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The Application of Pipette-Tip and Magnetic Dummy-Template Molecularly Imprinted Solid-Phase Extraction Coupled with High-Performance Liquid Chromatography with Diode Array and Spectrofluorimetric Detection for the Determination of Coumarins in Cosmetic Samples

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Abstract: In this study, adsorbents based on molecularly imprinted polymers (MIPs) in two solid-phase extraction application forms, pipette tip and magnetic extraction, were used for the selective extraction of coumarins. The pipette-tip solid-phase extraction reduced solvent volumes; the magnetic MIP extraction was simple and effective for phase separation. Parameters affecting extraction, such as the amount of adsorbent, type of washing solvent, volume of the elution solvent, and extraction times for magnetic extraction, were optimized. The MIP-based adsorbents displayed high selectivity and extraction efficiency, resulting in recoveries ranging from 70.3 to 102.0% (RSD % less than 5.5%) for five coumarins under study, 6,7-dihydroxycoumarin-6-β-D-glucoside, coumarin, 7-methoxycoumarin, 6-methylcoumarin, and dicoumarol. The extracts were analyzed by high-performance liquid chromatography with diode array (DAD) and fluorescence (FLD) detectors, reaching limits of quantification of 0.5 and 0.9 $\mu g \cdot mL^{-1}$ for coumarin and dicoumarol detected by DAD and 0.001–0.012 $\mu g \cdot mL^{-1}$ for the other prohibited simple coumarins when used as a fragrance (detected by FLD). The proposed method was validated and its applicability was shown for the analysis of cosmetic samples like shower gel and perfume.

Keywords: molecularly imprinted polymers; solid-phase extraction; HPLC; coumarins; personal care products; safety testing

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1. Introduction

Cosmetics (shower gels, spray, perfumes, body lotions, and toothpaste, among others) play an important role in everyone's daily life in cleaning, perfuming, and beautifying. Cosmetics usually consist of many ingredients, among which are fragrance chemicals, preservatives, dyes, oils, emulsifiers, etc. Some of them might cause various undesirable side effects, like contact allergies, rashes, and dermatitis. The fragrance ingredients in personal care products include coumarin and its derivatives. Coumarins are formed of a benzene and α-pyrone ring, with an oxygen atom in the α-position. They represent a large group of naturally occurring compounds found in a wide variety of plants, essential oils, fungi, and bacteria [1–3]. In addition to their pleasant aroma, coumarins exhibit several biological activities, such as anti-inflammatory, anti-HIV, antiviral, antioxidant, antimicrobial, and anti-asthmatic effects [4–6]. They may also act as constituents of sunscreen formulations to enhance tanning induced by ultraviolet radiation [7,8]. According to the EU (EU regulation EU No. 2017/1410 amending Annexes II (prohibited substances) and III (restricted substances) of Cosmetics Regulation 1223/2009), some coumarins, dicumarol, cyclocoumarol, acenocoumarol, 3,4-dihydrocoumarin, 7-methoxycoumarin, 7-methylcoumarin,

4-methyl-7-ethoxycoumarin, and furocoumarins (e.g., 8-methoxypsoralen, 5-methoxypsoralen, and imperatorin), among others, are listed as prohibited substances when used as fragrance ingredients. Furthermore, coumarins are included in lists of potentially allergic or photoallergic fragrance substances, and no coumarins should be used in cosmetic products for infants and toddlers [9].

There are several analytical methods [10] for the determination of coumarins, such as spectrofluorimetry [11,12], high-performance liquid chromatography (HPLC) [13,14], high-performance thin-layer chromatography (HPTLC) [15], and gas chromatography (GC) [16,17]. A fluorescence resonance energy transfer sensor was also developed for the detection of coumarin through the host–guest interaction between β-cyclodextrin and coumarin [18]. Sample preparation is a crucial step in cosmetics analysis, as the complex matrices may interfere with the target analytes. Trends in sample preparation for cosmetics analysis have been reviewed previously [19,20]. Extraction procedures such as traditional liquid–liquid extraction (LLE) and solid–liquid extraction (SLE), as well as advanced techniques such as ultrasound-assisted extraction (UAE) [21], supercritical fluid extraction (SFE) [13], solid-phase extraction (SPE) [21], or matrix solid-phase dispersion (MSPD) [22,23], were used for the extraction of coumarins from different types of cosmetics. However, trends are focused toward the environmental friendliness of procedures and the minimization of solvent volumes, sample amounts, and time consumption without decreasing method performance. An innovative approach in sample preparation and analyte preconcentration is SPE based on selective molecularly imprinted polymeric adsorbents (MIPs) containing binding sites, stereochemically shaped by a template (targeted analyte or analogue as a dummy template), for specific interactions with target analytes (or analogues) [24,25]. The utilization of MIPs in the analysis of cosmetics and other personal care products is mainly as selective adsorbents for SPE (MISPE) and MIP-based sensors. Analytical methods applied for MIP extraction are focused mainly on four families of the most-used emerging pollutants: organic UV filters (benzophenone), preservatives (parabens), antimicrobials (triclosan and triclocarban), and musks (musk ketone, amongst others) [26]. An overview of methods for the analysis of cosmetic samples, such as creams, shampoos, bath lotions, toothpaste, and body lotion, is documented Table S1 (Supplementary Material) [27–37]. MIPs are applied as selective adsorbents for SPE in conventional column form, microextractions, MSPD, or magnetic MIP extraction. MIP-based extraction allows for a higher recovery for targeted compounds, e.g., bisphenol A, parabens, drugs, the antibacterial and antifungal agent triclosan, and others. The extraction of coumarins by MISPE was used in an analysis of wines and plant extracts [38,39].

In recent years, green analytical chemistry principles have also been increasingly implemented in methods of cosmetics analysis. The miniaturization of classical extraction procedures, the substitution of hazardous chemicals and solvents with environmentally friendly alternatives, and the reusability of extraction media are the main objectives in the development and modification of these methods. Green chemistry concepts were also applied in the field of the synthesis of molecular imprinting materials [40]. Related to this, the main objective of this work was to develop a simple, selective, and sensitive method for personal care product analysis, such as shower gels and deodorants. Sample pre-treatment included the extraction procedures with the laboratory-fabricated MIP adsorbents selective for coumarins. The application of the miniaturized pipette-tip MISPE procedure, as well as batch extraction with MIPs coated on magnetic particles, is documented. The proposed extraction methods show the use of MIP-based adsorbents in the analysis of samples of different viscosities.

2. Materials and Methods

2.1. Chemicals and Samples

Analytical standards of coumarins, coumarin (99%), dicoumarol (98%), 6,7-dihydroxycoumarin-6-β-D-glucoside (esculin; 98%), 7-hydroxycoumarin (umbelliferone; 99%), 7-methoxycoumarin (herniarin; 98%), and 6-methylcoumarin (99%), and

reagents used in the synthesis of the MIPs, methacrylic acid, 2,2′azobisisobutyronitrile, and ethylene glycol dimethacrylate (all analytical grade), were obtained from Merck-Sigma Aldrich (Darmstadt, Germany). Methanol, ethanol, and chloroform (HPLC grade) and acetic acid (99%), acetone, oleic acid, iron(III) chloride hexahydrate (99%), iron(II) chloride tetrahydrate (98%), sodium hydroxide (analytical grade), and polyvinylpyrrolidone (for synthesis) were purchased from Centralchem (Bratislava, Slovakia). Nitrogen (99.9%) was purchased from Messer Tatragas (Bratislava, Slovakia). The water was distilled and purified (resistivity of 18.2 MΩ/cm) using a laboratory water purification system.

Cosmetic samples (shower gel 1, shower gel 2, shower gel 3; deodorant 1, deodorant 2) were obtained from local markets. Samples were stored in original packages at laboratory temperature.

2.2. Preparation of Standard Solutions

The stock solutions of coumarins (1×10^3 μg·mL^{-1}) were prepared by dissolving the accurately weighed reference compound in methanol and stored at 4 °C. Working mixed standard solutions were prepared from standard stock solutions by diluting with the methanol–water mixture (20:80 v/v) to obtain the final concentration in an interval of 0.3×10^{-3} μg·mL^{-1}–100 μg·mL^{-1}.

2.3. MIP and Fe_3O_4/MIP Synthesis

MIPs were fabricated using a previously optimized procedure [39]. The mixture of 7-hydroxycoumarin (0.7 mmol), methacrylic acid (2.9 mmol), and chloroform (7.5 mL) was stirred in a glass tube for 15 min followed by the addition of ethylene glycol dimethacrylate (11.75 mmol) and 2,2′-azobisisobutyronitrile (0.18 mmol). The mixture was polymerized in an oil bath for 24 h at 60 °C. The polymer block was crushed, sieved through an 80 μm sieve, and washed with acetone to remove fine particles. Finally, the sorbent was treated by Soxhlet extraction with methanol–acetic acid (90:10 v/v) for 48 h to remove the template. Figure 1 shows a schematic diagram of MIP formation.

The Fe_3O_4/MIP was synthesized according to a procedure described previously [41]. Magnetic particles were prepared by the coprecipitation method. $FeCl_2 \cdot 4H_2O$ (0.01 mol) and $FeCl_3 \cdot 6H_2O$ (0.2 mol) were dissolved in deionized water (100 mL). The temperature of the mixture was increased to 80 °C and a sodium hydroxide solution (40 mL) was added dropwise. The reaction mixture was kept at 80 °C under nitrogen for one hour. Black precipitates of Fe_3O_4 were washed with deionized water until the pH became neutral. The Fe_3O_4 particles were washed with acetone (100 mL) and dried under vacuum at 55 °C. For the synthesis of MIPs, methacrylic acid (8 mmol) and 7-hydroxycoumarin (1 mmol) were dissolved in chloroform (20 mL) and stirred for 30 min (mixture I). An amount of 1 g of Fe_3O_4 particles was mixed with oleic acid (1 mL) and stirred for 10 min under nitrogen (mixture I). Mixtures I and II were mixed with 20 mmol of ethylene glycol dimethacrylate under stirring for 30 min in nitrogen atmosphere (mixture III). In the next step, polyvinylpyrrolidone (0.4 g) dissolved in ethanol (100 mL) at 60 °C was mixed with mixture III and 2,2′-azobisisobutyronitrile (0.1 g) and polymerized under nitrogen atmosphere at 60 °C for 24 h. The Fe_3O_4/MIP was separated from the solution using an external magnet and washed with deionized water (500 mL, five cycles). Finally, the template was removed by washing with methanol–acetic acid (9/1 v/v, 100 mL) under stirring for 48 h (solvent was changed every 12 h). Figure 1 shows a schematic diagram of the Fe_3O_4/MIP formation.

2.4. Sample Preparation

Solid-phase extractions were performed with laboratory-fabricated MIP-7-hydroxycoumarin and Fe_3O_4/MIP-7-hydroxycoumarin.

Pipette-tip SPE with MIP adsorbent: The MIP (20 mg; amounts of 10, 20, 35, and 50 mg were tested to study the amount of adsorbent) was packed in a 1 mL polypropylene pipette tip, and the adsorbent was closed with cotton from both sides (Figure 1). The pipette tip was coupled with a plastic syringe. The cartridge was conditioned with methanol

(1 mL) and water (1 mL), and subsequently a deodorant sample or standard solution of coumarins (0.5 mL) was passed through the cartridge. The cartridge was then washed with water (0.3 mL), and finally the analytes were eluted with methanol–acetic acid (90:10, *v*/*v*; 0.5 mL). The extract was diluted (1:1, *v*/*v*) with the methanol–water mixture (20:80 *v*/*v*) and filtered through a 0.22 µm nylon membrane filter, and an aliquot of 20 µL was injected into the HPLC.

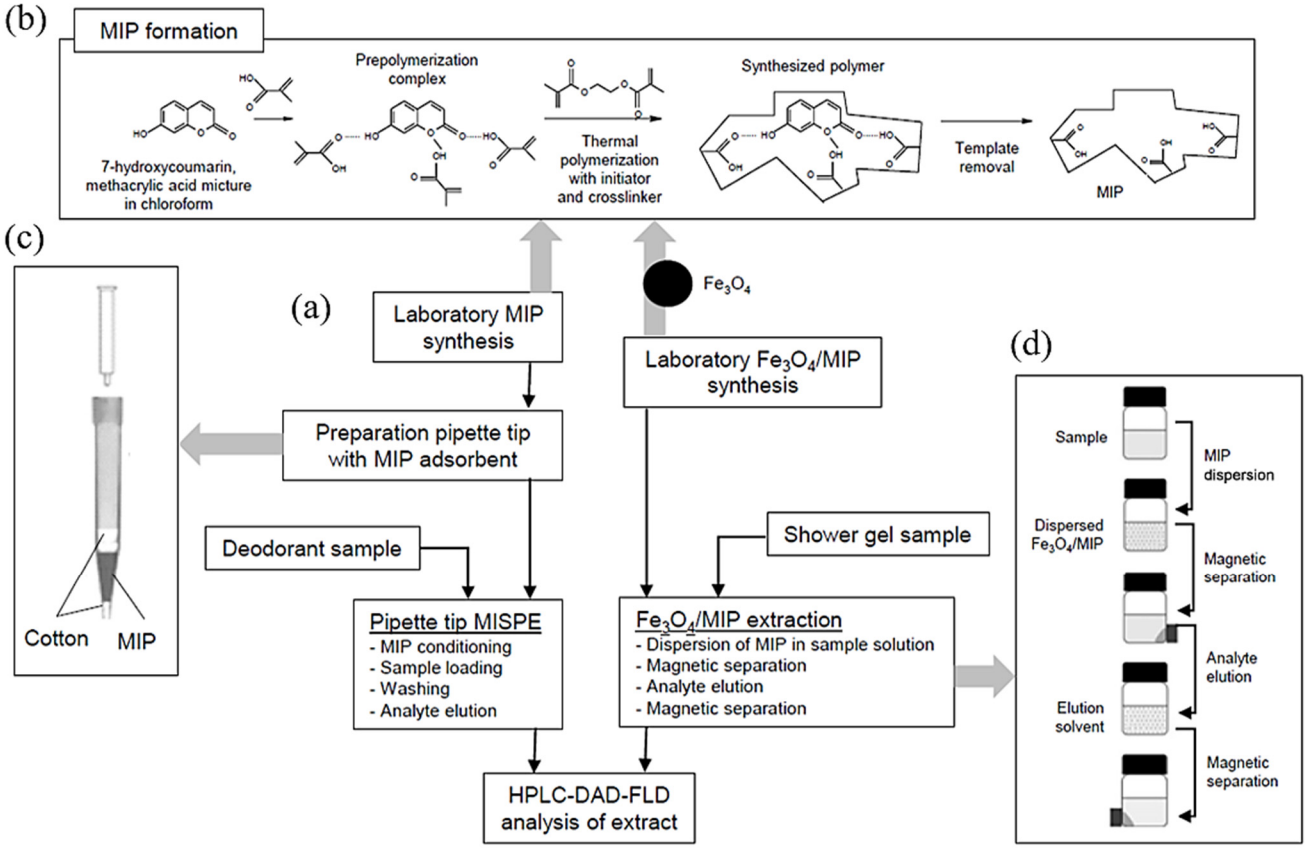


Figure 1. Schematic diagram of procedures in sample analysis (**a**), schematic illustration of MIP and Fe_3O_4/MIP preparation (**b**), pipette-tip preparation procedures (**c**), and magnetic extraction (**d**).

SPE with Fe_3O_4/MIP adsorbent (Figure 1): Fe_3O_4/MIP-7-hydroxycoumarin (100 mg; amounts of 50, 100, 150, and 200 mg were tested for the study the amount of adsorbent) was mixed with a shower gel sample or standard solution of coumarins (1 mL). The mixture was shaken on a mechanical mixer for 30 min (200 rpm) at 25 °C. Subsequently, the magnetic precipitate was isolated from the solution using a magnet and washed with water (2 mL) for 5 min in a mechanical mixer (200 rpm) before being dried at 60 °C under vacuum. Subsequently, methanol–acetic acid (90:10, *v*/*v*; 3 mL) was added to the adsorbent, and analytes were eluted under shaking on a mechanical mixer for 30 min (200 rpm). The adsorbent was separated using a magnet and the supernatant was diluted (1:1, *v*/*v*) with mixture of methanol–water (20:80 *v*/*v*) and filtered through a 0.22 µm nylon membrane filter. An aliquot of 20 µL was injected into the HPLC.

2.5. HPLC Instrumentation and Separation

The analyses were performed using HPLC Agilent Technologies, series 1200, which consisted of a binary pump, an autosampler, a column oven, a diode array detector (DAD), and a fluorescence detector (FLD). Chromatographic separations were carried out using the analytical column Kinetex C18 (100 mm × 4.6 mm I.D., 5 µm particle size) (Phenomenex, Torrance, CA, USA). A 20 µL solution was injected into the chromatographic system with a mobile phase consisting of a mixture of methanol–acetic acid (99:1, *v*/*v*) (component A) and

a 1% aqueous solution of acetic acid (component B) pumped at a flow rate of 1.0 mL.min^{-1}. The separation was carried out with gradient elution: from a 0 to 12 min linear gradient for the A component from 20 to 45%, then to 100% for A over 0.5 min. The composition was then maintained at 100% of A for 6 min, followed by a reverse gradient over 0.5 min and kept at 20:80 (v/v) A:B for 3 min. The temperature of the column was set at 23 °C. The chromatograms were recorded at 280 nm for coumarin and 6-methylcoumarin, 300 nm for dicoumarol, and 320 nm for 6,7-dihydroxycoumarin-6-β-D-glucoside, 7-hydroxycoumarin, and 7-methoxycoumarin. The UV spectra were scanned in the wavelength range of 190–400 nm. The fluorescence detector was used for the detection of all compounds, excluding coumarin and dicoumarol. Excitation and emission wavelengths were set at 320 nm (λex) and 450 nm (λem), respectively. The fluorescence spectra were scanned in the wavelength range of 340–500 nm.

2.6. Method Evaluation

The proposed method was evaluated in terms of some chromatographic characteristics and validation parameters. The HPLC system suitability test was performed using six repeated injections of the standard solution at 5 μg·mL^{-1}. Chromatographic parameters, such as repeatability of elution times, peak areas, high equivalent of a theoretical plate, and resolution, were evaluated. The validation parameters of the method represent linearity, limit of detection (LOD), limit of quantification (LOQ), recovery, and intraday and interday precisions. The linearity of the method was determined by constructing calibration curves (a graph of mean peak areas versus the corresponding concentration of analytes) of the analytes in the concentration ranges from the LOQ to 100 μg·mL^{-1} and the LOQ to 1 μg·mL^{-1} for the DAD and FLD, respectively (six concentration levels, three replicate measurements of each solution). To calculate the calibration equation and the correlation coefficient values, the regression analysis by the least squares method was used. The LOD and LOQ values were calculated from the slope of the calibration curves (b) and the standard deviation of the intercept of the calibration curve (s_a) using the equations LOD = 3.3 s_a/b and LOQ = 10 s_a/b. SPE with MIP-based adsorbents in pipette tip and batch mode was conducted for samples (shower gel 1 and deodorant 1) spiked with coumarins (10 μg·mL^{-1}/20 μg·mL^{-1} of coumarin, 20 μg·mL^{-1} of dicoumarol; 20 × 10^{-3} μg·mL^{-1} of 6,7-dihydroxycoumarin-6-β-D-glucoside, 7-methoxycoumarin, and 6-methylcoumarin) to determine a recovery of the method. Intraday precisions were evaluated for three preparations of spiked samples under working conditions. Interday precisions were evaluated for six replicates of the spiked samples over three consecutive days. The results were expressed in terms of relative standard deviation percentage (RSD %).

3. Results and Discussion

The work in this study included several steps (Figure 1): (i) sample pre-treatment using laboratory-fabricated MIP adsorbents selective for coumarins, (ii) development of the HPLC-DAD-FLD method, and (iii) an analysis of personal care products.

3.1. RP-HPLC-DAD-FLD Analysis

In this study, some details of the HPLC analysis were evaluated. The reversed-phase HPLC method of the C18 type was preferred due to the polarity of the analytes and compatibility with the extracts. The separation conditions were selected after testing different parameters, such as the composition of the mobile phase, the type of stationary phase, and the isocratic or gradient elution mode. The composition of the mobile phases was adjusted to provide efficient separation of the six targeted coumarins with acceptable resolution (Rs > 1.5), good peak symmetry (As = 0.8–1.2), and reasonable run time. Different C18 columns, Symmetry C18 (150 mm × 3.9 mm I.D., 5 μm particle size), Arion polar C18 (150 mm × 4.6 mm I.D., 5 μm particle size), and Kinetex C18 (100 mm × 4.6 mm I.D., 5 μm particle size) were tested. Considering the results, the Kinetex C18 core–shell column was selected for the purpose of this study, showing satisfactory column efficiency, resolution,

symmetry, and analysis time using the binary mobile phase gradient consisting of methanol, water, and an acidic additive. Table 1 documents the chromatographic characteristics of the selected coumarins. The retention times and peak areas were reproducible under the selected experimental conditions and reached RSD % values of less than 1.1% (retention time) and 5.0% (peak area; 5 μg mL^{-1}). Figure 2a,b show the typical chromatograms of coumarin standards separation in an analysis time of up to 20 min, recorded by DAD and FLD. 7-Hydroxycoumarin was included in the standard mixture to assess MIP bleeding. The main advantage of the core–shell-type stationary phase was the efficient separation of the analytes in a shorter analysis time compared to the traditional 5 μm fully porous phase (analysis time approximately 40 min) [42] and a similar performance as fully porous sub-2 μm adsorbents (analysis time less than 6 min, resolution 1.5–9.8) [43]. For quantitative analytical purposes, the UV detection wavelength was set at 280 nm for coumarin, 300 nm for dicoumarol, and 320 nm for 6,7-dihydroxycoumarin-6-β-D-glucoside, 6-methylcoumarin, 7-hydroxycoumarin, and 7-methoxycoumarin. The fluorescence detection wavelengths were set at 320 nm (λex) and 450 nm (λem), based on fluorescence spectra evaluation.

Table 1. Chromatographic characteristics for HPLC separation of coumarins.

Compound	t_R (min)	*Rs*	*As*	HEPT (μm)
6,7-Dihydroxycoumarin-6-β-D-glucoside	2.52	12.18	1.2	8.5
7-Hydroxycoumarin	6.55	4.40	1.2	7.1
Coumarin	8.31	7.57	1.1	5.7
7-Methoxycoumarin	11.40	4.55	1.1	3.5
6-Methylcoumarin	14.63	12.40	1.1	3.6
Dicoumarol	17.85		1.2	4.0

Coumarin concentrations 5 μg·mL^{-1}; n = 6; t_R—retention time; *Rs*—resolution; *As*—peak symmetry; HEPT—height equivalent of a theoretical plate.

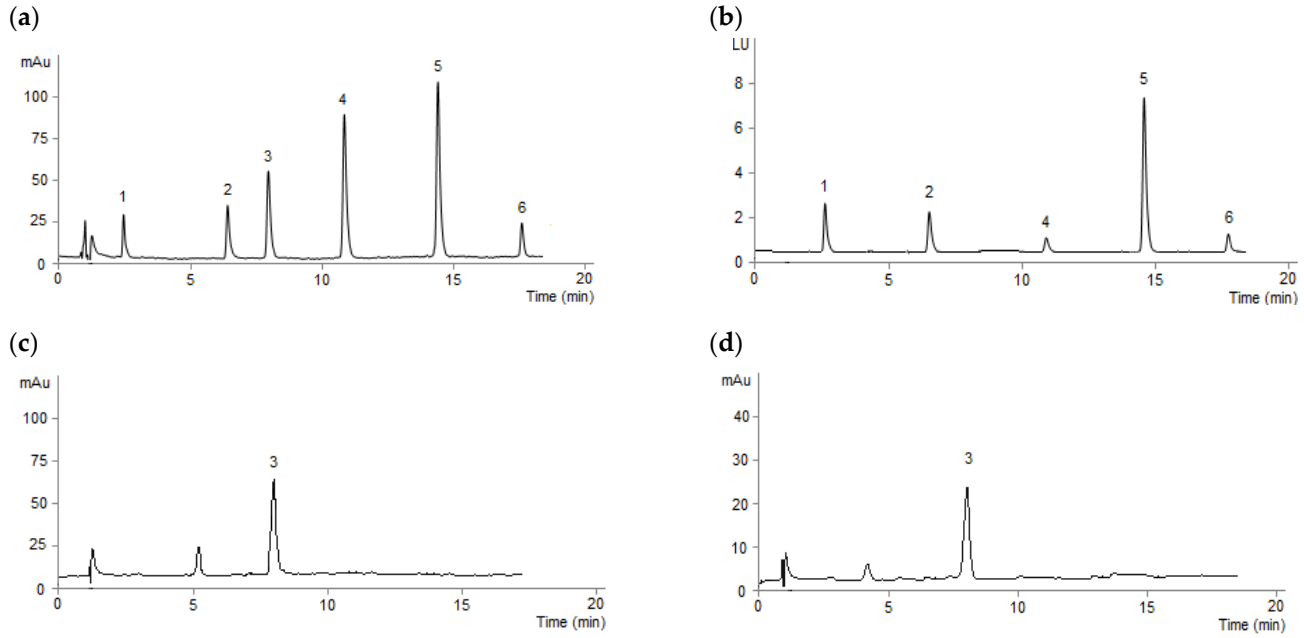


Figure 2. HPLC chromatograms of a standard solution of coumarins from DAD (λ = 280 nm) (**a**) and FLD (λex = 320 nm, λem = 450 nm) (**b**) and chromatograms from DAD (λ = 280 nm) for MISPE extract of deodorant sample 2 (**c**) and Fe_3O_4/MISPE extract of shower gel sample 2 (**d**). Peak identification: 1-6,7-dihydroxycoumarin-6-β-D-glucoside, 2-7-hydroxycoumarin, 3-coumarin, 4-7-methoxycoumarin, 5-6-methylcoumarin, and 6-dicoumarol.

3.2. Extraction Procedure with MIP-Based Adsorbents

MIP adsorbents have high selectivity to the target analyte, leading to effective extraction and elimination of interferences or matrix effects in the process of chemical analysis. In this study, we used the laboratory-fabricated group-selective MIP adsorbents prepared by thermal bulk polymerization and on the magnetite surface (Fe_3O_4/MIP) using 7-hydroxycoumarin as a template. This dummy template was selected as a structural analogue to the targeted compounds, as it is not a monitored compound in cosmetic products (the dummy template did not have any impact on the analysis of the targeted analytes since the leakage of the template cannot be avoided during the SPE elution step). Specific adsorption capacities of 270 μg per 1 g of MIP prepared by bulk polymerization and 80 μg per 1 g of Fe_3O_4/MIP (evaluated with dummy template) were satisfactory for use in the cosmetics analysis. The selected adsorbents were selective for targeted analytes reaching recognition coefficients α(MIP)/α(Fe_3O_4/MIP) of 1.2/1.4 for coumarin, 1.1/1.1 for dicoumarol, 1.2/1.2 for 6,7-dihydroxycoumarin-6-β-D-glucoside, 1.5/1.3 for 7-methoxycoumarin, and 1.6/1.4 for 6-methylcoumarin (α—the ratio of the amount of analyte adsorbed in the imprinted and blank adsorbents) [39,41].

The application of MIP-based adsorbents in the cosmetic analysis was realized using two extraction approaches, pipette-tip SPE and magnetic extraction. To select the optimal extraction conditions, the effects of adsorbent amount, type of washing solvent, volume of elution solvent, and adsorption time for batch extraction with the Fe_3O_4/MIP on the efficiency of the extraction procedures (expressed as recovery value, in %) were investigated. The samples of shower gel 1 and deodorant 1 spiked with coumarin at a concentration level of 5 μg·mL^{-1} were used. First, to eliminate interferences, the type of washing solvent (water and methanol) was tested for both types of extraction procedures. The methanol recovered 30–58% of coumarin, so this solvent was not suitable in the washing process. A loss of analyte of less than 2% was obtained using water as the washing solvent, so this solvent was finally applied.

To efficiently elute the coumarin, different volumes of elution solvent were tested. The elution solvent, methanol–acetic acid (90:10, v/v), was identical to the synthesis procedure for the removal of the template. Volumes less than 0.5 mL and 3.0 mL, for pipette-tip SPE and magnetic MIP extraction, respectively, were insufficient to elute the analyte, as documented in the graphs in Figure 3a,c (dependences shown for coumarin). Aliquots of 0.5 mL and 3.0 mL (for pipette-tip SPE and magnetic MIP extraction, respectively) of methanol–acetic acid 90:10 (v/v) showed recoveries higher than 95% and were finally applied in extraction procedures.

The influence of the amount of adsorbents for the pipette-tip MISPE and Fe_3O_4/MIP extraction procedures on the recovery of coumarin (Figure 3b,d) showed a moderate increase in trend when the amount of adsorbent increased from 10 to 20 mg and from 50 to 100 mg, respectively. The appropriate amounts of 20 mg and 100 mg were chosen for the pipette-tip MISPE and Fe_3O_4/MIP extraction, respectively.

Furthermore, the adsorption time was investigated for batch extraction with the Fe_3O_4/MIP (Figure 3e). The short extraction period may lead to incomplete extraction, whereas a long extraction time could increase the total analysis time, and in addition may cause decomposition of the analytes as well as a decrease in recovery. The extraction time interval of 15 min to 60 min was investigated to reach the optimum at 30 min, with recoveries greater than 93% (RSD % less than 8%).

3.3. Method Evaluation

The analytical method was validated, including parameters such as linearity, LOD, LOQ, accuracy, and precision. The relationship between the average peak area and the concentration of the analyte in the standard solution showed satisfactory linearity in the concentration range from the LOQ to 100 μg·mL^{-1} for the DAD and from the LOQ to 1 μg·mL^{-1} for the FLD. The correlation coefficients were found to be higher than 0.99, indicating that the method has satisfactory linearity (Table 2) in the concentration ranges

studied. The calculated LODs and LOQs showed values in ng.mL^{-1} for the method with FLD and in µg·mL^{-1} ranges for DAD. UV detection is commonly available in HPLC equipment and is suitable for the detection of all the coumarins under study. The HPLC method with FLD provides better sensitivity and selectivity for coumarins with native fluorescence properties. In this study, DAD was used for the detection of coumarin and dicoumarol (LODs of dicoumarol were similar for both detection types). The monitoring of coumarins (especially prohibited coumarins) at trace concentration levels is appropriate using FLD [42,43]. Thus, the developed method combining HPLC with DAD and FLD enables the detection of coumarins in cosmetics and provides a wider range of monitored compounds.

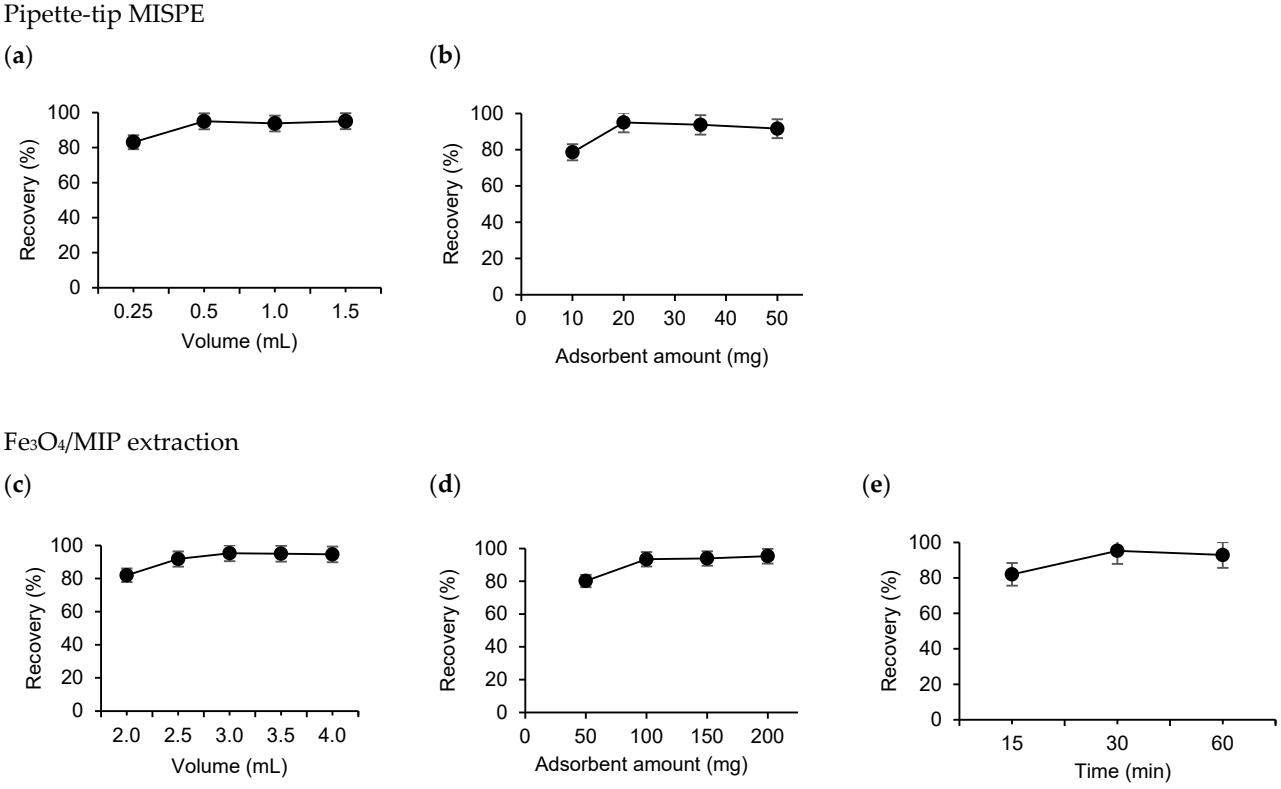


Figure 3. Effect of the volume of the elution solvent (methanol–acetic acid 90:10 *v*/*v*) (**a**,**c**), effect of the amount of adsorbent (**b**,**d**), and effect of the extraction time (**e**) on the recovery of coumarin for the pipette-tip MISPE and Fe_3O_4/MIP extraction.

Table 2. Linear range, coefficient of determination, LOD, and LOQ for coumarins.

Analyte	Detection Type	R^2	LOD (µg·mL^{-1})	LOQ (µg·mL^{-1})
6,7-Dihydroxycoumarin-6-β-D-glucoside	DAD	0.9993	0.3	1.0
	FLD	0.9993	0.001	0.003
Coumarin	DAD	0.9995	0.2	0.5
	FLD	na	na	na
7-Methoxycoumarin	DAD	0.9987	0.1	0.4
	FLD	0.9986	0.004	0.012
6-Methylcoumarin	DAD	0.9981	0.1	0.3
	FLD	0.9988	0.3×10^{-3}	0.001
Dicoumarol	DAD	0.9985	0.3	0.9
	FLD	0.9878	0.2	0.6

R^2—coefficient of determination; na—not applicable.

Recovery and precision tests were performed for the shower gel and deodorant samples spiked with mixed coumarin standards. Samples were kept for 1 h at laboratory temperature (23 °C) to absorb additives before extraction: Fe_3O_4/MIP extraction for the shower gel and pipette-tip MISPE for the deodorant. The accuracy of the method evaluated by recovery values ranged from 70.3 to 102.0% (Table 3). Therefore, the recovery values were acceptable for all the analytes studied. The intraday and interday precision evaluated by RSD % reached values less than 5.5%. Considering all of the above data for method validation, the current HPLC-DAD-FLD method and sample pre-treatment procedures employed in the present work can be regarded as suitable and applicable for the quantification of the selected coumarins in cosmetic samples.

Table 3. Recovery and precision results for extraction of coumarins.

Compound	Recovery (%)	Intraday Precision [a] (RSD %)	Interday Precision [b] (RSD %)
Fe_3O_4/MIP extraction [c]			
6,7-Dihydroxycoumarin-6-β-D-glucoside	73.2	4.2	4.8
7-Hydroxycoumarin	93.7	3.6	5.0
Coumarin	86.9/81.2	3.7/4.1	3.8/5.2
7-Methoxycoumarin	84.2	4.9	5.5
6-Methylcoumarin	85.0	3.5	4.9
Dicoumarol	70.3	3.7	4.5
Pipette-tip MISPE [d]			
6,7-dihydroxycoumarin-6-β-D-glucoside	72.4	3.1	3.1
7-hydroxycoumarin	94.6	2.4	3.8
Coumarin	94.1/102.0	3.5/2.8	4.5/3.3
7-methoxycoumarin	89.5	2.9	4.3
6-methylcoumarin	85.4	3.2	3.6
Dicoumarol	73.8	3.7	5.1

[a] n = 3, [b] n = 6, [c] shower gel 1 spiked with coumarins (10 $\mu g \cdot mL^{-1}$/20 $\mu g \cdot mL^{-1}$ of coumarin, 20 $\mu g \cdot mL^{-1}$ of dicoumarol; 20×10^{-3} $\mu g \cdot mL^{-1}$ of 6,7-dihydroxycoumarin-6-β-D-glucoside, 7-methoxycoumarin, and 6-methylcoumarin), [d] deodorant 1 spiked with coumarins (10 $\mu g \cdot mL^{-1}$/20 $\mu g \cdot mL^{-1}$ of coumarin, 20 $\mu g \cdot mL^{-1}$ of dicoumarol; 20×10^{-3} $\mu g \cdot mL^{-1}$ of 6,7-dihydroxycoumarin-6-β-D-glucoside, 7-methoxycoumarin, and 6-methylcoumarin).

3.4. Comparison of the Methods and Analysis of the Method Performance

A comparison of the pipette-tip MISPE and Fe_3O_4/MISPE–HPLC-DAD-FLD methods developed for the determination of coumarins in personal care products with other reported methods is listed in Table 4 [15,18,44–48]. HPLC methods have a high separation power compared to voltammetry and fluorescence methods and are useful mainly for the analysis of real samples with complex matrices, including cosmetic samples. The proposed method offers a simple and variable sample pre-treatment procedure and simultaneous determination of coumarins with sufficient sensitivity and recovery. Depending on the sample viscosity, the sample application form of MIP-based extraction is optional. Thus far, no methodology has been published for the determination of coumarins in cosmetic products combined with magnetic MIP-based extraction or pipette-tip SPE. In any case, as the authors documented in previous work, SPE with MIPs (7-hydroxycoumarin) in the traditional column form achieved a satisfactory recovery (comparable or even higher) compared to commercial adsorbents (C18 type and styrene-divinylbenzene copolymer resins) [49].

Table 4. Analytical characteristics of the methods for the determination of coumarins in cosmetics, including method proposed in this study.

Analyte	Sample	Method	Recovery (%)	LOD/LOQ	Ref.
6-Methylcoumarin	Toothpaste	UAE–HPLC-DAD	-	5×10^{-3} μg/ns	[14]
Coumarin; 7-Methoxycoumarin; 6-Methylcoumarin; Dicoumarol; 7-Ethoxy-4-methyl-coumarin	Cream	UAE–HPLC-UV	80–94	0.032–0.045 $\mu g \cdot mL^{-1}$/ns	[44]
6-Methyl-7-hydroxycoumarin; 7-Hydroxycoumarin; 4-Methyl-7-hydroxy-coumarin; 6,7-Dihydroxycoumarin; Dicoumarol; Coumarin; 7-Methoxycoumarin	Cream, lotion, shampoos, lipstick	SPE(Oasis HLB)–UPLC-MS/MS	80–93	ns/5×10^{-3}–15×10^{-3} $\mu g \cdot mL^{-1}$	[21]
Coumarin	Perfume	Dilution, HPLC-Q-TOF-MS	-	-	[45]
Coumarin	Deodorant, body lotion, cream, conditioner, bath additive	HPTLC with postchromatographic derivatization with KOH	-	0.5×10^{-3}/1.3×10^{-3} $\mu g \cdot mL^{-1}$	[15]
Coumarin	Fragrance product	GC-ECD	99–110	5×10^{-3} $\mu g \cdot mL^{-1}$/ns	[46]
Coumarin	Fragrance products	GC-MS	80–116	1.0 $\mu g \cdot mL^{-1}$/ns	[47]
Coumarin	Sun block, mist spray, emulsion	Fluorescent sensor	96–103	0.11 $\mu g \cdot mL^{-1}$/ns	[18]
Coumarin	Aqueous media	Square wave voltammetry with BDDE	92–104	0.23/0.66 $\mu g \cdot mL^{-1}$	[48]
6,7-Dihydroxycoumarin-6-β-D-glucoside; 7-Hydroxycoumarin; Coumarin; 7-Methoxycoumarin; 6-Methylcoumarin; Dicoumarol	Perfume, shower gel	Pipette-tip MISPE–HPLC-DAD-FLD Fe_3O_4/MISPE–HPLC-DAD-FLD	72–102 70–94	0.3×10^{-3}–$0.3/1 \times 10^{-3}$–1 $\mu g \cdot mL^{-1}$	This work

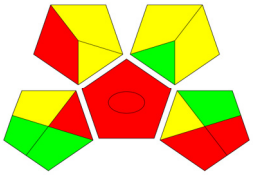
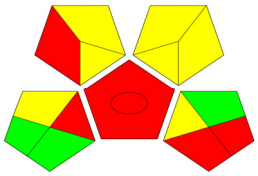
ns—not stated; BDDE—boron-doped diamond electrode; ECD—electron capture detector; HLB—hydrophilic–lipophilic balanced sorbent; MS—mass spectrometry; Q-TOF-MS—quadrupole time-of-flight mass spectrometry; UAE—ultrasound-assisted extraction, UPLC—ultra-performance liquid chromatography.

Recent trends in SPE focus on reducing sample and solvent volumes and increasing sample throughput. Pipette-tip SPE, as a miniaturized form of SPE that uses the small bed volume and sorbent mass in the pipette tip, significantly reduces washing and eluting solvent volumes, saves time in the evaporation step, and increases sample throughput [50]. In this work, 5 times less adsorbent compared to conventional SPE (100 mg) and 3–4 times less solvent volume were used. The benefit of Fe_3O_4/MISPE over traditional extraction methods is simple phase separation, eliminating the filtration and centrifugation steps [51,52]. Although this procedure is time consuming (90 min), it is more suitable for the treatment of viscous samples. Comparing other methods with the MIP-based SPE techniques used in this work showed good accuracy (70.3 to 102.0%; RSD % 3.1–5.5%).

In method development, some green analytical chemistry principles have been implemented through the miniaturization of the classical extraction procedure and the reusable application of adsorbents. Two approaches, the Analytical Eco-Scale [53] and the Green Analytical Procedure Index (GAPI) [54,55], were applied to evaluate the greenness level of the analytical procedures. The Analytical Eco-Scale concept assesses the method based on the number of hazards, expressed as penalty points. For each parameter of the analytical procedure (reagent type and quantity, occupational hazard, energy consumption, and waste generated), penalty points are calculated and subtracted from 100. A score greater than 75 indicates an excellent green procedure, a score ranging from 75 to 50 indicates an acceptable green analysis, and a score greater than 50 indicates an unsatisfactory green analysis [53]. The calculated penalty points (PP = 22 for the method with pipette-tip MISPE, PP = 23 for the method with Fe_3O_4/MISPE) are mainly assigned to the amount and type of solvents for extraction and HPLC separation (waste from the HPLC mobile phase) (Table 5).

The Eco-Scale score values were 78 for the pipette-tip MISPE–HPLC-DAD-FLD method and 77 for Fe_3O_4/MISPE–HPLC-DAD-FLD. These indicate the excellent greenness of the proposed methods. The GAPI approach evaluates fifteen parameters of the analytical method, utilizing five pentagrams to assess the environmental influence of the main fields of the procedure: general method type, sample collection, sample preparation, reagents and solvents required, and instrumentation [54,55]. In this work, the GAPI pentagram had four green, six yellow, and five red fields for pipette-tip MISPE and three green, seven yellow, and five red fields for Fe_3O_4/MISPE (Table 5). The red parts were related to the application of methanol as an extraction solvent (NFPA health rating 2, NFPA fire rating 3) and the amount of waste. The higher greenness of the method with pipette-tip MISPE result from the lower amounts of solvents in the extraction step. The advantage of both extraction methods in comparison to the SPE method with traditional adsorbents is the reusability of the MIP-based adsorbent.

Table 5. Greenness assessment of the methods coupled with pipette-tip MISPE and Fe_3O_4/MISPE developed for the determination of coumarins in cosmetics.

Pipette-Tip MISPE–HPLC-DAD-FLD			
Eco-Scale		**PPs**	**GAPI** [a]
Reagents	Methanol (8.2 mL)	7	
	Acetic acid (1 mL)	5	
	MIP (0.06 g)	1	
Instruments	HPLC-DAD-FLD	1	
	Occupational hazards	0	
	Waste (18.5 mL)	8	
Total PPs		22	
Score		78	
Fe_3O_4/MISPE–HPLC-DAD-FLD			
Eco-Scale		**PPs**	**GAPI** [a]
Reagents	Methanol (9.5 mL)	7	
	Acetic acid (1.0 mL)	5	
	Fe_3O_4/MIP (0.3 g)	1	
Instruments	HPLC-DAD-FLD	1	
	Mixer	0	
	Vacuum evaporator	1	
	Occupational hazards		
	Waste (13.4 mL)	8	
Total PPs		23	
Score		77	

[a] green/yellow/red color of pentagram part depicts low/medium/high environmental impact involved in each step of analytical methodology.

3.5. Analysis of Real Samples

The proposed MIP-based sample pre-treatment techniques under optimal conditions were used for the extraction of coumarins from five cosmetic samples (deodorant and shower gel). Among these, coumarin was detected in some tested samples; however, other coumarin derivatives were not detected over the LOD using the more sensitive HPLC-FLD method. The coumarin in the tested samples was verified by retention characteristics and UV spectra. As representative examples, the HPLC-DAD chromatograms obtained from the analysis of the deodorant 2 and shower gel 2 extracts treated with MISPE and Fe_3O_4/MISPE are shown in panels (c) and (d) of Figure 2, respectively. The matrices are remarkably clean, and no evident interferences are present. The coumarin concentration in the tested cosmetic samples varied between 0.5 and 15.4 $mg \cdot L^{-1}$ (deodorant 1: below the LOD; deodorant 2: 0.5 ± 0.1 $mg \cdot L^{-1}$; shower gel 1: below the LOD; shower gel 2: 0.8 ± 0.1 $mg \cdot L^{-1}$; shower gel 3: 15.4 ± 0.7 $mg \cdot L^{-1}$). Higher coumarin contents were deter-

mined in rinse-off cosmetic products such as shower gels. The other coumarin derivatives under study were not detected in the tested samples at concentration levels up to the LOD.

The Cosmetics Regulation (Council Directive of 27 July 1976 on the approximation of the laws of the Member States relating to cosmetic products (76/768/EEC)) requires the declaration of coumarin in the ingredient list of cosmetics from levels of 0.01% (rinse-off products) and 0.001% (leave-on products). Furthermore, the International Fragrance Association and the Research Institute for Fragrance Materials recommend specific limits for the use of coumarin in different end products for manufacturers in the perfume and cosmetic industry [56].

4. Conclusions

This paper reported MIP-based solid-phase extraction procedures applicable for sample pre-treatment prior to HPLC-DAD-FLD determination of coumarins in personal care products. Two formats of SPE were presented, showing their applicability depending on sample consistency: pipette-tip MISPE for low-viscosity samples such as deodorants and magnetic Fe_3O_4/MIP extraction for high-viscosity samples such as shampoo. The results showed that the proposed sample preparation methods are advantageous, simple, fast, and selective. In addition, elements of green analytical chemistry were applied, such as miniaturization and reusable adsorbents. This work supports the advancement of cosmetic products and offers a valuable tool for quality control. The proposed extraction protocols can be mutually complementary and applicable for the analysis of a wide range of cosmetic samples. A prospective application of the methods could be in the analysis of other matrices, e.g., natural samples and plants, to determine coumarins as significant bioactive compounds. In a further study, it would be appropriate to test the applicability of MIPs synthesized for other templates from the group of coumarins (e.g., coumarin, dicoumarol, and others).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr12030582/s1, Table S1: Applications of MIP-based extractions as sample pre-treatment methods in cosmetics analysis.

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