

Trace level analysis of per- and polyfluoroalkyl substances (PFAS) in solid cosmetics following a methanol extraction

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INTRODUCTION

WHAT. Per- and polyfluoroalkyl substances (PFAS) comprise a large and diverse group of synthetic chemicals which have been produced since the 1950s and have been consistently used since then. However, the large number and structural diversity of PFAS makes it difficult to comprehensively assess exposure to this class of contaminants. PFOS and PFOA are probably the most famous PFAS compounds, as they were the first to garner publicity with their use in the manufacturing process for Teflon™. These are only two out of thousands of potential PFAS compounds in use.[1]

WHERE. The properties of PFAS make useful low molecular weight surfactants or polymeric materials in an array of industrial applications and consumer products. PFAS are used in the production of many consumer products such as non-stick and water-resistant coatings, surfactants, polymerization aids, in firefighting foams, and even in cosmetic products (CPs). Examples of fluorinated ingredients in CPs include: per/polyfluorinated acrylate polymers, naphthalenes, alkanes/alkenes, alcohols, siloxanes, silanes, sulfonamides, ethers, esters, phosphate esters, and acids.[2]

WHY. PFAS are a group of chemicals of concern and have been reported widely around the globe. PFAS have been linked to a variety of health effects including elevated cholesterol, reproductive impacts, and are potentially carcinogenic. According to the European Commission's database on cosmetic ingredients (CosIng), these substances are used in CPs as emulsifiers, anti-statics, stabilizers, film formers, viscosity regulators, etc.

HOW. The common feature among each class are fully or partially fluorinated carbon tails. This C-F tail is connected to a head group which varies from group to group. Within each group, individual PFAS vary by the length of the C-F chain. Due to the strong electronegativity and small atomic size of fluorine, the perfluoroalkyl moiety (-C_nF_{2n+1}) imparts unique properties to molecules including high surface activity, chemical, and thermal stability.

LAW. A number of regulatory restrictions and substitution measures have been implemented over the last decade with the aim of reducing environmental emissions and human exposure to PFAS, but not for cosmetics yet.

AIM. The focus of this study was proof-of-concept to show that low concentrations of PFAS can be detected in solid, wax-free cosmetics (Figure 1) using liquid chromatography coupled to tandem quadrupole mass spectrometry (LC-MS/MS) using a simplified solid-phase extraction (SPE)-free workflow.

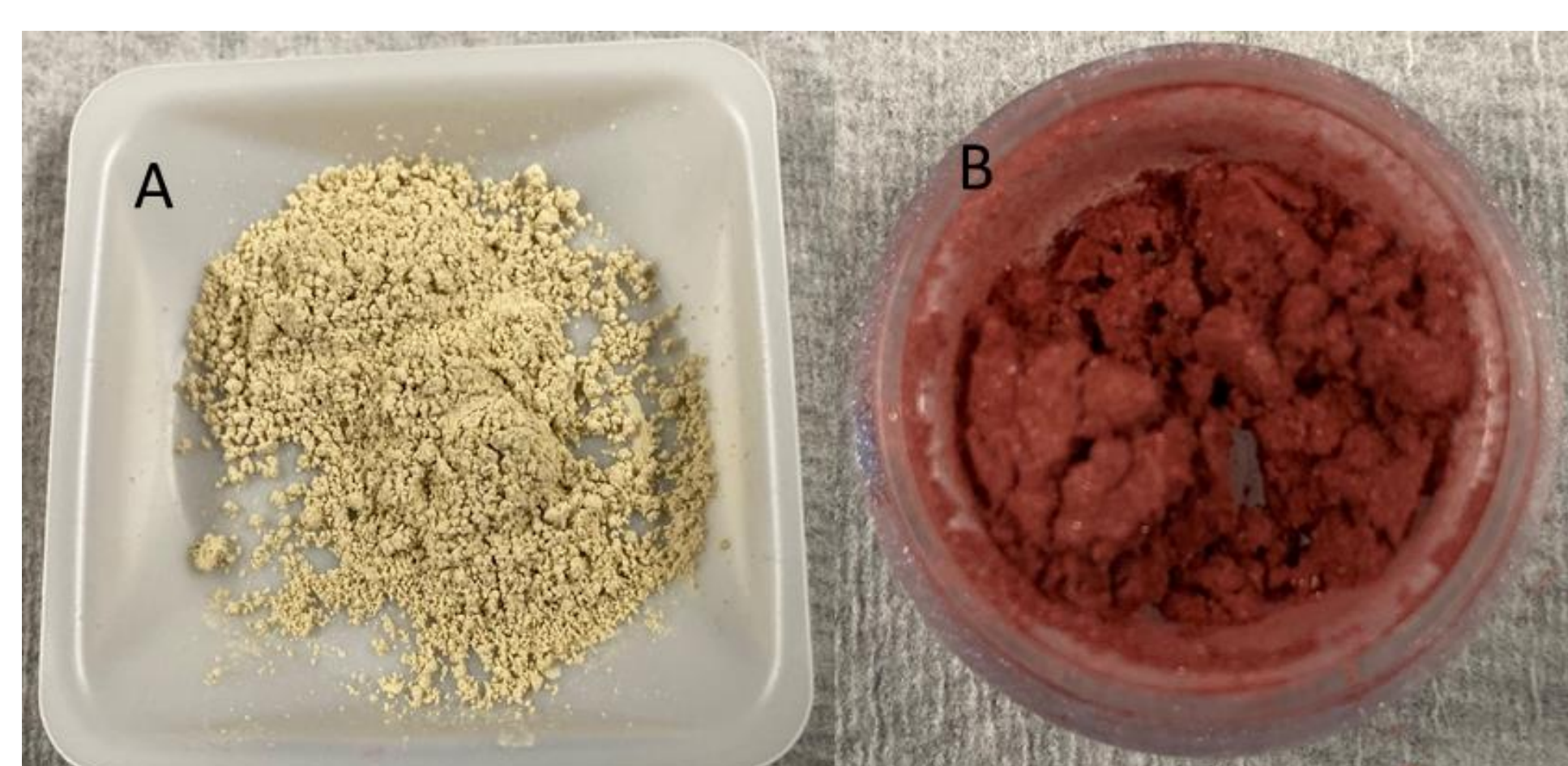


Figure 1. Solid cosmetics used in this study. A = foundation; B = eye shadow.

METHOD

It is critical for the analysis to acknowledge the difficulties associated with sample contamination. Since PFAS can be found practically everywhere, care must be taken to reduce risks of contamination from sample collection to sample preparation to sample analysis. It is important to use suitable laboratory products and solvents that have been evaluated for PFAS contamination prior to use. The steps of the sample work-up procedure are outlined below.

- 1 g sample
- Spike MPFAC-24ES + M3HFPO-DA (2.5 ng/mL)
- 10 mL of MeOH
- Sonicate for 30 min
- Filter: GMF filter followed by 0.22 um GHP syringe filter
- Dilute 5 mL extract 1:1 with 2 mM ammonium acetate
- Spin 70 min @ 3900 rpm
- Spike MPFAC-C-IS (5 ng/mL)
- Transfer to vial

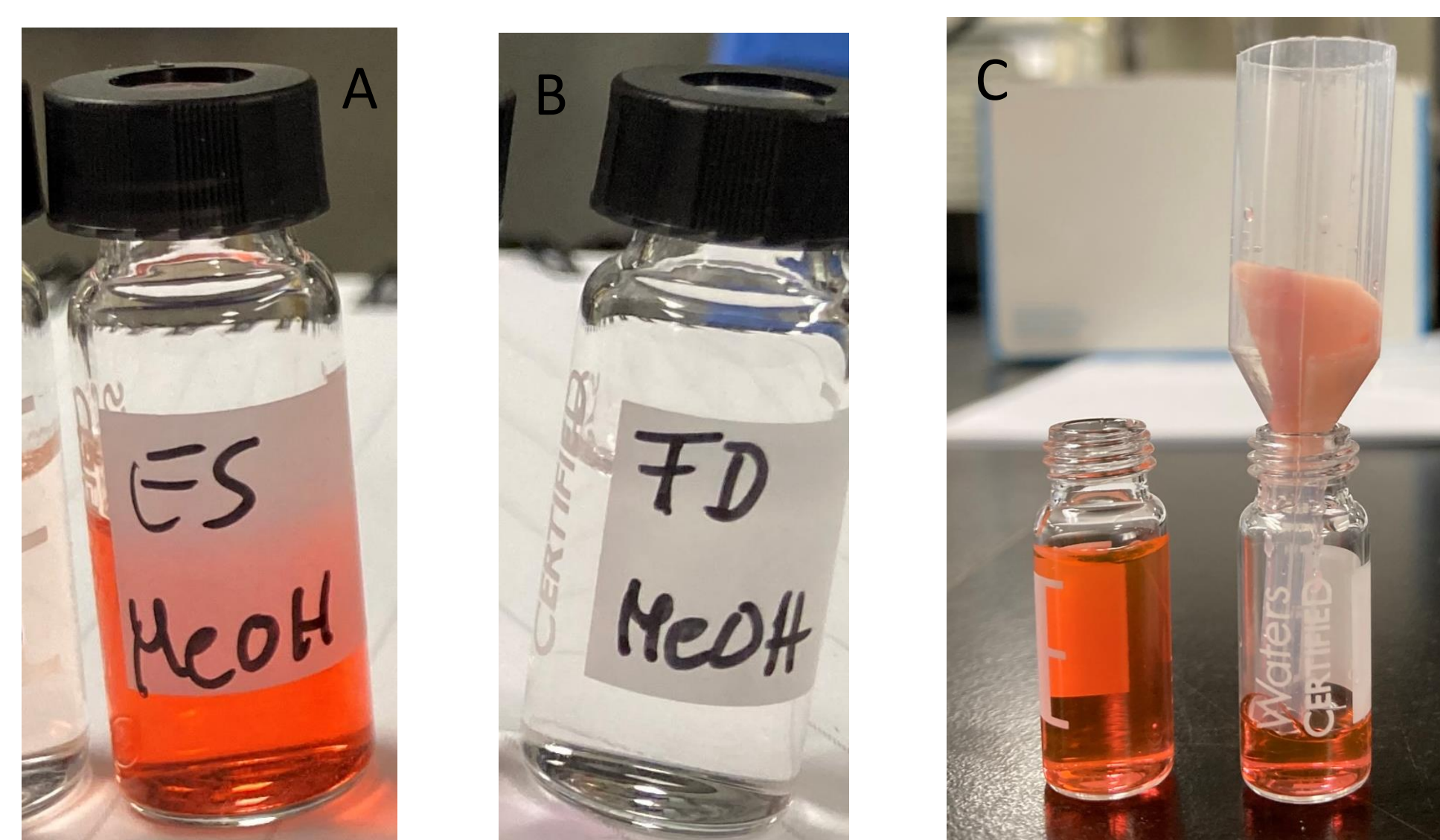


Figure 2. A = methanol extracts of eye shadow (ES); B = foundation (FD); C = filtration set-up for solid removal.

EXPERIMENTAL

MS Parameters

Instrument: Xevo TQ-S micro
Ionization Mode: ESI-
Capillary Voltage: 0.5 kV
Desolvation Temperature: 350 °C
Desolvation Flow: 900 L/h
Cone Flow: 150 L/h



LC Parameters

Instrument: ACQUITY I-Class PLUS with PFAS Kit (Fig.3)
Column: ACQUITY BEH C18 2.1x100 mm, 1.7 µm
Mobile Phase A: Water + 2 mM ammonium acetate
Mobile Phase B: Methanol + 2 mM ammonium acetate
Injection Volume: 10 µL
Gradient: See Table 1

The isolator column is installed after the mobile phase solvent mixer, prior to the sample injection valve, and provide chromatographic delay of system contaminants.



Figure 3. PFAS kit.

Table 1. LC gradient used in method.

Time (min)	Flow (mL/min)	%A	%B
0	0.3	95	5
1	0.3	75	25
6	0.3	50	50
13	0.3	15	85
14	0.3	5	95
17	0.3	5	95
18	0.3	95	5
22	0.3	95	5



RESULTS & DISCUSSION

The variation in chemical structure and properties across the entire suite of thousands of PFAS makes extraction and analysis challenging. This targeted study focused on a panel of about 30 PFAS covering a wide variety of PFAS chemistries with different alkyl chain lengths from C4 to C10 or higher. This list includes legacy PFAS such as the carboxylates and sulfonates, precursors, and emerging PFAS, like. Isotopically labeled standards were spiked into the samples both prior to extraction (extraction standard) and after extraction (injection standard). Extraction standards were used to determine recovery of the method. Table 2 lists the PFAS standard panel consisting of injection standards (IS) and extraction standards (ExS).

Table 2. PFAS standards used in analysis.

PFAS	Type of Standard	PFAS	Type of Standard
PFBA	ExS, IS	N-MeFOSAA	ExS
PFPeA	ExS	N-EtFOSAA	ExS
PFHeA	ExS	PFBS	ExS
PFHpA	ExS	PFPeS	ExS
PFOA	ExS, IS	PFHxS	ExS
PFNA	ExS	PFHpS	ExS
PFDA	ExS, IS	PFOS	ExS, IS
PFUdA	ExS	PFNS	
PFDoA	ExS	PFDS	
PFTeDA	ExS	4:2FTS	ExS
PFTeDA	ExS	6:2FTS	ExS
FBSA		8:2FTS	ExS
FHxSA		NaDONA	
FOSA	ExS	9CI-PF3ONS	
HFPO-DA (GenX)	ExS	11CI-PF3OUdS	

Direct analysis is not feasible with this instrumental set-up, because of the complexity of the sample matrix. Recent publications use various methods for the extraction of PFAS from cosmetics samples. Since the focus of this study was only on solid cosmetics, a simple direct extraction using methanol was evaluated. Methanol is a suitable solvent for PFAS extraction and takes advantage of the non-polar C-F alkyl chain present in every PFAS structure. Furthermore, the wetting behavior of MeOH was superior to water, which would aid the extraction. Figure 4 depicts the PFAS detected in the eye shadow as an example.

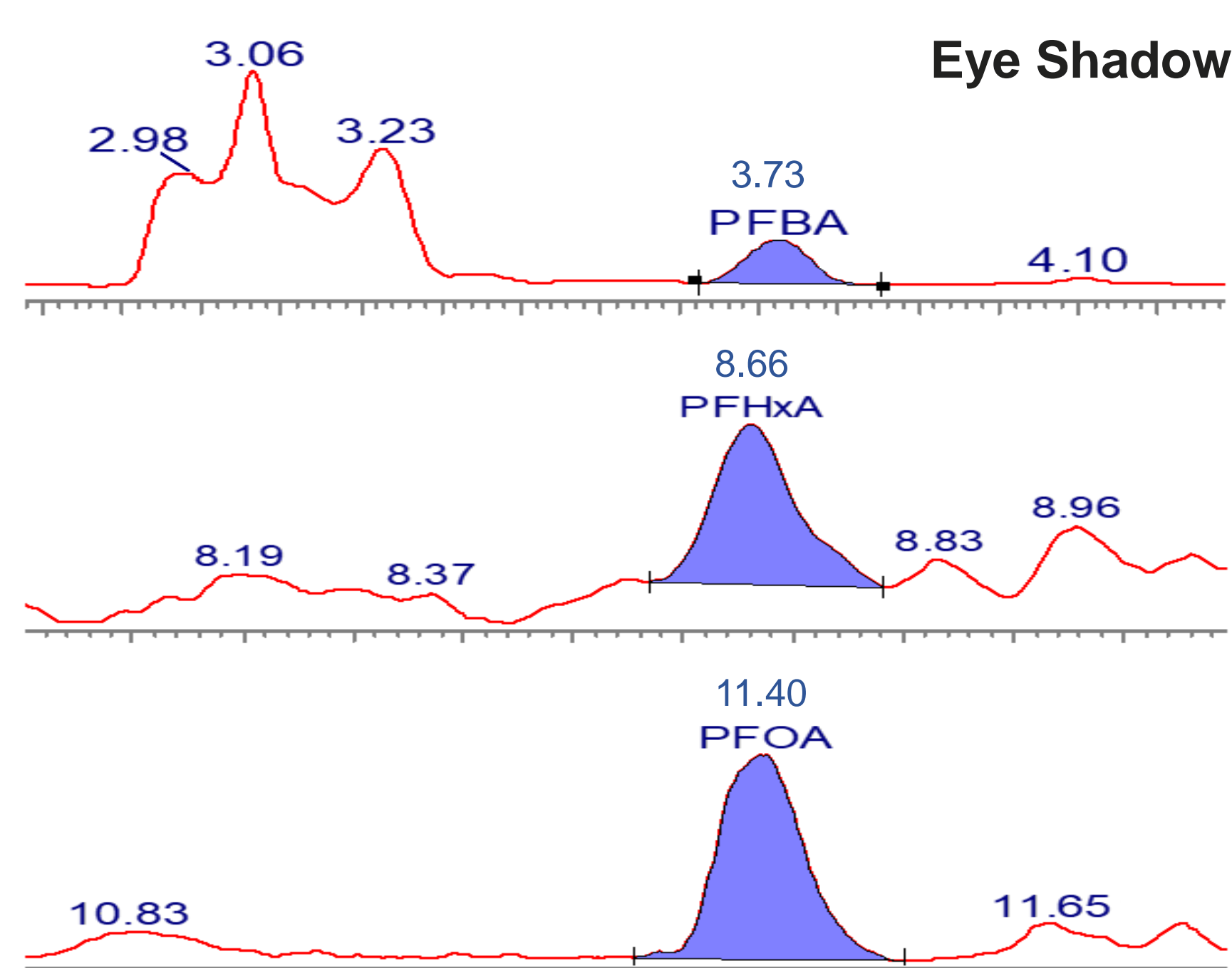


Figure 4. Staggered raw data of the eye shadow sample exhibiting non-standard PFAS

Concentrations of the detected PFAS compounds from eye shadow (ES) and powdered foundation (FD) are reported in Table 3. Perfluorobutanoic acid (PFBA), perfluoro-n-octanoic acid (PFOA) and perfluoro-n-tetradecanoic acid (PFTeDA) were detected in both eye shadow and foundation, whereas perfluoro-n-hexanoic acid (PFHxA) and perfluoro-1-butane-sulfonate (PFBS) were also detected in eye shadow. Detected PFAS concentrations ranged from 0.2 - 2.9 ng/g in the samples tested.

Table 3. Detected PFAS in eye shadow (ES) and foundation (FD).

Sample	Compound	Concentration (ng/mL)	Concentration (ng/g)
ES	PFBA	0.29	2.9
ES	PFHxA	0.02	0.2
ES	PFOA	0.12	1.2
ES	PFTeDA	0.02	0.2
ES	PFBS	0.02	0.2
FD	PFBA	0.18	1.8
FD	PFOA	0.01	0.1
FD	PFTeDA	0.02	0.2

Figure 5 illustrates the recovery trend for the spiked standard panel. It ranges from 65 to 140% that can be considered acceptable.

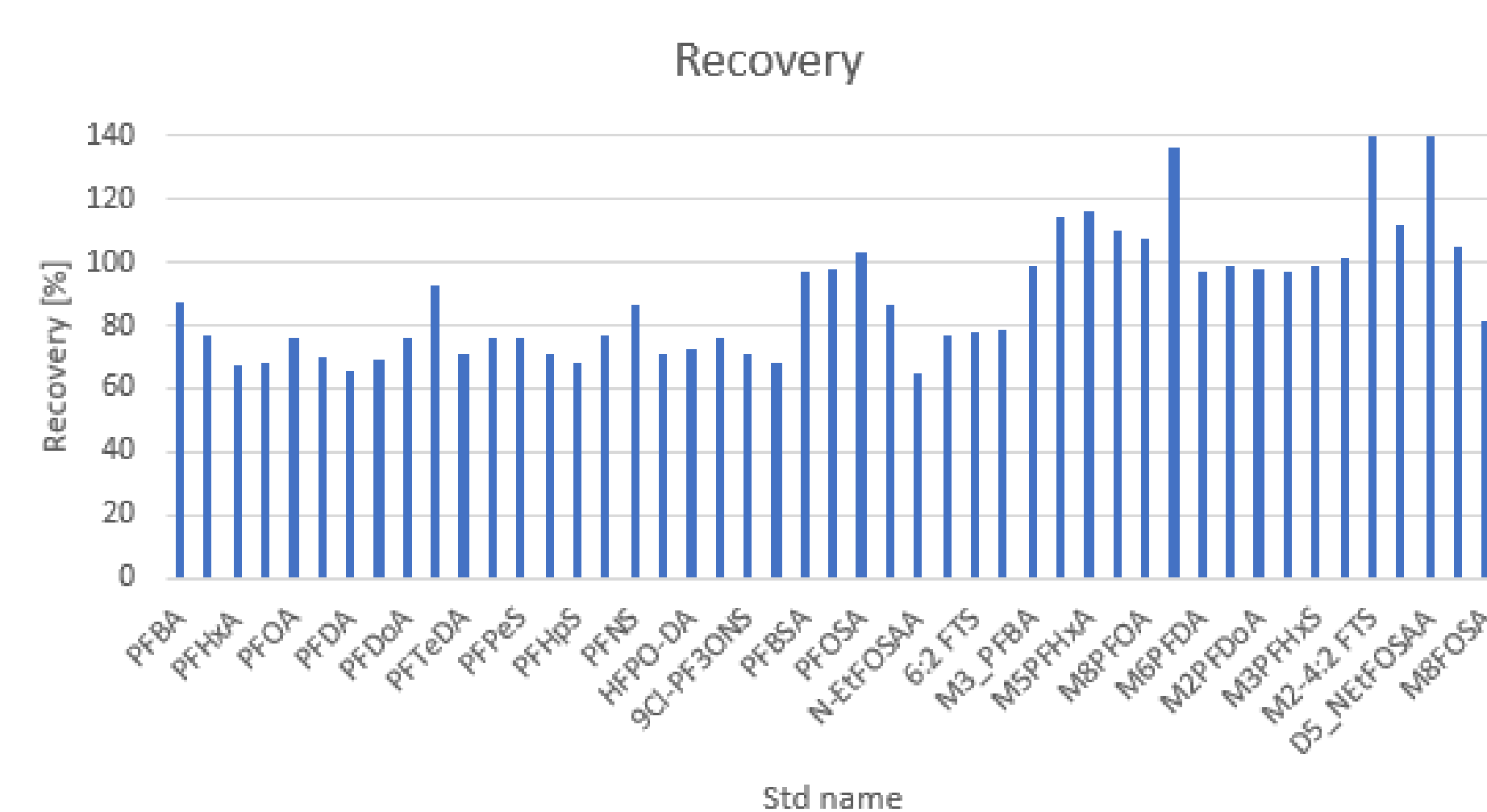


Figure 5. Recovery plot of spiked standards.

Sodium dodecafluoro-3H-4,8-dioxa-nonane-1-sulfonate (NaDONA) as a solvent-based standard was used as an example at 0.05 ppb (ng/mL) to demonstrate the sensitivity level of this simplified method. Determined concentration is 24.7 ppb. The calibration response ranged from 0.01 - 50 ppb (Figure 6A). The ion ratio (green) was used to confirm the target compounds with two characteristic MRM transitions and was consistently within the generally accepted 20% limit at low and high levels (Figures 6B-C).

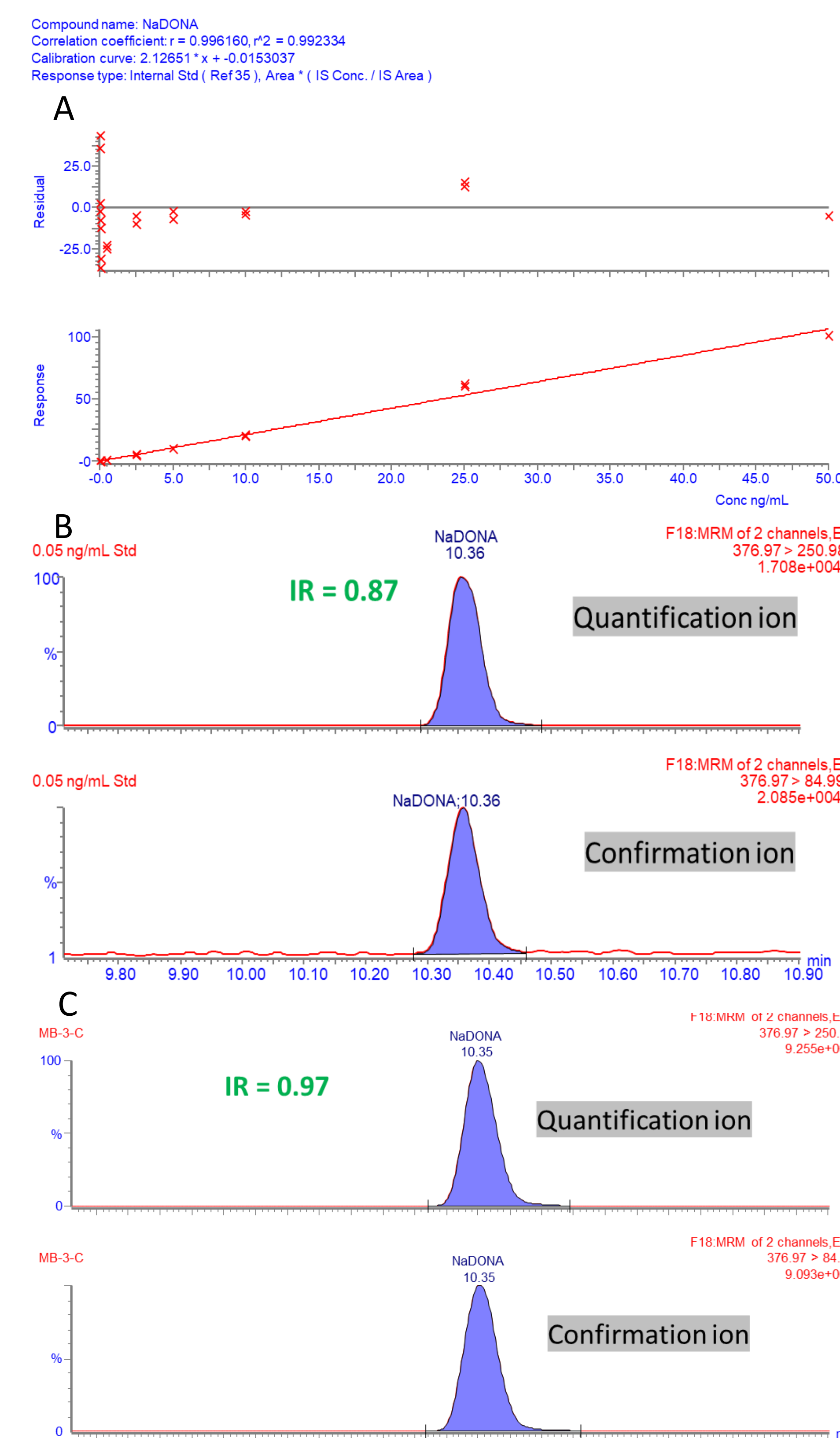


Figure 6. A = calibration range with residuals plot; B & C = ion ratios for two characteristic MRM transitions of NaDONA.

CONCLUSION

This study proved that a simplified sample work-up procedure can be applied to solid cosmetics products to extract non-standard PFAS compounds. The Xevo TQ-S micro provides excellent sensitivity to detect PFAS at trace levels.

References

- [1] Peaslee, G. F. et al. Fluorinated Compounds in North American Cosmetics. Environ. Sci. Technol. Lett. 2021, 8(7), 538-544.
- [2] Schaidler, L. A.; Balan, S. A.; Blum, A.; Andrews, D. Q.; Strynar, M. J.; Dickinson, M. E.; Lunderberg, D. M.; Lang, J. R.; Peaslee, G. F. Fluorinated Compounds in U.S. Fast Food Packaging. Environ. Sci. Technol. Lett. 2017, 4 (3), 105-111.