



NOTE

Detection and Comparison of 10 Metals in Brachymystax Lenok from the Genhe River and Ussuri River

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Assessment on heavy metals pollution of aquatic products has been paid more and more attention. Brachymystax lenok from Genhe river and Ussuri river of northeastern China were detected the contents of heavy metals to evaluate its safety. The results proved that the detecting method in these conditions is accurate and precise. Brachymystax lenok muscle contains many kinds of mineral elements, Cu, Pb, Zn, Cr, Fe, Ca, Na and Mn, but contents of harmful elements are very low, so Brachymystax lenok from both rivers are safe in terms of heavy metals. Compared with Brachymystax lenok from Ussuri river, Brachymystax lenok from Genhe river contains more Cu, Pb, Zn, Cr Fe and Ca and less Na and Mn, which should be relative to water environment, so we should control the river water environment.

Key Words: Brachymystax lenok, Genhe river, Ussuri river, Heavy metals, ICP-MS.

With the quick development, assessment on heavy metals pollution of aquatic products has been paid more and more attention^{1,2}. Brachymystax lenok belonging to salmoniformes head, salmonidae family, salmonids gorbuscha genus, which is widely distributed in northern China, especially Heilongjiang river and Wusuli river and its tributaries of Northeastern China, the upstream Luan river and White river in North China, the Irtys river in Xinjiang and its tributaries. Part of the rivers in Siberia of Russia, Mongolia and North Korea is also an important distribution region for Brachymystax lenok.

Brachymystax lenok, as one the most ferocious freshwater fish species, usually feed on animals, its foods mainly include small fish, fish eggs, shrimp and other aquatic insects, so Brachymystax lenok often enriched many metal elements through the food chain³, but contents of heavy metals in Brachymystax lenok has not been reported.

Today, there are many methods of detecting heavy metals, ICP-MS which has virtues of high precise and accurate and multielement determination has becomes one of the most popular method⁴⁻¹⁰. In this paper, Brachymystax lenoks from Genhe river and Ussuri river were sampled and detected the contents of heavy metals to evaluate its safety.

Sample preparation and instruments: The samples are wild fishes caught from the Genhe river and Ussuri river in October 2010 whose body weight was 1.6 ± 0.3 kg. Sampling its muscle, chopped and stir adequately. Weigh 0.5 g muscle minced in 70 % nitric acid 10 mL, digested, the microwave

digestion conditions was shown in Table-1. After cooling, the supernatant was filtered for detecting.

TABLE-1
MICROWAVE DIGESTION TEMPERATURE
CONTROL PROGRAM

Maximum power (W)	Climb time (min)	Temperature (°C)	Hold time (min)
1200W	15	180	10

The instrument was Agilent7500 ICP-MS (USA, Agilent Company) the PQ Excell instrument (PE Company, USA), MARS X system high pressure microwave digestion system (USA, CEM company), Argon (Purity: 99.995 %), Na, Ca, Zn, Cu, Mn, Pb, Cd, Cr, Ni, Fe multi-element standard solution (100 µg/mL, Agilent company); Na, Ca, Zn, Cu, Mn, Pb, Cd, Cr, Ni, Fe solid reference material (GBW08517 Kelp standard material composition analysis, Tianjin HuaKerufeng standard materials company), Li, Y, Ce, Tl MS tuning solution (10 µg/mL, Agilent company).

Detecting methods: Test methods used common external standard method, that is, the standard curve method. Diluting multi element standard solution into concentrations of 0, 10, 20, 50, 100 and 200 µg L⁻¹ with 1 % HNO₃ as the standard series of working fluid to detect the concentrations of Na, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb. The operating conditions of ICP-MS were showed in Table-2.

TABLE-2
PARAMETERS OF ICP-MS

Parameters	RF power (W)	Carrier gas flow (L.min ⁻¹)	Cooling gas flow (L.min ⁻¹)	Atomization temperature (°C)	Integration time (s)	Repeats
Value	1250	1.0	12.5	2.0	0.3	3

The contents of different heavy metals vary greatly, so the linear range of criteria curve should be selected according to the actual situation. Na, Ca, Mn and Fe have higher concentration, so their linear ranges were selected from 0 to 2000 mg kg⁻¹, other elements were selected from 0 to 200 mg kg⁻¹, the detected curve equation and correlation coefficient were showed in Table-3.

TABLE-3
CALIBRATION AND MASS OF ISOTOPE BY ICP-MS

Elements	Linear range (ng.mL ⁻¹)	Curve equation	Correlation coefficient	Isotope mass number
Cu	0-200.0	Y=3.593X-0.612	0.9995	63
Pb	0-200.0	Y=0.819X+0.025	0.9991	208
Zn	0-200.0	Y=0.771X+0.634	0.9995	66
Cd	0-200.0	Y=0.105X+0.02126	0.9996	111
Ni	0-200.0	Y=0.218X+0.024	0.9995	60
Cr	0-200.0	Y=0.099X+0.038	0.9998	53
Fe	0-20000.0	Y=0.026X+0.847	0.9997	57
Mn	0-2000.0	Y=1.205X+0.203	0.9991	55
Ca	0-2000.0	Y=0.003X+0.193	0.9992	43
Na	0-2000.0	Y=0.912X+23.024	0.9997	23

Accuracy of the precision of method: Ten kinds of mineral elements (Cu, Pb, Zn, Cd, Cr, Ni, Fe, Ca, Na and Mn) were detected by ICP-MS. Their recoveries are from 86.5 to 102.8 %, limits of detection range from 0.007 ng.mL⁻¹ to 0.095 ng.mL⁻¹ and relative standard deviations (RSD) range from 1.8 to 4.9 % and detecting limits are all lower than 0.095 ng mL⁻¹ (Table-4), which proved that the detecting method in these conditions is accurate and precise.

TABLE-4
RESULT OF THE STANDARD SAMPLES (n=7)

Elements	Recovery (%)	Relative standard deviation (RSD, %)	Detection limits (ng.mL ⁻¹)
Cu	99.0	3.2	0.025
Pb	86.5	4.6	0.095
Zn	101.4	3.9	0.006
Cd	97.4	2.1	0.001
Cr	98.4	1.8	0.007
Ni	97.1	2.3	0.036
Fe	102.8	4.9	0.016
Ca	100.4	4.7	0.032
Na	100.8	4.9	0.008
Mn	96.4	2.3	0.005

Content of heavy metals in Brachymystax lenok muscle from Genhe river and Ussuri river: Brachymystax lenok muscle contains many kinds of mineral elements, Cu, Pb, Zn, Cr, Fe, Ca, Na and Mn, but we didn't find Cd and Ni, in Brachymystax lenok muscle from both rivers. In the detected elements, concentrations of Ca and Na, as macroelements were

the highest, reached more than 400 mg kg⁻¹, but other elements which is usually harmful to human health are very low, so Brachymystax lenok from both rivers are safe in terms of heavy metals (Table-5).

TABLE-5
CONCENTRATIONS OF TRACE ELEMENTS IN BRACHYMYSTAX LENOK FROM GENHE RIVER AND USSURI RIVER (mg.kg⁻¹, n=15)

Elements	Brachymystax lenok from Genhe river	Brachymystax lenok from Ussuri river
Cu	0.396 ± 0.032	0.280 ± 0.027
Pb	0.016 ± 0.003	0.009 ± 0.001
Zn	4.910 ± 0.43	4.330 ± 0.29
Cd	null	null
Cr	0.041 ± 0.002	null
Ni	null	null
Fe	1.030 ± 0.06	0.760 ± 0.020
Ca	507.700 ± 21	485.300 ± 30
Na	650.300 ± 32	695.200 ± 36
Mn	null	0.047 ± 0.006

Compared with Brachymystax lenok from Ussuri river, Brachymystax lenok from Genhe river contains more Cu, Pb, Zn, Cr Fe and Ca and less Na and Mn, which should be relative to water environment, so we should control the river water environment.

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