Food Chemistry 239 (2018) 865–871

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Determination of fatty acids and lipid classes in salmon oil by near infrared spectroscopy

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ARTICLE INFO

Article history:
Received 15 March 2017
Received in revised form 14 June 2017
Accepted 29 June 2017
Available online 30 June 2017

Keywords:
Near infrared spectroscopy
Partial least square
Fatty acids
Lipid class
Omega-3
Omega-6

ABSTRACT

Near-infrared (NIR) spectroscopy was evaluated as a rapid method for the determination of oleic, palmitic, linoleic and linolenic acids as well as omega-3, omega-6, and to predict polyunsaturated, monounsaturated and saturated fatty acids, together with triacylglycerides, diglycerides, free fatty acids and ergosterol in salmon oil. To do it, Partial Least Squares (PLS) regression models were applied to correlate NIR spectra with aforementioned fatty acids and lipid classes. Results obtained were validated in front of reference procedures based on high performance thin layer and gas chromatography. PLS-NIR has a good predictive capability with relative root mean square error of prediction (RRMSEP) values below or equal to 1.8% and provides rapid analysis without the use of any chemicals making it an environmentally friendly methodology.

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1. Introduction

The determination of lipids and evaluation of fatty acids composition in foods is of a great importance for human health. Fish and shellfish are important sources of long-chain omega-3 polyunsaturated fatty acids (LCn-3PUFAs). A high intake of LCn-3PUFAs, produces beneficial effects in the human health reducing the impact of cardiovascular diseases, diabetes, cancer, obesity, autoimmune diseases, rheumatoid arthritis, asthma and depression (Lavie, Milani, Mehra, & Ventura, 2009; Simopoulos, 2002; Patterson, Wall, Fitzgerald, Ross, & Stanton, 2012).

The most important LCn-3PUFAs are eicosapentaenoic acid (EPA; C20:5n-3) and docosahexaenoioc acid (DHA; C22:6n-3) (Calder & Yaqoob, 2009) although docosapentaenoic acid (DPA; C22:5n-3) can be also important (Kaur, Cameron-Smith, Garg, & Sinclair, 2011), being α-linolenic acid (ALA; C18:3n-3) the precursor of EPA and DHA (Kim, Nam, Sik, Hayes, & Lee, 2014). On the other hand high intakes of long-chain omega-6 polyunsaturated fatty acids (LCn-6PUFAs) have opposite properties than those of LCn-3PUFAs (Simopoulos, 2002) (Patterson et al., 2012), being Linoleic acid (LA; C18:2n-6) the precursor of arachidonic acid (AA; 20:4n-6) (Kim et al., 2014). OA is the major monounsaturated fatty acid (MUFA) present in salmon oil and belongs to the family of omega-9 fatty acids, being correlated the high MUFA content of fish oil with cardioprotective effects (Covaset al., 2006). On the contrary, Wu, Song, Xu, Zhang, and Zou (2007) demonstrated that palmitic acid (PA; C16:0) and OA affect cholesterol and fatty acid metabolism in an opposite manner than oleic acid. SFAs affect involved factors in cholesterol metabolism (Mensink, 2013). For the aforementioned reasons, a deep knowledge of the presence and concentration of lipids in fish oil is mandatory.

Salmon oil contains triglycerides (TAGs) as major components at a level of 75%, diglycerides (DAGs) at 17% and monoglycerides (MAGs) as minor components. Additionally there are free fatty acids (FFAs) and ergosterol at levels of 6% and 2% of total lipids, respectively.

On the other hand, predominant fatty acids present in salmon oil are OA, LA, PA and ALA with values around 39%, 17%, 11% and 5%, respectively. In general, total SFAs concern 20% of extracted oil while MUFAs and PUFAs are around 44% and 34%, respectively (Cascant et al., 2017).

Chromatography is the main technique commonly employed to determine fatty acids and lipids in fish oil samples. Thin-layer chromatography (TLC) and its refined version high-performance thin-layer chromatography (HPTLC) are frequently used in numerous separations, identification of the individual lipids and their quantitative determinations in foods (Fuchs, Süß, Teuber, Eibisch, & Schiller, 2011). HPTLC technique is a sequential procedure that could not be fully automatized. Its use in lipid analysis involves

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http://dx.doi.org/10.1016/j.foodchem.2017.06.158
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the following steps: i) sample and standard preparation with chloroform solvent, ii) TLC plate conditioning, where silica gel plates are washed with a mixture chloroform/methanol and dried at 110 °C for 60 min, iii) application of sample and standards in TLC plate, iv) mobile phase preparation, which depends of lipid class determination, due to their differences in polarity of lipids, v) immersion of the stationary phase plate in mobile phase, vi) automatic developing distance, vii) final drying, viii) visualisation and, ix) quantitative evaluation of the generated densitometric data. In addition to time consuming, a possible lipid oxidation could be due based on TLC plate exposition to atmospheric oxygen and, the limitation of the preparative applications in TLC plate (Fuchs et al., 2011). On the other hand, fatty acids can be measured by using gas chromatography (GC) (Zhang, Wang, & Liu, 2015; Laakso & Hiltunen, 2002). Prior to the analysis by GC fatty acids are liberated from glycerides and converted to their methyl esters (FAMEs) which are more volatile than FFAs (Laakso & Hiltunen, 2002; Morrison & Smith, 1964). GC methods for fatty acids and lipids require several manipulative steps with high time and energy consume, which reduces their applicability for quality control in a sustainable way.

Fourier Transform-Infrared (FT-IR) spectroscopy in the middle region and Raman measurements have been used to predict the amount of omega-3 and omega-6 in melted fat from pork adipose tissue (Olsen, Rukke, Egelandsdal, & Isaksson, 2008). Floriano Ribeiro, Peralta-Zamora, Pereira Ramos, and Pereira-Netto (2013) used mid and near infrared reflectance spectroscopy, with multivariate calibration, to predict LA and ALA content in flax seeds and flax seed flours. Cozzolino, Murray, Chree, and Scaife (2005) employed near infrared (NIR) spectroscopy with partial least squares (PLS) for the determination of FFA in fish oil and, Bekhit, Grung, and Mjøs (2014) investigated the potential of FT-IR, NIR and Raman spectroscopy, with PLS regression models to predict concentrations of EPA, DHA and omega-3 in fish oil supplements. Karlsdottir, Arason, Kristinsson, and Sveinsdottir (2014) evaluated the feasibility of using NIR spectroscopy to determine lipid composition of two lean fish species, hoki and saithe, namely total lipid content, phospholipid, PUFAs and MUFAs.

NIR spectroscopy, combined with chemometric tools, can provide an alternative to the chromatography methods to determine fatty acids, fatty acid families and lipid classes. NIR measurements are fast and non-destructive, they do not require any sample pretreatment step, nor the use of reagents and solvents, and not generates residues, making it an environmentally friendly methodologies. Moreover, NIR also allows the simultaneous determination of several analytes or parameters in a same sample from a single and direct measurement. Additionally, samples can be measured inside closed glass vials, thus avoiding sample alteration and cross-contamination. On concluding, NIR spectroscopy can be a good alternative to traditional methods due to their applicability for quality control in a sustainable way.

The aim of the present study has been to evaluate NIR technique in combination with partial least square for the simultaneous determination of i) fatty acids as OA, PA, ALA, LA, ii) fatty acid families as omega-3, omega-6, PUFAs, MUFAs and SFAs and, iii) lipid classes as TAGs, DAGS, FFAs and ergosterol in salmon oil. PLS-NIR regression models were built and assayed to evaluate the aforementioned parameters in oil extracts of salmon fish, being compared the predicted values with reference data obtained by HPTLC and CG-FID.

2. Experimental

2.1. Materials, samples and reagents

n-Hexane (HPLC grade), methanol, sulfuric acid, sodium chloride, chloroform, methyl acetate, acetic acid, diethyl ether and potassium chloride were of analytical grade and were supplied by VWR International (Darmstadt, Germany).

Atlantic Salmon (*Salmon salar*) samples were bought at the local market and were stored at −20 °C. Samples were lyophilized, pulverized and stored in hermetic bags until extraction. Twenty-five grams of lyophilized salmon samples were extracted under reflux during 8 h with 300 mL of solvent. After this time, the content of the distillation flask was evaporated under reduced pressure by using a rotary evaporator (Cascantet al., 2017). A total of 54 salmon oil samples and mixtures of them were used in this study.

2.2. Reference procedure

2.2.1. High Performance Thin Layer Chromatography (HPTLC)

Lipid classes were obtained by using a High Performance Thin Layer Chromatography (HPTLC) from CAMAG (Muttenz, Switzerland). Lipids were detected and quantified using a CAMAG 3 TLC scanning densitometer with identification of the classes against known polar and neutral lipid standards. Lipid classes were identified and quantified using a calibration curve of each target molecule by using winCATS-Planar Chromatography Manager (version 1.3.3; CAMAG) for retention factor (Rf) and peak area of the calculations. Values obtained were expressed as percentage of lipid class in total lipids and used as reference for PLS-NIR models building (Cascant et al., 2017; Breil, Meullemiestre, Vian, & Chemat, 2016).

Lipid extracts were loaded as spots onto 20 × 10 cm silica gel 60 F254 HP-TLC plates from Merck (Darmstadt, Germany) using an ATS 5 automatic TLC sampler. HPTLC plates of silica gel 60 F254 were previously washed with a mixture of chloroform/methanol (2:1, v/v), followed by drying at 110 °C for 60 min on the TLC Plate Heater (CAMAG, Muttenz, Switzerland). A mixture of methyl acet ate/isopropanol/chloroform/methanol/KCl (0.25% solution) in a ratio of 25:25:25:10:9 (*v*/*v*/*v*/*v*/*v*) was used as eluent to separate polar lipids running to a height of 7 cm from the origin. On another plate, a mixture of *n*-hexane/diethyl ether/glacial acetic acid, in a ratio of 70:30:2 (*v*/*v*/*v*), was used till a height of 7 cm from the origin to separate neutral lipids. After drying, the plate was dipped for 2 s in a modified (10 mg of primuline, 160 mL of acetone, 40 mL of water), then scanned using a TLC Scanner 3 with WinCATs software (CAMAG).

Standard solutions were prepared using chloroform as solvent at concentration levels of 0.2 mg mL^{-1} of lipid in each solution. For samples, approximately 1 mg mL^{-1} of pure oil was obtained in chloroform. All solutions were stored in the dark at −20 °C until their analysis.

2.2.2. Gas chromatography

Samples were prepared from extracted oils using acid-catalyzed *trans*-methylation (Morrison & Smith, 1964). 400 µL of triheptadecanoin (C17:0 TAG, from Sigma Aldrich) 2 mg mL^{-1} in hexane solution was used as internal standard. 1 ml of methanolic sulfuric acid (5% v/v) was added to approximately 20 mg of extracted oil and the mixture was heated at 85 °C for 90 min. When the solution reached the room temperature, 1.5 ml of sodium chloride (0.9%) and 1 ml of *n*-hexane were added. The flask was shaken vigorously during 30 s before centrifugation at 4000 rpm for 2 min and the organic layer was transferred to a GC vial before direct injection in the gas chromatograph.

Fatty acid methyl esters were separated, identified and quantified by using a 7820 A gas chromatography (GC) system from Agilent technologies (California, USA) using flame ionization detector (GC-FID) and autosampler. GC was performed by a BD-EN14103 capillary column (30 m × 0.32 mm × 0.25 µm) using helium as carrier gas at the speed of 33 cm s^{-1}. 2 µl of samples were injected in split mode (split ratio: 1:20) a 250 °C. The oven temperature program was operated as follows: initial temperature at 50 °C for

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