An Overview of the Analytical Methods for the Determination of Organic Ultraviolet Filters in Cosmetic Products and Human Samples

Izabela Narloch and Grażyna Wejnerowska *

Department of Food Analysis and Environmental Protection, Faculty of Chemical Technology and Engineering, UTP University of Science and Technology, 3 Seminaryjna Street, 85-326 Bydgoszcz, Poland; izabela.narloch@utp.edu.pl
* Correspondence: grazyna.wejnerowska@utp.edu.pl; Tel.: +48-52-374-90-41

Abstract: UV filters are a group of compounds commonly used in different cosmetic products to absorb UV radiation. They are classified into a variety of chemical groups, such as benzophenones, salicylates, benzotriazoles, cinnamates, p-aminobenzoates, triazines, camphor derivatives, etc. Different tests have shown that some of these chemicals are absorbed through the skin and metabolised or bioaccumulated. These processes can cause negative health effects, including mutagenic and cancerogenic ones. Due to the absence of official monitoring protocols, there is an increased number of analytical methods that enable the determination of those compounds in cosmetic samples to ensure user safety, as well as in biological fluids and tissues samples, to obtain more information regarding their behaviour in the human body. This review aimed to show and discuss the published studies concerning analytical methods for the determination of organic UV filters in cosmetic and biological samples. It focused on sample preparation, analytical techniques, and analytical performance (limit of detection, accuracy, and repeatability).

Keywords: analytical methodologies; cosmetics products; human samples; organic ultraviolet filters; sample preparation

1. Introduction

In recent decades, there has been a progressive increase in UV radiation due to the depletion of the stratospheric ozone layer. This promotes an increase in the number of harmful effects on human health such as skin burns, skin photoaging, damage to the skin’s immunological system, pterygium, or skin cancer [1,2]. Accordingly, the number of personal care products containing UV filters has increased rapidly to protect human skin from damaging exposure to sunlight. The currently estimated volume production of UV filters reaches 26.9 million tons [3]. UV filters are frequently added to all types of personal care products such as lotions, shampoos, creams, aftershave products, make-up products, etc. [4–6].

The European Union (EU) Regulation 1223/2009—Cosmetics Regulation defines UV filters as “substances which are exclusively or mainly intended to protect the skin against certain UV radiation by absorbing, reflecting or scattering UV radiation” [7]. UV filters are classified into two groups: organic (chemical) UV filters, which absorb UV light, as well as inorganic (physical) UV filters, which reflect and scatter UV radiation. Chemical UV filters are organic molecules capable of absorbing high UV-A and UV-B range radiation. The UV filters have one or more benzene rings and sometimes are conjugated with carbonyl groups [8]. They can be classified into different groups according to their chemical structure: benzophenone derivatives, p-aminobenzoic acid and its derivatives, salicylates, cinnamates, camphor derivatives, triazine derivatives, benzotriazole derivatives, benzimidazole derivatives, and others (Table 1) [9]. One of the most widely used family
of UV filters are benzophenones, in particular BP-3, which in 2012 was classified by the US Environmental Protection Agency (US EPA) as “high production volume chemical” [3]. The scale of the problem of the existence of UV filters in the environment was presented by Astle et al. [3], who performed research among Swiss sunbathers on the use of UV filters during one tourist season. On their basis, it was estimated that about 1249 kg of ethylhexyl methoxycinnamate, 152 kg of octocrylene, 145 kg of 4-MBC, and 122 kg of avobenzene were released into Lake Zürich. Therefore, these compounds are the most frequently determined UV filters.

To protect consumers’ health, the substances that can be used as UV filters in personal care products and their maximum allowed concentrations are strictly defined in each country [8]. The European Union regulations permit the use of 29 UV filters in cosmetics in concentrations ranging from 2 to 25% (Table 1). However, only two are inorganic (titanium dioxide and zinc oxide) [7]. Organic UV filters have a hydrophilic or lipophilic character and most of them are classified as water-resistant [8].

Despite the limitations on their use in UV filters, there are no established official analytical methods for the determination of these compounds in cosmetics products. However, to maintain the safety and adequate effectiveness of products containing UV filters, analytical methods should be developed to control the content of UV filters in them [10].

Moreover, due to the daily use of cosmetics containing UV filters, such compounds are absorbed through the skin into the body, where they can be metabolized and eventually bioaccumulated and/or excreted. The dermal absorption may result in harmful health effects like dermatitis but also more serious effects, such as mutagenic, cancerogenic, and/or estrogenic activity [11]. Therefore, because of the adverse effects of UV filters on human health and their potential bioaccumulation, such biological samples as urine, plasma, breast milk, semen, or tissues must be checked for their presence.

In this context, this review aimed to provide a comprehensive overview of the developments related to the determination of UV filters in cosmetic samples and biological fluids and tissues, with special emphasis on sample preparation and analytical techniques, as well as the achieved detection limits, accuracy, and repeatability.

2. Analytical Methods for UV Filter Determination in Cosmetic Samples

2.1. Sample Preparation

Cosmetic sample preparation depends on sample type, target analytes, and the technique that is to be used. In general, the preparation of a cosmetic sample does not require a complex pre-treatment sample. This is because the UV filter content in the cosmetic samples is at a sufficiently high level for the sample treatment not to require the extraction and concentration steps. Additionally, in most cases (approximately 90%), liquid chromatography is used for analysis, which enables direct analysis of matrices such as cosmetics. It was alleged that in recent decades the methods of determining UV filters in cosmetics have not been modified too much [11,12].

The initial preparation of the sample consists of dissolving a cosmetic sample in a carefully selected solvent (typically ethanol, methanol, ethyl acetate, water, tetrahydrofuran). The step of dissolving the cosmetic sample may be preceded by homogenisation. Depending on the cosmetic product’s type (i.e., consistency), the next steps in the procedure may include sonicating the sample for a few minutes (5–30 min, 40 °C) [10,13–33], magnetic mixing [34,35], mechanical shaking [20,36], vortexing (3–4 min), [25,29,32,37], or centrifuging (1–20 min, 3500–14,800 rpm) [14,19,20,25,27,29,32,33], which can help accelerate the solubilisation. The obtained supernatant is often filtered as well (e.g., 0.45 µm nylon membrane filter) [10,13–18,21–26,37] and/or evaporated [19,25,27,29,33,38].
| Chemical Name                                      | INCI Name       | Abbreviation | CAS Number | Structure | Max. Concentration (%) | Log K_{ow} | pK_a | Solubility (g/L) |
|---------------------------------------------------|-----------------|--------------|------------|-----------|------------------------|------------|------|-----------------|
| **Benzophenone derivatives**                      |                 |              |            |           |                        |            |      |                 |
| 2-Hydroxy-4-methoxybenzophenone/Oxybenzone        | Benzophenone-3  | BP-3         | 131-57-7   |           | 10                     | 3.79       | 7.56 | 0.21            |
| 2-Hydroxy-4-benzophenone-5-sulfonic acid and its sodium salt/Sulisobenzoate | Benzophenone-4, Benzophenone-5 | BP-4, BP-5 | 4065-45-6/6628-37-1 |           | 5 (as acid)            | 0.37       | −0.70 | 0.65            |
| Benzoic acid, 2-[4-(diethylamino)-2-hydroxybenzoyl]-hexylester | Diethylamino Hydroxybenzoyl Hexyl Benzoate | DHHB | 302776-68-7 |           | 10                     | 6.54       | 7.29 | 9.5 \times 10^{-4} |
| **p-Aminobenzoic acid derivatives**               |                 |              |            |           |                        |            |      |                 |
| Ethoxylated ethyl-4-aminobenzoate                 | PEG-25 PABA     | PEG-25 PABA  | 116242-27-4|           | 10                     | −0.66      | -    | -               |
| 2-Ethylhexyl-4-(dimethylamino)benzoate/Padimate O (USAN:BAN) | Ethylhexyl Dimethyl PABA | OD-PABA | 21245-02-3 |           | 8                      | 6.15       | 2.39 | 0.0021          |
| **Salicylates**                                    |                 |              |            |           |                        |            |      |                 |
| Benzoic acid, 2-hydroxy-3,3,5-trimethylcyclohexyl ester/Homosalate | Homosalate     | HS           | 118-56-9   |           | 10                     | 6.16       | 8.09 | 0.02            |
Table 1. Cont.

| Chemical Name | INCI Name a | Abbreviation | CAS Number | Structure | Max. Concentration (%) | Log \( K_{\text{ow}} \) a | \( p_{\text{Ka}} \) a | Solubility (g/L) \( \text{ab} \) |
|---------------|-------------|--------------|------------|-----------|------------------------|-------------------------|----------------|------------------------|
| 2-Ethylhexyl salicylate/Octisalate | Ethylhexyl Salicylate | EHS | 118-60-5 | ![Structure](image1.png) | 5 | 5.97 | 8.13 | 0.028 |
| 2-Ethylhexyl-4-methoxycinnamate/Octinoxate | Ethylhexyl Methoxycinnamate | OMC | 5466-77-3 | ![Structure](image2.png) | 10 | 5.8 | - | 0.15 |
| Isopentyl-4-methoxycinnamate/Amiloxate | Isoamyl p-Methoxycinnamate | IMC | 71617-10-2 | ![Structure](image3.png) | 10 | 4.33 | - | 0.06 |
| 2-Phenyldibenzimidazole-5-sulfonic acid and its potassium, sodium, and triethanolamine salts/Ensulizole | PhenylDibenzimidazole Sulfonic Acid | PMDSA | 27503-81-7 | ![Structure](image4.png) | 8 (as acid) | -0.16 | -0.87 | 0.26 |
| Sodium salt of 2,2′-bis(1,4-phenylene)-1H-benzimidazole-4,6-disulfonic acid/Bisdisulizole | Disodium Phenyl Dibenzimidazole Tetrasulfonate | DPDT | 180898-37-7 | ![Structure](image5.png) | 10 (as acid) | -6.79 | -0.27 | 0.5 |
| Phenol,2-(2H-benzotriazol-2-yl)-4-methyl6-(2-methyl-3-(1,3,3,3-tetramethyl-1-trimethylsilyl)oxy)-disiloxanyl)propyl | Drometrizole Trisiloxane | DTS | 155633-54-8 | ![Structure](image6.png) | 15 | 10.38 | 1.2 | \( 5.5 \times 10^{-10} \) |
Table 1. Cont.

| Chemical Name                                                                 | INCI Name \(^a\) | Abbreviation | CAS Number       | Structure     | Max. Concentration (%) | Log \(K_{ow} \) \(^a\) | \(pK_a \) \(^a\) | Solubility (g/L) \(^{ab}\) |
|-------------------------------------------------------------------------------|-------------------|--------------|------------------|---------------|------------------------|-----------------|----------------|-----------------|
| 2,2’-Methylene-bis[6-(2H-benzotriazol-2-yl)-4-[1,1,3,3-tetramethylbutyl]phenol]/Bisocitrizole |                   | MBP          | 103597-45-1      | ![Structure](structure1.png) | 10                     | 12.46           | 7.56           | 3 \times 10^{-6} |

Camphor derivatives

| N,N,N-Trimethyl-4-(2-oxoborn-3-ylidenemethyl)anilinium methyl sulfate      | Camphor Benzalkonium Methosulfate | CBM          | 52793-97-2      | ![Structure](structure2.png) | 6                      | 0.28            | -              | 0.007           |

| 3,3’-(1,4-Phenylenebis[bis[hept-1-ylmethanesulfonic acid]]-2,2',7,7-dimethyl-2-oxobicyclo[2,2,1]hept-3-yl)methanesulfonic acid and its salts/Camphor Sulfonic Acid | Terephthalylidene Dicamphor Sulfonic Acid | PDSA | 92761-26-7, 90457-82-2 | ![Structure](structure3.png) | 10 (as acid) | 3.83            | -1.05           | 0.014           |

| Alpha-(2-Oxoborn-3-ylidene)-toluene-4-sulphonic acid and its salts         | Benzyldiene Camphor Sulfonic Acid | BCSA        | 56039-58-8      | ![Structure](structure4.png) | 6 (as acid) | 2.22            | -0.7            | 0.038           |

| 3-(4-Methylbenzylidene)-d1 camphor/Enzacamene                              | 4-Methylbenzylidene Camphor       | 4-MBC        | 38102-62-4/36861-47-9 | ![Structure](structure5.png) | 4                      | 4.95            | -              | 0.0051          |
Table 1. Cont.

| Chemical Name                                                                 | INCI Name a | Abbreviation | CAS Number   | Structure | Max. Concentration (%) | Log Kow b | pKa c | Solubility (g/L) ab |
|------------------------------------------------------------------------------|-------------|--------------|--------------|-----------|------------------------|-----------|------|-------------------|
| Polymer of N-[2 and 4]-[(2-oxoborn-3-ylidene)methyl-benzyl] acrylamide        | Polyacrylamidomethyl Benzylidene Camphor | PBC          | 113783-61-2 |           | 6                      | -         | -    | -                 |
| Benzoic acid, 4,4-((6-((4-((1,1-dimethyllethyl)amino)carbonyl)phenyl)amino)-1,3,5-triazine-2,4-diyl)dimino)bis-bis (2-ethylhexyl) ester/ Iscotrizinol (USAN) | Diethylhexyl Butamido Triazone | DBT          | 154702-15-5 |           | 10                     | 14.03     | 3.04 | 4.6 \times 10^{-7} |
| 3,3′-(1,4-Phenylene)bis(5,6-diphenyl-1,2,4-triazine)                          | Phenylene Bis-Diphenyl triazine     | -            | 55514-22-2  |           | 5                      | -         | -    | -                 |
| 2,4,6-Triamino-(p-carbo-2'-ethylhexyloxy)-1,3,5-triazine                       | Ethylhexyl Triazone                | ET           | 88122-99-0  |           | 5                      | 17.05     | 3.17 | -                 |
| 2,2′-(6-(4-Methoxyphenyl)-1,3,5-triazine-2,4-diyl)bis(2-ethylhexyloxyphenol)/ Bemotrizinol | Bio-Ethylhexyloxyphenol Methoxyphenyl Triazine | EMT          | 187393-00-6 |           | 10                     | 8.03      | 6.37 | 4.9 \times 10^{-8} |
## Table 1. Cont.

| Chemical Name | INCI Name | Abbreviation | CAS Number | Structure | Max. Concentration (%) | Log $K_{ow}$ | $pK_a$ | Solubility (g/L) $^{ab}$ |
|---------------|-----------|--------------|------------|-----------|------------------------|-------------|-------|-------------------------|
| Butyl Methoxydibenzoyl-methane | BMP | 70356-09-1 | | | 5 | 4.51 | 9.74 | 0.037 |
| Octocrylene | OC | 6197-30-4 | | | 10 (as acid) | 6.88 | - | $2 \times 10^{-4}$ |
| Polyisilicone-15 | BMP | 207574-74-1 | | | 10 | - | - | - |
| Methoxypropylamino | 1419401-88-9 | | | | 3 | - | - | - |

$^a$ From Cadena-Aizaga M.I. et al. [39]. $^b$ Solubility in water at 25°C.
These procedures are aimed at completely dissolving the sample or leaching the target analytes (e.g., in case of difficult-to-dissolve samples such as wax-balms, lipsticks, or foundations containing insoluble compounds). The achieved high recoveries (Table 2), amounting from 80 to 113%, confirm the effectiveness of these procedures.

Table 2. Published studies on UV filters determination in cosmetic samples.

| UV Filters | Matrix | Analytical Technique | Analytical Performance | Ref. |
|------------|--------|----------------------|------------------------|------|
| BP-3, IMC, MBC, DHHB, OC, EHS, HS, DBT, ET, DTS, MBP, EMT | Sunscreens, facial creams, lip balms, after shave creams | LC-UV/Vis; type of column: C<sub>18</sub>; column temperature: 60 °C; mobile phase: ethanol/formic acid (aq); mobile phase modifier: hydroxypropyl-β-cyclodextrin (HP-β-CD) | LOD: 0.02–0.22 µg mL<sup>−1</sup>; LOQ: 0.07–0.74 µg mL<sup>−1</sup>; R: 98–104%; RSD: 0.9–7.1% | [10] |
| PMDSA, BP-4, BP-3, MBC, DHHB, EMC, OC, MBP, EMT, ET, BDM | Emulsion, oil | HPLC-UV/Vis; type of column: C<sub>4</sub> or C<sub>18</sub>; column temp.: 35 °C; mobile phase: gradient acetonitrile/perchloric acid (aq) or isocratic methanol/acetonitrile or isocratic methanol/perchloric acid (aq) | LOD: 0.1–1.2 µg mL<sup>−1</sup>; LOQ: no data; R: 93.9–103.4%; RSD: 0.2–1% | [13] |
| BP-1, BP-2, BP-3 | Emulsion | MEKC-UV/Vis; type of capillary: a 51 cm uncoated fused-silica; surfactant: sodium tetraborate containing sodium dodecyl sulfate | LOD<sub>10</sub>: 3.90 × 10<sup>−8</sup>–10<sup>−7</sup> mol/L; LOD: no data; LOQ: no data; R: 89.5–102.5%; RSD: 1.14–8.09% | [14] |
| PMDSA, PABA, BP-4, BP-3, IMC, MBC, OC, EMC, HS, EHS, MBBT | Creams, lotions, foundation, loose powder, lipstick | HPLC-UV/Vis; type of column: C<sub>18</sub>; column temp.: 40 °C; mobile phase: gradient ethanol/tetrahydrofuran/perchloric acid (aq) | LOD: 0.04–1.66 µg mL<sup>−1</sup>; LOQ: 0.13–5.52 µg mL<sup>−1</sup>; R: 97–101.4%; RSD: 0.38–2.42% | [15] |
| PMDSA, BP-3, IMC, DHHB, OC, EMC, EHS, BDM, DBT, ET, MBP, EMT | Emulsion, sticks, powder | HPLC-UV/Vis; type of column: C<sub>18</sub>; column temp.: 30 °C; mobile phase: gradient ethanol/1% phosphoric acid (aq) | LOD: 200–500 ng mL<sup>−1</sup>; LOQ: 700–6700 ng mL<sup>−1</sup>; R: 98.5–102.2%; RSD: 0.51–1.72% | [16] |
| HS, EDP, EHC, EHS, MBC, BDM, BP-3, OC, PHBA, BC | Cream, milk, lotion, oil, lipstick | DART-MS (ESI<sup>+</sup>) | LOD: 2.5–460 ng g<sup>−1</sup>; LOQ: no data; R: 71–120%; RSD: 4–30% | [17] |
| EMC, IMC, EHS, MBC, BP-3, EDP, OC, BDM | Cream, lotion, spray | HPLC-UV/Vis; type of column: C<sub>18</sub>; column temp.: 30 °C; mobile phase: gradient acetonitrile/acetic acid (aq) | LOD: 0.03–1.5 mg L<sup>−1</sup>; LOQ: 0.08–4.6 mg L<sup>−1</sup>; R: 98–102%; RSD: 0.97–6.1% | [18] |
| BP-4, BP-3, ODP, OMC, EHS | Cream, lotion, lipstick, foundation | HPLC-UV/Vis; type of column: C<sub>18</sub>; column temp.: 40 °C; mobile phase: gradient methanol/pure water (80:20; v/v) | LOD: 1–100 ng L<sup>−1</sup>; LOQ: 4–340 ng L<sup>−1</sup>; R: 98–102%; RSD: 4.5% | [19] |
| OC | Emulsion | SWV/mercury electrode; a mixture of Britton–Robinson (BR) buffer and ethanol (7:3; v/v) as the supporting electrolyte | LOD: no data; LOQ: no data; R: 9.7–106%; RSD: 1–3.42% | [20] |
| EMC, BP-3, EHS, OC | Emulsion | LC-UV/Vis; type of column: C<sub>18</sub>; mobile phase: methanol/water (85:15; v/v) | LOD: no data; LOQ: no data; R: 99.67–101%; RSD: 0.04–1.5% | [21] |
| UV Filters | Matrix | Analytical Technique | Analytical Performance a | Ref. |
|------------|--------|----------------------|--------------------------|------|
| BDM, BP-3, EMC | Cream | HPTLC-DS.; type of column: C<sub>18</sub> or silica gel; mobile phase: acetonitrile/water (18:2) or cyclohexane/diethyl ether/n-hexane/acetone (14:2:1:2) | LOD: no data; LOQ: no data; R: 92.7–102.4%; RSD: no data | [22] |
| PABA, PMDSA, BP-3, MBC, BP-4, OC, EDP, EMC, BDM, HS, EHS, DBT, ET, DTS | Cream | HPLC-UV/Vis; type of column: C<sub>18</sub>; mobile phase: gradient ethanol/phosphate buffer | LOD: 0.01–1.99 mg L<sup>−1</sup>; LOQ: 0.02–6.02 mg L<sup>−1</sup>; R: 90.91–109.98%; RSD: 0.16–12.69% | [23] |
| BP-3, BP-4 | Shampoo, gel, perfume, cream | MEKC-UV/Vis; type of capillary: a 64.5 cm uncoated fused-silica; surfactant: sodium dodecyl sulfate/γ-cyclodextrin | LOD: 0.91–2.26 µg mL<sup>−1</sup>; LOQ: 2.72–6.79 µg mL<sup>−1</sup>; R: 90.4–107.4%; RSD: 5.7–12% | [24] |
| BP-3, BP-4, BP-6, BP-8, OC, EMC, PABA | Lotion, cream | MEKC-UV/Vis; type of capillary: a 30.2 cm uncoated fused-silica; surfactant: sodium dodecyl sulfate | LOD: no data; LOQ: no data; R: 90.4–107.4%; RSD: no data | [25] |
| BP-3, BP-3, IMC, MBC, OC, EHS, EMC, BDM, HS | Cream | HPLC-UV/Vis; type of column: C<sub>18</sub>; column temp.: 35 °C; mobile phase: isocratic ethanol/acetic acid (aq) (70:30; v/v) | LOD: no data; LOQ: no data; R: 95.08–104.57%; RSD: no data | [26] |
| BP-3, EMC, OC, EHS, MBC, EDP | Cream, lipstick, blemish balm cream | LTP-MS | LOD: no data; LOQ: no data; R: no data; RSD: 0.8–28.6% | [27] |
| PMDSA, BP-2, BP-1, BP-8, BP-6, BP-3, EHS, BP-10, HS, IMC, BDM, DHHB, BDM, BP-12 | Lotion, cream, lipstick | HPLC-MS/MS (ESI); type of column: C<sub>18</sub>; column temp.: 30 °C; mobile phase: gradient methanol/0.1% ammonium hydroxide (aq) | LOD: 2–20 mg kg<sup>−1</sup>; LOQ: 5–50 mg kg<sup>−1</sup>; R: 86.9–103.5%; RSD: 1–6.8% | [28] |
| EHS, EMC, BP-3, OC, EMT, BDM, DHHB, ET, DBT | Cream | UHPSFC-PDA; type of column: Torus 2-PIC; column temp.: 40 °C; mobile phase: gradient CO<sub>2</sub>/methanol/water/ammonium acetate | LOD: 0.2–1.7 mg kg<sup>−1</sup>; LOQ: 1–10.8 mg kg<sup>−1</sup>; R: 97.5–103.2%; RSD: 0.7–1.6% | [29] |
| BP-1, BP-2, BP-3, BP-8, HBP | Toothpaste, shampoo, face cleansers, sunscreens, body lotions, gels, hair gels, lotions, mask, hand sanitizer | HPLC-MS/MS (ESI); type of column: C<sub>18</sub>; column temp.: 40 °C; mobile phase: gradient methanol/acetonitrile/water | LOD: 0.002–0.197 ng mL<sup>−1</sup>; LOQ: 0.001–0.059 ng mL<sup>−1</sup>; R: 61.9–116%; RSD: no data | [30] |
| BP-1 | Nail product | GC-MS/MS (EI<sup>+</sup>); type of column: ZB-SemiVolatiles; oven temp.: 40 °C/2 min—5 °C/1 min to 65 °C—50 °C/1 min to 300 °C/5 min | LOD: 18.3–2370 µg g<sup>−1</sup>; LOQ: no data; R: 101–105%; RSD: 0.69–1.13% | [31] |
| BDM, EMT, OMC, OC, ET | Lotion | HPLC-UV/Vis; type of column: C<sub>18</sub>; mobile phase: acetonitrile/0.25% formic acid (aq) | LOD: 15 ng mL<sup>−1</sup>; LOQ: no data; R: 88.1–104.7%; RSD: 0.8–5.4% | [32] |
| BDM | Emulsion | LC-UV/Vis; type of column: C<sub>18</sub>; column temp.: 42 °C; mobile phase: acetonitrile/0.5% phosphoric acid (aq) | LOD: 0.05796 µg mL<sup>−1</sup>; LOQ: 0.19322 µg mL<sup>−1</sup>; R: no data; RSD: 0.46–2.83% | [33] |
### Table 2. Cont.

| UV Filters            | Matrix                        | Analytical Technique                  | Analytical Performance | Ref. |
|-----------------------|-------------------------------|---------------------------------------|------------------------|------|
| EMC, MBC, BP-1, BP-2, | Cream, nail polish, lipstick, | GC-MS/MS (EI); type of column: SLB-5 ms; | LOD: 0.0027–0.56 µg g⁻¹ | [35] |
| BP-6, BP-4, OC, PABA, | hair gel                      | oven temp.: 100 °C/1 min—25 °C/1 min—290 °C/5 min | LOQ: 0.009–1.9 µg g⁻¹ |      |
| EDP, EHS, HS, IMC, BP-3, |                               |                                       | R: 37.4–110.5%         |      |
| BP-8, BS, MA          |                               |                                       | RSD: 3.9–9.1%          |      |
| ET                   | Cream, lotion                 | TLC-DS; type of layer: silica gel; mobile phase: cyclohexanediethyl ether (1:1) | LOD: 0.03 µg spot⁻¹ |      |
| PMDSA, BDM, OC, EHS  |                               |                                       | LOQ: 0.1 µg spot⁻¹     |      |
|                     |                               |                                       | R: 95–105%             |      |
|                     |                               |                                       | RSD: 4.5–5%            |      |
| EMR, MBC, BP-1, BP-2, | Lipsticks, hair gel, cream,   | HPLC-MS/MS; type of column: C₁₈; oven temp.: 30 °C; mobile phase: gradient methanol/0.1% formic acid/ammonia (aq) | LOD: 0.0039–0.031 µg g⁻¹ | [36] |
| BP-6, BDM, BP-4, PMDSA, | nail polish                   |                                       | LOQ: 0.0013–0.1 µg g⁻¹ |      |
| MA, OC, EDP, IMC, BP-3, |                               |                                       | R: 81.7–102%           |      |
| BP-8                 |                               |                                       | RSD: 4.5–13%           |      |
| BDM, BP-3, EMC, EMT  | Emulsion                      | HPLC-UV/Vis; type of column: C₁₈; column temp.: 25 °C; mobile phase: gradient tetrahydrofuran/acetonitrile/acetic acid (aq) | LOD: no data | [37] |
|                     |                               |                                       | LOQ: no data           |      |
|                     |                               |                                       | R: 90.3–113.2%         |      |
|                     |                               |                                       | RSD: 2.8–5%            |      |
| BP-4                 | Shampoo                       | TLC-UV/Vis; type of layer: silica gel 60 plates; mobile phase: acetate/ethanol/water/phosphate buffer (15:7:5:1; v/v/v/v) | LOD: 0.03 µg spot⁻¹ | [38] |
| EHS, EMC, BP-3, OC,  | Cream                         | SFC-UV/Vis; type of column: 2-ethyl pyridine; column temp.: 30 °C; mobile phase: gradient CO₂/methanol/ethanol (97:1.5:1.5) | LOD: no data | [40] |
| BDM, DHHB, ET, DBT   |                               |                                       | LOQ: no data           |      |
|                     |                               |                                       | R: no data             |      |
|                     |                               |                                       | RSD: no data           |      |

* LOD and LOQ expressed as: w/w when referred to sample or w/v when referred to sample solution.

Despite the UV filters being the basic components of the samples, no special extraction techniques are needed. However, some authors proposed the use of extraction techniques such as pressurised liquid extraction [35,38], cloud point extraction [14], dispersive liquid–liquid microextraction [27], or hollow fibre liquid-phase microextraction [19].

### 2.2. Analytical Techniques

Since the UV filters are part of the cosmetic products, their determination by direct measurement without a prior separation step is impossible. As such, chromatography methods are typically used. The most common chromatographic technique for determining UV filters is liquid chromatography; this is because UV filters have very high boiling points. In the majority of publications, the reversed-phase liquid chromatography coupled with a UV/Vis spectrometry detector with a single wavelength or with a diode-array is commonly used for this purpose. The application of a diode-array detector makes it possible to receive the whole UV spectrum for all peaks. The most used stationary phase is the traditional octadecylsilica type (C18), but octysilica (C8) and amide (C16) have been used as well [9]. In the case of reversed-phase separations, the most used solvents include water, methanol, tetrahydrofuran, acetonitrile, or their mixtures. The more environmentally friendly analytical methods include using the ethanol–water mixture in the mobile phase [6,12,19,22]. Isocratic or gradient elution modes are practised as well. Some substances can be added to the eluent to cut back peak tailing, such as acetic acid in the case of BP-3 [14,35]. Such reagents as phosphate, sodium acetate, and ammonium...
acetate are used for buffering. Hydroxypropyl-β-cyclodextrin is used as a mobile phase modifier to improve the resolution between varied analytes [6].

Therefore, gas chromatography is used in derivatization procedures with silylating reagents that can increase UV filter volatility, as well as sensitivity. Some publications [32,35] describe the use of gas chromatography coupled with mass spectrometry with electron impact, with N,O-Bis(trimethylsilyl) trifluoroacetamide and acetic anhydride used as the derivatizing reagents.

Apart from liquid and gas chromatography, there are also a few other separation techniques. One of them is micellar electrokinetic chromatography [14,24,25,27], which utilises uncoated silica capillaries and sodium dodecyl sulphate as a surfactant. Others include thin-layer chromatography [22,36,37,41], supercritical fluid chromatography [30,42], and square wave voltammetry [20]. Table 2 shows the published reports on the determination of individual UV filters, including the sample preparation step and the analytical methodology, as well as the results obtained in terms of the limits of quantification, recovery method, and its precision.

3. Analytical Methods for UV Filter Determination in Biological Samples

Upon classifying published studies dealing with the determination of UV filters in human samples according to the studied matrix (Tables 3–5), it is clearly visible that the most studied biological matrix is urine (~61%), followed by blood, plasma, or serum (~20%). Other matrices such as milk (~7%), tissues (~5%), and nail, semen, or saliva (~8%) have only been analysed intermittently (Figure 1).

![Figure 1. Biological sample types in the determination of UV filters.](image)

To date, most research work is focused on the analysis of BP-3 and its metabolites, which have been widely determined in all types of biological samples. Other UV filters that have been analysed, albeit less often, include EMC, OMC, PABA, BDM, EDP, ES, HS, TDS, etc.

3.1. Sample Preparation

To determine UV filters in biological samples, the extraction (~75%) and microextraction (~25%) techniques have been used (Figure 2). Extraction techniques include liquid–liquid extraction (LLE) (~28%), solid-phase extraction (SPE) (~28%), fabric phase sorptive extraction (FPSE) (~5%), as well as the less frequently used accelerated solvent extraction (ASE); microwave-assisted digestion/extraction (MAE); microporous membrane liquid–liquid extraction (MMLLE); matrix solid–phase dispersion (MSPD); sequential injection solid-phase extraction (SI SPE); Quick, Easy, Cheap, Effective, Rugged, and Safe Extraction (QuEChERSExtraction); solid–liquid extraction (SLE); ultrasound-assisted extraction (UAE); and ultrasound-assisted dispersive solid-phase extraction (USAD-SPE) (each ~2%).
In the last decades, a gradual increase in the use of microextraction methods for the isolation and enrichment of analytes in the tested samples has been observed. In the work of Jiménez-Díaz et al. from 2014 [43] on methods for determining UV filters in human samples, the contribution of microextraction methods was only about 7%. Microextraction techniques include the dispersive liquid–liquid microextraction (DLLME) (~10%), as well as the less frequently employed air-assisted liquid–liquid microextraction (AALLME), bar adsorptive microextraction (BAμE), hollow-fibre liquid-phase microextraction (HFLPME), microextraction by packed sorbent (MEPS), stir bar sorptive extraction (SBSE), single-drop microextraction (SDME), solid-phase microextraction (SPME), microextraction using a monolithic stirring extraction unit (MUMSEU), and vortex-assisted dispersive liquid–liquid microextraction (VADLLME) (each of them accounts for ~2%) (Figure 3).

![Figure 2. Division of analytical techniques into extraction and microextraction techniques.](image)

![Figure 3. Microextraction techniques used for the determination of UV filters in biological samples.](image)

Urine is the most frequently analysed sample. In urine, the compounds usually occur in free and conjugated forms; hydrolysis is often required to determine their total content (free plus conjugated). Without the hydrolysis step, it is only possible to determine the content of the free ones. The difference between free and conjugated content gives the total conjugated content. Older studies typically used 6 M hydrochloric acid to hydrolyse the bounded compounds [44,45]. Today, enzymatic hydrolysis is achieved by incubating a urine sample with β-glucuronidase or with β-glucuronidase/sulfatase (under specific conditions such as pH, temperature, and time) [46–68]. After enzymatic hydrolysis, the enzyme is denatured by treated with cold acetonitrile, methanol, or acetic acid to stop the reaction and then separated by centrifugation. The supernatant undergoes the next sample preparation step.

Table 3 summarises the extraction techniques used in the methods for determining UV filters in urine published in the literature. Liquid–liquid extraction (LLE) [51,55,57,58,63,66,69] and solid-phase extraction (SPE) [46–50,56,59,62,64,65,70–72] are the most popular extraction techniques used to determine the UV filters. Accelerated solvent extraction (ASE) [62],...
Table 3. Published papers on UV filters determination in urine.

| UV Filters | Extraction Technique | Analytical Technique | Analytical Performance | Comments | Ref. |
|------------|----------------------|----------------------|-----------------------|----------|------|
| BP-3       | SPE (C$_{18}$)       | HPLC-UV/Vis; type of column: C$_{18}$; mobile phase: isocratic methanol/water (70:30) | No data | Total content | [44] |
| BP-3       | SPE (Bond Elut Certify LRC) | UPLC-MS/MS (ESI$^+$); type of column: Kinetex Phenyl-Hexyl; column temp.: 35 °C; mobile phase: water/acetonitrile/acetic acid (aq) | LOD: 0.3–0.5 ng mL$^{-1}$ LOQ: no data R: 97–105% RSD: 1.7–20% | Total and free forms content | [46] |
| BP-3       | Online SPE (RP$_{18}$) | HPLC-MS/MS (APCI$^+$/ESI$^-$); type of column: RP$_{18}$; mobile phase: gradient methanol/water | LOD: 0.2 ng mL$^{-1}$ LOQ: no data R: 96% RSD: 9.03–11.7% | Total content | [50] |
| BP-1, BP-2, BP-8, 4-OH-BP | LLE (solvent: ethyl acetate) | HPLC-MS/MS (ESI$^+$ / ESI$^-$); type of column: C$_{18}$; mobile phase: methanol/water (90:10; v/v) | LOD: no data LOQ: 0.7–2.0 ng mL$^{-1}$ R: 84–112% RSD: no data | Total content | [51] |
| BP-3       | SDME (acceptor phase:[C$_{6}$MIM][PF$_{6}$]; 25 min; 900 rpm) | LC-UV; type of column: RP$_{18}$; mobile phase: ethanol/1% acetic acid aq (60:40; v/v) | LOD: 1.3 ng mL$^{-1}$ LOQ: no data R: no data RSD: 6% | Free forms | [52] |
| BP, BP-OH, 2-OH-BP, BP-3, BP-10 | SBSE (PDMS; 60 min; 500 rpm) | GC-MS; type of column: DB-5 ms; oven temp.: 40 °C/1 min—5 °C/1 min to 190 °C—15 °C/1 min to 280 °C/3 min | LOD: 0.05–0.1 ng mL$^{-1}$ LOQ: 0.2–0.5 ng mL$^{-1}$ R: 98.7–101.7% RSD: 1.5–4.8% | Free forms | [53] |
| BP, BP-OH, 2-OH-BP, BP-3, BP-10 | HFLPME (toluene; 15 min; 500 rpm) | GC-MS (EI); type of column: DB-5 ms; oven temp.: 40 °C/1 min—5 °C/1 min to 190 °C—15 °C/1 min to 280 °C/4 min | LOD: 5–10 pg mL$^{-1}$ LOQ: 21–50 pg mL$^{-1}$ R: 89.3–100.2% RSD: 2.5–9.3% | Total content | [54] |
| BP-1, BP-3, BP-8, BP-2, 4-OH-BP | LLE (solvent: 50% MTBE/ethyl acetate) | HPLC-MS/MS (ESI$^+$); type of column: C$_{18}$; mobile phase: gradient methanol/water | LOD: 0.08–0.28 mg mL$^{-1}$ LOQ: 0.28–0.9 mg mL$^{-1}$ R: 85.2–99.6% RSD: 2.8–4.5% | Total content | [55] |
| BP-1, BP-3, BP-8, THB | SPE (C$_{18}$) | LC-MS/MS (ESI$^+$); type of column: Mediterranean SEA 18; mobile phase: gradient methanol/water/0.1% formic acid aq | LOD: 1 ng mL$^{-1}$ LOQ: 2.4 ng mL$^{-1}$ R: 84–111% RSD: no data | Total content | [56] |
### Table 3. Cont.

| UV Filters                          | Extraction Technique | Analytical Technique | Analytical Performance | Comments                  | Ref.  |
|-------------------------------------|----------------------|----------------------|------------------------|---------------------------|-------|
| BP-1, BP-2, BP-3, BP-8, 4-OH-BP     | LLE (solvent: 50% MTBE/ethyl acetate) | HPLC-MS/MS (ESI); type of column: C18; mobile phase: gradient methanol/water | LOD: 0.013–0.28 ng mL\(^{-1}\) | LOQ: no data | R: 85.2–99.6% | RSD: 1.4–4.5% | Total content | [57] |
| BP-1, BP-2, BP-3, BP-7, 4-OH-BP, 4-MBP, 4-MBC, 3-BC | LLE | On-line TurboFlow-LC–MS/MS; type of column: TurboFlow Cyclone P and Hypersil Gold aQ | LOD: 0.2–1.0 ng mL\(^{-1}\) | LOQ: no data | R: 77.1–108% | RSD: 5.7–15.1% | Total and free form content | [58] |
| EDP                                | Automated SPE (C\(_{18}\) HD) | LC-MS/MS (ESI\(^{+}\)); type of column: Mediterranean SEA C\(_{18}\); mobile phase: gradient methanol/acetonitrile/water/0.2% formic acid | LOD: 0.3–1.1 ng mL\(^{-1}\) | LOQ: 0.9–3.5 ng mL\(^{-1}\) | R: 91–107% | RSD: no data | Total and free forms content | [59] |
| BP-3, OMC, OS, HS                  | LLE (solvent: acetonitrile) | HPLC-DAD; type of column: C\(_{18}\); mobile phase: gradient methanol/water (75:25; v/v) | LOD: 0.03–0.2 µg mL\(^{-1}\) | LOQ: 0.1–0.4 µg mL\(^{-1}\) | R: 86.8–92.2% | RSD: 3.0–4.4% | Total content | [60] |
| BP-1, BP-2, BP-3, BP-8, 4-OH-BP    | DLLME (disperser solvent: acetone; extraction solvent: trichloromethane) | UHPLC-MS/MS | LOD: 0.1–0.2 ng mL\(^{-1}\) | LOQ: 0.3–0.6 ng mL\(^{-1}\) | R: 88–104% | RSD: 0.5–22.5% | Total and free forms content | [61] |
| BP-3, 4-MBC, HS, OC                | ASE & SPE | GC-MS/MS | LOD: 0.47–0.59 pg mL\(^{-1}\) | LOQ: no data | R: 70.5–110.7% | RSD: <5.04% | Total and free forms content | [62] |
| BMDDBM, CDAA, EHS, 5-OH-EHS, OC    | LLE (solvent: acetonitrile) | LC-LC-MS/MS (ESI); type of column: RP-18 ADS; mobile phase: gradient methanol/water/trichloromethane | LOD: 0.1–1.5 µL\(^{-1}\) | LOQ: 0.2–4.1 µL\(^{-1}\) | R: 94.2–113.6% | RSD: 2.6–16.5% | Total content | [63] |
| 5OH-EHS, 5oxo-EHS, 5cx-EPS         | Online SPE (TurboFlow Phenyl) | HPLC-MS/MS (ESI); type of column: XDB-C18; mobile phase: gradient acetonitrile/water/0.05% acetic acid | LOD: no data | LOQ: 0.01–0.15 µg mL\(^{-1}\) | R: 96–106% | RSD: 1.2–2.4% | Total and free forms content | [64] |
| BP-3                                | Online SPE (RP\(_{18}\)) | HPLC-MS/MS (ESI); type of column: XDB-C18; mobile phase: gradient methanol/water | LOD: 0.16 µg L\(^{-1}\) | LOQ: no data | R: 101% | RSD: 5% | Total and free forms content | [65] |
| BP-1, BP-2, BP-3, BP-8, 4-OH-BP    | LLE (solvent: ethyl tert-butyl ether/ethyl acetate (5:1; v/v)) | UHPLC-TQMS (ESI\(^{+}\)); type of column: C\(_{18}\); mobile phase: gradient methanol/water/acetonitrile | LOD: 0.01–0.2 ng mL\(^{-1}\) | LOQ: no data | R: 90.7–110.1% | RSD: 6.9–14.2% | Total and free forms content | [66] |
| BP-1, BP-2, BP-3, BP-8, 4-OH-BP    | VADLLME (disperser solvent: 2-propanol; extraction solvent: dichloromethane) | LC-MS/MS; type of column: C\(_{18}\); mobile phase: gradient methanol/water/acetonitrile | LOD: 0.02–0.03 ng mL\(^{-1}\) | LOQ: 0.05–0.4 ng mL\(^{-1}\) | R: no data | RSD: 1.2–12% | Total content | [67] |
| BP-1, BP-2, BP-3, BP-8, 4-OH-BP    | AALLME (extraction solvent: 1.2-dichloroethane) | LC-MS/MS (ESI); type of column: C\(_{18}\); mobile phase: water/methanol | LOD: 0.02–0.06 ng mL\(^{-1}\) | LOQ: 0.05–0.20 ng mL\(^{-1}\) | R: no data | RSD: <15% | Total content | [68] |
| PABA, 4-AHA, 4-AM, 4-OCH\(_{3}\)-AHA | LLE & SPE (solvent: ethyl acetate; C\(_{18}\)) | HPLC-ECD; type of column: C\(_{18}\); mobile phase: methanol/phosphate buffer (pH 5.5) (20:80; v/v) | LOD: no data | LOQ: 0.04–0.18 ng mL\(^{-1}\) | R: 96–99% | RSD: 0.2–3.8% | Total content | [69] |
| BP-1, BP-3                          | SPE (C\(_{3}\)) | HPLC-UV; type of column: C\(_{18}\); mobile phase: acetonitrile/water | LOD: 2–40 ng mL\(^{-1}\) | LOQ: no data | R: no data | RSD: 6.6–13% | Total and free form content | [70] |
The liquid–liquid extraction is a time-consuming technique, which requires large volumes of organic solvents, and is not automated. It uses different types of organic solvents such as ethyl acetate, a mixture of methyl tert-butyl ether: ethyl acetate, ethanol, methanol, and acetonitrile. The solid-phase extraction is used in manual mode or an online configuration or in commercially available automated workstations. Octadecyl silica sorbents (C18) are widely used for UV filter analysis using SPE in manual mode; divinylbenzene/N-vinylpyrrolidone copolymer (HLB) is an alternative option in this regard. The microextraction techniques are based on the equilibrium processes. Additionally, solid-phase microextraction (SPME) is based on the division of the analyte between the urine sample and a sorbent such as carbowax-DVB fibre. Stir-bar sorptive extraction (SBSE) uses the polymer coating of polydimethylsiloxane as a sorbent. Another microextraction technique is the microextraction by packed sorbent (MEPS), which uses the C18 sorbent to extract analytes. Yet another technique is the dispersive liquid–liquid microextraction (DLLME), which uses solvents (dispersing—acetone and extracting—trichloromethane). Different microextraction methods include hollow-fibre liquid-phase microextraction (HFLPME),

| UV Filters | Extraction Technique | Analytical Technique | Analytical Performance | Comments | Ref. |
|------------|----------------------|----------------------|------------------------|----------|------|
| PMDSA      | Online SPE           | SIA-FL               | LOD: 12 ng mL\(^{-1}\) | Free forms | [71] |
|            |                      |                      | LOQ: no data R: no data RSD: 2-13% |          |      |
| PEG-25 PABA| SPE (C\(_{18}\))     | LC-FL; mobile phase: dimethylfuran | LOD: 2.6 ng mL\(^{-1}\) | Total content | [72] |
|            |                      |                      | LOQ: no data R: 91–100% RSD: 3–10% |          |      |
| BP-4, 4-DHB, BP-2, BP-1, BP-8, BZ | FPSE | HPLC-PDA; type of column: C\(_{18}\); mobile phase: methanol/phosphate buffer (pH 3) (45:55; \(v/v\)) | LOD: 0.03 μg mL\(^{-1}\) | Total content | [73] |
|            |                      |                      | LOQ: 0.1 μg mL\(^{-1}\) R: no data RSD: 2.3–14.4% |          |      |
| EDP        | In-vial MMLLE (hydrophobic PTFE membranes) | GC-MS; type of column: SPB-5; oven temp.: 60 °C/1.5 min—30 °C/1 min to 275 °C/20 min | LOD: no data | Total content | [74] |
|            |                      |                      | LOQ: 0.11 µg L\(^{-1}\) R: no data RSD: 7.4% |          |      |
| BP-3, BP-4 | SI SPE (C\(_{18}\) and diethylaminopropyl) | LC/UV; type of column: RP\(_{18}\); mobile phase: ethanol/acetate buffer/1% acetic acid | LOD: 30–60 ng mL\(^{-1}\) | Total content | [75] |
|            |                      |                      | LOQ: no data R: no data RSD: 6–13% | Free forms |      |
| BP-1, BP-2, BP-8, 4-OH-BP | MEPS (C\(_{18}\)) | LC-MS/MS; mobile phase: water/methanol | LOD: 0.005–0.03 ng mL\(^{-1}\) | Total and free forms content | [78] |
|            |                      |                      | LOQ: 0.02–0.10 ng mL\(^{-1}\) R: 18–118% RSD: 1–16% |          |      |
| BP-1, BP-3, BP-8 | SPME (Carbowax/DVB) | GC-MS; type of column: DB5-MS; Oven temp.: 50 °C/0.1 min—30 °C/1 min to 150 °C/18 °C/1 min to 250 °C/1 min to 275 °C/20 min | LOD: 5–10 ng mL\(^{-1}\) | Total content | [79] |
|            |                      |                      | LOQ: no data R: no data RSD: 5–8% |          |      |
| BP, BP-1, BP-3, 4-OH-BP | BAµE | HPLC-DAD; type of column: Sea-18; mobile phase: methanol/water (75:25; \(v/v\)) | LOD(P2): <1.0 µg L\(^{-1}\) | Total content | [76] |
|            |                      |                      | LOQ(P2): <0.3 µg L\(^{-1}\) LOD(AC4): <1.5 µg L\(^{-1}\) LOQ(AC4): <0.4 µg L\(^{-1}\) |          |      |
| OMC, BP-3, OC, OS, HS | DLLME (disperser solvent: carbon tetrachloride; extraction solvent: acetonitrile) | HPLC-DAD; type of column: C\(_{18}\); mobile phase: isocratic water/methanol/acetonitrile (8:42:50; \(v/v/v\)) | LOD: no data | Total content | [77] |
|            |                      |                      | LOQ: 3–45 ng mL\(^{-1}\) R: 86.9–97.3% RSD: 0.1–6.4% |          |      |
| BP-1, BP-2, BP-3, BP-8, 4-OH-BP | Microextraction using a monolithic stirring extraction unit (150 min; 1100 rpm) | UPLC-DAD; mobile phase: acetonitrile/water | LOD: 1–10 µg L\(^{-1}\) | Total content | [80] |
|            |                      |                      | LOQ: 5–20 µg L\(^{-1}\) R: 71–114 % RSD: 5.6–9.1% |          |      |
based on the use of polypropylene porous hollow fibre, air-assisted liquid-liquid microextraction (AALLME), bar adsorptive microextraction (BAµE), single-drop microextraction (SDME), and vortex-assisted dispersive liquid–liquid microextraction (VADLLME). The final steps are attaining lyophilisation and redissolution of the residue in the solvent.

When examining plasma or serum, blood must undergo additional treatment to isolate them (Table 4). Plasma also includes large proteins such as albumin or immunoglobulin. Such treatment consists in the centrifugation of fresh blood with the addition of an anticoagulant. Serum, however, is prepared by centrifuging blood samples without anticoagulant. To determinate the total compound content, the hydrolysis step must be performed with either acid [81] or an enzyme solution [82–85]. In the case of blood, serum, or plasma samples, protein precipitation is commonly used to reduce matrix interferences. This is performed by mixing the sample with such organic solvents as acetonitrile [60,63,86], methanol [73,81], acetone [83], or formic acid [84,85]. Proteins are denatured, precipitated, and separated through centrifugation.

Table 4. Published studies on UV filters determination in blood, plasma, and serum.

| UV Filters | Matrix            | Extraction Technique                                      | Analytical Technique                        | Analytical Performance | Comments                  | Ref. |
|------------|-------------------|----------------------------------------------------------|--------------------------------------------|------------------------|---------------------------|------|
| BP-3, BP-1, BP-8 | Serum            | DLLME (disperser solvent: acetonitrile; extraction solvent: chloroform) | LC-MS/MS (ESI⁺); type of column: C₁₈; mobile phase: gradient methanol/water/0.1% formic acid | LOD: 7–8 µg L⁻¹  LOQ: 22–28 µg L⁻¹  R: 77–104%  RSD: 8–9% | Total content | [45] |
| BP-3, OMC, OS, HS | Plasma           | LLE (solvent: acetonitrile)                               | HPLC-DAD; type of column: C₁₈; mobile phase: gradient methanol/water (75:25; v/v) | LOD: 0.03–0.2 µg mL⁻¹  LOQ: 0.1–0.4 µg mL⁻¹  R: 90.8–103.8%  RSD: 2.1–4.4% | Total content | [60] |
| BP-3, OMC, OS, HS | Bovine serum albumin | LLE (solvent: acetonitrile)                               | HPLC-DAD; type of column: C₁₈; mobile phase: gradient methanol/water (75:25; v/v) | LOD: 0.03–0.2 µg mL⁻¹  LOQ: 0.1–0.4 µg mL⁻¹  R: 97.9–102.3%  RSD: 1.2–3.3% | Total content | [60] |
| BP-1, BP-2, BP-3, BP-6, BP-8, 4-OH-BP | Menstrual blood | DLLME (disperser solvent: acetonitrile; extraction solvent: trichloromethane) | UHPLC-MS/MS (ESI); type of column: C₁₈; mobile phase: chloroform | LOD: 0.2–0.3 ng mL⁻¹  LOQ: no data  R: 97–100%  RSD: 2.8–1.59% | Total and free forms content | [82] |
| BP-1, BP-2, BP-3, BP-6, BP-8, 4-OH-BP | Serum            | DLLME (disperser solvent: acetonitrile; extraction solvent: trichloromethane) | UPLC-MS/MS (ESI⁺); type of column: C₁₈; mobile phase: ammoniacal aq/0.1% ammonia in methanol | LOD: 0.1–0.3 ng mL⁻¹  LOQ: 0.4–0.9 ng mL⁻¹  R: 97–106%  RSD: 1.9–13.7% | Total and free forms content | [83] |
| BP-3                | Serum            | Online SPE                                               | HPLC-MS/MS (APPI)                          | LOD: 0.5 ng mL⁻¹  LOQ: no data  R: 96%  RSD: 7.7–8.7% | Total content | [84,85] |
| OC, BMDMBM, CDAA    | Plasma           | LLE (solvent: acetonitrile)                               | LC-LS-MS/MS (ESI); type of column: C₁₈; mobile phase: methanol/water | LOD: 1.1–6.5 µg L⁻¹  LOQ: 3.5–20.7 µg L⁻¹  R: 89.0–112.8%  RSD: 3.0–4.9% | Total content | [63] |
| BP-3                | Plasma           | LLE (solvent: acetonitrile)                               | UHPLC-DAD; type of column: C₁₈; mobile phase: acetonitrile/water | LOD: no data  LOQ: no data  R: 94–99%  RSD: 2.3–4.6% | Total content | [86] |
| BP-4, 4-DHB, BP-2, BP-1, BP-8, BZ | Whole blood     | FPSE                                                     | HPLC-PDA; type of column: C₁₈; mobile phase: methanol/phosphate buffer (pH 3) (45:55; v/v) | LOD: 0.03 µg mL⁻¹  LOQ: 0.1 µg mL⁻¹  R: no data  RSD: 0.4–10.8% | Total content | [73] |
### Table 4. Cont.

| UV Filters | Matrix | Extraction Technique | Analytical Technique | Analytical Performance | Comments | Ref. |
|------------|--------|----------------------|----------------------|------------------------|----------|------|
| BP-4, 4-DHB, BP-2, BP-1, BP-8, BZ | Plasma | FPSE | HPLC-PDA; type of column: C18; mobile phase: methanol/phosphate buffer (pH 3) (45:55; v/v) | LOD: 0.03 μg mL⁻¹; LOQ: 0.1 μg mL⁻¹ | Total content | [73] |
| BP-3, BP-1, 4-OH-BP, BP-8, 4-DHB, BP-2, BP-4, BMDBM | Umbilical cord blood | LLE (solvent: MTBE) | LC-MS/MS (ESI⁺; ESI⁻); type of column: RP18; mobile phase: methanol/water | LOD: 0.05–0.42 ng mL⁻¹; LOQ: 0.18–1.39 ng mL⁻¹; R: 14.3–146.4%; RSD: 0.5–33.8% | Total content | [81] |
| BP, 4-MBP | Plasma | LLE-SPE (solvent: MTBE; Oasis Prime-HLB) | HPLC/MS/MS (ESI); type of column: C18; mobile phase: 0.1% formic acid in water/0.1% formic acid in methanol | LOD: 0.8–2 pg mL⁻¹; LOQ: 3.5–7 pg mL⁻¹; R: 87–97%; RSD: 3.1–9.1% | Total content | [87] |

### Table 5. Published studies on UV filters determination in semen, saliva, milk, nail, and placental tissue.

| UV Filters | Matrix | Extraction Technique | Analytical Technique | Analytical Performance | Comments | Ref. |
|------------|--------|----------------------|----------------------|------------------------|----------|------|
| BP-1, BP-3, BP-8, THB | Semen | SPE (C18) | LC-MS/MS (ESI⁺); type of column: Mediterranean SEA 18; mobile phase: gradient mobile phase: 0.1% formic acid in water/0.1% formic acid in methanol | LOD: 0.03–0.04 ng mL⁻¹; LOQ: 0.08–0.13 ng mL⁻¹; R: 98–115%; RSD: no data | Total content | [56] |
| BP-3, OMC, OS, HS | Epidermal membranes | LLE (solvent: acetonitrile) | HPLC-DAD; type of column: C18; mobile phase: gradient methanol/water (75:25; v/v) | LOD: 0.03–0.2 μg mL⁻¹; LOQ: 0.1–0.4 μg mL⁻¹; R: 98.5–99.9%; RSD: 1.8–3.2% | Total content | [60] |
| OC, 3-BC, 4MBC, OMC, EDP, BP-1, BP-3, BP-6, BP-8, 4-OH-BP | Milk | QuEChERS Extraction; SALLE & d-SPE (sorbent: polysecondary amine and magnesium sulphate) | UHPLC/MS/MS (API); type of column: C18; mobile phase: gradient acetonitrile/water/0.1% formic acid | LOD: 0.1–0.2 ng mL⁻¹; LOQ: 0.4–0.6 ng mL⁻¹; R: 87–112%; RSD: 8–14% | Total content | [88] |
| BP-3 | Breast milk | Online SPE (RP18) | HPLC/MS/MS (APCI); type of column: RP18; mobile phase: gradient methanol/water | LOD: 0.015 ng mL⁻¹; LOQ: no data; R: 94.7%; RSD: 12.7–18% | Total and free forms content | [89] |
| BP-1, BP-3, 4-OH-BP, 4DHB, 4MBC, ODPABA, EtPABA, THB-PBT | Breast milk | Online TFC | HPLC/MS/MS (ESI); type of column: Cyclone and C18; mobile phase: gradient methanol/water/0.1% formic acid | LOD: 0.1–1.15 ng g⁻¹; LOQ: 0.3–5.1 ng g⁻¹; R: no data; RSD: 1–12% | Total content | [90] |
| BP-3 | Milk | Online SPE (RP18) | HPLC/MS/MS (APCI); type of column: RP18; mobile phase: methanol/water | LOD: 0.4 ng mL⁻¹; LOQ: no data; R: 102%; RSD: 8.8–12% | Total and free forms content | [91] |
| BP-1, BP-3, BP-6, BP-8, 4-OH-BP | Breast milk | USAD-SPE (15 min of sonification; sorbents: C18, polysecondary amine and magnesium sulphate) | UHPLC/MS/MS (ESI⁺); type of column: C18; mobile phase: gradient aqueous ammonium formate solution (pH 9)/0.025% ammonium in MeOH | LOD: 0.1–0.2 ng mL⁻¹; LOQ: 0.3–0.6 ng mL⁻¹; R: 90.9–109.5%; RSD: 2.0–12.3% | Total content | [92] |
| BP-1, BP-2, BP-3, BP-6, BP-8, 4-OH-BF, THB, AVB | Nail | MAE (20 min, 1000 W of power) | UHPLC/MS/MS (ESI⁺); type of column: C18; mobile phase: gradient methanol/water/0.1% formic acid | LOD: 0.2–1.15 ng g⁻¹; LOQ: 1.0–5.0 ng g⁻¹; R: 90.2–112.2%; RSD: 8.6–12.3% | Total content | [93] |
| BP-1, BP-2, BP-3, BP-6, BP-8, 4-OH-BP | Placental tissue | MSPD (solvent: ethyl acetate) | UHPLC/MS/MS (ESI⁺); type of column: RP18; mobile phase: gradient 0.1% ammoniacal aq solution/0.1% ammonium in methanol | LOD: 0.1 ng g⁻¹; LOQ: 0.2–0.4 ng g⁻¹; R: 95–106%; RSD: 4.5–11.8% | Free forms | [94] |
| BP-1, BP-2, BP-3, BP-4, 4-OH-BP | Placental tissue | SLE (solvent: ethyl acetate) | LC-MS/MS (ESI⁺); type of column: RP18; mobile phase: gradient methanol/water | LOD: 0.02–0.36 ng mL⁻¹; LOQ: 0.05–1.20 ng mL⁻¹; R: 72–110%; RSD: 4–40% | Total content | [95] |
Table 5. Cont.

| UV Filters            | Matrix                | Extraction Technique                                      | Analytical Technique                                      | Analytical Performance               | Comments | Ref.    |
|-----------------------|-----------------------|----------------------------------------------------------|-----------------------------------------------------------|-------------------------------------|----------|---------|
| BP-1, BP-2, BP-3, BP-8, 4-OH-BP | Saliva                | DLLME (disperser solvent: acetone; extraction solvent: trichloromethane) | LC-MS/MS; type of column: C18; mobile phase: gradient methanol/water | LOD: 0.01–0.15 ng mL⁻¹  
LOQ: 0.05–0.40 ng mL⁻¹ | R: no data  
RSD: 1–19% | Total content [96] |
| EDP, 3-BC, MBC, OMC, OC, BP-1, BP-3, BP-6, BP-8, 4-OH-BP | Placenta tissue       | UAE (disperser solvent: anisole; extraction solvent: anisole; 3 min of sonificiation) | UHPLC-MS/MS; type of column: C18; mobile phase: gradient acetonitrile/0.25% formic acid aq | LOD: 0.05–0.2 µg kg⁻¹  
LOQ: 0.15–0.5 µg kg⁻¹ | R: 90–112%  
RSD: 3–15% | Total content [97] |

The most popular extraction technique in the case of plasma, serum, or blood samples is liquid–liquid extraction with the use of such organic solvents as acetonitrile [60,63,86], as well as a methyl tert-butyl ether [81,87] (Table 4). Another technique is dispersive liquid–liquid microextraction (DLLME) with the use of acetone as the disperser solvent and trichloromethane as the extraction solvent [82,83] or acetone as the disperser solvent and chloroform as the extraction solvent [45]. Solid-phase extraction with the C18 sorbent [84,85] and fabric phase sorptive extraction (FPSE) [73] have also been employed.

In the case of milk, semen, and silica samples, determination takes place in the same way as for urine and plasma samples, and as such, the first step is the acid or enzymatic hydrolysis [69,88–90]. Afterwards, acetonitrile [88,90], formic acid [56], isopropanol [89], or methanol [91] is added to precipitate proteins. Finally, in the case of other biological samples such as placenta, nail, or epidermal membrane tissue, homogenisation takes place as well. The samples are shaken and mixed to enable tissue break up (Table 5).

The extraction techniques used in the determination of UV filters in milk, semen, and tissue samples are the same as in the case of urine, i.e., solid-phase extraction, in manual mode [56] and online configuration [89,91]; the ultrasound-assisted dispersive solid-phase extraction (USAD-SPE) is employed as well [92]. Microwave-assisted digestion/extraction (MAE) [93], matrix solid-phase dispersion (MSPD) [94], solid–liquid extraction (SLE) [95], dispersive liquid–liquid microextraction [96], and ultrasound-assisted extraction (UAE) [97] have also been applied for this purpose (Table 5).

3.2. Analytical Techniques

Even if an exhaustive initial sample treatment is performed to eliminate possible interfering compounds from the sample, an adequate analytical separation technique must still be selected to improve analyte determination. Tables 3–5 present the most used analytical techniques for the detection and quantification of UV filters in biological samples. Liquid chromatography and gas chromatography coupled with MS or MS/MS is the most frequent choice. The choice of either GC or LC is mainly based on the physicochemical properties of the target compounds. GC is usually employed to determine volatile analytes, whereas LC is applied to quantify both more polar and less volatile compounds.

Liquid chromatography has been used most widely for the determination of UV filters in biological samples. LC coupled with mass spectrometry detectors in tandem is the preferable option. Various ionisation sources have also been used. The most frequently used ionisation mode has been electrospray ionisation (ESI) [45,46,51,55,59,63–65,81–83,87,90,92,94–97]. Moreover, it was found that ESI⁺ has better efficiency than ESI⁻ [56]. It is a soft ionisation technique suitable for polar and mildly non-polar compounds. Nevertheless, since ion suppression or improvement in the complex matrix may occur, atmospheric pressure chemical ionisation (APCI) [47–49,75,77] and atmospheric pressure photoionisation (APPI) [84,85] have also been used. In all mentioned cases, the determination was carried by multiple reaction monitoring (MRM) mode of the most intense transition, with another one employed to confirm the presence of UV filters in biological matrices at very low concentration levels. Yet another type of detector coupled to liquid chromatography is based on UV/Vis spectroscopy. It is often used due to the fact that UV filters exhibit a high absorbance in the UV range of the electromagnetic spectrum [44,52,60,70,75–77,80,86]. Liquid chromatography coupled with a fluorometric detector has been scarcely used because most UV filters do not
exhibit fluorescence properties. LC-FL was only used twice—in determining PBSA [71], as well as PEG-25 and PABA [72] in urine samples.

While gas chromatography has been used less often, in most cases it is coupled with mass spectrometry with electron impact [53,54,62,74,79]. In the case of UV filters, a derivatisation step is required before the GC analysis. UV filters have been typically derivatized by using such silylating reagents as N,O-Bis (trimethylsilyl) trifluoroacetamide with trimethylchlorosilane (BSTFA-TMCS) [62] or N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) [54].

Lastly, despite comprehensive sample preparation and the use of carefully select analytical techniques, it must be noted that final results may sometimes be affected by the “matrix effect.” This phenomenon may impact quantitative recoveries when using external calibration. As such, it may cause differences in the behaviour of the analyte with the accompanying matrix compounds that one can use to enhance or decrease the signal (e.g., ion suppression in the mass spectrum) or affect the extraction efficiency when the extraction technique is used. This negative effect has been adjusted for by using a matrix-matched calibration (the use of the same matrix without analytes to prepare the standard calibration solutions). In other cases, the standard addition calibration method or an isotopic internal standard was used.

3.3. Accuracy and Sensitivity

Tables 3–5 show information about achieved results for different analytical methods used for the determination of UV filters in biological samples.

The analytical methods presented in it resulted in recoveries enabling exhaustive quantification of the target UV filters in the biological matrices, using external or matrix-matched or standard addition calibration. Thus, in the case of urine samples, the greatest recoveries have been achieved for BP-2 (118%) using microextraction by packed sorbent [78] and for EHS (113%) using liquid–liquid extraction [63]. In the case of blood, plasma, and serum samples, the best recoveries have been obtained for BP-1 (146.4%) using liquid–liquid extraction [81]. In milk samples, the highest-level recoveries have been achieved for BP-3 (112%) by using salt-assisted liquid–liquid extraction coupled with dispersive solid-phase extraction [88]. The recoveries in the case of the determination of OMC in placenta tissue by using ultrasound-assisted extraction amounted up to 112% [97].

In terms of sensitivity, the published methods (Tables 3–5) enable the determination of UV filters in the low pg mL\(^{-1}\) range.

In the urine samples, the lowest limit of detection (LOD) has been achieved for BP-3 (5 pg mL\(^{-1}\)) using hollow-fibre liquid-phase microextraction [42]. The LOD for BP-3, 4-MBC, OC, and HS (0.47–0.59 pg mL\(^{-1}\)) was obtained by using accelerated solvent extraction coupled with solid-phase extraction [62]. In the plasma sample, the LOD was at a level of 0.8 pg mL\(^{-1}\) for BP; it was determined using liquid–liquid extraction in conjunction with solid-phase extraction [87].

In the milk sample, the best LOD has been achieved for BP-6 and BP-1 (0.1 ng mL\(^{-1}\)) using salt-assisted liquid–liquid extraction coupled with dispersive solid-phase extraction [69]. In the determination of 4-OH-BP in the tissue sample, the LOD of 0.02–10 ng mL\(^{-1}\) has been obtained using solid–liquid extraction [95].

The low levels achieved in the determination of UV filters in biological samples have been influenced by the use of sensitive analytical techniques (e.g., MS/MS), as well as such enrichment techniques as LLE, SPE, MALLE, SPME, SBSE, SDME, HF-LPME, and MALLME.

4. Conclusions

Organic UV filters are a family of cosmetic ingredients most widely used in a common variety of cosmetic products to protect consumers from UV solar radiation. Since compounds belonging to this group can be metabolised, excreted, and/or bioaccumulated,
UV filters may be harmful to the human body. This has made analysing UV filters both in cosmetics products and biological samples a necessity.

Liquid chromatography with MS or UV detection is the dominant method for the determination of UV filters. The large majority of published works used conventional C18 or C8 separation columns. Due to the low level of UV filters in the biological samples (e.g., urine, blood, milk), it is necessary to perform the extraction and clean-up steps before the determination procedure to improve the detection limits. LLE and SPE are the most widely used sample preparation and enrichment methods among all those used. However, these conventional techniques present some drawbacks, such as the consumption of large volumes of sample and often toxic organic solvents, but they are time consuming. Nonetheless, such modern microextraction techniques as MEPS, SPME, SBSE, or DLLME are used as well. However, they are only used in 25% of analytical procedures. Due to the trends of modern analytical techniques towards “Green Analytical Chemistry,” they should in the future replace the classic methods of preparing samples for research. This is because of their many advantages, i.e., time-consuming and labour intensity, and above all because they are solvent-free methods.

This review paid special attention to the analytical performance, e.g., limits of detection, accuracy, and repeatability for developed and validated analytical methods. Organic UV filters have been determined to be prevalent in all kinds of biological matrices and are associated with specific markers connected to metabolism, physiological development, and harmful effects in the human body.

Author Contributions: Conceptualization, I.N. and G.W.; writing—original draft preparation, I.N.; writing—review and ending, I.N. and G.W.; supervision, G.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

[C_{6}MIM][PF_{6}]: hexyl-3-methylimidazolium hexafluorophosphate
2-OH-BP: 2-hydroxybenzophenone
3-BC: 3-benzophenone camphor
4-AHA: p-aminohippuric acid
4-AMB: p-acetamidobenzoic acid
4-DHB: 4,4-dihydroxybenzophenone
4-MBC: 3-(4-methylbenzylidene)-camphor
4-OCH_{3}-AHA: p-acetamidohippuric acid
4-OH-BP: 4-hydroxybenzophenone
5cx-EPS: 5-(((2-hydroxybenzoyl)oxy)methyl)heptanoic acid
5-OH-EHS: 5-hydroxy-2-ethylhexyl salicylate
5oxo-EHS: 2-ethyl-5-oxohexyl 2-hydroxybenzoate
AALME: air-assisted liquid–liquid microextraction
Ac: Acetone
APCI: atmosphere pressure chemical ionisation
API: atmosphere pressure ionisation
APPI: atmosphere pressure photoionisation
ASE: accelerated solvent extraction
BMDMBM: butyl methoxydibenzoylmethane/avobenzene
BAμE: bar adsorptive microextraction
| Abbreviation | Full Form |
|--------------|-----------|
| BC:          | benzyl cinnamate |
| BDM:         | butyl methoxydibenzoylmethane |
| EMT:         | bis-ethylhexyl oxyphenol methoxyphenyl triazine |
| BP:          | Benzophenone |
| BP-1:        | 2,4-dihydroxybenzophenone |
| BP-10:       | 2-hydroxy-4-methoxy-4′-methylbenzophenone |
| BP-12:       | (2-hydroxy-4-octoxy-phenyl)-phenyl-methane |
| BP-2:        | 2,2′,4,4′-tetrahydroxybenzophenone |
| BP-3:        | 2-hydroxy-4-methoxybenzophenone |
| BP-4:        | 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid |
| BP-6:        | 2,2′-dihydroxy-4,4′-dimethoxybenzophenone |
| BP-7:        | 5-chloro-2-hydroxybenzophenone |
| BP-8:        | 2,2′-dihydroxy-4-methoxybenzophenone |
| BP-OH:       | Benzhydrol |
| BS:          | benzyl salicylate |
| BZT:         | Benzotriazole |
| C18:         | Octadecyl |
| CDAA:        | 2-cyano-3,3-diphenyl acrylic acid |
| CPE:         | cloud point extraction |
| DAD:         | diode-array detection |
| DART-MS:     | direct-analysis-in-real-time mass spectrometry |
| DBT:         | diethylhexyl butamino triazone |
| DCM:         | Dichloromethane |
| DEA:         | Diethylaminopropyl |
| DHHB:        | diethylamino hydroxybenzoyl hexyl benzoate |
| DLLME:       | dispersive liquid–liquid microextraction |
| DMF:         | n,n-dimethylformamide |
| DTS:         | drometrizole trisiloxane |
| DS:          | Densitometry |
| d-SPE:       | dispersive solid-phase extraction |
| EA:          | ethyl acetate |
| ECD:         | electron captur detector |
| EDP:         | 2-ethylhexyl 4-(n,n-dimethylamino)benzoate |
| EHC:         | ethylhexyl cinnamate |
| EHS:         | 2-ethylhexyl salicylate |
| EI:          | electron impact |
| EMC:         | ethylhexyl methoxycinnamate |
| EHS:         | ethylhexyl salicylate |
| ESI:         | electrospray ionisation |
| ET:          | ethylhexyl triazone |
| EtOH:        | Ethanol |
| EtPABA:      | ethyl p-aminobenzoic acid |
| FL:          | Fluorescence |
| FPSE:        | fabric phase sorptive extraction |
| GC:          | gas chromatography |
| HFPLME:      | hollow-fiber liquid-phase microextraction |
| HPLC:        | high-performance liquid chromatography |
| HS:          | salicylic acid 3,3,5-trimethcyclohexyl ester |
| HTLC:        | high-temperature liquid chromatographic |
| IMC:         | isoamyl p-methoxycinnamate |
| LC:          | liquid chromatography |
| LD:          | liquid desorption |
| LLE:         | liquid–liquid extraction |
| LOD:         | limit of detection |
| log $K_{o/w}$:| log octanol/water partition coefficient |
| LOQ:         | limit of quantification |
| LTP-MS:      | low temperature plasma ionisation mass spectrometry |
MA: menthyl anthranilate
MAE: microwave-assisted extraction
MBBT: methylene bis-benzotriazolyl tetramethyl butyl phenol
MBC: 4-methylbenzylidene camphor
MBP: methylene bis-benzotriazoyl tetramethylbutylphenol
MeCN: Acetonitrile
MEKC: micellar electrokinetic capillary chromatography
MeOH: Methanol
MEPS: microextraction by packed sorbent
MMLLE: microporous membrane liquid–liquid extraction
MS/MS: tandem mass spectrometry
MS: mass spectrometry
MSPD: matrix solid phase dispersion
MTBE: methyl tert-butyl ether
NaCl: sodium chloride
OC: 4-methylbenzilidene camphor/octocrylane
ODP: octyl dimethyl PABA
ODPABA: 2-ethylhexyl 4-(dimethylamino)benzoate
OMC: 2-ethylhexyl p-methoxycinnamate
OS: 2-ethylhexylsalicylate
PABA: p-aminobenzoic acid
PMDSA: 2-phenylbenzimidazole-5-sulphonic acid
PDA: photodiode-array detection
PEG-25 PABA: polyethylene glycol 25 paminobenzoic acid
PHBA: 4-hydroxy benzoic acid
PLE: pressurized liquid extraction
PKa: acid dissociation constant
PSA: primary-secondary amine
QuEChERSExtraction: Quick, Easy, Cheap, Effective, Rugged, and Safe Extraction
R: Recovery
RSD: relative standard deviation
SALLE: salt-assisted liquid–liquid extraction
SBSE: stir bar sorptive extraction
SDME: single-drop microextraction
SFC: supercritical fluid chromatography
SIA: sequential injection analysis
SI SPE: sequential injection solid-phase extraction
SLE: solid–liquid extraction
SPE: solid-phase extraction
SPME: solid-phase microextraction
SWV: squarewave voltammetry
TBHPBT: 2-(5-tert-butyl-2-hydroxyphenyl)benzotriazole
TCM: trichloroamine
TFA: trifluoroacetic acid
TFC: turbulent flow chromatography
THB: 2,3,4-trihydroxybenzophenone
TLC: thin-layer chromatography
UAE: ultrasound-assisted extraction
UHPLC: ultra-high-performance liquid chromatography
UHPSFC: ultra-high performance supercritical fluid chromatography
UPLC: ultra-performance liquid chromatography
USAD-SPE: ultrasound-assisted dispersive solid phase extraction
UV/Vis: ultraviolet/visible spectrometry
VADLLME: vortex-assisted dispersive liquid–liquid microextraction
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