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A modified commercial gas chromatograph for the continuous monitoring of the thermal degradation of sunflower oil and off-line solid phase extraction gas–chromatography–mass spectrometry characterization of released volatiles☆

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ABSTRACT

A homemade flow cell attached to a commercial Gas Chromatograph equipped with a Flame Ionization Detector (FID) has been designed for the continuous monitoring of volatile compounds released during heating edible oils. Analytical parameters such as mass of sample, temperature and flow rates have been optimized and the obtained results have been compared with the corresponding thermographs from standard TG systems. Results show that under optimum conditions, the profiles of volatiles released upon heating are comparable to the profiles of TG curves, suggesting that the FID based system could be an alternative to TGA. Additionally, volatiles have been retained in a Lichrolut EN® resin, eluted and analyzed by Gas Chromatography–Mass Spectrometry. In this case, forty five compounds have been identified (acids, alcohols, alkanes, aldehydes, ketones and furans) and compared with the FID signals, working both in air or nitrogen atmosphere. It has been concluded that the oxidative thermal degradation is prevented in the presence of a nitrogen atmosphere.

1. Introduction

The degradation or decomposition of edible oils during cooking gives rise to a complex mixture of chemical substances [1–3], which modifies the organoleptic properties of foods, may produce toxic molecules with harmful effects for health [4–7] and may produce unpleasant odours. Most investigations into these processes are based on the characterization of the remaining edible oil in solution. These studies have demonstrated that during the cooking process the decomposition of edible oil (mainly triglycerides) produces different kinds of compounds such as peroxides, aldehydes, acetones, fatty acids and alcohols. Despite the fact that the degradation of edible oils is very complex (the quantity and nature of these compounds depends on several factors such as the kind of edible oil, the frying temperature, the presence of antioxidants and the oxygen exposure to edible oil [1]), numerous methods have been developed to study the process [8–13].

Thermogravimetry (TG) is one of the most widely accepted techniques. Several authors have studied the physico-chemical properties of edible oils related to the oxidation process [14–19] by means of this technique. TG has been proposed as a viable option for use as a quality control measure in the food industry because it allows to evaluate oxidative stability of oils and fats [20]. This parameter is important because oxidation of unsaturated lipids is one of the major causes of the development of off-flavour compounds and the reduction in nutritive value of this kind of products [21] and therefore of the lost of quality.

This characterization is important from the point of view of chemical composition, but it would be convenient to be able to complement TG information with the specific profiles of volatile compounds generated during the cooking process from the points of view of health and food quality. The deterioration of edible oils gives rise to volatile aldehydes, fatty acids and alcohols as secondary oxidation products. In particular, polycyclic aromatic hydrocarbons [4], acrylamide [5] and acrolein [7], are reported to have adverse effects on human health due to their toxic, mutagenic and carcinogenic properties.

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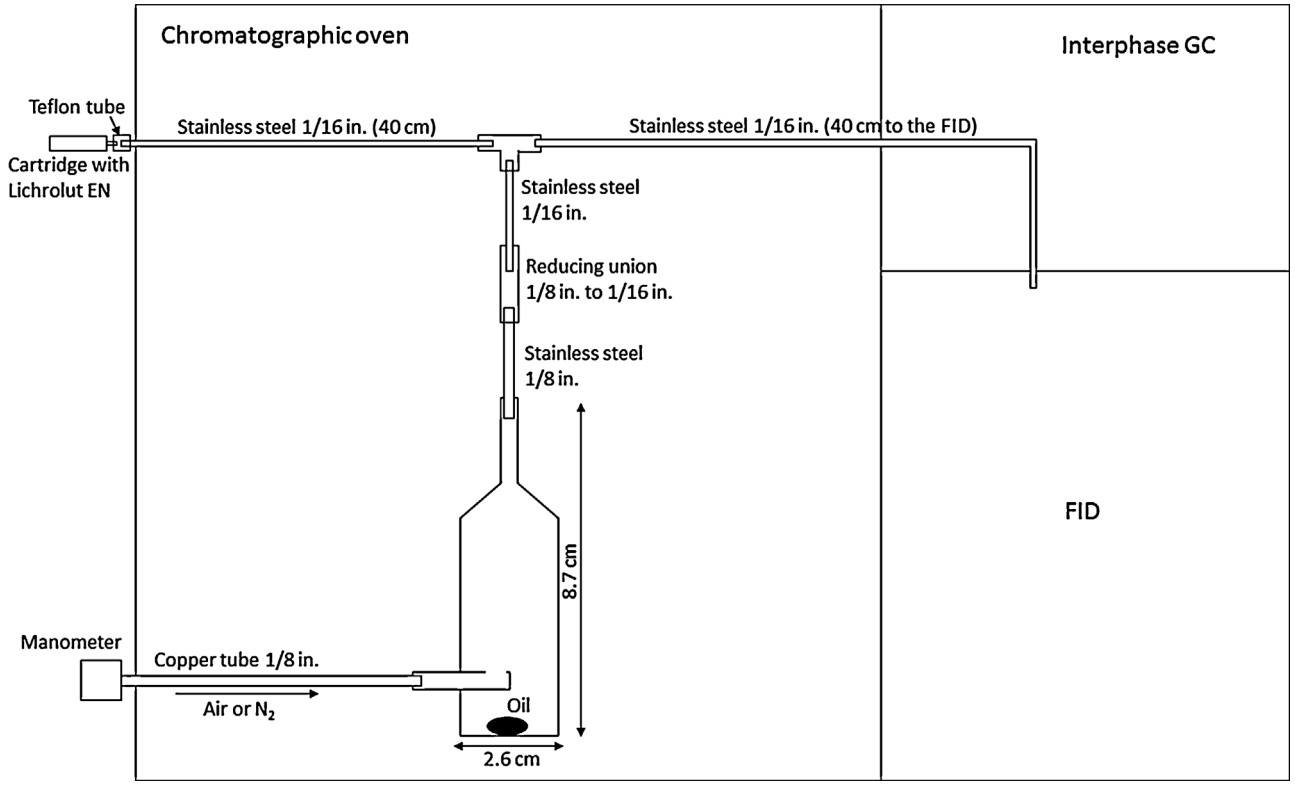

Fig. 1. Schematic representation of chromatograph oven with FID or trapping by SPE.

Most of the techniques used to analyze edible oil decomposition are based on analysis of the liquid phase. Some of them are non-continuum methods requiring different sampling procedures and their results may be difficult to relate to the standard TG plots.

This work describes the development of a new methodology for the continuous monitoring of the thermal degradation of edible oils using a modified Gas Chromatograph-Flame Ionization Detector (GC-FID) equipment which may also be used as a sampling system in order to analyze the released Volatile Organic Compounds (VOCs) by other techniques, such as Gas Chromatography–Mass Spectrometry (GC–MS).

2. Materials and methods

2.1. Materials, chemicals and standards

The high oleic sunflower oil (HOSO) samples examined were purchased from local shops. FAM profile revealed that the major components were oleic (73.1%) and linoleic acid (16.9%). The AV was 0.50 mg KOH/g oil ($s = 0.004$, $n = 6$).

Pentanal ≥ 97%, heptanal ≥ 92%, hexanoic acid ≥ 98%, octanal ≥ 99%, nonanal ≥ 95%, (*E*)-2-octenal ≥ 94%, heptanoic acid ≥ 99%, (*E*)-2-nonenal 97%, octanoic acid ≥ 98%, (*E*)-2-decenal ≥ 95%, (*E*)-2-undecenal ≥ 90%, (*E,E*)-2,4-decadienal 85%, (*E,E*)-2,4-heptadienal 88%, and glyceryl trioleate were supplied by Aldrich-Spain (Madrid, Spain). Hexanal ≥ 97%, (*E*)-2-hexenal ≥ 97%, pentanoic acid ≥ 99%, (*E*)-2-heptenal ≥ 96%, nonanoic acid ≥ 97% and an alkane solution (C8–C20), 40 mg L^{-1} in hexane were obtained from Fluka-Spain (Madrid, Spain).

Dichloromethane and methanol were of chromatographic grade and were purchased from Merck (Darmstadt, Germany).

Lichrolut EN® resins (styrene/divinylbenzene copolymer) were supplied by Merck.

2.2. Instruments

Thermograms were obtained from a SDT 2960, TA Instruments, using 2 or 5 mg of the corresponding sample with heating rates of 8 °C min^{-1} under nitrogen and air atmospheres (150 cm^3 min^{-1}) from 25 to 500 °C.

2.3. Flame Ionization Detector (FID) analysis

In the same way that TG analyses the mass lost by a sample along a heating programme, we present a new device based on a gas chromatography oven. A flow cell replaces the chromatography column. VOCs generated during heating of the sample are continuously detected and measured by the flame ionization detector (FID). Fig. 1 shows a scheme of the installation.

FID signals were obtained with a modified Perkin Elmer 3920B gas chromatograph in which the chromatographic column was replaced by a home-made glass cell. The sample quantity (10, 25 or 50 mg) was placed in the homemade glass cell, which was heated in the oven of the gas chromatograph and connected to a carrier gas (nitrogen or air) to purge the cell and lead the compounds to the FID. Temperature ranged from 25 to 390 °C. Heating rates of 4, 8 and 16 °C min^{-1} under a flow rate of 150 cm^3 min^{-1} of either nitrogen or synthetic air as a carrier gas were studied. The working conditions of the FID detector were 2.5 bar of air, 1.5 bar of H_2, a temperature of 400 °C, range 100 and ×8 attenuation.

Besides FID analysis, this versatile equipment is able to be used as a sampling system in order to analyze VOCs by other techniques.

2.4. Solid Phase Extraction–Gas Chromatography–Mass Spectrometry (SPE–GC–MS) analysis

For GC–MS analysis, 50 mg of the corresponding sample were subjected to the same procedure as the FID analysis, but replacing