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. 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 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, and even in cosmetic products (CPs).[2] Examples of fluorinated ingredients in CPs include: per/polyfluorinated acrylate polymers, naphthalenes, alkanes/alkenes, alcohols, siloxanes, silanes, sulfonamides, ethers, esters, phosphate esters, and acids.[3]

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. 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. However, the FDA will be looking into bringing on methodologies for testing consumer products for PFAS in the future.

IMPACT. This will pose an important step to safeguard end-users but will bear a burden on the industry as the sample preparation is challenging and time consuming and overall analyses including instrumentation is expensive.

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.

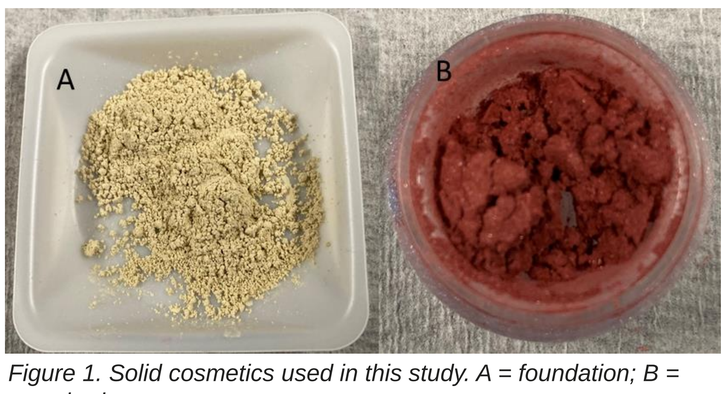

Figure 1. Solid cosmetics used in this study. A = foundation; B = eye shadow.

METHOD

It is critical for the analysis to acknowledge the difficulties associated with sample contamination. Since PFAS are ubiquitious in many common laboratory products, 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 and refer to Figure 2.

- 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

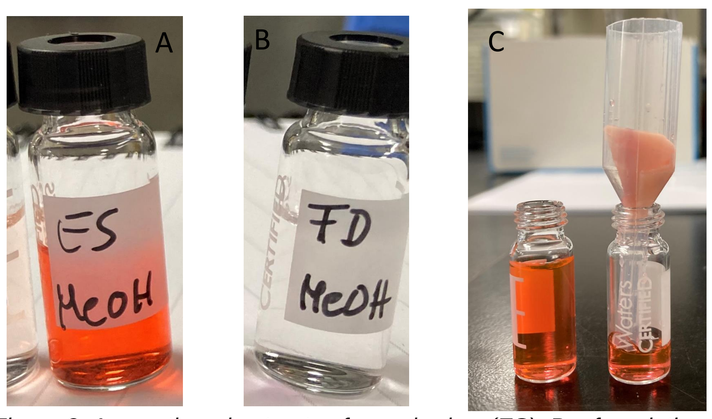

Figure 2. A = methanol extracts of eye shadow (ES); B = foundation (FD); C = filtration set-up for solid removal.

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**
Column: ACQUITY BEH C18 2.1×100 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

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

All standards were obtained from Wellington Laboratories. The method contained a total of 30 PFAS including the following compounds: Carboxylates: C4-C14; Sulfonates: C4-C10; Ethers: GenX, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUdS; Precursors: FBSA, FHxSA, FOSA, NMeFOSAA, NEtFOSAA, 4:2 FTS, 6:2 FTS, 8:2 FTS. Isotope labelled extraction (MPFAC-24ES) and injection standards (MPFAC-C-IS) were used during extraction and analysis to perform isotope dilution calculations. The extraction standards (ExS) were spiked in the samples prior to sample preparation and used to correct the native compounds for recovery and matrix effects. The injection standard (IS) was added to the sample after clean-up when the sample was reconstituted and used to correct the extraction standards for reconstitution variations, matrix effects, and injection variation (Table 2).

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	
PFOA	ExS, IS	PFHxS	ExS
PFNA	ExS	PFHpS	
PFDA	ExS, IS	PFOS	ExS, IS
PFUdA	ExS	PFNS	
PFDoA	ExS	PFDS	
PFTrDA		4:2FTS	ExS
PFTeDA	ExS	6:2FTS	ExS
FBSA		8:2FTS	ExS
FHxSA		NaDONA	
FOSA	ExS	9Cl-PF3ONS	
HFPO-DA (GenX)	ExS	11Cl-PF3OUdS	

Direct analysis is not feasible with this instrumental set-up, because of the complexity of the sample matrix. 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 methanol was superior to water, which would aid the extraction.

Figure 3 illustrates the recovery trend for the spiked extraction and injection standard panel. It ranges from 65 to 110% that can be considered good.

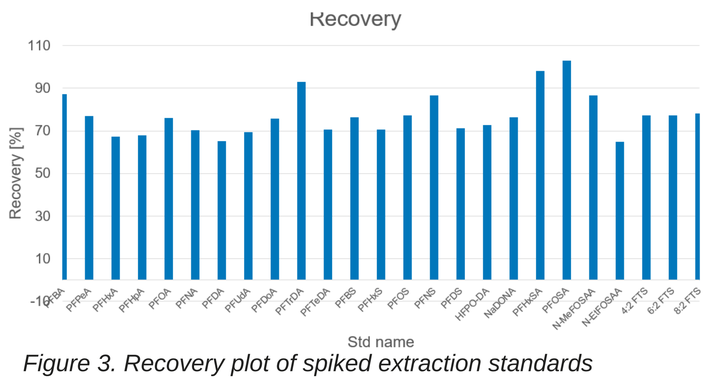

Figure 3. Recovery plot of spiked extraction standards

The sensitivity of the method can be demonstrated in the following examples of sodium dodecafluoro-3H-4,8-dioxa-nonane-1-sulfonate (NaDONA). Figure 4A demonstrates the calibration response in the range of 0.01-50 ng/mL. Triplicate injections were made of each concentration, demonstrating excellent linearity and reproducibility. Figure 4B shows the chromatograms of the two MRM transitions monitored for NaDONA in a 0.05 ng/mL solvent standard with the ion ratio highlighted in green. Figure 4C exhibits NaDONA spiked into a blank sample prior to extraction, also denoting the ion ratio. The ion ratio was used to confirm detected PFAS in the samples. All PFAS exhibited ion ratios with the generally accepted 20% limit at low and high levels.

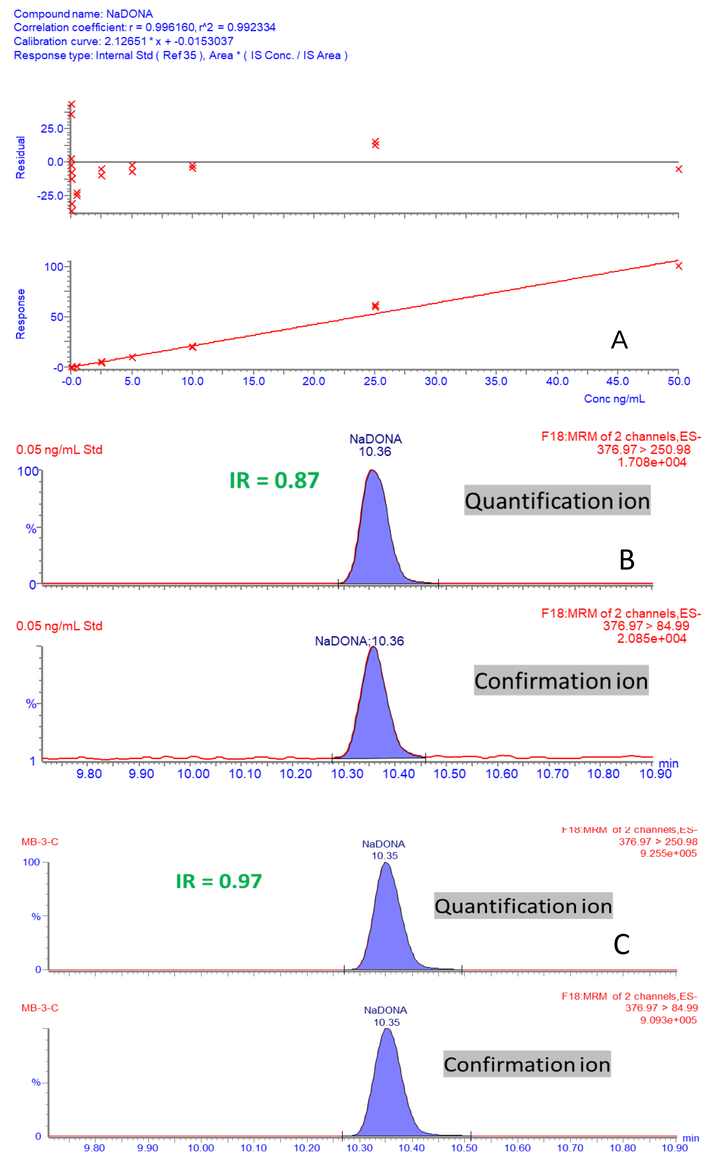

Figure 4.A = calibration range with residuals plot; B & C = ion ratios for two characteristic MRM transitions of NaDONA.

The extracted ion chromatograms (EIC) of quantification ions of one non-standard PFAS compound detected in a blank sample of eye shadow and confirmation ion from extraction standards were used to demonstrate a successful extraction procedure as is depicted in Figure 5. Detected PFAS concentrations ranged from 0.2-2.9 ng/g in the samples tested. Results from the blank samples of eye shadow and powdered foundation are reported in Table 3.

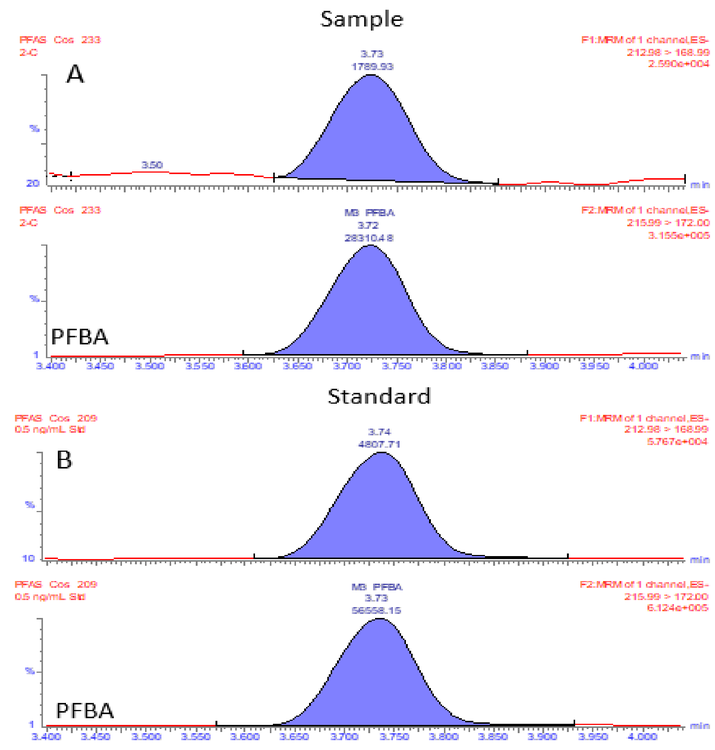

Figure 5. A = EIC of the quantitation ion for PFBA detected in the blank eye shadow sample; B = EIC of the confirmation ion for PFBA in a 0.5 ng/mL standard solution.

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

Sample	Compound	Concentration (ng/mL)	Concentraiton (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

CONCLUSION

This preliminary study proved that a simplified methanol extraction procedure is sufficient for solid cosmetics products. Trace level, non-standard PFAS compounds were extracted and detected in eye shadow and powdered foundation. The selective Xevo TQ-S micro tandem quadrupole mass spectrometer provided excellent sensitivity and 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] Perkins, T. Toxic 'forever chemicals' widespread in top makeup brands, study finds. The Guardian;15 Jun 2021.
[3] Schaider, 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.

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