



Determining quality parameters of fish oils by means of ^1H nuclear magnetic resonance, mid-infrared, and near-infrared spectroscopy in combination with multivariate statistics



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ARTICLE INFO

Keywords:

Nuclear magnetic resonance spectroscopy
Infrared spectroscopy
Artificial neural networks
Peroxide value
Anisidine value
Data fusion

ABSTRACT

Fish oil is becoming increasingly popular as a dietary supplement as well as for its use in animal feed, which is mainly due to its high contents of the health promoting omega-3 fatty acids. However, these polyunsaturated fatty acids are highly susceptible to oxidation, which results in a decrease of the fish oil quality. This study investigated the potential of ^1H NMR, FT-MIR, and FT-NIR spectroscopy in the quality assessment of fish oils. A total of 84 different fish oils, of which 22 were subjected to accelerated storage with varying temperature and light exposure, were used to develop models for predicting the peroxide value (PV), the anisidine value (AnV), and the acid value (AV). Predictions were based on comprehensive spectroscopic data in combination with *Artificial Neural Networks* (ANN) as well as *Partial Least Squares Regression* (PLSR). The best ANN model for PV was obtained from NMR data, with a predictive coefficient of determination (Q^2) of 0.961 and a *Root Mean Square Error of Prediction* (RMSEP) of $1.5 \text{ meq O}_2 \text{ kg}^{-1}$. The combined MIR/NIR data provided the most reliable ANN model for AnV ($Q^2 = 0.993$; RMSEP = 0.74). For AV, the ANN model based on the MIR data yielded a Q^2 of 0.988 and an RMSEP of $0.43 \text{ mg NaOH g}^{-1}$. In most cases, the accuracy of the ANN models was superior to the respective PLSR models. Variable selection and data dimensionality reduction turned out to improve the performance of the ANN models in some cases. The application of ^1H NMR, FT-MIR, and FT-NIR spectroscopy in combination with ANN can be considered very promising for a rapid, reliable, and sustainable assessment of fish oil quality.

1. Introduction

Fish oil contains high amounts of omega-3 fatty acids. These polyunsaturated fatty acids, in particular the long-chain docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA), are (semi-)essential nutrients that have been proven to contribute to the prevention of cardiovascular diseases and improved brain development (Cottin, Sanders, & Hall, 2011; Lauritzen et al., 2016). This is why they are often included in dietary supplements and incorporated in animal feed. However, due to their high level of unsaturation, DHA and EPA are susceptible to lipid

oxidation (EFSA BIOHAZ, 2010; Xu, Riccioli, & Sun, 2015). Several wet-chemical methods are available to evaluate fish oil quality and degree of oxidation. The peroxide value (PV) and the anisidine value (AnV) are markers of lipid oxidation, while the acid value (AV) indicates the degree of lipid hydrolysis. Free fatty acids have a higher susceptibility to oxidation. The determination of these quality parameters according to the reference methods is time-, work-, and solvent-consuming and requires high sample amounts (Cheng et al., 2013; EFSA BIOHAZ, 2010; Skiera, 2013; Xu et al., 2015).

Spectroscopic techniques, such as ^1H NMR, MIR, and NIR

Abbreviations: AV, acid value; ANN, Artificial Neural Networks; AnV, anisidine value; ATR, attenuated total reflectance; CARS, Competitive Adaptive Reweighted Sampling; DGF, German Society for Fat Science; DHA, docosahexaenoic acid; DTGS, deuterated triglycine sulfate; EPA, eicosapentaenoic acid; MAE, average mean square error; MC-UVE, Monte Carlo-Uninformative Variable Elimination; MLR, Multiple Linear Regression; MW-PLSR, Moving window Partial Least Squares Regression; NIPALS, Non-linear Iterative Partial Least Squares; SEP, Standard Error of Prediction; SPA, Successive Projections Algorithm; PLSR, Partial Least Squares Regression; PV, peroxide value; RMSEC, Root Mean Square Error of Calibration; RMSECV, Root Mean Square Error of Cross-Validation; RMSEP, Root Mean Square Error of Prediction; RPD, Ratio of Performance to Deviation; RPROP, Resilient Backpropagation; Std. BP, Standard Backpropagation; TBARS, thiobarbituric acid reactive substances; TMS, tetramethylsilane

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<https://doi.org/10.1016/j.foodres.2017.12.041>

Received 15 August 2017; Received in revised form 7 November 2017; Accepted 14 December 2017

Available online 16 December 2017

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spectroscopy, have gained increasing importance in the analysis of edible oils and animal fats in recent years. They are rapid and non-destructive methods that can provide comprehensive information in a single analysis, including initially non-targeted information. They do not need any or only minor sample preparation, require only small sample amounts, and may be automated (Cheng et al., 2013; Guillén & Ruiz, 2001; Skiera, 2013; Xu et al., 2015). They have been identified as promising tools in overcoming modern analytical challenges, such as the detection of food fraud and medicinal diagnostics (Li, Vosegaard, & Guo, 2017; Ropodi, Panagou, & Nychas, 2016). In parallel to the continuous advancement of spectroscopic instrumentation, the science of chemometrics has emerged, which is the extraction of information from chemical systems by mathematical and statistical methods. Chemometrics open up new possibilities for the processing and interpretation of the vast amounts of data acquired by modern instruments (Ropodi et al., 2016).

In the field of fish oil analysis, ^1H NMR, MIR, and NIR spectroscopy have often been used to determine fatty acid profiles (Azizian, Kramer, Ehler, & Curtis, 2010; Igarashi et al., 2000; Wu et al., 2014), although gas chromatography remains the standard method for this purpose (DGF, 2012). Some studies also determined the oxidation level or the degree of lipid hydrolysis (Cozzolino, Murray, Chree, & Scaife, 2005; Klaypradit, Kerdpiboon, & Singh, 2011; Poon, 2009; Skiera, Steliopoulos, Kuballa, Holzgrabe, & Diehl, 2012a; Zhang & Lee, 1997). As far as the analysis of other edible oils is concerned, MIR and NIR spectroscopy are frequently applied in combination with multivariate statistics (Armenta, Garrigues, & de la Guardia, 2007; Pizarro, Esteban-Díez, Rodríguez-Tecedor, & González-Sáiz, 2013; Rao et al., 2009; Yu, Du, van de Voort, Yue, & Li, 2009), i.e., *Partial Least Squares Regression* (PLSR) in most cases. Three of those studies used *Artificial Neural Networks* (ANN) to determine lipid oxidation parameters (Allouche, López, Beltrán Maza, & Jiménez Márquez, 2015; Klaypradit et al., 2011; Lazim et al., 2013) of which one was not only based on NIR data, but also on technological variables (Allouche et al., 2015). Klaypradit et al. (2011) determined the PV and the AnV of menhaden oil using attenuated total reflectance (ATR)-FT-MIR spectroscopy and Lazim et al. (2013) modelled the PV of palm oil by FT-MIR spectroscopy. MIR/NIR data fusion has been found to improve prediction performance in contexts such as authentication (Borràs et al., 2015).

Although there are a number of studies that investigated lipid oxidation in edible oils by ^1H NMR spectroscopy (Guillén & Ruiz, 2001; Martínez-Yusta, Goicoechea, & Guillén, 2014; Skiera, Steliopoulos, Kuballa, Holzgrabe, & Diehl, 2012b), only one described the use of ^1H NMR spectroscopy to predict lipid oxidation parameters of edible oils using multivariate statistics (Giese, Winkelmann, Rohn, & Fritsche, 2017). Giese et al. (2017) created a PLSR model for the PV, the AnV, and the AV of fish oil. Skiera et al. (2012a–c) determined the PV, the AnV, and the AV of various edible oils by integrating specific signals in the ^1H NMR spectra before applying *Deming Regression*. In those studies, the traditional wet-chemical and NMR methods were compared based on 95% confidence intervals and the relative sensitivity according to Mandel (1964). The authors concluded that both methods exhibited similar analytical performance. They found considerable deviations for black seed oils, pumpkin seed oils, and olive oils when determining PV.

The present study aimed to elucidate the potential of ^1H NMR, FT-MIR, and FT-NIR spectroscopy for the quality assessment of fish oils. In particular, the objectives were a) to generate ANN models for the prediction of PV, AnV, and AV from the spectral data; b) to identify the most suitable data preprocessing methods including spectral pretreatment, variable selection, and data dimensionality reduction; and c) to compare the accuracy of the ANN models to models generated by PLSR and to the wet-chemical reference methods for the determination of PV, AnV, and AV.

2. Materials and methods

2.1. Fish oils

A total of 84 different fish oils were used in this study including both refined and unrefined oils. In most cases, the fish species was not specified. 23 fish oils were provided by Lipromar GmbH, Cuxhaven, Germany. All the samples were analyzed by ^1H NMR, MIR, and NIR spectroscopy as well as by the wet-chemical reference methods. In order to expand the calibration range, 22 of the Lipromar oils were subjected to accelerated storage and analyzed periodically. Table 1 gives an overview of the samples and the conditions applied in the storage trials. Table S1 in the supplementary material characterizes the samples with regard to PV, AnV, and AV.

2.2. Storage trials

22 fish oil samples (approx. 40 mL) bottled in closed 50 mL polypropylene centrifugation tubes were subjected to storage trials and analyzed periodically by ^1H NMR, FT-MIR, and FT-NIR spectroscopy as well as the wet-chemical methods for determining PV, AnV, and AV. When samples were withdrawn during the storage period, they were either immediately analyzed or frozen at $-22\text{ }^\circ\text{C}$ until analysis.

2.3. Chemicals

2,2,4-trimethylpentane, diethyl ether (> 99.8%), starch (from potato), and thymolphthalein were obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. Chloroform- d_1 (99.8%, 0.03% TMS) was purchased from Deutero GmbH, Kastellaun, Germany. Acetic acid (100%), potassium iodate, tween 60, and sodium thiosulfate standard solution (0.01 mol L^{-1}) were obtained from Merck KGaA, Darmstadt, Germany. Ethanol, sodium hydroxide standard solution (0.1 mol L^{-1}), and hydrochloric acid (4 mol L^{-1}) were purchased from VWR International, Darmstadt, Germany. Potassium iodide (pure) was obtained from AppliChem GmbH, Darmstadt, Germany, and *p*-anisidine (99%) from Alfa Aesar GmbH & Co. KG, Karlsruhe, Germany.

2.4. Peroxide value

PV was determined according to Wheeler with visual endpoint determination using the official DGF standard method C-VI 6a – part 1 (05) (DGF, 2012). A Dosimat 775 (Deutsche Metrohm GmbH & Co. KG, Filderstadt, Germany) was used for titration. All the samples were analyzed in duplicate.

2.5. Anisidine value

AnV was determined according to the DGF method C-VI 6e (12) (DGF, 2012). A 60 UV-Vis spectrophotometer (Agilent Technologies, Inc., Santa Clara, CA, USA) was used. All the measurements were carried out in duplicate.

2.6. Acid value

AV was determined according to DIN EN ISO 660:2009 (DIN, 2009) with visual endpoint determination. A Dosimat 775 (Deutsche Metrohm GmbH & Co. KG, Filderstadt, Germany) was used for titration. The samples were measured in duplicate except for five samples where single measurements were carried out due to limited available sample quantities.

2.7. ^1H NMR spectroscopy

The ^1H NMR measurements were carried out as described by Giese et al. (2017). $140 \pm 2\text{ mg}$ fish oil were weighed into a 2 mL reaction

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