Determining the rancidity of a bakery product

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As is well known, baked products are often made using large quantities of fatty substances. The nature and concentration of the lipids of which they are composed are highly variable depending on the type of product and the recipe. In general, the fats most used in their preparation are butter, margarine, hydrogenated vegetable oils, lard and olive oil.

Both the baked goods and the oils and fats as such, which are used in their preparation, are subject to rancidity, that is to the deterioration of their lipid component. In addition to altering the nutritional qualities of the fatty matter, this phenomenon also leads to the formation of unpleasant odours and flavours (off-flavours) which compromise the sensory qualities.

The rancidity of fats

Rancidity consists of a series of chemical reactions involving fats that have produced the formation of unpleasant compounds. Two types of rancidity are distinguished according to the type of reactions involved: hydrolytic and oxidative.

Hydrolytic rancidity

Hydrolytic rancidity is caused by hydrolysis reactions, which as a final result generate the release of **free fatty acids (FFA).** These reactions occur in the presence of water and are catalysed by various factors such as:

- enzymes (lipases), already present in the food or released by microorganisms;
- an acidic or basic environment.

Hydrolytic rancidity, also called simply acidity, is typical of those baked products with a high water content, especially if stored too long and in unsuitable conditions.

Oxidative rancidity

Oxidative rancidity can be considered as the consequence of the reactions between atmospheric oxygen and the fatty substance, in particular with the fatty acids that compose it.
This type of oxidation occurs in two distinct phases characterised by the formation of different chemical compounds. The first products of oxidation are the **peroxides of fatty acids** called **products of the primary oxidation of a lipid**. These compounds are relatively stable and in themselves are odourless but they can easily decompose resulting in numerous smaller molecules such as aldehydes and ketones, called **secondary oxidation products**, which are the real culprits of the rancid aroma and which produce an increase of the value of **p-Anisidine**.
The formation of peroxides and subsequently of aldehydes and ketones can take place through several mechanisms:

- autoxidation;
- photo-oxidation;
- enzymatic reactions.

Self-oxidation is a radical reaction whose start is catalysed by the presence of metal ions, peroxides, heat and UV radiation. Photoxidation, instead, takes place with a different mechanism in which light radiation intervenes.

Therefore, in order to control the hydrolytic and oxidative rancidity of baked goods, determining the concentration of free fatty acids (FFA), peroxides, aldehydes and ketones (p-Anisidine) in the finished product and in the raw materials used in their preparation is of fundamental importance.

CDRFoodLab®

The analytical control

In the CDR ChemicalLab "Francesco Bonicolini" research laboratory we set out to develop a simple and fast system to determine the shelf-life of baked products that can be easily used by food companies even on the production line.

For this purpose, using the **CDR FoodLab®** analysis system, a study was carried out in which the progress of the rancidity of a series of baked products subjected to thermal stress was assessed.

The study

The study was conducted on muffins, croissants, two different types of hazelnut spreads and on biscuits such as "shortbread"; for the entire duration of the study all these products were subjected to a temperature of 50 ±2 °C inside a stove to speed up the rancidity process. The following are the nutritional values and in particular the fats contained in the various bakery products selected for the study.

Average values	For 100 g
Power	2252 kJ 539 kcal
Fats	30.9 g
of which: saturated fatty acids	10.6 g
Carbohydrates	57.5 g
of which sugars	56.3 g
Protein	6.3 g
salt	0.107 g

Table 1 . Nutritional values spread 1

Average values	For 100 g
Power	2210 kJ 529 kcal
Fats	30 g
of which: saturated fatty acids	7.5 g
Carbohydrates	55 g
of which sugars	55 g
Protein	9.2 g
salt	0.2 g

Table 2. Nutritional values spread 2

Average values	For 100 g
Energy	2012 kJ 479 kcal
Fats	19 g
of which: saturated fatty acids	4.6 g
Carbohydrates	68 g
of which sugars	22 g
Fibre	2.6 g
Protein	7.2 g
salt	0.66 g

Table 3 . Nutritional values shortbread

Average values	For 100 g
Energy	1825 kJ 437 kcal
Fats	23 g
of which: saturated fatty acids	5.1 g
Carbohydrates	51 g
of which sugars	30 g
Fibre	1.5 g
Protein	5.7 g
salt	0.75 g

Table 4. Nutritional values muffins

Average values	For 100 g
Energy	1727 kJ 414 kcal
Fats	23 g
of which: saturated fatty acids	12.6 g
Carbohydrates	40.1 g
of which sugars	11.5 g
Fibre	4.1 g
Protein	9.5 g
salt	0.600 g

Table 5 . Nutrition values croissants

Type of product	Type of oil or fat	Total percentage of fats
Spread 1	*Palm oil*	30.9%
Spread 2	*Anhydrous milk butter* *Cocoa butter*	30%
Shortbread	*Sunflower oil* *Butter*	19%
Croissants	*Vegetable margarine* *Butter* *Sunflower oil*	23%
Muffin	*Sunflower oil* *Coconut oil* *Cocoa butter*	23%

Table 6. Percentage and type of fat of each product

A sample of each baked product was taken from the stove at regular intervals and treated with the fat extraction method developed in the CDR laboratories for this type of food.

The CDR method for extracting the sample is simple, does not involve any risk for the operator and the environmental impact is minimised as it does not require toxic solvents, expensive waste disposal or extractor hoods.

The fat extraction method is as follows:

- weigh 10g of product (after shredding with a dedicated blender, if necessary)
- add 5 mL EXTRAFLUID (code *300133)
- shake well
- microwave the mixture to help dissolve the fats
- centrifuge for approximately 3 minutes at least 5000rpm

The supernatant obtained (Fig.1) from the centrifugation of the treated product is used to perform the analyses of Acidity (for free fatty acids), Peroxides (for the products of primary oxidation) and p-Anisidine (for the products of the secondary oxidation).

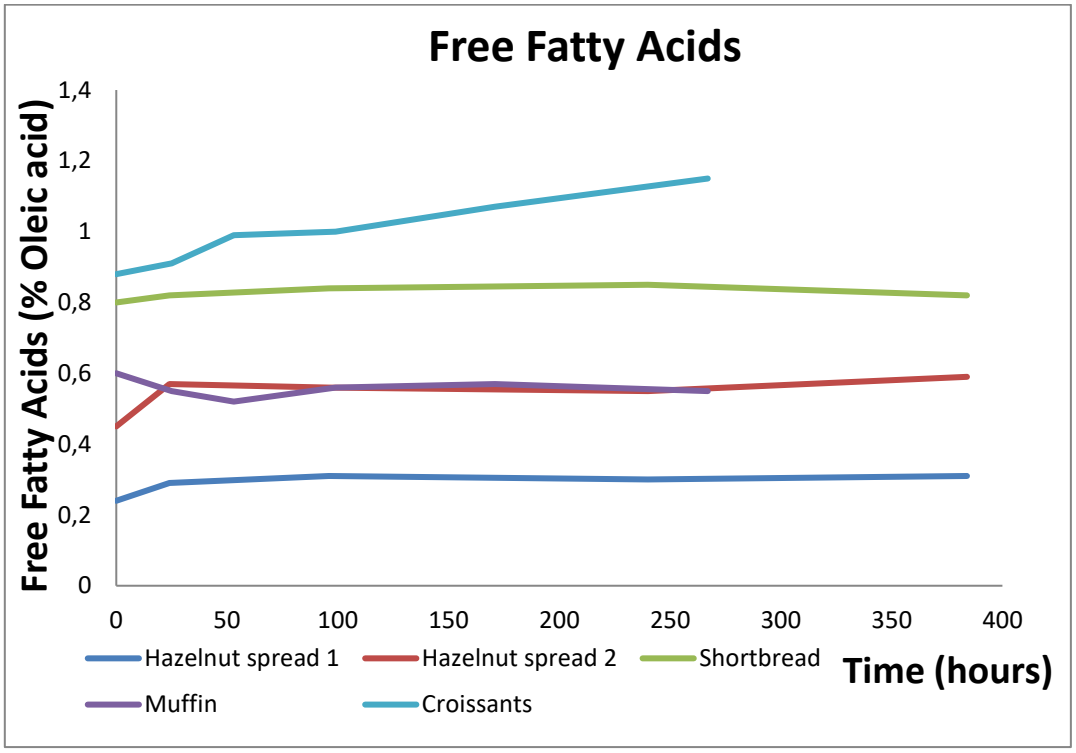
Figure 1. Fatty substance extraction with the CDR FoodLab® system

These analyses were carried out quickly and easily with the CDR FoodLab® system which is used to determine the parameters in question both on the oils and fats used as ingredients, and on the fat extracted from the finished products, such as snacks, biscuits, spreads and dry baked goods.

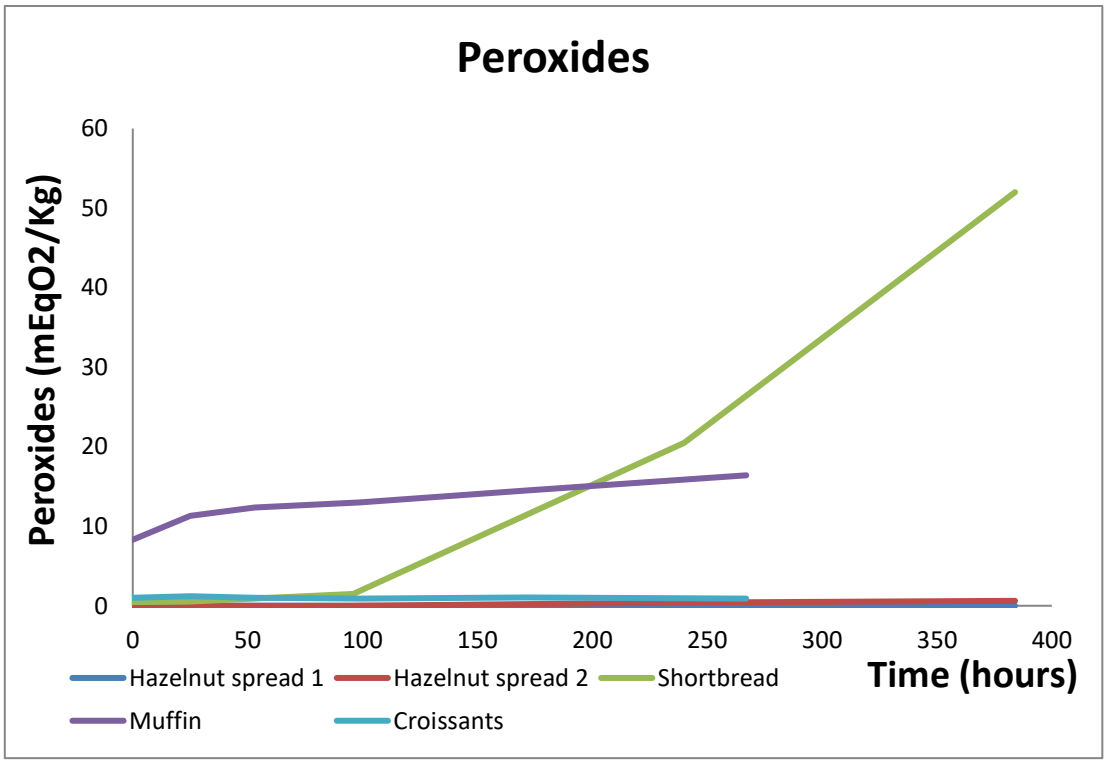
Compared to classic methods, CDR FoodLab® is used to analyse micro-quantities of sample. This characteristic means that, to perform the analyses, it is sufficient to extract a minimum quantity (1-2 g) of fatty matter from the oven product whose state of rancidity is to be determined.

The use of classic methods for performing the same analyses would be unthinkable, given the high quantity of fatty substance that would need to be extracted for the analysis.

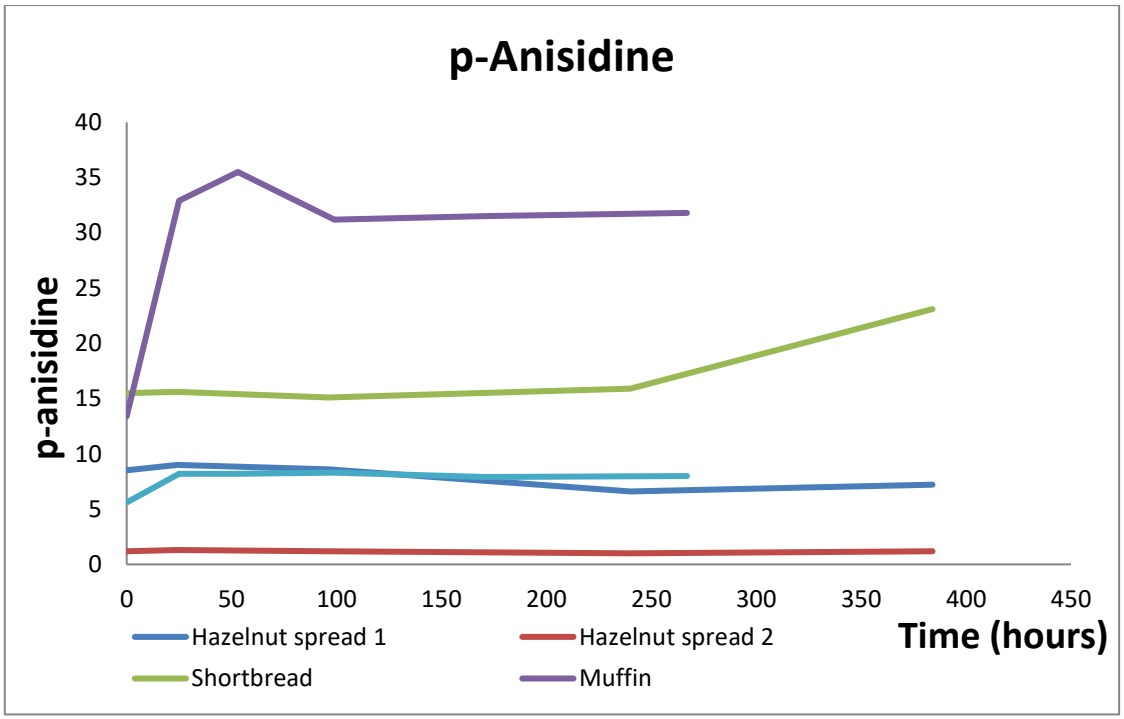
Below are the results of the analyses carried out over the course of the study



Graph 1 . Analysis of acidity over time on spread 1, spread 2, shortbread, croissants and muffins



Graph 2 . Analysis of the Peroxides over time on spread 1, spread 2, shortbread, croissants and muffins



Graph 3 . Analysis of p-Anisidine over time on spread 1, spread 2, shortbread, croissants and muffins

Data analysis

As can be seen from the graphs, the samples and therefore the analyses on spreads and shortbread, compared to the other products, lasted longer, increasing the time between one sampling and the next. This is because it was noted that these three products were particularly more stable than the others.

Regarding the acidity, a certain stability of all products was noted, except in the case of croissants, for which an increase occurred probably due to the higher percentage of humidity of the product compared to the others. The oscillations of the acidity values that can be seen in the graph, around a constant value, are attributable to the fact that each analysis was performed on a different sample, as it is necessary to analyse the product immediately after opening the package and each product is individually packed.

Instead, by analysing the results of the peroxide analysis, the extreme stability of both the spreads and the croissants can be seen, while a slight increase in the peroxides on the muffins and an exponential growth on the shortbread are evident.

By examining the data of p-Anisidine in the case of the two spreads, a difference in value of this parameter can be seen. Spread 2 starts from a lower p-Anisidine value and remains constant over the test. Spread 1 instead starts from a higher p-Anisidine value and then decreases slightly in the final phase. This decrease can be explained by a loss by volatility of the secondary oxidation products or by chemical reaction of the same during the stress test.

In the case of croissants, an increase in the p-Anisidine datum is noted which, after a short time, settles at a constant value. In the case of shortbread, the value remains constant up to approximately 200 hours before starting a linear ascent. Muffins undergo sudden secondary oxidation in the initial stress phase with the p-Anisidine datum practically tripled in approximately 50 hours of product stress. This value drops by a few units in the continuation of the stress test. In this case also, like spread 1, a reduction due to chemical reaction of the volatile compounds formed can be assumed.

Conclusions

The rancid state of a finished product can be determined by analysing Free Fatty Acids, Peroxide Value and p-Anisidine Value in the fat that composes it.

Performing this series of analysis is therefore useful to undertake research on how to improve the quality and stability over time of your product to increase its shelf-life.

By extracting a minimum quantity of fat with the system developed in the CDR research laboratories, it is possible to determine the shelf-life of a finished product quickly and easily with the CDR FoodLab® analysis system. This system is used to determine, in just a few minutes and simply, the parameters in question both on oils and fats used as ingredients, and on finished products such as snacks, biscuits, spreads and dry baked products with a simple photometric method.

The extraction system developed by CDR allows the extraction of the sample to be analysed simply and quickly, avoiding risks for the operator and for the environment.

With CDR FoodLab® it is also possible to analyse lactose for "lactose-free" products, the alcohol content in the finished product and in the alcoholic solutions used for its preservation, providing a complete series of analyses useful for the quality control of baked products and spreads. The analyses are carried out quickly and easily also on the production line without the need for personnel with experience in laboratory techniques.

Unlike traditional or reference methods, no titrations and long analysis times, glassware, calibration or maintenance of the instrument are required. The results are related to those of the reference methods. With CDR FoodLab®, acidity, peroxides and p-Anisidine analyses can be performed in just 5 minutes on oil or fat as raw material or on that extracted from the finished product.

The CDR FoodLab® analysis system is a valuable aid for companies of all sizes that manufacture bakery products because it makes quality control from raw materials to the finished product quick and easy and facilitates research in improving the shelf-life of this sometimes very complex type of product.