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A critical evaluation of the analytical techniques in the photodegradation monitoring of edible oils

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ABSTRACT

The performance of the widely used analytical techniques in monitoring the changes from light on edible oils was compared. Flax, soybean, peanut, sunflower, olive and corn oils were subdued to forced irradiation and analyzed by IR spectroscopy, UV-visible spectroscopy and HPLC. The stressing test was executed in agreement with international rules and the samples were analyzed at time intervals up to 540 min.

The results recorded by the spectrometric techniques were completely different. All IR spectra recorded along the test were superimposable, indicating full stability of all oils even after multivariate elaboration by principal component analysis. In contrast, UV spectra showed a constant variation, stating a clear photolability. HPLC-DAD determination of the main fatty acids confirmed the photodegradation of the samples, showing a clear decrease in their concentration.

This study provides information on the photostability of various edible oils, which could be useful for their proper storage. Moreover, the results clearly indicate that the IR spectrometry is not appropriate to evaluate the photostability of the oils. On the contrary, UV spectrometry is able to provide a rapid evaluation of the degradation degree and HPLC an effective assessment on the degradation of some important components such as the unsaturated fatty acids.

1. Introduction

The interest in the study of vegetable oils has increased in recent years because of their versatility not only in food but also in the pharmaceutical, cosmetic and technological fields (Hughes, Marangoni, Wright, Rogers, & Rush, 2009; Sai Sateesh, Arfat, & Kunal, 2016).

Most of the research focuses on the variety and composition of the oils and several methods for determination of fatty acids, peroxide value, tocopherols, sterols and pigments such as chlorophyll and carotenoids have been proposed (Pienkowska, Dudkowiak, Muszynski, & Frackowiak, 2005; Pienkowska, Planner, & Frackowiak, 2002; Roman, Heyd, Broyart, Castillo, & Maillard, 2013).

The studies on the stability of the oils have also increased considerably in the last years, both to guarantee consumers high quality products and to provide the correct information on their correct storage. The overall stability of the oils, and above all their resistance to the oxidation process, depends on their composition and on the conditions on which they are subjected. Usually, oxidation occurs if the oil is exposed to air, heating, exposure to light, catalysts, etc. Despite other degradation mechanisms are known, the oil degradation is characterized by a radical mechanism that leads to hydroperoxides that in turn evolve into aldehydes, ketones, lactones, alcohols and acids (Chen, Mc Clements, & Decker, 2011; Goburdhun, Jhaumeer-Laulloo, & Musruck, 2001; Guillén & Cabo, 1999; Guillén & Cabo, 2000; Guillén & Cabo, 2002; Guillén & Cabo, 1997; van de Voort, Sedman, & Russin, 2001; Vlachos et al., 2006). The pigments, above all chlorophyll, play an important role in assessing quality and organoleptic characteristics of the oil and their degradation is mainly caused by light and heat (Choe & Min, 2006).

The protection of the oils from light and temperature appears so of great importance to ensure that the products maintain the full original nutritional and organoleptic characteristics. Several papers have been published on the monitoring of oil oxidation (Genovese, Caporaso, & Sacchi, 2015; Wójcicki, Khmelinskii, Sikorski, & Sikorska, 2015) but the studies on the consequences of exposure to light or heat of the oils are few and almost all centered on the olive oil (Ammari, Bouveresse, Eveleigh, Boughanmi, & Rutledge,

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2013; Zeb & Murkovic, 2013). Thermal degradation has been monitored by spectroscopy and chromatography (Wenle et al., 2015). In a recent paper, modifications that occurred in some oils when heated to high temperatures have been reported (Gonçalves, Março, & Valderrama, 2014).

Photostability studies have increased over the last 20 years, but mainly focused in the pharmaceutical field, because in many cases the formation of toxic products or devoid of pharmacological activity has been demonstrated (Ragno, Ioele et al., 2006; Ragno, Risoli, Ioele, Cione, & De Luca, 2006; Vetuschi & Ragno, 1990). In the food sector, the exposure to light can result in alteration processes of the products causing loss of organoleptic properties or decrease of nutrients (Siddeeg & Xia, 2015; Torrecilla, Vidal, Aroca-Santos, Wang, & Cancilla, 2015). This issue is particularly important for the edible oils where the presence of readily oxidizable components is relevant.

In this work, the performance of the analytical techniques currently used in the control of the oils have been compared to evaluate their ability in monitoring the changes occurring under light irradiation. The study has been applied on a series of edible oils, comprising peanut, sunflower, corn, olive, linseed and soy oils.

Olive oil is certainly the most famous for its organoleptic characteristics and healthy ingredients that make it a major player in the Mediterranean Diet (De Luca, Restuccia, Clodoveo, Puoci, & Ragno, 2016; Oguz & Banu, 2015). Linseed oil is known as a major source of omega-3 fatty acids but is equally known for its easy oxidation (Guillén & Uriarte, 2012a; Lazzari & Chiantore, 1999; Nykter, Kymäläinen, Gates, & Sjöberg, 2006). The oil of peanut seeds, also thanks to its organoleptic properties, is more used than olive oil. It contains a considerable dose of vitamin E (Akhtar, Khalid, Ahmed, Shahzad, & Suleria, 2014; Chang, Sreedharan, & Schneider, 2013), which retards the process of rancidity than other oils, but is also more susceptible to contamination by aflatoxins (Ruijie et al., 2011). The soybean oil is rich in polyunsaturated fatty acids, above all linoleic and alpha-linolenic acids (Juárez, Osawa, Acuña, Sammán, & Gonçalves, 2011). It is used to flavor raw food or for producing margarine, after hydrogenation. It is not suitable for frying, as it is unstable to oxidation and high temperature (Wenle et al., 2015). The sunflower oil is very rich in vitamin E and is used for frying because quite stable at high temperatures (Guillén & Uriarte, 2012b). The corn oil is rich in polyunsaturated fatty acids of the omega-6 and omega-9 class, but is devoid of omega-3 fatty acids (Goicoechea & Guillén, 2015).

The Fourier transform infrared spectrometry (FTIR) has emerged in recent years in food analysis because of its rapidity in both sample preparation and analysis. FTIR is mainly used for the characterization of the oils because intensity and frequency of the spectral signals are characteristic of the origin and composition of the samples (Sherazi, Talpur, Mahesar, Kandhro, & Arain, 2009; Siong & Woei, 2012). The changes in frequency or absorbance of some bands have been used to assess the oxidation degree of olive oil. FTIR has been also used to determine adulteration of olive oil with various vegetable oils (sunflower oil, soybean oil, sesame oil, corn oil) (Ozen & Mauer, 2002; Ozen, & Mauer, 2003). FTIR analysis has been used coupled with multivariate data techniques for different aims in vegetable oils such as identification of origin or variety and detection of adulteration (De Luca et al., 2012; De Luca et al., 2016; Terouzi et al., 2011).

Chromatographic techniques have been used to determine the composition of edible oils and analyze adulteration processes. HPLC is often used to evaluate the composition of fatty acids with the focus on omega-3 and -6 (Guarrasi, Mangione, Sanfratello, Martorana, & Bulone, 2010; Hori et al., 2012; Zeb & Murkovic, 2013).

Some care is today dedicated to protect the olive oil from light, packing it into darkened glass bottles. Less caution has instead given to the photoprotection of seed oils, many of which are still marketed in glass or transparent plastic bottles. However, scientific investigation on the photodegradation of the oils is scarce and information about the analytical methods more suitable is poor.

This work aims to verify the performance of the widely used analytical techniques in assessing any alteration by light irradiation on a series of edible oils. The photodegradation tests were conducted in accordance with international rules (International Conference on Harmonization, 2003). The oil samples were analyzed by FTIR and UV spectroscopy and HPLC, just before the experiments and at several time intervals up to 9 h of total irradiation. FTIR analysis was directly performed on the oil samples through ATR sampler, while UV analysis was performed after appropriate dilution with hexane. HPLC analysis was targeted to the determination of the main fatty acids after appropriate extraction procedure.

2. Materials and methods

2.1. Chemicals

Corn, linseed, olive, peanut, soybean and sunflower oils were purchased commercially and stored in the dark at 25 °C. N-hexane for UV–vis analysis, sodium hydroxide, hydrochloric acid, petroleum ether, formic acid 98% (lab grade); acetonitrile and methanol, both of chromatographic grade; linoleic, linolenic and oleic acids (standard grade), were all purchased from Sigma-Aldrich (Milan, Italy).

2.2. Instruments

The stressing irradiation tests were conducted by using a cabinet Suntest CPS+ (Heraeus, Italy) equipped with a Xenon lamp, which emits light superimposable to the solar spectrum. Specific spectral regions can be selected through the interposition of suitable filters and the internal temperature fixed by means of a refrigeration unit linked to the cabinet.

UV analysis was performed by an UV spectrophotometer Agilent 8453 with diode array detector (Agilent Technologies, CA, USA).

FTIR spectra were carried out by using a Perkin Elmer Spectrum two, equipped with sampler ATR. The spectra are recorded by placing the sample on an optical crystal with high refractive index. This generates a reflected beam, which is absorbed up to few μm in the sample and originating in turn a second beam that is recorded as a spectrum.

HPLC analysis was carried out by using a HP 1100 pump fitted with a diode array detector G1315B (Agilent Technologies) and a Rheodyne 7725 manual injector. The LC column was a C18 Gemini (Phenomenex), 250 × 4.6 mm x 5 mm. The injection volume was 20 μl.

2.3. UV and IR analysis

The samples for UV analysis were prepared by diluting 1.0 g of oil in hexane and then opportunely diluting this solution up to obtain a concentration of 0.8 mg/mL. FTIR analysis were made by placing a drop of the samples on the ATR surface and infrared spectra were recorded in the range 4000–450 cm^{-1}. Scan number and resolution were fixed at 8 scans and 4 cm^{-1}, respectively. The spectrum of the ATR element versus room air was used as background. Before each analysis, the ATR plate was cleaned by scrubbing it with hexane and ethanol.