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Evaluation of frying oil subjected to prolonged thermal treatment: volatile organic compounds (VOC) analysis by DHS-HRGC-MS and ^{1}H-NMR spectroscopy

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It is known that fats and oils, when subjected to prolonged heating for frying, are subjected to a series of chemical-physical modifications, the effects of which can be observed in the variation of the sensory and nutritional characteristics.

The main factors influencing the entity of these transformations are represented by the temperature and the time of the treatment, the nature of foods being fried, the presence of metals that catalyze the oxidation phenomena, and the composition of the frying oil.

In order to prevent possible consumer risks due to the excessive and inappropriate use of frying oils and fats, the Italian Ministry of Health, in Circular n.1 of January 11, 1991, established that the concentration of total polar compounds (TPC), indicators of the state of triglyceride alteration, does not exceed 25 g /100 g in oils and fats used for frying food, a limit that reflects similar provisions established by legislation in other countries. In current analytical practice, the TPC evaluation method by preparative column chromatography is quite laborious and it is not repeatable and accurate. The aims of this study were to develop an accurate and repeatable method to evaluate the volatile organic compounds (VOC) which are formed during frying and find new possible markers correlated with TPC data, which should be suitable for routine use in order to determine the degree of triglycerides alteration. In particular, the markers have been studied by dynamic head space analysis (DHS) combined with high resolution gas-chromatography (HRGC) equipped with mass spectrometry (MS) and ^{1}H-NMR spectroscopy.

Introduction

Deep fat frying is an important, ubiquitous and highly versatile process, which has been used since antiquity to cook a wide range of products. During frying, a variety of reactions cause a spectrum of physical and chemical changes. By effect of oxygen, food moisture and high temperature, the oil undergoes three deleterious reactions: hydrolysis caused by water, oxidation and thermal alteration caused by oxygen and heat (Chang et al., 1978; Frankel, 1998). The main reactions lead to polymerization and homolitic β-scission of hydroperoxides. Decomposition products are also formed as a result of reactions between food ingredients and oil affecting products' taste, flavour and shelf-

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life (Dobarganes et al., 2000). Oxidation play a significant role due to the development of rancid flavours that reduce the organoleptic characteristics, and the formation of oxidized products that may cause a health hazard (Katan et al., 1984; Willett & Ascherio, 1994). Selective absorption may also occur, enriching the food product with breakdown oil compounds. It is important to note that oxygen plays an important role on the deterioration of the oil during frying. Under ambient conditions, autoxidation occurs by free radical mechanism where hydroperoxides play a primary role (Dobarganes and Velasco, 2002). Oxygen is essential, but rarely a limiting factor during frying. The alkyl radical interacts with atmospheric oxygen resulting in a very fast reaction. Retarding oxidation is normally feasible at low oxygen concentration lower than 2%. Hydroperoxides do not accumulate due to their instability at frying temperature; they decompose spontaneously to form dimers and volatile products (Frankel, 1998). Free radicals are involved in the reaction as intermediates. Therefore oxygen is critical in oil deterioration during frying. This fact should be incorporated into fryer design where both airflow and oil turbulence need to be minimized. The effect of water on hydrolysis has frequently been shown to be detrimental to oil quality, and external spraying of the frying oil with water remarkably increased the acid value. However, water can also serve as a physical barrier generating a steam “blanket” over the oil and preventing contact between oxygen and oil (Vitrac et al., 2000). It can also play a role as a physical agent for “steaming out” the volatile oxidative products from the oil and enhancing their evaporation. Volatile compounds have been object of several study (Mookherjee et al. 1965; Aparicio and Morales, 1994; Mildner-Szkudlarz et al., 2008; Van Loon et al., 2005; Pangioli et al., 2002). Abundant amounts of hexanal and t,t-2,4-decadienal, oxidation products of linoleic acid, which was the most abundant fatty acid found in the frying oils, were detected. The aim of our study was to identify among VOC possible markers to follow oil thermoxidation.

2. Materials and methods

In this study we have carry out two experiments: in the first, the oil has been used to fry frozen pre-fried potatoes (McCain), in the second, the oil has been thermoxidized without foodstuff for the same time.

The oil mix selected was a blend of fractionated and deodorized palm oil, sunflower oil and soybean oil (Olita Star).

The frying process took place at temperatures around 180°C and the potatoes (200 g) was deep fried for 6 minutes every hour for a daily treatment time of 4 hours for a total time of 40 hours for 10 workdays.

The deep fat fryer batch volume was 3,0 L and in both experiments new oil was added (100 ml to day) to compensate for the oil absorbed into the deep frozen pre-fried potatoes.

Both experiments took place in the same frying conditions. Frying oil, used to fry the deep frozen potatoes, and oil heated up in the fryer without potatoes, were sampled every 12 frying hours (every 3 days).

The samples were preserved in the dark at temperature -20°C ± 2 until analyses and subjected to the determinations of: TPC; VOC by DHS-HRGC-MS; aldehydes by ^{1}H-NMR spectroscopy.

TPC were determined by preparative column chromatography as described by Hein et al (1998).

The oil samples were analysed by DHS with "Purge and Trap" technique (Tekmar Instruments, Manchester, UK). The sample (2 mL), was added with 60 µl of solution (200 ppm) of internal standard (isobuthyl acetate). VOC analysis was carried out using Gas-Chromatography Agilent 6890N GC System with mass spectrometer Agilent 5973 N. Carrier gas, helium at a flow rate of 1,2 ml/min. Oven temperature program was: 45°C for 3 min., 10°C/min ramp to 240°C (1 min); 15°C/min ramp to 270°C (1 min). The mass spectra were generated at 70 eV in the range 35-400 uma. The VOC identification was achieved by comparison of the mass spectra and GC retention times with those, when available, of the pure standards compounds and data system library of the GC-MS equipment (NIST 02 and WILEY 275).

The ^{1}H NMR spectra were recorded on a AV Bruker spectrometer operating at 400 MHz. Each oil sample (100 µL) was mixed with 250 µL of deuterated chloroform and 250 µL of a solution 1mmol/L of TBB (Tribromobenzol) as internal reference in $CDCL_3$ and 40 µL of DMSO. The mixture was introduced into a 5 mm diameter tube. The acquisition parameters were: spectral width 13 ppm, relaxation delay 3 s, number of scans 2500, acquisition time 3s with a total accumulation time of 2h and 5 min. The experiment was carried out at 25°C. Spectra were acquired periodically throughout the oxidation process. The assignment of the signals was made as in previous studies (Sacchi et al., 1997). The area of the signals was determined by using the equipment software and the integrations were made three times to obtain average values.

3 Results And Discussion

The CPT continuously increased during both thermal treatment (data not shown). According to the chromatograms obtained by DHS-GC-MS technique, 36 compounds were identified. Among these, the 2E,4E-decadienal and the 2E-undecenal shown a good correlation with TPC values (figure 1) and could be proposed as valid alternative to monitor the thermal degradation of frying oils.

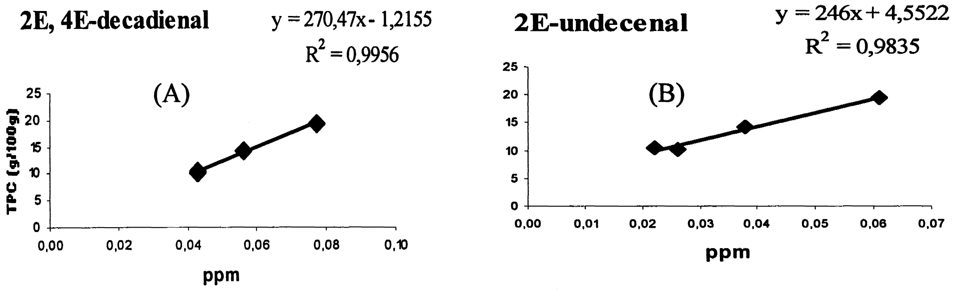

*Fig.1- Correlation between TPC and 2E,4E-decadienal (ppm) (A) and 2E-undecenal (ppm) (**B**) in the frying oil.*

NMR spectra confirmed that 2-alkenals and alka-2,4-dienals are the major compounds formed during thermal treatments (Fig. 2 and 3) and showed their increase during the thermal stress.

The oil only heated (Fig. 2) shows a major amounts of aldehydes with respect to the fryied oil as shown in figure 3. This fact is probably due to the matrix effect and to the presence in the frying oil of frozen potatoes (Guillen and Ruiz, 2001; 2005; 2006; 2008; Sacchi et al., 1996; 2001).

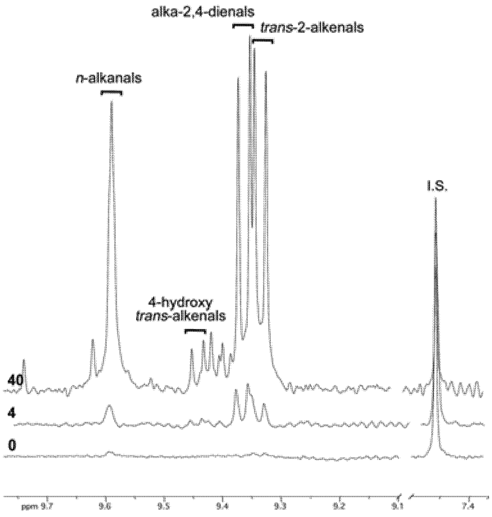

Fig.2- ^{1}H-NMR spectra of thermo-oxidized oil: 0 (initial time), 4 and 40 hours of treatment.

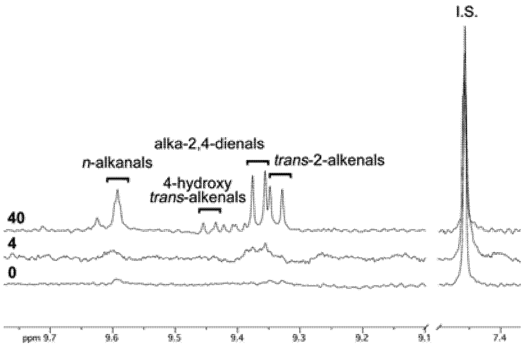

Fig.3- ^{1}H-NMR spectra of fryed oil: 0 (initial time), 4 and 40 hours of treatment.

Based on these preliminary assessments the evaluation of unsaturated aldehydes can be used as a reliable marker to verifying the thermal degradation of vegetable oils subjected to thermal stressing and frying. Further studies are in progress to confirm these findings and evaluate the reliability of these markers.

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