Estimation of Mercury in various Local Fish Species and Relevant Waters

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Summary: Employing the flameless atomic absorption technique a method of general utility is proposed for the estimation of mercury content in fish. The method is based on the reduction of organic/inorganic mercury to elemental mercury using tin(II) chloride as the reductant. Marine and fresh water whole fish samples (wet weight 2-3 kg) of the following common species: Salmon, mallie, mashir, bangha and pomphlet are analysed. The estimated mercury content of these fish is examined in relation to that of the relevant water. A linear regression analysis of the data indicates the potential use of fish as an indicator of a local mercury pollution source.

Introduction

The possible presence of mercury in human food is one of the most serious aspects of the overall problem of pollution by mercury. It has been shown that most foods, with the exception of fish, contain low levels of mercury, not exceeding 0.050 ppm on dry weight basis. A great deal of data are available on the mercury content of fish in both the marine and fresh water environments [3,4,5,6]. Mercury is considered to be non-essential element for living organisms, and has been studied extensively for its distribution in fish [7,8,9,10]. It is well known that there is a distinct increase in the concentration of mercury in marine environment as a function of time. Much of the mercury is spread from the air through smoke and fumes from factories and by paper-burning/ garbage-disposal plants installed in advanced countries. It is also added to the water through direct discharge and through agricultural drainage of mercury compounds used as seed disinfectants.

The greatest increase in mercury concentration (by about a factor of 100-1000) takes place between water and fish. A further concentration increase (by another factor of 10 or more) occurs between fish and fish-eating animals and brids [11]. Fish apparently can accumulate mercury more than other aqutic organisms, both directly from water (sea and fresh) and indirectly through the food chain [12]. Fish thus pose a potential mercury pollution threat to man.

The study of fish muscle tissues is one of the means for investigating the amount of mercury entering the human

body by food chain enrichment, and has, therefore, been investigated more than other organs. The muscle becomes enriched by the metal when the concentration becomes high [13]. This fact suggests the use of fish as indicator organisms for the study of mercury pollution [14].

In addition, the distribution of mercury in body organs can be studied through this approach. The problems related to the affinity of the metal for the organs can then be solved by investigating uptake kinetics and regulating mechanism involved. An attempt has been made in the present investigation to initiate a base-line study related to the above cited objectives. Mercury levels in fresh water and sea-water fish are estimated to ascertain whether mercury content is species specific and/or water source specific. Based on tin(II) chloride reduction method, estimation of mercury concentrations in fish and the relevant sea and fresh waters are made by the flameless atomic absorption method under optimum conditions. Various fish species studied include pomphlet silver (pampus argenteus) and black (parastromateus), mallie (wallago attu), mashair (torputitora), bangun bengal (labeo boggut) and punjab (micropthalmus). The sampling was done at upper reaches of the rivers Jhelum and Indus, hilly streems of northern areas, and the Arabian sea shore. The data obtained are analysed statistically to investigate into a possibility of the above cited correlation and the potential use of fish as a probable pollution indicator.

Experimental

All the reagents used were of Merck GR origin of extra high purity (min. 99.9%). Deionized water was used throughout this work. The mercury stock solution at a concentration of 200.0 mg/1 was prepared bydissolving appropriate amount of mercuric chloride in 0.5 M sulphuric acid. Known aliquots of this standard were diluted with 0.5 M sulphuric acid to prepare working standards with concentrations ranging between 0.050 mg/1 - 0.250 mg/1 mercury. A 6% (W/V) solution of $KMnO_4$ was prepared in deionized water. A 20% (W/V) solution of $NH_2OH.HCl$ was made in water. The stannous chloride reduction solution (10% W/v) was prepared in 0.5 M HCl and stored over tin in a glass bottle. The calibration solutions were prepared fresh before each measurement.

The sample solution was prepared as follows. Placed a known amount (approximately 1 g) of the homogenized whole fish muscle sample in a tared reduction flask. Reweighed the flask to obtain the exact weight of the sample. Added 5 cm^3 of sulphuric acid (Sp.gr. 1.8) to the sample flask and placed the flask in a preregulated water bath at 65°C. When the sample digestion was complete (as indicated by the development of a coloured homogenous solution) placed the flask in an ice bath to cool down to room temperature. Added 50 cm^3 of 6% (W/V) potassium permanganate solution, removed the flask from ice bath and placed it in water bath at 65°C for two hours. Removed the flask from water bath and allowed it to cool to room temperature. Then 15.0 cm^3 of the $NH_2OH.HCl$ solution was added to the sample solution to reduce excess of $KMnO_4$. Reagent blanks were checked by treating them as the sample. Introduced 2.0 cm^3 of the stannous chloride solution in the flask containing the standard or sample and inserted the ground-glass joint to the

Table-1: Estimated Mercury Concentrations in Various Fish* and Waters

lo.	Fish Sample Code	Location/ No. of Samples	Sample Description	Estimated average Hg Concentration** Fish (mg/kg ± 2S)	Water (µg/1 ± 2S)
	F1/SW	Arabian Sea/3	Salmon	0.150 ± 0.005	0.012 ± 0.001
	F2/SW	Arabian Sea/3	Pomphlet	0.154 ± 0.005	0.012 ± 0.001
	F3/FW	River Jhelum/3	Mallie (Wallagoattu)	0.198 ± 0.006	0.040 ± 0.002
	F3/FW	River Indus/2	Mallie (Wallagoattu)	0.238 ± 0.004	0.049 ± 0.002
	F4/FW	Rawal Canal/2	Mashir (Torputitora)	0.199 ± 0.005	0.038 ± 0.003
	F5/FW	Margala spring/3	Bangha (labeo Bogutt)	0.184 + 0.006	0.041 ± 0.003
	F6/FW-L1	Rawal Lake, down-stream/2	Pomphlet silver (pampus argenteus)	0.240 ± 0.004	0.029 ± 0.002
	F7/Fw-L2	Rawal Lake, up-stream/1	Pomphlet silver (pampus argenteus)	0.056 ± 0.003	0.021 ± 0.002

W = Sea water; FW = Fresh water; L1, L2 = Lake waters; ** = based on five parallel runs for all samples. * = on wet weight basis.

flask. The contents were shaken gently for 15-20 seconds and the mercury produced was expelled into the absorption cell by air. The absorptions were recorded onto an X-Y recorder. The amount of mercury present in various samples was quantified after adjustment of the blank absorbance from the sample absorbance. A Hitachi atomic absorption spectrophotometer was used in this investigation at optimum conditions for the estimation of mercury. FAO reference standards were used throughout the work for intercalibration and exact quantification. The observed agreement was within ± 2.0%. The method for the estimation of mercury in water based on flameless absorption has been described previously [15]. Recovery experiments were also conducted with most samples through standard additions of mercury in duplicate runs.

Results and Discussion

Table 1 summarizes the estimated mercury contents in values fish and the relevant waters. The various appearing in the Table have been averaged for five parallel measurements on each sample pertaining to individual fish species or water samples. The recovery experiments suggest that about 98% mercury is removed from the solution matrix by a single step reduction. An examination of the data in Table 1 shows that the percent spread in the estimated values with respect to the average lies between 1.7% - 5.3%; it being smaller for high mercury content and bigger for low mercury content.

It may be observed that maximum mercury content is found in case of sample F7, while minimum concentration is found in samples F8. The mercury contents of other fish lie within this extremum limit. It is observed that mercury is present in local fish in varying levels subject to the location and/or species involved. The nature of water also plays an important role. it is known that in the marine environment the heavy metal content in fish is usually low [16]. The present study supports this view. The concentration of mercury in sea fish is found to be lowr than that found in other water sources under study. The pomphlet silver fish samples F7 and F8, belonging to the Rawal Lake, have shown substantial difference in their mercury content. The downstream (distribution reservoir) fish is richer in mercury, perhaps as a result of longer stay time of water in the lake. On the other hand, the upstream (main storage reservoir) fish (F8) has a relatively lower mercury content since it stays all the while in fresh incoming water.

The mercury cotent in rivers is knwon to be high as compared with lakes and canals [17,18,19]. Same is found to be almost true for the mercury content of fish in these waters; the only exception being sample F7. However, a direct comparison of this sort is, in fact, oversimplification of the actual situation. The weight of the fish plays an important role for its capacity for mercury uptake. An attempt was made during the present investigation to collect fresh water fish samples ranging in body weight between 2-3 kg as this size is very popular among fish eaters. This was done to check whether a correlation exists between the mercury content and the age/weight of the fish.

A linear regression analysis of the data indicates that the mercury content in water has a bearing on that of the relevant fish. The correlation coefficient computed on this basis comes out to be + 0.60. While the

mathematical analysis of the experimental figures warrants this sort of relationship, the matrix of the problem is undoubtedly more complex. The mercury distribution in a given fish is a multivariable problem as it is in water. Surface and subsurface waters, sediments and underground rock formations all contribute to mercury accumulation. The greatest increase in mercury concentration takes place between water and fish. Hence, there is, in general, no direct proportionality between the concentration of mercury in a given mass of water and fish, but this may serve as a general index for a possible mercury pollution of a given source of water inhabitating fish of various kinds. For arriving at an exact correlation of this type, temporal studies incorporating weight /size and age of the fish are, therefore, perequisite.

Despite the great number of variables affecting the merucry content in fish, the present data show that marine and fresh water fish are to a certain extent suitable as indicators of mercury levels in these water sources. Thus, any probable local sources of pollution may be detected by comparing the metal level to the background level, although the background may differ from species to species and from region to region. Hence, any fish is suitable for this purpose [20,21].

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