Supporting Information for

A quinoxaline-based conjugated microporous polymer-coating for solid phase microextraction of polycyclic aromatic hydrocarbons in environmental sample

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Experimental Instruments and reagents

A gas chromatography-mass spectrometer (GC-MS, 7890A, Agilent Technologies, Santa Clara, CA, USA), X-ray powder diffractometer (XRD, Thermo Fisher Scientific, Waltham, MA, USA), EVO-18 scanning electron microscope (SEM, Carl Zeiss AG, Oberkochen, Germany), PerkinElmer-65 Fourier transform infrared spectrometer (FTIR, Shandong AoLaiDe Instrument Co., Ltd., Shandong, China), thermogravimetric analyzer (TGA, HQT-4, Beijing Hengjiu Experimental Equipment Co., Ltd., Beijing, China), automatic specific surface area analyzer (BET, Autosorb IQ, Quantachrome Instruments, Boynton Beach, FL, USA), X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific, Waltham, MA, USA), and solid-state nuclear magnetic resonance spectrometer (^{13}C NMR, 400 MHz, Bruker Corporation, Billerica, MA, USA) were used in this study.

Naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (FL), and pyrene (Pyr) were all of analytical grade and purchased from Saan Chemical Technology Co., Ltd. (Shanghai, China); their chemical structures (Fig. S1) and physicochemical properties are summarized in Table S1. Cyclohexanehexone octahydrate (98%) and 3-bromo-1,2-phenylenediamine (98%) were obtained from Aladdin Industrial Corporation (Shanghai, China). Tetrakis(triphenylphosphine)palladium(0) (99%) and 1,3,5-triethynylbenzene (M2, 98%) were purchased from Henan Pusi Chemical Products Co., Ltd. (Zhengzhou, China). All solvents and reagents were of analytical grade unless otherwise stated.

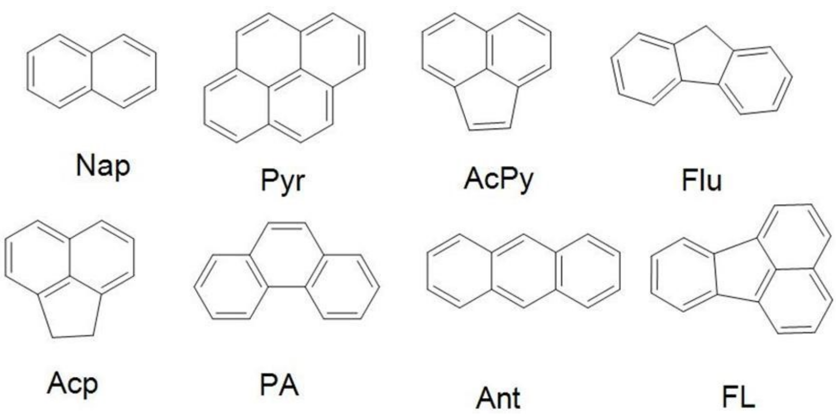


Figure S1.The structure of 8 PAHs

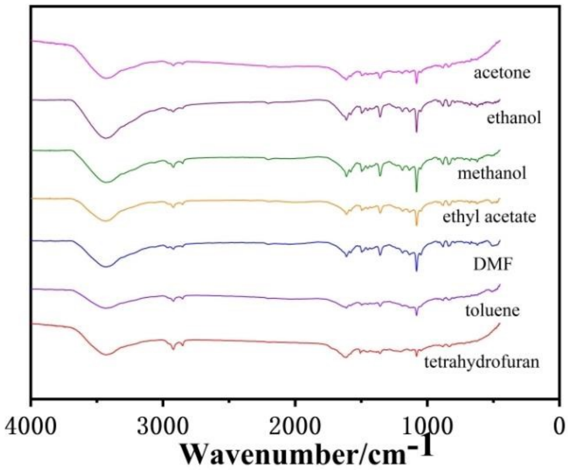


Figure S2. Chemical stability of CMP materials in various organic solvents

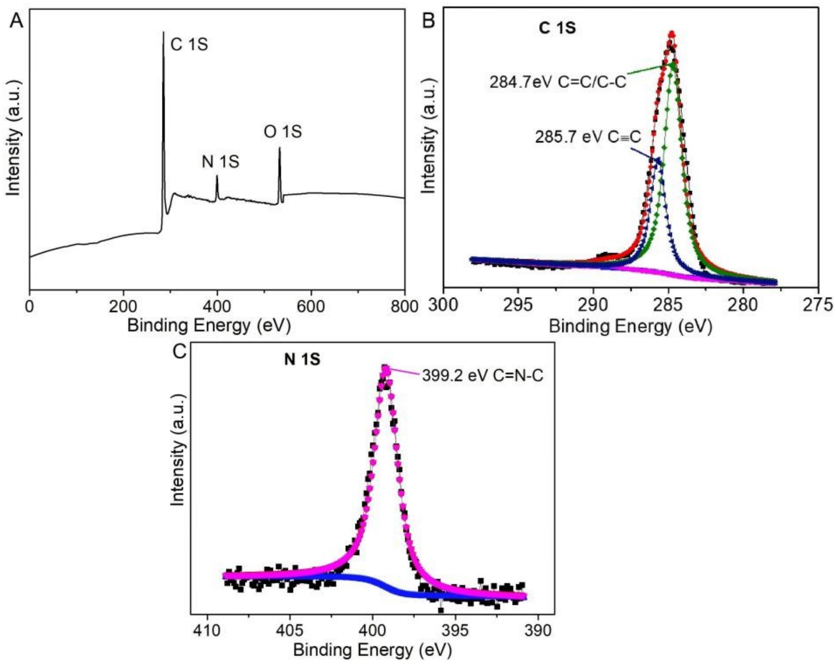


Figure S3. (A) XPS survey spectrum, (B) C 1s and (C) N 1s spectrum of CMP-1.

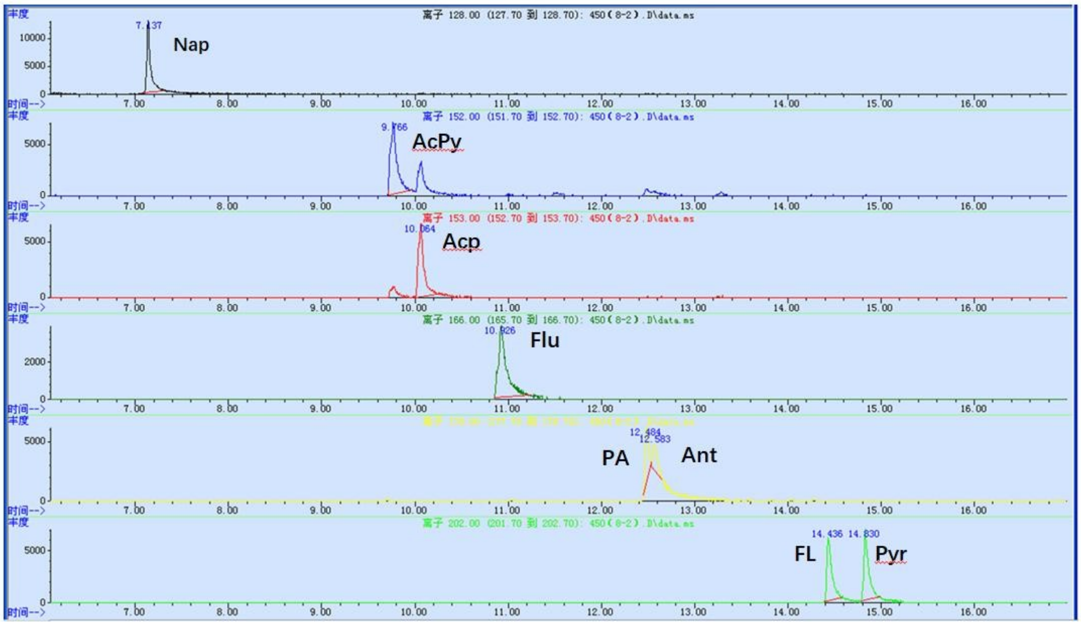


Figure S4. Ion chromatogram of extraction of 8 PAHs

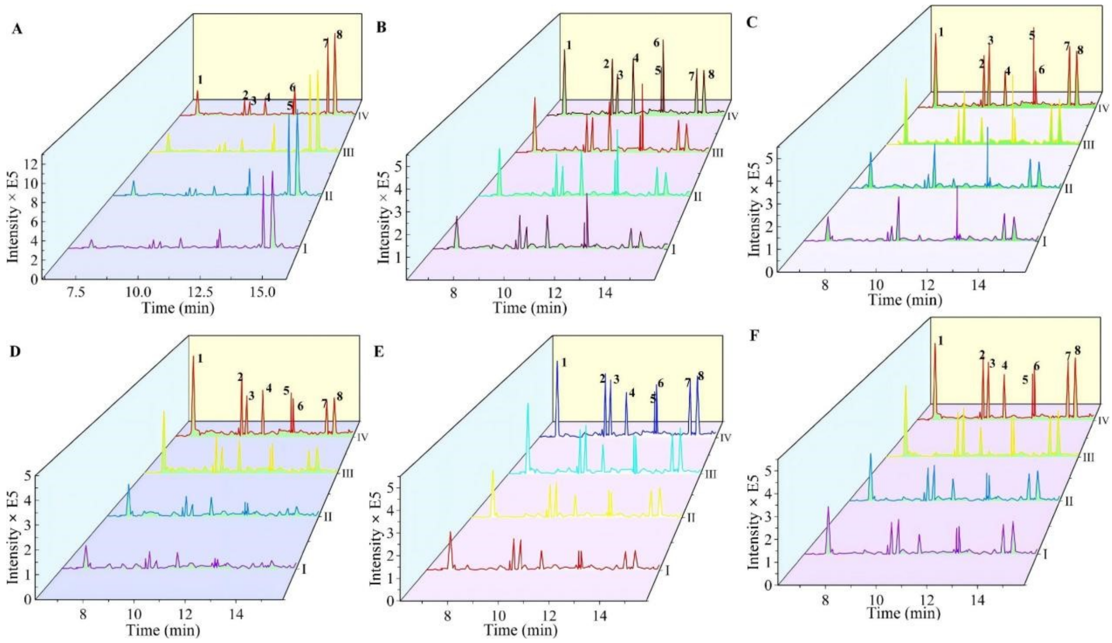


Figure S5. Chromatograms of polycyclic aromatic hydrocarbons (PAHs) in water samples (ABC) obtained by the established method: (I) unspiked; (II) spiked with 5 ng/mL; (III) spiked with 150 ng/mL; (IV) spiked with 300 ng/mL. Chromatograms of soil samples (DEF): (I) unspiked; (II) spiked with 30 ng/mL; (III) spiked with 300 ng/mL; (IV) spiked with 500 ng/mL.

(A)Artificial lake water, (B) Rain water, (C) Jinlong Lake water, (D) Sugarcane field soil, (E)Roadside soil, (F)Gas station soil,

1: Nap; 2: AcPy; 3: Acp; 4: Flu; 5: PA; 6: Ant; 7: FL; 8: Pyr

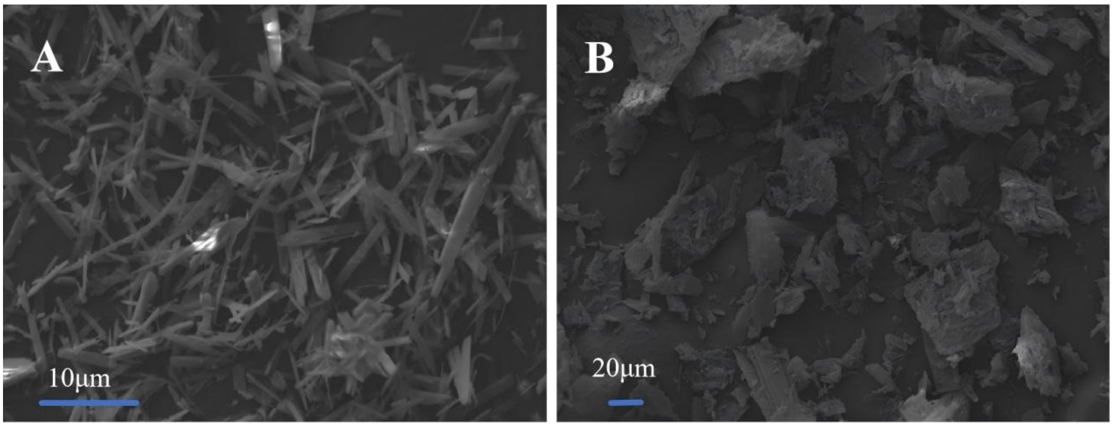


Figure S6. SEM images of (A) monomer M1 and (B) monomer M2

Table S1 Pore properties of polymer CMP-1

Sample	$^{a}S_{BET}$ (m^2 g^{-1})	$^{b}S_{Langmuir}$ (m^2 g^{-1})	$^{c}S_{micro}$ (m^2 g^{-1})	V_0 (cm^3 g^{-1})	BJH Adsorption average pore diameter Porie size (Å)
CMP-1	128.89	349.91	20.65	0.2	83.14

Table S2 Qualitative and quantitative information of 8 polycyclic aromatic hydrocarbons

PAHs	Retention Time/min	Quantitative ion	Qualitative ion
Nap	7.137	128	57、105、77
AcPy	9.766	152	135、55、85
AcP	10.064	153	57、76、91
Flu	10.926	166	82、135、149
PA	12.484	178	71、135、152
Ant	12.583	178	85、135、152
FL	14.436	202	57、85、152
Pyr	14.830	202	73、100、135

Table S3 Eight reference materials for polycyclic aromatic hydrocarbons

PAHs	Melting Point/°C	Boiling point/°C	Flash Point/°C	Density
Nap	80-82	218	174	0.98
AcPy	78-82	280	122	0.899
AcP	90-94	279	135	1.06
Flu	114.77	294	151	1.203
PA	98-100	340	99-101	1.063
Ant	215	340	121	1.24
FL	109-110	384	-18	1.252
Pyr	148	393.5	210	1.271

Table S4 Test results of 8 polycyclic aromatic hydrocarbons in actual samples (river water, rain water, Jinlong lake water)

Samples		Nap	AcPy	AcP	Flu	PA	Ant	FL	Pyr
Artificial lake water	Found	272.7	244.0	212.9	275.6	272.6	589.3	1173.0	1150.0
	Recovery[a] RSD(%)	102.9 ±7.2	90.3 ±6.8	92.1 ±9.8	103.9 ±6.5	107.5 ±9.3	116.4 ±8.1	106.7 ±9.5	82.3 ±7.8
	Recovery[b] RSD(%)	86.4 ±5.3	88.5 ±4.0	91.3 ±6.0	87.2 ±10.4	90.7 ±12.9	87.7 ±5.5	84.0 ±2.5	83.5 ±0.8
	Recovery[c] RSD(%)	84.2 ±4.0	88.7 ±4.0	87.7 ±6.2	85.7 ±3.9	86.6 ±3.8	105.7 ±4.0	102.9 ±1.5	83.5 ±2.3
Rain water	Found	266.6	139.6	90.1	145.8	284.1	220.4	515.2	306.7
	Recovery[a]	102.8	105.9	101.2	88.1	94.7	111.7	114.6	98.2
	RSD(%)	±5.5	±6.2	±7.4	±4.2	±7.9	±8.6	±5.4	±3.8
	Recovery[b] RSD (%)	91.4 ±3.3	93.7 ±10.4	82.0 ±6.8	90.8 ±9.2	94.2 ±9.8	83.5 ±2.2	95.7 ±4.5	84.5 ±5.3
	Recovery[c] RSD(%)	85.4 ±6.7	89.1 ±8.4	85.9 ±12.3	88.1 ±2.8	80.2 ±1.8	85.6 ±2.6	98.3 ±2.1	84.8 ±2.6
Jinlong Lake water	Found	339.1	354.8	333.2	494.9	393.2	604.4	284.6	243.6
	Recovery[a]	85.2	102.4	94.8	114.2	84.7	110.7	114.6	118.2
	RSD(%)	±4.9	±5.0	±2.9	±3.7	±7.9	±2.6	±3.4	±6.8
	Recovery[b] RSD(%)	86.3 ±7.8	93.2 ±2.6	88.7 ±6.9	83.2 ±8.6	88.3 ±2.7	108.2 ±1.3	106.3 ±2.7	84.7 ±7.8
	Recovery[c] RSD(%)	86.2 ±1.8	81.2± 2.9	84.0 ±4.9	82.0 ±2.2	87.8 ±7.6	83.0 ±2.2	87.8 ±6.0	91.7 ±5.0

[a] Recovery of spiked 5 ng/mL; [b] Recovery of spiked 150 ng/mL; [c] Recovery of spiked 300 ng/mL

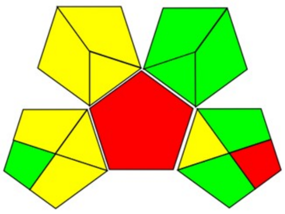
Table S5 Test results of 8 polycyclic aromatic hydrocarbons in actual samples (sugarcane field soil, roadside soil, gas station soil)

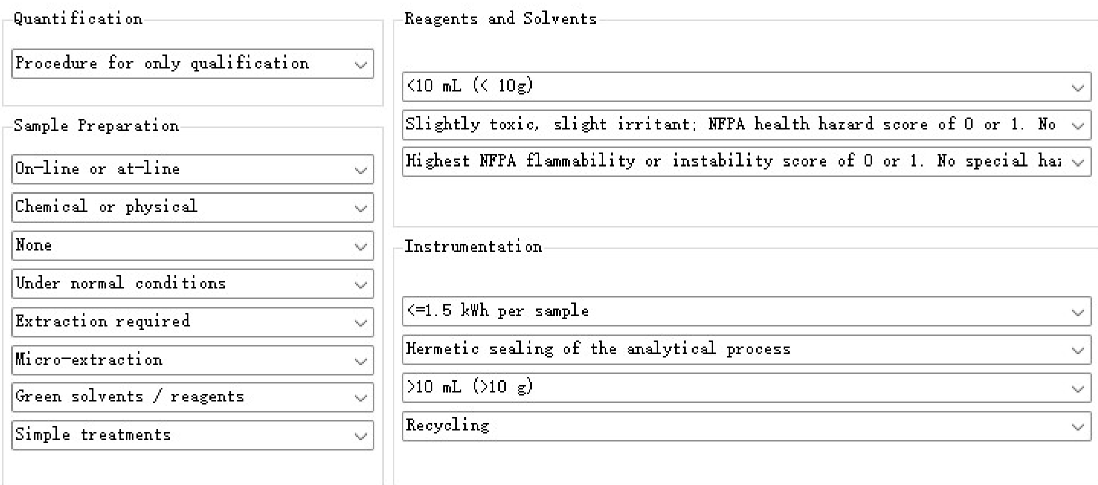
Samples		Nap	AcPy	AcP	Flu	PA	Ant	FL	Pyr
Sugarcane field soil	Found	231.9	237.9	155.5	215.8	208.1	155.8	144.2	151.6
	Recovery[a] RSD(%)	85.2 ±4.2	106.6 ±6.6	79.5 ±7.3	80.4 ±5.1	84.3 ±5.5	81.7 ±2.5	82.3 ±6.9	79.1 ±2.0
	Recovery[b] RSD(%)	89.4 ±3.6	92.5 ±4.4	76.8 ±4.5	75.5 ±4.7	70.6 ±8.4	78.9 ±6.4	80.6 ±13.8	81.6 ±6.3
	Recovery[c] RSD(%)	88.3 ±3.9	86.8 ±2.1	71.4 ±4.1	70.7 ±4.5	75.7 ±5.4	75.2 ±11.3	81.8 ±13.1	71.1 ±7.7
Roadside soil	Found	271.9	215.4	464.91	140.8	588.1	108.5	287.2	257.6
	Recovery[a] RSD(%)	83.2 ±4.5	96.3 ±7.6	79.7 ±5.3	75.0 ±6.4	78.6 ±2.5	78.2 ±2.5	85.7 ±6.9	77.4 ±2.0
	Recovery[b] RSD (%)	86.7 ±4.3	87.9 ±2.6	72.7 ±3.1	74.8 ±14.9	71.6 ±2.4	78.1 ±12.6	82.4 ±8.4	70.8 ±2.3
	Recovery[c] RSD(%)	90.0 ±5.1	97.0 ±7.2	75.0 ±2.5	72.5 ±6.9	71.0 ±4.3	79.6 ±5.5	81.0 ±3.3	73.0 ±2.8
Gas station soil	Found	344.8	307.6	382.5	257.6	324.8	265.5	272.4	279.7
	Recovery[a] RSD(%)	85.2 ±4.2	84.6 ±6.6	79.5 ±5.3	82.0 ±3.1	73.3 ±2.5	78.7 ±2.5	85.3 ±6.9	79.1 ±2.0
	Recovery[b] RSD(%)	94.2 ±5.2	97.7 ±6.0	76.8 ±2.1	78.8 ±2.3	71.5 ±4.0	75.1 ±10.7	82.7 ±7.4	72.3 ±9.7
	Recovery[c] RSD(%)	88.9 ±4.5	90.0 ±5.1	82.2 ±6.3	78.1 ±4.2	74.5 ±3.5	70.7 ±7.9	79.3 ±6.0	76.8 ±6.6

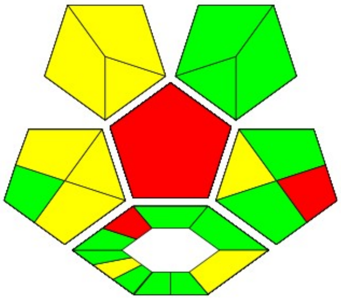
[a] Recovery of spiked 30 ng/mL; [b] Recovery of spiked 300 ng/mL; [c] Recovery of spiked 500 ng/mL

Table S6 Enrichment factors of 8 PAHs in different samples by coating

Compound	Log$K_{o/w}$	Artificial lake water EFs	Rain water EFs	Jinlong Lake water EFs	**Water EFs**	Sugarcane field soil EFs	Roadside soil EFs	Gas station soil EFs	**Soil EFs**
Nap	3.35	4730	4720	4030	4493	960	830	970	920
AcPy	3.94	2570	3230	3160	2987	710	790	730	743
AcP	3.75	1590	1870	2260	1907	650	610	520	593
Flu	4.18	2240	2310	2890	2480	340	360	490	397
PA	4.46	1990	2080	1930	2000	820	710	940	823
Ant	4.47	4420	4640	4500	4520	220	270	360	283
FL	5.19	7060	7180	7460	7233	530	490	530	517







SAMPLE PREPARATION AND ANALYSIS

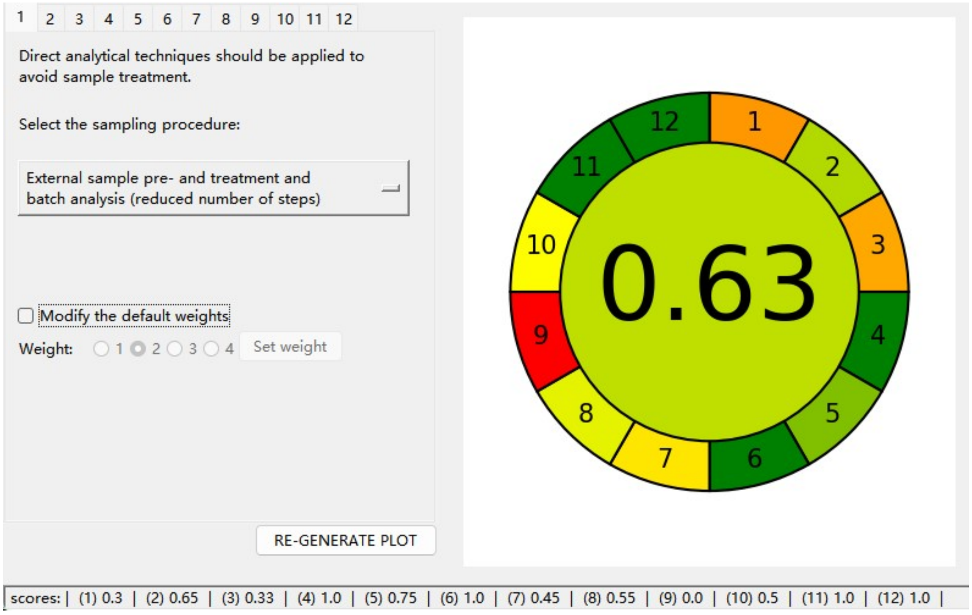
Sample preparation

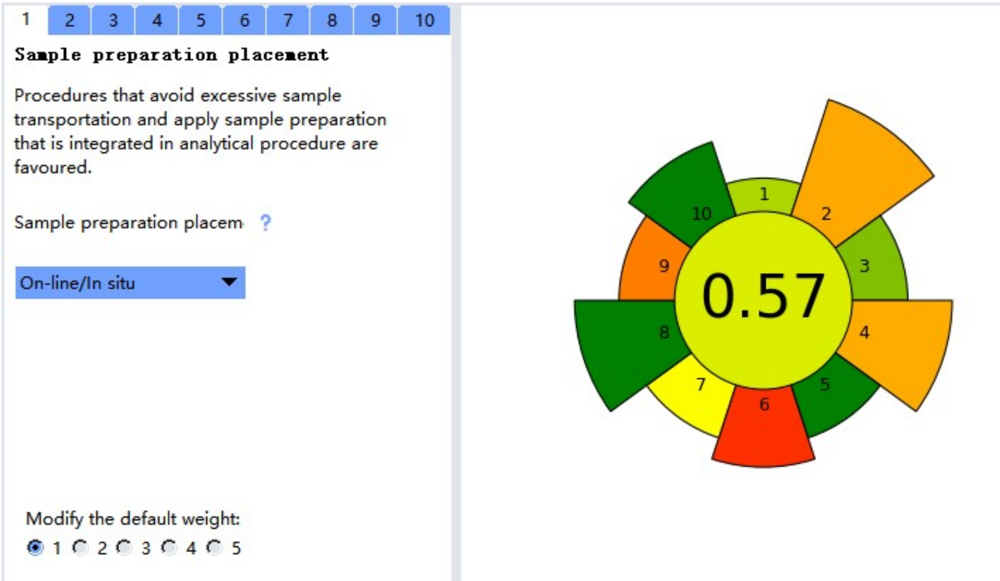
1. Collection:	On-line or at-line
2. Preservation:	Chemical or physical
3. Transport:	None
4. Storage:	Under normal condition
5. Type of method:	Extraction required
6. Scale of extraction:	Micro-extraction
7. Solvents/reagents used:	Green solvents/reagents
8. Additional treatments:	Simple treatments
Reagents and solvents	
9. Amount:	< 10 mL (< 10 g)
10. Health hazard:	Slightly toxic, slight irrita
11. Safety hazard:	Highest NFPA flammabil
instrumentation	
12. Energy:	<= 1.5 kWh per sample
13. Occupational hazard:	Hermetic sealing of the
14. Waste:	> 10 mL (>10 g)
15. Waste treatment:	Recycling
Method type	
Type of analysis:	Qualitative

PRE-ANALYSIS PROCESSES

Yield and conditions

I. Yield:	>89%
II. Temperature/time:	Room temp., < 1 h
Relation to Green Economy	
III. Number of rules met:	3-4
Reagents and solvents	
IVa. Health hazard:	Slightly toxic, slight irrita
IVb. Safety hazard:	Highest NFPA flammabil
Instrumentation	
Va. Technical setup:	Common setup
Vb. Energy:	≤1.5 kWh per sample
Vc. Occupational hazard:	Hermetization of analyti
Workup and purification	
VIa. End products workup, purification:	None or simple procese
VIb. Purity:	<97%
E-factor	
VII. E-factor input:	0 Apply


1 2 3 4 5 6 7 8 9 10 11 12
Direct analytical techniques should be applied to avoid sample treatment.
Select the sampling procedure:
External sample pre- and treatment and batch analysis (reduced number of steps)
Modify the default weights
Weight: 1 2 3 4 Set weight
RE-GENERATE PLOT
0.63
scores: | (1) 0.3 | (2) 0.65 | (3) 0.33 | (4) 1.0 | (5) 0.75 | (6) 1.0 | (7) 0.45 | (8) 0.55 | (9) 0.0 | (10) 0.5 | (11) 1.0 | (12) 1.0 |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Sample preparation placement
Procedures that avoid excessive sample transportation and apply sample preparation that is integrated in analytical procedure are favoured.
Sample preparation placem
On-line/In situ
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