Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Determination of polyfluoroalkyl substances in cosmetic products using dispersed liquid-liquid extraction coupled with UHPLC- MS/MS

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Text S1. The Raw extract, ENVI Carb, and WAX-SPE test procedure

For the preparation of raw extract solution (without clean-up), a cream sample (0.5 g, accurate to 0.01 g) was taken in a 10 mL centrifuge tube, followed by addition 3 mL of saturated sodium chloride solution. The slurry was vortexed for 1 min for dispersion prior to addition of 2 mL of acetonitrile. The sample was vortexed again for 2 min and centrifuged for 10 min at 5000 r/min. The upper organic layer was transferred to another 10 mL plugged centrifuge tube. The whole procedure was repeated twice more and the extracts were combined. Finally, acetonitrile was added to the 5 mL scale mark, and mixed. The solution was filtered through a 0.2 mm polypropylene filter before the LC-MS/MS analysis.

For the preparation of ENVI-Carb clean-up solution, the extraction process was the same as that of the raw extract. After the volume was fixed to 5 mL with acetonitrile, 500 mg ENVI Carb packing was added to the solution. Subsequently, this solution was vortexed for 5 min and centrifuged for 5 min at 10000 r/min, and the solution was filtered through a 0.2 mm polypropylene filter before the LC-MS/MS analysis.

The WAX solution was prepared as described in Sections 2.3.1 and 2.4.

Text S2. Details of LC-HRMS

The UHPLC Q-Exactive Orbitrap MS^n mass spectrometer equipped with an electrospray ionization (ESI) source was used for the determination of impurities using three purification methods. The chromatographic column, mobile phase, and mobile phase gradient are the same as mentioned in Section 2.5. The sample injection volume was 1 μL. The mass spectrometer analysis was operated in the ESI^+ (Fig. 2) and ESI^- (Fig. 3) modes. The high-resolution mass spectrum was collected in the full scan mode in the mass range m/z 100-1000. The spray voltage was set to 3.0 kV (ESI^+) and -2.5 kV (ESI^-); the sheath gas flow rate and aux gas flow rate were set to 45 arb and 12 arb, respectively; the capillary temperature and heater temperature were set to 350 °C and 320 °C, respectively; the S-lens RF level was 50.

Text S3. Determination of the eluent volume

Large solvent effect was observed when target compounds were directly detected in the eluent (0.1% ammonia-methanol solution). Therefore, the eluate must be evaporated under nitrogen conditions to remove the solvent. Large volumes of eluent introduce large quantities of impurities and increase the nitrogen blowing time; thus, it is vital to use a minimum volume of the eluent. In this study, the recovery of the target compounds using different volumes of eluent (4, 3, 2, and 1 mL) was investigated (Fig. S4). Elution

with 2 mL of 0.1% ammonia-methanol solution exhibited the highest recovery rate; the recovery rate did not change significantly with further increase in the eluent volume.

Table S1. MS/MS parameters for PFAS and IS, as well as target analytes corrected with each internal standard.

No.	Analyte	Precursor ion (m/z)	Product ion (m/z)	Declustering Potential (V)	Collision energy (eV)	Internal Standards
1	PFPeA	263	219*	-40	-10	M5PFPeA
			69	-40	-50	
2	L-PFBS	299	80*	-90	-70	M3PFBS
			99	-90	-38	
3	PFHxA	313	269*	-45	-13	M5PFHxA
			119	-45	-27	
4	L-PFPeS	349	80*	-19	-50	M3PFBS
			99	-19	-50	
5	PFHpA	363	319*	-30	-14	M4PFHpA
			169	-30	-24	
6	L-PFHxS	399	80*	-90	-90	M3PFHxS
			99	-90	-72	
7	PFOA	413	369*	-40	-14	M8PFOA
			169	-40	-24	
8	L-PFHpS	449	80*	-60	-52	M8PFOS
			99	-23	-85	
9	PFNA	463	419*	-35	-16	M9PFNA
			169	-35	-24	
10	L-PFOS	499	80*	-105	-110	M8PFOS
			99	-105	-98	
11	L-PFNS	549	80*	-24	-87	M8PFOS
			99	-24	-87	
12	PFDA	513	469*	-40	-18	M6PFDA
			219	-40	-26	
13	PFUdA	563	519*	-70	-16	M7PFUdA
			319	-70	-28	
14	L-PFDS	599	80*	-120	-124	M8PFOS
			99	-120	-110	
15	PFDoA	613	569*	-70	-18	MPFDoA
			169	-70	-36	
16	L-PFDoS	699	80*	-35	-138	M8PFOS
			99	-61	-130	
17	PFTrDA	663	619*	-65	-20	MPFDoA
			169	-65	-38	
18	M5PFPeA (Internal Standards)	268	223	-40	-10	-
19	M3PFBS (IS)	302	80	-90	-70	-
20	M5PFHxA (IS)	318	273	-45	-13	-
21	M4PFHpA (IS)	367	322	-30	-14	-

22	M3PFHxS (IS)	402	80	-90	-90	-
23	M8PFOA (IS)	421	376	-40	-14	-
24	M9PFNA (IS)	472	427	-35	-16	-
25	M8PFOS (IS)	507	80	-105	-110	-
26	M6PFDA (IS)	519	474	-40	-18	-
27	M7PFUdA (IS)	570	525	-70	-16	-
28	MPFDoA (IS)	615	570	-70	-18	-

*Quantifying ions

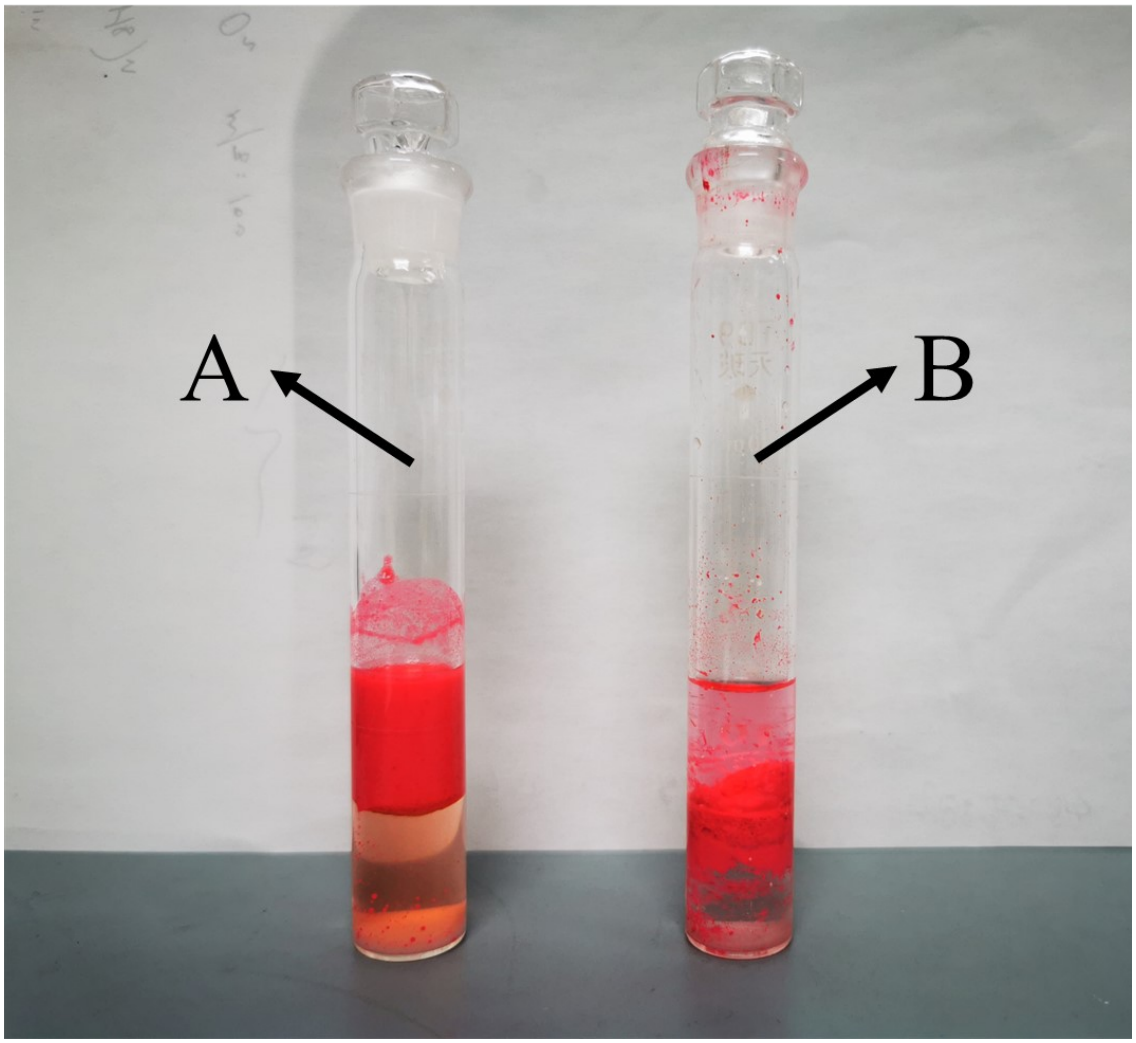

Figure S1. Comparison of lipstick dispersion in different extractants. A (0.5 g lipstick is fully dispersed in tetrahydrofuran-saturated-sodium-chloride-acetonitrile), B (0.5 g lipstick cannot be fully dispersed in saturated-sodium-chloride-acetoni trile).

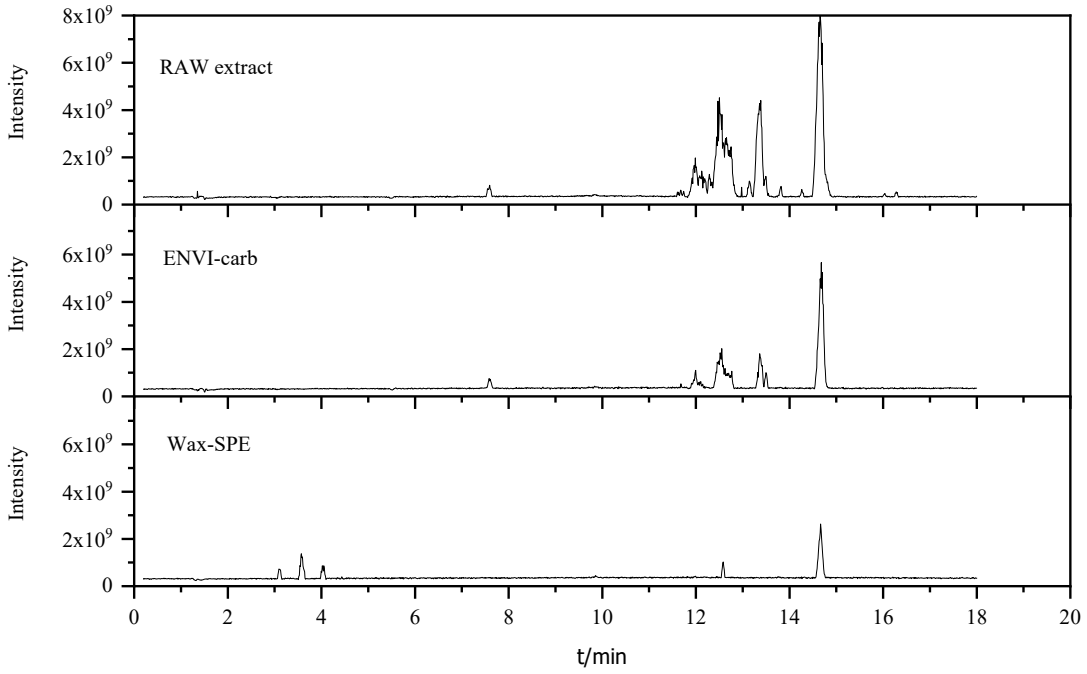

Figure S2. LC-HRMS (ESI^+) full scan chromatograms of a cream purified using three different procedures.

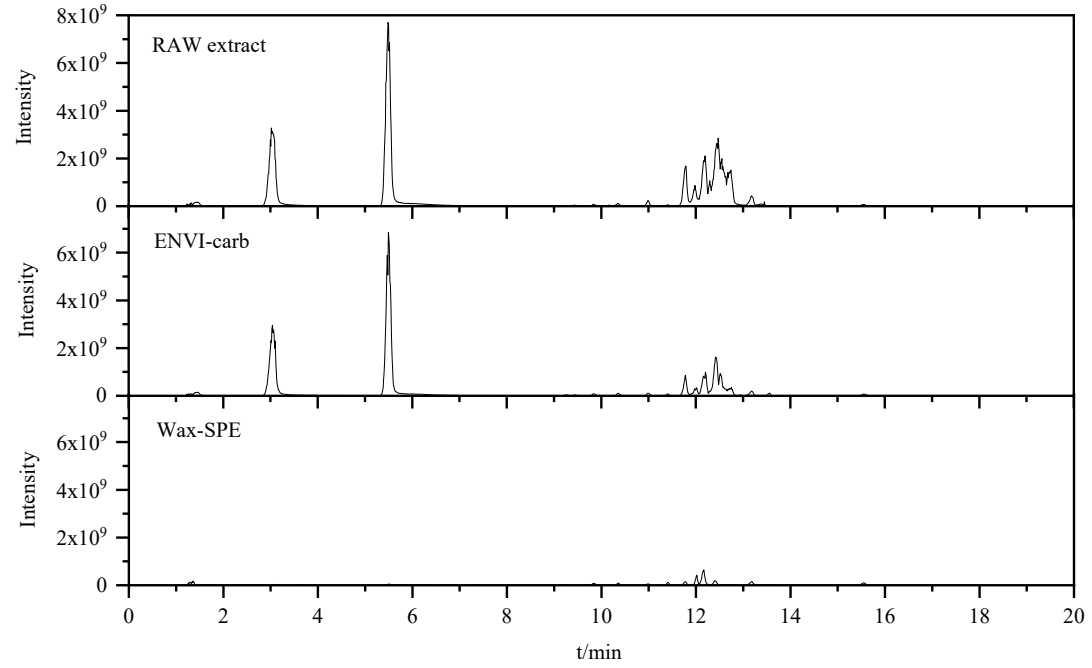

Figure S3. LC-HRMS (ESI^-) full scan chromatograms of a cream purified using three different procedures.

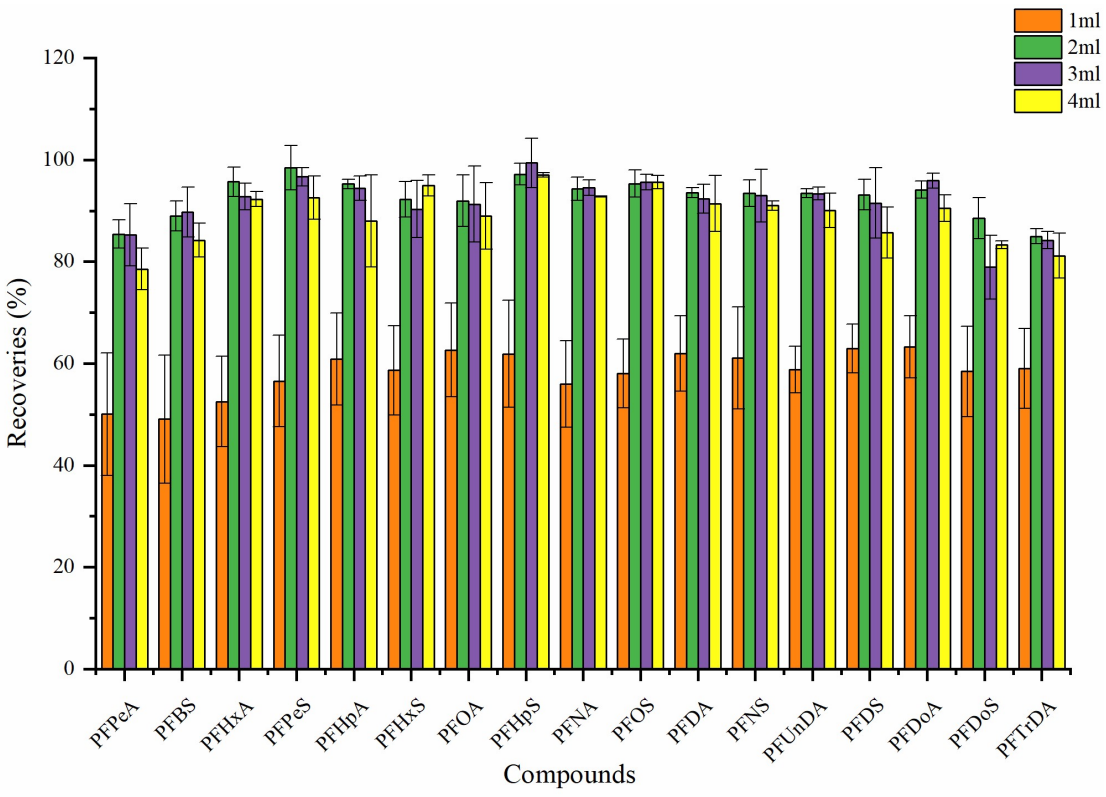

Figure S4. Recoveries of the 17 target compounds using different eluent volumes.

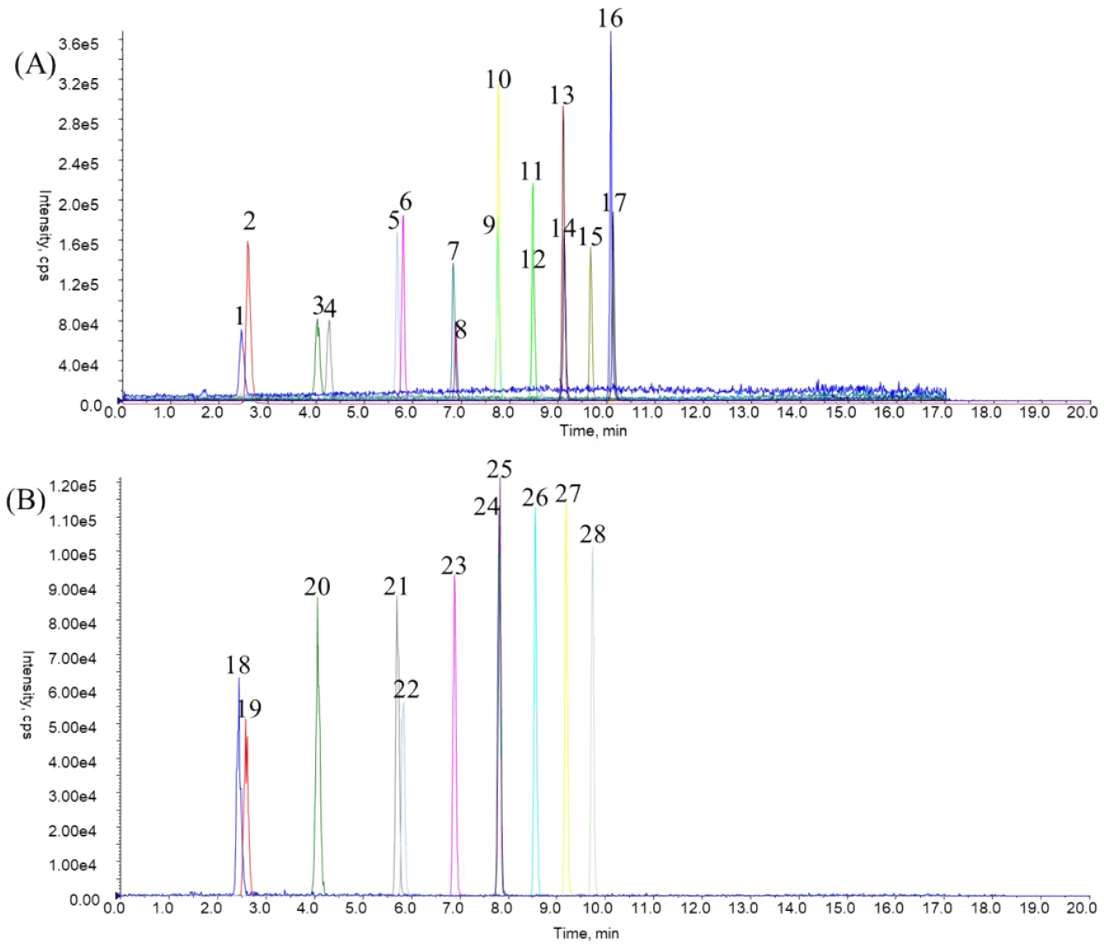

Figure S5. MRM chromatograms of 17 polyfluoroalkyl substances (A) and 11 internal standards (B) (the compound numbering refers to that in Table S1, the solvent is 50% methanol-water).

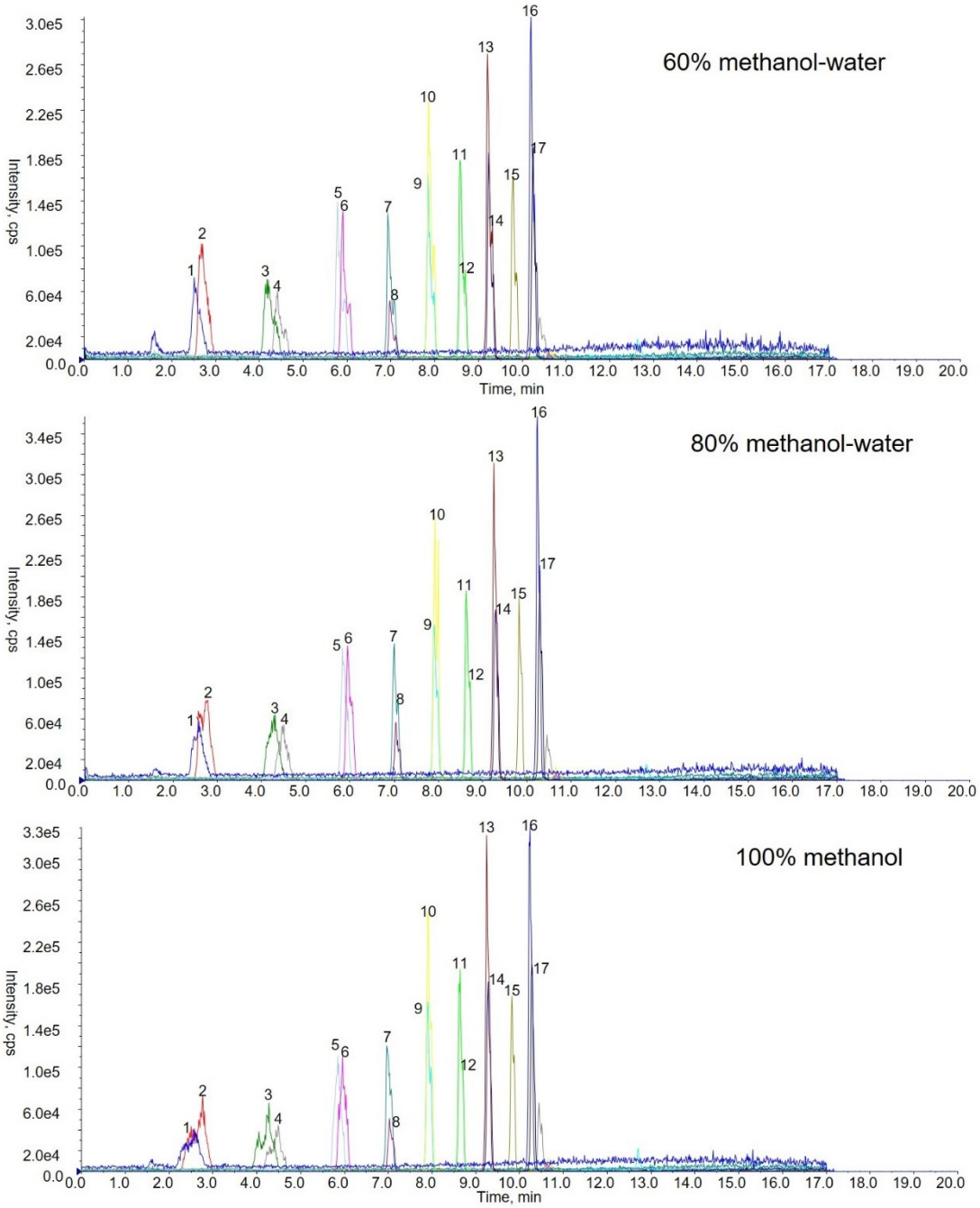

Figure S6. Peak shapes at different methanol-water ratios. (with the proportion of methanol in the solution increases, the peak shapes of PFPeA, PFBS, PFHxA, etc. get distorted peak, the compound numbering refers to that in Table S1)