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Application of factorial design in optimization of anion exchange resin based methylation of vegetable oil and fats

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ABSTRACT

A simple, rapid and fairly selective method for the preparation of fatty acid methyl esters (FAMEs) based on anion exchange resin Amberlite IRA-904 catalyzed transesterification of vegetable oil/fat with iodomethane has been described. The vegetable oil and animal fats used were sunflower oil, palm oil, vanaspati (hydrogenated vegetable oil), olive oil, tallow and butter. A Plackett–Burman factorial experimental design was used as a multivariate strategy for the evaluation of the effects of varying several variables at once. The effects of five different variables amount of resin, strength of sodium hydroxide, volume of iodomethane, heating time and temperature of thermostatic water bath, on the yield of fatty acid methyl esters (FAMEs) have been investigated. From these studies, certain variable showed up as significant, and they were optimized by a using 2^3+star central composite design, which involved 16 experiments. The best conditions for transesterification reaction were as follows: amount of resin 2 g, strength of sodium hydroxide 0.25 N, volume of iodomethane 400 µl, heating time 2 min at 70 °C. A standard IUPAC method was used to prepare FAMEs from vegetable oil/fats for comparative purpose. Finally samples of oil/fat obtained from both methods were analysed by Gas liquid chromatography. Analytical results for the FAMEs by resin based proposed method, and conventional IUPAC method showed a good agreement, thus indicating the possibility of using Amberlite IRA-904 based transesterification instead of intensive treatments inherent with the conventional time-consuming methods.

Industrial relevance: Fatty acids are the main components of edible oil and fats, therefore determination of fatty acid composition is so far one of the important parameters for quality evaluation and nutritional value determination of edible oil and fats. The analysis of fatty acid is usually carried out by Gas liquid chromatography (GLC) after conversion of volatile fatty acid methyl esters (FAME) although other ester may be prepared for specific purpose.

The endeavor of present work was to improve the FAMEs preparation method, proposing the development of anion exchange resin Amberlite IRA-904 based transesterification of edible oil/fat with iodomethane as alkylating reagent. The present method besides being rapid and reproducible avoids the use of classical saponification, washing of esters and solvent extraction step.

1. Introduction

The analysis of food components has recently acquired special importance due to strict quality control requirements, concern for correct nutrition habits and greater knowledge of food components and associated diseases. In these perspectives, the accurate characterization of the fatty acid composition of oils and fats is mandatory (Eras, Dolcet, Ferran, & Canela, 2004). The analysis of fatty acid is usually carried out by Gas liquid chromatography (GLC) after conversion of volatile fatty acid methyl esters (FAME) although other ester may be prepared for specific purpose (Christie, 1989).

Previous methods for the preparation of FAMEs include alkaline catalysis (Destaillats & Angers, 2002; Ichihara, Shibahara, Yamamoto, & Nakayama, 1996), acid catalysis (Eder, 1995; Seppänen-Laakso, Laakso, & Hiltunen, 2002) and combined catalysis (Liu, 1994; Stransky & Jursik, 1996; Carrapiso & Garcia, 2000; Eras, Montañes, Ferran, & Canela, 2001). Potassium hydroxide, sodium hydroxide and sodium methoxide are the most common catalyst used in basic catalysis, whereas among acidic catalysts HCl, H_2SO_4 and BF_3 are commonly employed. HCl has been considered a mild and useful derivatization reagent (Stoffel, Chu, & Ahrens, 1959) due to almost quantitative yield but its transmethylation capacity is low, thus requiring reaction times

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more than 30 min. In addition to constraint, the use of H_2SO_4 has been reported to lead the decomposition of polyunsaturated fatty acids (PUFA) under certain conditions (Christie, 1989). BF_3 reveals a high methylation power, hence requiring a short time period to react. However some reports (Brondz, 2002; Rosenfeld, 2002) have claimed that BF_3 leads to irreversible damage of GC column, because traces of this compound migrate to the organic extracting phase.

Basic catalysis is faster than acid catalysis, however alkali catalyst reactions require strict anhydrous conditions, which may be difficult to fulfill in case of biological samples. Moreover, alkaline counterparts are unable to methylate free fatty acids. Potassium hydroxide and boron triflouride, both in methanol can be used in combined catalysis, which involves a two-step process. A second acid catalysis step avoids this problem but increases sample preparation time (Jordi, Farnando, Javier, & Ramon, 2001). The disadvantage in using homogeneous catalyst is their miscibility in the reaction medium, which causes separation problems. Moreover, at higher acid catalyst concentrations, equipment corrosion and secondary reactions can occur (Rosenfeld, 2002; Wood, 1993). Hence, the use of heterogeneous catalyst such as zeolites and ion-exchange resins has clear advantages since they are noncorrosive and are easy to separate from the reaction mixture; furthermore, no washing of the ester is required, presenting fewer disposal problems (Sasidharan & Kumar, 2004; Jiménez, Garvin, & Costa-Lopez, 2002; Suppes, Dasari, Doskocil, Mankidy, & Goff, 2004).

Lately Bondioli (2004) has reported that the cationic resins are active at low temperatures and owing to their molecular sieve action, produce few by products and may be highly selective. More recently Simone, Elizabeth, Regina, Jorge, and Marcelli (2005) have described transesterification of Brazilian vegetable oils with methanol over ion-exchange resins, but the method requires long reaction time with extraction and washing steps. Several methods of optimization can be used for the preparation of FAMEs from different edible oil/fats, but some methods are time-consuming: for instance, the study of each variable separately. Procedures for optimization of factors by multivariate techniques have been encouraged, as they are faster, more economical and effective, and allow more than one variable to be optimized simultaneously (Ferreira, Bezerra, Dos Santos, & Neto, 2003; Dos Santos, Dos Santos, & Ferreira, 2003).

Among the different groups of designs, Plackett–Burman designs, introduced in 1946 by Plackett and Burman (1946), allow us to discover the most significant variables for a certain system with only few experiments. They are used as a screening method in order to select the variables that have influence on a system but they do not give the optimum value for each variable. In order to obtain the optimum values for each variable involved in a certain system, central composite designs are the most widely used design framework (Olivero, Nocerino, & Deming, 1995). These design structures are based on full two-level factorial design by center point replication and inclusion of an axial portion (Gardiner, & Gettinby, 1998). The optimization procedures based on these approaches are nowadays being applied to optimize some sample pre-treatments and operating conditions for some analytical techniques (Lavilla, Perez-Cid, & Bendicho, 1998; Lespes, Seby, Sarrandin, & Potin-Gautier, 1994; Koch, Harrington, Reimer, & Cullen, 1997; Heyden et al., 1995).

The aim of present work was to improve the FAMEs preparation, proposing the development of anion exchange Amberlite IRA-904 transesterification of edible oil/fat with iodomethane as alkylating reagent. The present method besides being rapid and reproducible avoids the use of classical saponification, washing of esters and solvent extraction step. The influence of variables on the yield of methyl esters was studied by factorial design method based on Plakett–Burman model and Central composite design was employed to obtain optimum values.

2. Experimental

2.1. Chemical and reagents

Amberlite IRA-904 (anionic Cl^- form) 16–50mesh size, hexane, iodomethane, potassium hydroxide and methanol were purchased from Fluka (Sigma-Aldrich, Madrid, Spain). FAMEm were purchased from Sigma Aldrich Co. (Seelze, Germany); conjugated linoleic acid (CLA *cis-9*, *trans-11*) was purchased from Matreya, Biotrend, Köln, Germany.

2.2. Oil/fat samples

Sunflower oil and butter samples were purchased from local retail store, while palm oil, vanaspati (blend of palm oil with sunflower/cotton seed oil) and tallow samples were obtained from Wazir Ali Industries private limited Hyderabad (Pakistan). The oil/fat samples were kept under nitrogen atmosphere in refrigerator. They were used without any further purification. Sample of vanaspati was warmed, homogenized, and used directly for the preparation of FAME, while butter oil was recovered by melting samples in acid wash beakers on a hot plate allowing phase separation, overnight at 95–100 °C in an oven.

2.3. Procedures for FAME preparation

Three sub-samples of each oil/fat sample were used for fatty acid composition determination with conventional BF_3–MeOH and proposed Amberlite IRA-904 anion exchange resin method. Each result is the average of triplicate analysis of the samples.

2.3.1. Proposed resin method

For optimization of different variables, amount of resin (0.5–2 g), sodium hydroxide strength (0.05–0.25 N), amount of 1 M iodomethane (100–400 µl) with varying temperature (40–70 °C) and time (2–5 min) were studied.

After optimization of variables 2.0 g of resin was taken in glass column (12 cm long and id 9.5 mm). 10 ml NaOH (0.25 N) was passed through the column to activate the resin, followed by rinsing with 5 ml of double distilled water and diethyl ether respectively. 100 mg of oil/fat sample, dissolved in 5 ml hexane was passed through the column. Treated resin was transferred to flask and mixed with 400 µl (1 M) of iodomethane dissolved in 5 ml hexane, fitted with condenser followed by heating of mixture at 70 °C in a thermostated water bath for 2 min. The resin was filtered off and filtrate was dried over anhydrous sodium sulphate. 1 µl of the filtrate was directly injected to the gas chromatograph. Initially each sample contained 0.5 mg of C-13:0 and C-17:0 (as the triglycerol) as an internal standard. Quantization was done by calculating response factor as earlier described by Golay, Dionisi, Hug, Giuffrida, and Destaillats (2007).

2.3.2. BF_3–MeOH method

Amounts (30 mg) of oil/fat, 1.5 ml of methanol and 1.5 ml of 14% boron trifluoride in MeOH were added to a 15-ml reaction vial equipped with a PTFE-lined cap. The mixture was vortex mixed and heated in a shaking bath at 80 °C for 60 min. It was then cooled and 2.5 ml of water and hexane were added. The mixture was vortex mixed for 15 min and the upper phase containing the FAMEs was recovered and analyzed as described below.

2.4. GC analysis

All FAME samples were analyzed on a Perkin Elmer gas chromatograph, model 8700, fitted with a non bonded biscynopropyl siloxane stationary-phase, polar capillary column SP-2340 (60 m×0.25 mm),