PAPER

ASSESSING OIL OXIDATIVE STABILITY IN TARALLINI BY OXITEST®

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ABSTRACT

The shelf life of the typical Italian bakery snack "tarallini" depends on the recipe and on the cooking and storage conditions. In this work, the lipid oxidative stability of tarallini was measured using an OXITEST® instrument, an accelerated oxidation test. The OXITEST® methodology was optimised taking into account sample amount and the sample particle size.

Homemade tarallini prepared using sunflower oil, extra virgin olive oil and a blend of extra virgin olive oil and lard were cooked for two different cooking times. The results showed a good ability of OXITEST® to discriminate between lipid unsaturation and cooking time, providing information on the lipid shelf life of complex food matrices, such as tarallini.

Keywords: accelerated oxidation, bakery products, OXITEST®, shelf life, Tarallini

1. INTRODUCTION

Lipid oxidation is one of the main deteriorating reactions in food chemistry; food quality is deeply affected by lipid oxidation (CALLIGARIS *et al*., 2008). In particular, it damages lipids, especially essential fatty acids (CHOE and MIN, 2006), in fat-rich foods, such as bakery products, biscuits and snacks. Moreover, lipid oxidation is a promoter of off-flavours, producing the worst sensorial properties, reducing nutritional value and increasing the production of potentially toxic compounds (VERLEYEN *et al*., 2005). Thus, bakery product formulation must consider the characteristics of the used lipids, the matrix effect that influences their contact with oxygen and the technological treatment (cooking) that the products undergo.

Due to influence of food composition on shelf life, formulation can play an important role in food quality, even in terms of lipid oxidation. In fact, the interaction of lipid oxidation products with sugar, proteins and Maillard reaction products greatly affect the development of lipid rancidity in complex food (FRENKEL, 1984).

Moreover, different other factors (temperature, light, oxygen partial pressure, etc.) could affect and enhance lipid oxidation during storage. In particular, among them, partial oxygen pressure affect oxidation rate (KACYN *et al*. 1983): higher is the headspace partial oxygen pressure and higher is the amount of oxygen dissolved in food. Consequently, the oxygen available for lipid oxidation is increased and, in the dark, it will be enough to reach a value of peroxide value of 10mEqO_2/kg of fat (PRZYBYLSKI and ESKIN, 1988).

In addition, fatty acid composition, in particular fatty acid unsaturation degree, storage time and pro- and antioxidant compounds significantly affect the auto-oxidation rate (CALLIGARIS *et al*., 2008).

Briefly, when the oxidation occurs, fatty acids are converted at first into hydroperoxide, can then decompose to form volatile molecules, hydroxylated, keto- or epoxy- compounds or react with other oxidised fatty acids to form dimers or polymers.

Many different methods have been developed to assess these oxidation compounds in various food ingredients and products. GC analyses of volatiles compounds, free fatty acid or mono and diglicerides, HPLC evaluation of oxidised fatty acid or spectrophotometric determination of peroxide value, conjugated diene and trienes are the main traditional methods applied to asses lipid oxidation in foods (VERARDO *et al*., 2010; VERARDO *et al*., 2011)

However, the lipid oxidation rate is usually slow at room temperature and the rancidity threshold, which is strictly related to the consumer rejection of foods, could take months.

Moreover, oxidation products analyses are often time consuming and for the food industry it is very important to check as quickly as possible the food stability (MÀRQUEZ-RUIS *et al*., 2003).

Thus, excessively time-consuming shelf-life tests are useless for industry needs, and it is essential to apply methods that give quick answers (GÓMEZ-ALONSO *et al*., 2004).

An interesting way to reduce the time of analysis of lipid oxidation compounds is using accelerated oxidation tests, allowing foods lipid stability assessment in a significantly shorter time than under real storage conditions (PRZYBYLSKI and ESKIN, 1988).

Usually, in this type of test, one or more parameters (temperature, oxygen pressure, light, etc.) (WAN *et al*., 2000) that can increase the lipid oxidation rate are modulated, but the temperature is the most critical factor affecting the oxidation rate; thus, it is the most commonly considered (RAGNARSSON and LABUZA, 1977; LABUZA and SCHMIDT, 1985; WATERMAN and ADAMI, 2005).

Several tests were developed to evaluate accelerated lipid oxidation. In particular, most of them like Rancimat or Oxidative Stability Instrument (OSI) tests are suitable only for oils

or fat extracted from foods, but are not applicable to the whole food. In this way, however, the effect of food matrix on lipid oxidation onset cannot be considered.
A newer instrument, the OXITEST® reactor, has been used to asses oils lipid oxidation in several studies (AMATO *et al*., 2015; CAVAZZA *et al*., 2015; CLAUS *et al*., 2015; CLAUS *et al*., 2015 b; MORA *et al*., 2009; Mora *et al*., 2011) but it is particularly fitted to investigate the oxidation sensitivity also in solid foods (VERARDO *et al*., 2013; KWON *et al*. 2015), such as bakery products, with limited preparation and without any fat extraction (VELP SCIENTIFICA, 2006; MARUYAMA *et al*., 2014; FERREIRA SILVA *et al*., 2015).
The OXITEST® reactor subjects the sample to an oxidative stress environment at high temperature and high oxygen pressure; the drop in oxygen pressure inside the oxidation chambers is monitored according to ability of the food to oxidise and is expressed as the induction period (IP) which is theoretically defined as the time required to obtain a continuous oxidation cycle in the oxidation process; it is measured as the time required for a sudden and rapid change in the oxidation rate (FRENKEL, 1998).
Considering the importance of the rapid determination of lipid oxidation in foods as a marker of quality during shelf life, the aim of this work was to evaluate the performance of OXITEST® as a new screening instrument to assess lipid stability directly on bakery products, tarallini, a typical Italian snack. In particular, the sample amount, particle size, and formulations were setted in order to enhance the discriminating power of the technique.
Traditionally, tarallini are a typical southern Italian salted snack formulated with wheat flour, oil, water, salt and white wine. The oil used during its preparation plays the main role in the oxidative stability and thus shelf life of this snack; homemade tarallini is generally prepared using extra virgin olive oil (EVOO), but the industrial one could be formulated with sunflower oil (cheaper than EVOO) or with a blend of EVOO and LARD, more expensive but with longer shelf life (CAPONIO *et al*., 2009). The longer shelf life is mainly due lower susceptibility of fat blend to lipid oxidation, related to the fatty acids composition of fats and the presence of natural antioxidants in EVOO.
In addition, cooking time is critical for tarallini quality. In particular, cooking time should be optimised for a golden colour without negatively altering the crunchiness and the texture of the product.
In fact, a cooking time or a cooking temperature too high could led to a product extremely dry and with a darker colour compared to the typical one. Moreover, a longer cooking enhance the heat stress promoting lipid oxidation onset and reducing the shelf life of the snack.

2. MATERIALS AND METHODS

2.1. Solvents and reagents

All of the solvents were purchased from VWR International (Radnor, Pennsylvania, USA). The reagents were provided by Sigma Aldrich (St. Louis, MO, USA).

2.2. Samples

The analysed samples were Italian typical salted snacks ("tarallini") prepared following three different recipes (reported in Table 1):
Recipe I: Wheat flour, water, salt and sunflower oil.
Recipe II: Sunflower oil was replaced with extra virgin olive oil (EVOO).
Recipe III: A blend of EVOO and lard (4:1 w/w) was used as a fat source.

Table 1: Recipes of formulated tarallini.

Ingredients	SO tarallini	EVO Tarallini	EVO/LA Tarallini
Wheat flour (g)	1000	1000	1000
Water (mL)	350	350	350
Salt (g)	20	20	20
Oil (g)			
* Sunflower oil	200	0	0
* Extravirgin olive oil	0	200	160
* Lard	0	0	40

In all of the recipes, the dough was kneaded for 15 minutes, manually formed (~4 cm diameter, 0.7 cm thickness) and then oven cooked at 220°C for different times: 8 and 11 minutes to evaluate the ability of the instrument to detect minimal differences in thermal-induced oxidation of the products. The cooking times were chosen based on the typical commercial golden colour of the products (8 minutes), and giving more heat stress, compatibly with the snack's crunchiness (11 minutes).
The samples that were used as control to optimise the OXITEST® analytical conditions were commercial tarallini snacks purchased from a local supermarket in Cesena (Italy). The commercial products that were used for the analytical optimisation conditions were formulated with wheat flour, water, salt and a mixture of EVOO and lard.
The oxidation tests evaluation with OXITEST® was carried immediately after sample production.

2.3. Fatty acid analysis of fats used for the formulation of tarallini snacks

The fatty acid methyl esters (FAMEs) of oils used for the lab scale tarallini productions were identified after alkaline treatment, as described by CHRISTIE (1989), on a GC-2010 Plus gas chromatograph (Shimadzu Corporation, Kyoto, Japan) equipped with a flame ionisation detector (FID) according to the method of VERARDO *et al*. (2013a). Peaks were identified by comparing peak retention times with GLC-463 from Nu-Check (Elysian, MN, USA) and FAME 189-19 standard mixtures from Sigma Aldrich Chemicals (St. Louis, MO, USA).
The fatty acids were expressed as weight percentages of total FAME.

2.4. OXITEST® analysis optimisation

The method of analysis was optimised using commercial samples. The OXITEST® reactor (Velp Scientifica, Usmate, Milan, Italy) was fitted with two separate oxidation chambers at 90°C with an oxygen pressure of 6 bar, as indicated by VELP SCIENTIFICA (2006).
At first, the ground commercial sample, milled mechanically using a water-cooled mill (IKA-WERKE M20 mill, speed 20000 rpm, maximum particle size 6-7 mm) (TFG), was analysed in different amounts (10, 20 and 30 g) to determine the best compromises between quantity, time of analysis and repeatability. Each sample was analysed three times and monitored twice during each test (in chambers A and B). The results, expressed as IPs, were obtained using the two-tangent method.
After establishing the sample amount, an OXITEST® analysis was performed on commercial samples with different particle sizes: whole product (WT) and after mechanical (TFG) (using IKA-WERKE M20 mill) and manual (TCG) milling. Briefly, 10 g

of tarallini was oxidised as whole (WT) after milling five times for 30 seconds using a water-cooled mill (TFG) and after grinding manually in a mortar (TCG) to obtain bigger particles.
Inter-days tests were performed to evaluate the instrument repeatability with different types of samples. Thus, each type of sample was monitored twice by the OXITEST® reactor over five days. *Intra*-day tests were not allowed by the experiment duration (greater than ten hours).

2.5. OXITEST® analytical conditions

All of the analyses were carried out under the same conditions of temperature (90°C) and oxygen pressure (6 bar). After optimisation of analytical conditions, the amount of handmade tarallini that was analysed was 10 g. The samples were analysed immediately after production.

2.6. Statistical analysis

One-way (Tukey's honest significant difference multiple comparison) and multifactorial analyses of variance (ANOVA), were carried out to establish significant differences. All of the statistical tests were evaluated using Statistica 8.0 software (StatSoft, Tulsa, OK, USA), and p values less than 0.05 were considered statistically significant.

3. RESULTS AND DISCUSSIONS

3.1. Chemical composition of SO, EVOO and EVOO/LARD

The analysis of the oils used as raw materials showed a high amount of unsaturated fatty acids, as expected. In EVOO, the most abundant fatty acid was oleic acid (C18:1), 70.0%, followed by palmitic acid (C16:0, 13.7%) and linoleic acid (C18:2 9.2%).
Linoleic (C18:2, 59.0%), oleic (C18:1, 28.9%) and palmitic (C16:0, 6.4%) acids were also the main fatty acids in sunflower oil.
The fatty acid composition of the EVOO/LARD (4:1 w/w) blend closely reflected the composition of EVOO, with some changes in the percent distribution of each fatty acid. Oleic acid (C18:1) accounted for 63.4%, palmitic acid (C16:0) 15.4%, and linoleic (C18:2) and stearic (C18:0) acids 9.7% and 4.3%, respectively, of the total fatty acids. In small quantities, this blend also contained saturated medium chain fatty acids, such as lauric acid (C12:0, 0.02%) and myristic acid (C14:0, 0.28%), typical of lard, as shown in Table 2.
The oxidative status of the fats used during formulation was assessed by an OXITEST® reactor, at the same condition applied for tarallini analyses (90°C, 6 bar oxygen pressure) but weighting 5 g of products. The results showed that EVOO was characterised by a similar and not significantly different oxidative stability compared to EVOO/LARD blend (1371 vs 1408 minutes, respectively) but by a greater oxidative stability than the one of sunflower oil (699 minutes), confirming the results reported by COMANDINI *et al*. (2009).

3.2. Optimisation of the analytical parameters of the OXITEST® reactor

Preliminary tests performed on commercial tarallini were aimed to to optimise the conditions of analysis of bakery products by OXITEST®; in particular they were aimed to determine the amount of sample and particle size that allow the best repeatability. Thus, different quantities loaded into the reactor chambers were tested. Moreover, once decide

the best amount to load, trying to reach the most homogenous and repeatable contact with oxygen, the samples were analysed as whole (WT) or ground mechanically with a mill (TFG) or manually with a mortar (TCG).

Table 2: Fatty acid composition (%) of fats used in tarallini formulation.

	SO	EVOO	EVOO/LA
C12:0	0.00±0.00	0.00±0.00	0.02±0.00
C14:0	0.07±0.00	0.00±0.00	0.28±0.02
C16:0	6.41±0.01	13.70±0.09	15.38±0.01
C16:1t	0.02±0.00	0.13±0.04	0.16±0.01
C16:1c	0.11±0.00	1.13±0.03	1.30±0.00
C17:0	0.06±0.00	0.13±0.00	0.20±0.01
C17:1c	0.03±0.00	0.21±0.01	0.22±0.01
C18:0	3.25±0.02	2.03±0.02	4.32±0.07
C18:1	28.90±0.22	70.01±0.05	63.36±0.21
C18:2 tt	0.23±0.05	0.00±0.00	0.00±0.00
C18:2 n6	58.97±0.24	9.22±0.09	9.73±0.00
C18:3n6	0.06±0.01	0.07±0.01	0.10±0.03
C18:3n3	0.09±0.02	0.57±0.01	0.58±0.01
C20:0	0.24±0.02	0.39±0.01	0.37±0.00
C20:1	0.15±0.04	0.30±0.02	0.42±0.02
C20:2	0.00±0.00	0.00±0.00	0.13±0.01
C20:3n6	0.10±0.06	0.37±0.14	0.90±0.13
C22:0	0.71±0.01	0.14±0.00	0.10±0.00
C20:5+C22:1	0.00±0.00	0.06±0.03	0.11±0.02
C22:2	0.06±0.00	0.52±0.02	0.44±0.02
C22:3+C22:4	0.00±0.00	0.16±0.06	0.39±0.09
C24:0	0.33±0.03	0.39±0.15	0.69±0.02
C24:1	0.10±0.00	0.15±0.01	0.33±0.08
C22:5	0.14±0.01	0.33±0.02	0.46±0.05

Oxidising 30, 20 and 10 g of TFG, the IP values were 757, 873 and 788 minutes, respectively, and there were no significant differences in term of IPs between the three amounts tested (Table 3). Thus, in order to save the sample to use, 10 g was chose as the amount to use in the following trials. Thirty grams of sample was the maximum quantity per plate in a single oxidation chamber; a higher amount, in fact, needed to be placed on more than one, causing a not-reliable comparison between trials with smaller amounts. Lower amounts were not chosen because quantities below 10 g did not allow the total covering of the steel plate in the oxidation chamber, leading to a possible irregular oxygen distribution on the sample and showing a non-linearity of response.
After choosing the more repeatable amount of sample and testing the instrument repeatability, the instrument capacity of discrimination for different sample particles size was tested.

Table 3: IP Values of different amounts of tarallini.

Samples	IP values (minutes)
TFG 30 g	757±38[a]
TFG 20 g	873±48[a]
TFG 10 g	788±37[a]

TFG: Tarallini fine ground, ground mechanically; **TCG**: Tarallini coarse ground, ground by mortar; **WT**, Whole tarallini). Different letters indicate significantly differences between values ($p < 0.05$).

As reported in Table 4, statistically significantly differences in the IPs were observed between the two different types of milled products (TCG and TFG) and between WT and the TCG. These differences could be due to the initial heating effects that, related to the milling process, increase the susceptibility to oxidation in TFG with a decrease in the IP value compared to TGC. Moreover, for ground products, as smaller was the particles size (TFG respect to TCG) as higher was the susceptibility of the product to lipid oxidation, as reported by TAN *et al*. (2002)
As concerning WT, the IP value was not significantly different to the one of TFG but significantly different from TGC. However should be noticed that WT IP showed a high standard deviation suggesting that OXITEST® were less repeatable when used on whole product compared to the ground one; this can be probably connected to the lower sample homogeneity (e.g slightly different shape and thickness) of the whole product, that could affect interaction between oxygen an oil fraction.

Table 4: IP values of whole tarallini and tarallini ground differently.

Samples	IP values (minutes)
TFG 10 g	788±37[a]
TCG 10 g	902±54[b]
WT 10 g	788±168[a]

(TFG: Tarallini fine ground, ground mechanically; **TCG**: Tarallini coarse ground, ground by mortar; **WT**, Whole tarallini). Different letters indicate significantly differences between values ($p < 0.05$).

The results showed that the larger the particles (TCG compared to the same quantity of TFG saqmple) and thus the smaller the surface area-to-volume ratio exposed to oxygen, the higher the IP.
However, the above hypothesis is confirmed only by ground products because the results obtained by the oxidation of the whole sample are very changeable, probably due to the shape of tarallini, which could lead to a different exposure to oxygen and different oxidation rates among trial tests. The whole product showed an induction period very close to that milled by grinder (TFG) but was characterised by a higher variation between replicates.
The results of *inter*-day experiment showed a lower CV (4.1%) for TFG compared to TCF (7.5%) and WT (23.2%). These results suggest the product ground mechanically (TFG) as the one to choose for OXITEST® analysis; thus, handmade tarallini was ground by a water-cooled mill before analysis (TFG).

3.3. Evaluation of the oxidative stability of handmade tarallini

To assess the effect of food composition ("matrix effect") on lipid rancidity, handmade tarallini formulated with three different fat sources were oxidised by the OXITEST® reactor, testing the reliability of this instrument for the screening of the oxidative stability of baked snacks.
Comparing the IP values of tarallini formulated with different recipes, it can be noticed that the most oxidable products were sunflower oil tarallini snacks, showing the lowest IPs (274 and 599 minutes). A low IP means high oxidation susceptibility.
Increasing lipid saturation (EVOO and EVOO/LARD as fatty sources), the IPs increased, reaching values more than double (1254 and 1150 minutes for EVOO snacks and 1192 and 1100 minutes for EVOO/LA tarallini) compared to those of sunflower snacks. This trend may be associated with the fatty acid composition of the fat used: the higher degree of unsaturation of sunflower oil reduces the oxidative stability of the produced snacks (Table 5).

Table 5: Induction period (IPs) of handmade tarallini snacks cooked for 8 and 11 minutes and reduction of IPs by increasing cooking time.

Samples	8 minutes cooking	11 minutes cooking	Reduction of IPs
EVOO	1254 ^{a}	1150 ^{a,b}	8.3%
EVOO/LA	1192 ^{a,b}	1100 ^{b}	7.7%
SO	599 ^{c}	274 ^{d}	54.3%

Different letters mean significantly differences between values ($p < 0.05$)

To better explain these results, the unsaturation degree was expressed as the "unsaturation point" and calculated as the sum of the main fatty acids weighted by the number of double bounds of the fatty acid.
Sunflower oil had the highest unsaturation point (147), followed by those of EVOO (88.5) and the EVOO/LARD blend (82.8). Although the EVOO/LARD blend had a lower unsaturation point compared to that of EVOO, it showed greater susceptibility to oxidation. This is probably due to the blend's lower content of natural antioxidants, typical of EVOO, which protects the fat against oxidation.
In addition to lipid unsaturation degree, cooking time also played a significant role in lipid oxidation onset in tarallini snacks as reported in Tables 5 and 6.
Cooking for a longer time decreases the IPs of the samples analysed due to an increase in the lipid oxidation rate. The effect of cooking time was emphasised in the products characterised by the higher unsaturation degree (SO tarallini), with a significant reduction of IP values (274 vs 599 minutes).
Even if the IP values decreased with 11 minutes of cooking, significant differences were not observed in tarallini made with EVOO or EVOO/LA when cooking time was changed. Anyway, the highest IP value was shown by tarallini made of EVOO and cooked for 8 minutes (IP=1254 minutes). This result may indicate that the phenolic compounds naturally present in EVOO have a strong antioxidant activity that can help to prevent lipid oxidation. The IP values of EVOO tarallini were higher, even if not significant, also

compared to that of a more saturated lipid (EVOO/LA tarallini), confirming the report of HRNCIRIK and FRITSCHE (2005) in different EVOO samples.

Table 6: Multifactorial ANOVA (univariate results).

Source of Variation	Probability
Oil	***
Baking time	***
Oil x Baking time	*

$p < 0.05$; *** $p < 0.001$

Thus, the cooking heating effect caused a significant increase in the oxidation onset only in snacks formulated with highly oxidable oils, such as sunflower oil. In this case, comparing snacks formulated with the same fat but cooked for different times, it can be seen that even only 3 minutes of cooking changes the oxidation stability of the products, suggesting that heat effect plays a dominant role in the high unsaturated lipid oxidation onset.
The CV (all values below 5%, except for tarallini made with EVOO and cooked for 11 minutes, where the CV was 9%) for handmade snacks confirms the good repeatability of the OXITEST® reactor even when fats with different susceptibilities to oxidation were used for formulations.

4. CONCLUSIONS

Tarallini ground in different ways and with different particle sizes showed different behaviour during the accelerated oxidation process due to the different surface/volume ratio and, consequently, different contact with oxygen. These results highlight the necessity to perform an analysis on ground foods, especially when their shape is not homogeneous.
The OXITEST® instrument also showed good performance for the discrimination of different fat used in snacks formulations. Moreover, baking tarallini for different cooking times led to an ~50% reduction of IPs, highlighting the power of the OXITEST® to discriminate between products under different thermal stresses.
Thus, OXITEST®, different from other accelerated shelf life tests, is suitable for solid, liquid and doughy foods (VELP SCIENTIFICA, 2006).
The possibility of screening lipid stability to oxidation with good repeatability of results in complex foods, such as bakery products, avoiding lipid extractions and with the minimal preparation of the sample, suggest the OXITEST® instrument as a good option to save time in the preliminary evaluation of lipid oxidation. Moreover, this instrument considers the complexity of formulated foods giving more reliable results due to interactions between compounds that can be considered.
Nevertheless, more investigations are needed to study this accelerated oxidation test with other foodstuffs.

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ABBREVIATIONS

IP, Induction Period; OXITEST, Oxidation Test; EVOO, Extra virgin olive oil; SO, Sunflower oil; LA, Lard; TFG, Tarallini fine ground; TCG, Tarallini coarse ground; WT, Whole tarallini.

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