Applications of near infrared spectroscopy for fish and fish products quality: a review

Wenqian Yu
Synthetic & Catalytic Chemistry, University of Toronto
kyue0411@gmail.com

Abstract: Fish and fish products are rich in significant nutrients such as protein and fat, and it is an important part of human diet. However, the deterioration of fish due to the influence of microorganisms and oxidation has not only wasted resources but also affected food safety. Therefore, the development of fast and simple detection technology is an important solution. This paper combines with domestic and foreign literatures, summarizes research papers based on Near-infrared (NIR)spectroscopy, discusses the basic principles, analysis process and modeling methods of NIR spectroscopy respectively, and reviews the application of NIR spectroscopy in physical and chemical indicators, microbial indicators, storage conditions, classification and identification, geographic traceability and other related aspects, which provides a reference for the further development and research of rapid detection technology for fish and fish products.

1. Introduction
Fish and fish products are important sources of human nutritional intake, containing high protein, mineral content, vitamins, and low fat (Zhou et al., 2019; Agyekum et al., 2020). It also contains polyunsaturated fatty acids, which are hardly found in other food sources (Moriarity et al., 2020). These nutrients have positive effects on human health, such as help prevent the development of heart diseases, as well as reducing the coronary heart disease (CHD) mortality rate (Wang et al., 2020). However, once the fish is slaughtered, due to the enzymatic decomposition of some nutrients (especially proteins, lipids, and nucleotides) and microbial spoilage by surface bacteria an unpleasant smell will be produced. Hence, the quality of fish is directly linked with fat oxidation, a breaking down of protein and adenosine triphosphate (ATP) (shown in Fig.1), a decrease in pH, and a production of peculiar smell (Rahman et al., 2015; Agyekum et al., 2020). Nowadays, with the increasing demand for fish consumption and the pursuit of quality of life, the requirements for fish quality are getting higher and higher. Indexes such as freshness, protein content, flesh color and texture are important for fish quality evaluation. Therefore, how to ensure these indexes of fish during transportation, storage and processing has become an increasingly significant research problem.
Currently, sensory, physical, chemical, biological and microbiological indicators are used to assess the quality of fish. Among them, sensory evaluation is relatively subjective, which depends on appearances, odor, flavor, and texture of fish. Therefore, it brings difficulties to qualitative analysis. In addition, the physical method includes texture analysis, colorimetric method, and electric noise (EN), and water-holding capacity (WHC), microbiological methods are aerobic and standard plate count, while pH, ATP decomposition, total volatile basic nitrogen (TVB-N) concentration, trimethylamine-nitrogen, K value and nucleotide degradation are used as parameters for chemical evaluation (Prabhakar et al., 2020; Ocaño-Higuera et al., 2011; Lalabadi et al., 2020). Although these traditional techniques provide a precise way for freshness evaluation of fish, there are still restrictions of being destructive, expensive, complicated, and time-consuming (Taheri-Garavand et al., 2019; Leghrib et al., 2020). For this reason, a convenient, non-destructive and less time-consuming method is necessary for fish quality evaluation.

At present, Near-infrared (NIR) spectroscopy is a rapid, non-destructive technique and convenient, which is not only widely applied in petrochemical (Reboucas et al., 2010), textile (Sun et al., 2019), pharmaceutical industries (Desai et al., 2020), but also agricultural products (Pierna et al., 2020), especially fish quality monitoring. The spectroscopy evaluates the chemical and biochemical properties of fish through various indicators, including protein, fat, water-holding capacity, TVB-N, TMA-K, peroxidation value, K value, pH, ATP decomposition (Prabhakar et al., 2020; Ocaño-Higuera et al., 2011; Lalabadi et al., 2020). This technology has the ability to provide quickly generated and comprehensive information as well as the measure multiple sets of analytical data at the same time (Trocino et al., 2012; Cai et al., 2011). Moreover, its reproducibility makes the evaluation process more economical and convenient. However, there are relatively few studies devoted to fish and fish products based on NIR. This review aims to give a summary of the basic knowledge of NIR spectroscopy and its application combining with chemometrics in the quality of fish and fish products so far. It highlights papers that were published in recent five years, but referring to earlier ten years as well, and it mainly focuses on the sensory, physical, chemical and biological parameters.

2. Near-infrared (NIR) spectroscopy
When there is a beam of light that irradiates through a sample, molecules in the sample absorb light selectively under certain frequency bands, thus the chemical bonds in molecules vibrate to generate the Near-infrared (NIR) spectrum. It shows the information of overtone and combination bands of fundamental vibration of chemical bonds in molecules that mainly contain hydrogen atoms, for example
N-H, O-H, and C-H groups. The range of NIR spectrum is from 780 nm-2500 nm (Baianu et al., 2011; Li et al., 2020), where the absorption between 780-1800 nm corresponding to the first, second, third and fourth overtones of C-H groups, and 1100-2400 nm associated with the first, second, and third combination of those groups. Besides, absorption at 840 nm, 960 nm and 1440 nm represent the first, second, and third overtones of O-H groups, respectively (Walsh et al., 2020). In addition, wavelength of first overtone and combination features of N-H are at 1500 and 2150 nm.

NIR spectroscopy is an economical and environmental-friendly monitoring method that does not require sample pretreatment (Nordey et al., 2017). It has been utilized extensively in many fields, such as medical science (Kim et al., 2020), forensic science (Coppey et al., 2020), and biochemistry. The analysis of NIR involves few steps listed below: 1) collection of NIR spectra of known samples and characterization of the properties of samples; 2) establishment and validation of model; 3) prediction of target parameters of unknown samples. It should be noted that models were built by chemometrics. Chemometrics is the application that uses the principle of statistics, mathematics and computer science while processing chemical information, in order to obtain construction and composition of the substance tested. Generally, partial least squares (PLS) (Zhang et al., 2020) and multiple linear regression (MLR) (Çerçi & Hürdoğan, 2020) were used to develop quantitative models, whereas support vector machines (SVM) (Zareef et al., 2020) and principal components analysis linear discriminant analysis (PCA-LDA) (Dumalisile et al., 2020) were used to build qualitative models. In addition, there are still some problems in NIR spectral analysis. First of all, there are some background interferences while collecting the spectra, including noise and overlapping bands. Furthermore, due to the weak absorption bands, it is hard to analyze and may lead to misreading of data (Guo et al., 2016; Barbin et al., 2014). For these reasons, it is required to pre-process of the original spectra. The spectral data preprocessing includes normalization, first and second derivation (shown in Fig.2), baseline, standard normal variate transformation (SNV) and multiplicative scatter correction (MSC), which helps to eliminate background noises (Qu et al., 2015).

Fig.2 (A) the original spectra, (B) the first-order derivative spectra, and (C) the second-order derivative spectra (Alishahi, 2010)

3. Application

3.1. Physical and chemical properties
The main components of fish are protein, fat, and water. Particularly protein with high contents is one of the most important nutrients in fish. The conformational changes of protein under different processing
and storage conditions will affect the quality of fish. Near-infrared spectroscopy has proven to be a valuable tool for studying the molecular mechanisms of protein structural reactions and protein folding, unfolding and misfolding. Khodabux et al. (2007) used the near infrared method to determine the fat, moisture, and protein in tuna successfully. Additionally, some related studies have been reported to predict and monitor the secondary structure of proteins by NIR or FT-NIR spectroscopy. Karlssottir et al. (2014) used Near-infrared spectroscopy to predict the total fat content and fatty acids of two fish (hoki (Macrouronus novaezelandiae) and saithe (Pollachius virens)), and the results showed that the independent verification coefficient (R2) of thiobarbituric acid reactive substances, total fat content and free fatty acids of saithe (Pollachius virens) were 0.76, 0.97, and 0.89 respectively. The corresponding values of sait hoki (Macrouronus novaezelandiae) he was 0.70, 0.96 and 0.89 respectively. And it has also been reported that NIR spectroscopy can better predict ergosterol, free fatty acids, triglycerides, and diglycerides in salmon oil (Cascant et al., 2018).

Zhou et al. (2020) used NIR spectroscopy combined with PLS-DA algorithm to set up an analysis model for predicting the chewiness, resilience, water holding capacity, shear force, elasticity, and hardness of the silver carp (Hypophthalmichthys molitrix). The results show that the relevant coefficients of the corresponding model are 0.92, 0.87, 0.95, 0.86, 0.83 and 0.89. Fourier transform near-infrared spectroscopy (FT-NIR) can also predict the K value, pH, the thiobarbituric acid value and total volatile basic nitrogen of bighead carp, and the R2 is 0.807, 0.945, 0.954 and 0.932 (Zhou, Wu, Chen, You & Xiong, 2019).

3.2. Microbial Indicators
The microbial indicator is one of an important indicator for evaluating fish freshness. Studies have shown that NIR spectroscopy is a reliable, convenient and useful technique for detecting microbial behavior and spoilage in fish. It is generally acknowledged that the quality of fish during storage and processing to a certain extent will be affected by the occurrence of microorganisms, especially bacteria and their active or passive transmission. Therefore, it is necessary to meet the microbiological safety standards because it prevents food-borne diseases and ensures the public Health and maintaining the high quality of fish and fish products are essential. Quantitative or qualitative detection of bacteria in fish usually leads to perceptions and decisions about the acceptability of their consumption and trade. However, conventional microbiological measurement methods related to sample collection, preparation, and testing are extremely time-consuming and tedious, which may be critical or unsatisfactory for real-time monitoring needs. In order to overcome the shortcomings of traditional methods, NIR spectroscopy as a rapid and non-destructive detection technology, has great significance for bacteria detection, and has been proven that it is a useful technology for reliable and rapid detection of fish and fish products quality. Tito et al. (2012) used NIR-spectroscopy to predict the number of microorganisms in salmon, however, the model had large error.

3.3. Storage Conditions
The NIR spectroscopy can detect the spectral changes of salmon fillets during storage and distinguish between frozen salmon and fresh salmon (Kimiya, Sivertsen & Heia, 2013). Based on the VIS-NIRs technology to establish a model to different fresh from frozen/thawed tuna fillets, the correct discrimination rate for fresh samples was 92%, and the correct discrimination rate of frozen/thawed samples was 82% (Reis et al., 2017).

3.4. Classification, Identification, and Geographical Traceability
NIR spectroscopy is used to distinguish different types of fish (Alamprese & Casiraghi, 2015). The combination of NIR spectroscopy and PLS-DA algorithm is applied for the differentiation of seven types of fish, including grass carp (Ctenopharyngodon idellu), carp (Cyprinus carpio), Sparidae (Parabramis), silver carp (Hypophthalmichthys molitrix), arrogant carp (Aristichthys nobilis), herring (Mylopharyngodon piceus), and crucian carp (Carassius auratus), with a 100% correct rate (Xiong, 2017). NIR spectroscopy combines with OPLS-DA algorithm discriminates wild bass and farmed bass
successfully with a 100% correct rate, as well as distinguishing between different rearing systems (extensive, semi-intensive or intensive), where extensive, semi-intensive and intensive rearing subjects provided 67%, 80%, and 100% correct classification rates respectively. Moreover, the spectrum can also be used to determine the geographic origin of fish, which can correctly distinguish 100% in the east, 88% in the middle, and 85% in the western Mediterranean (Ghidini et al., 2019). In addition, the combination of NIR spectroscopy and LDA algorithm distinguishes all fish fillets and patties with 100% accuracy (Grassi, Casiraghi & Alamprese, 2018).

4. Conclusion
This article summarizes the application of NIR spectroscopy in the analysis and detection of fish and fish products, and elaborates the detection principle, analysis process and how to build up models of NIR spectrum, it also discusses the detection of some basic indicators such as the water content, protein and fat content of fish; the detection of microorganisms on the surface of fish and fish products; as well as the application analysis of storage conditions, classification, identification and geographic traceability. This helps to provide a reference for the future development of simple, efficient, fast and accurate NIR spectroscopy technology, and to technical support for the development of fish industry.

Reference
[1] Agyekum, A. A., Kutsanedzie, F. Y. H., Annavaram, V., Mintah, B. K., Asare, E. K., & Wang, B. (2020). FT-NIR coupled chemometric methods rapid prediction of K-value in fish. Vibrational Spectroscopy, 108, 103044.
[2] Agyekum, A. A., Kutsanedzie, F. Y., Annavaram, V., Mintah, B. K., Asare, E. K., and Wang, B. (2020) FT-NIR coupled chemometric methods rapid prediction of K-value in fish. Vibrational Spectroscopy 108, 103044.
[3] Alamprese, C., & Casiraghi, E. (2015). Application of FT-NIR and FT-IR spectroscopy to fish fillet authentication. LWT - Food Science and Technology, 63(1), 720-725.
[4] Baianu, I., Guo, J., Nelson, R., You, T., and Costescu, D. (2011) NIR Calibrations for Soybean Seeds and Soy Food Composition Analysis: Total Carbohydrates, Oil, Proteins and Water Contents [v.2]. Nature Precedings.
[5] Barbin, D. F., Ana Lucia De Souza Madureira Felicio, Sun, D.-W., Nixdorf, S. L., and Hirooka, E. Y. (2014) Application of infrared spectral techniques on quality and compositional attributes of coffee: An overview. Food Research International 61, 23–32.
[6] Cai, J., Chen, Q., Wan, X., and Zhao, J. (2011) Determination of total volatile basic nitrogen (TVB-N) content and Warner–Bratzler shear force (WBSF) in pork using Fourier transform near infrared (FT-NIR) spectroscopy. Food Chemistry 126, 1354–1360.
[7] Cascant, M. M., Breil, C., Fabiano-Tixier, A. S., Chemat, F., Garrigues, S., & de la Guardia, M. (2018). Determination of fatty acids and lipid classes in salmon oil by near infrared spectroscopy. Food Chemistry, 239, 865-871.
[8] Çerçi, K. N., and Hürdoğan, E. (2020) Comparative study of multiple linear regression (MLR) and artificial neural network (ANN) techniques to model a solid desiccant wheel. International Communications in Heat and Mass Transfer 116, 104713.
[9] Coppey, F., Bécue, A., Sacrè, P.-Y., Ziemons, E. M., Hubert, P., and Esseiva, P. (2020) Providing illicit drugs results in five seconds using ultra-portable NIR technology: An opportunity for forensic laboratories to cope with the trend toward the decentralization of forensic capabilities. Forensic Science International 110498.
[10] Desai, P. M., Acharya, S., Armstrong, C., Wu, E. L., and Zaidi, S. A. (2020) Underpinning mechanistic understanding of the segregation phenomena of pharmaceutical blends using a near-infrared (NIR) spectrometer embedded segregation tester. European Journal of Pharmaceutical Sciences 154, 105516.
[11] Dumalisile, P., Manley, M., Hoffman, L., and Williams, P. J. (2020) Near-Infrared (NIR) Spectroscopy to Differentiate Longissimus thoracis et lumborum (LTL) Muscles of Game
Species. Food Analytical Methods 13, 1220–1233.

[12] Ghidini, S., Varrà, M. O., Dall'Asta, C., Badiani, A., Ianieri, A., & Zanardi, E. (2019). Rapid authentication of European sea bass (Dicentrarchus labrax L.) according to production method, farming system, and geographical origin by near infrared spectroscopy coupled with chemometrics. Food Chemistry, 280, 321-327.

[13] Grassi, S., Casiraghi, E., & Alamprese, C. (2018). Handheld NIR device: A non-targeted approach to assess authenticity of fish fillets and patties. Food Chemistry, 243, 382-388.

[14] Guo, Y., Ni, Y., and Kokot, S. (2016) Evaluation of chemical components and properties of the jujube fruit using near infrared spectroscopy and chemometrics. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 153, 79–86. Barbin, D. F., Ana Lucia De Souza Madureira Felicio, Sun, D.-W., Nixdorf, S. L., and Hirooka, E. Y. (2014) Application of infrared spectral techniques on quality and compositional attributes of coffee: An overview. Food Research International 61, 23–32.

[15] I.G. Martín, N. Álvarez-García, C. González-Pérez, V. Villaescusa-García

[16] Karlsdottir, M. G., Arason, S., Kristinsson, H. G., & Sveinsdottir, K. (2014). The application of near infrared spectroscopy to study lipid characteristics and deterioration of frozen lean fish muscles. Food Chemistry, 159, 420-427.

[17] Khodabux, K., L Omelette, M. S. S., Jhaumeer-Laulloo, S., Ramasami, P., & Rondeau, P. (2007). Chemical and near-infrared determination of moisture, fat and protein in tuna fishes. Food Chemistry, 102(3), 669-675.

[18] Kim, S. H., Park, J. H., Kwon, J. S., Cho, J. G., Park, K. G., Park, C. H., Yoo, J. J., Atala, A., Choi, H. S., Kim, M. S., and Lee, S. J. (2020) NIR fluorescence for monitoring in vivo scaffold degradation along with stem cell tracking in bone tissue engineering. Biomaterials 258, 120267.

[19] Kimiya, T., Sivertsen, A. H., & Heia, K. (2013). VIS/NIR spectroscopy for non-destructive freshness assessment of Atlantic salmon (Salmo salar L.) fillets. Journal of Food Engineering, 116(3), 758-764.

[20] Lalabadi, H. M., Sadeghi, M., and Mireei, S. A. (2020) Fish freshness categorization from eyes and gills color features using multi-class artificial neural network and support vector machines. Aquacultural Engineering 90, 102076.

[21] Leghríb, R., Aantri, Y., Sanchez, J. B., Berger, F., and Kaaya, A. (2020) Assessing the freshness of Agadir blue fish using a metal oxide gas sensing array. Materials Today: Proceedings 22, 1–5.

[22] Li, X., Zhang, L., Zhang, Y., Wang, D., Wang, X., Yu, L., Zhang, W., and Li, P. (2020) Review of NIR spectroscopy methods for nondestructive quality analysis of oilseeds and edible oils. Trends in Food Science & Technology 101, 172–181.

[23] Moriarity, R. J., Libera, E. N., and Tsuji, L. J. (2020) Subsistence fishing in the Eeyou Istchee (James Bay, Quebec, Canada): A regional investigation of fish consumption as a route of exposure to methylmercury. Chemosphere 258, 127413.

[24] Nordey, T., Joas, J., Davrieux, F., Chillet, M., and Léchaudel, M. (2017) Robust NIRS models for non-destructive prediction of mango internal quality. Scientia Horticulturae 216, 51–57.

[25] Ocaña-Higuera, V., Maeda-Martínez, A., Marquez-Rios, E., Canizales-Rodriguez, D., Castillo-Yáñez, F., Ruiz-Bustos, E., Graciano-Verdugo, A., and Plascencia-Jatomea, M. (2011) Freshness assessment of raw fish stored in ice by biochemical, chemical and physical methods. Food Chemistry 125, 49–54.

[26] of inorganic elements in animal feeds by NIRS technology and a fibre-optic probe, Talanta 69 (2006) 711–715.

[27] Pierna, J. A. F., Vermeulen, P., Eylenbosch, D., Burger, J., Bodson, B., Dardenne, P., and Baeten, V. (2020) Chemometrics in NIR Hyperspectral Imaging: Theory and Applications in the Agricultural Crops and Products Sector. Comprehensive Chemometrics 361–379.

[28] Prabhakar, P. K., Vatsa, S., Srivastav, P. P., and Pathak, S. S. (2020) A comprehensive review on
freshness of fish and assessment: Analytical methods and recent innovations. Food Research International 133, 109157.

[29] Qu, J.-H., Liu, D., Cheng, J.-H., Sun, D.-W., Ma, J., Pu, H., and Zeng, X.-A. (2015) Applications of Near-infrared Spectroscopy in Food Safety Evaluation and Control: A Review of Recent Advances. Critical Reviews in Food Science and Nutrition 55, 1939–1954.

[30] Rahman, A., Kondo, N., Ogawa, Y., Suzuki, T., Shirataki, Y., and Wakita, Y. (2015) Prediction of K value for fish flesh based on ultraviolet–visible spectroscopy of fish eye fluid using partial least squares regression. Computers and Electronics in Agriculture 117, 149–153.

[31] Reboucas, M. V., Santos, J. B. D., Domingos, D., and Massa, A. R. C. (2016) Near-infrared spectroscopic prediction of chemical composition of a series of petrochemical process streams for aromatics production. Vibrational Spectroscopy 52, 97–102.

[32] Reis, M. M., Martínez, E., Saitua, E., Rodríguez, R., Pérez, I., & Olabarrieta, I. (2015). Non-invasive differentiation between fresh and frozen/thawed tuna fillets using near infrared spectroscopy (Vis-NIRS). LWT, 78, 129-137.

[33] Sun, X., Yuan, H., Song, C., Li, X., Hu, A., Yu, S., and Ren, Z. (2019) A novel drying-free identification method of cashmere textiles by NIR spectroscopy combined with an adaptive representation learning classification method. Microchemical Journal 149, 104018.

[34] Taheri-Garavand, A., Fatahi, S., Banan, A., and Makino, Y. (2019) Real-time nondestructive monitoring of Common Carp Fish freshness using robust vision-based intelligent modeling approaches. Computers and Electronics in Agriculture 159, 16–27.

[35] Tito, N. B., Rodemann, T., & Powell, S. M. (2012). Use of near infrared spectroscopy to predict microbial numbers on Atlantic salmon. Food Microbiology, 32(2), 431-436.

[36] Trocino, A., Xiccato, G., Majolini, D., Tazzoli, M., Bertotto, D., Pascoli, F., and Palazzi, R. (2012) Assessing the quality of organic and conventionally-farmed European sea bass (Dicentrarchus labrax). Food Chemistry 131, 427–433.

[37] Walsh, K. B., Blasco, J., Zude-Sasse, M., and Sun, X. (2020) Visible-NIR ‘point’ spectroscopy in postharvest fruit and vegetable assessment: The science behind three decades of commercial use. Postharvest Biology and Technology 168, 111246.

[38] Wang, S., Dong, D., Li, P., Hua, X., Zheng, N., Sun, S., Hou, S., An, Q., Li, P., Li, Y., Song, X., and Li, X. (2020) Mercury concentration and fatty acid composition in muscle tissue of marine fish species harvested from Liaodong Gulf: An intelligence quotient and coronary heart disease risk assessment. Science of The Total Environment 726, 138586.

[39] Xiong, H. L. W. X. (2017). Classification of freshwater fish species by linear discriminant analysis based on near infrared reflectance spectroscopy. Journal of Near Infrared Spectroscopy, 25(1), 54-62.

[40] Zareef, M., Chen, Q., Hassan, M. M., Arslan, M., Hashim, M. M., Ahmad, W., Kutsanedzie, F. Y. H., and Agyekum, A. A. (2020) An Overview on the Applications of Typical Non-linear Algorithms Coupled With NIR Spectroscopy in Food Analysis. Food Engineering Reviews 12, 173–190.

[41] Zhang, C., Wu, W., Zhou, L., Cheng, H., Ye, X., and He, Y. (2020) Developing deep learning based regression approaches for determination of chemical compositions in dry black goji berries (Lycium ruthenicum Murr.) using near-infrared hyperspectral imaging. Food Chemistry 319, 126536.

[42] Zhou, J., Wu, X., Chen, Z., You, J., & Xiong, S. (2019). Evaluation of freshness in freshwater fish based on near infrared reflectance spectroscopy and chemometrics. LWT, 106, 145-150.

[43] Zhou, J., Wu, X., You, J., & Xiong, S. (2020). Rapid determination of the textural properties of silver carp (Hypophthalmichthys molitrix) using near-infrared reflectance spectroscopy and chemometrics. LWT, 129, 109545.