# Total Mercury–Monomethylmercury Content of Several Species of Fish

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The toxicity of mercury, especially of its vapor, has been known to man almost since the discovery of the element. In the past several years mercury has been found as a contaminant of marine and fresh-water fish. Recently epidemics of poisoning, termed Minamata disease, occurred in Minamata and Niigata, Japan. The causative agent in both incidents was shown to be fish contaminated with an alkylmercury compound, monomethylmercury. Since alkylmercury compounds are known to be several times more toxic than alkoxyalkyl, aryl, inorganic, or elemental mercury, it is important to know which form or forms of mercury is present in fish.

Recently various researchers have attempted to determine how much of the mercury present in fish is in the methyl form. Data from Sweden (1) have shown that the mercury present in the edible portion (fillet) of fish is essentially all methylmercury. Data from Japan (2) have indicated the proportion of methylmercury to total mercury in fish is about 50%. Some data from the United States (3) have shown 30-102% of the mercury in lake trout to be the monomethyl from. These latter findings are based on analysis of whole fish, whereas the Swedish and Japanese data concern only the edible portion of fish.

Because of this conflict, the monomethylmercury and total mercury content of the edible portion, generally fillet, of several species of fish has been determined. Included were white bass, perch, northern pike, tuna fish, and swordfish. Portions of each sample were analyzed for total mercury and monomethylmercury in different laboratories.

## Experimental

Four sets of fish samples obtained from several sources were used for the comparative analyses. Thirty-six samples were analyzed; they consisted of 20 swordfish, 11 tuna fish, two northern pike, two white bass, and one perch.



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Each of the 20 swordfish samples was prepared at the Baltimore laboratory of the Food and Drug Administration (FDA) in the following manner. Frozen swordfish steaks (bone and skin removed) were chopped in a 4-quart rotary Hobart food chopper and thoroughly mixed. One pint of sample was put through a small meat grinder four times, thoroughly mixed, and then divided into two parts. Total mercury was determined in FDA's Baltimore laboratory by the method of Munns and Holland (4). Methylmercury was determined in FDA's Washington, D. C., laboratory by the procedure of Westöö (5, 6,7,8) as described by Kamps and McMahon (9).

A total of 11 samples of canned tuna fish, either oil or water pack, from various sources were prepared in three different laboratories. Liquid in the oil pack tuna fish was included in the sample; liquid in the water pack tuna was discarded before sample preparation. Tuna fish samples 1-5 were prepared in FDA's New York laboratory. Samples were prepared by grinding in a Hobart food chopper and thoroughly mixing the ground material, and a portion of each prepared sample was provided to the two analyzing laboratories. Tuna fish samples 6 and 7 were prepared in FDA's Buffalo laboratory by grinding the entire sample in a Hobart food chopper and mixing. Samples 8-11 each consisted of one 7-ounce can of tuna fish and were prepared in a Washington, D. C., laboratory of FDA by passing the entire contents of the can through a small meat grinder four times and then thoroughly mixing the ground sample. Analyses for total mercury on all samples of tuna fish, done at FDA's Cincinnati laboratory, utilized the procedure of Munns and Holland (4). Methylmercury was determined in the Washington, D. C., laboratory by the method of Westöö as described by Kamps and McMahon (9).

Samples of two Swedish northern pike, kindly supplied by Dr. Gunnel Westöö, were analyzed without extensive sample preparation. Ten-gram portions of white muscle (fillet) were sliced from the frozen fish and immediately analyzed for methylmercury in FDA's Washington, D. C., laboratory. The samples had been analyzed in the Swedish laboratories by methods involving both gas chromatography (methylmercury) and neutron activation (total mercury).

Two samples of white bass and one sample of perch were analyzed for methylmercury by FDA's Washington, D. C., laboratory. The samples had been prepared for a check sample program by the Department of Interior's Bureau of Commercial Fisheries laboratory in Ann Arbor, Michigan. The white bass had been prepared by removing the viscera, head, tail, scales, and fins, followed by thorough grinding and mixing of the remainder of the fish. The perch had been prepared by filleting (skin removed), followed by thorough grinding and mixing.

The samples of bass and perch had been analyzed for total mercury by 16 laboratories using a variety of methods as a part of the check sample program. These methods utilized: (a) several digestion procedures followed by determination with cold vapor atomic absorption (e.g., (4)); (b) the official AOAC procedure with colorimetric determination (10), in some cases modified by using the digestion procedure described by Polley and Miller (11); and (c) neutron activation analysis. The Washington, D. C., laboratory of FDA performed analyses for methylmercury (9) on the same samples for comparative purposes.

## Results and Discussion

The results from the analysis of 36 samples of fish show that the mercury present is essentially all in the form of (mono) methylmercury. Mercury and methylmercury were determined in the edible portion of swordfish, tuna, northern pike, white bass, and perch. Results expressed as parts per million (ppm) mercury are given in Tables 1-4.

Table 1 presents results from the analysis of 20 samples of frozen swordfish steak for total and methylmercury. Total mercury ranged from 0.49 to 2.60 ppm. The proportion of methylmercury to total mercury in the samples ranged from 93 to 113% with an average value of 102%.

Results from the analysis of 11 samples of canned tuna fish are given in Table 2. The samples were prepared in three different laboratories; only 4 of the 11 samples were analyzed in the laboratory in which they were prepared. Total mercury ranged from 0.04 to 0.55 ppm. Results ranged from 0.04 to 0.58 ppm for methylmercury expressed as ppm mercury. The quantity of methylmercury in samples 1-7 ranged from 90 to 125% of the total mercury.

The results reported for samples 8-11 were determined at or below the limit of detection of the method and should not be considered quantitative.

Seven of the tuna fish samples (Table 2) were analyzed in duplicate. The maximum difference between duplicates for total mercury (0.38 to 0.43 ppm) occurred in sample 4; the maximum difference between duplicates for methylmercury (0.53 to 0.59 ppm) occurred in sample 7. The maximum difference between total mercury and methylmercury occurred in sample 4 where the methylmercury found was 125% of the total mercury.

TABLE 1

Total Mercury - Methylmercury Content of Frozen Swordfish Steak

| Mercury (ppm) | | Methyl, % |
|---|---|---|
| Methyl[a] | Total | of Total |
| 0.75 | 0.73 | 103 |
| 0.84 | 0.81 | 104 |
| 0.62 | 0.63 | 98 |
| 0.75 | 0.77 | 97 |
| 0.70 | 0.69 | 101 |
| 0.80 | 0.77 | 104 |
| 0.82 | 0.77 | 106 |
| 0.99 | 1.0 | 99 |
| 1.10 | 1.1 | 100 |
| 0.73 | 0.72 | 101 |
| 1.08 | 1.1 | 98 |
| 2.44[b] | 2.3 | 106 |
| 1.51 | 1.6 | 94 |
| 1.12 | 0.99 | 113 |
| 1.56 | 1.4 | 111 |
| 0.61 | 0.60 | 102 |
| 0.49 | 0.48 | 102 |
| 0.71 | 0.76 | 93 |
| 1.52 | 1.5 | 101 |
| 2.25 | 2.3 | 98 |

[a]Methylmercury chloride expressed as ppm of mercury.
[b]Average of 3 determinations (2.36, 2.37, and 2.60).

Duplicate analyses of tuna fish samples 1-7 for methylmercury involved the addition of mercuric chloride solution to one of the two portions (6,9). Similar results between duplicates show that the cysteine partitioning was providing adequate cleanup and also that the sample did not contain a significant amount of dimethylmercury. Duplicate results for methylmercury given in Table 2 are essentially the same, indicating that accurate determinations were being made with the usual procedure.

Table 3 presents the data from the analyses of samples of two Swedish northern pike. The results for methylmercury obtained in the Washington, D. C. laboratory are slightly higher than those obtained in Sweden on the same two fish; moisture lost when the sample thawed in transit from Sweden is the probable cause of this difference. Methylmercury found in the two fish by FDA was 113 and 107%, respectively, of the total mercury values determined in Sweden, and methylmercury determined in Sweden was 97 and 100%, respectively, of the total mercury.

TABLE 2

Total Mercury - Methylmercury Content of Canned Tuna Fish

| | Mercury (ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Methyl[a] | | | Total | | | Methyl, % |
| Sample | Orig. | Dupl.[b] | Av. | Orig. | Dupl. | Av. | of Total |
| 1 | 0.38 | 0.40 | 0.39 | 0.34 | 0.34 | 0.34 | 115 |
| 2 | 0.51 | 0.51 | 0.51 | 0.53 | 0.54 | 0.54 | 94 |
| 3 | 0.35 | 0.36 | 0.36 | 0.31 | 0.31 | 0.31 | 116 |
| 4 | 0.50 | 0.51 | 0.50 | 0.38 | 0.43 | 0.40 | 125 |
| 5 | 0.35 | 0.36 | 0.36 | 0.40 | 0.40 | 0.40 | 90 |
| 6 | 0.55 | 0.60 | 0.58 | 0.53 | 0.55 | 0.54 | 107 |
| 7 | 0.53[c] | 0.59 | 0.56 | 0.49 | 0.53 | 0.51 | 110 |
| 8 | 0.05[c] | --[d] | | 0.04 | -- | | 125 |
| 9 | 0.12 | -- | | 0.12 | -- | | 100 |
| 10 | 0.07[b] | -- | | 0.07 | -- | | 100 |
| 11 | 0.04[b] | -- | | 0.06 | -- | | 67 |

[a]Methylmercury chloride expressed as ppm mercury.
[b]$HgCl_2$ solution (9) added to check adequacy of cleanup and show absence of dimethylmercury.
[c]Results at or below the limit of detection of the method.
[d]No duplicate analysis.

TABLE 3

Total Mercury - Methylmercury Content of Northern Pike

| | Mercury (ppm) | | |
|---|---|---|---|
| | Methyl (GLC)[a] | | Total (NAA) |
| Sample | FDA | Sweden | Sweden |
| 1 | 2.19[b] | 1.88 | 1.94 |
| 2 | 1.20[c] | 1.10 | 1.10 |
| 2 | 1.17[c] | 1.10 | 1.10 |

[a]Methylmercury chloride, expressed as ppm mercury.
[b]Analyzed October 21, 1970.
[c]Reanalyzed October 23, 1970.

Table 4 presents the data obtained from the analyses of the two samples of white bass and one sample of perch prepared by the Bureau of Commercial Fisheries laboratory. Summaries of results for total mercury from 16 laboratories are listed according to the determinative step used in the various methods; the number of laboratories using each determinative step is given. Results for methylmercury were obtained only by the method using GLC (9) and only in one laboratory. Although levels of total mercury found by the 16 laboratories cover a wide range, the averages compare closely with the averages of duplicate results for methylmercury. The data show that the mercury present in these samples of white bass and perch is essentially methylmercury.

TABLE 4

Total Mercury - Methylmercury Results from Three Check Samples

| Determinative Method | Mercury (ppm) White Bass No. 1 Av. | White Bass No. 1 Range | White Bass No. 2 Av. | White Bass No. 2 Range | Perch Av. | Perch Range |
|---|---|---|---|---|---|---|
| AA[a] | 0.61 | 0.42-0.74 | 0.65 | 0.53-0.83 | 0.25 | 0.12-0.38 |
| Colorimetry[b] | 0.57 | 0.33-0.72 | 0.68 | 0.51-0.80 | 0.22 | 0.12-0.30 |
| NAA[c] | 0.64 | 0.62-0.67 | 0.69 | 0.67-0.69 | 0.23 | 0.21-0.26 |
| GLC[d] | 0.64 | 0.65-0.64[e] | 0.65 | 0.67-0.63[e] | 0.30 | 0.30-0.29[e] |

[a]Atomic absorption; 10 laboratories.
[b]Four laboratories.
[c]Neutron activation analysis; 2 laboratories.
[d]Results are given as methylmercury chloride expressed as ppm mercury; 1 laboratory.
[e]Duplicate analyses on different days.

These data presented on five fish species indicate that mercury present in edible portions of fish is methylmercury. With the exception of the two samples of white bass, only fillet (no skin or bone) was included in the samples. Bache et al. (3) reported that in whole lake trout (viscera and scales included) the proportion of methylmercury to total mercury in 27 samples ranged from 30.8 to 101.9%. It is possible that a fish recently exposed to heavy inorganic mercury contamination would contain significantly less methylmercury than total mercury in the edible portion.

In any comparative study, preparation of the samples to be analyzed is of prime importance. Accurate results are dependent upon the homogeneity of the material being analyzed. Westöö (8) has shown that the mercury residue present in the white muscle (fillet) of northern pike is homogeneous. With other fish species, particularly fish of high fat content, homogeneous distribution of the mercury residue cannot be assumed. Close attention to preparation (grinding, mixing, etc.) is a necessity if comparative results are to be meaningful.

The special attention given to preparation of the swordfish samples in this study is reflected in the excellent agreement between the totalmercury-methylmercury findings. The data in Table 1 show that 15 of 20 comparative results (mercury versus total mercury) varied less than 5% from one another, and that the maximum difference was 13%.

Size of the sample analyzed may also affect sample preparation requirements. Analysis for total mercury used a 5-g sample and analysis for methylmercury used a 10-g sample. Methods which use a significantly smaller sample (1.0 - 0.2 g or less) make sample homogeneity an absolute necessity.

## Summary

Data are presented which show the total mercury versus monomethylmercury content in the edible portion of five species of fish. Mercury content ranged from 0.04 to 2.60 ppm. The proportion of methylmercury to total mercury ranged from 67 to 125%.

Comparative data from the 36 samples analyzed show that mercury in the edible portion of these swordfish, tuna fish, northern pike, white bass, and perch is essentially all monomethylmercury.

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