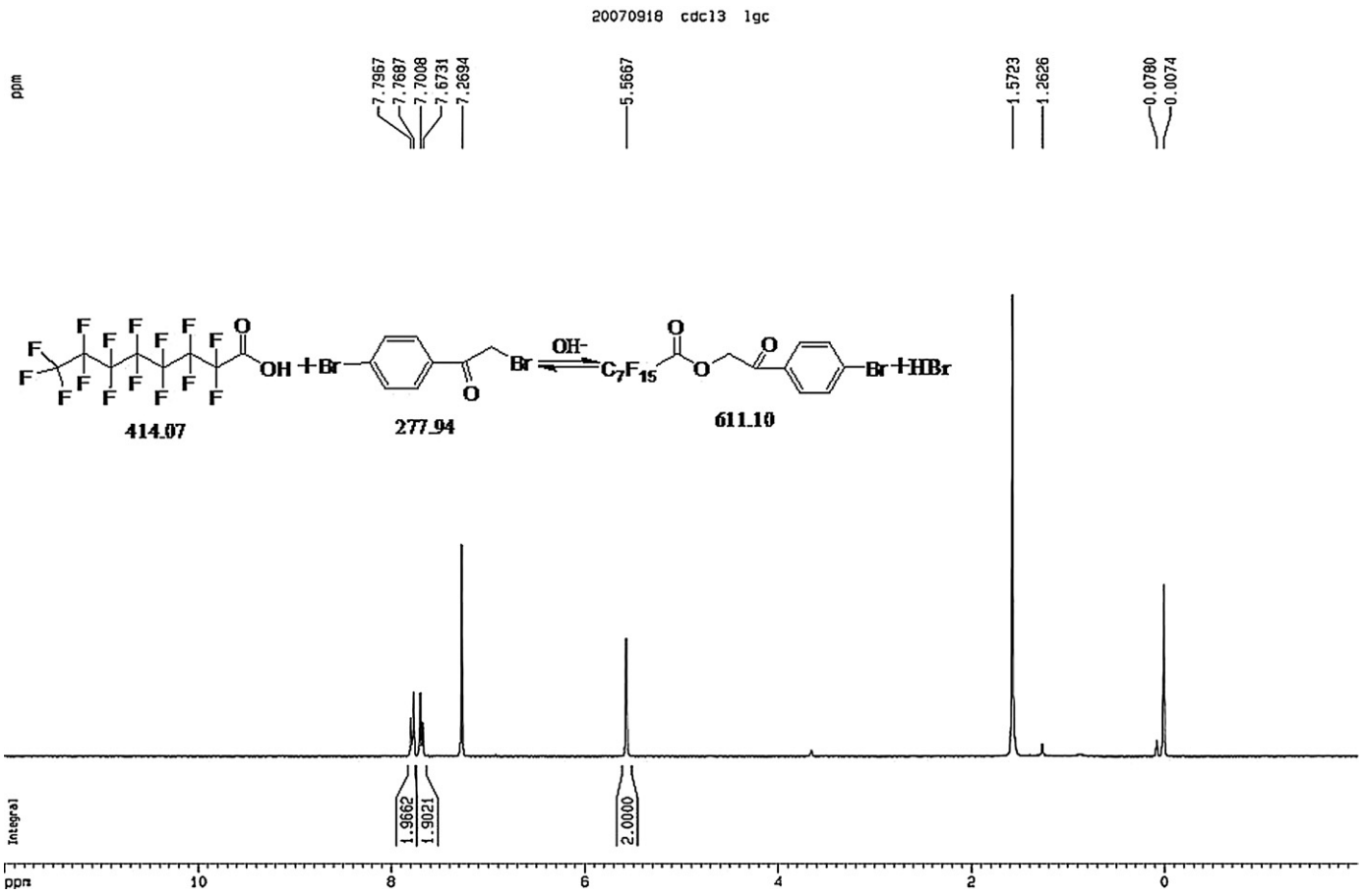

Fig. 1. Reaction scheme and ^{1}H spectrum of Br-PFOA.

2.5. High performance liquid chromatography and tandem mass spectrometry

For the separation, a C_{18} HPLC analytical column (250 mm × 4.6 mm, 5 μm, Grace Vydac, USA) was operated at a temperature of 30 °C for target separation with a constant flow of the mobile phase at 1 mL min^{-1}. For UPLC–MS/MS analyses, a C_{18} 4 mm × 10 mm Grace Vydac guard column (Supelco, Bellefonte, PA, USA) was used to trap any contaminants in the mobile phase and/or the HPLC system. For the UPLC BEH C_{18} column (2.1 mm × 50 mm, i.d. 1.7 μm), the mobile phase was a mixture of ACN and H_2O (ACN: H_2O = 8:2), and all solvents used as the mobile phase were previously filtered through 0.45 μm nylon membranes. The flow rate of the mobile phase was kept at 0.3 mL min^{-1}. DAD was used for quantitation and 260 nm was selected as the ultraviolet absorption wavelength. The UPLC–ESI-MS method was used for evaluation and application testing, respectively, and the ESI source was operated in the negative ionization mode. Nitrogen gas was used as the desolvation gas, nebulizer gas and collision gas in the ESI source. The ion spray voltage was set to −4.5 kV, cone voltage was 14 V, and the heater gas temperature was maintained at 300 °C. MRM transitions of $[M-H]^-$ precursor ions → product ions were selected for each analyte and the relative collision energies optimized (Table 1). Curtain, collision, nebulizer, and auxiliary gases of the MS/MS were set at 15, 6, 35, and 45 arbitrary units, respectively.

Analyst 1.3.2 software (Applied Bioscience, Foster City, CA, USA) was used for instrument control and data manipulation. Results of the optimization are shown in Table 1.

3. Results and discussion

3.1. Optimization of the derivatization procedure

Several parameters such as derivatization temperature, derivatization time, and amount of catalyst which significantly affected the derivatization yield were carefully considered and optimized. As the boiling point of acetonitrile is 83 °C, a temperature range of 50–80 °C was considered and 80 °C was finally selected (Fig. S3). Thirty minutes was chosen as a reasonable reaction time (Fig. S4). Under these conditions, a satisfactory derivatization yield was obtained when the molar ratio of the derivatization reagent/18-crown-6 was 20:1. Moisture was avoided as BPBr is unstable and moisture-sensitive. The yield was only 27% when moisture was not excluded, but increased to 92% when the reaction was protected under N_2. Under the optimized reaction conditions, the conversion yield of the PFCAs determined ranged from 86 to 92% with low %RSD.

3.2. ESI–MS/MS analysis of PFCA derivatives

In order to perform ESI-MS/MS analysis on the derivatives of the five PFCAs, parameters such as cone voltage, collision-induced dissociation energy and the best fragmentation pattern were optimized by direct injection of the standards. The ESI-MS/MS experimental parameters optimized are summarized in Table 1, and the mass spectra in negative ion mode during initial Q1 scans of the derivatives are presented in Fig. 2(A–E). The derivatives of PFCAs have ester groups and a single bromide atom which are

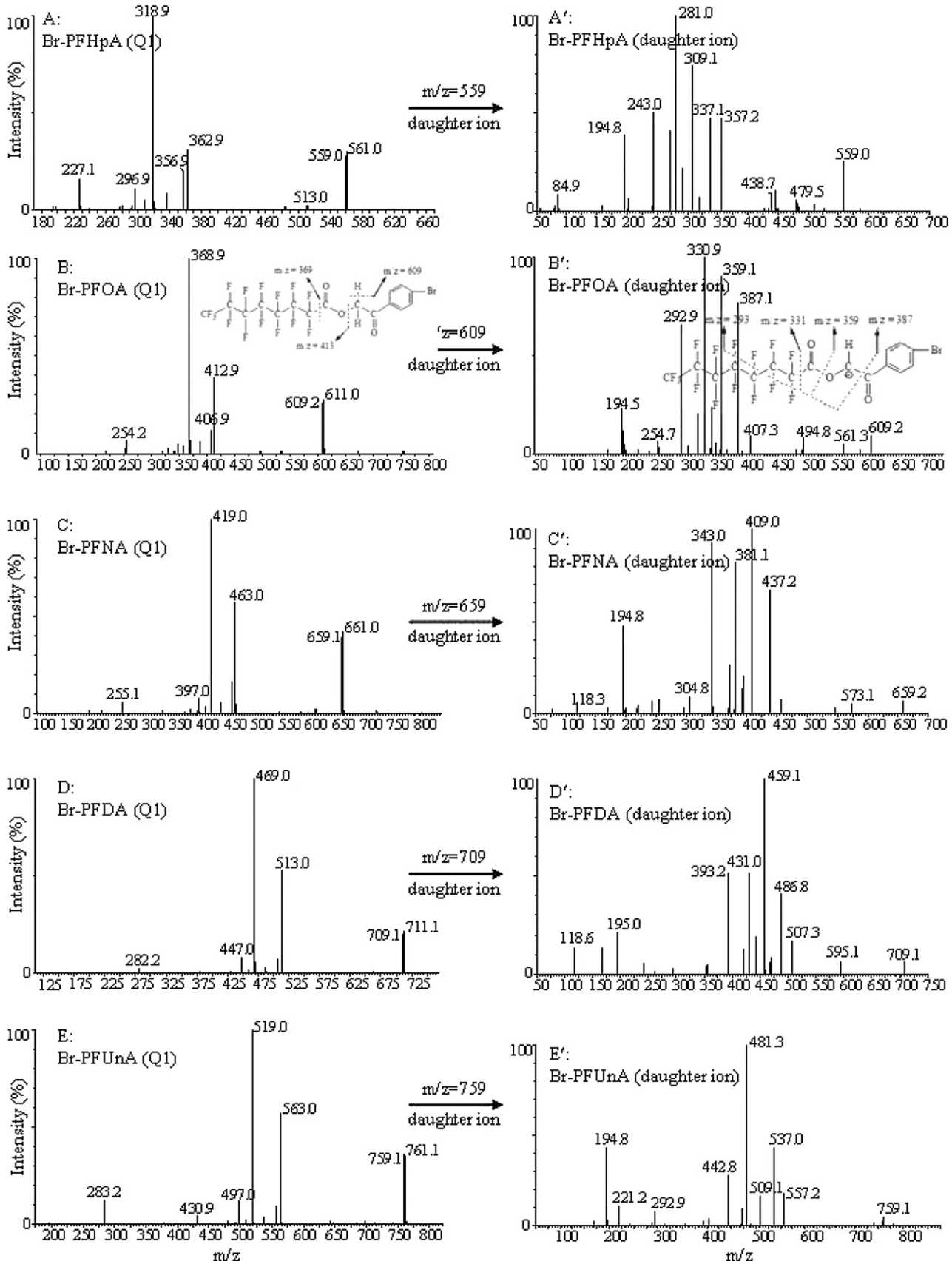

Fig. 2. Mass spectra (negative-ion mode) of Br-PFCAs (10 μg L^{-1}). Leaf column mass spectra (A, B, C, D and E) obtained from initial Q1 scans of the derivatives; light column mass spectra (A′, B′, C′, D′ and E′) are daughter ions of the corresponding parent ions which were obtained from initial Q1 scans of the derivatives. Refer to Table 1 for abbreviations of the analytes.

Table 1
ESI parameters and MRMs transitions for derivatives of PFCAs.

Compound	Molecular formula	Cone voltage (V)	Relative collision energy (%)	Precursor ion $[M-H]^{-1}$	MRM 1 $[M-H-2F_2-3CO-C_6H_4Br]^{-1}$	MRM 2 $[M-H-F_2-3CO-C_6H_4Br]^{-1}$	MRM 3 $[M-H-F_2-2CO-C_6H_4Br]^{-1}$	MRM 4 $[M-H-F_2-CO-C_6H_4Br]^{-1}$	Difference of m/z
Br-PFHpA	$CF_3(CF_2)_5COOCH_2COC_6H_4Br$	14	52	559.0	243.0	281.0	309.1	337.2	
Br-PFOA	$CF_3(CF_2)_6COOCH_2COC_6H_4Br$	14	61	609.2	292.9	330.9	359.1	387.1	50
Br-PFNA	$CF_3(CF_2)_7COOCH_2COC_6H_4Br$	14	52	659.1	343.0	381.1	409.0	437.2	50
Br-PFDA	$CF_3(CF_2)_8COOCH_2COC_6H_4Br$	14	63	709.1	393.2	431.0	459.1	486.8	50
Br-PFUnA	$CF_3(CF_2)_9COOCH_2COC_6H_4Br$	16	46	759.1	442.8	481.3	509.1	537.0	50

favorable for the production of valuable mass spectra. As shown in Fig. 2B, as example, there were two fragment ions near the molecular weight of the derivatives with nearly the same abundance but differed in two mass to charge ratios (m/z = 609 and m/z = 611), which were characteristic fragment ions of a substance that contained one bromide atom. Furthermore, the same pattern of four large peaks appeared in the spectrum of each derivative, and the m/z 50 (CF_2) difference in each derivative was observed from the difference in molecular weights. Fig. 2B shows an example (Br-PFOA) with high abundance of m/z 609/611/413/369 in negative ion mode, in which, m/z 609 and 611 represent the molecular ion $[M-H]^-$ and the naturally occurring bromide-81 isotope $[M-H+2]^-$, respectively. This molecular ion produced abundant ions at m/z 413 and 369 (Fig. 2B). The peak at m/z 413 is due to the neutral loss of the BPBr substituent ($[M-H-BPBr]^-$) (it is clearly verified through the absence of the characteristic bromine isotopic cluster ions), and m/z 369 ($[M-H-BPBr-CO_2]^-$) is due to the loss of BPBr and CO_2, where CO_2 is typical of carboxylic acid-containing compounds. The fragmentations with chemical structure are shown in Fig. 2B.

When the sample matrix is complex, some co-extractors in the sample will produce interference signals and affect the accuracy. One of the most important aspects when analyzing low levels of compounds using LC–MS/MS, is to minimize the interference ions that increase the background signal from the mobile phase and sample matrix. One method is to use multiple reactions monitoring (MRM) mode, which is one of the functions of MS/MS. For each derivative of the PFCAs, the molecular ions were used as parent ions, and serial daughter ions of molecular ions were monitored to confirm the presence of the molecule and to quantify the levels of the chemicals. As shown in Table 1 and Fig. 2, daughter ions produced from each derivative molecular ion showed the same mass spectrum profiles as in the initial Q1 scans, with a shift in mass of 222 [$F_2 + CO + C_6H_5Br$], 250 [$F_2 + 2CO + C_6H_5Br$], 278 [$F_2 + 3CO + C_6H_5Br$] and 316 [$2F_2 + 3CO + C_6H_5Br$] for four daughter ions (Fig. 2B′). This was found to be the most reliable for identification and quantification purposes. In the case of Br-PFOA, the daughter-ion scan spectrum was obtained from the characteristic ion of Br-PFOA at 609 m/z. As in Fig. 2B′, characteristic daughter ions appeared at 387, 359, 331 and 293 m/z. The daughter ion at 293 m/z was used for quantification, and 331 and 387 m/z were used for confirmation. The above mass spectrum information ensured accurate identification of the analytes, even when the sample matrices were complex.

3.3. LC–UV–ESI-MS/MS

The aim of our study was to establish both a rapid and multidimensional detection method for the quantification of PFCAs from natural environmental samples. We focused not only on developing an adequate ESI-MS/MS detection method, but also on a fast and reproducible LC–UV separation and detection method using a derivatization technique.

A series of preliminary experiments were carried out to optimize the chromatographic separation conditions for the PFCA esters (Br-PFCAs). As shown in Fig. 3A, the five derivatives were clearly separated within less than 6 min of the total run time with high resolution and sharp peaks. It is known that PFCAs have no UV absorbing capacity due to the absence of UV-absorbent groups in their chemical structure. On the other hand, the derivatives contained benzyl groups with a strong ultraviolet (UV) absorbance (1.82×10^6 molar absorptivity, Fig. S5). The strong absorbance of UV light by benzyl groups allows easy analysis of PFCAs in samples using a common UV detector equipped with a LC system. Therefore, the proposed method is highly suitable for the laboratory analysis of PFCAs. Furthermore, UV detection of a sample is non-destructive,

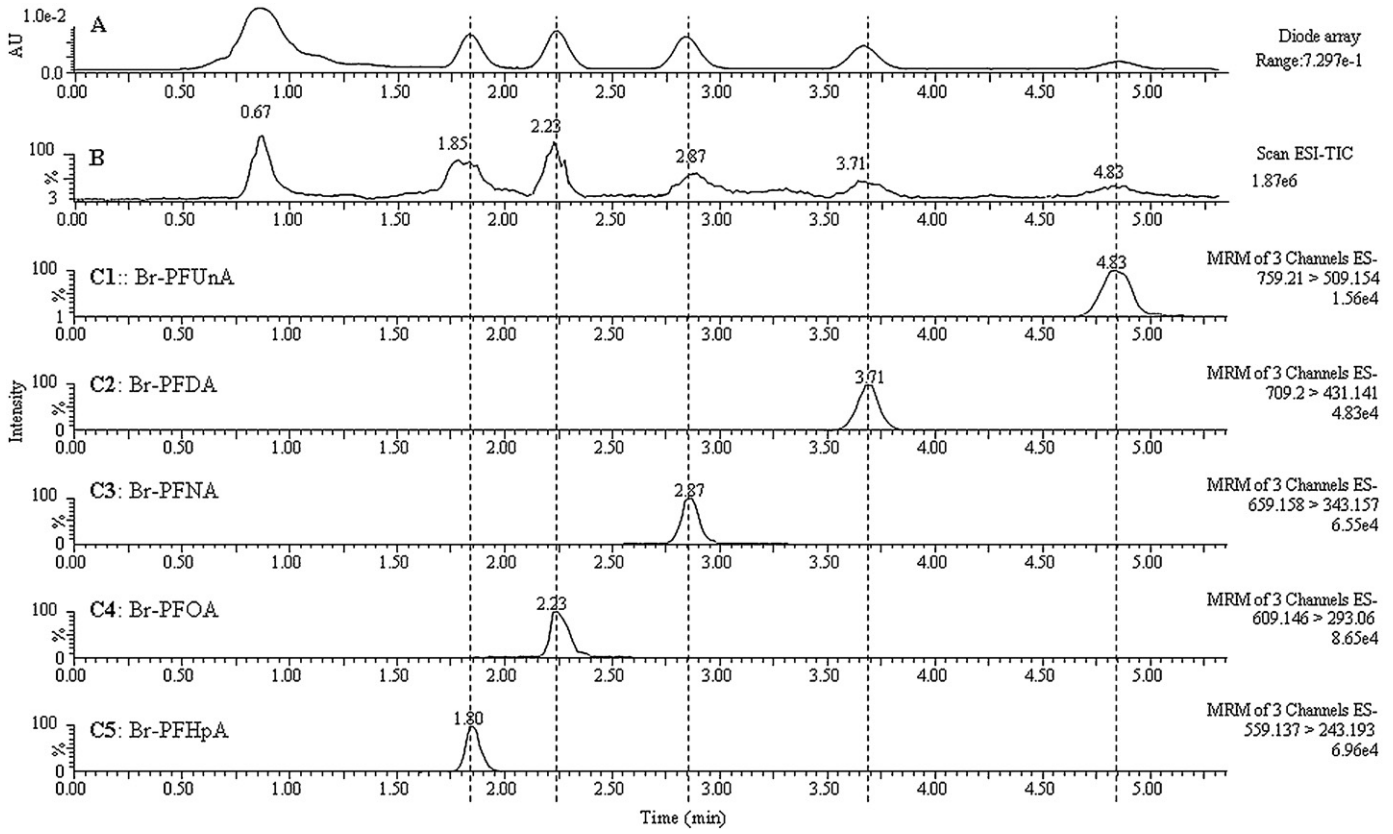

Fig. 3. LC–UV–EIS-MS/MS profile of Br-PFCA standards (10 μg L^{-1}). (A) Determined by DAD detector at 260 nm; (B) Determined by ESI-MS during initial Q1 scans; (C) MRMs ion-chromatograms.

so the eluant can be safely introduced into MS for further detailed and reliable information.

The LC–UV–ESI-MS/MS tests were performed using 10 μg mL^{-1} of Br-PFCAs dissolved in methanol solution. As shown in Fig. 3, each peak which appeared in the LC–UV chromatogram clearly and exactly matched with the total ion current (TIC) chromatogram and MRM chromatograms obtained from ESI-MS/MS analysis. This indicates that the PFCAs can be multidimensionally determined using UV and MS detection coupled with liquid chromatography after conversion to their corresponding Br-PFCAs derivatives. Like any other multidimensional analytical technique, both selectivity and specificity of the proposed method will be greatly increased in real complex sample analysis.

3.4. Background

The background values of LC–MS/MS analysis for PFCAs were high and background noise was also high. Contamination from fluoropolymers in various laboratory consumables may be one source of background signals. The sample must be devoid of any fluorinated substances during the preparation procedure. Moreover, background signals can occur when the mobile phase flows through the internal fluoropolymer parts of the HPLC system (most notably PFOA can be leached) during the instrumentation analysis procedure, causing background problems [14,23,26]. The PFCAs were converted into their corresponding derivatives (Br-PFCAs) before LC analysis in this study, as a result, interferences which originated from the LC instrument system were successfully avoided in the whole instrument analytical procedure including the sample injection step.

A tap water sample was analyzed by LC–UV–ESI-MS/MS after being subjected to the derivatization and clean-up procedure to verify the feasibility of accurate qualitative and quantitative analysis of PFCAs. As shown in Fig. 4, no background signal was detected in the UV chromatography which was also confirmed in the MRM chromatography, thus, as expected, the method successfully eliminated the background interference.

3.5. Evaluation of the method performance

In this study, five PFCAs in a standard mixture were used to evaluate the analytical performance and validate the proposed method. Linearity and the limits of detection (LODs) were evaluated using deionized water spiked with five PFCAs at five different concentration levels (5, 20, 100, 200 and 1000 ng mL^{-1}) and subjected to the derivatization procedure. Three replicate analyses were performed for each spiked water sample to evaluate repeatability. The linear range spanned 3 orders of magnitude for all analytes, with correlation coefficients (r) varying between 0.98 and 0.99 (Fig. 5), therefore, a direct proportional relationship between the amount of corresponding derivatives and initial PFCA concentrations was demonstrated. The LODs were verified by injection of the derivatives arising from different concentration levels of PFCAs and calculated based on three times the signal to noise ratio as per published guidelines. As shown in Table 2, all the analytes showed LODs of 5 ng mL^{-1}. The developed method revealed good repeatability with relative standard deviation (RSD) values of 5.2% to 9.8%, and the recoveries were higher than 85% for all PFCAs.

3.6. Application

Some components present in environmental sample extracts may affect derivatization yield, sensitivity and accuracy of the

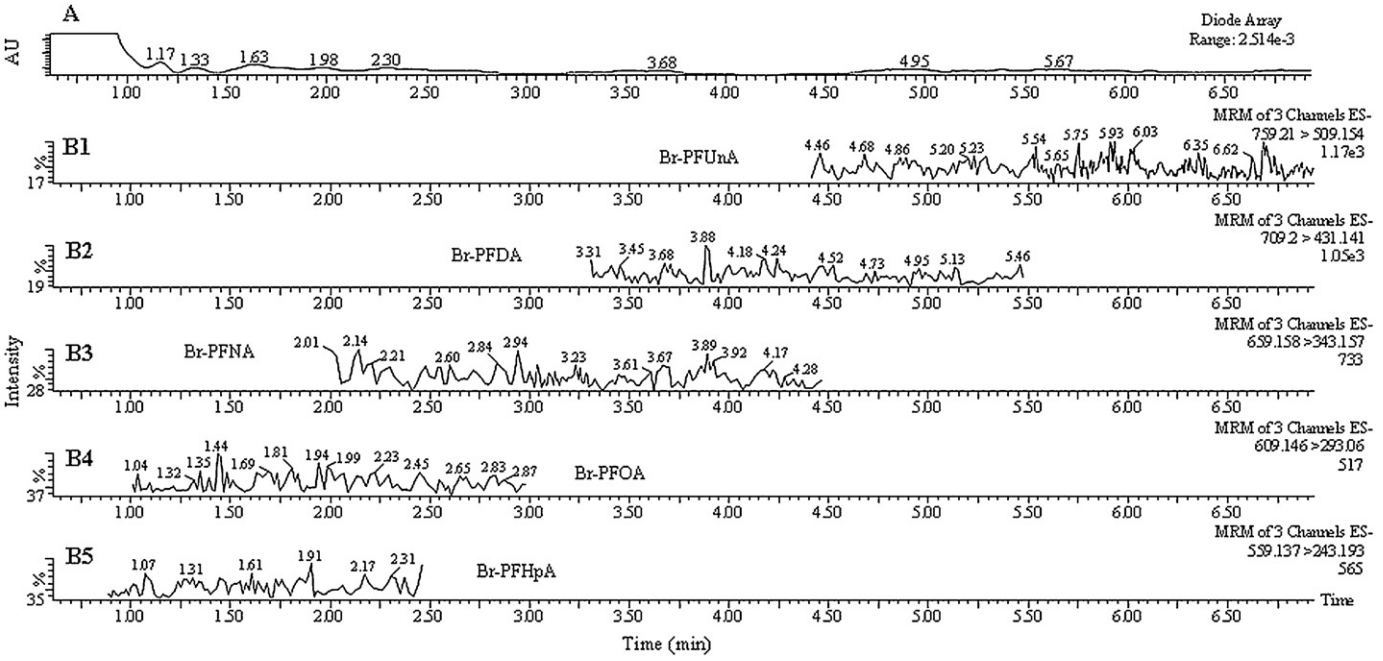

Fig. 4. LC–UV–ESI-MS/MS profile of a blank tap water. (A) LC–UV chromatogram; (B) MRMs ion-chromatograms.

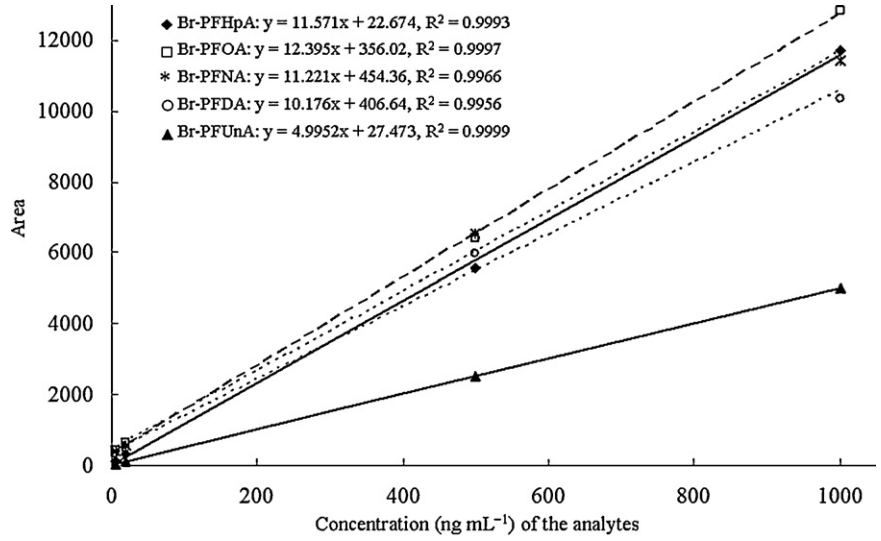

Fig. 5. Calibration curves of the derivatives of the five PFCAs.

Table 2
Method performance.

Compound	Linear range ($\mu g\,L^{-1}$)	Correlation coefficient ($R2$)	LOD $S/N = 3$ ($\mu g\,L^{-1}$)	RSD (%) $n = 3$	Yield (%)
PFHpA	5–1000	0.9982	5	5.2	86.5
PFOA	5–1000	0.9912	5	9.8	92.2
PFNA	5–1000	0.9932	5	7.6	87.4
PFDA	5–1000	0.9938	5	6.5	89.2
PFUnA	5–1000	0.9981	5	9.4	88.6

Table 3
Analytical results for the analysis of five PFCAs in water sample from Tumen River.

Compound	Concentration ($ng\,g^{-1}$)	Intra-day RSD (%)	Inter-day RSD (%)	Recovery (%)
PFHpA	3.87 ± 0.29	7.4	5.1	89.2
PFOA	82.43 ± 4.95	6.0	7.2	90.5
PFNA	2.20 ± 0.23	10.3	11.5	85.7
PFDA	nd	–	–	–
PFUnA	nd	–	–	–

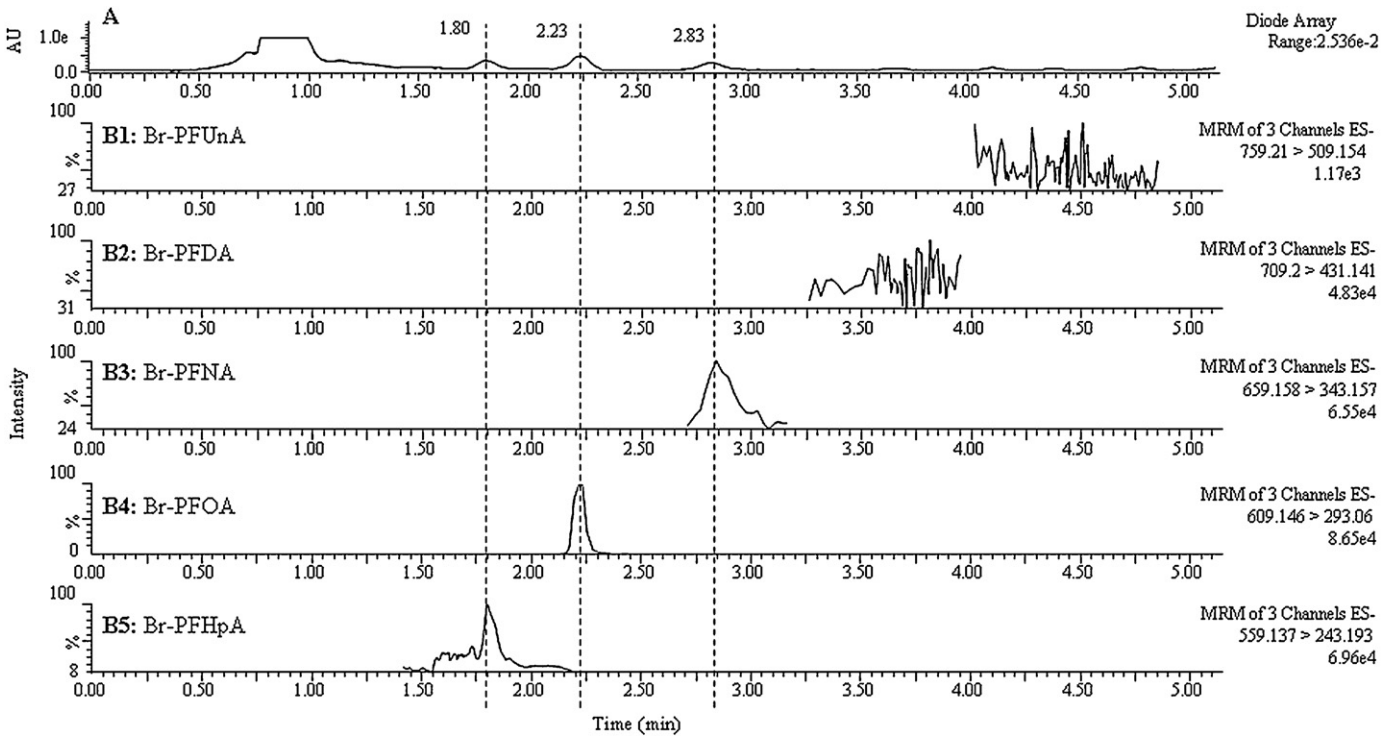

Fig. 6. UV and MRM chromatography of river water sample. (A) LC–UV chromatogram; (B) MRMs ion-chromatograms.

instrument. To examine the applicability and reliability of the described method, a water sample taken from the Tumen River was collected and three replicate samples were subsequently analyzed by the derivatization-LC–UV–ESI-MS/MS technique. A typical chromatogram of derivatized PFCAs from the Tumen River water extract is shown in Fig. 6. Among the five target analytes, Br-PFHpA, Br-PFOA and Br-PFNA were detected, and the concentration levels were 3.8 ± 0.3, 82.4 ± 5.0 and $2.2 \pm 0.2\ \mathrm{ng\,mL^{-1}}$, respectively. The results for each set of experiments are summarized in Table 3 (concentration, RSD (intra- and inter-day), recovery). The method showed a low RSD of approximately 10% in the intra-day analysis, and when the sample was measured on three different days, a RSD in the same range was observed. Work is currently underway on environmental PFCA analyte monitoring utilizing this LC–UV–ESI-MS/MS technique.

4. Conclusions

The coupling of derivatization with LC–UV–ESI-MS/MS represents a versatile tool for the rapid and reliable determination of low levels of PFCAs from complex mixtures, significantly reducing background noise which frequently occurred in previous studies. The PFCA analytes were simply converted to their corresponding Br-PFCAs using p-bromophenacyl bromide as a derivatization reagent under moderate reaction conditions. The conversion yield ranged from 86% to 92% with a low %RSD. The identities of the peaks assigned to the PFCAs were confirmed by their retention times during LC–UV and MRM mass spectrometry. The multidimensional determination (UV and MS) of PFCA analytes is possible from a complex environmental matrix with high sensitivity and selectivity. Furthermore, the selectivity of derivatization following LC–UV–ESI-MS/MS shows the potential application of this method in various complex matrices such as sediments and organisms. This work is currently underway in our laboratory.

Acknowledgements

The authors wish to thank Dr. Narayanan Kannan for his valuable comments and English editing of this manuscript. This study was supported by the grant-in-aid from the National Natural Science Foundation of China (no. 21027009).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2012.02.047.

References

[1] M.-H. Li, Environ. Toxicol. 24 (2009) 95.
[2] T. Ohya, N. Kudo, E. Suzuki, Y. Kawashima, J. Chromatogr. B 720 (1998) 1.
[3] P. de Voogt, M. Sáez, Trends Anal. Chem. 25 (2006) 326.
[4] C.L. Tseng, L.L. Liu, C.M. Chen, W.H. Ding, J. Chromatogr. A 1105 (2006) 119.
[5] B.D. Key, R.D. Howell, C.S. Criddle, Environ. Sci. Technol. 31 (1997) 2445.
[6] K. Prevedouros, I.T. Cousins, R.C. Buck, S.H. Korzeniowski, Environ. Sci. Technol. 40 (2006) 32.
[7] S.P.J. van Leeuwen, J. de Boer, J. Chromatogr. A 1153 (2007) 172.
[8] K.J. Hansen, H.O. Johnson, J.S. Eldridge, J.L. Butenhoff, L.A. Dick, Environ. Sci. Technol. 36 (2002) 1681.
[9] M. Loewen, T. Halldorson, F. Wang, G. Tomy, Environ. Sci. Technol. 39 (2005) 2944.
[10] M. Houde, T.A.D. Bujas, J. Small, R.S. Wells, P.A. Fair, G.D. Bossart, K.R. Solomon, D.C.G. Muir, Environ. Sci. Technol. 40 (2006) 4138.
[11] J. Olivero-Verbel, L. Tao, B. Johnson-Restrepo, J. Guette-Fernández, R. Baldiris-Avila, I. O'byrne-Hoyos, K. Kannan, Environ. Pollut. 142 (2006) 367.
[12] L.W.Y. Yeung, M.K. So, G. Jiang, S. Taniyasu, N. Yamashita, M. Song, Y. Wu, J. Li, J.P. Giesy, K.S. Guruge, P.K.S. Lam, Environ. Sci. Technol. 40 (2006) 715.
[13] R. Renner, Environ. Sci. Technol. 42 (2008) 648.
[14] B.F. Scott, C.A. Moody, C. Spencer, J.M. Small, D.C.G. Muir, S.A. Mabury, Environ. Sci. Technol. 40 (2006) 6405.
[15] R. Alzaga, C. Salgado-Petinal, E. Jover, J.M. Bayona, J. Chromatogr. A 1083 (2005) 1.
[16] J.P. Benskin, M. Bataineh, J.W. Martin, Anal. Chem. 7 (2007) 6455.
[17] C.R. Powley, S.W. George, T.W. Ryan, R.C. Buck, Anal. Chem. 77 (2005) 6353.
[18] N. Yamashita, K. Kannan, S. Taniyasu, Y. Horii, T. Okazawa, G. Petrick, T. Gamo, Environ. Sci. Technol. 38 (2004) 5522.

[19] V. Dufková, R. Čabala, D. Maradová, M. Štícha, J. Chromatogr. A 1216 (2009) 8659.
[20] W.M. Henderson, E.J. Weber, S.E. Duirk, J.W. Washington, M.A. Smith, J. Chromatogr. B 846 (2007) 155.
[21] C.A. Moody, J.A. Field, Environ. Sci. Technol. 33 (1999) 2800.
[22] P. Hušek, P. Šimek, E. Tvrzická, Anal. Chim. Acta 465 (2002) 433.
[23] J.W. Martin, K. Kannan, P. de Vougt, J. Field, J. Franklin, J. Geisy, T.D. Harner, D. Muir, B. Scott, M. Kaiser, U. Jarnberg, K. Jones, S. Mabury, H. Schroeder, M. Simcik, C. Sottani, B. Van Bavelm, A. Karrman, G. Lindstrom, S. van Leewen, Environ. Sci. Technol. 38 (2004) 248A.
[24] B.S. Larsen, M.A. Kaiser, Anal. Chem. 79 (2007) 3966.
[25] H.D. Durst, M. Milano, E.J. Kikta Jr., S.A. Connelly, E. Grushka, Anal. Chem. 47 (1975) 1797.
[26] J.W. Washington, W. Matthew Henderson, J. Jackson Ellington, T.M. Jenkins, J.J. Evans, J. Chromatogr. A 1181 (2008) 21.