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Short communication

## Reliable and sensitive ultra-short chain per- and polyfluorinated alkyl substances (PFAS) analysis in food: a polar reverse-phase chromatography approach

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## ABSTRACT

Food contamination by per- and polyfluoroalkyl substances (PFAS), especially ultra-short-chain (USC) compounds, poses a growing concern due to their environmental persistence and potential health risks. Despite the developing regulatory framework, analytical challenges persist in quantifying polar USC-PFAS in complex content food matrices. This study presents the development and validation of a novel high-performance liquid chromatography coupled to a tandem mass spectrometer (HPLC-MS/MS) method for the accurate determination of USC-PFAS (carbon chain length from one to four, C1–C4) in tomato-based products (i.e. concentrate, puree, and pulp), that, due to their high water content, are prone to USC-PFAS contamination. Leveraging a polar analytical column and a delay column, the method effectively mitigates system-related interferences, especially for trifluoroacetic acid (TFA) and achieves enhanced retention and sensitivity. Target compounds included Difluoroacetic acid (DFA), TFA, Perfluoropropanoic acid (PFPrA), Perfluorobutanoic acid (PFBA), Perfluoromethanesulfonic acid (PFMeS), Perfluoroethanesulfonic acid (PFEtS), Perfluoropropanesulfonic acid (PFPrS), and Perfluorobutanesulfonic acid (PFBS). The quantification based on isotope dilution ensures high accuracy and precision. The method demonstrated excellent linearity ( $R^2 \geq 0.99$ ), recoveries within 65–135 %, and low relative standard deviation (RSD) values (<10 %). PFBA was detected across all tested tomato products, with concentrations ranging from 0.056 to 0.265  $\mu\text{g}/\text{kg}$ , indicating potential endogenous contamination potentially linked to processing concentration effects. This study fills a critical methodological gap, offering a robust analytical tool for USC-PFAS monitoring in complex food matrices, and supporting improved food safety regulation.

## 1. Introduction

Food safety is a key concern for industries and consumers, and in particular, accurate quantification of contaminants is essential for ensuring food integrity. Nowadays, per- and polyfluoroalkyl substances (PFAS) are receiving significant attention from the scientific community due to their resistance to degradation in water, air, and soil, leading to persistence in the environment, primarily from industrial sources, and subsequent contamination of food [1]. PFAS are linked to serious health issues, including cancer, liver damage, and immune system suppression

[2]. Therefore, reliable and standardized methods are crucial for monitoring PFAS levels in food, enabling effective regulation and public health protection. A specific interest is developing for the quantification of polar short- and ultra-short chain (USC) PFAS in high water content foods due to their mobility and bioavailability in aqueous environments, which facilitates the absorption of hydrophilic short-chain PFAS from soil [3], potentially leading to increased human exposure through dietary intake [4]. While current studies in literature on USC-PFAS focus on simple matrices, such as drinking water [5], without addressing matrix complexity and potential interferences, this study addresses the

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need for a targeted analytical method to quantify USC-PFAS in complex and high-water content matrices and specifically on tomato-based products specifically concentrates, puree, and pulp. Tomatoes, rich in pigments and hydrophilic molecules, present significant matrix interferences for USC-PFAS analysis. The analysis focused on quantifying compounds from C1 to C4, such as TFA, PFPrA, PFBA, PFMeS, PFEtS, PFPrS, PFBS and DFA, although not strictly a short-chain PFAS, is also a metabolite of pesticides like flupyradifurone. A new chromatographic method was developed to optimize retention and enhance sensitivity for these challenging analytes, providing a robust tool for PFAS detection in complex food matrices.

## 2. Experimental section

### 2.1. Materials and methods

LC/MS grade methanol, acetonitrile, formic acid, water, tert-butylmethyl ether (TBME) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) were from Carlo Erba (Milan, Italy). Tetrabutylammonium hydrogen sulfate (TBA) was from Merck (Darmstadt, Germany). Native PFAS Reference Standard ISO21675-PFAS-R1 (including PFBA and PFBS) was from AccuStandard (New Haven, Connecticut, USA). Perfluoropropanesulfonic acid (PFPrS), Perfluoroethanoic acid (TFA), Perfluoropropionic acid (PFPrA), 2H-Perfluoroethanoic acid (DFA), and Trifluoroacetate-1-<sup>13</sup>C (<sup>13</sup>C-TFA) were from Chiron (Trondheim, Norway). Method 8327 surrogate spiking mixture (including <sup>13</sup>C<sub>3</sub>-PFBA and <sup>13</sup>C<sub>4</sub>-PFBS), <sup>13</sup>C<sub>3</sub>-perfluoropropanoic acid (<sup>13</sup>C<sub>3</sub>-PFPrA), sodium trifluoromethanesulfonate (PFMeS), and sodium perfluoroethanesulfonate (PFEtS) were from Cambridge isotope label standards (Tewksbury, Massachusetts, USA).

### 2.2. Sample extraction procedure

The extraction of concentrates, puree, and pulp tomato samples was conducted following the ion pair protocol described in EURL-POPs guidance [6]. The experimental design included the preparation of four distinct sample types: a procedural blank, a matrix blank (non-contaminated tomato), a tomato sample spiked with isotopically labeled PFAS only, and a tomato sample spiked with both native and labeled analytes at 1x, 10x and 100x targeted LOQ level. Each extraction was performed in quadruplicate, two replicates by two different operators in different days, on 2 g of tomato matrices. Spiking was carried out in order to achieve target concentrations in the final extract of 0.0188 µg/kg, 0.188 µg/kg, 1.88 µg/kg for DFA, TFA, PFPrA (group 1), 0.150 µg/kg for <sup>13</sup>C-TFA, and <sup>13</sup>C<sub>3</sub>-PFPrA and 0.00750 µg/kg, 0.0750 µg/kg, and 0.750 µg/kg for PFMeS, PFEtS, PFPrS, PFBA, PFBS (group 2), 0.0750 µg/kg for <sup>13</sup>C<sub>3</sub>-PFBA, and <sup>13</sup>C<sub>4</sub>-PFBS. After extraction and solvent evaporation, the dried residues were reconstituted in 300 µL of a methanol:water (1:2, v/v) containing 1 % formic acid. The injection volume for LC-MS/MS analysis was set to 10 µL.

### 2.3. HPLC-MS/MS method

Chromatographic separation was carried out using an Exion UHPLC system (Sciex, Framingham, MA, USA) operated in reverse-phase mode with a mobile phase gradient. The analytical column employed was a Luna® Polar Pesticide column (3 µm, 150 × 2.1 mm) and a Luna® Polar Pesticide (3 µm, 100 × 2.1 mm) as delay column, both supplied by Phenomenex (Torrance, CA, USA). Specifically, the delay column was placed between the mixing chamber and the injector to postpone the elution of interferences originating from the mobile phases. This stationary phase has proven to be effective in retaining highly polar analytes such as DFA and TFA, justifying its use as a delay column. The mobile phases consisted of (A) water with 0.3 % formic acid (HCOOH) and (B) acetonitrile (CH<sub>3</sub>CN) with 0.3 % formic acid. The column temperature was maintained at 45 °C, and the flow rate was set at 0.400 mL/min. The gradient program initiated at 2 % B, ramping to 15 % B over 5

min, followed by a sharp increase to 95 % B within 2 min. This condition was held for 7 min before returning to the initial composition (2 % B) for an 11-minute re-equilibration period. Mass spectrometric detection was performed using a QTRAP® 6500+ mass spectrometer (Sciex, Framingham, MA, USA) coupled to the UHPLC system via an IonDrive® Turbo V ion source. Instrument parameters were optimized by direct infusion for the detection of ultra-short per- and polyfluoroalkyl substances (USC-PFAS). The source was operated with a curtain gas setting of 35, collision gas set to “medium,” IonSpray voltage at -4000 V, source temperature at 400 °C, and ion source gases 1 and 2 set to 35 a.u. and 45 a.u., respectively. The triple quadrupole (TQ) mass spectrometer was operated in multiple reaction monitoring (MRM) mode. Each analyte was monitored using two distinct MRM transitions, allowing both identification and quantification of USC-PFAS. All mass spectrometric parameters, including precursor and product ions, dwell time, declustering potential (DP), entrance potential (EP), collision energy (CE), and collision cell exit potential (CXP), were individually optimized (Table 1).

### 2.4. HPLC-MS/MS validation

Quantification of PFAS was carried out using external calibration prepared at seven concentration levels, applying an isotope dilution approach. Calibration standards for DFA, TFA, and PFPrA were prepared at concentrations of 0, 0.015, 0.038, 0.075, 0.150, 0.375, 0.750, and 1.875 (µg/kg) each containing a fixed concentration of 0.150 µg/kg of the corresponding isotopically labeled internal standards (<sup>13</sup>C-TFA and <sup>13</sup>C<sub>3</sub>-PFPrA). For PFMeS, PFEtS, PFPrS, PFBA, and PFBS, calibration levels were set at 0, 0.002, 0.008, 0.015, 0.038, 0.075, 0.300, and 0.750 (µg/kg), with a fixed internal standard concentration of 0.075 µg/kg for <sup>13</sup>C<sub>3</sub>-PFBA and <sup>13</sup>C<sub>4</sub>-PFBS. All calibration solutions were prepared in a solvent mixture composed of methanol and water (1:2, v/v) with 1 % HCOOH. Calibration curves were constructed by plotting the response (defined as the area ratio of the native compound to its isotopically labeled analogue) against the nominal concentration of the native analyte. In cases where a direct isotopically labeled analogue was not available, a structurally similar internal standard was used: <sup>13</sup>C-TFA for DFA and <sup>13</sup>C<sub>4</sub>-PFBS for all sulfonated PFAS. TFA calibration curves

**Table 1**

MRM parameters optimized for each analyte, including parent and daughter ions, dwell time, DP, EP, CE, and CXP. Quantifier transitions are indicated with an asterisk (\*).

ID	Q1 Mass (Da)	Q3 Mass (Da)	Dwell Time (msec)	DP (V)	EP (V)	CE (V)	CXP (V)
DFA_1*	95.0	50.8	80	-50	-14	-19	-11
DFA_2	95.0	95.0	80	-50	-14	-5	-11
TFA_1*	113.0	68.9	80	-1	-3	-15	-6
TFA_2	113.0	19.0	80	-1	-3	-40	-10
PFPrA_1*	163.0	118.9	80	-4	-14	-15	-10
PFPrA_2	163.0	19.0	80	-4	-14	-40	-10
PFBA_1*	212.9	168.9	110	-23	-7	-14	-18
PFBA_2	212.9	212.9	110	-23	-7	-5	-18
PFMeS_1*	149.0	80.0	80	-20	-5	-31	-7
PFMeS_2	149.0	98.9	80	-20	-5	-31	-7
PFEtS_1	199.0	80.0	80	-42	-7	-32	-14
PFEtS_2*	199.0	98.9	80	-42	-7	-32	-14
PFPrS_1*	249.0	80.0	90	-17	-5	-65	-15
PFPrS_2	249.0	98.9	90	-17	-5	-35	-15
PFBS_1	299.0	80.0	130	-50	-12	-73	-9
PFBS_2*	299.0	98.9	130	-50	-12	-40	-9
<sup>13</sup> C_TFA_1*	114.0	69.0	80	-1	-3	-17	-8
<sup>13</sup> C_TFA_2	114.0	114.0	80	-1	-3	-5	-8
<sup>13</sup> C <sub>3</sub> _PFPrA_1*	166.0	121.0	80	-3	-10	-14	-13
<sup>13</sup> C <sub>3</sub> _PFPrA_2	166.0	19.0	80	-3	-10	-37	-13
<sup>13</sup> C <sub>3</sub> _PFBA_1*	216.0	171.9	110	-19	-6	-12	-18
<sup>13</sup> C <sub>3</sub> _PFBA_2	216.0	216.0	110	-19	-6	-5	-18
<sup>13</sup> C <sub>4</sub> _PFBS_1	303.0	80.0	130	-26	-12	-66	-12
<sup>13</sup> C <sub>4</sub> _PFBS_2*	303.0	98.9	130	-26	-12	-36	-12

needed to be corrected for the contribution of the native abundance of  $^{13}\text{C}$  [7] in the native standard, which at higher concentration could contribute almost 5 % to the  $^{13}\text{C}$ -TFA internal standard. To fully validate the chromatographic method, all the parameters calculation were performed, including linearity ( $R^2$ ), instrumental LOD and LOQ, ion ratio diff % between quantifier and qualifier transition in solvent (Sv) and matrix (Mx), working range of the calibration curves, intraday repeatability (intra RSD %) and interday reproducibility (inter RSD %) of retention times, retention factor (k), efficiency ( $N_{W1/2}$ ), peak asymmetry ( $A_s$ ), comparing all of them in both solvent and matrix conditions [8,9]. All the results are shown in Table 2.

Retention time deviation between solvent and matrix is below 0.5 % for all analytes, indicating excellent retention time stability across conditions. The retention factor (k) values are acceptable for all compounds, including DFA and TFA, which are typically more difficult to retain; their retention times are clearly distinguishable from the void time, confirming adequate retention. Column efficiency, expressed as the number of theoretical plates, ranges from 2828 to 5304 in solvent and from 2763 to 6886 in matrix, demonstrating that matrix components do not adversely affect chromatographic efficiency. All peaks exhibit acceptable symmetry, with asymmetry factors ( $A_s$ ) below 2. Furthermore, intra-day and inter-day precision, expressed as RSD %, are below 0.15 % and 0.34 %, respectively, confirming the robustness and reproducibility of the method.

To assess potential matrix interferences, an additional curve generated using an extracted concentrated tomato matrix as the solvent was prepared. The method's linearity was demonstrated by the linear regression method, and all calibration curves— including those in matrix — showed an  $R^2$  value of  $\geq 0.99$ . The linear regression model in solvent was validated by interpolating the response of the highest concentration in the matrix into the solvent-based curve, with all resulting deviations all below 10 %.

To establish a suitable limit of quantification (LOQ), we calculated parameters to achieve apparent recoveries (AR %) between 65 % and 135 % and relative standard deviations (RSD %) below 25 %. The results will be further discussed in detail (see Section 3).

### 3. Result and discussion

Despite growing attention to USC-PFAS, chromatographic methods tailored to their analysis remain scarce, primarily due to their high polarity and poor retention under reversed-phase conditions. Most reported methods [11,12] rely on HILIC in isocratic mode or anion-exchange chromatography, both of which present issues such as

high background noise (particularly for TFA), limited robustness, and low suitability for complex matrices like plant-based foods. Moreover, the available studies focus mainly on relatively simple aqueous matrices (e.g., tap or bottled water), and do not adequately address the matrix effects and analytical challenges posed by food or plant samples. Notably, none of the reported methods consider the use of delay columns to mitigate solvent-derived contamination an important factor when detecting trace levels of highly mobile and ubiquitous analytes like USC-PFAS. In fact, one of the major challenges in PFAS analysis is the ubiquitous presence of these compounds, which becomes particularly critical when targeting USC-PFAS such as TFA. TFA, frequently employed as a coupling agent, is a common source of background contamination and is readily detected even in high-purity, HPLC-MS-grade solvents. Traditional C18 columns are not suitable for the determination of TFA, as it typically elutes at the system's dead time. Moreover, background signals originating from the analytical system itself are not effectively isolated by conventional C18 delay columns, further complicating the analysis. In this study, the use of a strongly polar analytical column allowed for improved retention of TFA, extending its elution time to approximately 4 min with around 20 % organic content in the mobile phase (Figure S1). Specifically, the Luna Polar Pesticide delay column effectively separated system-derived interferences (Fig. 1), where system interferences, are clearly resolved from the analytical TFA peak.

The method validated in this work allows minimizing TFA interference from reagents and standards. The solvent blank had a signal area of  $1.01 \times 10^6$ , indicating minor contamination from the dilution solvent. Additionally, TFA was detected also at the 0  $\mu\text{g}/\text{kg}$  point, containing only labeled PFAS standards, resulting in a signal area of  $4.26 \times 10^6$ . However, the analyte at 0.750  $\mu\text{g}/\text{kg}$  yielded a signal area of  $4.43 \times 10^6$ , demonstrating the method's good sensitivity and dynamic range. The method's precision was assessed by integrating the areas of labeled PFAS in calibration curves across  $>30$  injections from different vials, both in solvent and matrix. The RSD % for  $^{13}\text{C}$ -TFA,  $^{13}\text{C}_3$ -PFPrA,  $^{13}\text{C}_3$ -PFBA, and  $^{13}\text{C}_4$ -PFBS were 5.6, 2.7, 5.2, and 3.2, respectively (Figure S2).

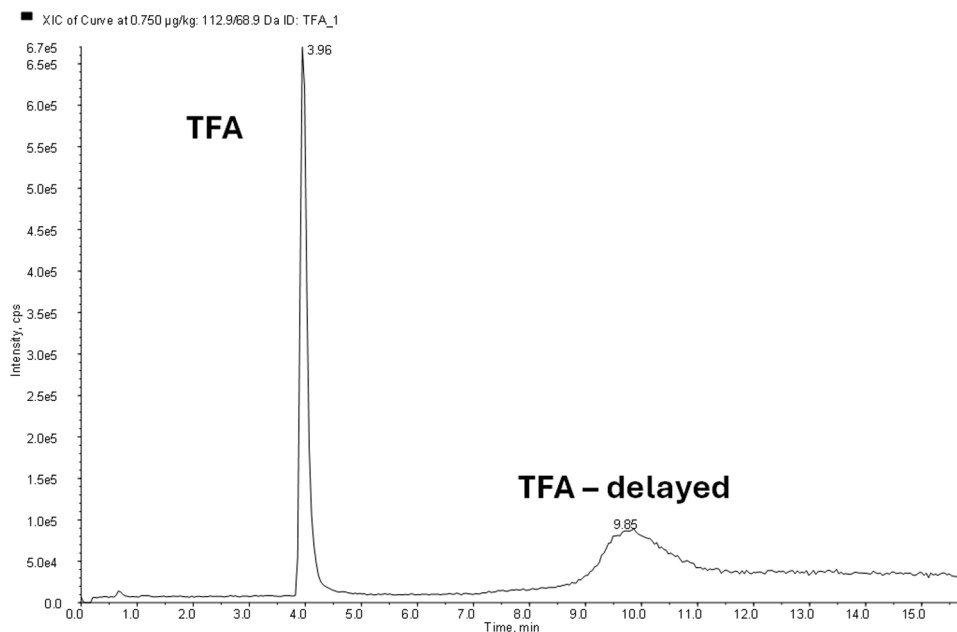
The final evaluation assessed the extraction efficiency and the method's ability to quantify USC-PFAS in tomato samples evaluating different criteria: apparent recovery (AR) %, relative standard deviation (RSD) %, and lowest validated LOQ (valLOQ), according to Tables 3, 4, 5, and 8 of EURL-POPs guidance [6]. Results are reported in Table 3.

Even if DFA was successfully validated in the chromatographic development, assessing an instrumental LOQ of 1.08  $\mu\text{g}/\text{kg}$ , the extraction performed still needs to be improved as at this stage it was not able to achieve a good recovery above 65 %. Regarding TFA, while iLOQ

**Table 2**

Chromatographic parameters evaluated: Equation, linearity ( $R^2$ ), instrumental iLOD and iLOQ, ion ratio diff % between quantifier and qualifier transition in solvent (Sv) and matrix (Mx), working range of the calibration curves, retention time of analytes (RT), repeatability (intra RSD %) and reproducibility (inter RSD %) of RT, retention factor (k), efficiency ( $N_{W1/2}$ ), peak asymmetry ( $A_s$ ).

	Eq ( $y = mx + q$ )	$R^2$	iLOD ( $\mu\text{g}/\text{kg}$ )	iLOQ ( $\mu\text{g}/\text{kg}$ )	Ion Ratio  diff %	Working range ( $\mu\text{g}/\text{kg}$ )				
DFA	$y = 0.65x + 0.075$	0.99	0.36	1.1	4.6	0.015 - 1.875				
TFA	$y = 17x + 4.7$	0.99	0.030	0.091	0.30	0.015 - 1.875				
PFPrA	$y = 7.4x + 0.060$	1.00	0.0040	0.012	6.3	0.015 - 1.875				
PFBA	$y = 11x + 0.018$	1.00	0.00030	0.0010	4.0	0.0015 - 0.750				
PFMeS	$y = 35x + 0.25$	1.00	0.0010	0.0030	4.9	0.0015 - 0.750				
PFEtS	$y = 3.7x + 0.026$	1.00	0.0080	0.024	1.3	0.0015 - 0.750				
PFPrS	$y = 19x + 0.083$	1.00	0.0010	0.0040	0.70	0.0015 - 0.750				
PFBS	$y = 10x + 0.0040$	1.00	0.0010	0.0030	6.4	0.0015 - 0.750				
	Sv RT (min)	Mx RT (min)	Sv k	Mx k	Sv $N_{W1/2}$	Mx $N_{W1/2}$	Sv $A_s$	Mx $A_s$	intra RSD %	inter RSD %
DFA	4.28	4.25	4.70	4.66	2828	2763	1.53	1.11	0.12	0.34
TFA	4.70	4.72	5.33	5.29	3093	2936	1.58	1.26	0.11	0.31
PFPrA	5.10	5.12	5.87	5.83	3418	3035	1.62	1.27	0.080	0.24
PFBA	5.70	5.71	6.66	6.62	3499	3826	1.97	1.48	0.090	0.20
PFMeS	5.12	5.14	5.90	5.86	3298	3170	1.40	1.39	0.080	0.29
PFEtS	5.64	5.67	6.60	6.56	3646	3568	1.70	1.34	0.15	0.33
PFPrS	6.52	6.52	7.72	7.70	4296	4374	1.52	1.37	0.070	0.18
PFBS	7.53	7.52	9.05	9.03	5304	6886	1.61	1.17	0.18	0.17



**Fig. 1.** MRM trace for TFA (transition 113.0 → 68.9 m/z): the sharp peak at 3.96 min corresponds to the analyte, while the broader signal around 10 min originates from system-related contributions separated by the delay column.

**Table 3**

Method validation parameters: Concentration spiked at the lowest validated level and concentration calculated from the calibration curves, apparent recovery % (AR %), RSD % across replicates from different operators and final validated LOQ (valLOQ). For TFA was used, according to Table 4 of EURL-POPs guidance document, the average of reagent blank (RB) findings multiplied by 3.3 times.

	Conc <sub>spiked</sub> (µg/kg)	Conc <sub>calc</sub> (µg/kg)	AR %	RSD %	valLOQ (µg/kg)
DFA	1.88	< LOQ	–	> 25	–
TFA	1.88	< LOQ	–	> 25	2.06 (3.3x RB)
PFPrA	0.0188	0.0148	78.8	15	0.0188
PFBA	0.00750	0.00800	107	9.9	0.00750
PFMeS	0.00750	0.00960	128	11	0.00750
PFEtS	0.0885	0.0885	118	9.6	0.0885
PFPrS	0.00750	0.00870	116	23	0.00750
PFBS	0.00750	0.00780	104	18	0.00750

was assessed at 0.091 µg/kg, unfortunately the average of eight different reagent blanks (RB) showed a concentration of (0.625 ± 0.066) µg/kg. According to Table 4 of EURL-POPs guidance document [6], considering this, the proper way to assess an LOQ was to use the formula 3.3x avgRB, resulting in a LOQ of 2.06 µg/kg. All of the other analytes were successfully validated at the LOQ reported in Table 3.

### 3.1. Endogenous occurrence of PFAS in tomato samples

After the screening of the first small round of concentrate, puree, and pulp tomato samples, available on the market, (3 batch each) an evaluation on endogenous occurrence of USC-PFAS was performed. Specifically, in tomato concentrates only PFBA, PFPrA, and PFMeS were detected, and as summarized in Fig. 2, showing chromatograms for a procedural blank (A), a concentrate (B), and a concentrate spiked with PFBA at 0.075 µg/kg (C) the PFBA contamination case is shown, being PFBA the only PFAS detected already mentioned in EU recommendation for fruit and vegetables [10].

The recovery of PFBA, as already showed for valLOQ in Table 3, ranged between 65 % and 135 %, with the absolute recovery calculated by interpolating the <sup>13</sup>C<sub>3</sub>-PFBA found in the extracted sample into the

calibration curve, yielding a recovery of 66.12 %. The apparent recovery in the tomato concentrate was calculated by subtracting the endogenous PFBA concentration, resulting in a recovery of 134.60 %, in compliance with the guidance document [6]. All three samples were positive, with concentrations of (0.265 ± 0.038) µg/kg found in the concentrate, (0.056 ± 0.005) µg/kg for pulp, and (0.063 ± 0.001) µg/kg for puree, which suggested an endogenous content increasing from the industrial process of tomatoes. By screening the other USC-PFAS, PFPrA was quantified in concentrate, puree, and pulp samples at, respectively, (0.733 ± 0.100) µg/kg, (0.440 ± 0.0400) µg/kg, (0.184 ± 0.0500) µg/kg, while PFMeS was found only in one concentrate with a concentration of (0.043 ± 0.0060) µg/kg.

## 4. Conclusions

This study introduces, for the first time, a novel approach for determining ultra-short-chain PFAS in complex food matrices, such as tomato products. A key innovation is the use of a polar analytical and delay column combination, which effectively separated analytes from system-derived interferences. This approach significantly reduced interference from reagents and standards, enhancing sensitivity and result reliability. This is further reflected in the excellent linearity of all analytes, including TFA, with R<sup>2</sup> values higher than 0.99 in both solvent and matrix conditions. Parameters like efficiency, peak asymmetry, retention factor, and ion ratio difference between solvent and matrix conditions were evaluated in order to successfully validate the chromatographic method developed. The method's robustness and precision were tested to achieve: interday RSD % below 0.4 for all analytes RT, and apparent recovery at the lowest validated levels (with exception of DFA and TFA which the extraction still needs to be improved aiming to reach lower LOQs) from 78.8 % to 127.5 %, with an RSD % < 25. The presence of PFBA, PFPrA, and PFMeS in commercial tomato samples was quantified, offering valuable insights into USC-PFAS contamination. While other works already studied approaches to quantify these analytes with LC-MS methods in water samples, the presented developed chromatographic approach will allow to assess contamination in food of plant origin such as tomato samples. This study advances food safety and public health protection by providing a reliable tool for PFAS detection in complex food matrices, supporting regulations and risk management.

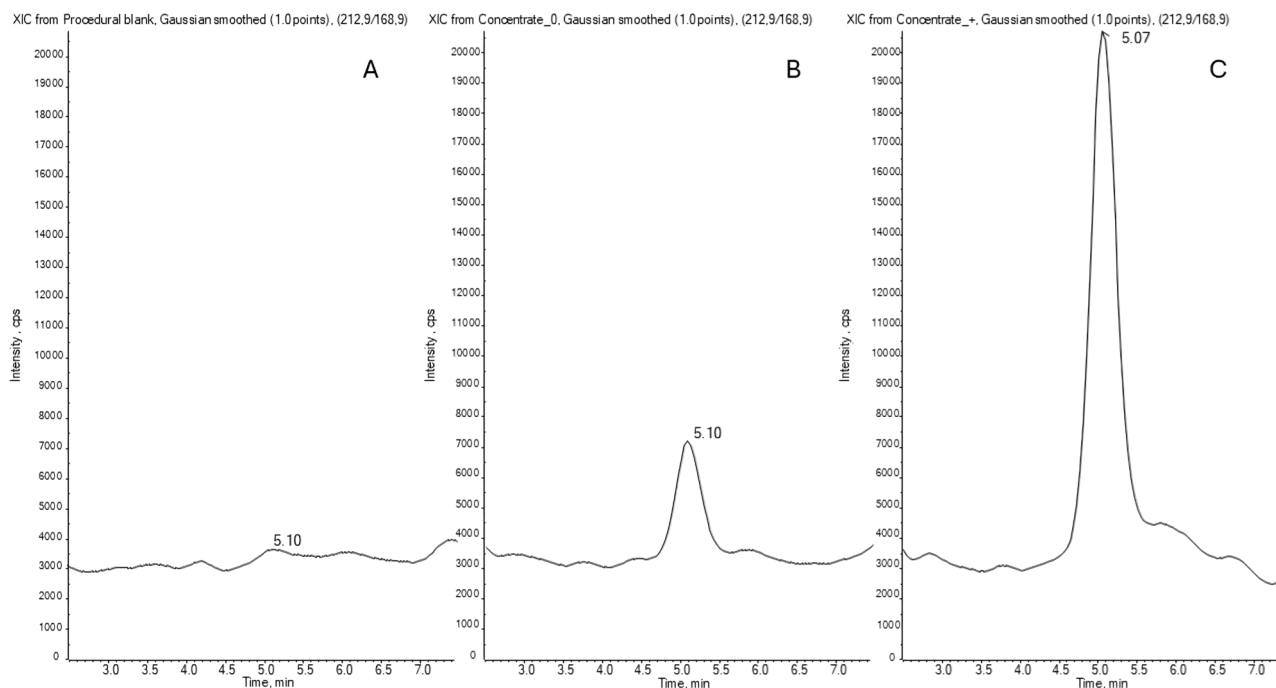


Fig. 2. PFBA peaks looking at the MRM transition from 212.9 m/z to 168.9 m/z. On the left is the procedural blank (A); in the middle is the negative extracted tomato containing only labelled PFBA (B); and on the right is the PFBA found in the spiked tomato at 0.075  $\mu\text{g}/\text{kg}$  (C).

## Abbreviations

PFAS, per- and polyfluoroalkyl substances; USC, ultra-short-chain; HPLC-MS/MS, high-performance liquid chromatography coupled to a tandem mass spectrometer; TFA, trifluoroacetic acid; DFA, difluoroacetic acid; PFPrA, perfluoropropanoic acid; PFBA, perfluorobutanoic acid (PFBA); PFMeS, perfluoromethanesulfonic acid; PFEtS, Perfluoroethanesulfonic acid (PFETs); PFPrS, perfluoropropanesulfonic acid; PFBS perfluorobutanesulfonic acid; RSD, relative standard deviation; TBME, tert-butylmethyl ether; TBA, tetrabutylammonium hydrogen sulfate; MRM, multiple reaction monitoring; DP, declustering potential; EP, entrance potential; CE, collision energy; CXP collision cell exit potential; LOQ, limit of quantification, AR %, apparent recoveries.

## CRediT authorship contribution statement

**Consolato Schiavone:** Writing – original draft, Methodology. **Francesco Romaniello:** Writing – review & editing, Methodology, Conceptualization. **Paola Brizio:** Validation, Conceptualization. **Michele Suman:** Methodology, Investigation. **Andrea M. Rossi:** Supervision, Data curation. **Chiara Portesi:** Writing – review & editing, Supervision.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.chroma.2025.466332](https://doi.org/10.1016/j.chroma.2025.466332).

## Data availability

Data will be made available on request.

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