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Chemical Quality Indices for Freshness Evaluation of Fish

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Abstract

The compounds formed in fish spoilage process have been frequently used to assess the quality of different species. Quality indices based mainly on the concentration of the products of nucleotide degradation and biogenic amine content have been proposed. However, these indicators must be calculated considering intrinsic and extrinsic factors that may affect both, biogenic amine formation and nucleotide degradation rate and pattern. In relation to the analytical methods, regardless the methodology chosen, the extraction stage is critical. High performance liquid chromatography is the technique indicated for both, biogenic amine analysis and determination of nucleotide degradation products.

Keywords: Analytical methods, Biogenic amines, HPLC, Quality index, Nucleotide degradation products

1. Introduction

After fish death, there is a gradual loss of freshness due to a series of *post mortem* enzymatic and bacterial reactions that determine the emergence of undesired odors and flavors due to the formation of organic compounds and the development of microorganisms that can be hazardous for the consumer (Mukundan et al., 1986; Gram and Dalgaard, 2002; Andrade et al., 2012; Cardozo et al., 2013; Rodrigues et al., 2013).

The Brazilian law, through Decree no 30.691 (Brazil, 1952) and Ordinance no 185 (Brazil, 1997), establishes limits for fish freshness evaluation based on total volatile base content, tertiary volatile base content, internal and external flesh pH, hydrogen sulfide and histamine content for species of the *Scombridae*, *Scombresocidae*, *Clupeidae*, *Coryphaenidae* and *Pomatomidae* families. However, it does not take into account other metabolites formed during a fish spoilage process that have been used for some time as quality indices, such as adenosine triphosphate degradation products and the presence of other biogenic amines (Carmo et al., 2010; Monteiro et al., 2010; Silva et al., 2011, Andrade et al., 2012; Rodrigues et al., 2013).

Assessing fish preservation based on official procedures has been considered a controversial issue because of the variety of species with individual peculiarities due to physiological aspects and capture methods.

Therefore, the objective of the present review is to conduct a study on quality index data, in order to support future analytical studies that contribute to effectively assess fish preservation, considering the physiological peculiarities of each species based on the concentration of biogenic amines and adenosine triphosphate degradation products highlighting the main analytical methods for the determination of those parameters.

2. Biogenic amines

Biogenic amines are organic compounds with basic character and low molecular weight formed by decarboxylation reactions of precursor amino acids or by amination and deamination of aldehydes and ketones and synthesized in the metabolism of plants, animals and microorganisms (Brink et al., 1990; Bardócz, 1995; Sillas Santos, 1996; Rodriguez et al., 2014).

Although considered endogenous in some foods, and present in low concentrations, they are usually formed as a result of bacterial action associated with the availability of free amino acids, conditions that favor bacterial growth and enzyme production (Sillas Santos, 1996; Silva et al., 2011; Cardozo et al., 2013). The amount and type of biogenic amine formed depend on food composition and the type of microorganism present in the matrix (Brink et al., 1990).

Numerous bacterial genera present in food such as *Bacillus*, *Citrobacter*, *Clostridium*, *Klebsiella*, *Escherichia*, *Proteus*, *Pseudomonas*, *Salmonella*, *Shigella*, *Photobacterium*, *Lactobacillus*, *Pediococcus* and *Streptococcus* have amino acid decarboxylase capability. These microorganisms can be naturally present in food, intentionally added or introduced by

contamination, as occurs by inadequate handling before, during or after food processing. The species *Morganella morganii*, certain *Klebsiella pneumoniae* strains and some of *Hafnia alvei* are prolific histamine producers, with particular importance in fish (Brink et al., 1990; Sillas Santos, 1996; Carmo et al., 2010; Lee et al., 2012).

Fish is highly susceptible to biogenic amine formation, especially histamine, putrescine, cadaverine and tyramine (Veciana-Nógues et al., 1997; Bunka et al., 2012; Hu et al., 2012). In general, high levels of biogenic amines found in seafood are caused by inadequate preservation with consequent microbial decarboxylation of amino acids (Hu et al., 2012). In addition, some species, particularly those belonging to the *Scombridae* family, such as tuna fish and bonito and those of the *Clupeidae* family, such as sardines, present high levels of free histamine in the muscle (Lehane and Olley, 2000; Oliveira et al., 2004; Kim et al., 2009; Lee et al., 2012). Histamine can be catabolized through two routes in fish muscle: by amino acid deamination forming urocanic acid, which is the main route in normal physiological conditions or by decarboxylation forming histamine, which is an important route in cases of bacterial contamination (Sillas Santos, 1996; Lehane and Olley, 2000).

The content of biogenic amines in fish can vary according to the season of the year, genetics, environment, food, sex, physiological stage, storage period and sampled tissue (Veciana-Nógues et al., 1997; Lee et al., 2012), and formation is directly influenced by the storage temperature (Silveira et al., 2001; Carmo et al., 2010).

The presence of biogenic amines in food, besides being a health problem due to its physiological and toxic effects (Önal, 2007), can be used as quality index, once they are formed by bacterial activity and are resistant to thermal treatment, thus reflecting the quality of the raw material and the hygienic conditions of food processing (Veciana-Nógues et al., 1997; Park et al., 2010; Sagratini et al., 2012).

2.1 Biogenic amine index

Biogenic amines are naturally present in very low levels in fresh fish and the presence of high amounts of these compounds is associated to bacterial degradation (Özogul and Özogul, 2006; Šimat and Dalgaard, 2011; Cunha et al., 2013). Assessing biogenic amine presence is important not only from a toxicological point of view, but because these substances can be used as indicators of food degree of freshness or spoilage (Alberto et al., 2002; Özogul and Özogul, 2006; Önal, 2007; Park et al., 2010; Sagratini et al., 2012; Silva et al., 2013).

Mietz and Karmas (1977), studying canned tuna to estimate the degree of freshness of the fish prior to processing, observed that on the spoiled samples, the putrescine, cadaverine and histamine content increased, while spermine and spermidine decreased compared to good quality food samples. Therefore, they suggested a Chemical Quality Index (QI) based on the concentration of the following biogenic amines:

$$Quality\ Index\ (QI) = \frac{histamine + putrescine + cadaverine}{spermine + spermidine}$$

The authors observed that the quality index increased when the sensory scoring of the canned product decreased. Thus, they suggested that a product with QI below 1 would have been processed with a first quality raw material, while those with values above 10, would indicate a raw material with very poor microbiological quality.

Veciana-Nóguez et al. (1997) assessing tuna stored at 0, 8 and 20ºC for 21, 9 and 4 days respectively, concluded that spermidine and spermine contents are not indicators of quality loss and that significant alterations in histamine, putrescine, cadaverine and tyramine concentrations during the studied period at the three storage temperatures were important to assess the spoilage process. In addition, they observed that sensory rejection of samples kept at 8ºC occurred on the 5th storage day, although the QI value of 10 proposed by Mietz and Karmas (1977) had not been attained. These results support the proposal of a Biogenic Amine Index (BAI) based on the sum of histamine, cadaverine, putrescine and tyramine levels considering values below 50 mg.kg^{-1} as indicative of good quality food.

Křížek et al. (2002) found that the index proposed by Mietz and Karmas (1977) has little application to assess the quality of carp (*Cyprinus carpio*) stored in non-hermetic packages kept at 3 and 15ºC for 13 and 4 days, respectively, due to the non-occurrence of spermine concentration decline. Putrescine content presented the best correlation with the sensory quality of the meat. Based on these results, the authors observed that good quality samples presented putrescine content up to 10 mg.kg^{-1}, acceptable quality between 10-20 mg.kg^{-1} and undesirable quality above 20 mg.kg^{-1}. Histamine and cadaverine formation kinetics were similar to putrescine formation kinetics, however histamine content increase was observed only in evidently spoiled samples. They considered, then, that the sum of putrescine and cadaverine contents might be used to assess carp quality.

Özogul and Özogul (2006) assessed biogenic amine concentration in sardines (*Sardina pilchardus*) kept at 4ºC in the air, packed under modified atmosphere (60% CO_2 and 40% N_2) and under vacuum. From QI calculation proposed by Mietz and Karmas (1977) and BAI suggested by Veciana-Nógues et al. (1997), they observed that both indices increased as a function of storage time and showed good correlation with the sensory alterations of the samples. The QI 10 established as the acceptance limit was attained in 4, 8 and 12 storage days in samples kept in the air, vacuum packed and packed under controlled atmosphere, respectively, times when the samples were sensory rejected. The BAI presented good correlation with fish sensory quality, however, according to the authors, establishing acceptance limits for samples packed in vacuum and modified atmosphere is still needed.

Bakar et al. (2010) studied biogenic amine content in barramundi (*Lates calcarifer*) stored at 0ºC and 4ºC for 15 days and calculated QI and BAI according to the formulas proposed by Mietz and Karmas (1977) and Veciana-Nógues et al. (1997). The results showed that both indices increased during storage time and therefore can be used to determine the degree of spoilage of this species.

Other freshness indices have been pointed out for different fish species based on the correlation of biogenic amine increase with storage period, such as cadaverine concentration in salmon (*Salmo gairdneri*) (Yamanaka et al., 1989), cadaverine and agmatine content in

smooth weakfish (Ruiz-Capillas and Moral, 2001) and putrescine and cadaverine content in trouts of the *Oncorhynchus keta* species (Rezaei et al., 2007; Rodrigues et al., 2013).

The biogenic amines indices from different fish species is listed in Table 1.

3. ATP degradation

Adenosine triphosphate is a high energy molecule that enables to keep actin and myosin filaments separated in the muscle. In living organisms ATP is regenerated from adenosine diphosphate (ADP) through oxidative phosphorylation. After the death of the animal, the cells continue, after a certain period of time, their normal physiological processes. As oxygen content decreases and creatinine phosphate reserve is consumed, ATP regeneration ends and ATP is rapidly degraded by a series of dephosphorylation and deamination reactions to different compounds (Ocaño-Higuera et al., 2009; Song et al., 2012).

ATP is thus converted, by dephosphorylation reactions initially to adenosine diphosphate (ADP) and then to adenosine monophosphate (AMP). AMP is in turn deaminated to inosine monophosphate (IMP) which degrades to inosine (HxR) and hypoxanthine (Hx). Several studies propose an alternative mechanism for marine invertebrates that considers a sequence of dephosphorilations to adenosine (Ade), which then degrades to HxR and Hx and, in some cases can form xanthine and uric acid (Saito et al., 1959; Venugopal, 2002).

Generally, ATP degradation occurs in a similar way on most marine species, however the degradation rate and pattern vary as a function of the specimen species, muscle type and biologic condition (sex, gonadal status), season of the year, water temperature, capture method and stress conditions during capture, handling and storage (Hattula et al., 1995; Özyurt et al., 2007; Morkore et al.; 2010).

Gram and Huss (1996) highlight that usually, after the fish death, the ATP molecules rapidly hydrolyze to IMP by the action of endogenous amines. The subsequent degradation of IMP to HxR and Hx is slower and with the participation of autolytic and microbial enzymes. Therefore, IMP is accumulated in the initial degradation stage and an increase of Hx and HxR levels is observed with time and consequent quality loss. IMP is the main responsible for the definition of fresh fish odor and flavor, while Hx has a direct effect on the bitter taste of spoiled fish. Lakshmanan et al. (1990) reported a negative relationship between the content of hypoxanthine and sensory quality of rock cod (*Epinephelus* spp.). Therefore, the content of ATP degradation metabolites has been widely used as biological indicators of fish freshness degree.

3.1 Quality indices based on ATP degradation

Saito et al. (1959) were the first authors to propose a quality index based on the concentration of different nucleotides, to assess fish freshness degree, defined as K value calculated by the formula:

$$K\ (\%) = \frac{HxR + Hx}{ATP + ADP + AMP + IMP + HxR + Hx}\ x\ 100$$

From the application of the K value, Saito et al. (1959) obtained values that allowed classifying some fish commercial species as:

- K < 20%: very fresh fish, suitable to be consumed raw.

- 20 < K < 40%: fish considered fresh to be consumed after cooking.

- K > 40%: fish inadequate for consumption.

As the passage of ATP to IMP is fast, Karube et al. (1984) modified K value and suggested a new calculation (Ki) defined as:

$$Ki\ (\%) = \frac{HxR + Hx}{IMP + HxR + Hx}\ x\ 100$$

Those authors highlighted that, for some species, ATP, AMP and IMP concentrations remain more or less constant up to two weeks. In this case, they should be considered in freshness evaluation.

Burns et al. (1985), studying samples of cod, mackerel and crab, proposed the G value based on the accumulation and/or degradation of Hx, IMP, AMP and HxR, according to the following formula:

$$G(\%) = \frac{Hx + HxR}{HxR + IMP + AMP}\ x\ 100$$

According to these authors, the G value is based on Hx accumulation also reflecting the disapearance of IMP, AMP and HxR.

Luong et al. (1992) highlight that, for some species, K and Ki values do not adequately reflect the alterations that occur, because they rapidly increase and then, they remain more or less constant. This is caused by a rapid accumulation of HxR and Hx. For these species, those authors proposed the value H based on Hx concentration considered as a good indicator of fish freshness under both points of view, physiological and sensory, as a function of the characteristic bitter taste of spoiled fish:

$$H(\%) = \frac{Hx}{IMP + Hx + HxR}\ x\ 100$$

Lakshmanan et al. (1996) when assessing mullet (*Liza corsula*) and pearlspot (*Etroplus suratensis*) stored at room temperature and in ice reported K values different from those

proposed by Saito et al. (1959). At room temperature, both species remained adequate for consumption up to 9-hour storage, when K value attained 50% and rejection occurred after 12-hour storage, with K values of 61.52 for mullet and 67.76 for pearlspot. Mullet and pearlspot ice stored samples were classified as first quality after 4 and 8 storage days with K values of 29.8% and 23.5%, respectively, good with K values of 50% after 8 and 13 storage days and rejected after 12 and 14 storage days with K values of 70.59% and 54.94%, respectively. Özogul et al. (2011) suggested K value of 80% as the acceptance limit for sole (*Solea sole*) samples after 16-18 storage days.

In canned sardines (*Sardinops sagax caerulea*) of three different brands, Vázquez-Ortiz et al. (1997), aiming at evaluating the quality of the raw material before thermal processing, once it does not interfere with nucleotide content, observed K value variation of 34.7-56.3 indicating the use of raw material of poor sensory quality. Similar results were described by Uriarte-Montoya et al. (2010) who observed an increase of K value throughout the canning process stages of this sardine species, from 14.1% to 22.8%. Both authors concluded that this index may be useful for freshness assessment of the fish used in the preparation of canned preserves.

Özogul et al. (2000) noted that herring (*Clupea harengus*) stored in ice and in modified atmosphere (60% CO_2 and 40% N_2) presented initial K values of 29% and 32% respectively, indicating poor quality raw material. In that study, the authors also verified that hypoxanthine increased more rapidly in ice stored fish than in fish stored in a modified atmosphere, indicating that the presence of carbon dioxide (CO_2) influences Hx accumulation. Similar results were obtained by Özogul and Özogul (2002) when they analyzed trouts (*Oncorhynchus mykiss*) stored in modified atmosphere (40%CO_2, 30%O_2 and 30% N_2) and in ice. In addition to K value, the authors calculated Ki and H values and observed that H value increased at a smaller rate than the other indices. They also reported that, although CO_2 presence influences Hx content throughout the storage period, the concentration of this gas did not affect K, Ki and H values.

Özogul et al. (2006a) calculated K, Ki, H and G values for European seabass (*Dicentrarchus labrax*) stored at 4ºC and in ice and observed a continuous increase of these indices throughout the storage period. Corroborating findings of Özogul and Özogul (2002), Özogul et al. (2006a) found that H value slowly increased not presenting a significant alteration during the initial eight storage days due to the constant increase of Hx concentration. In addition, the authors reported that a rapid increase of K, Ki and G values occurred due to the accentuated drop of IMP and no significant difference was observed among those values. Similar results were observed by Özogul et al. (2006b) when assessing eel (*Anguilla anguilla*) and Özogul et al. (2008) when assessing white grouper (*Epinephelus aeneus*). The authors also calculated the P value of eles and observed that the lowest value obtained was G value. The authors attributed acceptance limits of 81%, 84%, 39% and 137%, for K, Ki, H and G respectively for grouper.

Huidobro et al. (2001) assessing gutted and entire giltheads (*Sparus aurata*) obtained by different sacrifice methods (immersion in water and ice, asphyxiation, anesthesia with

subsequent percussion and percussion) observed that ATP degradation products could not be used separately as indicators of this species freshness, however the relationship expressed as K value presented good correlation with freshness status, with no significant differences among slaughter methods and *post-mortem* treatment. The K value of 20% was reached after seven storage days, presenting a slower evolution when compared to other species, reaching 50-60% only after 25 storage days, when the sensory and microbiologic evaluations showed values compatible with quality loss. The authors compared K and Ki values and noted that Ki differed from K during the refrigerated storage, due to rapid ATP degradation to IMP in this species, which allowed to infer that this value did not add relevant analytical information for quality assessment.

In ice stored matrinxã (*Brycon cephalus*) specimens, Batista et al. (2004) observed that during the initial storage days, there was no significant variation of K index (2.01 to 3.29%) and that, after 16 days, the K value attained 19.56 maintaining a significant correlation with sensory, physicochemical and bacteriological parameters and the fish was considered adequate for consumption, according to the classification proposed by Saito et al. (1959). After 23 storage days K value attained an average of 28.87%, maintaining freshness characteristics.

Siripatrawan et al. (2009), studying mollusks of the *Haliotis asinina* species noted that ATP alone could not be used as freshness index, due to its rapid conversion to IMP. The authors observed Hx increase but did not detect inosine presence. They concluded that, for the studied species, K value is not a good indicator of degree of freshness.

4. Analytical methods

According to Önal (2007) the main applications of biogenic amine analysis refer to quality control of raw materials, intermediary and final products, monitoring of fermentation processes, process control, besides the technical-scientific aspects.

The complexity of the matrix to be analyzed, presence of interfering substances and low concentration are considered limiting factors in the analysis of these compounds in food (Shalaby, 1999; Alberto et al., 2002; Önal, 2007). The solvents more commonly used for the extraction of these compounds are trichloroacetic acid (Pacheco-Aguilar et al., 1998; Mendes et al., 1999; Shalaby, 1999; Ruiz-Capillas and Moral, 2001; Oliveira et al., 2004; Özogul et al. 2006a; Özogul et al., 2006b; Özogul and Özogul, 2006; Rezaei et al., 2007; Özogul et al., 2008; Anderson, 2008; Bakar et al., 2010), perchloric aid (Yamanaka et al., 1989; Křížek et al., 2002; Shakila et al., 2003; Dadáková et al., 2009; Kim et al., 2009) and methanol (Kim et al., 2001; Du et al., 2002).

Several analytical methods have been developed to assess biogenic amines in different foodstuffs. Spectrofluorimetry, thin layer chromatography, high performance liquid chromatography (HPLC), gas chromatography, capillary electrophoresis, and polymerase chain reaction (PCR) are mentioned as the more relevant from the analytical point of view (Shalaby, 1999; Lapa-Guimarães and Pickova, 2004; Önal, 2007).

Spectrofluorimetry has been used to determine amines individually (Andrade et al., 2012) and is considered by the AOAC as the official method in the USA and adopted as such in Brazil for the quantitative analysis of histamine in fish (AOAC, 2002; Brazil, 1997). However, recently high performance liquid chromatography (HPLC) became the official method in Brazil for the determination of histamine and other biogenic amines (cadaverine, putrescine, spermidine, spermine) in fish through Normative Instruction no 25 (Brazil, 2011). The technique involves acid extraction of the amines, pre-column off-line derivatization with dansyl chloride in alkaline pH, followed by separation and quantification by HPLC with elution gradient and ultraviolet detection. According to Park et al. (2010) HPLC is a selective and sensitive technique and the most frequently used for biogenic amine determination due to its high resolution.

Thin layer chromatography is a simple, fast and low-cost semi-quantitative method for the separation and estimation of biogenic amines in food (Shalaby, 1999; Carmo et al., 2010; Andrade et al., 2010; Lapa-Guimarães and Pickova, 2004; Önal, 2007; Monteiro et al., 2010; Andrade et al., 2012; Rodrigues et al., 2012) used in routine quality control in industries and warehouses.

Due to the lack of chromophores and fluorescent properties of most biogenic amines, chemical derivatization is performed to increase the sensitivity in the determination of these compounds (Alberto et al., 2002; Park et al., 2010). Önal (2007) highlights that the analytical procedures adopted are usually based on the formation of fluorescent derivatives with different derivatization agents such as dansyl chloride, benzoyl chloride, fluorescein, 9-fluorenylmethyl chloroformate, naphtalene-2,3 dicarboxaldehyde and o-phtaldehyde (OPA). The use of the derivatization agent 6- aminoquinolyl-N-hydroxysuccinimidyl carbamate (AQC) is a major breakthrough in the detection of biogenic amines because, among other factors, it has great stability and sensitivity to fluorescent detection (Martínez et al., 2000; Ordóñez et al., 2013).

Many methods have been reported for the analysis of ATP and its degradation products, such as the use of cationic-ionic exchange columns (Saito et al. 1959), enzyme sensor system (Karube et al. 1984), capillary electrophoresis (Luong et al., 1992) and high performance liquid chromatography (HPLC), the latter as the most frequently described in several studies (Burns et al., 1985; Lakshmanan et al., 1996; Vázquez-Ortiz et al., 1996; Özogul et al., 2000; Huidobro et al., 2001; Özogul et al., 2008; Siripatrawan et al., 2009; Uriarte-Montoya et al., 2010; Özogul et al., 2011). Perchloric acid is the reagent more frequently used in the extraction stage. Compound separation is usually performed in reverse phase columns using phosphate buffers as mobile phase or by ion-pair methods. Organic solvents such as methanol and acetonitrile can be used to reduce the run time (Özogul et al., 2000).

5. Conclusion

Quality indices based on the concentration of ATP degradation products and level of biogenic amines are widely used to assess fish freshness, because they present good correlation with the changes that occur during the storage period. However, aspects related to fish species,

type of sampled tissue, stress suffered by the fish during capture, storage temperature, among other factors must be considered when establishing values to be reliably used.

In relation to the analytical methods, the extraction phase is one of the most important stages because of the elimination of interfering substances. The methodology commonly used for both, biogenic amine and ATP degradation product detection is high performance liquid chromatography, mainly because it allows the rapid and simultaneous detection of more than one compound in the same sample and analysis.

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Table 1. Biogenic amines indice in samples fish

Sample fish	Cientific name	Biogenic amines indice	References
Tuna	-	HI + PU + CA / SM + SD	Mietz and Karmas (1977)
Tuna	*Thunnus thynnus*	HI + CA + PU + TY	Veciana-Nóguez et al. (1997)
Carp	*Cyprinus carpio*	PU and CA	Křížek et al. (2002)
Salmon	*Salmo gairdneri*	CA	Yamanaka et al. (1989)
Sardine	*Sardina pilchardus*	HI + PU + CA / SM + SD and HI + CA + PU + TY	Özogul and Özogul (2006)
Barramundi	*Lates calcarifer*	HI + PU + CA / SM + SD and HI + CA + PU + TY	Bakar et al. (2010)
Hake	*Merluccius merluccius*, L.	CA and AG	Ruiz-Capillas and Moral (2001)
Trout	*Oncorhynchus keta*	PU and CA	Rezaei et al. (2007) and Rodrigues et al. (2013)

HI: histamine; PU: putrescine; CA: cadaverine; SM: spermine; SD: spermidine; TY: tiramine; AG: agmatine