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1 **Optimization method for quantification of sunscreen organic ultraviolet filters in coastal**
2 **sands**

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4

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10

11 **Running title**

12 Quantification of organic UV filters in sands

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15 **List of abbreviations**

16 BEMT: *bis*-Ethylhexyloxyphenol methoxyphenyl triazine; BM: Butyl

17 methoxydibenzoylmethane; BP: Benzophenone; BP3: Benzophenone-3; BS: Butyloctyl

18 salicylate; EM: 2-Ethylhexyl 4-methoxycinnamate; ES: Ethylhexyl salicylate; FLD:

19 Fluorescence detection; HS: Homosalate; LOD: Limit of detection; LOQ: Limit of

20 quantification; MBBT: Methylene *bis*-benzotriazolyl tetramethylbutylphenol; OC:

21 Octocrylene.

22 **Keywords**

23 UV filters, extraction, quantification, liquid chromatography, mass spectrometry

24

25 **Abstract**

26 Most organic UV filters are very lipophilic and some of them are difficult to quantify in the
27 environment. This article describes a method optimization for quantification of these
28 compounds in sand samples with diverse compositions. The standard additions method was
29 used. The search for a unique HPLC method to analyze all these filters along with the search
30 for optimal detection conditions are presented in detail. The best extraction solvent was
31 methanol, and the best conditions for analysis and detection involved the use of an HPLC
32 system equipped with a biphenyl column (2.6 μm , 150 x 4.6 mm) and an Orbitrap MS
33 detector. We also demonstrated that sample freeze-drying can induce significant loss of
34 some of the UV filters.

35

36

37 1. Introduction

38

39 Emerging pollutants, such as UV filters, are of concern to legislators, industry members, and
40 consumers because of the risk of accumulation, persistence (or pseudo-persistence), and
41 the potential impact of these non-natural compounds on organisms and ecosystems. These
42 compounds are listed by the U.S. EPA as high-production volume manufactured chemicals (>
43 500 metric tons per year) and are used in a large number of cosmetic preparations and
44 industrial products. They are used in sun creams against sunburn, but also in anti-aging and
45 moisturizing products. Environmental contamination by these chemicals is often associated
46 with water and snow recreational activities, and especially with sewage discharges [1].

47 Recently, the focus of contamination has been on coral reefs, but these chemicals are found
48 in marine and aquatic environments, including Arctic and Antarctic coastlines, rivers and
49 lake systems worldwide, as well as potable water sources. Water and sediment
50 contamination is the most commonly screened sample matrix, but contaminated biological
51 matrices include corals, subsistence fish, migratory birds and their eggs, sea turtle, marine
52 mammals, vegetable produce (e.g., lettuce, tomato, cucumber), and marine algae [2–7].

53

54 In the past five years, there has been a building body of evidence that the pollution induced
55 by these chemicals threaten ecological integrity and biodiversity [4]. For example,

56 benzophenone-3 (oxybenzone; BP3) is toxic to the larval stages of both coral and fish, and
57 induces a multi-generational toxic effect from just a single exposure to the parent [8–11].

58 Octocrylene has also been shown to be environmentally toxic to coral and fish [12–14].

59 Other UV filters, such as the methoxycinnamates (octinoxate), camphors (4-methybenzyl
60 camphor), and salicylic acid derivatives (e.g., homosalate) can be toxic to early-stage

61 developmental in animals, induce cytotoxicity and genotoxicity, and are potential endocrine
62 disruptors [15–17]. Several of these UV filters exhibit acute and chronic toxicity to plants
63 and algae [18–24].

64

65 Most organic UV filters used in sunscreens are markedly lipophilic and poorly soluble in
66 water. These compounds tend to accumulate in sands and sediments [25–27], and can
67 bioaccumulate and biomagnify throughout the marine food chain, from filter feeders to
68 large predators [4,28,29].

69

70 There are persistent difficulties in the successful extraction and quantification of these
71 compounds in different environmental matrices, which can be a result of their
72 physicochemical properties and relative structural diversity. In our previous work [27], we
73 experienced difficulties in the quantification of some of the low molecular weight filters
74 such as BP3 or butyl methoxydibenzoylmethane (BM). The recovery rates of these two UV
75 filters from sediment samples were 47% and 2%, respectively. Here, we demonstrate the
76 adoption of optimizing processing steps that significantly improve the detection and
77 quantitation of several organic UV-filters.

78

79 2. Materials and methods

80

81 2.1. Chemicals and solvents

82

83 The names and molecular structures of the studied sunscreens are shown in Table 1.

84 Benzophenone (BP), methylene bis-benzotriazolyl tetramethylbutylphenol (MBBT) and
85 benzophenone-3 (BP3) were purchased from Sigma-Aldrich (Lyon, France), while bis-
86 ethylhexyloxyphenol methoxyphenyl triazine (BEMT), butyl methoxydibenzoylmethane
87 (BM), homosalate (HS), ethylhexyl salicylate (ES) and octocrylene (OC) were kindly provided
88 by Pierre Fabre Laboratories. Butyloctyl salicylate (BS) was obtained from Innospec Active
89 Chemicals. Ethylhexyl methoxycinnamate (EM) was obtained from Accustandard (Cat#
90 ALR144N). UHPLC/MS-grade acetonitrile (ACN), dichloromethane (DCM), methanol (MeOH),
91 water, isopropanol, acetone, and formic acid (98 %) were obtained from Sigma-Aldrich. To
92 avoid contamination, glassware was cleaned with dichloromethane and dried at 450 °C for 2
93 hours. Clean volcanic Hawaii sand was collected at Mau'umae Beach, island of Hawai'i,
94 Hawaii, U.S.A. Clean aragonite was collected from Children's Bay Cay, Exumas, Bahamas.
95 Fontainebleau sand was purchased from VWR (Fontenay-sous-Bois, France).

96

97 *2.2. Preparation of solutions for spiking and extraction, standard protocol*

98

99 A stock solution was prepared by dissolving ~100 mg (measured with an accuracy of 0.1 mg)
100 of each of the 10 compounds into DCM (volume adjusted at 100 mL in a volumetric flask).

101

102 Replicated sand samples were spiked with final target concentrations of 10, 50, 100, 200,
103 500 or 1000 ng/g sand by addition of a diluted solution in DCM prepared from the stock
104 solution. The dilution factor was adjusted so that 50 µL of solution was added with a glass
105 syringe to reach the targeted spiking concentration. All dilutions were made by withdrawing
106 the required volume from the stock or an intermediate solution with a glass syringe and
107 Teflon plunger and adjusting to the required volume in a volumetric flask. The withdrawn

108 solution volume was in general above 500 μL and never below 250 (250 μL to 15 mL). After
109 adding the DCM solutions into the sand (~ 2 g), the solvent was left to evaporate for 4 h at
110 room temperature under a fume hood. The extraction solutions containing the standards at
111 different concentrations were prepared in the same way by dilution of the stock solution
112 into the appropriate extraction solvents (in general MeOH, but also acetonitrile or
113 MeOH/DCM 20/80 for experiment in Table 3). The standard addition concentrations were
114 2000, 500, 200, 150, 100, 50, and 0 ng/mL, calculated exactly based on exact concentrations
115 of each compound in the stock solution.

116

117 *2.3. Tubes for extraction and standard extraction procedure*

118

119 For extraction, 7 sand samples taken from the same batch of sand (2 g, measured accurately
120 with less than 1 % difference between pseudo-replicates [*i.e.*, same sand with different
121 standard addition concentrations in extraction solutions]) were prepared in tubes and
122 covered with extraction solvent (2 mL, with 0, 50, 10, 150, 200, 500, or 2000 ng/mL of the
123 compounds to be quantified). After this, the tubes were tilted at 20° to the horizontal and
124 shaken at 110 r.p.m. for 40 h with an Infors HT Orbitron shaker; thus, they had to be
125 rigorously sealed even if the solvent did not reach the cap in this configuration. The tubes
126 used in this study were Pyrex™ borosilicate glass round bottom 16×125 culture tubes with
127 screw cap and PTFE lined rubber disc (Analytic Lab, Montpellier, France), but nearly a
128 quarter of the tubes had to be discarded because of neck deformities that prevented them
129 from being closed tightly leading to solvent evaporation and inaccurate measurements (see
130 figure S1 in supporting information).

131

132 After this time, some rare tubes may require a quick centrifugation step (typically 30 s). An
133 indefinite volume of supernatant was collected with a Pasteur pipette (roughly 0.5 mL) and
134 poured into a HPLC vial for analysis.

135

136 *2.4. HPLC method and quantification*

137

138 HPLC-UV-Fluo analyses were performed on a Dionex Ultimate 3000 system equipped with a
139 diode array and a fluorescence detector. In UV, the effluents were monitored at 254 nm for
140 BP, 357 nm for BM, and 305 nm for BEMT, BP3, EM, and MBBT. In FLD, the excitation
141 wavelength was 306 nm and the emission wavelength 450 nm for the detection of the three
142 salicylates (BS, ES, HS) [30]. HS is present as a mixture of two diastereomers. The minor one
143 eluted first and accounted for 16 % of all HS. Since the relative proportion of the minor
144 isomer was similar in all products we tested, it was possible to ignore this isomer for
145 quantification. If it is integrated neither in the standard nor in the samples, then the HS
146 concentration can be accurately measured. In HPLC-UV, the volumes injected were 5 or 15
147 μL , but in both cases the method proved to be less sensitive than UHPLC-MS, including for
148 salicylates.

149

150 UHPLC-MS analyses were conducted on an Ultimate 3000TM UHPLC system coupled to a Q
151 Exactive Focus Orbitrap spectrometer (Thermo Fisher Scientific). Analyses of extracts and
152 standards (5 μL injected) were performed in the electrospray positive ionization mode in the
153 range of 80–1200 Da in centroid mode. The tune parameters were as follows: spray voltage:
154 3.5 kV; sheath flow rate: 75; aux gas pressure: 20; capillary temperature: 350 °C; heater

155 temperature: 430 °C; S-lens RF level: 55. The analyses were conducted in FullMS mode, the
156 resolution was set to 70,000, and the AGC target was 3×10^6 .

157

158 With both HPLC and UHPLC systems, the column was a Phenomenex Kinetex Biphenyl 2.6
159 μm , 150 x 4.6 mm. The column temperature was set to 50 °C, and the flow rate was 1
160 $\text{mL}\cdot\text{min}^{-1}$. The mobile phase was a mixture of water (solution A) with increasing proportions
161 of MeOH (solution B), both solvents modified with 0.1% formic acid, and a washing mixture
162 of ACN (40 %), isopropanol (40 %) and acetone (20 %) (solution C). The gradient was as
163 follows: 40% B 5 min before injection, then from 1 to 8 min, a non-linear gradient increase
164 of B up to 100 % (curve 2), followed by 100 % B for 4 min. Then, from 12 to 14 min, a linear
165 gradient increase of C to 100%, followed by 100% C for 6 min. System washing with C
166 significantly reduced carryover of the most retained filters (mainly OC, MBBT, and BEMT –
167 see Table 2). From 20 to 22 min, an increased gradient of B to 100 % followed by 100 % B for
168 2 min prepared the system for the next injection. A gradient table and gradient figure are
169 provided in supporting information (Table S1, Figure S2). Under these conditions, the
170 pressure in the system was between 200 and 400 bars, allowing the method to be used by
171 HPLC and UHPLC applications. The flow was diverted (not injected into the mass
172 spectrometer) before injection, up to 1.5 min after injection. The detectors were on from 0
173 to 17 min. Compound retention times (t_R) are listed in Table 1.

174

175 In UV and fluorescence detection, the peaks were integrated manually. The optimal UV
176 wavelength for each compound is provided in Table 1.

177

178 In MS, the peaks were integrated automatically after smoothing (moving mean 7) using the
179 Genesis algorithm in Thermo FreeStyle®. The integrations of the most difficult peaks were
180 corrected manually if need be (salicylates, BEMT or BM). Also, the Excel pivot table tool was
181 used in the sum mode to sum all automatic integrations corresponding to one peak. This
182 was very useful for BM peak integration because BM peak was split without return to
183 baseline between the two maxima (Figure 1). The concentration calculation is detailed in
184 our previous work [31].

185

186 3. Results and discussion

187

188 *3.1. Compounds used in the study*

189

190 The present work was conducted on 9 UV filters of varying polarities (Table 1). These 9
191 compounds are amongst the most used UV filters worldwide in industry and the most
192 detected in environmental matrices (Ramos 2015). However, not all of these compounds are
193 registered as UV filters. In Europe, BS is registered as hair conditioning, skin conditioning,
194 and solvent [32]. In the USA, the FDA will produce a final monograph (as required by the
195 Sunscreen Innovation Act) which will decide on the use of 12 UV filters in different
196 formulations to be generally recognized as safe and effective (GRASE) [33]. Current public
197 records are considered by the FDA as insufficient to support positive GRASE determinations
198 for BM, BP-3, EM, ES, HS, OC. These ingredients are classified as Category III. BEMT and
199 MBBT are allowed as UV filters in Europe, but not in the USA. Benzophenone is not
200 permitted in dermatological sun creams, but it is used as a UV stabilizer in fragrances. It was

201 included in this work because it was demonstrated to accumulate upon aging in cosmetics
202 formulated with OC by two independent research groups [31,34].

203

204 *3.2. Improving HPLC method and limiting HPLC carryover*

205

206 There is likely no ideal method to analyze all these 10 compounds in a single HPLC injection.
207 Nevertheless, we have optimized the analytical conditions to drastically improve the peak
208 shape of the 10 analytes, to limit cross-contamination and to improve detection. Eventually,
209 we were able to determine that the use of a Biphenyl 2.6 μm , 150 x 4.6 mm core-shell
210 column at 50 °C was an acceptable compromise (Figure 1). We were surprised to discover
211 that the peak shapes were substantially better with methanol rather than acetonitrile as
212 eluting solvent, even for more lipophilic filters. A cleansing solvent composed of acetonitrile,
213 isopropanol, and acetone was used at the end of the analyses to reduce carryover.
214 However, a small proportion of cross-contamination could not be avoided with some of the
215 UV filters studied (Table 2). The average blank peak integration for each compound was
216 used to correct the integration values by subtraction.

217

218 In this experiment, BEMT detection was efficient, although the BEMT peak was significantly
219 tailed. However, reliable integration values could be obtained for BEMT above LOQ (Table
220 2). The other compounds yielded symmetrical peaks. One issue was the low detectability of
221 the three salicylates. These compounds fragment extensively in ESI and neither the
222 protonated molecular ion nor higher MW adducts were detected. In their MS spectrum, the
223 common major ion was at m/z 139.0390 and corresponded to protonated salicylic acid. This
224 ion was used to monitor the concentration of BS, ES, and HS. HS is commercialized as a ~9:1

225 mixture of diastereomers eluting at 7.36 and 7.22 min, respectively. The minor isomer does
226 not need to be integrated for quantification since it will also be present in the contaminated
227 sand samples in the same relative proportion.

228

229 It should be mentioned that we have also tested UV and fluorescence detection (FLD). We
230 believed that FLD in particular could significantly improve the detection and quantification
231 limits of salicylates, which absorb at 305 nm and emit at 410 nm. However, this was not the
232 case and the LOD and LOQ were higher with both UV detection and FLD for all tested
233 compounds.

234

235 For BM, the peak shape could not be improved because it results from the equilibration
236 between the different existing tautomers of BM. However, the detection of BM was very
237 sensitive and the LOD and LOQ were acceptable for environmental quantification with this
238 method.

239

240 *3.3. Optimizing extraction protocol and extraction solvent*

241

242 Usually, sand and environmental samples are homogenized and freeze-dried before
243 extraction [35–37]). The most commonly used solid-liquid extraction techniques are soxhlet,
244 microwave-assisted, ultrasound, vortex, and pressurized liquid extraction. The latter is
245 widely used for extraction and quantification of UV filters [36]. This technique has the
246 advantage of being adaptable to an automatic extractor (ASE), of using small volumes of
247 solvent, and of usually increasing the extraction rate of UV filters.

248

249 In our historical experience with environmental chemical analysis, we first extracted UV
250 filters from sand and sediments by pressurized liquid extraction with an automatic extractor
251 (ASE) using a mixture of MeOH and dichloromethane as extraction solvent. However, the
252 method proved to be unsuitable for the analysis of a very large number of samples due to
253 extraction time. For reasons that we did not understand at this time, it was not robust
254 enough. Overall, the many manipulations of the samples during extraction led to significant
255 losses and therefore low recovery rate for several compounds. An ultrasound-assisted
256 extraction was preferred, with a prior freeze-drying step. The same solvent mixture was
257 chosen and extraction was performed with a 10-minute sonication step before drying and
258 analysis of the extracts. This method resulted in recovery rates ranging from 2% (for BM) to
259 80% (for MBBT) [27]. We later discovered that the low recovery rates for some of the UV
260 filters were due to analyte evaporation, freeze-drying (see 3.4), and sample manipulation. In
261 an effort to significantly reduce the number of sample transfers and to better account for
262 the properties of the matrices to be extracted, we have developed an extraction protocol
263 using the standard addition method. In our protocol, the sand was weighed into extraction
264 tubes, the solvent was added, and the tubes were properly sealed and shaken for 40 h. Then
265 the supernatant was analyzed directly by LC-MS.

266

267 In a first step, we spiked aragonitic sand (2 g) with a concentration of 100 ng/g of each
268 compound to be determined. We extracted this sand with 3 different solvents, acetonitrile,
269 methanol, and a 2:8 mixture of methanol and dichloromethane (Table 3). Here the standard
270 addition concentrations were in the 0-200 ng/mL range, with 2 mL of each solvent added for
271 extraction. Overall, the pollutant concentration measurements with the 3 solvents were
272 quite reliable. The results were somewhat inaccurate for the salicylates (in particular BS and

273 ES), but this was because the highest standard addition concentration was 200 ng/L in this
274 experiment. The linearity was not very good in this concentration range. We will see later
275 that by adding a point at 500 ng/L, the results are more reliable. Comparing the solvents of
276 extraction, it seems that acetonitrile and methanol performed the same. The relatively
277 lower efficiency of the DCM/MeOH mixture is odd given the extraction efficiency of this
278 mixture. It could be due to the volatility of DCM. Based on this experiment, MeOH was
279 selected for further experiments. ACN would have been equally efficient.

280

281 The advantage of the standard addition method is that it allows each analyte to be
282 quantified as an internal standard. It can therefore be used even when labeled internal
283 standards (labeled with ^{13}C or D) are not available. However, the method is very sensitive to
284 the slope of the linear regression and any outlier must be discarded. It is also important to
285 ensure that the measured concentrations are within the linearity range of the method; the
286 previous experiment demonstrated that the ideal standard addition concentration range is
287 not the same for all compounds. In the next experiment, we tested the impact of different
288 standard addition concentration ranges (0-200, 500 or 2000 ng/mL, *i.e.*, 0-400, 1000 or 4000
289 ng) on the results obtained for different sand nominal pollutant concentrations (Table 3).

290

291 Overall, the dataset in Table 4 demonstrates that the standard addition range has a strong
292 impact on the accuracy of the quantifications, and that the impact is not the same for all
293 compounds. The highest standard addition concentration (4000 ng), and sometimes the
294 second-highest one were not well aligned for some of the UV filters (with 5 μL injected on
295 column), thereby artificially increasing the experimental result at the lowest nominal
296 concentrations. This was the case for BM, BP3, EM, ES, HS and OC. For these compounds,

297 standard additions in the 0-400 ng range are satisfactory unless the nominal concentration
298 in the sand is higher than 200 ng/g. Although the salicylates signal in ESI⁺ is somewhat weak,
299 the results obtained with ES and HS were satisfactory even when the sand nominal
300 concentration was below the LOD (Table 2). Nonetheless, and based on our various
301 experiments, it seems prudent to keep a point at 1000 ng (500 ng/mL) in the standard
302 additions for ES and HS. In this way, the linear regression line can be calculated with two
303 points above LOD. This would reduce the variability compared to a linear regression
304 calculated on a maximum concentration of 200 ng/mL (400 ng). The example of BS is
305 remarkably clear. BS can only be quantified accurately with the 1000 ng point, in which case
306 the quantification is acceptable even at low nominal concentrations in sand.

307

308 Another limitation is in the quantification of BEMT and OC, which are not accurate below
309 200 and 100 ng, respectively. Finally, the case of BP and MBBT is interesting. For both
310 compounds, the range of 0-400 ng for the standard additions was satisfactory for
311 quantification, even at high nominal concentrations. This is due to the good linearity of the
312 MS response in the full concentration range. Overall, for these two molecules, we
313 recommend using the standard addition range of 0 to 400 ng for 2 g of sand at least up to
314 the nominal concentration of 1,000 ng/g sand, with 2 g sand in the experiment. In the event
315 that the nominal concentration would be higher, it would be possible to use less sand in the
316 extraction as long as the weight accuracy is satisfactory.

317

318 At last, it should be mentioned that three different sands were tested for extraction
319 (aragonite, Fontainebleau sand, and a volcanic sand collected in Hawaii) and no differences
320 were observed in the extraction efficiency and quantification results (data not shown).

321

322 *3.4. Freeze-drying can alter quantification data*

323

324 Freeze-drying of wet samples is useful because it allows for the determination of the dry
325 mass of sample to be extracted. Moreover, it is commonly believed that the extraction yield
326 is better on a freeze-dried sample. As mentioned previously, we suspected for some time
327 that evaporation or freeze-drying steps might decrease the UV filter recovery rates in some
328 cases due to partial evaporation or sublimation of the compounds to be tested [4]. We
329 tested this hypothesis with the 10 compounds used in this work. Sand samples were spiked
330 at 400 ng (200 ng/g), humidified with pure water, and freeze-dried for 2 days. The
331 quantification results with and without freeze-drying are provided in Figure 2.

332

333 Without freeze-drying, the results are all close to the expected spiking concentration of 400
334 ng/2 g sand. With freeze-drying, some of the UV filter concentrations decrease significantly.
335 This phenomenon is pronounced for BM, BP, BS, EM, ES, and HS, with a loss of more than
336 50% of the nominal amount in the aragonitic sand sample. This clearly demonstrates that
337 freeze-drying is not always an acceptable option. The choice of whether or not to freeze-dry
338 a sample should be made with the knowledge that a significant proportion of certain
339 compounds may be lost in the process. Nevertheless, the contamination data calculated
340 from dry matter weight remains the standard. In this context, it is possible to weigh the wet
341 sand and then freeze-dry all the samples after extraction in order to recalculate the dry
342 mass concentrations. Any excess water can be removed by laying the sample out on filter
343 paper.

344

345 Finally, it is reasonable to postulate that the effect of freeze-drying will not always be
346 identical depending on the nature of the sample to be extracted. In particular, it can be
347 assumed that more lipophilic animal tissues will retain more of these notoriously lipophilic
348 UV filters.

349

350 **4. Concluding remarks**

351

352 In conclusion, we were able to establish a general method for the determination of UV filter
353 concentrations in samples derived from diverse coastal sand compositions. The HPLC system
354 uses a biphenyl column, methanol as eluting solvent, and mass spectrometric detection. The
355 extraction is better performed with methanol. The standard addition method was used and
356 this work established the concentrations range to be used according to the nature of the
357 pollutant to be quantified and its nominal concentration in the environmental sample.
358 Finally, sample freeze-drying may not be a good option for the quantification of more
359 volatile UV filters such as BM, BP, BS, EM, ES, and HS.

360

361 **Declaration of competing interest**

362

363 The authors declare no competing financial interest.

364

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366

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371

372 **Conflict of interest statement**

373

374 The authors have declared no conflict of interest.

375

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377

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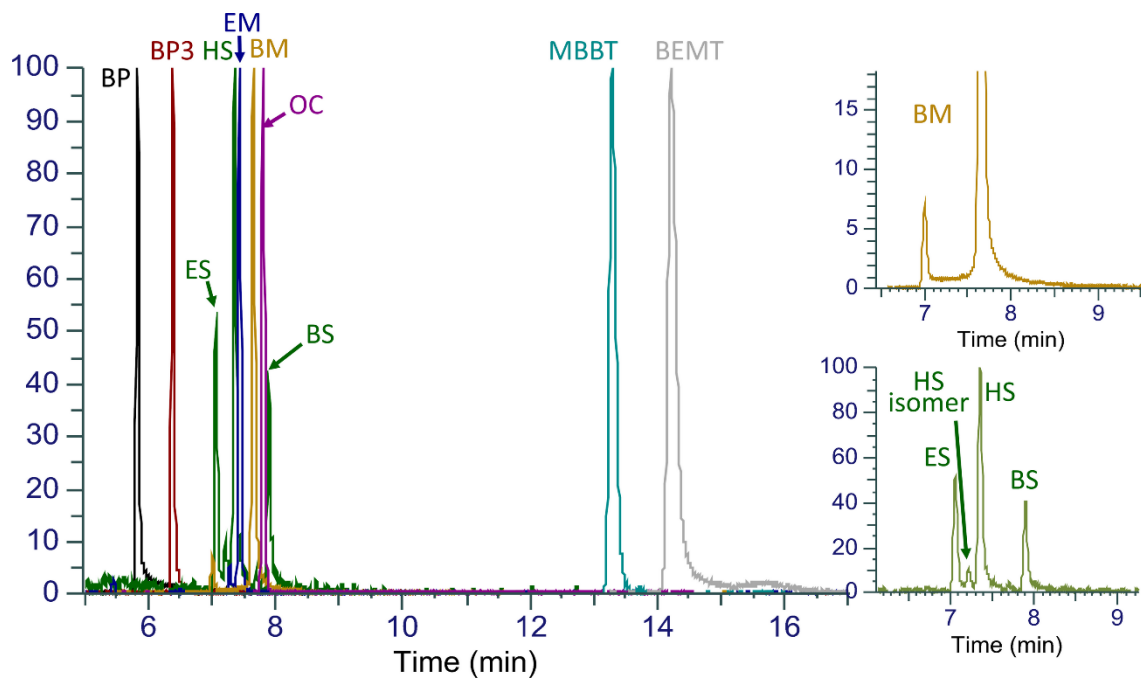
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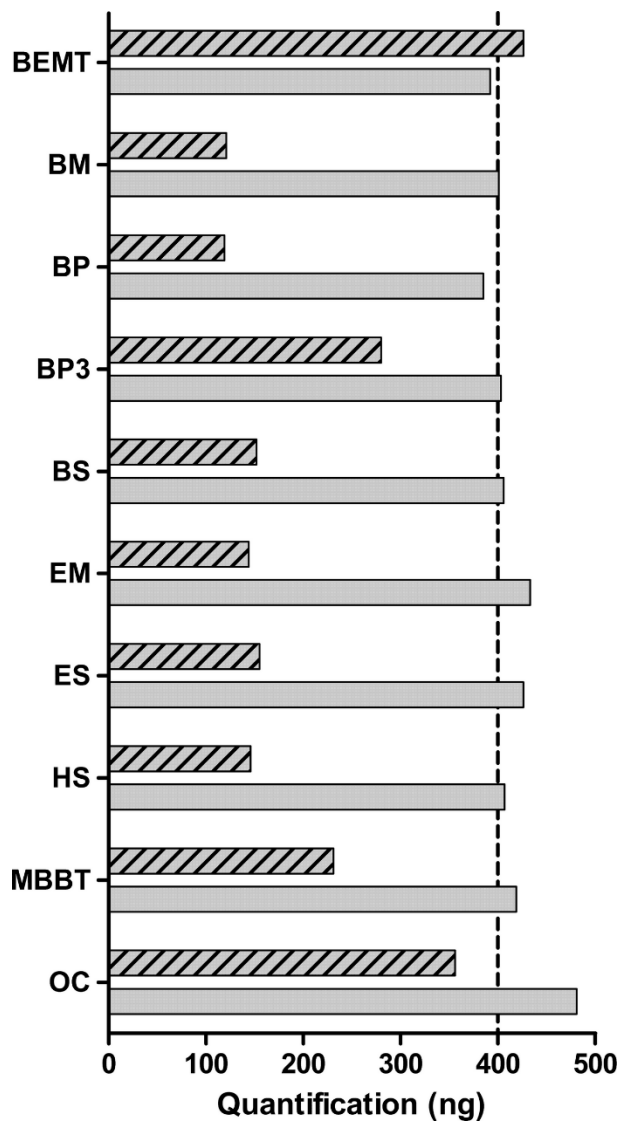
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501 **FIGURE 1** Extracted ion chromatograms for the 10 studied compounds after optimization of
 502 analytical conditions, injection 500 ng/mL, 5 μ L. On the top right, expansion of BM peak
 503 baseline (20 % of the y-axis). On the bottom right, expansion of the salicylates extracted ion
 504 chromatogram at m/z 139.0390.

505



506

507 **FIGURE 2** Compared quantification accuracy. Freeze-dried samples are indicated in the grey-

508 hatched bars. Samples not subject to freeze-drying are indicated in the solid-black bars.

509 Sample matrix was aragonitic sand spiked with 200 ng/g per analyte.

510

511

512 **TABLE 1** UV filters used in this study

Abbr.	CosIng name ^a	Alternative names ^b	Formula	CAS	Monitored ion in MS	t _R (min)	UV/FLD (nm)
BEMT	bis-Ethylhexyloxyphenol methoxyphenyl triazine	Bemotrizinol, Tinosorb S	C ₃₈ H ₄₉ N ₃ O ₅	18739 3-00-6	628.3748 [M+H] ⁺	13.73	340
BM	Butyl methoxydibenzoylmethane	Avobenzone, 4- <i>tert</i> -Butyl-4'-methoxydibenzoylmethane	C ₂₀ H ₂₂ O ₃	70356 -09-1	311.1644 [M+H] ⁺	7.51	357
BP	Benzophenone	Diphenylketone	C ₁₃ H ₁₀ O	119- 61-9	183.0805 [M+H] ⁺	5.76	254
BP-3	Benzophenone-3	Oxybenzone, 2-Hydroxy-4-methoxybenzophenone	C ₁₄ H ₁₂ O ₃	131- 57-7	229.0860 [M+H] ⁺	6.29	254
BS	Butyloctyl salicylate	2-Butyloctyl 2-hydroxybenzoate	C ₁₉ H ₃₀ O ₃	19008 5-41-7	139.0390 (frag.)	7.76	λ _{abs} 306 λ _{em} 450
EM	Ethylhexyl methoxycinnamate	Octinoxate, Octyl methoxycinnamate	C ₁₈ H ₂₆ O ₃	83834 -59-7	291.1955 [M+H] ⁺	7.31	305
ES	Ethylhexyl salicylate	Octyl salicylate, Octisalate	C ₁₅ H ₂₂ O ₃	118- 60-5	139.0390 (frag.)	6.94	λ _{abs} 306 λ _{em} 450
HS	Homosalate		C ₁₆ H ₂₂ O ₃	118- 56-9	139.0390 (frag.)	7.24	λ _{abs} 306 λ _{em} 450
MBBT	Methylene bis-benzotriazolyl tetramethylbutylphenol	Bisotrizole Tinosorb M Parsol Max	C ₄₁ H ₅₀ N ₆ O ₂	10359 7-45-1	659.4068 [M+H] ⁺	12.88	305 nm
OC	Octocrylene	Octocrilene, Uvinul N-539	C ₂₄ H ₂₇ NO ₂	6197- 30-4	384.1933 [M+Na] ⁺	7.68	305 nm

^a International Nomenclature of Cosmetic Ingredients
^b International Nonproprietary Names (INN), International Nomenclature of Cosmetic Ingredients (INCI), Commercial names, or names from the "Food and Drug Administration (FDA) proposed rule for sunscreen drug products for over the counter human use", published in 2019.

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514

515 **TABLE 2** Carryover, peaks tailing factor, limit of detection (LOD) and limit of quantification
 516 (LOQ) for all compounds tested

	Carryover (%)	Tailing factor	LOD (vial, ng/mL)	LOQ (vial in ng/mL, or sand in ng/g)
BEMT	0.3	2.0	4.3	43
BM	<0.1	1.4	6.8	68
BP	2.2	1.2	1.4	14
BP3	0.1	1.2	1.8	18
BS	0.0	0.9	18.7	187
EM	0.5	1.1	1.8	18
ES	0.0	1.0	18.6	186
HS	0.0	1.3	14.4	144
MBBT	0.1	1.4	7.0	70
OC	1.4	1.1	4.6	46

517

518 **TABLE 3** Compared extraction solvents efficiency

	Extraction solvent:			
	ACN	MeOH	MeOH-DCM	
	Theor. (ng) ^a	Exp. (ng) ^b	Exp. (ng) ^b	Exp. (ng) ^b
BEMT	201	185	183	133
BM	200	193	182	176
BP	199	163	162	136
BP3	203	199	200	162
BS	205	359	302	299
EM	207	198	189	184
ES	201	462	228	218
HS	201	217	228	267
MBBT	208	228	230	170
OC	199	232	217	248

519 ^a Theoretical amount based on sand spiking (ng for 2 g of sand)

520 ^b Experimental quantification measured by the standard additions method

521

522

523 **TABLE 4** Compared quantification of the tested compounds at different sand spiked
 524 concentrations and impact of the standard addition maximum concentrations. The correct
 525 results are in bold.

SA range (ng) ^a		Spiking ^b						
		0 ng	20 ng	100 ng	200 ng ^c	400 ng	1000 ng	2000 ng
BEMT	0-400	259	161	56	183	555	1028	1914
	0-1000	87	192	249		392	1076	2220
	0-4000	221	186	369		530	760	2681
BM	0-400	0	19	99	182	387	1005	1960
	0-1000	9	31	105		401	1018	2301
	0-4000	58	68	148		487	1018	2366
BP	0-400	-1	18	90	162	362	920	1877
	0-1000	0	28	92		372	969	2208
	0-4000	24	20	78		385	881	2091
BP3	0-400	5	22	102	200	403	1072	2205
	0-1000	8	35	108		461	1037	2241
	0-4000	36	59	135		467	1601	2271
BS	0-400	13	11	134	302	388	771	2549
	0-1000	3	25	105		406	1043	2568
	0-4000	6	29	46		327	659	1756
EM	0-400	6	35	67	189	486	1083	2419
	0-1000	1	38	131		433	1015	2515
	0-4000	34	43	160		462	1586	2363
ES	0-400	-1	28	129	228	526	968	1609
	0-1000	12	51	97		426	927	2625
	0-4000	41	23	104		357	660	2117
HS	0-400	9	34	122	228	394	928	2511
	0-1000	6	36	115		407	1065	2258
	0-4000	22	2	101		372	610	2048
MBBT	0-400	9	24	101	230	419	1028	2075
	0-1000	10	40	130		441	1064	2546
	0-4000	61	73	164		511	1408	2394
OC	0-400	16	70	125	217	452	1232	3731
	0-1000	38	77	130		481	1158	2368
	0-4000	136	156	223		624	1461	2694

526 ^a Standard addition range with 2 mL of solvent. 0-400: 0, 50, 100, 150, 200 ng/mL; 0-1000: 0-400 + 500 ng/mL;
 527 0-4000: 0-1000 + 2000 ng/mL.

528 ^b Theoretical sand spiking amount, for 2 g sand.

529 ^c This column is from Table 3, for comparison.

530