Fishmeal Freshness Assessment - An Overview Of Analytical Methods Available.

By Jean-Francois Herve - American Seafoods Company.

Defining and therefore measuring fishmeal freshness can be challenging. Yet, the freshness of pet food ingredients can affect the palatability, nutrition and safety of the resulting product. Flavors caused by chemical or microbiological deterioration of the ingredients can result in food refusal, since animals rely on their sense of smell and taste to differentiate safe, nutritious foods from those that taste bad or may contain toxic substances.

Assessing timely the quality of a fishmeal is critical to deliver a safe, nutritious product cats and dogs will enjoy.

At American Seafoods, we take freshness very seriously. And we understand the consequences of marine ingredient quality on the product consumed, on pets and on their parents..

The initial quality of raw materials, considering their freshness, microbiological load, and physical damage, is an important factor, which influences the quality of the end product. Fuselli et al. (1994) and Cascado et al. (2005). Including measures of spoilage specific to raw materials brings another dimension to the freshness definition. Ours includes the following criteria:

- Quantification of chemical compounds reflective of raw materials spoilage pre-production of the fishmeal.
- Fishmeal Lipid and protein oxidation speed over time. Oxidation usually happens postproduction of the ingredient during storage. This area will not be covered in this paper.
- Sensory assessment and description of “freshness” by pet parents, although they may not have clear words to express precisely what they consider fresh
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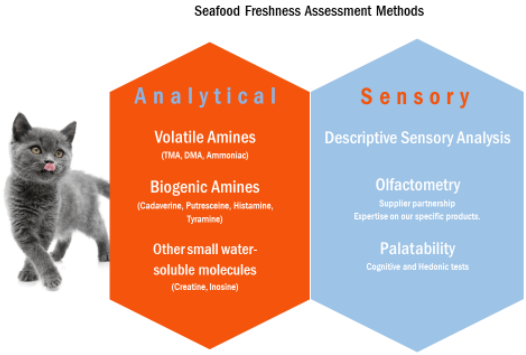

- vs. not so fresh. Yet, a consistently fresh product will heavily contribute to their brand loyalty.

- Preference assessment by cats and dogs themselves.

Not all these layers provide the same answer, even if they all need to be well understood and controlled. A food processor will expect to know as soon as possible and at the lowest possible cost if an ingredient can be processed and what is the quality of the resulting diet. Therefore, the objective of this article is to review the methods available that can help measuring freshness proactively, and to clarify what are their limits.

The traditional sensory method (Alur and others 1991; Perez-Villarreal and Howgate1987; Cox and Lovell 1973) is probably the easiest way to judge seafood quality and can be used with either cooked or raw products. However, it needs specially trained personnel and the subjective judgements of odor, degree of melanosis, or the color of the body causes more disagreements of the results than objective evaluations. So what are the rapid methods available to determine how fresh fishmeal is?

1 - Volatile amines as an indicator of freshness in fishmeal.

Processing of seafood generates a large amount of by-products (skin, bones, liver, head, offals etc.) used for the production of fishmeal. Because of the presence of bacteria on the surface of fish skin and intestine, the spoilage of by-products is a very fast process resulting in the degradation of biomolecules

If you have ever caught fresh fish, you know that it does not have a particularly strong odor. However, after a few hours, a “fishy” smell can be identified. What causes that smell has to do with some interesting physiology unique to sea creatures. Water in the open ocean is about 3% salt by weight, but the optimal levels of dissolved minerals inside an animal cell is less than 1%. In order to maintain fluid balance, ocean creatures must fill their cells with amino acids and amines to counter the saltiness of seawater. Ocean fish tend to rely on trimethylamine oxide (TMAO) for this purpose.

The problem is that when fish is killed, bacteria and fish enzymes convert TMAO into trimethylamine (TMA),

which gives off the characteristic “fishy” odor. TMA is a small water-soluble molecule classified as volatile amine and is part of a larger group constituted of mostly three molecules, ammonia,dimethylamine (DMA) and trimethylamine (TMA). DMA and TMA result of the degradation oftrimethylamine oxide (TMAO)

Volatile amines are the characteristic molecules responsible for the fishy odor and flavor present in fish several days after the catch and together with the sensory parameters, they are the most common criteria for assessing the fish. The significance and the use of these criteria have been underlined by numerous authors and synthesis about the suitability of\volatile amines as freshness/spoilage of seafood have been published by Oehlenschläger (1997 a, b) and in FAO Fisheries Technical Paper 348 (Huss, 1995).

Ammonia-N is, a small and extremely volatile compound is a poor indicator of fish freshness and cannot considered as an effective marker of fish spoilage. It is the ultimate level of protein degradation. For that reason, It will not provide any information on early stage of spoilage.

DMA-N can be considered as an effective marker of fish freshness however, its use is limited to those fish species which contain the enzyme TMAO-ase such as Alaska Pollock, Pacific whiting and Cod, and it can be used to monitor the quality of frozen-stored gadoid fish.

TMA-N is an excellent indicator for the spoilage of gadoid fish; it is useful, as a rapid means of objectively measuring the eating quality of many demersal fish especially on the medium-later phases of spoilage but it cannot be used as a freshness indicator (constant level during the first days of iced storage).

Total Volatile Amines (TVN) is one of the most commonly used criteria for assessing fish freshness and quality. However, the values are specie-dependent and methods and laboratory provide very variable results (AOAC vs. Conway), making the use of a standard value impossible across different producers and species. Moreover, TVN detects only late phases of alteration.

2 - Biogenic amines as an indicator of fishmeal freshness

Biogenic amines are low-molecular-mass substances, essential for proper health for all organisms. These compounds could be detrimental to human health with various toxicological effects when they are present in high concentrations. Therefore, biogenic amines monitoring in food samples is a matter of utmost importance, and their accurate determination is considered indispensable. Tyramine, cadaverine, putrescine and histamine are the most common BAs in meat and meat products. As for the BAs level regulations, histamine is currently the only BAs having official limits in fish products, despite the fact that BAs have been described as having a certain potential toxicity in food products in general.

The maximum acceptable histamine levels in fish have been established in the USA by the Food and Drug Administration at a maximum limit of 50 mg kg−1at the port.

As a supplier of fish products to the pet food industry, American Seafoods is responsible for . providing the best quality possible. We recently launched a freshness standard encompassing several of the rapid methods described above:

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ULBA™ ULTRA LOW BIOGENIC AMINES

ULBA™ fishmeal Freshness Standard includes but

Does not restrict to the following quality parameters:

TVB-N < 60 MG N/100 G	Measured by HPLC.
TMA < LIMIT OF DETECTION	Colorimetric sensor array
H + P + C + T* < 100 PPM	HPLC SPME-GC Method

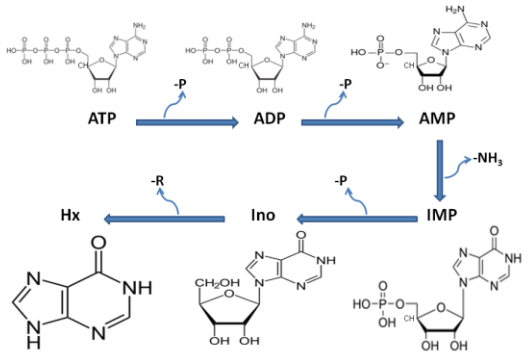
* Histamine, Putrescine, Cadaverine and Tyramine

Classical reversed-phase high-performance liquid chromatography (RP-HPLC) has been employed for the BAs quantitative determination in different types of food because of its sensitivity, high resolution, great versatility and relatively simple sample treatment.

3 - Determination of Fish Freshness by Electrochemical Impedance Spectroscopy (K Value).

Inosine monophosphate (IMP) is one of the molecules responsible for Umami taste (taste of amino acid L-glutamate + 5'-ribonucleotides). Highest levels of IMP are present in the early post-mortem ATP degradation pathway in fish and meat tissue (freshness pathway). The result of the IMP degradation is an increased content of hypoxanthine (Hx). Therefore, it makes sense-tracking IMP/Hx ratio in order to have an early detection of spoilage in seafood and fishmeals.

Biochemical structure of freshness pathway characterized by ATP depletion following the arrest of cellular respiration post-mortem in muscle tissue.



The method based on the K value (Karube et al. 1984; Saito et al. 1959) measures the autolytic process that takes place immediately after the fish's death.

It is the ratio (HxR + Hx)/(ATP + ADP + AMP + IMP + HxR + Hx), where HxR is inosine, Hx is hypoxanthine, IMP is inosine 5'-monophosphate, AMP is adenosine 5'-phosphate, and ADP is adenosine diphosphate. It has been shown that K values increases with spoilage. A higher % Hx indicates muscle aging and has been correlated with bacterial (Battle et al., 2001; Tsai, Cassesn, Briskey, and Greaser, 1972; Yano et al., 1995; A.S. Hernandez-Casares et al. 2010) spoilage in fish muscle.

K value is considered the gold standard in the service of scientific research in terms of reliability and accuracy and is adopted by the Japanese seafood industry.

4 – Bacteriological assessment.

This method uses the relationship between the increase in microbial number and the decrease in sensory quality to indicate the degree of spoilage (Ward and Hackney 1991; Liston 1980; Matches 1982; Nickelson and Vanderzant 1976). The unique advantage of this method is its ability to identify specific microorganisms that cause the unacceptable flavor and odor (Cox and Lovell 1973) but negative results may be produced if the microorganisms are destroyed during thermal treatment, which is the case of fishmeals.

5 - Molecular weight Analysis.

Characterization of fishmeal through NIR (comparative profile between extremely fresh fishmeal produced with fresh raw materials and fishmeal produced with low quality raw materials/ spoiled raw materials). The profile will analysis can provide useful information.

Disadvantage: method is supplier or source and specie specific, but can be one of the most effective method to rapidly assess the freshness of a specific fishmeal and determined supplier.

6 - E-Nose and Near Infrared to assess freshness.

E-Nose is a device allowing relatively rapidly the identification and quantification of different classes of compounds, representing microbial metabolites that are characteristic for the onset of spoilage odors.

Research shows that both e-nose and VIS/NIR spectroscopy can be used to generate an estimate of fish quality. By being able to model both time and specific indicators, these two technologies show the robust nature that is normally seen in sensory panels. While maintaining these advantages, both technologies yield a repeatable and nondestructive testing method that has not been available in the past. These methods are also complicated, time-consuming, and laboratory-based.

We are confident the definition will evolve soon due to consumers' awareness, incorporating sensory science and oxidation management. One-step at a time.