Simultaneous Selective Enrichment of Methylparaben, Propylparaben, and Butylparaben from Cosmetics Samples Based on Syringe-to-Syringe Magnetic Fluid Phase Microextraction

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Simultaneous Selective Enrichment of Methylparaben, Propylparaben, and Butylparaben from Cosmetics Samples Based on Syringe-to-Syringe Magnetic Fluid Phase Microextraction

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Abstract

Present work is the preparation of novel magnetic nanofluids based on deep eutectic solvent and used for the rapid microextraction of methylparaben (MP), propylparaben (PP), and butylparaben (BP) from cosmetics samples using syringe-to-syringe dispersive magnetic nanofluid microextraction procedure (SS-DMNF-ME). The optimization of the extraction of MP, PP, and BP was performed through central composite design (CCD). The optimum extraction conditions were assessed by optimizing pH, nanofluid volume, NaCl concentration, cycle number, and methanol volume. pH 8.0, 200 μL of magnetic nanofluid, 6% w/v of NaCl, eight cycles of injection/back injection, and 80 μL of methanol were the optimum extraction conditions, with the maximum recoveries of 98.62%, 100.92%, and 99.13% for MP, PP, and BP, respectively. The figures of merit calculated under the optimum condition were achieved from the CCD, and the developed method exhibited the low limits of quantitation (4.3, 3.0, and 2.7 ng mL⁻¹) and detection (1.3, 0.9, and 0.8 ng mL⁻¹) for MP, PP, and BP, respectively, as well as excellent linearity with R² > 0.99. The relative recoveries of three parabens in the actual samples were 85.99–99.07% with relative standard deviations ≤5.52%. In comparison to other extraction methods, SS-DMNF-ME was readily and rapidly determined MP, PP, and BP using HPLC-UV, and experimental data showed the efficiency, robustness, and reliability of the proposed method.

Graphical abstract

Keywords

Simultaneous selective enrichment, Magnetic nanofluid, Syringe-to-syringe magnetic liquid phase microextraction, Parabens, Cosmetics samples

1. Introduction

Parabens are synthetic chemicals typically applied as protective additives, and their most common and crucial types are methylparaben (MP), propylparaben (PP), and butylparaben (BP). Parabens are stable in a range of physical and environmental conditions and have ability to inhibit the development of undesirable microorganisms. Owing to this preventive feature, they can effectively reduce the use of antimicrobial agents and increase shelf life, as well as can be employed as preservative additives in personal care products, cosmetics, food, beverages, and pharmaceuticals. Parabens are highly efficient against yeasts, molds, and Gram-positive bacteria, but they have no effect on viruses and little effect on bacterial spores [[1], [2], [3]]. Their low concentrations can be found in a broad variety of products. Parabens are important due to their frequent contact with many people and have irritant contact dermatitis, antiandrogenic activity, disruption to the endocrine-disrupting system, and the development of malignant melanomas or female breast cancer. The role
of parabens in breast cancer (lower levels of 20 ng g⁻¹) have been evidenced in some recent investigations; therefore, it is speculated that these chemicals can influence the development and growth of tumors [4,5]. As a result of the widespread use of parabens and their derivatives in drug, food, and cosmetics samples, their determination is an important subject. In the investigation of parabens in matrices of complex sample, methods of sample preparation show an essential role in preconcentration, isolation, clean-up, and determination of the parabens prior to their instrumental analysis [2].

Very recently, solid-phase extraction (SPE), magnetic solid-phase extraction (MSPE), liquid phase microextraction (LPME), and solid-phase microextraction (SPME) have been used as sample preparation methods for the preconcentration of parabens prior to chromatographic analysis [6,7]. Dispersive LPME approach has newly attracted more attentions in virtue of the simplicity, rapidity, high extraction recoveries, and high enrichment factors (EFs) [8].

The collection of extraction phase after the microextraction process is highly critical; for this reason, magnetic nanofluid-based LPME has received special attention because of its exceptional characteristics of physicochemical stability, tenability, and easy preparation. Carrier liquids and magnetic solids create magnetic fluids that show both fluid and magnetic properties [9]. Nanofluids are uniform and stable solid-liquid composite materials containing of magnetic nanoparticles suspended in base fluids [10]. In recent years, nanofluids have got the focus of analytical chemistry research, mostly due to their capability of improving coefficient of mass transfer in microextraction processes [11]. Generally, in nanofluids, the magnetic nanoparticles are being coated by a shell made of a suitable material to preclude the particles from agglomeration or magnetostatic interactions and ameliorate their selectivity or affinity towards the special targets [12].

One of the major challenges is searching for new organic liquids that can possess eco-friendly advantages. Thus, many efforts have been devoted to the alteration in the conventional carriers and utilization of alternative solvents for the synthesis of new magnetic nanofluids with appropriate attributes [10]. Therefore, deep eutectic solvents (DESs) can serve as an alternative to traditional organic solvents [13]. Moreover, as a novel class of green solvents, DESs can be a suitable replacement for ionic liquids and volatile organic compounds owing to low volatility, low toxicity, good thermal and chemical stability, biodegradability, adjustable viscosity, easy preparation, and low costs [14]. DESs are compounds made by mixing a proper amount of hydrogen bond donor (HBD) and acceptor (HBA) [15,16]. The mixture of these two materials, due to the generation of hydrogen bonds and Van der Waals interactions, results in an eutectic mixture with the lower melting point than each individual component (HBA and HBD). DESs not only include the superior features of ionic liquids but also avoids numerous limitations in view of their biocompatibility, biodegradability, and nontoxicity [17].

The aim of this research work was to improve an efficient and a simple extraction method in order to determine MP, PP, and BP as protective additives. To this end, a new magnetic nanofluid was prepared from magnetic nanoparticles, and DES was suggested as a new extraction phase for the microextraction of MP, PP, and BP from cosmetics materials. To offer favorable repeatability and quantitative recoveries, some experimental factors, such as pH, nanofluid volume, NaCl concentration, cycle number, and methanol volume, were investigated by central composite design (CCD). The validity of the technique was experienced with reproducibility and repeatability studies. In the end, the proposed technique was employed to extract and determine the MP, PP, and BP from cosmetics samples. Among the innovations of the offered technique are practicality and cheapness, as well as the use of accessible devices.
2. Experimental

2.1. Apparatus, chemicals, and HPLC conditions
All reagents—such as FeCl$_3$·6H$_2$O (≥99%), FeCl$_2$·4H$_2$O (≥99.0%), NH$_4$OH (30–33% NH$_3$ in H$_2$O), methanol (≥99.9%), acetonitrile (99.8%), decanoic acid (≥98%), MP (analytical standard), PB (analytical standard), BP (analytical standard), DL-menthol (99%), oleic acid (OA; ≥99%), NaOH (≥98%), and HCl (37%)—were purchased from Merck, Darmstadt, Germany. The apparatus used in this study is listed in the supplementary data.

HPLC analysis was conducted using a liquid chromatograph (Agilent 1100 series, Wilmington, DE, USA). The system was equipped with a micro vacuum degasser, quaternary pump, and a wavelength detector (models G1379A, G1311A, and G13658, respectively), as well as with a sample injection valve (20-μL sample loop) and an Agilent C18 column (4.6 mm i. d. 250 mm, 5 μm). A 50:50 (v/v) mixture of acetonitrile and water (0.2% acid acetic) was used as the mobile phase. All the measurements were performed at ambient temperature by a wavelength ultraviolet detector operated at 280 nm.

2.2. Synthesis of Fe$_3$O$_4$ nanoparticles coated with OA
FeCl$_2$·4H$_2$O (0.4 g) and FeCl$_3$·6H$_2$O (1.1 g) were first added to 150 mL of distilled water and kept at 60 °C under vigorous stirring for 15 min. Subsequently, at the same conditions, in the presence of N$_2$ atmosphere and after the addition of 20 mL of NH$_4$OH (25%), the pH of solution reached ~11. The black suspension achieved in the result of this process was stirred vigorously under N$_2$ gas and at 50 °C for 2 h Fe$_3$O$_4$ magnetic nanoparticles were readily isolated by a strong magnet, washed several times by deionized water and dried [18], [19], [20]. Next, nanoparticles were coated with OA by mixing 0.5 g of Fe$_3$O$_4$ nanoparticles with 10% v/v OA, followed by the formation of the viscous solution via vigorous stirring by a magnetic stirrer at 150 rpm for 2 h [21]. The suspended particles were rinsed five times with 10 mL of the mixture of acetone and methanol (1:1 v/v) in order that the excess content of OA was removed. Finally, after separating by magnetic decantation, the prepared suspension (Fe$_3$O$_4$-OA) was dried under vacuum for a period of 24 h.

2.3. Preparation of hydrophobic DESs
Hydrophobic DES was prepared in a jacketed glass vessel by mixing decanoic acid with DL-Menthol (1:1 M ratios) with a magnetic stirrer at 300 rpm and about 100 °C until a homogeneous liquid was formed in the absence of any solid. The prepared solution was slowly cooled down to the ambient temperature [22], [23], [24].

2.4. Preparation of magnetic nanofluid
The preparation of magnetic nanofluid was conducted through dispersing 50 mg of OA-coated Fe$_3$O$_4$ nanoparticles, as magnetic nanoparticles, in a 1-mL volume of DES. The sonication of the mixture was performed for about 30 min until the dispersion of all the potential clusters of nanoparticles and the achievement of a stable magnetic nanofluid. The resultant magnetic nanofluid was kept at 4–8 °C for two weeks and later was used [10,25].

2.5. Syringe-to-syringe dispersive magnetic nanofluid microextraction procedure (SS-DMNF-ME)
In this method, two medical syringes (20 mL, V. MED) were connected to each other through one metal interface and used as a microextraction flask. For under study method, 10 mL of the sample solution, including MP, PP, and BP (100 ng mL$^{-1}$ of each paraben) and 6% w/v of NaCl, was adjusted at pH 8.0, and the sample solution was drawn into syringe 1 and mixed thoroughly with 200 μL of magnetic nanofluid. Following the connection of syringe 1 to syringe 2, the content of syringe 1 (a mixture of magnetic nanofluid and sample solution) was swiftly injected into syringe 2, and vice versa. The injection/back injection cycle was accomplished eight times. Afterward, magnetic nanofluid was simply isolated from the aqueous solution with an external
magnet, and the solution of supernatant was separated. After removing the magnet and adding methanol (80 μL), as the precipitation reagent, for desorption of DES from magnetic nanoparticles to the syringe 1, the strong magnet was again inserted to the bottom of the syringe 1 until the phase separation was obtained. Next, 20 μL of the extract was injected into HPLC to estimate the content of MP, PP, and BP. In the final step, the EF, preconcentration factor (PF), and extraction recovery (ER) were calculated. EF was considered as the ratio of the slopes of calibration curve of after (m_after) to before (m_before) preconcentration process, while PF was estimated based on the volume ratio of the aqueous solution (Vaq) to extraction phase (Vex).

\[
1) \ EF = \frac{m_{after}}{m_{before}}
\]

\[
2) \ PF = \frac{V_{aq}}{V_{ex}}
\]

Based on the following equation, ER, which is the percentage of total amount of analyte (n₀) transferred into the final phase (n_fin), was calculated.

\[
3) \ ER\% = \frac{n_{0}}{n_{fin}} \times 100 = \frac{C_{ex} \times V_{ex}}{C_{aq} \times V_{aq}} \times 100
\]

where \( V_{ex} \) and \( V_{aq} \) represent the volumes of extraction phase and the aqueous solution, respectively, and \( C_{ex} \) and \( C_{aq} \) indicate the concentrations of analyte in the final extraction phase and the aqueous solution, respectively [26].

2.6. Design of experiments

For estimation and explanation of responses and the effect of variable interaction, CCD is an effective modeling tool [27]. It includes less number of experimental runs needed for multicomponent optimization of factors and their interactions [28,29]. The influence of operating parameters, i.e. pH, nanofluid volume, NaCl concentration (% w/v), cycle number, and methanol volume (μL), and their interaction, on the extraction of MP, PP, and BP from cosmetics samples was examined. The range and level of these parameters are shown in Table S1. The analysis of variance (ANOVA) was applied to investigate the effect of the independent parameters on the extraction recovery. The adjusted determination coefficient (R² adj) was applied to know the role of five independent variables in the ER, as a function for the linear and quadratic model. The relationship between the aforesaid variables and their effects on the ER of MP, PP, and BP were illustrated in a three-dimensional graphical representation [30]. In addition, a second-order equation was improved to describe the relationship of the parameters with ER [28].

3. Results and discussion

3.1. Characterization and identification of materials

FE-SEM image of the Fe₃O₄ nanoparticles (Fig. 1a) represented particles of an equal size and a spherical shape, while the TEM image (Fig. 1b) illustrated particles of a unified size ranging from 10 to 30 nm. The XRD pattern of Fe₃O₄ nanoparticles (Fig. 1c) revealed a peak with the intensity of its pure form without any impurity. This result comes from diffraction peaks at 2θ value of 30.0°, 35.6°, 37.0°, 43.1°, 47.0°, 53.4°, 57.3°, and 62.8° (JCPDS NO. 88–0866) from the crystal planes (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (4 2 2), (5 1 1) and (4 4 0), respectively.
Fig. 1. (a) FE-SEM image, (b) TEM image, and (c) XRD pattern of the Fe₃O₄ nanoparticle.

3.2. Statistical analysis

As a computational method, ANOVA is employed to assess the contribution of each variable in the studied responses [31]. Table S2 presents the ANOVA results for the proposed model. F-value generally indicates that the model is significant for dependent factors. Herein, the F-values of the model were 99.52, 121.47, and 89.24 for the extraction of MP, PP, and BP, respectively, which demonstrate the model significance. The P-value <0.05 defines that the model terms are significant, which are required to be applied in the model equations [32,33]. The observed equations of the model in terms of coded factors, based on ANOVA results, were improved for the extraction of three above-mentioned parabens as follows:

$$\text{ER}_{\text{MP}}(\%) = +35.3 + 8.30A + 0.13B + 3.10C - 1.00D - 0.003AB + 0.04AC + 0.40AD + 0.02AE + 0.0031BC + 0.005BD + 0.0004BE - 0.32CD + 0.0044CE - 0.02DE - 0.35A^2 - 0.00005B^2 - 0.16C^2 - 0.10D^2 - 0.002E^2$$

$$\text{ER}_{\text{PP}}(\%) = +17.93 + 8.26A + 0.28B + 0.57C + 1.39D + 0.0009AB + 0.10AC + 0.46AD + 0.02AE + 0.03BC - 0.02BD + 0.0004BE - 0.35CD - 0.04CE + 0.04DE - 0.47A^2 - 0.0004B^2 - 0.18C^2 - 0.10D^2 - 0.002E^2$$
\[
\text{ER}_{\text{BP}}(\%) = -17.69 + 19.29A + 0.17B + 5.45C - 0.07D + 0.0007AB - 0.16AC + 0.16AD - 0.03AE + 0.01BC - 0.009BD + 0.0005BE - 0.27CD - 0.04CE + 0.03DE - 0.82A^2 - 0.0001B^2 - 0.14C^2 + 0.06D^2 + 0.001E^2
\]

All the independent variables had an effect on the extraction recovery; however, pH was the most effective factor as in the above equations, it has the highest coefficient. Mathematical models for the extraction of three parabens were statistically adequate due to the nonsignificant lack of fit (P > 0.05) and significant regression (P < 0.05) [34]. The model represented the lack of fit P-values of 0.4281, 0.3037, and 0.2223 for the extraction of MP, PP, and BP, respectively. Besides, the results displayed that the coefficient of variation (CV) was <10% for the extraction of the three parabens, as well as was reproducible, reliable, and precise. A high CV demonstrates that the disparity in the mean value is great, disclosing the inadequacy of response model [35]. The characteristic factors denoting the quality of the selected polynomial model in terms of fitting data are the adequate precision, \(R^2\), \(R^2\) adj. The \(R^2\) was equal to 0.9945, 0.9955, and 0.9939, and \(R^2\) adj values were 0.9845, 0.9873, and 0.9827 for the extraction of MP, PP, and BP, respectively. A minor difference between \(R^2\) and \(R^2\) adj values is suggestive of the adequate fitting of the data. Comparing the predicted value at the design points with the average prediction error shows the adequate precision, which should be greater than 4 to validate an appropriate model [36]. Therefore, the values of 39.605, 38.269, and 38.956 represents the adequacy of the designed model for the extraction of MP, PP, and BP, respectively. Fig. 2 exhibits the relationship of the actual data with the predicted ones. Obviously, linear distribution of the actual data reflects that there is sufficient consistency among the obtained data from the model and actual data.

![Fig. 2. Correlation of predicted and experimental values for the extraction recoveries of analytes.](image)

3.3. Effect of factors
The sample pH was investigated in the range of 2–10. The \(pK_a\) of MP, PP, and BP were 8.15, 8.4, and 8.5, respectively. Thus, the three parabens, under acidic pH and basic pH, exist as positive and negative ions, which elevates their water solubility and lessen their transfer to the extraction phase. The ER increased at pH values varied from 2.0 to 8.0, but at the pH values higher than 8, it obviously decreased (Fig. 3). The fluctuation in ER indicates that hydrophobic and electrostatic interactions are involved in the extraction recoveries. At pH 8.0, the three parabens were in their forms, and the highest extraction recoveries were achieved at pH ~8.0. The volume of the non-ionized extraction phase can directly influence the extraction efficiency recovery. However, an insufficient extraction phase cannot provide enough amount of extract for the analysis of chromatography, and the reproducibility will be weak. Moreover, the excessive extraction phase would make the signal response reduce remarkably [37,38]. In order to find the optimal volume of magnetic nanofluid, the experiments involving various volumes of the magnetic nanofluid were performed in the range of 100–300 μL. Fig. 3 shows that the extraction percentage declined rapidly with the growth of magnetic nanofluid volume. This observation
uncovers that the magnetic nanofluid has favorable performance for the extraction recoveries of MP, PP, and BP. It means that a very small volume of extractant is sufficient to meet the requirement for the extraction to achieve high EF, which is very beneficial to the enhancement of the sensitivity of the suggested method. In microextraction, the addition of salt is a common method that can affect the extraction efficiency by raising the ionic strength; however, a high ionic strength could lead to an inefficient rate of mass transfer and low extraction recoveries [39]. The influence of salt addition was examined by using NaCl concentration in the aqueous solution in the range of 0–8% (w/v). The extraction of MP, PP, and BP was highest when the concentration of NaCl was 6% (Fig. 3). The number of injection/back injection of the aqueous phase and the magnetic nanofluid mixture was measured as the numbers of extraction cycle. Accordingly, it is reasonable to conclude that the growth of the turbidity of the solution, which results from the complete dispersion of the magnetic nanofluid into the aqueous solution, is highly depends on increasing the number of extraction cycle. This behavior gives rise to maximizing the contact area of the aqueous phase with the extraction phase [8], thereby enhancing the extraction efficiency of the method. To evaluate the extraction cycle numbers, the injection/back injection of the mixture was examined in the range of 1–9 cycles. The results indicated that the extraction of three parabens raised to eight times and then remained constant (Fig. 3). The volume of methanol was investigated by measuring its varying volume in the range of 20–100 μL, to find the best volume for the desorption process. As it is apparent from the results, the extraction of MP, PP, and BP increased up to 80 μL and then decreased (Fig. 3). This alteration can be attributed to the fact that at volumes less than 80 μL, the DES cannot be desorbed completely from the magnetic nanoparticle, and as a result, low extraction is obtained. On the other hand, at volumes higher than 80 μL, the extraction started to decrease due to diluted MP, PP, and BP.
3.4. Optimum conditions

Desirability function was selected to maximize the extraction recoveries of MP, PP, and BP and used to define the profiles for the predicted values and desirability. Based on the desirability function of 1.0 (Fig. 4), the maximum recoveries of 98.62%, 100.92%, and 99.13% for MP, PP, and BP, respectively, were predicted under the following conditions: pH 8.0, 200 μL of magnetic nanofluid, 6% w/v of NaCl, eight cycles of injection/back injection, and 80 μL of methanol.
Fig. 4. Optimization plot for the determination of analytes.

3.5. Method validation

The performance of SS-DMNF-ME under the optimum conditions was examined in terms of the linear range, limit of quantification (LOQ), limit of detection (LOD), PF, EF, and intra- and inter-day precision (RSD%) (Table 1). The chromatogram and calibration curves (Fig. 5) were linear with R^2 of higher than 0.99, ranging from 5 to 700 ng mL\(^{-1}\). LODs estimated based on 3Sd/m [40] were 1.3, 0.9, and 0.8 ng mL\(^{-1}\), and LOQs based on 10Sd/m were 4.3, 3.0, and 2.7 ng mL\(^{-1}\) for MP, PP, and BP, respectively. The PF estimated for MP, PP, and BP based on 10 mL/200 μL was found to be 50, and the EF was calculated to be 79.5, 82.5, and 85.9, respectively. The intra-day precision (repeatability) showed as RSD%, and the determination of the three parabens at 100 ng mL\(^{-1}\) on a single day was 3.95%, 3.39%, and 2.60%, while the inter-day precision (reproducibility) on five consecutive days was achieved to as 3.50%, 3.83%, and 4.42% for the extraction of MP, PP, and BP, respectively.

Table 1. Performance characteristics of the preconcentration procedure.

<table>
<thead>
<tr>
<th>Quantitative analysis</th>
<th>MP</th>
<th>PP</th>
<th>BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample volume (mL)</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Extraction phase (μL)</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Linear range (ng mL(^{-1}))</td>
<td>5–700</td>
<td>5–700</td>
<td>5–700</td>
</tr>
<tr>
<td>Coefficients of determination (R^2)</td>
<td>0.9983</td>
<td>0.9990</td>
<td>0.9996</td>
</tr>
<tr>
<td>Limit of detections (LOD) (ng mL(^{-1}))</td>
<td>1.3</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Limit of quantification (LOQ) (ng mL(^{-1}))</td>
<td>4.3</td>
<td>3.0</td>
<td>2.7</td>
</tr>
<tr>
<td>Repeatability (ER%±RSD%, n = 5)</td>
<td>97.82 ± 3.95</td>
<td>99.01 ± 3.39</td>
<td>98.27 ± 2.60</td>
</tr>
<tr>
<td>Reproducibility (ER%±RSD%, n = 5)</td>
<td>97.15 ± 3.50</td>
<td>98.61 ± 3.83</td>
<td>96.92 ± 4.42</td>
</tr>
<tr>
<td>Preconcentration factor</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Enrichment factor</td>
<td>79.5</td>
<td>82.5</td>
<td>85.9</td>
</tr>
</tbody>
</table>
Fig. 5. The chromatogram (a) and calibration curves (b) of linear ranges for analytes in the range of 5–700 ng mL\(^{-1}\).

3.6. Application of the method in real samples

The real applicability of the SS-DMNF-ME method was validated for the monitoring of MP, PP, and BP in real samples. Under the optimum extraction conditions, water and the five cosmetics samples were analyzed. Table 2 shows the relative recoveries achieved for the MP, PP, and BP in water and the five cosmetics samples. In water and cosmetics samples, relative recovery (RR \%) indicated the reduction of the negative effects of the matrix. Based on the data in Table 2, reasonable recoveries ranging from 85.99\% to 99.07\% with RSDs ≤5.52\% verify that the proposed method has favorable accuracy and acceptable repeatability for the evaluation of MP, PP, and BP in water and cosmetics samples.

Table 2. Application of the proposed method for the determination of MP, PP, and BP in cosmetics samples (n = 3).

<table>
<thead>
<tr>
<th>Real samples</th>
<th>Added</th>
<th>Found(_{MP})</th>
<th>Found(_{PP})</th>
<th>Found(_{BP})</th>
<th>RR(_{MP})(^a)</th>
<th>RR(_{PP})</th>
<th>RR(_{BP})</th>
<th>RSD(_{MP})</th>
<th>RSD(_{PP})</th>
<th>RSD(_{BP})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0</td>
<td>ND(^b)</td>
<td>ND(^b)</td>
<td>ND(^b)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>100(^c)</td>
<td>97.20(^c)</td>
<td>98.81(^c)</td>
<td>99.07(^c)</td>
<td>97.20</td>
<td>98.81</td>
<td>99.07</td>
<td>1.42</td>
<td>2.62</td>
<td>1.85</td>
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<tr>
<td>Lipstick</td>
<td>0</td>
<td>ND</td>
<td>8.2</td>
<td>9.46</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td></td>
<td>100</td>
<td>92.25</td>
<td>100.79</td>
<td>103.81</td>
<td>92.25</td>
<td>92.59</td>
<td>94.35</td>
<td>3.77</td>
<td>4.13</td>
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<tr>
<td>Eyeliner</td>
<td>0</td>
<td>7.31</td>
<td>10.52</td>
<td>6.65</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>96.61</td>
<td>101.32</td>
<td>98.38</td>
<td>89.3</td>
<td>90.8</td>
<td>91.73</td>
<td>5.52</td>
<td>4.49</td>
<td>5.20</td>
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<tr>
<td>Blusher</td>
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<td>4.9</td>
<td>1.83</td>
<td>3.09</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
</tr>
<tr>
<td></td>
<td>100</td>
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<td>92.55</td>
<td>94.53</td>
<td>87.49</td>
<td>90.72</td>
<td>91.44</td>
<td>4.51</td>
<td>3.95</td>
<td>3.64</td>
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<tr>
<td>Eye shadow</td>
<td>0</td>
<td>8.22</td>
<td>4.81</td>
<td>5.52</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
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<td>89.06</td>
<td>5.16</td>
<td>4.50</td>
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*a* Relative recovery.  
*b* Not detected.  
*c* ng mL⁻¹.

The typical chromatograms of the blank water sample (a) and spiked with 100 ng mL⁻¹ of analytes before (b) and after (c) SS-DMNF-ME are illustrated in Fig. 6. It was observed that not only the detection sensitivity was obviously improved but also the interferences were reduced by treating with SS-DMNF-ME.

**Fig. 6.** Chromatograms of the blank water sample (a) and spiked with 100 ng mL⁻¹ of analytes before (b) and after (c) SS-DMNF-ME.

### 3.7. Comparison with other methods

In comparison to other methods reported in the literature (Table 3), SS-DMNF-ME has advantages of reducing the use of harmful and toxic organic solvents. The established method is applicable for the extraction and determination of a trace amount of MP, PP, and BP in cosmetics samples, with high sensitivity. In addition, the LOD, EF, and linear range of SS-DMNF-ME technique showed more satisfactory results than those reported in
other studies. Meanwhile, SS-DMNF-ME required less analysis time and was highly simple. Considering the above superiorities, the SS-DMNF-ME can be considered as an ideal method for the quantification of MP, PP, and BP in cosmetics samples.

Table 3. Comparison of the characteristic performance data obtained by using SS-MSPME with those of other methods for the determination of MP, PP, and BP in cosmetics samples.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Method</th>
<th>LOD</th>
<th>Linear range</th>
<th>Analysis time</th>
<th>EF</th>
<th>References</th>
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<td>100–10000</td>
<td>&gt;4</td>
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<td>10</td>
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<td>SS-DMNF-ME-HPLC-UV</td>
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<td>SDME-GC-MS</td>
<td>0.001</td>
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<td>0.8</td>
<td>5–700</td>
<td>5</td>
<td>85.9</td>
<td>Present Work</td>
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</table>

SDME-GC-MS: Single drop microextraction-gas chromatography-mass spectrometry.

4. Conclusions
In this study, an effective, a simple and a green analytical method was proposed. The technique was conducted based on the syringe-to-syringe dispersive magnetic nanofluid for the preconcentration of MP, PP, and BP in cosmetics samples prior to its determination by HPLC-UV. In the extraction process, the effective factors were optimized by CCD and specified best conditions. The proposed method required only a small amount of magnetic nanofluid to achieve quantitative recovery in a short time. In addition, the method attained favorable LOD, repeatability, linearity, and extraction recovery. Therefore, SS-DMNF-ME can serve as a rapid preparation technique and is suitable for the analysis of MP, PP, and BP in cosmetics samples.
Credit author contribution statement
Ebrahim Alipanahpour Dil: Conceptualization, Methodology, Investigation, Formal analysis, Validation, Writing - original draft. Mehrorang Ghaedi: Supervision, Resources, Writing - review & editing. Arash Asfaram: Formal analysis, Validation, Writing - original draft. Lobat Tayebi: Validation, Writing - review & editing.

Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data
The following is the Supplementary data to this article: Download: Download Word document (27KB)

Multimedia component 1.

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