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EXTRACTION OF PARABENS FROM COSMETIC AND ENVIRONMENTAL WATER SAMPLES COUPLED WITH UV-VISIBLE SPECTROSCOPY**

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An effective and fast vortex-assisted dispersive liquid-liquid extraction method was developed for the extraction of paraben in cosmetic samples and water samples. The paraben was determined and quantified using ultraviolet-visible (UV-Vis) spectrometry. A response surface methodology (RSM) based on the central composite design was used for the optimization of factors (composition of the extractant, volume of extractant, extraction time, centrifugation time, and centrifugation velocity) affecting the extraction efficiency of the procedure. The optimum parameters for vortex-assisted dispersive liquid-liquid extraction (VA-DLLE) are: chloroform used as the extractant solvent, 5 ml volume of extractant, 3 min extraction time, 5 min centrifugation time, and 2400 rpm centrifugation velocity. The limit of detection (LOD) and the limit of quantification (LOQ) for paraben are 0.0476 and 0.1442 μg/mL, respectively. Spiked cosmetic samples have the extraction recoveries in the range of 81.2–96.8%, whereas spiked water sample extraction recoveries were in the range of 88.8–100.63%. Each sample was repeated ($n = 2$), with a relative standard deviation of <5.74% for cosmetic samples and <9.03% for water samples. In conclusion, this extraction method is fast and inexpensive for the extraction of paraben.

Keywords: *vortex-assisted dispersive liquid-liquid extraction method, extraction of parabens, cosmetic and environmental samples.*

ЭКСТРАКЦИЯ ПАРАБЕНОВ В ПРОБАХ КОСМЕТИЧЕСКОЙ И ПРИРОДНОЙ ВОДЫ В СОЧЕТАНИИ СО СПЕКТРОСКОПИЕЙ В УФ-ВИДИМОЙ ОБЛАСТИ

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Разработан эффективный и быстрый метод жидкостно-жидкостной экстракции с помощью вихревой дисперсии для экстракции парабенов из проб косметической и природной воды. Для обнаружения и количественной оценки парабена использована спектрометрия в УФ-видимой области.

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Методология поверхности отклика (RSM), основанная на центральной композитной конструкции, использована для оптимизации факторов (состава и объема экстрагента, времени экстракции, времени и скорости центрифугирования), влияющих на эффективность экстракции. Оптимальные параметры вихревой дисперсионной жидкостно-жидкостной экстракции (VA-DLLE): хлороформ, используемый в качестве экстрагирующего растворителя, объем экстрагента 5 мл, время экстракции 3 мин, время центрифугирования 5 мин и скорость центрифугирования 2400 об/мин. Для парабена предел обнаружения LOD = 0.0476 и предел количественного определения LOQ = 0.1442. Образцы косметических средств с добавками имеют степень извлечения при экстракции в диапазоне 81.2–96.8%, тогда как эффективность извлечения образцов с добавленной водой при экстракции находится в диапазоне 88.8–100.63%. Для каждого образца эксперимент повторялся (n = 2) с относительным стандартным отклонением <5.74% для косметических образцов и < 9.03% для образцов воды.

Ключевые слова: *вихревой дисперсионный метод жидкостно-жидкостной экстракции, экстракция парабенов, косметические и природные образцы.*

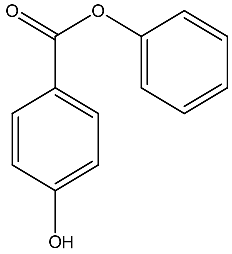
Introduction. Paraben is *p*-hydroxybenzoic acid from a group of alkyl esters. This includes methyl paraben, ethyl paraben, propyl paraben, butyl paraben, iso-butyl paraben, and benzyl paraben [1]. The antimicrobial activity of paraben will increase with increase in the esters chain group [2]. Esters with longer alkyl group have limitations due to low solubility in water. In order to comply with the needed antimicrobial activity, paraben is used as mixtures to obtain a synergetic effect [3]. In the study of Chen et al., paraben was used as a preservative in food, cosmetics, and pharmaceutical purposes due to its properties: neutral pH, odorless, tasteless, no decoloration, stable in air, and resistance to hydrolysis in aqueous and acidic solutions [4]. The use of paraben in large quantities is categorized as safe because paraben is easily absorbed and metabolized to *p*-hydroxybenzoic acid, which is less toxic than the parent compound [5]. The use of paraben as a preservative has increased due to its low toxicity and because of its broad antimicrobial activity spectrum, chemically stability, and low cost. Recent studies have shown that exposure to paraben can disrupt the endocrine system and can endanger the health of human being and animals [6]. Paraben can cause breast cancer due to the exposure of paraben to the skin through the application of deodorant. Studies have also shown that paraben can have a negative effect on the reproductive system [7]. In addition, paraben can cause serious diseases such as cancer through the replacement of the *p*-hydroxy in the aromatic ring, which contributes to estrogenic activity in the body [8].

Analytical control for cosmetic products is compulsory to ensure the quality and safety of the products. Various analytical studies have been conducted to extract paraben through the conventional and modern method. The conventional methods used are acid digestion, liquid-liquid extraction, and distillation, while the modern methods are improvements of the conventional method [9]. Many methods to extract paraben have been established such as liquid phase extraction (LPE), liquid-liquid extraction (LLE), solid phase extraction (SPE), and ultrasonic-assisted extraction (UAE) [10]. Recent studies have shown the use of microextraction to extract paraben, such as solid phase microextraction (SPME) and liquid phase microextraction (LPME). Liquid phase extraction is further developed in the form of cloud point extraction (CPE), dispersive liquid-liquid microextraction (DLLME), and vortex-assisted microextraction (VME) [4, 11, 12]. These solvent extraction-based methods, including LLE, dispersive liquid-liquid extraction (DLLE), and DLLME, can easily be modified or combined with other sample preparation techniques for particular purposes [13]. In this way, ultrasound-assisted dispersive liquid–liquid extraction (UADLLE) [14], ultrasound-assisted matrix solid-phase dispersive liquid extraction (UAMSPDLE) [13], and dispersive derivatization liquid–liquid extraction (DDLLE) [15] have been developed as good alternatives to the conventional LLE. This study attempted to develop the vortex-assisted dispersive liquid-liquid extraction (VA-DLLE) as an alternative for the conventional LLE method. The conventional LLE are not reliable for the current research since this method uses a large volume of solvents and bulky apparatus and is time consuming and expensive.

Extraction is an important process in many industries, especially in pharmacy and environmental industries, which is generally used for quantification and isolation of compounds of interest [16]. However, various factors such as extraction temperature, time, power, frequency, along with solvent concentrations and pH, are known to influence the extraction processes. Two types of techniques are generally used for optimization; the classical single factor experiments and the response surface methodology (RSM). The former is a one-factor-at-a-time approach, in which only one factor is varying at a time while all others are kept constant. This is time-consuming and suffers from a lack of information on the interaction of the factors. RSM is a multi-factorial study that can be done at a single time [17]. RSM is an effective mathematical and statistical tool for performing, improving, and optimizing the independent factors that influence responses in a given set of experiments. RSM not only defines the effect of independent variables but also their interaction effects [17]. RSM can be used to optimize the operating parameters in order to achieve maximum yield using a mathematical model [18]. RSM has been shown to be a reliable tool that provides statistically acceptable results [19].

This study attempted to develop the vortex-assisted dispersive liquid-liquid extraction (VA-DLLE) as an alternative for the conventional LLE method. The novelty of this method is the use of small amounts of solvent for extraction, which is carried out in the general apparatus without the need for large volumes of solvents and bulky apparatus. The vortex method has been added for improving the extraction of DLLE. The fast extraction is carried out in 5 min, and the samples are ready to be analyzed using UV-Vis spectrophotometry. Overall, the develop method is easily implemented because of the low operating cost. RSM was implemented in this study to set the optimum condition for the extraction of benzyl paraben in real water and cosmetic samples.

Experimental. The selected analyte, benzyl paraben



Benzylparaben

used in this study was purchased from Dow Corning Shanghai, China and supplied by Dow Corning Malaysia. Standard paraben solution is prepared in acetonitrile solvent and kept at 4°C until analysis to prevent degradation. The solvents used are chloroform purchased from Sigma Aldrich, butylimidazolium bromide, dichloromethane, and acetonitrile purchased from Merck, Germany.

Instrumentations. Quantification of benzyl paraben was performed using ultraviolet-visible (UV-Vis) spectrophotometer at wavelength 234 nm. A blank was used for the detection of paraben in the mixture of acetonitrile and chloroform at ratio of 1:1 for both solvents. A Vortex Heidolph Reax Top was used as a mixer for mixing extractant solvent and in real cosmetic and water sample analysis. Acentrifuge type Sartorius is used at a speed of 2400 rpm.

Preparation of extractant solvent. A 2-ml portion of extractant solvent (chloroform and dichloromethane), 3 ml of dispersive solvent (butylimidazolium bromide), and 5 ml of ultra-pure water was mixed in a 15 mL centrifuge tube. The mixture in the centrifuge tube was vortexed for 2 min and centrifuge for 5 min at 3500 rpm. A sediment phase and an aqueous phase was generated and observed. The sediment phase (extractant solvent) is removed using syringe and stored at room temperature before used for the extraction of paraben.

Vortex-assisted dispersive liquid-liquid extraction procedure. A 2-ml portion of 0.6 mg/L standard paraben, 5 mL of extractant solvents, and 4 mL of ultra-pure water were mixed in a 15 mL centrifuge tube. The mixture in the centrifuge tube was vortexed for 1, 3, and 5 min, and the samples were centrifuged for 1, 3, and 5 min at various centrifuge velocities (1500, 2500, and 3500 rpm). A cloudy solution with two layers was formed, which consists of sediment and aqueous phases. The sediment phase was removed using a syringe for analysis using a UV-Vis spectrophotometer. The procedure is shown in Fig. 1. The optimization of parameters of extraction was performed using the experimental design approach based on the central composite design (CCD). The factors investigated include the composition of extractant solvent, volume of extractant solvent, extraction time, centrifugation time, and centrifugation velocity (Table 1). Statistical analysis was performed using Design-Expert software (Version 6, Stat-Ease Inc.).

TABLE 1. Factors and Levels of Experimental Design

Factors	Variables	Central point (0)	Low Level (–1)	High Level (+)
A	Centrifugation velocity, rpm	2500.00	1500.00	3500.00
B	Extraction Time, min	3.00	1.00	5.00
C	Volume of extractant solvent, mL	3.50	2.00	5.00
D	Centrifugation time, min	3.00	1.00	5.00
E	Composition of extractant solvent	Chloroform	Chloroform	Dichloromethane

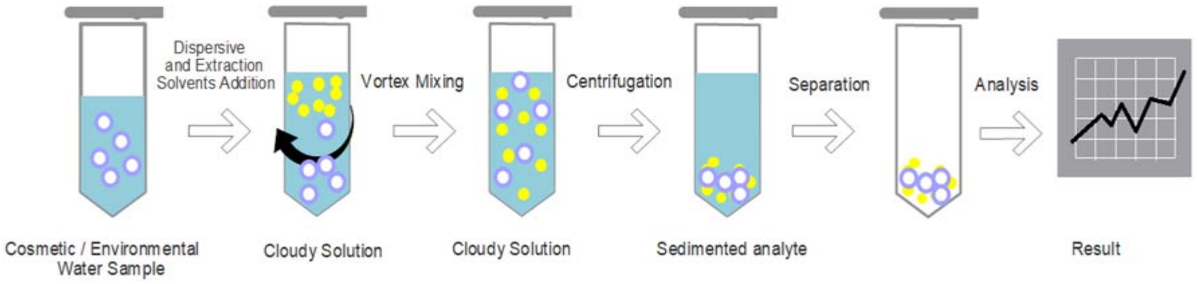


Fig. 1. Procedure of VA-DLLE.

Real sample preparation. The randomly chosen cosmetic samples were moisturizer, toner, body lotion, and body soap, which were bought at a local shop in Bangi, Selangor. The cosmetic samples were diluted with ultra-pure water at a dilution factor of 1:100 and were filtered using a 0.45 μm membrane filter to remove all the impurities in the cosmetic samples. Water samples were taken from rivers and lakes in the Klang Valley area, which are Sungai Langat, Sungai Buah, Sungai Kantan, Tasik Cempaka, and Tasik Idaman. Water samples were filtered using a 0.45 μm membrane filter to remove suspended particles before analysis.

Results and discussion. *Optimization of parameters.* The optimization of parameters of influence, such as composition of extractant solvent, volume of extractant solvent, extraction time, centrifugation time, and centrifugation velocity, was performed using RSM based on CCD. Figure 2 shows the analysis of variance (ANOVA) represented in terms of a Pareto chart to explore the significance of the parameters affecting vortex-assisted dispersive liquid-liquid extraction. Figure 2 shows that the effect of all parameters was significant as the desirability of all parameters is approximately equal to 1. RSM was used to observe the changes in response to the contributing factors.

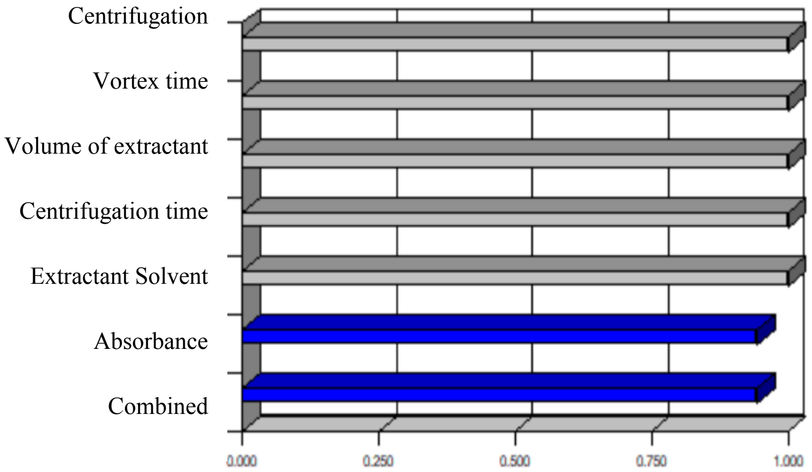


Fig. 2. Pareto chart of standardized effects for variables in the extraction of paraben.

TABLE 2. Summary of ANOVA Analysis for VA-DLLE

Source	Sum of square	Degree of freedom	Mean square	*F*-value	*P*-value ($\alpha = 0.05$)
Model	74.04	19	3.90	39.19	< 0.0001
A	8.388E-003	1	8.388E-003	0.084	0.7730
B	4.715E-003	1	4.715E-003	0.047	0.8287
C	2.67	1	2.67	26.89	< 0.0001
D	0.90	1	0.90	9.03	0.0046
E	66.59	1	66.59	669.65	< 0.0001
A2	0.58	1	0.58	5.84	0.0203
B2	0.13	1	0.13	1.30	0.2602
C2	2.515E-005	1	2.515E-005	2.529E-004	0.9874
D2	0.046	1	0.046	0.46	0.5010
AB	0.020	1	0.020	0.20	0.6548
AC	0.024	1	0.024	0.24	0.6273
AD	0.081	1	0.081	0.82	0.3714
AE	1.691E-003	1	1.691E-003	0.017	0.8969
BC	0.015	1	0.015	0.15	0.7031
BD	0.066	1	0.066	0.67	0.4189
BE	0.16	1	0.16	1.59	0.2153
CD	0.17	1	0.17	1.66	0.2049
CE	0.011	1	0.011	0.11	0.7435
DE	1.10	1	1.10	11.05	0.0019
Residual	3.98	40	0.099		
‘Lack of Fit’	3.62	30	0.12	3.40	0.0227
Pure error	0.35	10	0.035		
Value of R^2	0.9490	Adjusted value of R^2	0.9248		

The analytical response using RSM was conducted in random order to lower the chances of biased data. Analysis of variance (ANOVA) was used to explore the significant effects of the VA-DLLE procedure. The summary of ANOVA suggests using the quadratic model to continue validation, as shown in Table 2; *P*-value = 0.0011 for the quadratic model shows it is smaller than $\alpha = 0.05$; *F*-value for the quadratic model shows that the model is significant and there is only a 0.01% chance for the “*F*-value model” to happen due to noise. A $P > F$ value less than 0.05 indicates that the model is significant. Significant sources for this experiment are C, D, E, A^2, and DE, which are; the volume of extractant solvent, centrifugation time, composition of extractant solvent, interaction of centrifugation velocity, and interaction of centrifugation time against the composition of extractant solvent. An R^2 value showing the quadratic model can explain 94.90% of interaction in the model. The equation of the regression model is as follows:

$$
\begin{aligned}
Y &= 1.86 - 0.015A + 0.011B + 0.27C + 0.16D - 1.05E - 0.33A^2 - \\
&- 0.16B^2 + 0.0022C^2 + 0.094D^2 + 0.025AB - 0.027AC - 0.050AD - \\
&- 0.0068AE - 0.021BC - 0.046BD - 0.066BE - 0.072CD - 0.017CE - 0.17DE,
\end{aligned}
$$

where *Y* is the absorption (nm); *A* is the centrifugation velocity (A); *B* is the extraction time (min); *C* is the volume of extractant solvent (mL); *D* is the centrifugation time (min); and *E* is the solvent composition of the extractant. The quadratic equation for the model illustrates the dependence of the analytical response (% recovery) with respect to the evaluated variables [20].

The 3D response surface plots showing the analytical response against individual factors are shown in Fig. 3a–c. Figure 3a illustrates the interaction between centrifugation time and vortex time. The interaction 3 dimensions (3D) graph shows that the absorbance is highest in the middle range of centrifugation time and vortex time. Figure 3b, which shows the interaction volume of extractant solvent with centrifugation time, indicates that the absorbance is only high when the volume of extractant solvent is at a high volume no matter how long the centrifugation time is. Although centrifugation time affects absorbance, the volume of extractant solvent exerts a greater effect towards absorbance. Referring to Fig. 3c, the absorbance is lowest when both centrifugation time and velocity are low. The highest absorbance is when centrifugation time is in the middle range and the centrifugation velocity is high. This shows that the effect of absorbance was dependent on these factors. The calculated optimum conditions suggested by RSM are: chloroform as the extractant solvent, 5 mL volume of extractant, 3 min extraction time, 5 min of centrifugation time, and 2400 rpm centrifugation velocity. The optimum conditions suggested by RSM and the results were not significantly different from the predicted values at 95% confidence interval. Validation on the real samples was done using the optimum conditions suggested by RSM.

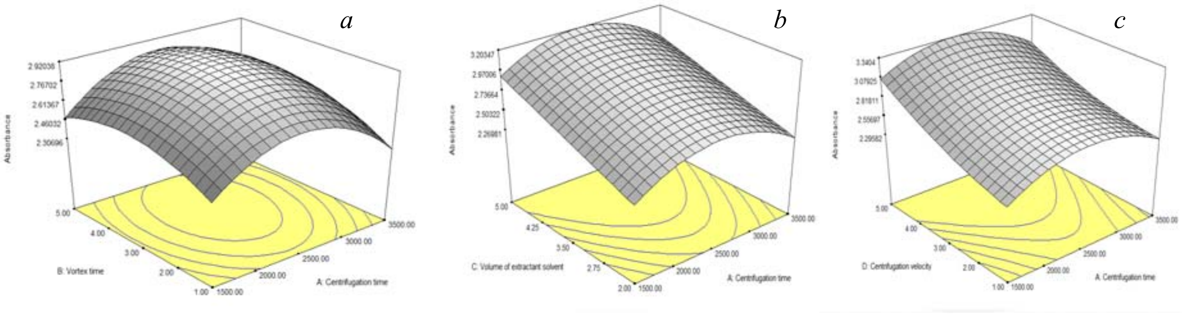


Fig. 3. Interaction between (a) centrifugation time with vortex time, (b) centrifugation time with volume of extractant solvent, and (c) centrifugation time with centrifugation velocity.

Analytical figures of merit. Under optimal conditions, the analytical performance of the proposed method for the extraction of paraben was investigated on linearity (0.1–1.0 mg/L), correlation coefficient ($R^2 = 0.9974$), limits of detection (LOD = 0.0476 mg/L), and limits of quantification (LOQ = 0.1542 mg/L). Five points (duplicate) calibration curves for the paraben were constructed by plotting the peak area of the signal acquired using UV-Vis spectroscopy as a function of concentrations of paraben. Figure 4 shows the spectrograph of UV-Vis of benzylparaben. A small value of LOD and LOQ indicated that the developed VA-DLLE is an effective method to detect paraben [21].

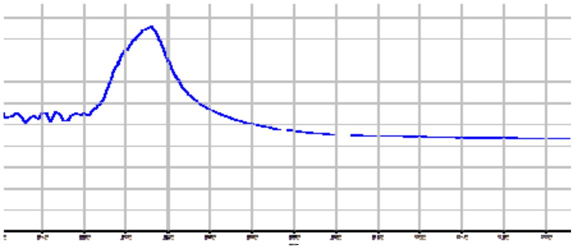


Fig. 4. UV-Vis absorption spectrograph.

Validation of real samples. The proposed method of VA-DLLE was used in the extraction of parabens in cosmetics (toner, moisturizer, shower cream and lotion) and environmental water samples that were analyzed by UV-Vis spectrometry after the VA-DLLE procedure. Under optimized conditions, the cosmetics and environmental water samples were spiked with 0.6 mg/L of benzyl paraben and analyzed according to the proposed procedure.

For spiked cosmetic samples, the RSD ranged from 2.1878% to 5.7466% (Table 3). For paraben extraction, the highest and lowest extraction recovery were 81.2199% and 96.8440% for toner and shower cream, respectively. For unspiked paraben cosmetic samples, the lowest paraben concentration was 0.8199 mg/L for toner samples and the highest was 1.0003 mg/L for lotion samples. For spiked water samples, the RSD ranged from 3.6726% to 9.0312% (Table 4). For paraben extraction, the highest and lowest extraction recovery are 100.63% and 88.78% for Sungai Buah and Sungai Langat, respectively. For unspiked water samples, the highest paraben concentration was 1.1269 mg/L for Sungai Kantan samples, and the lowest was 0.9516 mg/L for Sungai Buah sample. According to AOAC guidelines, the acceptable recovery for 1.0 mg/L is 75–120% [22]. Thus, it can be concluded that the extraction performance on cosmetic and water samples using VA-DLLE method is effective.

TABLE 3. Analysis of Paraben in Cosmetic Samples

Cosmetic samples	Spiked with 0.6 mg/L paraben		Unspiked
	Extraction recovery, %	Relative standard deviation (RSD)	Concentration, mg/L
Toner	81.2199	2.6671	0.8199
Moisturizer	91.5314	2.1878	0.9229
Shower cream	96.8440	4.2600	0.9063
Lotion	96.1320	5.7466	1.0003

TABLE 4. Analysis of Paraben in Environmental Water Sample

Water samples	Spiked with 0.6 mg/L paraben		Unspiked
	Extraction recovery, %	Relative standard deviation (RSD)	Concentration, mg/L
Sungai Kantan	91.9478	6.6396	1.1269
Tasik Cempaka	93.7778	4.4298	1.0809
Sungai Langat	88.7814	3.6726	1.0445
Sungai Buah	100.6324	9.0312	0.9516
Tasik Idaman	95.7234	7.9472	1.0821

TABLE 5. Comparison of the Developed VA-DLLE Method with Other Methods for Determination of Parabens

Parabens	Matrices	Method	Recovery, %	LODs, μg/mL	References
Methyl, ethyl, propyl, isopropyl, butyl, isobutyl, benzyl paraben	Wastewater, river water	SPE/HPLC-UV	66.8–109.3	0.08–0.44	[23]
Methyl, propyl paraben	Underground water	HF-MMLLE/ HPLC-DAD	67.0–116.0	500–4600	[24]
Methyl, ethyl, propyl paraben	Toothpaste, mouth rinse, shampoo, tap water, river water	DLLME/HPLC-UV	90.2–111.0	5–20	[25]
Methyl, ethyl, propyl paraben	Water, beer and beverage samples	DLLME/HPLC-UV	95.0–103.0	0.3–0.5	[26]
Methyl, ethyl, propyl, benzyl paraben	Shower cream, moisturizer, cleanser, make-up remover, lotions	CPE/HPLC-UV	68.0–112.0	0.01–0.02	[27]
Benzyl paraben	Cosmetic and water samples	VA-DLLE/UV-Vis	81.0–100.6	0.0476	This work

SPE: solid phase extraction, HPLC-UV: high performance liquid chromatography with ultraviolet detector, HF-MMLLE: hollow fiber-microporous membrane liquid-liquid extraction, HPLC-DAD: high performance liquid chromatography with diode array detector.

Comparison of developed VA-DLLE method with other existing methods. The extraction efficiencies of the developed VA-DLLE method to extract benzyl paraben were compared with other methods of determination of parabens (Table 5). Comparison of the % recovery, RSD, and LOD revealed that the currently developed method was as efficient compared to the previously reported methods. The analytical performance of the developed VA-DLLE method was comparable to those reported in Table 5. The results obtained in this work showed that the VA-DLLE method is efficient and is also a simple technique for extraction of paraben from cosmetic and environmental water samples.

Conclusions. In this study we proposed a simple and effective method to extract paraben from cosmetic and environmental water samples. Its procedure was based on VA-DLLE method followed by UV-Vis spectrometry analysis of paraben present in the samples with the assistance of response surface methodology (RSM) based on the central composite design (CCD). The obtained limit of detection (LOD) of benzyl paraben was 0.0476 μg/mL, and good recoveries were obtained in the ranges 88.8–199.6% and 81.2–96.8% for spiked water samples and cosmetic samples, respectively.

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