无损检测技术在鱼类及其产品监测中的应用

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摘　要: 鱼类及其产品的质量安全深受消费者关注, 然而鱼肉在加工运输贮藏阶段易发生品质上的变化, 因而对鱼类及其产品的质量安全监控显得十分重要。无损检测技术依据鱼类及其产品的光谱学特性、声学特性及电磁学特性, 可以高效无损地实时监控鱼类及其产品的质量安全。现阶段, 国外发达国家已将无损检测技术应用到工业化检测并取得了较好的结果。

关键词: 鱼类及其产品; 质量安全; 无损检测

Non-destructive techniques for quality evaluation and safety assessment of fish and fish products-a review

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ABSTRACT: The quality and safety of fish and fish products are paid great attention by consumers. Because the quality of fish flesh is easy to decline during processing, transporting, and storage, the evaluation and control are significantly important. Non-destructive techniques which are based on spectroscopic, acoustic, electromagnetic properties could be used for quality and safety assessment of fish and fish products. Recently, non-destructive techniques are popular in developed countries and satisfied results are received in industries.

KEY WORDS: fish and fish products; quality and safety assessment; non-destructive techniques

鱼肉因其营养健康深受国内外消费者欢迎[1,2], 但是鱼类及其产品的质量及安全的工业级别检测还存在很多问题和挑战[3], 如何进行质量安全实时监控是生产商和消费者都十分关注的问题。现有很多对鱼类及其产品的微生物检测、理化检测、新鲜程度评定、感官品质评估等传统的分析方法, 例如基于平板培养的微生物检测[4]; 按照 AOAC 规范对水分含量(AOAC 930.15)及水分活度(AOAC 978.18)、蛋白质含量(AOAC 991.20)及氨基酸组成(AOAC 985.28)、脂肪含量(AOAC 989.05)及脂肪酸组成(AOAC 973.26, AOAC 991.39)、灰分(AOAC 920.153)、酸度(AOAC 920.124)的分析; 通过生物胺[5]、TVB-N(total volatile base nitrogen, 挥发性盐基氮)[6]测定鱼肉及其产品的新鲜程度; 利用 TBARS(硫代巴比妥酸法) [7]测定脂质的氧化; 利用 NPN(non-protein nitrogen, 非蛋白氮)和 AAN(amino acid nitrogen, 氨基态氮)以及电泳技术测定鱼肉蛋白水解及聚集状态[6,8]; 采用质构仪、流变仪对鱼肉产品的凝胶流变特性及其感官品质进行

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分析[9]。尽管在这其中, 有的方法权威准确, 然而这些方法一般耗时费力, 需要技术娴熟的测验人员, 而且破坏原材料, 不适合实时监控[3,10]。

为了弥补传统分析方法的缺陷, 许多国外学者转而研究监控鱼类及其产品质量安全的无损检测技术[3, 11-14]。无损检测技术可以避免破坏性测量造成的样品损失; 并且检测速度快, 机械化自动化程度高, 节约了时间和劳动力[15]; 实时监控可以跟踪源头从而满足消费者的需求[10]。无损检测技术在果蔬[16-18]、乳品[19-21]的品质控制上已经得到广泛的应用, 但在我国的水产品加工、贮藏、运输过程中的质量安全检测领域尚处于发展阶段。

无损检测技术依据鱼类原料及产品的光谱学特性、声学特性、以及电磁学特性, 可以测定样品的外观属性, 例如识别鱼体表面缺陷[12, 14, 22]、测量质量尺寸[23-26]、描述质构色泽等感官品质[10, 27, 28]; 还可以分析样品的本质属性, 例如鱼类产品的水分含量和水分活度[29-38]、盐含量[33,39]、蛋白质[40-43]、脂类[44-46]等; 同时也可以检测鱼类及其产品的新鲜度[47-51]和卫生状况[3, 52-54]。

1 光谱学特性

基于样品光谱学特性的无损检测技术主要有机器视觉[24,25,55]、可见光光谱法[28,47,56]、红外光谱法[40-48,52,54,57]、核磁共振[13,30,44,58,59]、核磁共振成像[30,31]、光谱成像[17,26,27,51,53,60]。表 1 列出了基于光谱学特性的无损检测技术在鱼类及其产品监测中的应用。

1.1 机器视觉技术

机器视觉技术主要应用于鱼种的鉴别, 鱼类质量尺寸的分级分选, 鱼体表面缺陷的识别[12,14,23-25,55]。传统检测方法采用人工观测分类, 不仅耗费了大量人力物力, 而且效率低, 影响了正常的商业运转。机器视觉可以通过高分辨率相机提供描述鱼肉外观的高品质画面, 捕捉颜色、重量、尺寸、形状、表面缺陷等信息, 实现了自动化高效无损检测[25]。

Dowlati 等[12]和 Mathiassen 等[14]利用机器视觉捕捉了鱼体表面缺陷, 包括鱼肉破裂、组织挫伤、血斑, 刀伤刮蹭伤、鱼头鱼尾缺失。Mathiassen 等[55]研究了多重成像模式组合下鲱鱼表面缺陷的可视性效果是否被强化, 结果表明, 自动化检测结合了漫反射, 交互及 3D 模式, 可以检测出大多数缺陷类型。X 射线探测仪产生的图像也可以用于机器视觉分析, 用于检测产品中的金属和鱼刺[61]。

1.2 可见光光谱技术

VIS(visible spectroscopy, 可见光)技术常用于测定鱼肉的新鲜度和贮藏时间。仪器可以记录反射、透射、漫反射光谱信息, 探针只需接触样品表面, 无需深入内部。图 1 显示了可见光频段范围。

采用可见光频段, 可以建立低脂鱼例如鳕鱼的新鲜度、冰上放置时间的预测模型[62], 这个模型的预测相关系数高达 0.97, 预测贮藏期的误差天数不超过 1.04 d。Sivertsen 等[47]利用可见光一小部分频段区分了冻藏—解冻鳕鱼和新鲜鳕鱼。

表 1 基于光谱学特性的无损检测技术在鱼类及其产品监控中的应用总结

Table 1 An over-review of spectroscopic techniques for non-destructive quality assessment of fish and fish products

无损检测技术	鱼的种类	检测指标	结果	参考文献
机器视觉	台湾罗非鱼	重量	R^2=0.9303	Liang 等 [63]
机器视觉	比目鱼等	尺寸	σ=1.2mm	White 等[24]
机器视觉	三文鱼	表面缺陷	R=0.514, P<0.001	Ashton 等[64]
VIS	大西洋鳕	新鲜度	R=0.97; 误差天数不超过 1.04d	Nilsen 等[62]
NIR	鲈鱼	水分含量	R^2=0.90	Majolini 等[32]
NIR	太平洋三文鱼	盐含量	R^2=0.83	Lin 等[39]
NMR	大西洋三文鱼	水分分布	温度升高, 水的流动性增加	Aursand 等[31]
HIS	鲭鱼等	湿度和脂肪含量	湿度: R=0.94, 脂肪含量: R=0.91	ElMasry 等[65]
HIS	鳕鱼	寄生虫	总检出率: 58%, 深色寄生虫检出率: 71%, 浅色寄生虫检出率: 46%	Sivertsen 等[53]

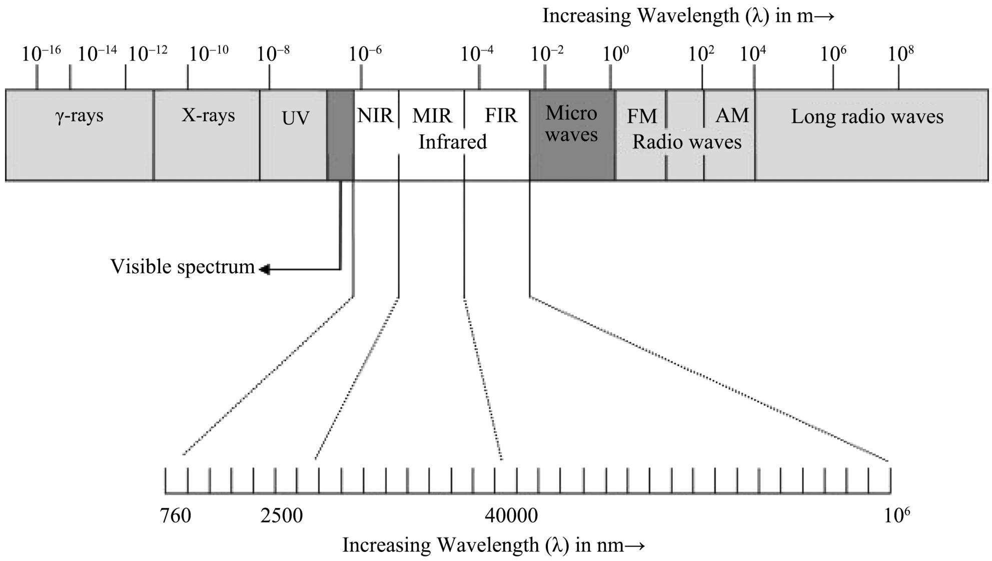

图 1　可见光和红外光谱波长分布图[66]

Fig. 1　VIS/IR spectroscopy[66]

1.3　红外光谱技术

IR(infrared spectroscopy, 红外光谱)可以细分为 NIR(near-infrared spectroscopy, 近红外)和 MIR (mid-infrared spectroscopy, 中红外)。NIR 与 VIS 类似, 也常用于新鲜度和贮藏时间的预测, 例如三文鱼之类的高脂鱼利用 NIR 可以构建高适性模型, 预测相关系数为 0.98, 误差天数不超过 1.20 d[62]。此外, IR 是分析鱼类产品成分和鱼类及其产品卫生状况的有力工具。

Lin 等[39]采用 SW-NIR(short-wave near-infrared, 短波红外光谱)研究了烟熏三文鱼的盐含量; Huang 等[33]在此基础上, 结合反向传播神经网络方法, 研究了烟熏三文鱼的盐含量。NIR(扫描光谱 1000~2500 nm)结合 PLS(partial least squares, 偏最小二乘法)多元回归模型可以预测鱼肉的粗蛋白含量, 相关系数 R^2=0.95, 有较高的准确性[57]; NIR 还可以预测蛋白质的二级结构, 从分子层面观测蛋白质链的打开和蛋白质的相互作用[40,41,43]; MIR 可以辨别出 α-螺旋, β-转角, β-折叠, 无规卷曲环境中的肽键[42]。NIR 还可以获得关于鱼肉脂质的数据, 例如 Khodabux 等[67]通过 NIR 光谱建立了金枪鱼总脂肪含量和游离脂肪含量的测定方法; Sánchez-Alonso 等[46]通过傅立叶转换红外技术实时监控了鳕鱼油水解过程。NIR 也被广泛应用在鱼类及其产品的水分含量和水分活度的测定中[32, 33, 35], 在 760 nm 到 2.5 μm 的范围内(图 1), 不同共价键的弯曲和伸缩振动的吸收值不同, 红外吸收光谱取决于分子的物理化学环境, 因而可根据红外吸收光谱测定水分含量[36]。根据寄生虫和鱼肉光谱学的相异性, NIR 技术可以检测出寄生虫[52], Sone 等[68]利用 NIR 观测获知三文鱼表面是否有细菌生长, 与此类似, Tito 等[54]结合 NIR 和 PCA/PLSA 模型预测了大西洋鲑鱼是否发生了腐败。

1.4　核磁共振技术

LF-NMR(low field-nuclear magnetic resonance, 低场核磁共振)技术主要应用于鱼类及其产品中各种有关水分指标的测定。通过测定横向弛豫时间可以对鱼类及其产品的质量安全进行控制[13,29,31,58]。不同类别的水中由于质子所处的环境不同, 因而横向弛豫时间也不相同, 水与肌肉组织结合越紧密, 弛豫时间越短, 依据弛豫图可以分析水分的变化及迁移[69]。图 2 为典型的弛豫图, 可以看出温度升高, T_{21} 和 T_{22} 的峰向长的弛豫时间移动, 说明鱼肉内部的水分流动性增加, 到了更高温度(55 ℃), T_{21} 和 T_{22} 两个峰变成了三个峰, Aursand 等推测 T_{21} 的峰是与肌肉蛋白质结合的水的响应峰, 在 55 ℃下, 蛋白质发生了变性, 蛋白质网络结构发生了改变, 其中的水分流动性增加而外排, 常被称为滴汁损失, 三个峰分别为与肌肉结合相对紧密的束缚水, 维系力微弱的束缚水, 和自由水的响应峰[58]。

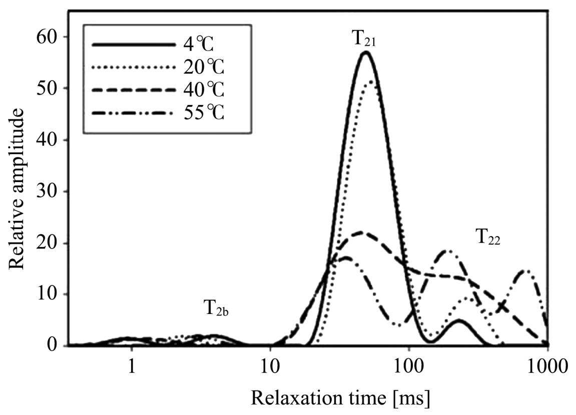

图 2 鲑鱼四个温度下横向弛豫时间图[58]

Fig. 2 Transverse relaxation time of salmon under 4 different temperatures[58]

1.5 核磁共振成像技术及光谱成像技术

核磁共振成像技术及光谱成像技术是近几年发展起来的新兴技术，它们结合了光谱技术和成像技术(图 3)，可以同时获取被检测样的空间信息和光谱信息，对于鱼类质量尺寸的分级分选，鱼类及其产品的新鲜度鉴别，样品的组成分析、感官评定，以及样品的卫生状况都可以进行检测。

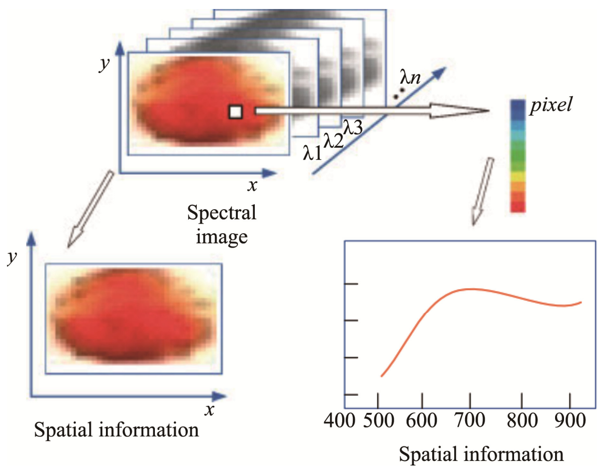

图 3 高光谱成像图解[70]

Fig. 3 Hyper spectral imaging (HSI) illustration[70]

例如, NMRI(nuclear magnetic resonance imaging, 核磁共振成像)可以扫描鱼肉整体并且提供 3D 图谱, 因而可以用于检测寄生虫[3];HIS(hyperspectral imaging, 高光谱成像)也被应用到寄生虫的检测中[53]。此外, ElMasry 等[65]利用近红外光谱(760~1040nm)成像技术决定了六种类别的鱼的水分分布。Erikson 等[56]证实了 VIS 成像可以检测出宰杀后和去除内脏的鲑鱼体腔内残余血，从而可以决定下一步是否需要清洗。Wu 等[27]采用高光谱成像方法(波长 400~1000 nm), 结合 SPSS 的 PLS 分析，探究了该方法检测鲑鱼鱼块质构的可靠性，结果表明，硬度、粘合性、粘性的相关系数 r 分别为 0.665、0.555、0.666，显示正相关，交互验证均方根误差分别为 4.09、0.067、0.504，说明高光谱成像方法用于大批次的质构无损检测有很高的应用前景。VIS 和高光谱成像两者结合，并使用 LS-SVM 模型，可以通过颜色鉴别出新鲜鱼肉和解冻鱼肉[51]。近两年, Menesatti 等[71]改进了 RGB 的校正方法，使得在任意的光照条件下，依然能对颜色做出正确的评估。

2 声学特性

超声波应用在肉制品中例如猪肉牛肉脂肪含量的无损检测已经普及[72-74]，然而应用在鱼肉脂肪含量的测定还鲜见报道。超声波检测是利用肉品在超声波作用下的反射、散射、透射、吸收特性和衰减系数、传播速度以及其本身的声阻抗和固有频率，根据一些主要参数的变化测定肉品的组成成分、肌肉厚度、脂肪厚度等，以实现快速无损在线检测与分级的方法。利用超声波衰减系数和传播速度的变化可以测定肉品(活体或尸体)的成分，如牛、羊、猪等的背膘厚以及脂肪含量。如果将来将超声波测定方法应用于水产工业，可以快速测定鱼脂含量。

3 电磁学特性

以电磁学为基础的生物阻抗分析不仅可以用于水分含量的测定，还可以辨别鱼肉的新鲜程度。

Bourdages 等[38]利用生物阻抗方法比较鳟鱼水分含量及干基质量，相关系数分别为：总水分含量 R^2=0.89，干重 R^2=0.80。Pérez-Esteve 等[49]比较了阻抗分析方法和传统检测新鲜度的 TVBN 方法，得出 R^2=0.72，总结出阻抗分析方法具有一定的应用前景。我国学者[50]对新鲜和解冻的草鱼、罗非鱼进行了阻抗测定，发现新鲜鱼的阻抗随电场频率变化值显著大于解冻鱼。

4 结论与展望

目前，国外发达国家研究并应用无损检测技术

对鱼类及其产品进行质量安全监控, 取得了一定的成果, 而我国的相关报道较少, 工业化检测仍以破坏性的传统检测方法为主。如果可以将无损检测技术应用于鱼类及其产品在产业化生产中的质量安全的在线监测, 可以实现工业化检测的革新, 不仅可以保证鱼类及其产品的质量安全,同时可以提高检测效率, 节省人力物力; 而且无损检测节约了鱼类资源, 减少了废弃物对环境的污染, 降低了有害化学试剂对检测人员的伤害。无损检测技术在鱼类及其产品质量安全监测中的应用将推动我国水产品工业的发展。

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