

## Supplementary Information

An environment-friendly approach by using deep eutectic solvent combined with liquid-liquid microextraction based on solidification of floating organic droplets for simultaneous determination of preservatives in beverages

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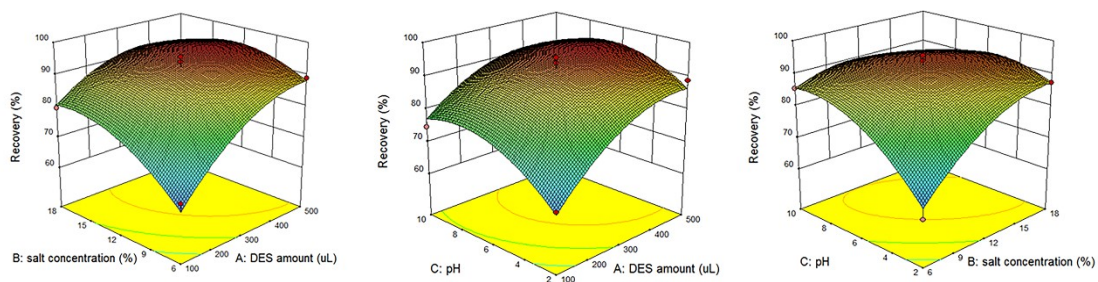
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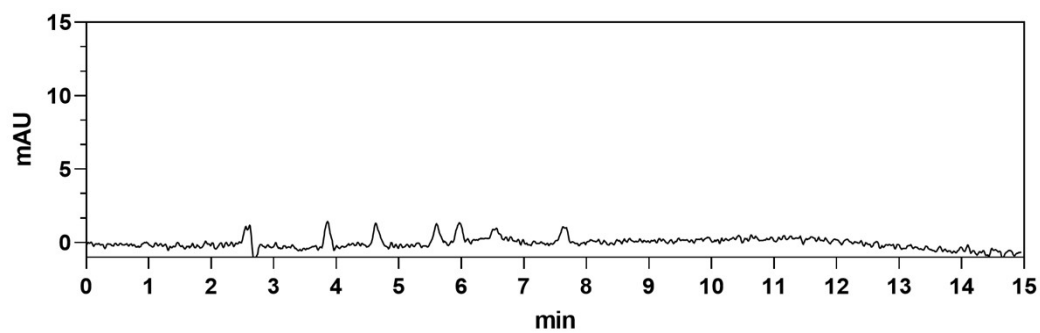
**E-mail:** wang2000@zju.edu.cn

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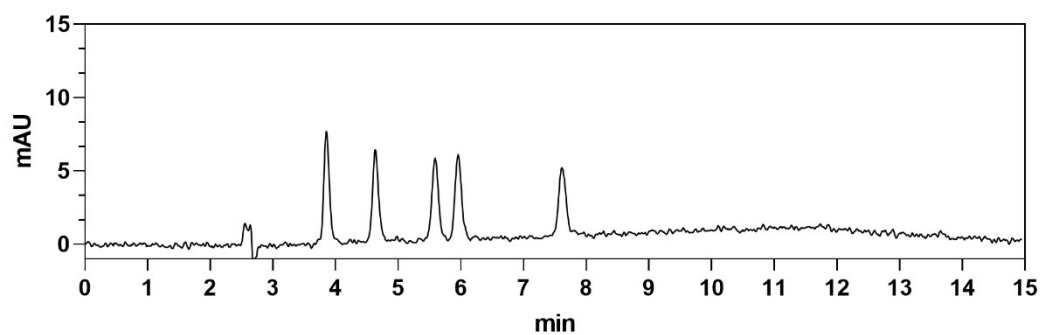


**Fig. S1.** 3D response surface plots showing the effect of three factors on the average recovery of the five target analytes: (A) DES amount ( $\mu\text{L}$ ) vs. salt concentration (%), (B) DES amount ( $\mu\text{L}$ ) vs. pH; salt concentration (%), (C) Salt concentration (%) vs. pH; DES amount ( $\mu\text{L}$ ).

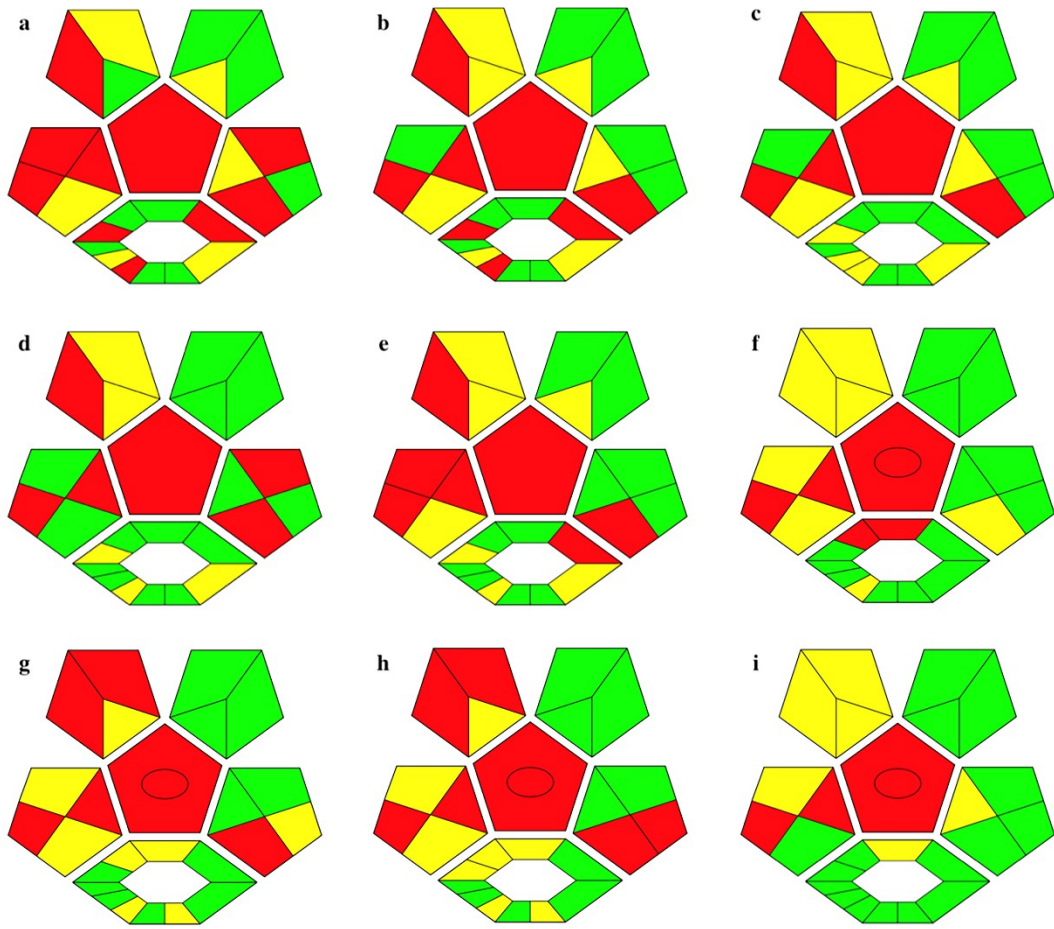
**a**



**b**



**Fig. S2.** The typical chromatograms of five preservatives at the level of LOD (a), and LOQ (b).



**Fig. S3.** Comparisons with previous reported methods (a: reference 13, b: reference 15, c: reference 16, d: reference 19, e: reference 24, f: reference 47, g: reference 48, h: reference 49, i: current study) using the ComplexGAPI tool.

**Table S1.** Response surface experiment results based on the Box-Behnken design for the average recovery (Y) and three variables ( $X_1$ – $X_3$ )

<i>Run</i>	Independent variables			Response	
	$X_1$	$X_2$	$X_3$	Y	
	DES amount ( $\mu\text{L}$ )	Salt concentration (%)	pH	Average recovery (%)	
1	300	12	6	92.0	
2	500	12	2	88.8	
3	300	18	10	85.4	
4	300	6	10	85.5	
5	100	6	6	65.0	
6	300	6	2	61.0	
7	500	6	6	89.0	
8	300	12	6	95.6	
9	300	12	6	90.4	
10	300	18	2	87.4	
11	100	12	2	64.8	
12	100	12	10	74.8	
13	500	12	10	88.8	
14	500	18	6	87.4	
15	300	12	6	94.0	
16	300	12	6	90.4	
17	100	18	6	79.6	

**Table S2.** Analysis of variance (ANOVA) for response surface quadratic model

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-Value (> F)	
Model	1770.30	9	196.70	20.44	0.0003	
X <sub>1</sub>	609.01	1	609.01	63.27	< 0.0001	
X <sub>2</sub>	193.06	1	193.06	20.06	0.0029	
X <sub>3</sub>	132.03	1	132.03	13.72	0.0076	
X <sub>1</sub> X <sub>2</sub>	65.61	1	65.61	6.82	0.0349	
X <sub>1</sub> X <sub>3</sub>	25.00	1	25.00	2.60	0.1511	
X <sub>2</sub> X <sub>3</sub>	175.56	1	175.56	18.24	0.0037	
X <sub>1</sub> <sup>2</sup>	171.25	1	171.25	17.79	0.0039	
X <sub>2</sub> <sup>2</sup>	144.22	1	144.22	14.98	0.0061	
X <sub>3</sub> <sup>2</sup>	194.84	1	194.84	20.24	0.0028	
Residual	67.38	7	9.63			
Lack of Pure	46.45	3	15.48	2.96	0.1609	not
Cor total	1837.67	16	5.23			
	R <sup>2</sup> =96.33%	Adj	C.V.%=3.71%			

**Table S3.** Comparison of proposed method with reported methods for determination of preservatives

Extraction methods	Matrix	Analytes	Solvent consumption	Extraction Time (min)	Recovery (%)	Ref
MSPD	Sea food	MP, EP, PP, BP	12 mL ACN	30	75.0-116.1	13
DVA MSPD	Leafy vegetables	MP, EP, PP, BP, BzP	8 mL MeOH	15	85.0-104.0	15
QuEChERS	Food	MP, EP, PP, SA, BA	16 ml ACN	15	91.0-107.0	16
DSPE	Flavors	MP, EP, PP, IBP, IPP, BP	1 mL ACN	6	88.3–106.6	19
LLME	Food	MP, EP, PP, BP, SA, BA, DHA	0.5 mL acetone, 0.05 mL trichloromethane	25	88.7–110.5	24
DLLME	Water, beverage, beer	MP, EP, PP	20 $\mu$ L magnetic ionic liquids to 250 mL of ACN	15	67.5-73.0	47
SPME	Waters and grape juices	PP, IPP, BP, IBP	ACN:water (40/60)	15	81.2-88.2	48
MSPE	Water	Mp, EP, PP, BzP	280 $\mu$ L ACN	18	72.0-119.0	49
LLME-SFO	Beverages	MP, EP, PP, IBP, IPP	0.3 mL DES	12	86.0- 110.2	Current study

MSPD, matrix solid-phase dispersion

DVA MSPD, double-vortex-assisted matrix solid-phase dispersion

DSPE, dispersive solid-phase extraction

DLLME, dispersive liquid liquid microextraction

SPME, Solid phase microextraction

MPSE, magnetic solid phase extraction

BP, butylparaben

BzP, benzylparaben

SA, sorbic acid;

BA, benzoic acid;

DHA, dehydroacetic acid;

IAP, iso-amyl paraben

AP, amyl paraben

HP, hexyl paraben

HPP, heptyl paraben



