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Mercury in an Assortment of Processed and Unprocessed Seafood Samples

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The physical properties of mercury have given this toxic element and its compounds industrial utility throughout history. Current uses for mercury include the manufacture of vapor lamps, switches, medical devices, chlorine (through the chlor-alkali process), and the extraction of gold from ore. The coupling of this widespread industrial use with mercury emissions from the combustion of coal and other fuels has led to human exposure. The most prevalent mercury exposure pathway for the general population is the ingestion of contaminated food, particularly marine fish (Knowles et al. 2003; Kraepiel et al. 2003). Mercury exposure can be especially dangerous to developing neonatal and fetal central nervous system tissues (Rodier 1994).

Because of the environmental prevalence and toxicity of mercury and its compounds, regular monitoring of the food supply is required. A number of analytical tools are available for the determination of mercury in fish samples. The most frequently employed method is cold vapor atomic absorption spectrometry (CVAAS). This analytical technique has been applied successfully to determine mercury levels in a number of fish species and seafood matrices (Alonso et al. 2000; Burger et al. 2001; Sager 2004). Sample analysis by CVAAS can be expensive and time-consuming, however, because it requires sample digestion prior to analysis. An alternate analytical approach that eliminates the need for sample digestion is thermal decomposition and amalgamation, followed by atomic absorption spectrometry. The potential utility of this approach for the determination of mercury in various fish tissues has recently been demonstrated (Cizdziel et al. 2001; Cizdziel et al. 2003). The goals of this investigation were to determine the mercury content in an assortment of commercially available processed tuna products and unprocessed fish fillet and seafood products by thermal decomposition, amalgamation, and atomic absorption spectrometry, and to thoroughly assess the accuracy and precision of this analytical approach.

MATERIALS AND METHODS

The assortment of study samples included eleven commercially available, processed tuna samples purchased from several vendors in the greater Raleigh-Durham area of North Carolina. Six of these processed products were labeled to

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contain albacore tuna, three were labeled to contain chunk light tuna, and two were labeled to contain solid white tuna. These products were either packaged in cans (eight samples) or pouches (three samples), and the tuna was packed in oil (four samples) or water (seven samples). Five manufacturers produced all of the processed samples in the assortment.

Several commercially available fish fillets and unprocessed seafood samples were also purchased from vendors in the greater Raleigh-Durham area. This assortment of unprocessed samples included a total of thirteen products, which were labeled as catfish fillets (two samples), tilapia fillets (two samples), shrimp (two samples), bay scallops (one sample), swordfish (two samples), tuna (two samples), monkfish (one sample), and black bass (one sample). These products were purchased fresh and were stored frozen until analysis.

Several certified reference materials (CRMs) from the National Research Council of Canada were used throughout this investigation. Aliquots of lobster hepatopancreas tissue (TORT-2), dogfish muscle tissue (DORM-2), and dogfish liver tissue (DOLT-2) were analyzed with the study samples to assess method accuracy. Several study samples were fortified with the CRMs to assess the potential matrix impact on mercury recovery. In addition, the TORT-2 CRM was used to calibrate the mercury analyzer prior to sample analysis and to verify instrument performance during sample analysis as a continuing instrument calibration check. The certified mercury concentrations of the TORT-2, DORM-2, and DOLT-2 materials are 0.27 ± 0.06 mg/kg, 4.64 ± 0.26 mg/kg, and 2.14 ± 0.28 mg/kg, respectively.

Prior to analysis, wet masses were obtained for all of the samples in this investigation. The samples were then frozen and subjected to a 48-hour lyophilization procedure. Dry masses were recorded, and the moisture loss on drying was calculated for each sample and was used to express determined mercury concentrations in terms of wet weight. Prior to aliquoting, each lyophilized sample was ground using a homogenizer.

All mercury data were collected using a Milestone DMA-80 direct mercury analyzer. Because this instrument uses an oxygenated decomposition furnace to liberate mercury directly from solid samples, sample digestion is not required prior to analysis. A nominal 0.05-g aliquot of each sample was weighed directly into a nickel boat and placed in the instrument autosampler tray for analysis.

RESULTS AND DISCUSSION

Prior to analysis, the instrument was calibrated using aliquots of the TORT-2 CRM, and low-level and high-level mercury curves were constructed. The regression equation for the low-level mercury (0 – 40 ng Hg) curve was: absorbance = $0.03369(x) - 0.00025(x^2)$, while the regression equation for the high-level (40 – 600 ng Hg) mercury curve was: absorbance = $0.00176(x)$. Aliquots of TORT-2 were also used as calibration check standards, which

bracketed a maximum of ten study samples. In order for the analysis of bracketed study samples to be considered valid, the mercury concentrations for the TORT-2 calibration check samples were required to fall within the tolerance limit reported on the CRM certificate of analysis (0.27 ± 0.06 mg/kg).

Data from the analysis of processed tuna samples and information about product packing (water/oil) and packaging (pouch/can) are presented in Table 1. The determined mercury concentrations for the processed tuna products ranged from 0.0329 to 0.412 mg/kg. Significant variability in the measured mercury content was observed across all tuna packing and packaging methods, even for products from the same manufacturer. Products that were labeled to contain albacore tuna generally had higher mercury levels than products that were labeled to contain light tuna, although overlap in mercury content was observed.

Mercury concentration data from the assortment of fish fillets and unprocessed seafood products are presented in Table 2. The mercury content in these products ranged from 0.00351 to 1.85 mg/kg. The determined mercury concentrations for the catfish fillet, tilapia fillet, shrimp, and scallop samples were all relatively low (less than 0.0400 mg/kg) compared to the other unprocessed seafood products. The tuna and swordfish fillet samples had higher mercury content relative to the ther test samples, with concentrations ranging from 0.0833 to 0.575 mg/kg and 0.872 to 1.85 mg/kg for tuna and swordfish, respectively.

The World Health Organization (WHO) has recently lowered the Provisional Tolerable Weekly Intake (PTWI) of methylmercury to 1.6-μg/kg body weight per week (WHO 2003). Using this standard, the PTWI for a 63-kg person would be approximately 100 μg (0.1 mg) of methylmercury. Because mercury is present almost completely in the methylated form for many fish species (Storelli et al. 2002; Baeyens et al. 2003), it was assumed that the mercury detected in the study samples was present as methylmercury. Based on this assumption, a 63-kg person would meet or exceed his or her PTWI with one eight-ounce serving for four out of the twenty-four processed and unprocessed study samples (processed albacore tuna in pouch from Manufacturer 4, swordfish fillet sample from Vendor 1, swordfish fillet sample from Vendor 4, and yellowfin tuna fillet sample from Vendor 4). In addition, the 100-μg PTWI level would be surpassed with two eight-ounce servings for five of the remaining processed tuna samples. These data are consistent with recent advice on fish consumption issued jointly by the United States Environmental Protection Agency and the United States Food and Drug Administration (USEPA and USFDA 2004).

During this investigation, numerous quality control samples were analyzed to assess method performance. Multiple replicates were analyzed for each test sample and percent relative standard deviation (%RSD) data are presented with the mercury concentration data in Tables 1 and 2. The %RSD was less than or equal to 10% for all but two of the samples and was less than 5.0% for a majority of the test samples, indicating a high level of method precision.

Table 1. Mean mercury concentration data for processed tuna products, expressed as mg Hg/kg wet weight.

Product Description	Replicates	Mean mg Hg/kg wet wt.
Manufacturer 1 Albacore Tuna in Water Packing: Pouch	4	0.116 (%RSD = 2.4)
Manufacturer 1 Solid White Albacore Tuna in Water Packing: Can	4	0.179 (%RSD = 1.4)
Manufacturer 1 Chunk Light Tuna in Soybean Oil Packing: Can	4	0.237 (%RSD = 11)
Manufacturer 2 Solid White Albacore Tuna in Water Packing: Can	4	0.210 (%RSD = 2.2)
Manufacturer 2 Albacore Tuna in Water Packing: Pouch	4	0.337 (%RSD = 1.2)
Manufacturer 2 Solid Light Tuna in Olive Oil Packing: Can	4	0.0447 (%RSD = 10)
Manufacturer 2 Chunk Light Tuna in Vegetable Oil Packing: Can	4	0.0329 (%RSD = 4.4)
Manufacturer 3 Solid White Tuna in Water Packing: Can	4	0.228 (%RSD = 1.5)
Manufacturer 4 Solid White Albacore Tuna in Water Packing: Can	3	0.222 (%RSD = 0.62)
Manufacturer 4 Albacore Tuna in Water Packing: Pouch	4	0.412 (%RSD = 4.6)
Manufacturer 5 Chunk Light Tuna in Soybean Oil Packing: Can	4	0.382 (%RSD = 9.6)

In addition to the replicate sample analyses, fourteen empty nickel boats were analyzed along with the samples and were treated as blanks. The method quantitation limit (MQL) was defined as ten times the standard deviation of the total mercury level (in ng) measured in these blank runs. The average mercury level in the blanks was 0.0443 ng, and the MQL was 0.2 ng. This can be expressed as 0.001 mg/kg wet weight by assuming a nominal 0.05-g sample mass and a 75% mass loss on drying. All of the study and quality control samples analyzed during this investigation were above the MQL.

Table 2. Mean mercury concentration data for unprocessed fish fillets and seafood products, expressed as mg Hg/kg wet weight.

Product Description	Replicates	Mean mg Hg/kg wet wt.
Vendor 1 Catfish Fillet	2	0.0109 (%RSD = 12)
Vendor 2 Catfish Fillet	2	0.00840 (%RSD = 2.6)
Vendor 3 Tilapia Fillet	2	0.0383 (%RSD = 8.8)
Vendor 2 Tilapia Fillet	2	0.00886 (%RSD = 4.9)
Vendor 1 Shrimp	2	0.0114 (%RSD = 9.2)
Vendor 4 Tiger Shrimp	2	0.0287 (%RSD = 3.6)
Vendor 4 Bay Scallops	2	0.00351 (%RSD = 4.7)
Vendor 1 Swordfish Fillet	4	1.85 (%RSD = 1.3)
Vendor 4 Swordfish Fillet	4	0.872 (%RSD = 0.81)
Vendor 1 Tuna Fillet	2	0.0833 (%RSD = 5.8)
Vendor 4 Yellowfin Tuna Fillet	2	0.575 (%RSD = 0.61)
Vendor 4 Monk Fish	2	0.0831 (%RSD = 1.4)
Vendor 3 Black Bass	2	0.0641 (%RSD = 6.4)

To assess method accuracy, multiple CRM aliquots were analyzed along with the study samples. Fifteen TORT-2 aliquots were analyzed, and the average concentration of mercury was determined to be 0.268 mg/kg (%RSD = 3.0). This corresponds to a 99.3% recovery of the certified value (0.27 mg/kg). Five replicates DORM-2 material and three replicates of DOLT-2 material were also analyzed. The average determined mercury concentration of the DORM-2 samples was 4.22 mg/kg (%RSD = 1.6), while the average mercury concentration of the DOLT-2 samples was 2.05 mg/kg (%RSD = 3.0). These values correspond to 90.9% and 95.8% mercury recoveries in the DORM-2 (certified as 4.64 mg/kg) and DOLT-2 (certified as 2.14 mg/kg) samples, respectively.

To determine the recovery of mercury in the presence of sample matrix, four study samples were fortified with aliquots of TORT-2, DORM-2, or DOLT-2. The albacore tuna in water sample from Manufacturer-1 was spiked with TORT-2, the albacore tuna in water sample from Manufacturer-2 was spiked with DORM-2, and the catfish fillet sample from Vendor-1 and the yellowfin tuna

fillet sample from Vendor-4 were spiked with DOLT-2. The mercury recoveries in these matrices were 104%, 90.5%, 105%, and 109%, respectively, indicating that the matrix impact was not significant.

The objectives of this investigation were to determine the mercury content in an assortment of commercially available processed tuna samples and unprocessed fish fillet and seafood samples by applying a direct mercury analysis technique and to assess the performance of the applied methodology. High levels of method accuracy and precision were observed through the analysis of numerous blank, CRM, duplicate, and matrix spike samples. Sample digestion was not required, making the technique faster and less expensive than conventional mercury analysis methods. The collected sample data provide further evidence that the concentration of mercury must be closely monitored in both processed and unprocessed seafood products, particularly for species that tend to bioaccumulate mercury.

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REFERENCES

Alonso D, Pineda P, Olivero J, Gonzalez H, Campos N (2000) Mercury levels in muscle of two fish species and sediments from the Cartagena Bay and the Ciénaga Grande de Santa Marta, Columbia. Environ Pollut 109: 157-163

Baeyens W, Leermakers M, Papina T, Saprykin A, Brion N, Noyen J, De Gieter M, Elskens M, Goeyens L (2003) Bioconcentration and biomagnification of mercury and methylmercury in North Sea and Schedldt estuary fish. Arch Environ Contam Toxicol 45: 498-508

Burger J, Gaines KF, Boring CS, Stephens, Jr. WL, Snodgrass J, Gochfeld M (2001) Mercury and selenium in fish from the Savannah River: species, trophic level, and locational differences. Environ Res Sect A 87: 108-118

Cizdziel J, Hinners T, Cross C, and Pollard J (2003) Distribution of mercury in the tissues of five species of freshwater fish from Lake Mead, USA. J Environ Monit 5: 802-807

Cizdziel JV, Hinners TA, Heithmar EM (2002) Determination of total mercury in fish tissues using combustion atomic absorption spectrometry with gold amalgamation. Water Air Soil Pollut 135: 355-370

Knowles TG, Farrington D, Kestin SC (2003) Mercury in UK imported fish and shellfish and UK-farmed fish and their products. Food Add Contam 20: 813-818

Kraepiel AML, Keller K, Chin HB, Malcolm EG, Morel FMM (2003) Sources and variations of mercury in tuna. Environ Sci Technol 37: 5551-5558

Rodier PM (1994) Vulnerable periods and processes during central nervous system development. Environ Health Perspect 102(supplement 2): 121-124

Sager DR (2004) Mercury in tissue of selected estuarine fishes from minimally Impacted bays of coastal Texas. Bull Environ Contam Toxicol 72: 149-

156
Storelli MM, Giacominelli Stuffler R, Marcotrigiano GO (2002) Total and methylmercury residues in tuna-fish from the Mediterranean Sea. Food Add and Contam 19:715-720
USEPA and USFDA (2004) What you need to know about mercury in fish and shellfish. EPA-823-R-04-005, Washington, DC
WHO (2003) Joint FAO/WHO expert committee on food additives. Sixty-first meeting, Summary and Conclusions, JECFA/61/SC: 1-22, Rome, Jun 10-19