Supplementary Materials

Comparison of the greenness assessment of chromatographic methods used for analysis of UV filters in cosmetic samples

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Descriptions of Methods 1-10:

Method 1 - solvent extraction followed by ultrasonication (in case of determination of the fat-soluble UV filters): 0.1 g cosmetic samples were dissolved with 25 mL of EtOH, followed by 10 min ultrasonic treatment. Next, 3 mL of the ethanolic sample stock solution was transferred to a 10 mL volumetric flask, and the flask was filled up to the mark with EtOH. Then, the extracted solvent was filtered using a 0.45 μm filter, and HPLC-UV/Vis analysis was performed (run time 40 min, 15 analytes). Additional reagents were used for HPLC analysis (mobile phase): 29.9 mL of EtOH and 10.1 mL 1% formic acid solution containing 20 mmol HP-β-CD.

Method 2 – solvent extraction followed by ultrasonication: 0.1 g cosmetic samples were dissolved with 4 mL of MeOH, followed by 30 min ultrasonic treatment. After the supernatant was collected, ultrasonic extraction was repeated twice with 3 and 2 mL of MeOH, respectively. Extracts were combined and reconstituted in 10 mL of MeOH, filtered through a 0.22 μm filter, and HPLC-MS/MS analysis was performed (run time 16.5 min, 5 analytes). Additional reagents were used for HPLC analysis (mobile phase): 2.5 mL of MeOH, and 2.5 mL of acetonitrile.

Method 3 - extraction with derivatization GC-MS/MS: 100 μL nail samples were dissolved with 700 μL of acetone, 100 μL of *N*,*O*-Bis(trimethylsilyl)trifluoroacetamide and 100 μL of internal standards. The samples were vortexed (3 min) and sonicated (20 min). The samples were again vortexed (3 min) and centrifugated (10 min). The supernatant was filtered through a 0.22 μm filter, and GC-MS/MS analysis was performed (run time 18 min , 1 analyte).

Method 4 – solid phase extraction (SPE): 0.1 g cosmetic samples were dissolved in 1000 mL of H_2O. The solutions were mixed using the magnetic stirrer for 15 min. The cartridges (C18, 1000

mg, 6 mL) were conditioned with 5 mL of ethyl acetate (EA) and 5 mL of dichloromethane (DCM). Next, extraction of 100 mL solutions were performed and the analytes were eluted with 5 mL mixture of EA/DCM (1:1, v/v). The eluates were evaporated to dryness under a gentle stream of N_2 at room temperature. The residues were redissolved in 0.5 mL of EA for GC-MS analysis (run time 20 min, 3 analytes).

Method 5 – accelerated solvent extraction (ASE) with single cell – pressurized liquid extraction (PLE): the mixture of 0.1 g cosmetic samples, 0.1 g of anhydydrate Na_2SO_4, and 0.8 g of Florisil were prepared. A cellulose filter was placed at each end of the PLE cell and the mixture was transferred to the PLE cell. Finally, the dead volume of the cell was filled with Florisil. The 10 mL of acetonitrile was used as solvent, and time of extraction was 11 min. The extracts were then derivatized by adding 0.2 mL of acetic anhydrate and 0.01 mL of pyridine. The solutions were maintained at 100°C for 60 min, and then allowed to cool down before GC-MS/MS analysis (run time 14 min, 16 analytes).

Method 6 – microextraction by packed sorbent (MEPS): 0.3 g cosmetic samples were dissolved in 500 mL of H_2O. The sorbent bed was conditioned by flushing 250 μL of EA/DCM (1:1, v/v) and 250 μL of water. Next, 2 mL of the sample was extracted – eight times × 250 μL. Then, the sorbent was washed with 250 μL of H_2O, and the cartridge was dried by pumping air through it (ten times × 250 μL). The analytes were eluted with 100 μL of EA (two times × 50μL) and GC-MS analysis was performed (run time 20 min, 3 analytes). After elution, the cartridge was washed three times with 250 μL of EA and three times with 250 μL of EA/DCM (1:1, v/v).

Method 7 – micro-matrix solid-phase dispersion (μ-MSPD): 0.1 g cosmetic samples were blended with 0.4 g of the anhydrate Na_2SO_4, and 0.4 g of the corresponding dispersing agent (Florisil or sand) until a homogenous mixture was obtained (5 min). The mixture was then

transferred into a 15 cm glass Pasteur, with glass wool at the bottom, containing 0.1 g of Florisil, and 1 mL of acetonitrile, and analyzed by GC-MS/MS (run time 27 min, 14 analytes).

Method 8 – stearic-acid-modified magnetic dispersive solid-phase microextraction (SA-MDSPME): 20 mg cosmetic samples were dissolved with 1 mL of acetonitrile, vortexed (4 min), and centrifugated (1 min). The solution was diluted 500 times with H_2O. Next, 2 mL of the sample solution was buffered with 1 mL of phosphate buffer solution (pH 2.5). The solutions were transferred into 20 mg of preconditioned SA-MNPs as adsorbent and vortexed (1 min). An external magnetic field was used to collect the analyte-rich SA-MNPs, and the supernatant was discarded. The analyte desorption was performed using 100 μL of acetonitrile as the eluent by vortex (1 min). The collected solution was diluted two times with H_2O, and analyzed by HPLC-DAD (run time 6 min, 3 analytes).

Method 9 – ultrasound-vortex-assisted dispersive liquid-liquid microextraction (US-VA-DLLME): 12.5 mg cosmetic samples were dissolved in 50 mL mixture of AC/H_2O (1:39, v/v), then 140 μL of MeOH (dispersant), and 160 μL of anisole (extractant) were added. The sample was vortexed (4 min) and ultrasonicated (3 min). The resulting cloudy solution was then centrifuged for 1 min. The 165 μL bottom phase was dried at 55°C, and the residue was re-dissolved in 20 μL of 2-vinyl naphthalene. The HPLC-DAD analysis was performed (run time 30 min, 5 analytes). Additional reagents were used for analysis (mobile phase): 7.5 mL of acetonitrile, and 0.033 mL of formic acid.

Method 10 - dynamic hollow fiber liquid-phase microextraction (dynamic HF-LPME-HPLC-UV): 0.01 g cosmetic samples were dissolved in 2 mL n-hexane. The samples were ultrasonicated (5 min) and centrifuged (3 min). The supernatant was filtered through a 0.22 μm filter dried at 60°C by nitrogen, and then sample was diluted to 100 mL with de-ionized water. In the meantime, the hollow fiber segments were ultrasonically cleaned in acetone (15

min) and then dried in the air. A disposable flow control valve line for the visiprepTM-DL as the external tube was installed on the sample injection syringe. Then an aqueous sample of 0.6 mL was loaded into the syringe. The hollow fiber attached to the microsyringe needle was inserted into the visiprep TM-DL external tube, and then 10 μL acceptor phase (toluene) was filled into the hollow fiber. The sample was continuously injected into the extractor by the pump. During the extraction, the analytes in the aqueous sample were largely extracted into the organic solvent by diffusion. The analyze-enriched acceptor phase was directly collected into the microsyringe after the extraction. Finally, 5 μL acceptor phases were used for HPLC analysis. The extraction was performed at ambient temperature (25 °C) for 10 min. The HPLC-UV analysis was performed (run time 25 min, 5 analytes). Additional reagents were used for analysis (mobile phase): a mixture of methanol-pure water (80:20, v/v).

Table S1. Results for the Methods 1-10 have been obtained from Analytical Greenness reports

Crite-rion	Criterion description	Weig-ht	Scores									
			Method 1	Method 2	Method 3	Method 4	Method 5	Method 6	Method 7	Method 8	Method 9	Method 10
1.	Direct analytical techniques should be applied to avoid sample treatment	2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
2.	Minimal sample size and minimal number of samples are goals	2	0.98	0.98	0.98	0.98	0.98	0.82	0.98	1.0	1.0	1.0
3.	If possible, measurements should be performed in situ	2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4.	Integration of analytical processes and operations saves energy and reduces the use of reagents	2	1.0	1.0	1.0	0.8	1.0	1.0	1.0	1.0	0.8	0.8
5.	Automated and miniaturized methods should be selected	2	0.0	0.0	0.0	0.0	0.25	0.5	0.5	0.5	0.5	0.75
6.	Derivatization should be avoided	2	1.0	1.0	0.51	1.0	0.37	1.0	1.0	1.0	1.0	1.0
7.	Generation of large volume of analytical waste should be avoided, and proper management of analytical waste should be provided	2	0.12	0.31	0.54	0.34	0.36	0.57	0.37	0.0	0.15	0.27
8.	Multi-analyte or multi-parameter methods are preferred versus methods using one analyte at a time	2	0.58	0.18	0.0	0.15	0.51	0.3	0.59	0.34	0.34	0.32
9.	The use of energy should be minimized	2	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.5	0.5
10.	Reagents obtained from renewable sources should be preferred	2	0.5	0.5	0.0	0.0	0.0	0.0	0.0	0.5	0.5	0.5
11.	Toxic reagents should be eliminated or replaced	2	0.0	0.15	0.51	0.15	0.19	0.48	0.2	0.26	0.0	0.12
12.	Operator's safety should be increased	2	0.8	0.8	0.8	0.8	0.6	0.8	0.8	0.8	0.6	0.6
Sum			0.48	0.43	0.39	0.38	0.38	0.48	0.48	0.52	0.47	0.51

Table S2. Results for the Methods 1-10 have been obtained from AGREEprep reports

Crite-rion	Criterion description	Weig-ht	Scores									
			Method 1	Method 2	Method 3	Method 4	Method 5	Method 6	Method 7	Method 8	Method 9	Method 10
1.	Sample preparation placement	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.	Hazardous materials	5	0.0	0.0	0.35	0.0	0.0	0.31	0.0	0.23	0.27	0.17
3.	Sustainability and renewability of materials	2	0.0	0.0	0.0	0.0	0.0	0.25	0.0	0.0	0.0	0.0
4.	Waste	4	0.06	0.23	0.44	0.2	0.23	0.49	0.24	0.0	0.0	0.44
5.	Size economy of the sample	2	1.0	1.0	1.0	1.0	1.0	0.84	1.0	1.0	1.0	1.0
6.	Sample throughput	3	0.16	0.0	0.04	0.0	0.0	0.21	0.16	0.16	0.16	0.1
7.	Integration and automation	2	0.25	0.25	0.25	0.19	0.5	0.25	0.25	0.25	0.19	0.38
8.	Energy consumption	4	1.0	0.67	0.84	0.69	0.02	0.85	1.0	1.0	0.87	0.98
9.	Post-sample preparation configuration for analysis	2	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
10.	Operator's safety	3	0.5	0.25	0.5	0.25	0.25	0.25	0.5	0.25	0.0	0.0
Sum			0.33	0.26	0.41	0.26	0.19	0.41	0.36	0.33	0.29	0.36