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Speciation of methylmercury in market seafood by thermal degradation, amalgamation and atomic absorption spectroscopy

Manuela Ruiz-de-Cenzano, Arancha Rochina-Marco, M. Luisa Cervera*, Miguel de la Guardia

Department of Analytical Chemistry, University of Valencia, 50th Dr. Moliner St., E-46100 Burjassot, Valencia, Spain

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ABSTRACT

Sample thermal decomposition followed by mercury amalgamation and atomic absorption has been employed for the determination of methylmercury (MeHg) in fish. The method involves HBr leaching of MeHg, extraction into toluene, and back-extraction into an aqueous L-cysteine solution. Preliminary studies were focused on the extraction efficiency, losses, contaminations, and species interconversion prevention. The limit of detection was 0.018 $\mu g\ g^{-1}$ (dry weight). The intraday precision for three replicate analysis at a concentration of 4.2 $\mu g\ g^{-1}$ (dry weight) was 3.5 percent, similar to the interday precision according to analysis of variance (ANOVA). The accuracy was guaranteed by the use of fortified samples involving 83–105 percent recoveries, and certified reference materials TORT-2 (lobster hepatopancreas) and DORM-3 (dogfish liver), providing 107 and 98 percent recovery of certified values. The greenness of the method was also evaluated with the analytical eco-scale being obtained a final score of 73 points which means an acceptable green analysis. The method was applied to fifty-seven market samples of different fish acquired from local markets in several sampling campaigns. The content of MeHg found varied between 0.0311 and 1.24 $\mu g\ g^{-1}$ (wet weight), with values that involve 33–129 percent of the total mercury content. Some considerations about food safety were also done taking into account data about Spanish fish consume and Tolerable Weekly Intake (TWI) established for MeHg.

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1. Introduction

Methylmercury (MeHg) is considered the most toxic mercury species due to its bioaccumulative character and biomagnification through the food chain (Driscoll et al., 2013). It is efficiently absorbed from the gastrointestinal tract and it is able to cross the placenta and the blood-brain barrier (Gundacker et al., 2010), thus creating neurological disorders, especially in foetus and children. Unfortunately, human intake of mercury occurs mainly as MeHg via fish consumption (European Food Safety Authority (EFSA), 2012).

The European Food Safety Authority (EFSA) recommended in 2012 a Tolerable Weekly intake (TWI) for MeHg of 1.3 $\mu g\ kg^{-1}$ body weight (bw), expressed as mercury, which provides a margin of about 40 as compared to the Lower Benchmark Dose on the 95 percent confidence level ($BMDL_{05}$) for the reduction in antibody response in rats (European Food Safety Authority (EFSA), 2012). In the European Union, Maximum Tolerated Level (ML) for mercury in fish is 0.5 mg kg^{-1} wet weight (ww) or 1.0 mg kg^{-1} ww (predatory fishes) (European Comission (EC), 2008). However, the best way of managing the risk of MeHg exposure is the combination of appropriate MLs and consumer advice, because patterns of fish consumption and mercury level in fish vary between countries. Hence, it is important to develop, maintain, and improve existing databases on MeHg focused on regional or national-based information (Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO), 2013).

The most commonly methods for MeHg determination involve the use of sophisticated hyphenated techniques with gas chromatography or liquid chromatography coupled to highly selective and sensitive detectors; such as atomic absorption spectroscopy (Jagtap et al., 2011), atomic fluorescence spectroscopy (Ohki et al., 2013), atomic emission spectroscopy, and inductively coupled plasma mass spectrometry (Tu et al., 2000).

Non-chromotagraphic methods employing cold vapour techniques, often in combination with preconcentration procedures, have been also developed as a simpler and cheaper alternative for MeHg determinations. They are based on the different behaviour of inorganic and organic mercury in front of reducing agents (Cava-Montesinos et

* Corresponding author.
E-mail addresses: manuela.ruiz@uv.es (M. Ruiz-de-Cenzano), aromar4@alumni.uv.es (A. Rochina-Marco), m.luisa.cervera@uv.es (M.L. Cervera), miguel.delaguardia@uv.es (M. de la Guardia).

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al., 2004) (Ashkenani et al., 2009), the selective retention or elution of species through a solid phase extraction system involving the use of different complexing or chelating agents (Vereda Alonso et al., 2008) (Wu et al., 2006), or alternatively the biosorption on microorganisms (bacteria, algae, yeast) (Tuzen et al., 2009a,b).

In recent years, the occurrence of direct mercury analyser instrumentation based on thermal degradation, amalgamation and atomic absorption (TDA-AAS) has improved the determination of total mercury at trace levels, because it allows an accurate quantification at very low concentrations in a very fast way. However, the use of this technique in mercury speciation requires a sample pre-treatment in order to separate the target species prior to the measurements. Some approaches have been published involving acid extraction of MeHg with HCl or HBr and double liquid–liquid extraction, first with toluene and then with cysteine or tiosulphate solution (see Table 1).

However, many of the available studies remain at the academical level or have been applied to a reduced number of samples or fish species. In line with the European Commission Joint Research Centre Institute for Reference Materials (EC-JRC-IRMM) which has recently run a collaborative trial in an attempt of standardise a method for MeHg determination (European Commission Joint Research Centre Institute for Reference Materials and Measurements (EC-JRC-IRMM), 2013), studies performed on certified reference materials should be now extended to field studies in order to substantiate the applicability of the available methodologies.

The purposes of this work were to assess the suitability of TDA-AAS methodology for MeHg determination in natural fish samples, also evaluating the greenness of the method, and to improve the existing databases regarding MeHg in fish consumed by the Spanish population.

2. Material and methods

2.1. Apparatus and instruments

Freeze-dry process was performed with a Telstar Cryodos system (Barcelona, Spain). Sample preparation involved the use of an analytical balance Mettler Toledo (Barcelona, Spain), a centrifuge Ortoalresa Mod Digicen 20 (Madrid, Spain) and a Milli-Q system Millipore (Bedford, USA) for ultrapure water. Mercury determination based on sample thermal degradation atomic absorption spectroscopy was made using a dual cell spectrophotometer Milestone instrument DMA-80 (Sorisole, Italy).

2.2. Reagents, standards and certified samples

All chemicals used were of the highest purity available and all solutions were prepared in ultrapure water with a resistivity 18.2 MΩ cm. HNO_3 69 percent (w/v) from Scharlau (Barcelona, Spain) was employed for cleaning glassware materials. In sample treatment, HBr 47 percent (w/v) and toluene, both from Scharlau, and L-cysteine solution from Sigma (Barcelona, Spain) were used. Oxygen N-50 was supplied by Carburos Metálicos (Barcelona, Spain).

Certified standard stock solution of 1000 mg L^{-1} Hg(II) was obtained from Merck (Darmstadt, Germany) and MeHg(II) chloride was obtained from Sigma-Aldrich (Madrid, Spain).

Certified reference materials TORT-2 (lobster hepatopancreas) and DORM-3 (dogfish liver) were obtained from the National Research Council of Canada (NRC) and Coal fly ash 1633c was provided by the National Institute of Standards and Technology of USA (NIST).

Table 1
Methods proposed in the literature for the determination of MeHg in fish by TDA-AAS.

Sample treatment	Type of sample	Origin	Accuracy (%)	Reference
Ultrasound extraction with HCl(15 mL)/toluene(5 mL), back-extraction into cysteine acetate(1 mL)	BCR 463,cod, flounder, turbot, perch, herring	Poland	(90.3–102)	(Kwasniak et al., 2012)
Microwave extraction with HCl(0.75 mL)/H_2O(1 mL)/ toluene(10 mL), back-extraction into cysteine acetate (2 mL) Acid leaching with H_2SO_4/KBr(5 mL)/ $CuSO_4$(1 mL), o-Hg extraction into toluene(5 mL, 3 times) and back-extraction into $Na_2S_2O_3$(5 mL)	BCR 463, sardine, anchovy, tuna fish	Spain	(92)	(Carbonell et al., 2009)
	BCR 463, TORT-2, *D. labrax*	Portugal	(97–105) (91–107)	(Válega et al., 2006)
	S. plana	Portugal		(Ahmad et al., 2012)
	S. canicula	Atlantic Ocean		(Coelho et al., 2010)
	TORT-2, *D.labrax*	Portugal	(75–91)	(Mieiro et al., 2011)
	TORT-2, *Liza aurata*	Portugal	(89.6 ± 4.58)	(Tavares et al., 2011)
Hydrolysis with HBr(10 mL), o-Hg extraction into toluene(20 mL) and back-extraction into cysteine (6 mL)	DORM-2, DOLT-3, SRM-2976, SRM-2977, *T. bernacchii, T. pennelli, G. acuticeps, C. hatus, C. mawsoni*	Antarctic	(84.3) (73.9) (92.8) (81.2)	(Maggi et al., 2009)
	DORM-2, DORM-3, TORT-2			(Scerbo and Barghigiani, 1998)
	DORM-2, *Lophius spp., Helicolenus dactylopterus, Aphanopus carbo, Lepidorhombus spp.*	Portugal	(94.63)	(Afonso et al., 2008)
	DORM-2, TORT-2, *Prionace glauca, Xiphias gladius*	Atlantic Ocean	(100) (93.42)	(Branco et al., 2004)
Hydrolysis with HBr(10 mL), o-Hg extraction into toluene(35 mL) and back-extraction into cysteine (6 mL)	DOLT-4, TORT-2, SRM 2974a, SRM 1566b, ERM CE464		(84.6 ± 33.6) (96.4 ± 21.0) (100.9 ± 29.0) (143.1 ± 71.4) (87.3 ± 15.2)	(European Commission Joint Research Centre Institute for Reference Materials and Measurements (EC-JRC-IRMM), 2013)
Tris–HCl buffer (with sequential additions of protease, NaOH, cysteine, $CuSO_4$, acidic NaBr) followed by extraction with toluene(0.5 mL) and $Na_2S_2O_3$(0.15 mL)	DOLT-3, TORT-2, NIST 1566 b		(98.6 ± 5.7) (97.9 ± 4.7) (97.2 ± 9.6)	(Nam and Basu, 2011)

BCR 463: tuna fish. DORM-2: dogfish muscle. DORM-3: dogfish liver. DOLT-3, DOLT-4: dogfish liver. ERM CE464: tuna fish. NIST 1566 b: oyster tissue. SRM-2974a, 2976, 2977: mussel tissue. SRM-1566b: oyster tissue. TORT-2: lobster hepatopancreas.

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