

# Supplementary Materials

## The Development of an Ultra-Performance Liquid Chromatography–Tandem Mass Spectrometry Method for Biogenic Amines in Fish Samples

Tong Li, Ruiguo Wang and Peilong Wang \*

Institute of Quality Standards and Testing Technology for Agro-Products,  
Chinese Academy of Agricultural Sciences, Beijing 10081, China; litong@caas.cn  
(T.L.); wangruiguo@caas.cn (R.W.)

\* Correspondence: wangpeilong@caas.cn; Tel.: +86-10-82106582

**Table S1.** Extraction recoveries of 14 BAs derivatives with different extraction reagents. FA means formic acid, AA means acetic acid, ACN means acetonitrile.

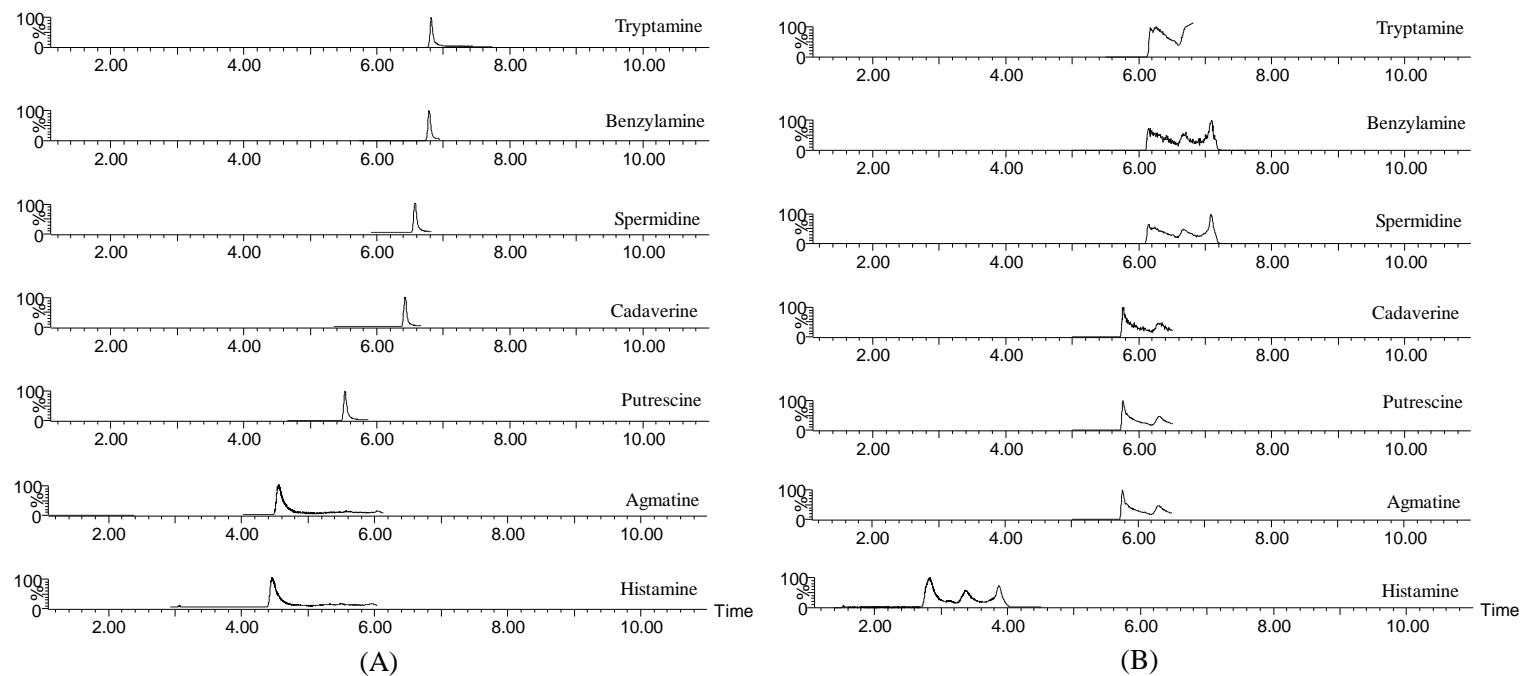
Name	extraction reagents				
	ACN	0.1% FA in ACN	0.5% FA in ACN	0.1% AA in ACN	0.5% FA in ACN
Histamine	55.1 ± 7.4%	80.1 ± 4.7%	82.4 ± 5.6%	44.2 ± 2.6%	80.1 ± 4.7%
Tyramine	32.1 ± 4.8%	75.2 ± 5.1%	76.1 ± 7.5%	52.1 ± 7.5%	75.2 ± 5.1%
Dopamine	28.9 ± 8.1%	91.3 ± 10.7%	91.2 ± 7.1%	48.2 ± 8.2%	91.3 ± 10.7%
Tryptamine	38.3 ± 5.2%	78.8 ± 4.2%	79.0 ± 11.8%	68.1 ± 12.4%	78.8 ± 4.2%
Serotonin	64.5 ± 7.4%	89.2 ± 6.1%	82.5 ± 13.0%	33.3 ± 10.0%	86.5 ± 7.7%
Putrescine	22.1 ± 8.2%	93.1 ± 3.4%	92.3 ± 6.7%	26.4 ± 12.0%	82.9 ± 13.4%
Spermine	27.3 ± 11.4%	92.1 ± 6.4%	84.2 ± 2.6%	44.2 ± 2.6%	90.4 ± 8.5%
Spermidine	61.2 ± 9.8%	75.2 ± 8.8%	78.1 ± 8.3%	31.7 ± 17.2%	69.3 ± 12.3%
Octopamine	32.1 ± 10.1%	91.6 ± 0.8%	91.2 ± 9.5%	29.2 ± 10.4%	90.4 ± 5.6%
Benzylamine	58.3 ± 9.2%	88.8 ± 6.2%	88.1 ± 11.0%	60.2 ± 9.2%	78.8 ± 2.6%
1- Phenylethylamine	33.5 ± 7.9%	89.2 ± 7.2%	92.5 ± 12.7%	62.5 ± 3.7%	82.7 ± 4.7%
Cadaverine	17.7 ± 8.6%	90.1 ± 8.4%	84.3 ± 6.3%	14.3 ± 8.2%	92.2 ± 6.4%
2-Phenethylamine	21.8 ± 17.5%	81.3 ± 5.7%	76.4 ± 16.2%	55.5 ± 12.7%	82.7 ± 10.4%
Agmatine	9.3 ± 15.3%	77.2 ± 6.4%	74.3 ± 5.7%	54.3 ± 6.3%	72.5 ± 9.4%

**Table S2.** Sensitivities of BAs (1000 nM) standard solution derived with benzoyl chloride, dansyl chloride and pyridine-3-sulfonyl chloride.

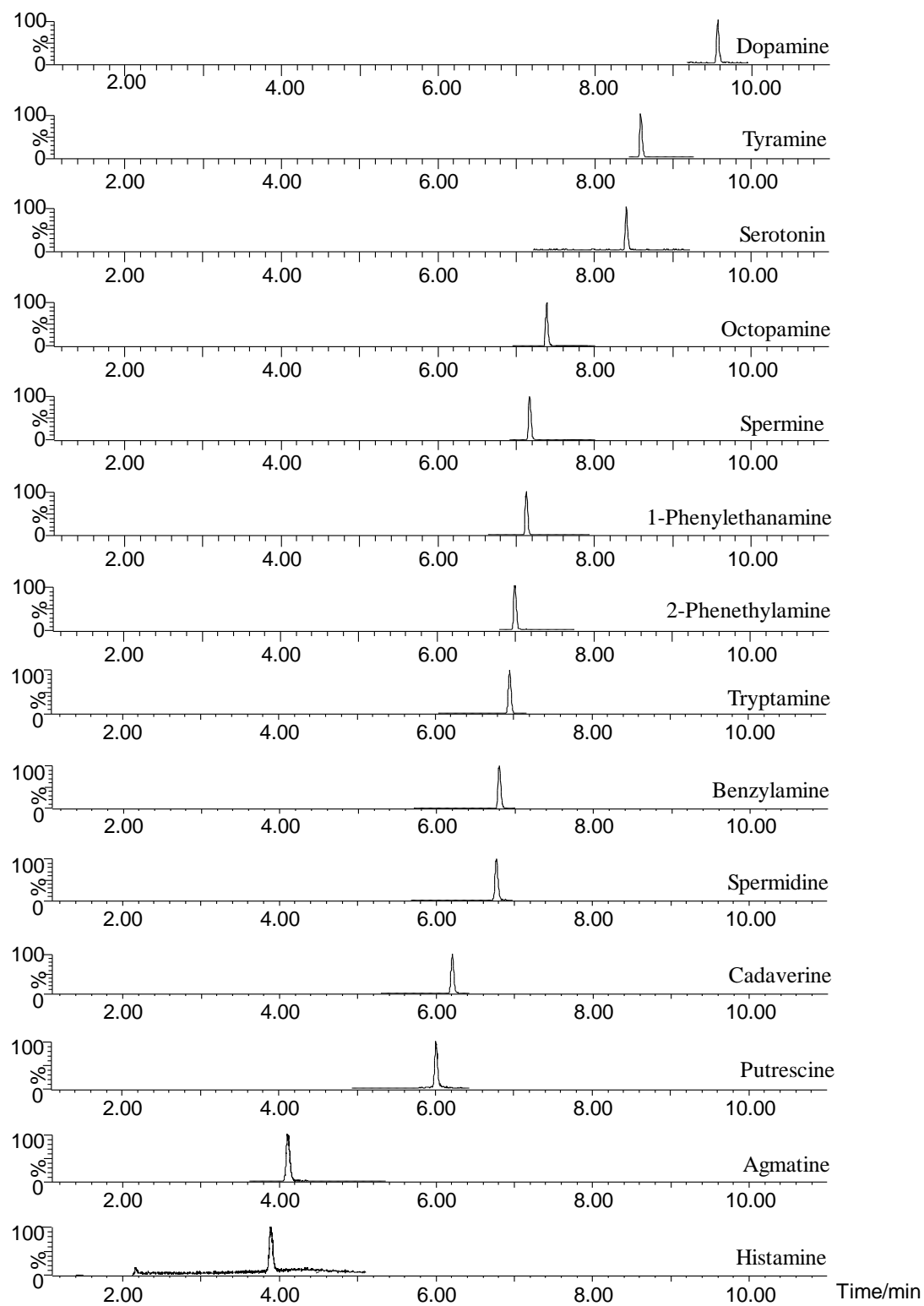
Name	derivatization reagents		
	benzoyl chloride	dansyl chloride	pyridine-3-sulfonyl chloride
Histamine	$4.66 \times 10^6$	$1.29 \times 10^6$	$9.27 \times 10^5$
Tyramine	$1.05 \times 10^7$	$4.93 \times 10^6$	$1.36 \times 10^6$
Dopamine	$1.37 \times 10^7$	$9.38 \times 10^5$	$8.03 \times 10^5$
Tryptamine	$1.62 \times 10^7$	$7.39 \times 10^6$	$1.07 \times 10^5$
Serotonin	$5.15 \times 10^6$	$3.87 \times 10^6$	$1.36 \times 10^6$
Putrescine	$2.70 \times 10^6$	$1.88 \times 10^6$	$1.08 \times 10^6$
Spermine	$1.96 \times 10^6$	$1.96 \times 10^6$	$1.33 \times 10^6$
Spermidine	$1.23 \times 10^6$	$1.06 \times 10^6$	$7.11 \times 10^5$
Octopamine	$2.70 \times 10^6$	$2.59 \times 10^6$	$2.16 \times 10^5$
Benzylamine	$1.86 \times 10^7$	$2.93 \times 10^6$	$3.40 \times 10^5$
1-Phenylethylamine	$1.91 \times 10^7$	$7.04 \times 10^5$	$5.87 \times 10^5$
Cadaverine	$2.30 \times 10^7$	$9.97 \times 10^6$	$7.11 \times 10^5$
2-Phenethylamine	$2.08 \times 10^7$	$8.56 \times 10^6$	$2.72 \times 10^6$
Agmatine	$1.37 \times 10^7$	$5.16 \times 10^6$	$3.40 \times 10^5$

**Table S3.** Response of each BAs derivatives under different conditions (concentration of benzoyl chloride and vortex time) of derivatization.

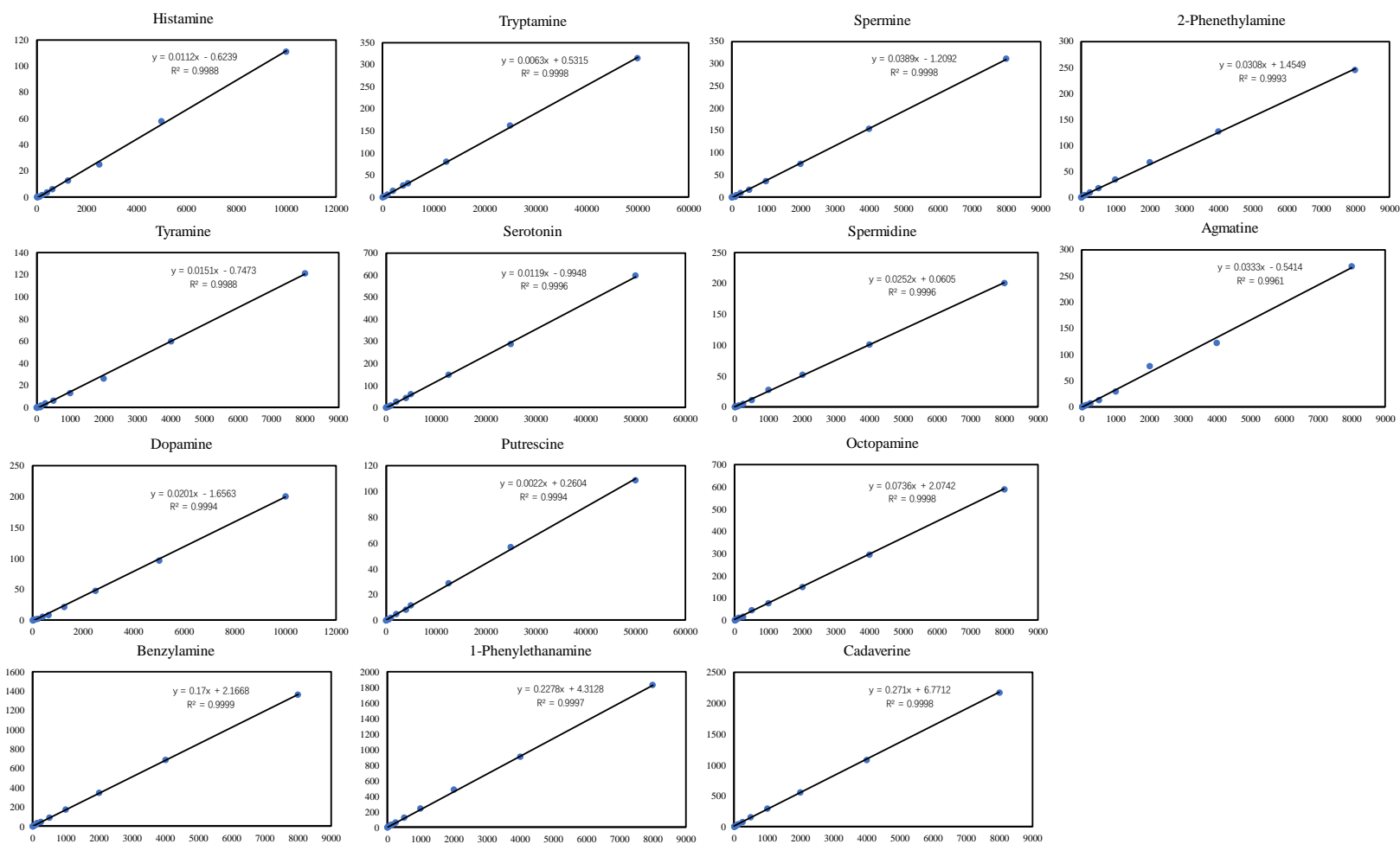
Name	Concentration of of benzoyl chloride					Reaction time			
	1%	2%	3%	4%	10%	5 min	10 min	20 min	30 min
Histamine	$8.40 \times 10^6$	$1.60 \times 10^7$	$1.52 \times 10^7$	$1.20 \times 10^7$	$8.80 \times 10^6$	$1.28 \times 10^7$	$1.40 \times 10^7$	$1.64 \times 10^7$	$1.60 \times 10^7$
Tyramine	$1.80 \times 10^7$	$4.64 \times 10^7$	$4.56 \times 10^7$	$3.60 \times 10^7$	$3.04 \times 10^7$	$3.60 \times 10^7$	$4.64 \times 10^7$	$4.76 \times 10^7$	$3.96 \times 10^7$
Dopamine	$2.16 \times 10^7$	$5.12 \times 10^7$	$4.84 \times 10^7$	$4.16 \times 10^7$	$2.40 \times 10^7$	$3.00 \times 10^7$	$3.44 \times 10^7$	$5.12 \times 10^7$	$4.04 \times 10^7$
Tryptamine	$2.68 \times 10^7$	$5.60 \times 10^7$	$3.96 \times 10^7$	$3.56 \times 10^7$	$3.04 \times 10^7$	$3.60 \times 10^7$	$4.88 \times 10^7$	$5.56 \times 10^7$	$5.60 \times 10^7$
Serotonin	$8.40 \times 10^6$	$1.76 \times 10^7$	$1.76 \times 10^7$	$1.64 \times 10^7$	$1.28 \times 10^7$	$4.00 \times 10^6$	$6.40 \times 10^6$	$1.80 \times 10^7$	$1.84 \times 10^7$
Putrescine	$4.80 \times 10^6$	$1.76 \times 10^7$	$1.36 \times 10^7$	$8.00 \times 10^6$	$4.40 \times 10^6$	$8.80 \times 10^6$	$1.56 \times 10^7$	$1.68 \times 10^7$	$1.76 \times 10^7$
Spermine	$2.40 \times 10^6$	$1.64 \times 10^7$	$6.40 \times 10^6$	$3.60 \times 10^6$	$3.60 \times 10^6$	$6.80 \times 10^6$	$1.32 \times 10^7$	$1.76 \times 10^7$	$1.68 \times 10^7$
Spermidine	$2.80 \times 10^6$	$1.68 \times 10^7$	$1.56 \times 10^7$	$3.20 \times 10^6$	$3.20 \times 10^6$	$1.12 \times 10^7$	$1.68 \times 10^7$	$1.80 \times 10^7$	$1.52 \times 10^7$
Octopamine	$3.60 \times 10^6$	$1.56 \times 10^7$	$1.28 \times 10^7$	$2.00 \times 10^6$	$1.60 \times 10^6$	$6.40 \times 10^6$	$1.56 \times 10^7$	$1.60 \times 10^7$	$1.52 \times 10^7$
Benzylamine	$3.08 \times 10^7$	$6.24 \times 10^7$	$5.64 \times 10^7$	$4.80 \times 10^6$	$2.60 \times 10^7$	$3.40 \times 10^7$	$4.92 \times 10^7$	$4.96 \times 10^7$	$4.88 \times 10^7$
1-Phenylethylamine	$3.08 \times 10^7$	$4.80 \times 10^7$	$4.32 \times 10^7$	$3.52 \times 10^6$	$2.24 \times 10^7$	$3.64 \times 10^7$	$4.80 \times 10^7$	$4.84 \times 10^7$	$4.68 \times 10^7$
Cadaverine	$3.92 \times 10^7$	$6.40 \times 10^7$	$5.16 \times 10^7$	$3.08 \times 10^6$	$2.68 \times 10^7$	$3.92 \times 10^7$	$5.44 \times 10^7$	$6.44 \times 10^7$	$6.36 \times 10^7$
2-Phenethylamine	$3.40 \times 10^7$	$8.00 \times 10^7$	$7.92 \times 10^7$	$6.80 \times 10^6$	$3.60 \times 10^7$	$3.40 \times 10^7$	$8.00 \times 10^7$	$8.44 \times 10^7$	$8.12 \times 10^7$
Agmatine	$2.24 \times 10^7$	$3.20 \times 10^7$	$2.64 \times 10^7$	$1.60 \times 10^6$	$8.40 \times 10^6$	$2.24 \times 10^7$	$3.20 \times 10^7$	$3.24 \times 10^7$	$3.04 \times 10^7$



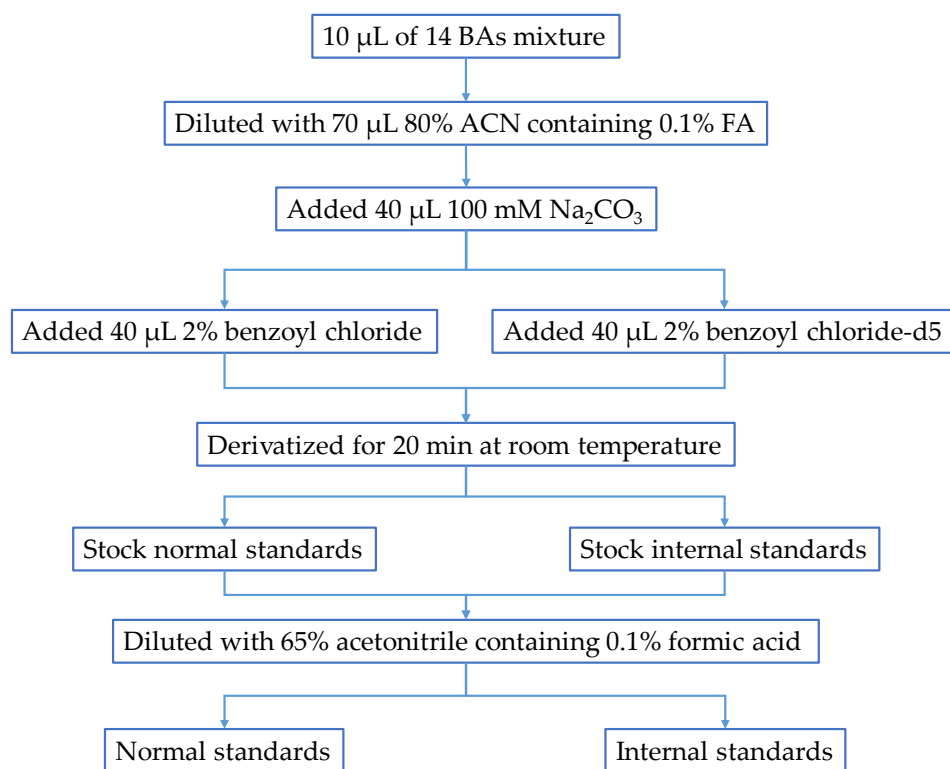
**Figure S1.** Chromatogram of 7 BAs derivatives in 1000 nM standards mixture. Results show that the chromatographic peak is obviously broadened or even trailing, when the flow rate was 0.2 mL/min (Figure S1A). Chromatography peak shapes were unsatisfactory, when the mobile phase A was water and phase B was acetonitrile (Figure S1B).



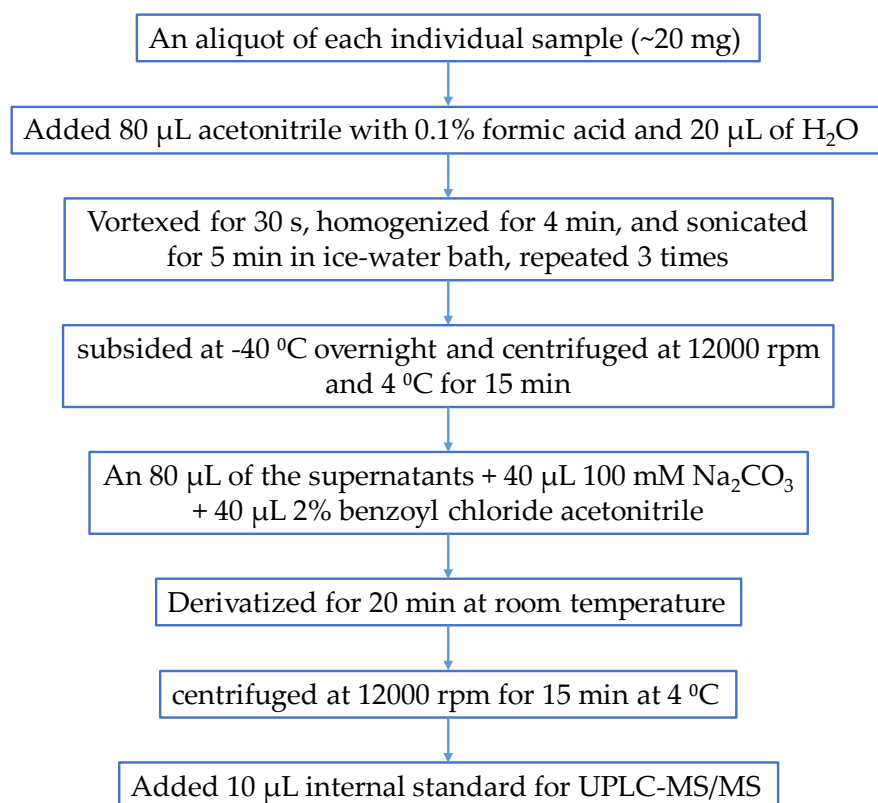
**Figure S2.** Chromatogram of 14 derivatized BAs in spiked fish sample (1000 nM).



**Figure S3.** Graphs of calibration curves with data points of 14 BAs derivatives.



**Figure S4.** A flow chart for the steps of derivatization of standards.



**Figure S5.** A flow chart for the steps of derivatization of fish samples.