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Concentration and Determination of Ultraviolet Filters in Environmental Water Samples with Ionic Liquid-Dispersive Liquid-Liquid Microextraction Followed by High Performance Liquid Chromatography

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A simple, sensitive and environmental friendly procedure was presented for the concentration and determination of extensively used five UV filters in water samples based on dispersive liquid-liquid microextraction (DLLME) followed by high performance liquid chromatography with UV detection (HPLC-UV). Hydrophobic 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide was used as an extraction solvent and extraction conditions were examined and investigated. Under optimized conditions, the linearity of UV filters was in the range 0.2-200 ng × mL^{-1} with corresponding correlation coefficient of 0.9943-0.9992. The recoveries ranged from 94 to 119 % and the relative standard deviations were between 3.6 and 8.4 % at a spiked level of 10 ng mL^{-1} (S/N = 3). Their limits of detection ranged from 0.02-0.16 ng × mL^{-1}. The proposed ionic liquid-DLLME-HPLC-UV procedure was successfully used for the concentration and determination of UV filters in the environment water samples. Satisfactory recoveries and precision were obtained.

Keywords: Sample preparation, Dispersive liquid-liquid microextraction, Ultraviolet filters, Ionic liquids.

INTRODUCTION

Due to their large molar extinction coefficients in both UVA and UVB ranges, ultraviolet (UV) filters are frequently used in sunscreens and cosmetics in order to protect the skin from UV radiation of sunlight[1]. Currently, these compounds are also integrated in numerous commercial formulations of personal care products such as lotions, creams, hair sprays, moisturizers, shampoo, lipsticks and hair dyes in amounts of 0.1-10 %. Moreover, some compounds can also be added as additives to textiles, plastics, paints, car polishes, *etc*.[2]. Their maximum permitted concentrations are regulated by the legislation in force in each country[3]. With the increasing popularity of all these personal care products, recent studies have shown that UV filters are found in river, rain, lakes and coastal sea water due to their release through wastewater from different activities such as washing clothes, showering, human excretion and industrial wastewater discharges. Although the levels found in environmental water are in the ng L^{-1} range, they are not far below the dose that causes toxic effects in animals[4]. Therefore, organic UV filters have recently been supposed to be emerging pollutants. To date, there are no official analytical methods for their detection in aquatic environment. Moreover, taking into account that the maximum residue limits for these emerging pollutants occur at ultra-trace levels, sensitive analytical methods are needed. Different reviews have reported UV-filter determination in environmental water samples in recent years[5-7].

Special emphasis was placed on microextraction techniques such as solid-phase microextraction[8-10], stir-bar sorptive extraction[11], single-drop microextraction[12,13] and dispersive liquid-liquid microextraction (DLLME)[14,15].

Dispersive liquid-liquid microextraction is a simple, rapid, inexpensive and highly efficient microextraction technique based on the use of an appropriate extractant and a disperser solvent with high miscibility in both extracting and aqueous phases[16]. Volatile and toxic chlorinated solvents usually employed as extraction solvents in conventional DLLME. For this reason, green and hydrophobic ionic liquids (ILs) were introduced into DLLME instead of toxic chlorinated solvents[17]. Currently, several descriptions dealt with ionic liquid-based DLLME of UV filters[18-20]. In this case, additional agitation such as ultrasound is generally needed to shorten the equilibrium time and improve sensitivity because common ionic liquids possess greater viscocity[21].

The purpose of this work is to study the analytical performance of 1-alkyl-3-methylimidazolium cation with inorganic and organic anions as extraction solvents in DLLME coupled to high performance liquid chromatography with UV detection

(HPLC-UV). Effect of ultrasound on ionic liquid-DLLME was examined. A simple, sensitive and environmentally friendly procedure was developed to concentrate and determine typical UV filters from environmental water in local area.

EXPERIMENTAL

1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF_6]), 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM][PF_6]) and 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ([BMIM)[TF_2N]) were obtained from Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China). 2,4-dihydroxybenzop-henone (BP) (purity 98 %, CAS No. 135-56-6), 2-hydroxy-4-methoxybenzophenone (BP-3) (purity 100 %, CAS No. 131-57-7), 2-ethylhexyl-4-methoxycinnamate (EHMC) (purity 98 %, CAS No. 5466-77-3) and 2-ethylhexyl 4-(N,N-dimethylamino) benzoate (OD-PABA) (purity 97 %, CAS No. 21245-02-3) were purchased from AccuStandard (New Haven, USA). 2-Ethylhexyl salicylate (EHS) (purity 99 %, CAS No. 118-60-5) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). HPLC-grade methanol was purchased from Shandong Yuwang Industry Co., Ltd. (Yucheng, China). HPLC-grade acetonitrile, acetone and ethanol were obtained from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Sodium chloride, concentrated hydrochloric acid and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

A stock solution containing UV filters (1000 μg mL^{-1} each) was prepared in methanol and stored at 4 °C in the refrigerator. A mixture of standard working solutions (50 ng mL^{-1} each) was daily prepared by ultrapure water with stock solution to study extraction performance under different conditions.

Separation and determination of UV filters were performed on Waters 600E multi-solvent delivery system (Milford, MA, USA) equipped with Waters 2487 dual l absorbance detector and a Waters Sunfire C18 chromatographic column (150 × 4.6 mm, 5 mm). A N2000 workstation (Zhejiang University, China) was used for the acquisition of data. The mobile phase consisted of methanol (90 %, v/v) and water (10 %, v/v). Injection volume was 20 μL for HPLC analysis. All UV filters were detected at 310 nm. The sample pH was measured with a PB-10 acidimeter (Beijing sartorius Instrument System Co., Ltd., China). Ultrapure water was obtained from the Sudreli-system (Chongqing, China). To remove background contamination, all glasswares were immersed in chromosulfuric acid for 0.5 h and rinsed with ultrapure water, avoiding direct contact with skin.

Real water samples: In this experiment, environment water samples include 4 river water (pH, 7.43-7.91), 1 rainwater (pH, 7.89) and 2 wastewater samples (pH, 7.71 and 7.93). The water samples of the Yellow river were freshly collected at different sites in Lanzhou section of the Yellow river. Rain water sample was taken inside school. Wastewater samples were collected from local wastewater treatment plants. All real water samples were collected in amber glass containers in July of 2013 and filtered through 0.45 μm micropore membranes, then stored in the dark at 4 °C, the pH value of water samples was adjusted to 7 prior to analysis.

Dispersive liquid-liquid microextraction procedure: A 5 mL aliquot of water sample were placed in a 15 mL screw cap glass conical test tube and then a mixture of 40 μL of ionic liquid and 100 μL of disperser solvent was rapidly injected into aqueous sample. The tube was tightly closed and the mixture was immersed into an ultrasonic water bath for 5 min extraction at ambient temperature to form a homogeneously cloudy solution. Subsequently the solution was centrifuged at 4000 rpm for 5 min. The dispersed fine droplets of ionic liquid phase were sedimented at the bottom of conical test tube. The upper aqueous phase was removed with a syringe and the sedimented phase was dissolved in 30 μL of methanol for direct HPLC analysis.

RESULTS AND DISCUSSION

Optimization of DLLME: Enrichment factor (EF) is generally defined as the ratio of the analyte concentration in the sedimented phase to the initial analyte concentration in the sample solution. It directly reflects the efficiency of DLLME and employed to optimize the extraction conditions.

Dependence of DLLME on the type of ionic liquids: Selection of appropriate extraction solvents is the first key step in DLLME. Therefore, four hydrophobic ionic liquids were examined as extraction solvents because their qualified density and solubility in 100 mL of water are 1.37 g mL^{-1} and 1.88 g for [BMIM][PF_6], 1.31 g mL^{-1} and 0.75 g for [HMIM][PF_6], 1.23 g mL^{-1}, 0.20 g for [OMIM][PF_6] as well as 1.42 g mL^{-1} and 0.80 g for [BMIM][TF_2N] at 25 °C. The DLLME performance of working solutions were examined by combination of 500 μL of acetone with 100, 45, 20 and 30 μL of individual [BMIM][PF_6], [HMIM][PF_6], [OMIM][PF_6] and [BMIM][TF_2N] to obtain 15 μL of sedimented phase. As shown in Fig. 1, the highest enrichment factors were achieved for all UV filters using [BMIM][TF_2N] and [OMIM][PF_6] as extraction solvents. In view of its very low viscosity, [BMIM][TF_2N] was selected as an extraction solvent in subsequent experiments.

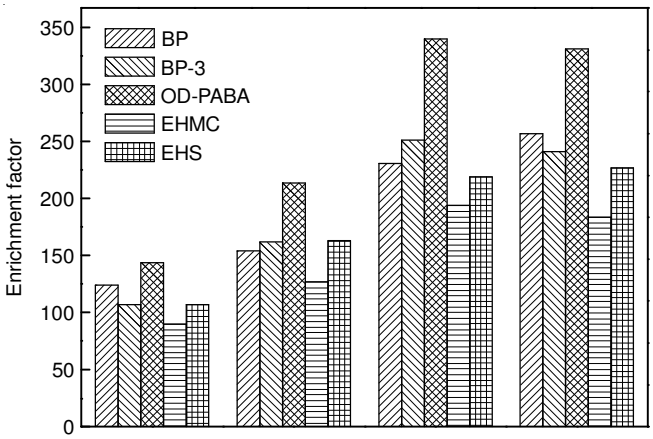

Fig. 1. Effect of different ionic liquids on DLLME. Extraction conditions: [BMIM][PF_6], 100 μL; [HMIM][PF_6], 30 μL; [OMIM][PF_6], 20 μL, [BMIM][TF_2N], 45 μL; acetone, 500 mL; pH, 7

Dependence of DLLME on the type of disperser solvents: The miscibility of disperser solvents in aqueous and organic phases plays an important role in DLLME. Their addition decreases the interfacial tension between two phases

and facilitates the formation of fine droplets in aqueous phase. As a result, this phenomenon greatly improves the diffusion of analytes from aqueous phase to organic phase and thereby shortens their equilibrium time. For this purpose, methanol, ethanol, acetonitrile and acetone were examined as disperser solvents. As shown in Fig. 2, methanol and ethanol exhibits the highest enrichment factors for all UV filters. Furthermore good chromatographic separation can be obtained because methanol was used in the mobile phase. Therefore, methanol was employed for subsequent study.

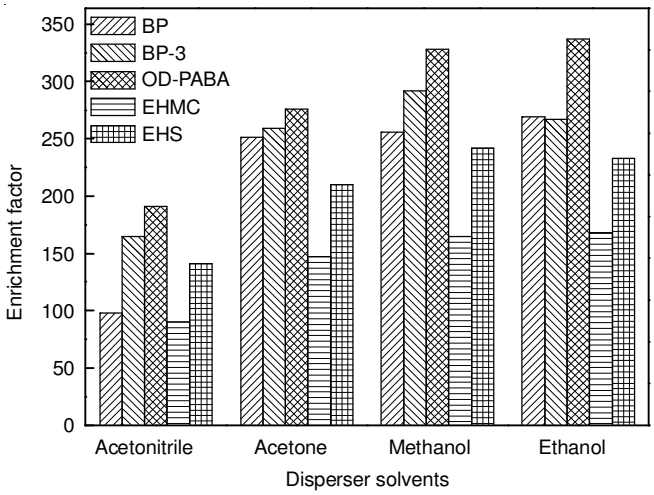

Fig. 2. Effect of disperser solvents on DLLME. Extraction conditions: [BMIM][TF_2N], 30 mL; Dispersers, 500 mL; pH, 7

Dependence of DLLME on the volume of [BMIM][TF_2N] and methanol: The volume of extraction and disperser solvents directly affects enrichment factors of analytes in DLLME. About 5 μL of sedimented phase was practically obtained when 20 μL of [BMIM][TF_2N] was employed within 500 μL of methanol, causing predictable systematic errors measured by a microsyringe. In contrast, addition of more [BMIM][TF_2N] results in more sedimented phase and more accurate volume measurements. Fig. 3 shows the effect of [BMIM][TF_2N] on DLLME. 40 μL of [BMIM][TF_2N] was used for further experiments in view of a compromise between high enrichment factors and sufficient volume of the sedimented phase for subsequent HPLC analysis after centrifugation.

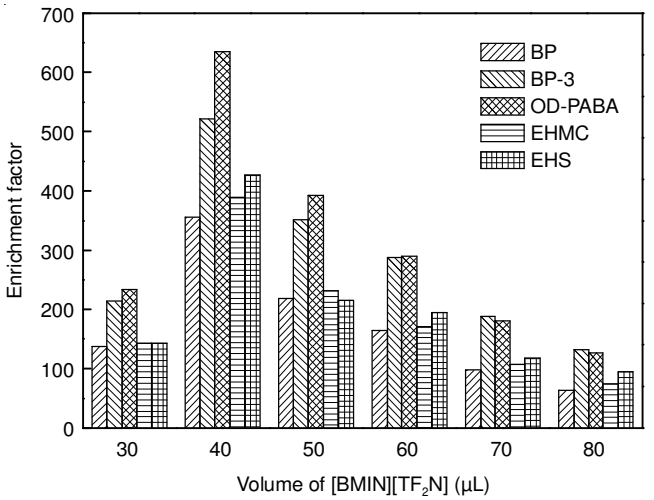

Fig. 3. Effect of [BMIM][TF_2N] on DLLME. Extraction conditions: methanol, 500 mL; pH, 7

On the other hand, methanol has a significant effect on the dispersion of [BMIM][TF_2N] in aqueous phase and the volume of sedimented phase. Less methanol could not properly disperse [BMIM][TF_2N] and thereby cloudy solution can not be completely formed. Fig. 4 shows the effect of methanol on DLLME. The results indicated that the enrichment factors decreased slowly with the increasing volume of methanol from 100 to 500 μL. The increased solubility of [BMIM][TF_2N] and UV filters in water phase should be responsible for this result. Therefore, 100 μL of methanol was employed for the following work.

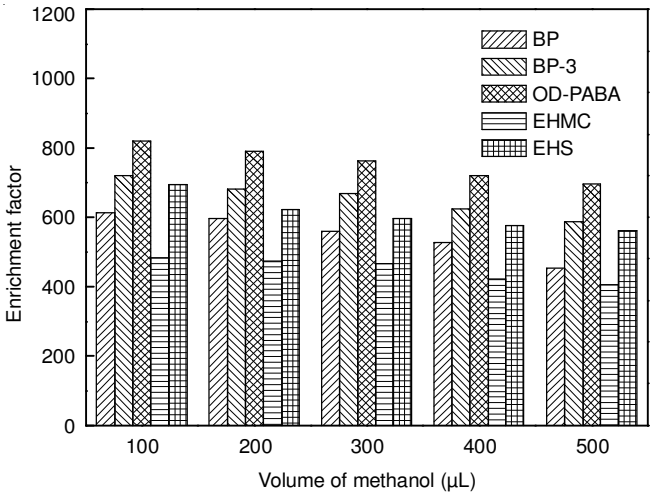

Fig. 4. Effect of methanol on DLLME. Extraction conditions: [BMIM][TF_2N], 40 mL; pH, 7

Dependence of ionic liquid-DLLME on ultrasonic time: The transition of UV filters from aqueous phase to ionic liquid phase was very fast and the equilibrium could be quickly achieved, which is the obvious advantage of DLLME technique. However, slight fluctuation of enrichment factors was observed in conventional ionic liquid-DLLME, frequently leading to poor repeatability. For this reason, ultrasound processing was examined to improve the dispersion of fine droplets of [BMIM][TF_2N]. As shown in Fig. 5, this step finally result in the excellent enrichment. The highest enrichment factors of UV filters were obtained within 5 min. Hence, 5 min was performed in the following ionic liquid-DLLME.

Dependence of USA-IL-DLLME on pH: In conventional DLLME, the neutral form of analytes is expected to be extracted in the organic extraction solvent more efficiently than the ionic form. Taking into account that hydroxylated UV filters are potentially ionisable compounds, effect of pH on ionic liquid-DLLME was investigated within the range of 2-10. The enrichment factors for all UV filters rapidly increased from pH 2 to 7. The best responses were achieved at pH 7. Therefore, a pH value of 7 was selected in ionic liquid-DLLME.

Dependence of USA-IL-DLLME on ionic strength: In DLLME, the greater ionic strength generally leads to the decreased solubility of both non-polar analytes and organic extraction solvents in aqueous phase as a result of the so-called salting-out effect. Fig. 6 shows the dependence of ionic liquid-

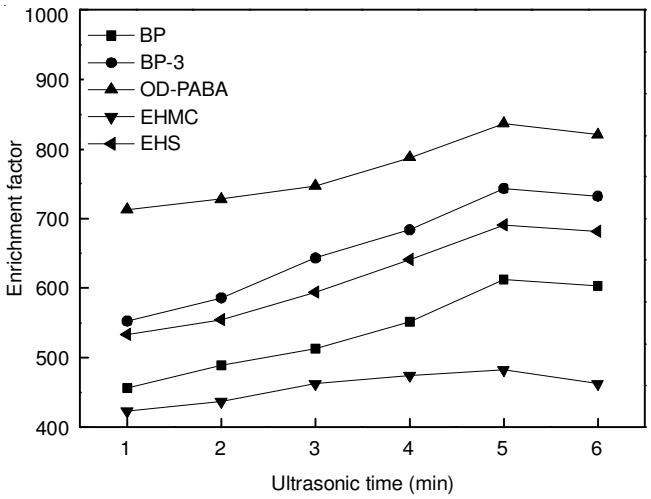

Fig. 5. Effect of ultrasonic time on DLLME. Extraction conditions: [BMIM][TF_2N], 40 mL; Methanol, 100 mL; pH, 7

DLLME on the concentration of NaCl from 0 to 20 % (w/v). The addition of salt has a significant negative effect on the enrichment factors of UV filters. This result is very different from that in conventional DLLME with chlorinated solvents as extraction solvent[14]. Apparently it can be attributed to the decreased concentration of UV filters in the sedimented [BMIM][TF_2N] phase. In fact, the effect of ionic strength on the solubility of [BMIM][TF_2N] is more significant than that of UV filters, resulting in more sedimented phase. Therefore, no salt addition would be the best choice.

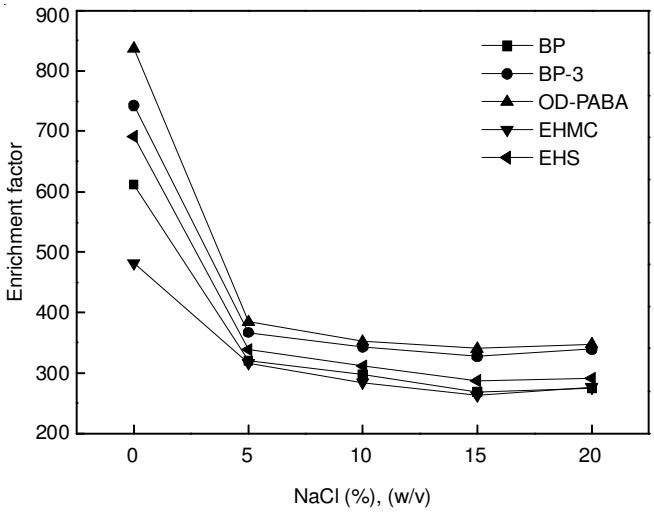

Fig. 6. Effect of ionic strength on DLLME. Extraction conditions: [BMIM][TF_2N], 40 mL; Methanol, 100 mL; pH, 7; Ultrasonic time, 5 min

Dependence of ionic liquid-DLLME on temperature: High temperature leads to the decreased viscosity of [BMIM][TF_2N] and improves mass transfer of targeted UV filters in aqueous phase. As a result, the influence of temperature on ionic liquid-DLLME was examined from 28 to 52 °C. It clearly indicates that the temperature has a significant negative effect on the enrichment factors of UV filters. This result should originate from the increased solubility of [BMIM][TF_2N] and UV filters in aqueous phase and the decreased concentration of UV filters in the sedimented [BMIM][TF_2N] phase. Therefore, heating was not recommended.

Analytical performance of USA-IL-DLLME-HPLC-UV: The linearity, accuracy, precision and sensitivity were examined to evaluate the current procedure under the optimum conditions. The analytical parameters are listed in Table-1. The recoveries (R) were achieved in the range of 94-119 % for the spiked water with each UV filter at a concentration of 10 ng mL^{-1}. RSDs were between 3.54 and 8.76 % (n = 5) and LODs ranged from 0.02-0.20 ng mL^{-1} calculated based on signal-to-noise ratio of 3. These data imply that the established USA-IL-DLLME-HPLC-UV procedure is reliable and suitable for the concentration and determination of UV filters in water.

Analysis of real water samples: The current procedure was applied to the preconcentration and determination of five popular UV filters in different environmental water samples under the optimized conditions. As can be seen in Table-2, BP, BP-3, OD-PABA and EHMC were detected in all environmental water samples with the exception of EHS, which was not present in any of water samples. The result may be due to the mandatory limits of this compound in sunscreen products in China[22]. These data clearly indicate that the Yellow River water has been slightly contaminated by UV filters. Direct release of sunscreens from local bathing areas and indirect inputs through local domestic wastewater may be responsible for this result because Lanzhou city is situated in the Loess Plateau of northwestern China, a dry area with less rain and intense sunlight exposure. Sunscreen cosmetics are very popular. Furthermore all water samples were spiked with 10 ng mL^{-1} of standard solutions to study matrix effects on the extraction performance. The acceptable relative recoveries were obtained over the range of 74-119, 92-101 and 93-106 % for UV filters in river water, rainwater and wastewater samples, respectively and the RSD values were achieved between 3.6 and 8.4 %. These data suggest that the matrix has minor effect on the current procedure for the extraction and determination of five popular UV filters in real water samples. The established procedure proved to be effective for the preconcentration and determination of UV filters in different environmental water samples.

TABLE-1
ANALYTICAL CHARACTERISTICS OF THE CURRENT METHOD (n = 5)

UV filters	Linearity (ng mL^{-1})	r^2	R (%)	RSD (%)	LOD (ng mL^{-1})	Enrichment factors
BP	0.1-200	0.9992	103	8.76	0.02	612
BP-3	0.2-200	0.9972	94	3.54	0.06	748
OD-PABA	0.5-200	0.9984	112	5.40	0.12	837
EHMC	0.2-500	0.9982	115	5.62	0.06	486
EHS	1.0-500	0.9943	119	4.68	0.16	689

Conditions: 40 µL [BMIM][TF_2N]; 100 µL methanol; pH, 7; Ultrasonic time, 5 min; Centrifugation time, 5 min; No addition of salt

TABLE-2
ANALYTICAL RESULTS OF UV FILTERS IN DIFFERENT ENVIRONMENTAL WATER SAMPLES (n = 5)

Samples	Locations	UV filters	Original (ng mL^{-1})	Spiked (ng mL^{-1})	Detected (ng mL^{-1})	R (%)	RSD (%)
River water	Bapanxia suspension bridge	BP	1.98	10	10.67	89.1	5.4
		BP-3	2.03	10	11.76	97.8	3.8
		OD-PABA	1.21	10	12.03	107	4.7
		EHMC	1.02	10	12.39	112	6.8
		EHS	ND*	10	11.07	111	5.3
River water	Yintan bridge	BP	4.02	10	13.43	95.8	6.4
		BP-3	2.19	10	11.96	98.1	5.7
		OD-PABA	1.28	10	10.45	92.6	4.7
		EHMC	1.27	10	13.29	118	4.5
		EHS	ND	10	12.72	127	6.2
River water	Downstream of the sewage plant	BP	1.62	10	10.87	93.6	5.7
		BP-3	1.18	10	11.39	102	3.6
		OD-PABA	1.52	10	11.32	98.3	5.3
		EHMC	0.73	10	10.2	95.1	6.8
		EHS	ND	10	10.72	107	5.2
River water	Donggang bridge	BP	5.6	10	13.95	89.4	7.1
		BP-3	1.0	10	10.69	97.2	6.5
		OD-PABA	0.94	10	11.02	101	6.2
		EHMC	1.17	10	10.88	97.4	5.8
		EHS	ND	10	11.45	115	6.4
River water	Shichuan bridge	BP	1.51	10	10.91	94.8	5.6
		BP-3	2.05	10	14.34	119	4.8
		OD-PABA	1.63	10	10.52	90.4	5.8
		EHMC	0.91	10	9.11	83.5	3.9
		EHS	ND	10	9.52	95.2	6.2
Rain water	Sports ground inside school	BP	5.49	10	15.72	101	5.3
		BP-3	2.21	10	11.23	92.0	4.6
		OD-PABA	1.66	10	11.05	94.8	7.2
		EHMC	1.01	10	10.91	99.1	6.4
		EHS	ND	10	9.37	93.7	7.6
Wastewater	The entrance of the waste water treatment plant	BP	2.31	10	12.72	103	5.3
		BP-3	1.81	10	11	93.1	4.9
		OD-PABA	2.02	10	12.17	101	8.1
		EHMC	1.04	10	10.23	92.7	5.7
		EHS	ND	10	10.38	104	6.6
Wastewater	The exit of the waste water treatment plant	BP	1.95	10	12.63	106	6.2
		BP-3	1.47	10	10.79	94.1	4.8
		OD-PABA	1.89	10	11.03	92.8	5.2
		EHMC	1.07	10	11.38	103	7.3
		EHS	ND	10	10.29	103	5.4

*ND, Not detected or lower than LOD; Conditions: [BMIM][TF_2N], 40 µL; Methanol, 100 µL; pH, 7; Ultrasonic time, 5 min; Centrifugation time, 5 min; No addition of salt

Conclusion

This study established a new sample pretreatment procedure for the concentration and determination of five most frequently used UV filters at ultra-trace level in different environmental water samples using a hydrophobic, environmentally friendly [BMIM][TF_2N] as an extraction solvent. Moreover [BMIM][TF_2N] has low viscosity and mass transfer of UV filters is rapid from aqueous phase to ionic liquid phase. Higher enrichment factors were achieved. Under the optimum conditions, this current procedure was successfully applied to the concentration, separation and determination of UV filters in environmental water samples. Especially UV detection was also demonstrated to be suitable for the determination of common UV filters due to their much higher molar absorptivity. Consequently, the proposed USA-IL-DLLME-HPLC-UV procedure is simple, inexpensive, environmentally benign and sensitive for the analysis of UV filters in real environmental water samples.

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REFERENCES

1. D.L. Giokas, A. Salvador and A. Chisvert, *Trends Anal. Chem.*, **26**, 360 (2007).
2. http://europa.eu.int/eurlex/en/lif/reg/en register 133016.html.
3. A. Salvador and A. Chisvert, Analysis of Cosmetic Products, Elsevier, Amsterdam, p. 83 (2007).
4. S.D. Richardson, *Anal. Chem.*, **81**, 4645 (2009).
5. A. Salvador and A. Chisvert, *Anal. Chim. Acta*, **537**, 1 (2005).
6. W.W. Buchberger, *J. Chromatogr. A*, **1218**, 603 (2011).
7. M. Pedrouzo, F. Borrull, R.M. Marce and E. Pocurull, *Trends Anal. Chem.*, **30**, 749 (2011).
8. D.A. Lambropoulou, D.L. Giokas, V.A. Sakkas, T.A. Albanis and M.I. Karayannis, *J. Chromatogr. A*, **967**, 243 (2002).
9. N. Negreira, I. Rodríguez, M. Ramil, E. Rubí and R. Cela, *Anal. Chim. Acta*, **638**, 36 (2009).

10. H.T. Liu, L. Liu, Y.Q. Xiong, X.M. Yang and T.G. Luan, *J. Chromatogr. A*, **1217**, 6747 (2010).
11. M.J. Gómez, S. Herrera, D. Solé, E. García-Calvo and A.R. Fernández-Alba, *Anal. Chem*., **83**, 2638 (2011).
12. L. Vidal, A. Chisvert, A. Canals and A. Salvador, *Talanta*, **81**, 549 (2010).
13. L. Vidal, A. Chisvert, A. Canals and A. Salvador, *J. Chromatogr. A*, **1174**, 95 (2007).
14. I. Tarazona, A. Chisvert, Z. León and A. Salvador, *J. Chromatogr. A*, **1217**, 4771 (2010).
15. Y.F. Zhang and H.K. Lee, *J. Chromatogr. A*, **1249**, 25 (2012).
16. M. Rezaee, Y. Assadi, M.-R. Milani Hosseini, E. Aghaee, F. Ahmadi and S. Berijani, *J. Chromatogr. A*, **1116**, 1 (2006).
17. Y. Liu, E.C. Zhao, W.T. Zhu, H.X. Gao and Z.Q. Zhou, *J. Chromatogr. A*, **1216**, 885 (2009).
18. L. Ye, J.J. Liu, X. Yang, Y. Peng and L. Xu, *J. Sep. Sci*., **34**, 700 (2011).
19. Y. Zhang and H.K. Lee, *Anal. Chim. Acta*, **750**, 120 (2012).
20. L.K. Xue, W.W. Ma, D.X. Zhang and X.Z. Du, *Anal. Methods*, **5**, 4213 (2013).
21. M.J. Trujillo-Rodríguez, P. Rocío-Bautista, V. Pino and A.M. Afonso, *Trends Analyt. Chem*., **51**, 87 (2013).
22. II People's Republic of China, Hygienic Standard for Cosmetics, Part 1/General, P. 75 (2007).