Electronic Supplementary Information

PLGA-based nanofibers with a biomimetic polynoradrenaline sheath for rapid *in vivo* sampling of tetrodotoxin and sulfonamides in pufferfish

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Liquid Extraction. The liquid extraction of fish dorsal-epaxial muscle was conducted according to the National Standard of China (GB/T 22951-2008). A fish was killed, and 10 g of dorsal-epaxial muscle was collected in a centrifugation tube after trituration. Aliquots of 20 μL of deuterated standards solution (5.0 μg mL^{-1}), 20 g of Na_2SO_4, and 25 mL of acetonitrile were added in the centrifugation tube; then, the tube was vortex-mixed at 400 rpm for 2 min, and centrifuged at 3,000 rpm for 3 min. The obtained supernatant was transferred to a 50 mL volumetric flask, while 20 mL of acetonitrile was added to the residue, followed by a repetition of the aforementioned process. Then, the extracts of the two-time operation were amalgamated, and acetonitrile was added to the scale line of the flask. 10 mL of the above solution was transferred to an evaporating pipe, which was dried with nitrogen stream in water bath at 45 °C afterwards. The residue was dissolved by adding 120 μL of acetonitrile, 880 μL of CH_3COONH_4 solution (10 mM), and 1 mL of n-hexane in the centrifugation tube; subsequently, the tube was vortex-mixed at 400 rpm for 1 min, and centrifuged at 3,000 rpm for 3 min. The supernatant n-hexane was discarded, and another 1 mL of n-hexane was added. The procedure was repeated several times, until the subnatant aqueous phase became into transparency liquid. Finally, the subnatant was purified through a filter membrane, and was transferred to the inset tube in an amber vial for LC-MS/MS analysis.

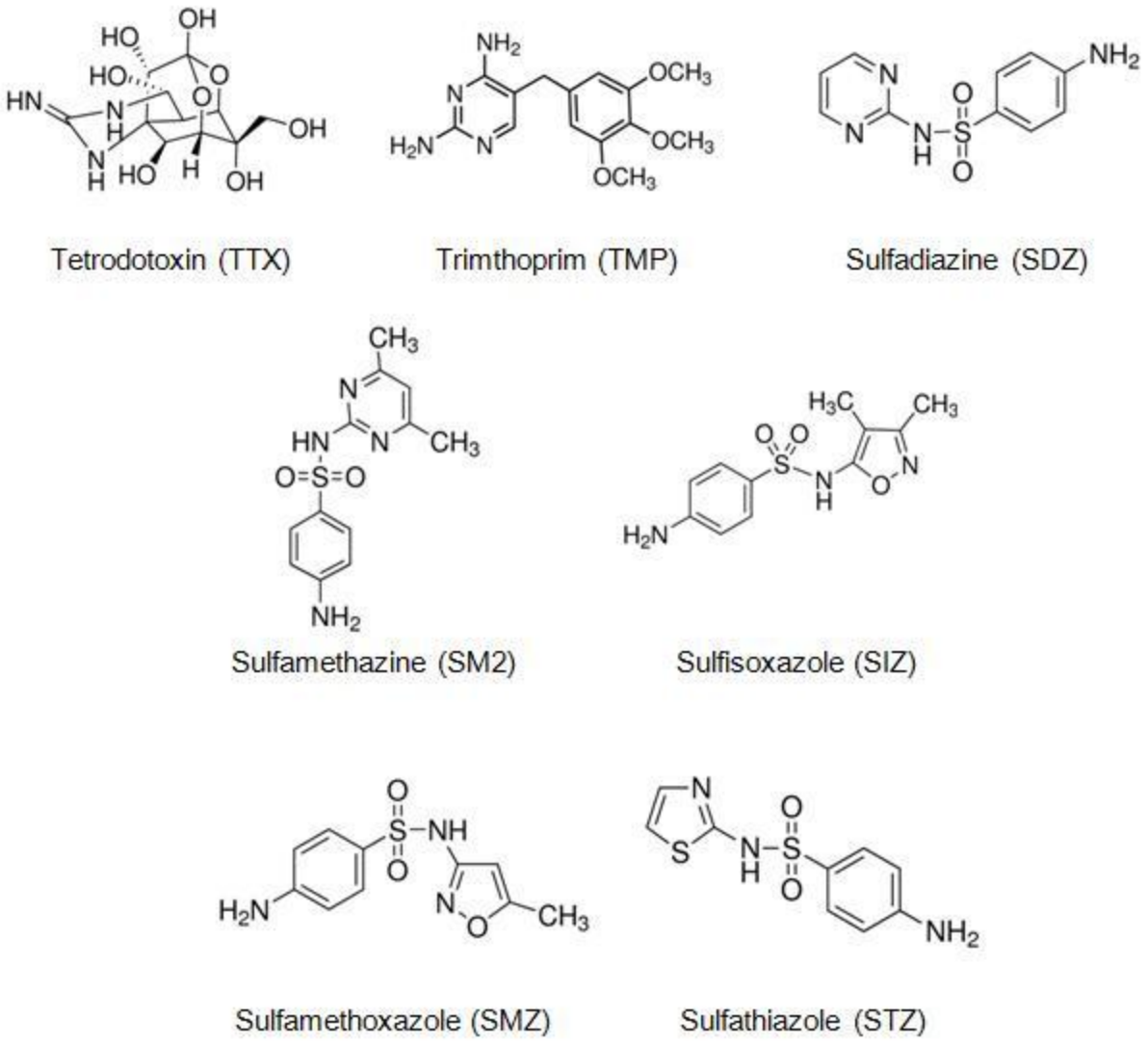

Fig. S1 Chemical structures of the seven analytes investigated in this study.

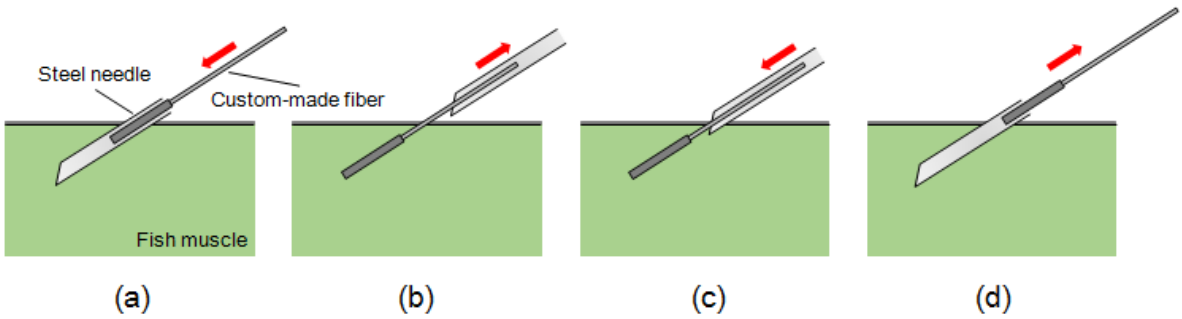

Fig. S2 Deployment of the novel SPME fiber in dorsal-epaxial muscle of living fish. (a) Deploy the fiber under the guidance of a steel needle, (b) remove the steel needle to expose the fiber to fish muscle, (c) put back the steel needle at the end of sampling, and (d) withdraw the fiber from fish muscle.

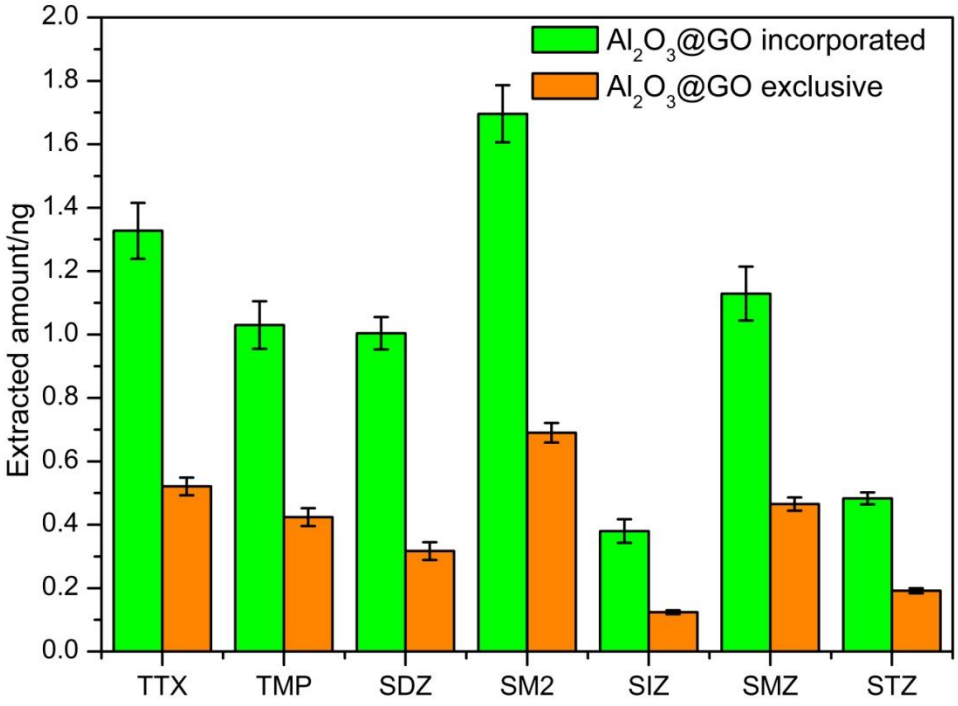

Fig. S3 Effect of Al_2O_3@GO incorporation on the extraction performance of the PLGA-based nanofibers.

Table S1 Regression slopes (k) and linear regression coefficients (R^2) of curves (signal to concentration, the units were omitted) derived from the matrix-free and matrix-impacted solutions (concentration range: 1-100 ng mL^{-1})

Matrix-	Index	TTX	TMP	SDZ	SM2	SIZ	SMZ	STZ
Free	k	173506	103752	55280	87102	92945	62526	59712
	R^2	0.9991	0.9985	0.9997	0.9990	0.9976	0.9988	0.9995
Impacted	k	168237	101926	57187	90332	93761	60194	55083
	R^2	0.9983	0.9964	0.9971	0.9969	0.9950	0.9962	0.9958

Tabe S2 Comparison of the sample preparation time (min) and LODs (ng g^{-1}) of the in vivo SPME method for TTX and SAs in this study with those in other works

Analytes	Methods	Sample preparation time[a]	LODs	References
TTX	SPME+LC-MS/MS	35	1.76	this work
	LE+mELISA	105	230	[1]
	LE+IAC+UPLC-MS/MS	67	0.1	[2]
	LE+LC-ESI-CID-MS/MS	10	80	[3]
SAs	SPME+LC-MS/MS	35	0.52-2.30	this work
	LE+pulsed-dc ESI-MS/MS	14	0.07-0.11	[4]
	LE+IAC+HPLC-UV	38	14.1-45.0	[5]
	QuEchERS+LC-MS/MS	57	0.01-0.04	[6]

[a]A conservative estimate based on the time cost for each step that was exactly mentioned in other works; sample preparation here refers to all the required procedures before the instrumental analysis or the deployment of detection devices, including extraction, possible desorption, and purification.

Table S3 Sampling rates (μg min^{-1}) of analytes determined with in vivo SPME in fish muscle

Analytes	Fish-1	Fish-2	Fish-3	Fish-4	Fish-5	Fish-6	Mean	RSDs
TTX	231.57	248.90	216.77	192.82	257.64	229.01	229.45	10.1%
TMP	294.29	320.15	375.83	339.06	282.75	371.47	330.59	11.7%
SDZ	59.12	46.22	48.57	63.95	42.50	52.18	52.09	15.6%
SM2	247.66	213.98	271.26	258.02	219.35	255.74	244.34	9.3%
SIZ	512.39	473.85	490.21	337.28	431.83	556.61	467.03	16.2%
SMZ	168.64	139.57	207.92	182.31	232.15	170.99	183.60	17.7%
STZ	202.78	271.33	249.06	176.11	221.83	192.45	218.93	16.4%

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