ASM Sc. J., 12, 2019
https://doi.org/10.32802/asmscj.2019.310

Vortex Assisted Extraction for Propylparaben Analysis in Cosmetics

Fatin Nur Afini Binti Bajuri[1], Beh Shiuan Yih[1],
Noorashikin Md Saleh[1*], Farhanini Yusoff[2] and Nik Nur Atiqah Nik Wee[1]

[1]*Chemical Engineering Programme, Research Centre for Sustainable Process Technology (CESPRO), Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Ehsan, Malaysia*
[2]*School of Marine and Environmental Sciences, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu Malaysia*

Propylparaben is an ester of para-hydroxybenzoic acid and commonly used as a preservative in the cosmetics, pharmaceuticals and food products. However, several recent reports demonstrated that paraben possesses an estrogenic activity and causes cancer for the consumer. Therefore, the extraction of propylparaben from cosmetics requires method that is easy, fast, user-friendly and accurate reproducible result. Conventional techniques such as liquid-liquid extraction (LLE) show some disadvantages such as the use of a large amount of solvent and time-consuming. Therefore, this present study aims to apply vortex assisted extraction (VAE) in determining the concentration of propylparaben in cosmetic samples and analyse using ultraviolet spectroscopy (UV-Vis). From the results, the calibration curve was found in the range of 0.2-1.0mg/L with a regression coefficient, r^2=0.9932 and relative standard deviation (RSD) less than 1%. The limit of detection (LOD) and quantification (LOQ) for VAE was 0.090mg/L and 0.302mg/L, respectively. Operating parameters for VAE (concentration of salt, type of solvent and extraction time) and LLE (concentration of salt, extraction time, type and volume of solvent) have been optimised and subsequently applied to the extraction using the real samples. Ten cosmetic products were chosen randomly such as shampoo, body wash, gargle, toner, mouth rinse, lotion, feminine wash, face mask, and scrub. The recoveries for VAE and LLE were 76.7% -103.4% (RSD=0.1-4.0%) and 62.5%-93.9% (RSD=<1%), respectively. Therefore, VAE is the best modern method for determination of propylparaben in cosmetics because it is simpler, faster with high percentage of recovery compared to other techniques.

Keywords: propylparaben; liquid-liquid extraction; vortex-assisted extraction

I. INTRODUCTION

Nowadays, cosmetics are elements that can attract the attention of the community. Some Asians often exaggerate in the use of cosmetics as absolute importance in the care of their appearance (Krishnan *et al.*, 2017). In the process of producing cosmetics, foods, pharmaceuticals and paper industries, preservatives are important ingredients to prevent the growth of microorganisms for longer product life (Huang *et al.*, 2013, Liao and Kannan, 2014).

Propylparaben is one of the common preservatives used in cosmetics, foods, and pharmaceuticals. These preservatives also have estrogenic properties, and 58.0% of cancer patients have been found with parabens in their breast cancer cells (Khanna and Darbre, 2013). According to Jain *et al.* (2015), the addition of alkyl chains in the ester group not only increases the function of anti-bacterial agent but

*Corresponding author's e-mail: noorashikin@ukm.edu.my

also increases its toxicity (Jain *et al.*, 2015). According to the Organization for Economic Cooperation and Development (OECD), endocrine disruptive compound (EDC) is defined as an exogenous compound or mixture that changes the endocrine system and causes a harmful effect towards human health. The effects of EDC on human nowadays are endometriosis, reduced number of sperms, increasing the chances of breast cancer as well as testicle and prostate cancer. Apart from that, infertility problems caused by parabens have been reported to be able to perform anti-androgen activity, which bonded with androgen receptors and thereby prevented transcription of testosterone (Esplugas *et al.*, 2007, Shalash *et al.*, 2017).

Additionally, the use of paraben is limited to 0.40% concentration in single usage while 0.80% concentration in a mixture. Thus, determination of paraben in cosmetic products becomes a concern in many studies conducted. Figure 1.1 shows the molecular structure of propylparaben.

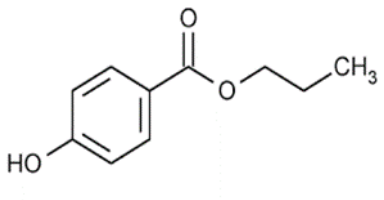

Figure 1. Propylparaben structure

Traditionally, methods that have been used in the determination of propyl paraben such as liquid-liquid extraction (LLE) involved long procedures and consumed large volume (5.0 – 60.0mL) of toxic organic solvents such as chloroform and dichloromethane. The formation of an emulsion resulting in losing of analytes is one of the major issues in LLE. In comparison, modern methods have shown to provide a more economical condition in removal of impurities and complex matrix from cosmetic samples and reduce the time of extraction than traditional methods (Chen *et al.*, 2018). Many modern methods for determination of paraben have been reported, including, liquid-phase microextraction (LPME), solid-phase microextraction (SPME) (Fei *et al.*, 2011) and fast syringe-assisted liquid-liquid microextraction (FSALLME) (Rajabi *et al.*, 2017). LPME has been reported as a more environmentally friendly process than SPME due to a higher mass transfer effect and shorter extraction time. Plus, SPME required a meticulous preparation to get the best polymer surface for paraben extraction (Fei *et al.*, 2011). Moreover, vortex-assisted dispersive liquid-liquid microextraction based on the solidification of a floating organic drop (VA-DLLME-SFO) allows an easy and facile separation of aqueous solutions from extraction solvents to establish an oil-in-water emulsion, and the use of a vortex results in a shorter extraction time compared to dispersive liquid-liquid microextraction (DLLME) (Chen *et al.*, 2018). Two phases separation to extract methyl phenol and paraben were successfully reported by Noorashikin *et al.* (2016) and Norseyrihan *et al.* (2016) respectively which using cloud point extraction (CPE) and replace solvent by surfactant which makes this method as a modern and green methods (Noorashikin *et al.*, 2016, Norseyrihan *et al.*, 2016).

Besides the modern and versatile methods that have been implemented nowadays, the vortex-assisted extraction (VAE) also has its speciality on the extraction of pollutants from environmental samples. Thus, this study proposed a green method that utilised mechanical agitation produced from VAE. Based on Shalash *et al.* (2017), VAE enhanced the efficiency of the extraction due to the mechanical agitation, which affected the mass transfer and emulsification process (Shalash *et al.*, 2017). It is also cheap to be practised for high quantitative revenue without reducing the efficiency rate and does not require any use of dispersing solvent (González-Hernández *et al.*, 2015). The scrutiny stride for the determination of pentachlorophenol (PCP) in the soil was improved using liquid-vortex aid (VAELLE) as the extraction method and gas chromatography (GC). Total PCP acquisitions in soil samples ranged from 89.5% to 98.9% (Yu *et al.*, 2015).

Thus, the purpose of this study is to compare the environmental friendly modern extraction method, VAE with the traditional method, LLE in combination with UV-Vis spectrophotometry in determination of propylparaben. This is a first attempt to study on development using vortex assisted extraction method for propylparaben in cosmetic samples using UV-Vis spectrophotometry. Several parameters involved in both methods were optimised such as temperature, volume of extraction solvent, concentrations of salt and extraction time. The analytical recoveries of propylparaben in ten different samples of cosmetics were compared between the proposed extraction method and previously reported methods.

II. MATERIALS AND METHODS

A. Reagents and Standards

Propylparaben (99.9%) was purchased from Sigma Aldrich (USA). Reagents such as acetonitrile (99.0%), n-hexane (99.0%), methanol (99.0%) and dichloromethane (99.0%) used are analytical grade and were purchased from Sigma Aldrich (USA). Magnesium sulfate, $MgSO_4$ was obtained from Merck (Germany). Deionised water was obtained from Millipore Milli-Q Plus water purification system. The stock solution of propylparaben was prepared in analytical grade acetonitrile at concentration of 1000mg/L. Working standard solutions were prepared by step-wise dilution from stock solution in acetonitrile.

B. Instrumentation

The purification and separation of the target analyte were performed by Perkin Elmer UV-Vis spectrophotometer (model Lambda 35, Tokyo) at absorbance 245nm using 1cm glass cells. A vortex-mixer (Heidolph, USA) was used to homogenise the solution in VAE method.

C. Cosmetic Samples Preparation

About 0.01g of cosmetic samples were weighed into 250mL beaker, and 100mL of deionised water was added. The mixture was stirred using magnetic stirrer. The mixture was filtered using 0.45µm filter before used in proposed method.

1. Procedure for Vortex-assisted Extraction (VAE)

A mixture of 2.50mL of propylparaben stock solution (0.4mg/L), 0.20mL of extracting solvent (acetonitrile) and 0.50ml of 1.50 M $MgSO_4$ were added into centrifuge tube. The centrifuge tube was then vigorously shaken using vortex for 1 min at 2500 rpm. The separation of the two phases occurred after standing the centrifuge tube for 1 min. The solvent-rich phase was isolated and analysed using UV-Vis as illustrated in Figure 2.

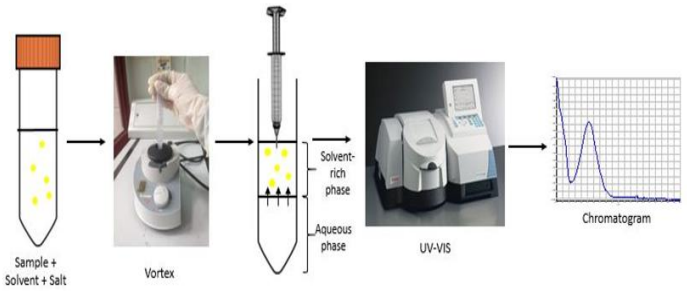

Figure 2. Procedures of VAE

2. Procedure for Liquid-liquid Extraction (LLE)

This method was adopted from Bedassa *et al.* (2017) with some modification. A mixture of 2.50mL stock solution, 0.5mL of 1.50 M $MgSO_4$ and 2.50mL of extracting solvent (acetonitrile) were added into separating funnel and shaken by hand intermittently over 1 min. The phases were allowed to separate for 10 min, and aqueous phase was removed. The solvent rich phase was isolated into vial and evaporated under N_2 gas stream. The sample was analysed using UV-Vis (Bedassa *et al.*, 2017). Figure 3 illustrates the procedures of LLE.

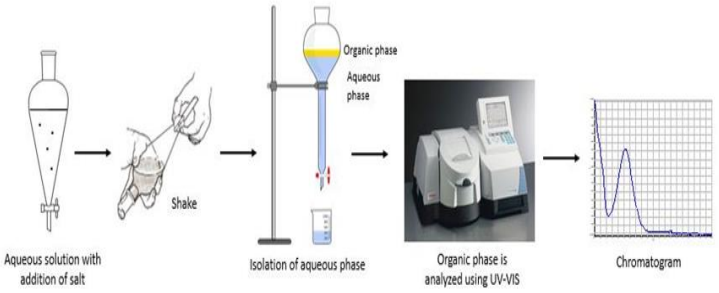

Figure 3. Procedures of LLE

III. RESULTS AND DISCUSSIONS

A. Optimisation of VAE technique

1. Effect of MgSO4 concentration

In this study, the addition of salt such as $MgSO_4$ is known to form solvent rich phase through salting out effect. Type of salt selection plays crucial role in the degree of phase separation, which reduces the mutual miscibility of the two liquids. For example, the aqueous sample and water-

miscible organic solvent, causing formation of a two-phase system with the simultaneous extraction of the target analytes into the organic phase (Bedassa *et al.*, 2017). Bedassa *et al.* (2017) and Zhang *et al.* (2009) reported that $MgSO_4$ has the highest peak area among other salts such as NaCl, Na_2CO_3 and $(NH_4)_2SO_4$ due to highest ionic strength per unit concentration of $MgSO_4$ in aqueous phase. Magnesium also is known as strong Lewis acid thus any strong Lewis base that has interaction with it would give an impact to the extraction recovery. Hence, $MgSO_4$ was selected in this study. The different concentrations of $MgSO_4$ ranged from 0.50 M, 1.00 M, 1.50 M, 2.00 M and 2.50 M in the samples were tested as shown in Figure 4. It was observed that concentration of extracted propylparaben increased from 0.50 M to 1.50 M salt as the amount of salt was sufficient to induce the required phase separation. Decline trend was shown from 2.00 M and above due to saturation when $MgSO_4$ was added (Du *et al.*, 2014). Undissolved salts in the solution caused the separation of both phases became difficult. Also, it reduced the efficiency of extraction. Therefore, 1.50 M of $MgSO_4$ was selected as the optimum concentration to get the best salting-out effect.

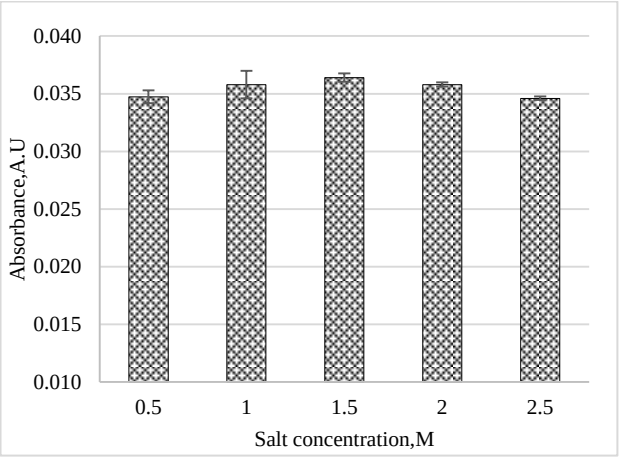

Figure 4. The effect of different concentration of MgSO4 on the concentration of extracted propylparaben

2. Effect of type of extraction solvent

A successful proposed method can be achieved through an appropriate selection of organic solvent for extraction of the desired analyte. The organic solvent should be miscible in water, highly polar and able to perform a two-phase separation with addition of salt. In the present study, four extraction solvents (acetonitrile, dichloromethane, n-hexane and methanol) were compared in single mixture to extract propylparaben into surfactant-rich phase. Experimental observations showed that dichloromethane and n-hexane were unable to induce phase separation. Good phase separation was introduced using acetonitrile alone because methanol was unable to dissolve $MgSO_4$, thus produced salt precipitation at the bottom of centrifuge tube. Acetonitrile is less harmful organic solvent than other solvents and frequently used in conventional LLE thus more favour with a green chemistry context (Teju *et al.*, 2017). Acetonitrile also has been widely used as extraction solvent in determination of fluoroquinolones in water, food, biological matrices and multi-residual pesticides respectively (Bedassa *et al.*, 2017; Du *et al.*, 2014; Tang and Weng, 2013). Therefore, acetonitrile was selected as an ideal extraction solvent for LLE method in determination of propylparaben due to high ability to form clear phase separation.

3. Effect of extraction time

Mixing of the sample using vortex would affect the kinetics of extraction and enhance contact angle between organic solvent and aqueous solution to form a two-phase system. In this study, the effect of vortex time was varied between 0.5 min, 1 min, 2 min and 3 min as shown in Figure 5. At time less than 1 min, the agitation was inadequately mixed and resulted in a lower absorbance. Maximum absorbance was achieved at 1 min of vortex time, which indicated that equilibrium was rapidly reached by interface contact between propylparaben and aqueous sample (Liu *et al.*, 2010). Extracted propylparaben concentration shows neither increased nor decreased after 1 min extraction time. Thus, 1 min extraction time was selected as the optimum condition using VAE method. Miralles *et al.* (2016) obtained 1 min of extraction time as optimum operation time using vortex mixer in determination of cosmetic products by vortex-assisted liquid-liquid semimicroextraction. In addition, Shalash *et al.* (2017) reported the optimum extraction time in the range of 15 s to 60 s at 2500 rpm and showed an increasing trend of efficiency within the range with constant efficiency after 1 min. The study also selected 1

min as an optimum extraction time.

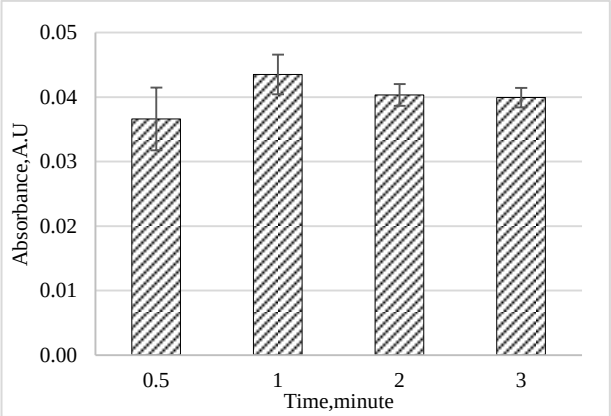

Figure 5. The effect of different extraction time on the concentration of extracted propylparaben

B. Optimisation of LLE technique

1. Effect of MgSO4 concentration

Different salt concentrations affect the degree of phase separation, which reduces the solubility of polar organic and separate water-miscible solvent in the dilute phase (Tang and Weng, 2013). The ability to precipitate hydrophilic substances should be strong. Considering the explanation from above subsection, $MgSO_4$ was selected for present study.

A salting out effect was studied by adding different concentrations of salt varied from 0.50 M, 1.00 M, 1.50 M and 2.00 M in Figure 6. It was observed that the concentration of propylparaben increased gradually with increased concentration of $MgSO_4$ up to 1.50 M. Propylparaben in the samples might diminish its solubility in the presence of salt. However, when the concentration of $MgSO_4$ was higher than 1.50 M, a slight decreased in the concentration of propylparaben was observed. It could be explained by increase in the viscosity of aqueous phase would reduce the mass transfer of the analyte from aqueous to organic phase (Pourhossein and Alizadeh, 2017). Besides, above 2.00 M of $MgSO_4$, the sample solution was saturated and interfered with the phase separation as discussed in above subsection. The results obtained by Bressan *et al.* (2017) in developed method using the salting-out effect agreed that anions contributed substantially to the generation of separation phase. Anion such as $S0_3^{2-}, C0_3^{2-}, S0_4^{2-}$ produced a better separation phase than anion such as $CH_3COO^-, Cl^-, HPO_4^{2-}$ *dan* NO_3^{2-} while cation did not play any role in this method (Bressan *et al.*, 2017). Thus, 1.50 M of $MgSO_4$ was chosen for subsequent experiments.

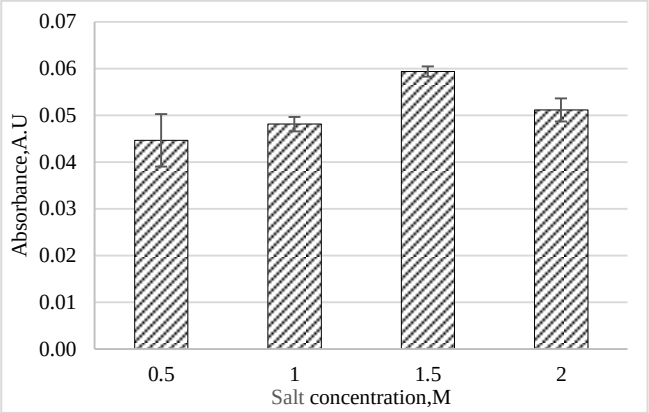

Figure 6. The effect of different concentration of $MgSO_4$ on the concentration of extracted propylparaben

Experimentally, both methods used 1.50 M of salt to induce the best separation of phases. However, anion only involved in salting-out effect during cation effect on salting-in mechanism. Both types of salt contained the same anion, SO_4^{2-}.

2. Effect of type of extraction solvent

Selection of organic solvent is vital in the extraction method, especially in extraction of propylparaben from cosmetic samples. Different types of solvent used in this study were described in above subsection. Similar results were obtained thus acetonitrile was chosen as extraction solvent for further analysis.

3. Effect of extraction time

To increase the concentration of propylparaben in a solvent-solvent phase, the contact angle between the two phases should be optimised in order to improve the effectiveness of extraction. Different extraction time; 0.5, 1.0, 2.0 and 3.0 min were tested as shown in Figure 7. By increasing the extraction time, the concentration of extracted propylparaben also increased and reached the maximum

concentration at 3.0 min. Hence, 3.0 min was used as the optimum time for this method.

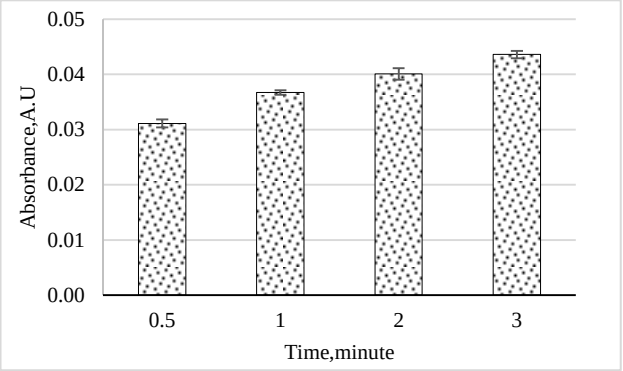

Figure 7. The effect of different extraction time on the concentration of extracted propylparaben

Effect of extraction time was compared between VAE and LLE methods. Based on Figure 5 and 7, the shortest extraction time was achieved by VAE at 1 min. LLE required 3 min extraction time, and the recovery of propylparaben was the lowest among the other extraction methods. Therefore, VAE is recommended as an extraction method for propylparaben based on the shortest extraction time.

4. Effect of solvent volume

The volume of extraction solvent plays a significant role in the efficiency of extraction method. The optimum volume of extraction solvent should promote a high extraction recovery as well as sufficient volume of organic phase for the subsequent analysis. In this study, the effect of acetonitrile volume was investigated in range 2.00 - 3.00mL as shown in Figure 8. The concentration of propylparaben increased with bigger volume of acetonitrile up to 2.50mL, and there was no significant improvement for concentration of propylparaben with 3.00mL of acetonitrile.

The proposed method implemented 2.50mL of acetonitrile, which produced a sufficient volume of the solvent-rich phase for UV-Vis. Subsequently, this method used a 1:1 (v:v) ratio sample to solvent. Previous studies conducted by Benn *et al.* (2011) and Bouchard and Ma (2008) used the similar ratio of 1:1 (v:v) sample to solvent with the volume of 5.00mL:5.00mL and 20.0mL:20.0mL, respectively in liquid-liquid extraction. However, it leads to higher consumption of solvent. In this study, an optimal volume of 2.50mL of acetonitrile was chosen in order to achieve higher concentration of propylparaben and minimal consumption of solvent.

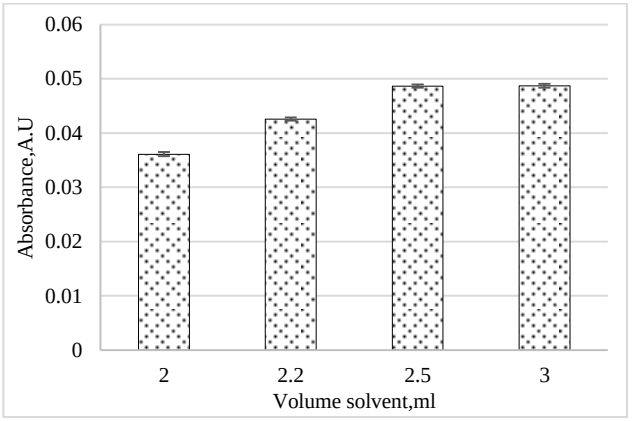

Figure 8. The effect of different volume of solvent on the concentration of extracted propylparaben

In comparison between VAE and LLE technique based on the volume of extraction solvent, VAE showed high recovery of propylparaben using 0.20mL of acetonitrile while LLE required 2.50mL of acetonitrile to produce similar recovery.

C. Figures of Merit

Table 1 shows the optimised condition for proposed methods. The linearity of the proposed methods was determined by injecting standard solutions of propylparaben at different concentrations. A series of concentrations were prepared from 0.20 - 1.00mg/L and the r-square value of the calibration curve was 0.993. The LOD and LOQ were 0.090mg/L and 0.302mg/L, respectively. The precision based on the relative standard deviation (RSD) of the peak area for a 0.400mg/L of propylparaben was calculated to be 0.170% for triplicate readings. These results provide concrete support for the proposed methods to be considered as highly sensitive for analysis of propylparaben in cosmetic samples.

Table 1. Optimised operating conditions for proposed methods, VAE and LLE

Parameter	Studied range	Optimum condition
VAE		
Concentration $MgSO_4$ (M)	0.50 - 2.50	1.50
Type of solvent	Acetonitrile, n-hexane, dichloromethane, methanol	Acetonitrile
Extraction time (min)	0.50 – 3.00	1.00
LLE		
Concentration MgSO4 (M)	0.50 - 2.50	1.50
Type of solvent	Acetonitrile, n-hexane, dichloromethane, methanol	Acetonitrile
Extraction time (min)	0.50 – 3.00	3.00
Volume of solvent (mL)	2.00 – 3.00	2.50

The percentage recovery of LLE and VAE calculated as:

$$R\% = \frac{C_{found}}{C_{initial}} \times 100\ \% \quad (1)$$

where C_{found} is the calculated concentration of the propylparaben using the calibration curve, and $C_{initial}$ is the spiked concentration of propylparaben in the cosmetic sample (González-Hernández *et al.*, 2015). Based on Table 2, the concentration of propylparaben in all cosmetic samples using VAE was found between 76.7% and 103.4% with the RSDs in the range 0.10% to 4.00%. Meanwhile, the concentration of propylparaben in all cosmetic samples using LLE was achieved between 62.5% and 93.9% with less than 1.00% RSD.

Table 2. The concentration of propylparaben (PP) in cosmetic samples (mg/L) and percentage of RSD (%) found using proposed extraction methods, VAE and LLE

Products	VAE			LLE	
	Unspiked PP (mg/L)	%Recovery of spiked PP (RSD)		Unspiked PP (mg/L)	%Recovery of spiked PP (RSD)
body wash	0.002	77.9 (3.25)		0.230	85.9 (0.06)
cleanser	n.d	99.9 (2.62)		n.d	58.8 (0.02)
face mask	n.d	93.1 (0.97)		n.d	69.3 (0.05)
lotion	n.d	103.4 (1.64)		n.d	65.9 (0.04)
shampoo	0.118	92.8 (1.79)		0.040	93.9 (0.05)
deodorant	0.102	76.7 (3.95)		0.024	81.0 (0.03)
feminine wash	0.075	87.5 (2.92)		n.d	62.5 (0.04)
toothpaste	0.181	81.6 (3.41)		n.d	70.4 (0.10)
gargle	0.542	90.2 (4.04)		0.640	70.9 (0.07)
Face toner	0.859	77.6 (4.00)		1.863	75.8 (0.17)

n.d = not detected.

Data given for %Recovery are based on the spiked PP 0.40mg/L.

Replicate sample: 3

From Table 2, propylparaben was not found in cleanser, facemask and lotion. All tested samples that contained propylparaben followed the regulation of propylparaben usage in cosmetics. As shown in Table 3, both proposed methods, VAE and LLE showed good recoveries of propylparaben from cosmetic samples in comparison with other extraction methods. In addition, a combination of vortex assisted in extraction method has been reported to enhance the recovery up to 112.0%, which affected by complex matrix of sample (Shalash *et al.*, 2017, Abu-Bakar *et al.*, 2014). In this study, the recovery of proposed methods was found up to 103.4%. This percentage of recovery is within the acceptable recovery range of 80.0-120.0% (2014) and higher recovery in comparison to SALLE method reported by Liu *et al.* (2010). Therefore, proposed methods showed improved recovery percentage of propylparaben apart from being simple, feasible and practical to be implemented in monitoring the concentration of propylparaben in cosmetic samples.

Table 3. Comparison of extraction methods used on paraben between previous literature and current study

Method	**Instrument**	**Sample**	**Analyte**	**Recovery,% (RSD,%)**	**LOD**	**Reference**
CPE-DC193C	HPLC-UV	Water	MP, EP, PP, AP	71.2-97.7 (0.15-7.6)	0.14-0.29 µg/mL	(Noorashikin *et al.*, 2013)
SPME	UPLC-DAD	Cosmetics	MP, EP, PP, BP	90.0-98.0 (<5.4)	0.12-0.15 µg/mL	(Fei *et al.*, 2011)
SPE	HPLC-ED	Shampoo	MP, EP, PP	93.1–104.4 (2.3–9.8)	n.s	(Martins *et al.*, 2011)
DLLME	GC-FID	Food, cosmetic and beverages	MP, EP, PP, BuP	81.6-101.2 (≤ 2.67	0.03–0.10 µg/mL	(Jain *et al.*, 2013)
SALLE	HPLC-UV	Water river, honey , urine	Sulphonamide	19.4-93.8 (n.s)	1.40-4.50 ng/mL	(Liu *et al.*, 2010)
SALLE	Synchronous fluorescence spectrometry	Soil sample and sediment	Polycyclic aromatic hydrocarbon	74.3-105.8(<8.8)	n.s	(Bressan *et al.*, 2017)
VALLLME	HPLC-DAD	Honey, Iced tea, coffee drink can	Phenolic acid	72.2-112.0 (n.s)	0.05–0.68 µg/L	(Shalash *et al.*, 2017)
SA-VALLME	HPLC-DAD	Fruit juices	Furfural and patulin	82.0-112.0 (0.57-6.90)	0.28-3.50 µg/L	(Abu-Bakar *et al.*, 2014)
FSALLME	GC-FID	Water sample, cosmetics	MP, EP, PP, BuP	51.0-59.0 (<9.40)	0.50–1.00 ng/mL	(Rajabi *et al.*, 2017)
Ultrasonic	HPLC-DAD	Cosmetics	MP, EP. PP, BuP	96.0 -111.0 (0.30-6.60)	n.s	(Xu *et al.*, 2016)
VAE	UV-Vis	Cosmetics	PP	76.7-103.4 (0.10-4.00)	0.090 mg/L	Current study
LLE	UV-Vis	Cosmetics	PP	62.5-93.9 (≤0.17)	0.090 mg/L	Current study

ED = *Electrochemical detection*, MSPD = *Matrix solid-phase dispersion* , *MP= Methylparaben, EP= ethylparaben, BuP= butylparaben,* PP=Propylparaben, BP = benzylparaben, SPME= *solid phase microextraction*, SPE = *Solid phase extraction*, DLLME= *Dispersive Liquid-liquid Microextraction*, SALLE = *Salting-out liquid-liquid extraction*, VALLLME= *Vortex-assisted liquid-liquid-liquid microextraction*, FSALLME = *Fast syringe-assisted liquid-liquid microextraction*, HPLC = *High performance liquid chromatography,* UPLC = *Ultra-performance liquid chromatography*, GC = *Gas chromatography, n.s = not stated*

Figure 9 and 10 represent the UV-Vis chromatograms of extracted paraben in different cosmetic samples using VAE and LLE.

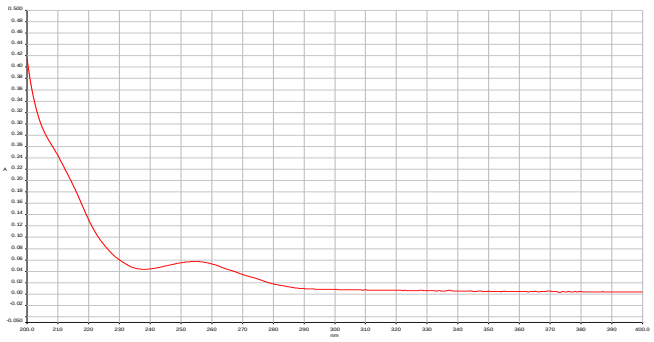

Figure 9. UV-Vis of extracted propylparaben in shampoo using VAE

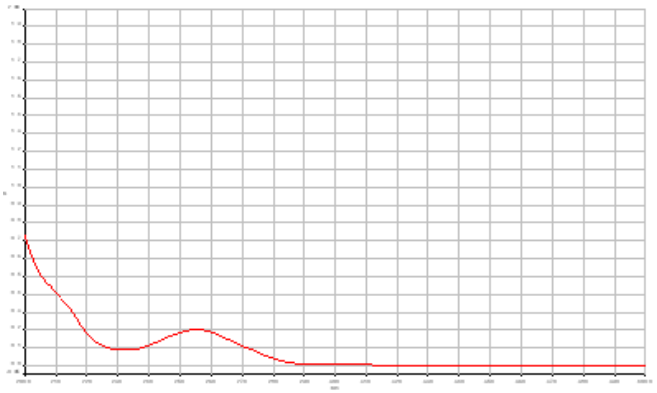

Figure 10. UV-Vis of extracted propylparaben in deodorant using LLE

IV. CONCLUSION

The development of environmentally friendly, low cost and simple method of LLE and VAE induced by salting out effect for determination of propylparaben in ten cosmetic products combined with UV-Vis were reported herein. Different operating parameters affecting the extraction performance such as type and concentration of salt, volume of solvent and extraction time were optimised. Hence, the optimum operating parameters were established. The proposed methods exhibited good linearity (r^2=0.9932) and recoveries for 10 real samples through validation method. The traditional method (LLE) consumes large amount of toxic extraction solvent, high labour cost, long procedures and low yield recoveries in extracting propylparaben. The modern technique proposed in this study, which was VAE shows an excellent performance in all required criteria of extraction technique. VAE is simple, more rapid, environmentally friendly, consumes less amount of solvent extraction, and short extraction time. VAE also was shown to have the best extraction percentage recoveries for propylparaben in cosmetics. As a conclusion, vortex-assisted extraction (VAE) induced by salting out effect was the most preferred technique compared to traditional method, LLE in determination of propylparaben in cosmetics.

V. ACKNOWLEDGEMENTS

The authors would like to thank Universiti Kebangsaan Malaysia for the grant as financial support. (Geran Galakan Penyelidik Muda (Reference Code: GGPM-2017-033).

VI. REFERENCES

[1] Guidelines for control of cosmetic products in Malaysia 2014. Spike, recovery, and linearity protocol for validating untested samples in r&d systems elisas experimental protocol only-not guaranteed, R & D Systems.

[2] Abu-Bakar, N-B, Makahleh, A & Saad, B 2014, 'Vortex-assisted liquid–liquid microextraction coupled with high performance liquid chromatography for the determination of furfurals and patulin in fruit juices', *Talanta*, vol. 120, pp. 47-54.

[3] Bedassa, T, Megersa, N & Gure, A 2017, 'Salting-out assisted liquid-liquid extraction for the determination of multiresidue pesticides in alcoholic beverages by high performance liquid chromatography', *Science*, vol. 5, pp. 38-45.

[4] Benn, TM, Westerhoff, P & Herckes, P 2011, 'Detection of fullerenes (c60 and c70) in commercial cosmetics', *Environmental Pollution*, vol. 159, pp. 1334-1342.

[5] Bouchard, D & Ma, X 2008, 'Extraction and high-performance liquid chromatographic analysis of c60, c70, and [6, 6]-phenyl c61-butyric acid methyl ester in synthetic and natural waters', *Journal of Chromatography A*, vol. 1203, pp. 153-159.

[6] Bressan, LP, do Nascimento, PC, Schmidt, ME, Faccin, H, de Machado, LC & Bohrer, D 2017, 'Salting-out assisted liquid-liquid extraction and partial least squares regression to assay low molecular weight polycyclic aromatic hydrocarbons leached from soils and sediments', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 173, pp. 749-756.

[7] Chen, C-W, Hsu, W-C, Lu, Y-C, Weng, J-R & Feng, C-H 2018, 'Determination of parabens using two microextraction methods coupled with capillary liquid chromatography-UV detection', *Food Chemistry*, vol. 241, pp. 411-418.

[8] Du, D, Dong, G, Wu, Y, Wang, J, Gao, M, Wang, X & Li, Y 2014, 'Salting-out induced liquid–liquid microextraction based on the system of acetonitrile/magnesium sulfate for trace-level quantitative analysis of fluoroquinolones in water, food and biological matrices by high-performance liquid chromatography with a fluorescence detector', *Analytical Methods*, vol. 6, pp. 6973-6980.

[9] Esplugas, S, Bila, DM, Krause, LGT & Dezotti, M 2007, 'Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (edcs) and pharmaceuticals and personal care products (ppcps) in water effluents', *Journal of Hazardous Materials*, vol. 149, pp. 631-642.

[10] Fei, T, Li, H, Ding, M, Ito, M & Lin, JM 2011, 'Determination of parabens in cosmetic products by solid - phase microextraction of poly (ethylene glycol) diacrylate thin film on fibers and ultra high - speed liquid chromatography with diode array detector', *Journal of Separation Science*, vol. 34, pp. 1599-1606.

[11] González-Hernández, P, Pino, V, Ayala, JH & Afonso, AM 2015, 'A simplified vortex-assisted

emulsification microextraction method for determining personal care products in environmental water samples by ultra-high-performance liquid chromatography', *Analytical Methods*, vol. 7, pp. 1825-1833.

[12] Huang, JQ, Hu, CC & Chiu, TC 2013, 'Determination of seven preservatives in cosmetic products by micellar electrokinetic chromatography', *International Journal of Cosmetic Science*, vol. 35, pp. 346-353.

[13] Jain, A, Soni, S & Verma, KK 2015, 'Determination of parabens in cosmetics by liquid-phase microextractions and high-performance liquid chromatography–diode array detection', *Journal of Liquid Chromatography & Related Technologies*, vol. 38, pp. 82-91.

[14] Jain, R, Mudiam, MKR, Chauhan, A, Ch, R, Murthy, R & Khan, HA 2013, 'Simultaneous derivatisation and preconcentration of parabens in food and other matrices by isobutyl chloroformate and dispersive liquid–liquid microextraction followed by gas chromatographic analysis', *Food Chemistry*, vol. 141, pp. 436-443.

[15] Khanna, S & Darbre, PD 2013, 'Parabens enable suspension growth of mcf - 10a immortalized, non - transformed human breast epithelial cells', *Journal of Applied Toxicology*, vol. 33, pp. 378-382.

[16] Krishnan, S, Amira, NS, Atilla, UN, Syafawani, S & Hafiz, M 2017, 'The usage of cosmetic in Malaysia: Understanding the major factors that affect the users', *Management*, vol. 7, pp. 48-51.

[17] Liao, C & Kannan, K 2014, 'Concentrations and composition profiles of parabens in currency bills and paper products including sanitary wipes', *Science of the Total Environment*, vol. 475, pp. 8-15.

[18] Liu, J, Jiang, M, Li, G, Xu, L & Xie, M 2010, 'Miniaturized salting-out liquid–liquid extraction of sulfonamides from different matrices', *Analytica Chimica Acta*, vol. 679, pp. 74-80.

[19] Martins, I, Carreira, FC, Canaes, LS, Junior, FAd SC, da Silva Cruz, LM & Rath, S 2011, 'Determination of parabens in shampoo using high performance liquid chromatography with amperometric detection on a boron-doped diamond electrode', *Talanta*, vol. 85, pp. 1-7.

[20] Miralles, P, Vrouvaki, I, Chisvert, A & Salvador, A 2016, 'Determination of alternative preservatives in cosmetic products by chromophoric derivatization followed by vortex-assisted liquid–liquid semimicroextraction and liquid chromatography', *Talanta*, vol. 154, pp. 1-6.

[21] Noorashikin, M, Nur Nadiah, A, Nurain, I, Siti Aisyah, A & Siti Zulaika, M 2016, 'Determination of phenol in water samples using cloud point extraction and UV spectrophotometry', *Desalination and Water Treatment*, vol. 57, pp. 15486-15494.

[22] Noorashikin, MS, Raoov, M, Mohamad, S & Abas, MR 2013, 'Cloud point extraction of parabens using non-ionic surfactant with cyclodextrin functionalized ionic liquid as a modifier', *International Journal of Molecular Sciences*, vol. 14, pp. 24531-24548.

[23] Norseyrihan, MS, Noorashikin, MS, Adibah, M & Farhanini, Y 2016, 'Cloud point extraction of methylphenol in water samples with low viscosity of non-ionic surfactant sylgard 309 coupled with

high-performance liquid chromatography', *Separation Science and Technology*, vol. 51, pp. 2386-2393.

[24] Pourhossein, A & Alizadeh, K 2017, 'Salt-assisted liquid-liquid extraction followed by high performance liquid chromatography for determination of carvedilol in human plasma', *Journal of Reports in Pharmaceutical Sciences*, vol. 7, pp. 79-87.

[25] Rajabi, M, Sarhadi, A, Bazregar, M, Asghari, A & Mirparizi, E 2017, 'Rapid derivatization and extraction of paraben preservatives by fast syringe-assisted liquid–liquid microextraction and their determination in cosmetic and aqueous sample solutions by gas chromatography', *Analytical Methods*, vol. 9, pp. 5963-5969.

[26] Shalash, M, Makahleh, A, Salhimi, SM & Saad, B 2017, 'Vortex-assisted liquid-liquid–liquid microextraction followed by high performance liquid chromatography for the simultaneous determination of fourteen phenolic acids in honey, iced tea and canned coffee drinks', *Talanta*, vol. 174, pp. 428-435.

[27] Tang, YQ & Weng, N 2013, 'Salting-out assisted liquid–liquid extraction for bioanalysis', *Bioanalysis*, vol. 5, pp. 1583-1598.

[28] Teju, E, Tadesse, B & Megersa, N 2017, 'Salting-out-assisted liquid–liquid extraction for the preconcentration and quantitative determination of eight herbicide residues simultaneously in different water samples with high-performance liquid chromatography', *Separation Science and Technology*, pp. 1-11.

[29] Xu, F, Zhao, D & Liu, Z 2016, 'Parabens analysis in cosmetics by ultrasonic extraction coupled with HPLC detection', in *6th International Conference on Mechatronics, Materials, Biotechnology and Environment*.

[30] Yu, X-S, Liu, Y, Lou, J, Feng, X-L, Wang, H-Z & Xu, J-M 2015, 'Determination of water-and methanol-extractable pentachlorophenol in soils using vortex-assisted liquid-liquid extraction and gas chromatography', *Chin J Anal Chem*, vol. 43, pp. 1389-1394.

[31] Zhang, J, Wu, H, Kim, E & El - Shourbagy, TA 2009, 'Salting - out assisted liquid/liquid extraction with acetonitrile: A new high throughput sample preparation technique for good laboratory practice bioanalysis using liquid chromatography-mass spectrometry', *Biomedical Chromatography*, vol. 23, pp. 419-425.