

Supplementary Information

Hexafluoroisopropanol-induced salt-free catanionic surfactant supramolecular solvent for direct immersion single-drop microextraction of sulfonamides and fluoroquinolones in water samples

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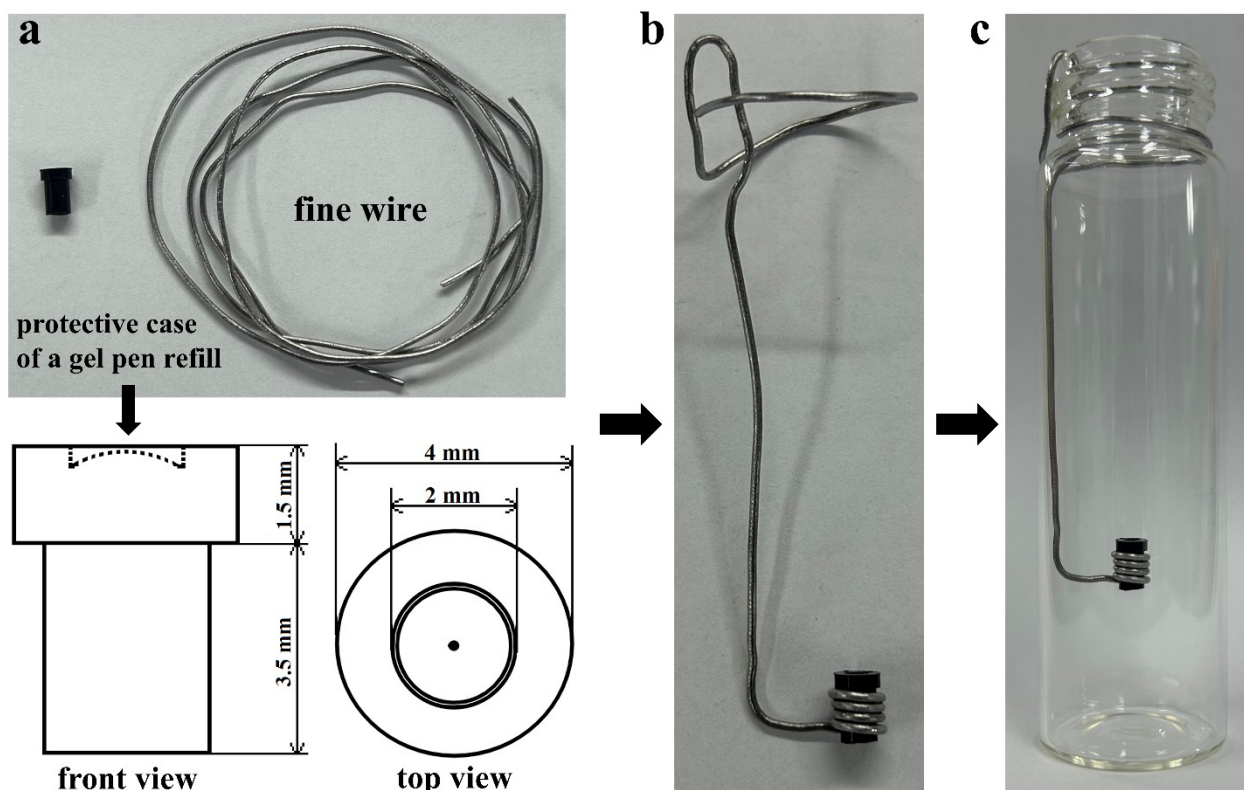


Fig. S1. Schematic and photographic illustration of the homemade droplet holder fabrication. (a) Schematic diagram showing the dimensions of the gel pen refill case, alongside the raw materials (pen refill case and fine wire); (b) The holder after wrapping with fine wire and forming the suspension hook; (c) The final assembly of the holder inside the sample vial.

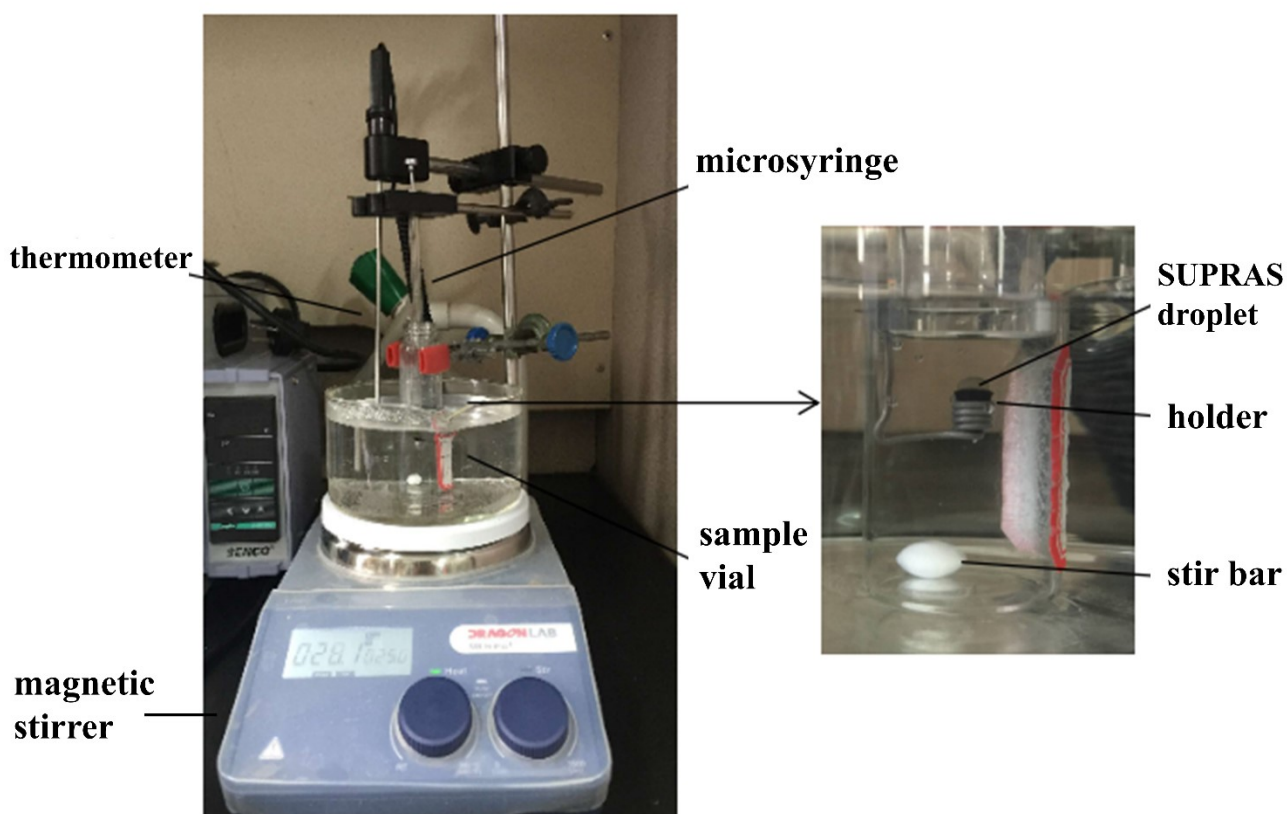


Fig. S2. Photograph of the experimental setup. The overall setup includes a magnetic stirrer, water bath, sample vial, microsyringe, and thermometer. The inset shows the SUPRAS single droplet supported by the homemade holder, along with the stir bar inside the vial.

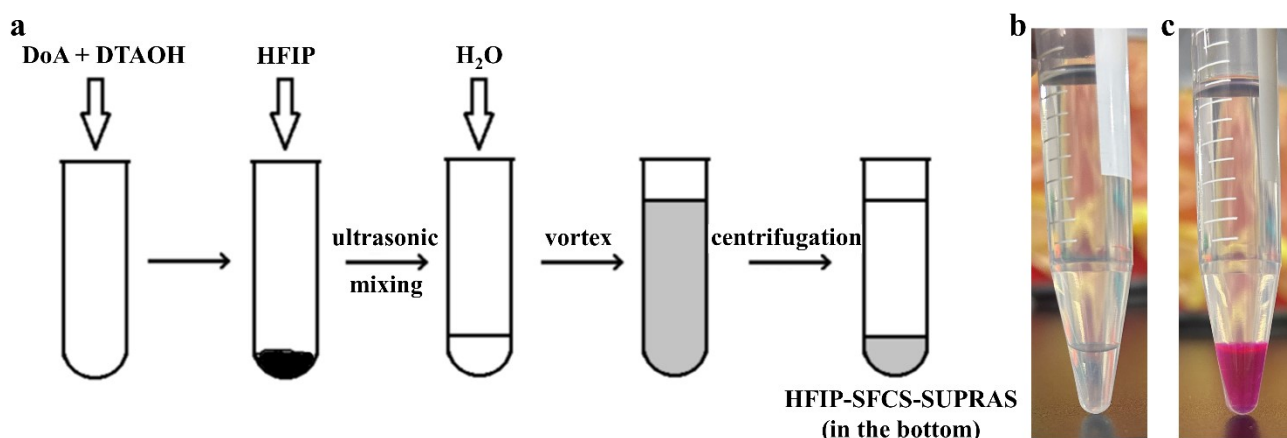


Fig. S3. Preparation and visualization of HFIP-SFCS-SUPRAS. (a) Schematic of the synthesis procedure; (b) Photograph of the phase-separated SUPRAS; (c) Nile red-stained SUPRAS for visual confirmation. Conditions: DoA/DTAOH = 7:3 (mol/mol), total surfactant concentration = 100 mM, HFIP = 10% (v/v).

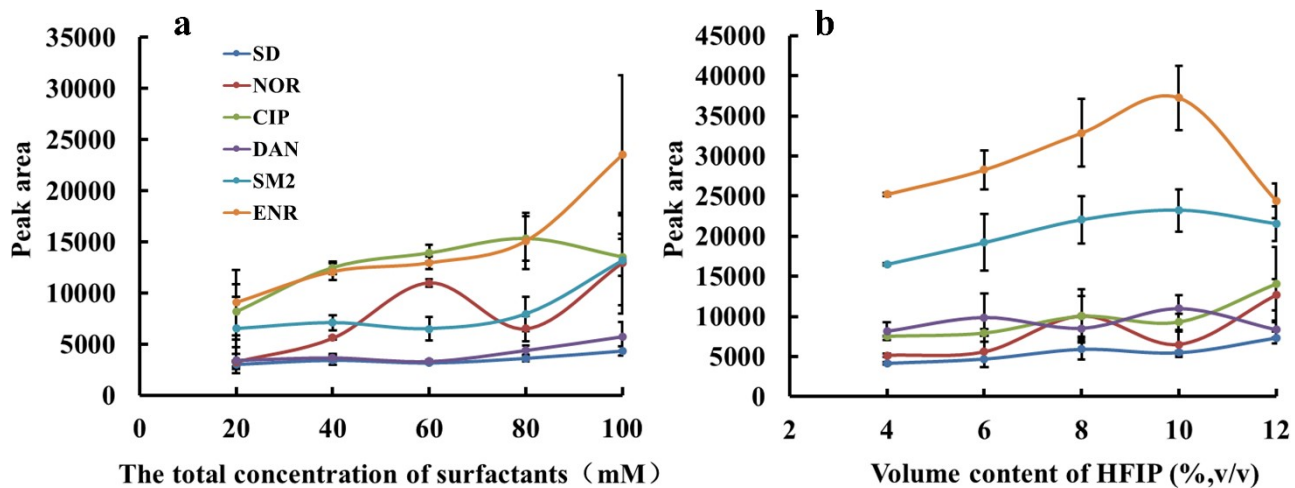


Fig. S4. Effects of total surfactant concentration (a) and HFIP content (b) on peak area of SAs and FQs. Conditions: extraction temperature = 25°C, stirring rate = 300 rpm, extraction time = 20 min, drop volume = 20 μ L (a) DoA/DTAOH = 1:1 (mol/mol), HFIP = 10% (v/v); (b) DoA/DTAOH = 1:1 (mol/mol), total surfactant concentration = 100 mM.

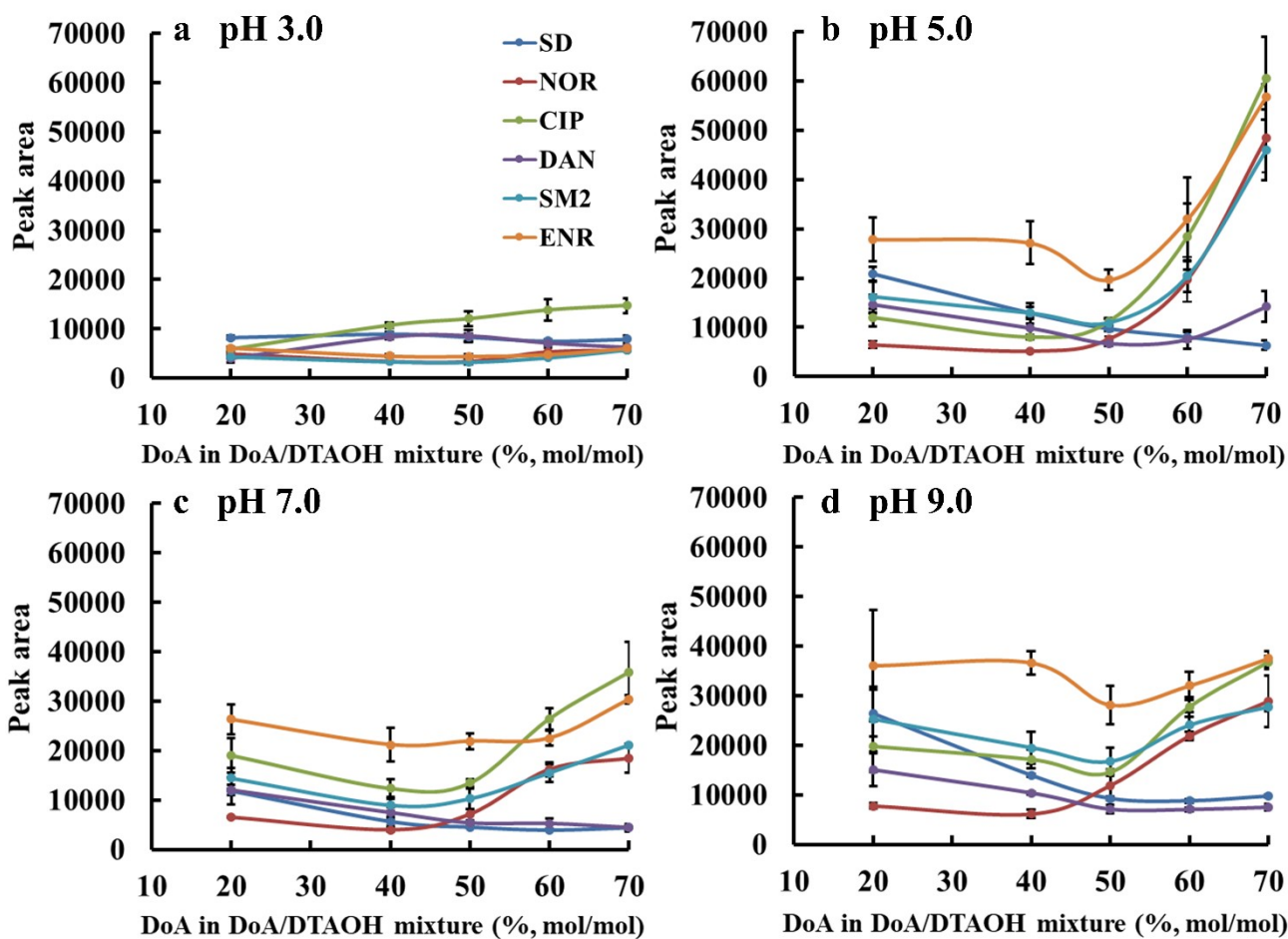


Fig. S5. Effects of DoA/DTAOH molar ratio and sample pH 3.0 (a), 5.0 (b), 7.0 (c), 9.0 (d) on peak area of SAs and FQs. Conditions: total surfactant concentration = 40 mM, HFIP = 10% (v/v), extraction temperature = 25°C, stirring rate = 300 rpm, extraction time = 20 min, drop volume = 20 μ L.

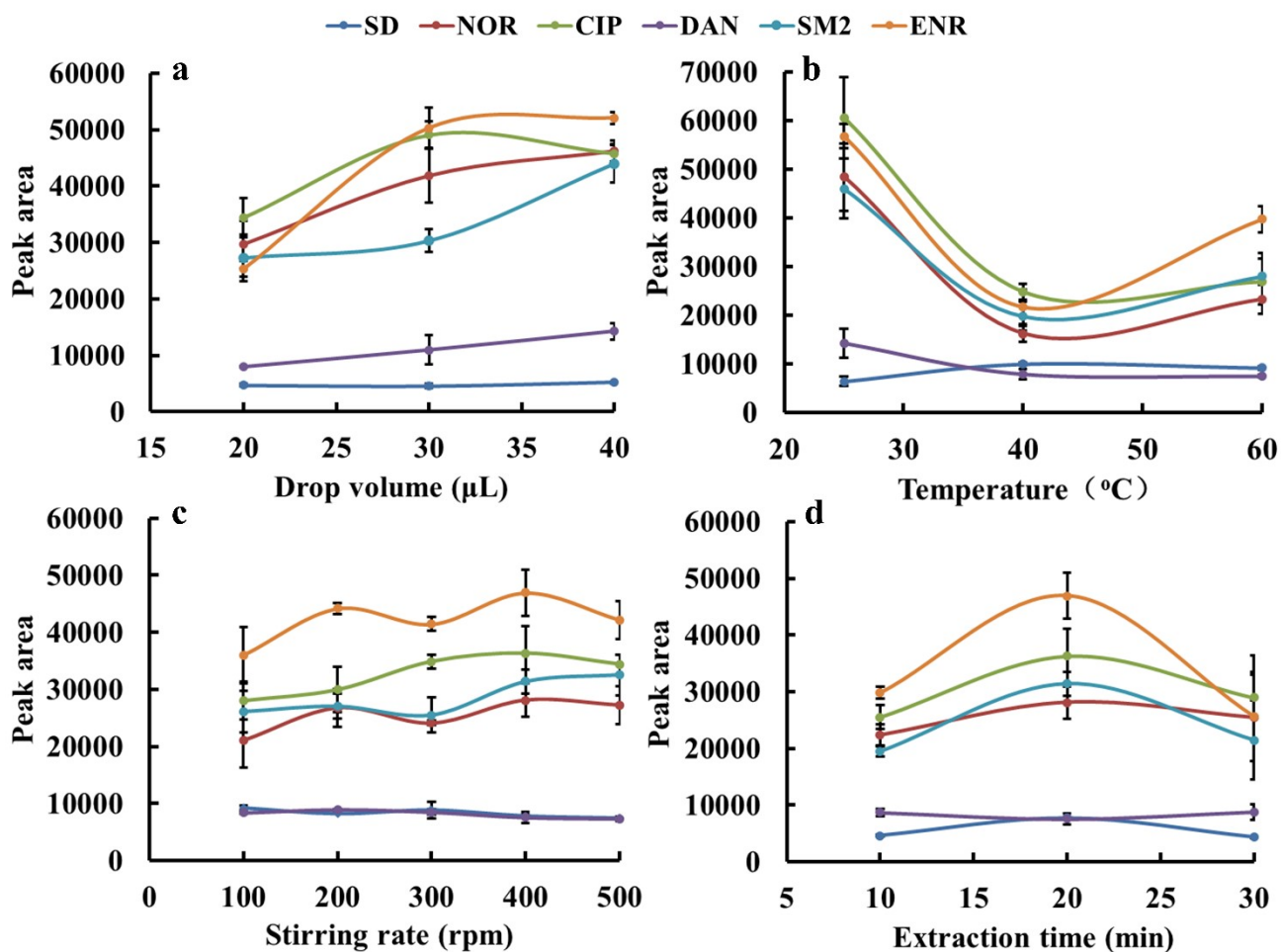


Fig. S6. Effects of drop volume (a), temperature (b), stirring rate (c) and extraction time (d) on peak area of SAs and FQs. Conditions: DoA/DTAOH = 1:1 (mol:mol), HFIP = 10% (v/v), total surfactant concentration = 100 mM.

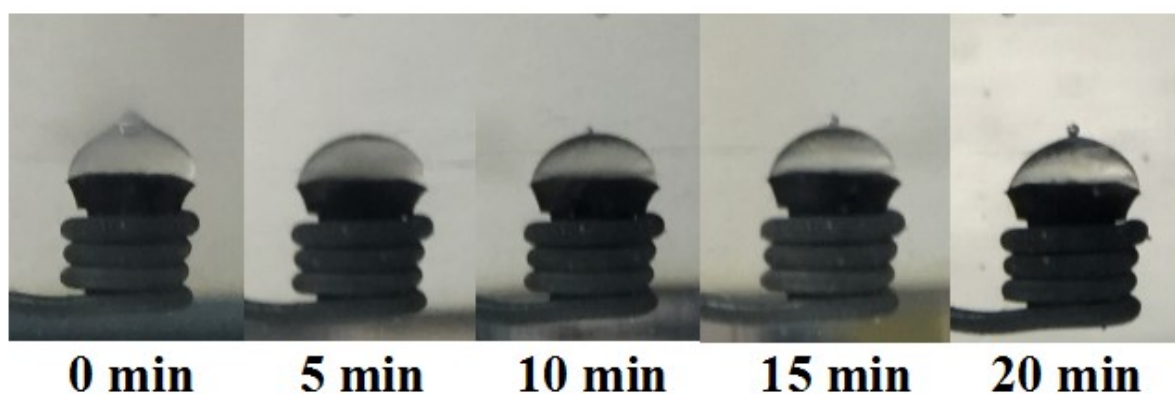


Fig. S7. The droplet on the base with different extraction times.

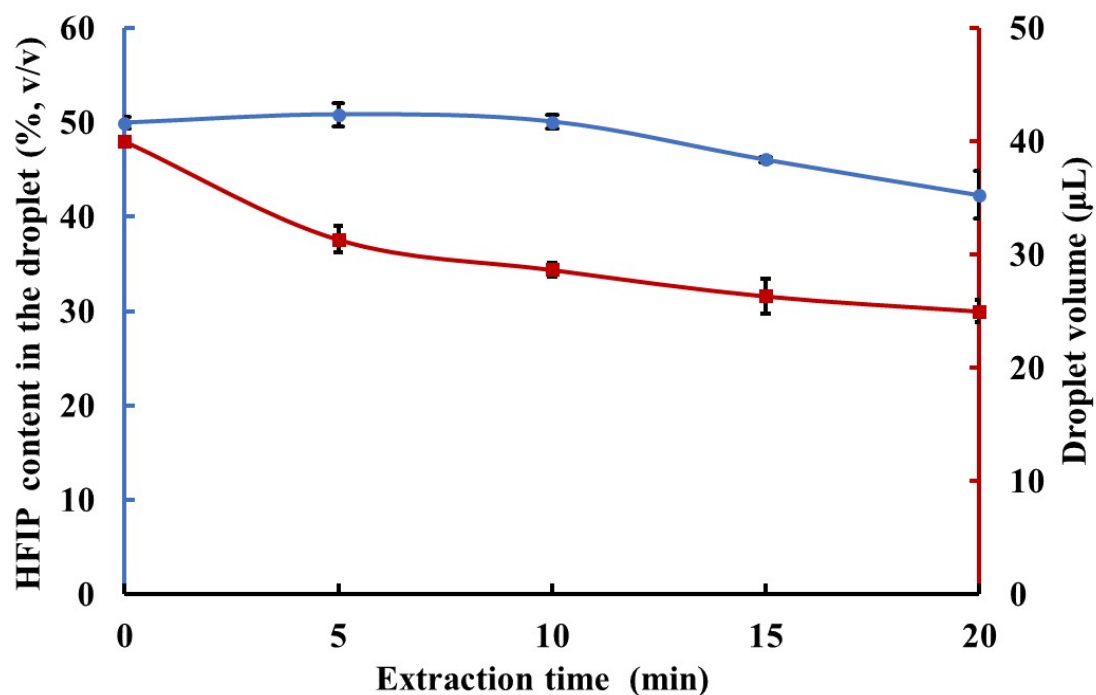


Fig. S8. SUPRAS droplet volume and HFIP content in the droplet with different extraction times.

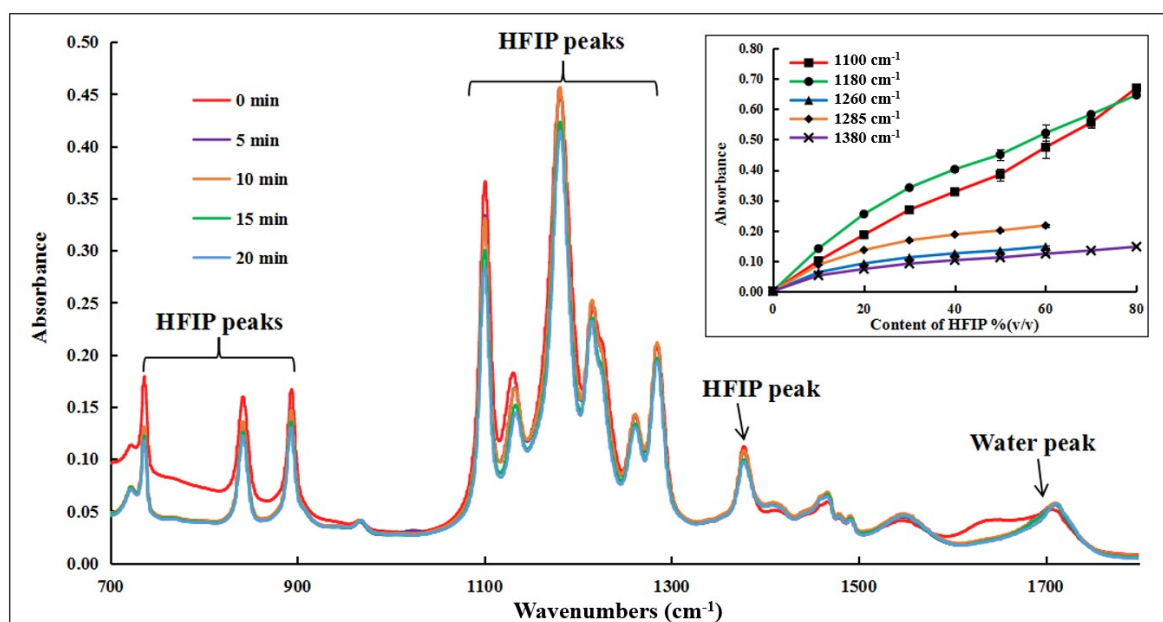


Fig. S9. ATR-FTIR spectra of the SUPRAS droplet with different extraction times. Calibration curves (inset) were made from the spectra of HFIP–water mixed solutions. The peaks at 1100, 1180, 1260, 1285, and 1380 cm^{-1} gave the most linear responses. Due to the high response and good correlation coefficient, the peak at 1180 cm^{-1} was chosen to quantify the HFIP content.

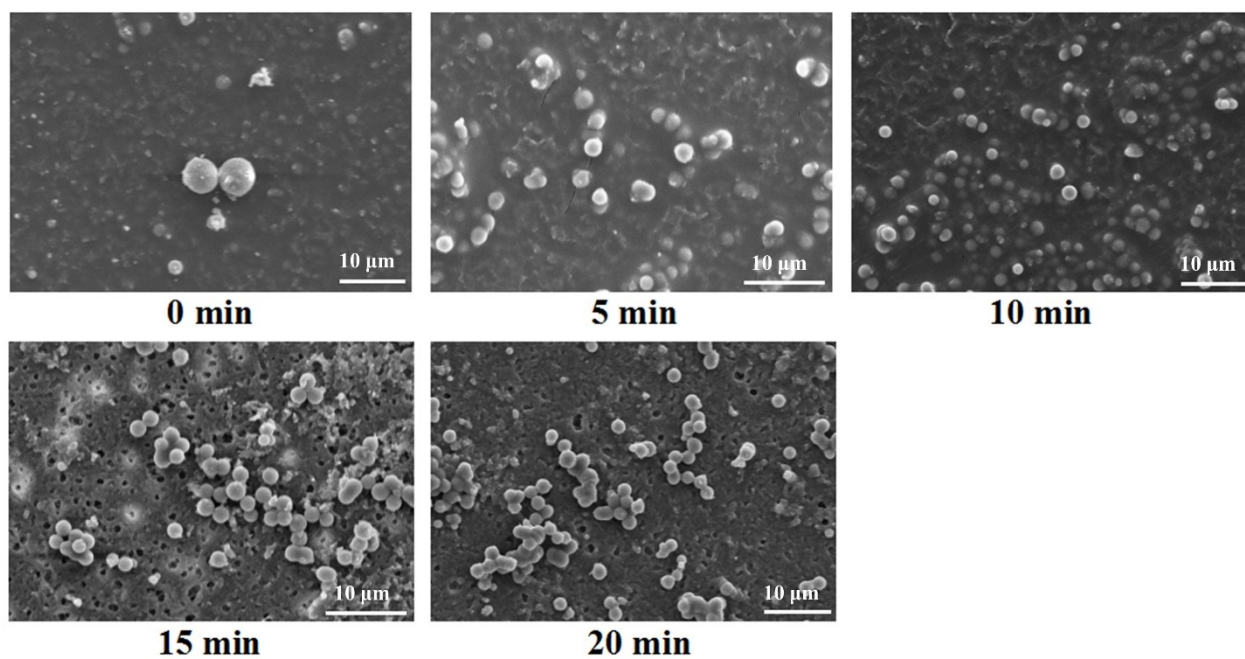


Fig. S10. Cryo-SEM images for HFIP-SFCS-SUPRAS droplet with different extraction times.

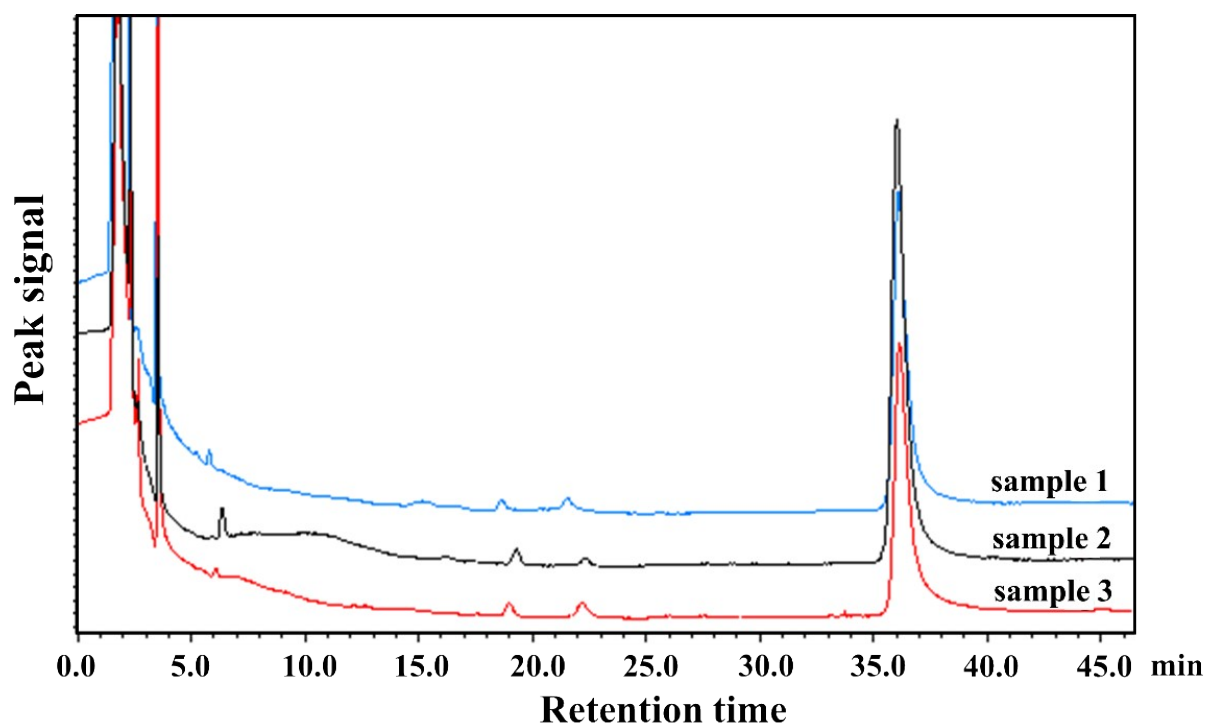
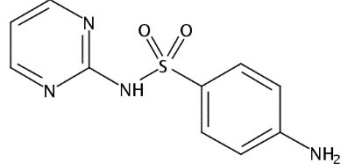
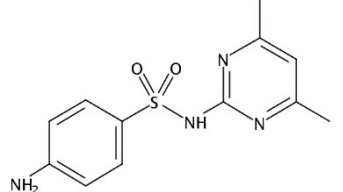
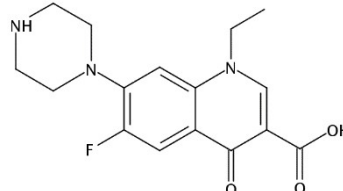
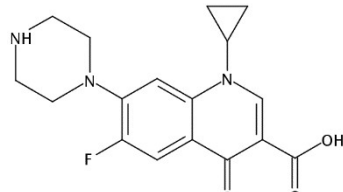
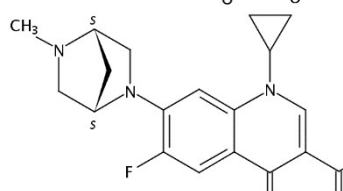
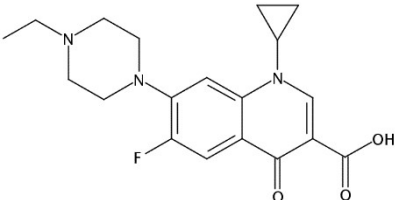


Fig. S11. Chromatograms for the determination of SAs and FQs in three lake water samples.

Table S1 Chemical structures and physical properties of studied analytes.

Analyte	CAS number	Chemical structure	Molecular weight ^a	pKa ^a	Log P ^a	HBA/HBD ^{a,b}
Sulfadiazine (SD)	68-35-9		250.28	1.64 ± 0.10 6.81 ± 0.10	-0.074 ± 0.255	6/3
Sulfamethazine (SM ₂)	57-68-1		278.33	1.69 ± 0.10 7.89 ± 0.10	0.296 ± 0.278	6/3
Norfloxacin (NOR)	70458-96-7		319.33	0.16 ± 0.20 8.68 ± 0.10	1.744 ± 0.831	6/2
Ciprofloxacin (CIP)	85721-33-1		331.34	6.43 ± 0.41 8.68 ± 0.10	1.625 ± 0.831	6/2
Danofloxacin (DAN)	112398-08-0		357.38	6.43 ± 0.41 9.00 ± 0.20	1.811 ± 0.909	6/1

Enrofloxacin (ENR)	93106-60-6		359.39	6.43 ± 0.41 7.76 ± 0.10	2.306 ± 0.819	6/1
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^a The data comes from SciFinder Scholar from Chemical Abstract Service-predicted properties.

^b HBA = Hydrogen bond acceptor, HBD = Hydrogen bond donor.

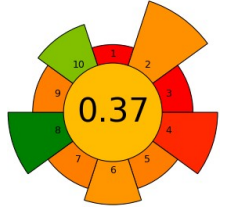
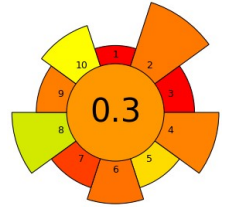
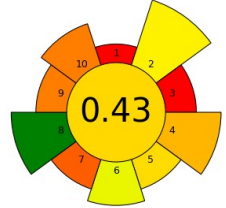
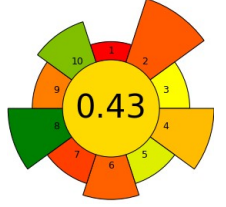
Table S2 Regression equations and coefficients for all HFIP peaks.

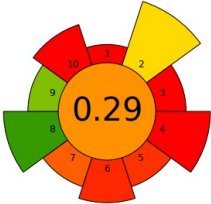
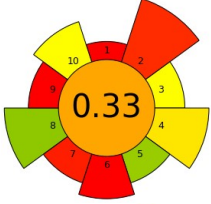
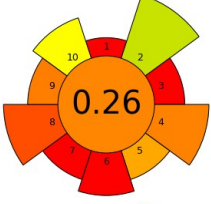
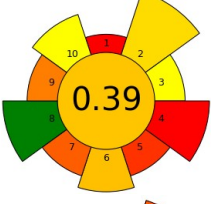
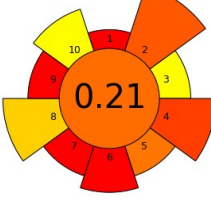
Wavenumber (cm ⁻¹)	Standard curve
1100	$y = 0.0077x + 0.0271$ ($R^2 = 0.9942$)
1180	$y = 0.0074x + 0.0805$ ($R^2 = 0.9822$)
1260	$y = 0.0018x + 0.0460$ ($R^2 = 0.9312$)
1285	$y = 0.0029x + 0.0589$ ($R^2 = 0.9586$)
1380	$y = 0.0014x + 0.0420$ ($R^2 = 0.9825$)

Table S3 Assessment of the greenness of the proposed method and other methods using AGREEprep metric tool.

Method	Sample preparation placement	Hazardous materials	Sustainability, renewability, and reusability of materials	Waste	Size economy of the sample	Sample throughput, h ⁻¹
SALLME	EX-situ	1.4 mL ACN	<25% of reagents and materials are sustainable or renewable, but can only be used once	~30 g (water, extraction solvent, ammo-nium sulfate, tubes, pipette tips)	18 mL	3.5
DLLME	EX-situ	685 μ L CHCl ₃ , 1.25 mL of ACN	<25% of reagents and materials are sustainable or renewable, but can only be used once	~10 g (water, extraction solvent, tubes, pipette tips)	5 mL	~2.6
HDES-LLME	EX-situ	174 μ L HDES, 200 μ L MeOH	<25% of reagents and materials are sustainable or renewable, but can only be used once	~5.4 g (water, HDES, MeOH, tubes, pipette tips)	5 mL	10
MOF@COF-ptSPE	EX-situ	~3 mL ACN	Materials are not sustainable or renewable, but are used several times	~5 g (water, ACN, MOF@COF, pipette tips)	2 mL	~2.3
PSB-SPME	EX-situ	180 μ L MeOH/AA, 70 μ L nitrite, 90 μ L HCl, 120 μ L NaOH, 60 μ L TTFA	<25% of reagents and materials are sustainable or renewable, but can only be used once	~50 g (water, fiber, desorption solution, derivatization reagents)	50 mL	~1.4
MIP-HFM	EX-situ	5.4 mL MeOH, 8 μ L FA	Materials are not sustainable or renewable, but are used several times	~3 g (water, fiber, MeOH)	0.8 mL	1
dt-MIP-DSPE	EX-situ	150 μ L MeOH/AA	<25% of reagents and materials are sustainable or renewable, but can only be used once	~10 g (water, sorbent, MeOH, AA, tubes, pipette tips)	10 mL	~0.3
MCMPs-MSPE	EX-situ	500 μ L MeOH/FA (99/1, v/v)	Materials are not sustainable or renewable, but are used several times	~50 g (water, sorbent, desorption solvent, tubes, pipette tips)	50 mL	5
WDMPM-DSPE	EX-situ	3 mL MeOH/FA (95/5, v/v)	Materials are not sustainable or renewable, but are used several times	~23 g (water, sorbent, desorption solvent, tubes, pipette tips)	20 mL	~0.9
HFIP-SFCS-SUPRAS-DI-SDME	EX-situ	40 μ L SUPRAS	Materials are not sustainable or renewable, but are used several times	~20 g (water, SUPRAS)	20 mL	3

Continued

Method	Integration and automation	Energy consumption	Post-sample preparation configuration for analysis	Operator's safety	Circle diagram	Ref.
SALLME	Manual systems with 2 steps (mixing, phase separation)	<10 Wh	HPLC-UV	1 hazard (ACN)		34
DLLME	Manual systems with more than 4 steps (vortex, centrifugation, evaporation, reconstitution)	~50 Wh	UHPLC-DAD	2 hazards (CHCl ₃ , ACN)		35
HDES-LLME	Manual systems with 3 steps (vortex, standing, dilution)	<10 Wh	HPLC-UV	3 hazards (1-octanol, N ₈₈₈₁ -Cl, MeOH)		36
MOF@COF-ptSPE	Manual systems with 4 steps (condition, loading, elution, washing)	<10 Wh	HPLC-UV	1 hazard (ACN)		37

PSB-SPME	Manual systems with 3 steps (extraction, desorption, derivatization)	~15 Wh	FO-LADS	6 hazards (MeOH, AA, nitrite, HCl, NaOH, TTFA)		38
MIP-HFM	Manual systems with 5 steps (condition, extraction, washing, desorption, dilution)	~30 Wh	HPLC-MS/MS	2 hazards (MeOH, FA)		39
dt-MIP-DSPE	Manual systems with 6 steps (ultrasonication, extraction, centrifugation, vacuum drying, desorption, centrifugation)	~270 Wh	HPLC-DAD	2 hazards (MeOH, AA)		40
MCMPs-MSPE	Manual systems with more than 3 steps (activation, adsorption, desorption)	~10 Wh	HPLC-DAD	2 hazards (MeOH, FA)		41
WDMPM-DSPE	Manual systems with 7 steps (extraction, centrifugation, evaporation, desorption, centrifugation, evaporation, reconstitution)	~100 Wh	HPLC-MS/MS	2 hazards (MeOH, FA)		42

HFIP-SFCS-SUPRAS-
DI-SDME

Manual systems with 1 step (extraction)

<10 Wh

HPLC-UV

3 hazards (DoA,
DTAOH, HFIP)



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work
