Asian Journal of Chemistry; Vol. 25, No. 7 (2013), 3665-3667

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13708

Determination of Total Mercury in Fish from Amur and Ussuri River of China by Microwave Digestion-ICP/MS Method

DONGLI QIN, ZHONGXIANG CHEN, HAITAO WANG, JIWEI ZHAO and ZHENBO MOU*

Heilongjiang River Fisheries Research Institute, Chinese Academy of Fishery Science, Harbin 150070, P.R. China

*Corresponding author: E-mail: mouzb1962@163.com; qdl978@163.com

(*Received*: 10 March 2012; *Accepted*: 7 January 2013) AJC-12670

Total mercury concentration in fishes from Fuyuan reach of the Amur and Ussuri River were determined by inductively coupled plasma-mass spectrometry. Sample analysis consisted of digestion of 0.5 g of muscle with nitric acid and hydrogen peroxide solution using microwave digestion, followed quantification of mercury by ICP-MS, Bi was used as an internal standard (ISTD). The mean recovery ranged from 95.2-105.8 % and the relative standard deviation (RSD) ranged from 2.84 to 7.22 % and the lower limit of detection was 0.001 mg/kg. The present study showed that total mercury in specimens of *Parasiburusasvtus* and *Pelteobagrus fulvidraco* were generally higher than in *Cyprinus carpio Linnaeu* and *Carassius auratu gibeliv*, but total mercury concentrations in all the samples below 0.3 mg/kg, limit recommended by China regulation.

Key Words: Amur River, Ussuri River, Total mercury, Fish, ICP-MS.

INTRODUCTION

Amur River and Ussuri River lies between China and Russia and is the boundary for two countries. In Fuyuan, the Ussuri River into Amur, where is the main natural fishing areas and one of the richest fishery resources in China's inland waters[1]. The Amur's largest tributary, the Songhua river was seriously polluted by mercury mostly in the last century[2,3]. Fuyuan is located in the downstream from the historical pollution source, information on Hg concentration and distribution in this region is scarce and inadequate. Fish may represent risk for human health since they can accumulate contaminants from aquatic environment and magnify them up the food chain[4-6] and Hg is one of the most toxic heavy metals in the environment[7]. For this reason, determination of Hg in fish is extremely important for human health.

There are many detection methods of mercury in fish samples, such as inductively coupled plasma optical emission spectrometry[8,9], inductively coupled plasma mass spectrometry[10-12], graphite furnace atomic absorption spectrometry[13], cold atomic absorption spectrometry[14,15], flame atomic absorption spectrometry[16], atomic fluorescence spectrometry[17,18], the automatic Hg analyzer[19,20], *etc*. In this paper, the total mercury in samples was determined by inductively coupled plasma mass spectrometry after closed-vessel microwave digestion since the method is precise, accurate and rapid in the trace elements detection[21,22].

EXPERIMENTAL

Samplings: In September 2011, fish were purchased directly from local fisherman on the water in Fuyuang reach of the Amur and Ussuri River. Collected specimens include *Cyprinus carpio Linnaeu*, *Carassius auratu gibeliv*, *Parasiburusasvtus* and *Pelteobagrus fulvidraco* were classified, measured and were brought back with polyethylene bags containing ice in and preserved at -20 ºC in laboratory. Fish was washed with deionized water, only the interior filets of fish muscle were analyzed to avoid potential surface contamination.

The standard stock solution of mercury (1000 µg/mL, Chinese National Standard Research Center). Internal standard stock solution (^{6}Li, Sc, Ge, Rh, In, Tb, Lu and Bi: 100 µg/mL, Agilent Part #5188-6525). Tuning solution (Li, Y, Ce, Tl and Co: 10 µg/L, Agilent Part # 5184-3566). Nitric acid and hydrogen peroxide solution are GR reagents. All water was distilled, deionized and further purified *via* a Millipore Milli-Q.

All of the glass vessels and PTFE digestion tanks were soaked overnight in 30 % HNO_3, rinsed with copious amounts of distilled deionized water, stored, capped and filled with deionized water, prior to use.

Sample preparation

Working stock solutions: The working stock solutions (Hg at concentrations of 0, 25, 50, 100, 250 and 500 µg/L and

ISTD at 50 µg/L) were prepared by diluting the standard stock solution with 5 % nitric acid water (v/v).

Calibration curve and quality controls: The calibration curve was made by adding 1 mL working stock solutions of Hg to PTFE digestion tank, respectively, processing steps with the same method 2.3.3 sample digestion procedure except for adding fish muscle, the final Hg concentrations of 0, 0.5, 1.0, 2.0, 5.0 and 10.0 µg/L with 1 µg/L of ISTD. Quality control samples were prepared using the same methodology.

Sample digestion procedure: Samples were digested using a MARS X microwave digestion system (CEM, USA). Briefly, 0.5 g fish muscle placed in a PTFE digestion tank with 5 mL nitric acid for 1 h, adding 2 mL hydrogen peroxide solution and then digested with the microwave digestion (conditions was shown in Table-1). Digestion solution was transferred to a 50 mL volumetric flask after cooling the digestion tank, adding 1 mL working stock solutions of ISTD and adding purity water to volume of 50 mL for detection.

TABLE-1
MICROWAVE DIGESTION CONTROL PROGRAM
(CONTROL TYPE: STANDARD CONTROL)

Step	Enter power		Method time (min)	Parameters (ºC)	Hold (min)
	Max	%			
1	1600W	100	5	110	3
2	1600W	100	4	150	8
3	1600W	100	3	180	25

ICP-MS conditions: Detection was performed on an Agilent 7500CX Inductively coupled plasma-mass spectrometry (Agilent Technologies Co. Ltd., USA). The optimized conditions of operating parameters were listed in Table-2.

TABLE-2
OPERATING PARAMETERS OF ICP-MS

Parameters	Value	Parameters	Value
RF power (w)	1500	Mass elem.	202Hg
RF matching	1.74	ISTD	209Bi
Sample depth (mm)	8.2	Integration time (s)	0.10
Carrier gas (L/min)	0.90	Repetition	3
Makeup gas (L/min)	0.24	Acquisition mode	Spectrum
Nebulizer pump(rps)	0.10	Uptake speed (rps)	0.40
S/C temp (ºC)	2	Uptake time (s)	45
Cooling gas (L/min)	15.0	Stabilization time (s)	30

RESULTS AND DISCUSSION

Standard curve and LOD: The analytical characteristics *i.e.*, calibration data and detection limit were evaluated. Calibration curve obtained using matrix-matched standards showed good linearity over the entire range of concentrations with quadratic correlation coefficients (R^2) is 0.9998. Limits of detection (LOD) was defined and determined as the minimum detectable amounts of analyze with a signal-to-noise ratio of 3:1[21]. LOD was obtained 0.001 mg/kg, ww (0.01 µg/L). The attained LOD are sufficiently low for fish safety monitoring purposes considering the maximum Hg level established in fish by China Regulation (GB/T 18406.4-2001, 0.3 mg/kg).

Determination of quality control samples: To check the accuracy of the method, recoveries of spiked standards solutions in the defined calibration range were measured in cod fish samples[21]. Spikings (n = 10) were realized before the digestion of samples, subjected to the complete analytical procedure. The result show that the mean recovery ranged from 95.2 to 105.8 % and the relative standard deviation (RSD) ranged from 2.84 to 7.22 %.

Hg in muscles of fish species: In Amur and Ussuri River, Hg mean amounts in muscle composites of the examined species were 0.091 ± 0.050 (ranging from 0.036-0.133), 0.067 ± 0.034 (0.011-0.101), 0.105 ± 0.059 (0.045-0.180), 0.121 ± 0.071 (0.020-0.210) and 0.098 ± 0.037 (0.063-0.137), 0.066 ± 0.032 (0.019-0.092), 0.179 ± 0.087 (0.102-0.273), 0.119 ± 0.052 (0.026-0.166) mg/kg for *Cyprinus carpio Linnaeu*, *Carassius auratu gibeliv*, *Parasiburusasvtus* and *Pelteobagrus fulvidraco*, respectively (Table-3). Comparisons revealed that Hg in fishes muscle concentrations were not significantly different between two rivers in Fuyuan section.

China law on total mercury concentrations in edible freshwater species sets a limit of 0.3 mg/kg of fresh weight[23]. The law can act as a reference for evaluating the mercury concentrations found in the studied species. For this reason, total mercury concentration in fish is reported in Table-3 as fresh weight. The result showed that the detected concentrations of Hg in all fishes muscle are below the maximum level recommended by China regulation.

Statistical comparisons revealed that Hg concentrations were significantly different ($p < 0.001$) between fish species[5]. In this investigation,the concentration of mercury in *Parasiburusasvtus* and *Pelteobagrus fulvidraco* were generally higher than in *Cyprinus carpio Linnaeu* and *Carassius auratu gibeliv* showed that the law for mercury distribution in fish Was: The concentration of mercury in fish in the bottom of the river > that of fish in the surface of the river and that of predatorial fish > that of herbivorous fish[24].

TABLE-3
TOTAL MERCURY CONCENTRATION (mg/kg FRESH WEIGHT) IN FISH LENGTH: cm

Station	Species	Length	Hg	Length	Hg	Length	Hg	Length	Hg	Length	Hg
Amur	*Cyprinus carpio Linnaeu*	23.5	0.036	17.5	0.133	24.4	0.105	–	–	–	–
	Carassius auratu gibeliv	14.1	0.071	13.4	0.069	19.1	0.011	14.0	0.082	12.7	0.101
	Parasiburusasvtus	32.0	0.120	28.1	0.045	31.2	0.180	33.4	0.075	–	–
	Pelteobagrus fulvidraco	15.1	0.147	22.7	0.137	15.2	0.034	14.7	0.195	13.9	0.020
	–	14.3	0.085	13.6	0.129	14.5	0.050	16.5	0.204	14.9	0.210
Ussuri	*Cyprinus carpio Linnaeu*	19.3	0.094	18.0	0.137	21.2	0.063	–	–	–	–
	Carassius auratu gibeliv	17.6	0.019	13.0	0.080	15.2	0.073	17.5	0.092	–	–
	Parasiburusasvtus	25.0	0.273	26.0	0.161	23.5	0.102	–	–	–	–
	Pelteobagrus fulvidraco	15.5	0.166	13.2	0.159	14.3	0.026	15.7	0.137	16.5	0.150
	–	15.6	0.052	15.9	0.145	–	–	–	–	–	–

Conclusion

The concentrations of total mercury in all specimens collected at Fuyang reach of the Amur and Ussuri River were not exceeded the criterion showed this region not to be affected by anthropogenic mercury contamination. However, Mercury bioaccumulation was particularly evident in *Parasiburusasvtus* and *Pelteobagrus fulvidraco*, so their frequent use for human consumption may represent a health hazard.

ACKNOWLEDGEMENTS

This work was supported by the Program: Basic and Specific Research of Heilongjiang River Fishery Research Institute (No: 2007HSY-ZH-25).

REFERENCES

1. C.Z. Dong, Y. Liu, J. Wang and H.B. Wang, *Chin. J. Fisheries*, **1**, 12 (2002) (in Chinese).
2. Z.S. Zhang, X.J. Sun, Q.C. Wang, D.M. Zheng, N. Zheng and X.G. Lv. *Water Air Soil Pollut*., **211**, 219 (2010).
3. C.Y. Lin, M.C. He, Y.X. Zhou, L.J. Hu, W. Guo, X.C. Quan and Z.F. Yang, *Soil Sediment Contamination*, **16**, 397 (2007).
4. R.J. Medeiros, L.M.G. dos Santos, A.S. Freire, R.E. Santelli, A.M. C.B. Braga, T.M. Krauss and S.C. Jacob, *Food Control*, **23**, 535 (2012).
5. C. Vieira, S. Morais, S. Ramos, C. Delerue-Matos and M.B.P.P. Oliveira, *Food Chem. Toxicol*., **49**, 923 (2011).
6. M. Tuzen, *Food Chem. Toxicol*., **47**, 1785 (2009).
7. M.I. Castro-González and M. Méndez-Armenta, *Environ. Toxicol. Pharmacol*., **26**, 263 (2008).
8. A.A. Fallah, S.S. Saei-Dehkordi, A. Nematollahi and T. Jafari, *Microchem. J*., **98**, 275 (2011).
9. C.M. Xiong and B. Hu, *J. Agric. Food Chem*., **55**, 10129 (2007).
10. S. Mol, *Biol. Trace Elem. Res*., **143**, 974 (2011).
11. K.X. Yang and S. Kamal, *Spectrochim. Acta B*, **62**, 1177 (2007).
12. SN/T 2208-2008, Determination of Sodium, Magnesium, Aluminum, Calcium, Chromium, Iron, Nickel, Copper, Zinc, Arsenic, Strontium, Molybdenum, Cadmium, Lead, Mercury, Selenium in Aquatic Products-Microwave Digestion-ICP/MS Method, The People's Republic of China Entry-Exit Inspection and Quarantine Standards (in Chinese).
13. J. Naozuka and C.S. Nomura, *J. Anal. Atom. Spectrom*., **23**, 2257 (2011).
14. R.B. Voegborlo and A.A. Adimado, *Food Chem.*, **123**, 936 (2010).
15. P. Rivaro, C. Ianni, F. Soggia and R. Frache, *Microchim. Acta*, **158**, 345 (2007).
16. P.J. Custódio, S. Pessanha, C. Pereira, M.L. Carvalho and M.L. Nunes, *Food Chem.*, **124**, 367 (2011).
17. G.G.A. de Carvalho, M.A. Feres, J.R. Ferreira and V.H. Kennedy, *Int. J. Environ. Anal. Chem*., **90**, 686 (2010).
18. I. Abua and E. Jonathan, *Food Chem*., **110**, 301 (2008).
19. P.J. Lechler, J.R. Miller, L.D. Lacerd, D. Vinson, J.-C. Bonzongo,W.B. Lyonsd and J.J. Warwick, *Sci. Total Environ*., **260**, 87 (2000).
20. R. Scerbo, T. Ristori, B. Stefanini, S. De Ranieri and C. Barghigiani, *Environ. Pollut*., **135**, 179 (2005).
21. H.T. Wang and P.R. Zhan, *Asian J. Chem*., **23**, 1881 (2011).
22. H.T. Wang and Z.B. Mou, *Asian J. Chem*., **23**, 4715 (2011).
23. GB/T 18406.4-2001, Safety Qualification for Agricultural Product-Safety Requirements for Non-Environmental Pollution Aquatic Products, The people's Republic of China National Standard (in Chinese).
24. L. Zhang, Q.-C. Wang and Z.-G. Shao, *Wetland Sci*., **3**, 27 (2005).