Chapter 4

Heavy Metal Residues in Fish and Fishery Products

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Heavy metals are toxic metals and above a normal level can affect the quality, safety and marketability of seafood. They have atomic weight higher than 40.04U and specific density > 5g/cm^3. Heavy metal contamination in fish and other aquatic organisms are highly depending upon geographic location, species and fish size, feeding pattern, solubility of chemical and their persistence in the environment. The major toxic heavy metals causing significant importance in seafood safety are Arsenic (As), Cadmium (Cd), Mercury (Hg) and Lead (Pb).

Compared to fish lead content is higher in shellfish as it is getting accumulated in hepatopancreas. The organic form of lead, tetra alkyl lead is mostly found in fish. In fishes Cd is mostly deposited in kidney and liver. In invertebrates like Cephalopods, it can go as high as 30 ppm in digestive glands. Hence the digestive gland must be removed immediately after catch. Both Cd and Pb are carcinogenic in nature. Mercury is one of the most toxic heavy metals in the environment. Among metal contaminants methyl mercury has elicited the most concern among consumers, affecting the nervous system. Arsenic is a widely distributed metalloid and a major contaminant in case of ground water. International Agency for Research on Cancer (IARC) has classified inorganic arsenic as a human carcinogen.

Being inhabitants of the aquatic ecosystem, fish and other aquatic species (molluscs, crustaceans, etc) carry the natural burden of heavy metal concentration. Heavy metals in fish and other aquatic organisms come from both natural and anthropogenic sources. The presence of toxic heavy metals such as lead, cadmium, mercury, arsenic, nickel, and chromium is of significant importance in seafood safety. Due to coastal pollution, in some areas of the Indian coast the enrichment factor for metals is very high (>100). In the aquatic environment, cadmium is also extensively distributed and bioaccumulation of cadmium by aquatic organisms is a well-recognized fact. The cephalopods (Squid, Cuttlefish, and Octopus) naturally bio-accumulate cadmium to toxic levels.

Similarly, predatory finfishes like Tuna, Marlin, Swordfish, and Barracuda, which contribute significantly to India’s fish production are associated with high mercury levels. Mercury is present in fish primarily in its organic form as methyl mercury and accumulates with age.

Methylmercury accumulates rapidly but depurates very slowly. Because of this reason most mercury in fish muscle is present as methylmercury.

Although more than 90% of the mercury in fish is found as methylmercury, the contents of methylmercury can vary considerably between species. Predatory species that are at the top of the food chain and have long life span accumulate higher levels of methylmercury. Methyl mercury is known to cross the blood-brain barrier and placenta and cause irreversible prenatal and post-natal damage in the ingested population. Tuna and swordfish are found to be the main source of high methyl mercury (MeHg) exposure, followed by cod, haddock, and octopus.

Although Codex prescribes a limit for methyl mercury, many country regulations are based on total mercury content. Estimation of methyl mercury requires the use of cost-prohibitive hyphenated equipments like HPLC-ICP-MS or IC-ICP-MS. Similarly, high Arsenic content is reported in seafood, but major chemical forms are organic (arsenobetaine and arsenosugars), which are non-toxic.

Determination of heavy metals in seafood

Principle: Plasma is a stream of highly ionized gas containing an equal number of electrons and positive ions. Plasma is electrically conductive. It is affected by a magnetic field. When plasma energy is given to an analysis sample from outside, the component elements (atoms) are excited. When the excited atoms return to a low energy position, emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays and the content of each element is determined based on the intensity of the rays.

To generate plasma, first argon gas is supplied to the torch coil, and high-frequency electric current is supplied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high-frequency current, argon gas is ionized and plasma is generated. This plasma has high electron density and temperature (10000K) and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the center of the torch tube. The steps leading to the emission are desolvation, vaporization, atomization, and ionization.

Sample digestion

The sample should be homogenous, representative of bulk, free of suspended particles, and free-flowing. Samples are digested in a microwave digestion unit. Take 0.25 to 0.5 g of the sample to the pre-cleaned digestion vessel. Add 8 ml nitric acid and slowly add 2 ml H_2O_2 to it. Keep it for 10 minutes. Close the vessel and keep it in a microwave digestion chamber for digestion. After digestion the samples are made up to 100 ml. digested sample is introduced to Inductively Coupled Plasma - optical emission spectrometry (ICP-OES) for analysis.