Front face fluorescence analysis to monitor food process contaminants

Fluoralys technology

Fluorescence is a natural phenomenon of light emission when a molecule has received light energy, with 10% of light-absorbing molecules being fluorescent. In food products a wide range of molecules, such as proteins, various vitamins and pigments, have this capability. Maillard products are highly fluorescent, therefore fluorescence can be detected with exceptionally high sensitivity, making it possible to detect trace amount of PCs in heat-treated food products.

To detect the natural fluorescence emitted by food products, a compact and robust analyzer, Fluoralys, was developed by Spectralys (Figure 1). It comprises the optical system required to perform front face fluorescence measurements. Four fibre coupled LED light sources for sample excitation, and one for fluorescence recovery are embedded in a probe. The probe is inserted into a chamber containing the sample at a given distance from a solid sample (biscuit) or inside the puree or milk (baby food). The fluorescence light is decomposed by a spectrometer and analysed using software in an embedded computer. The software sends the measurement to a remote database and applies decomposition and prediction models producing a result, such as PC concentration, in 30 sec.

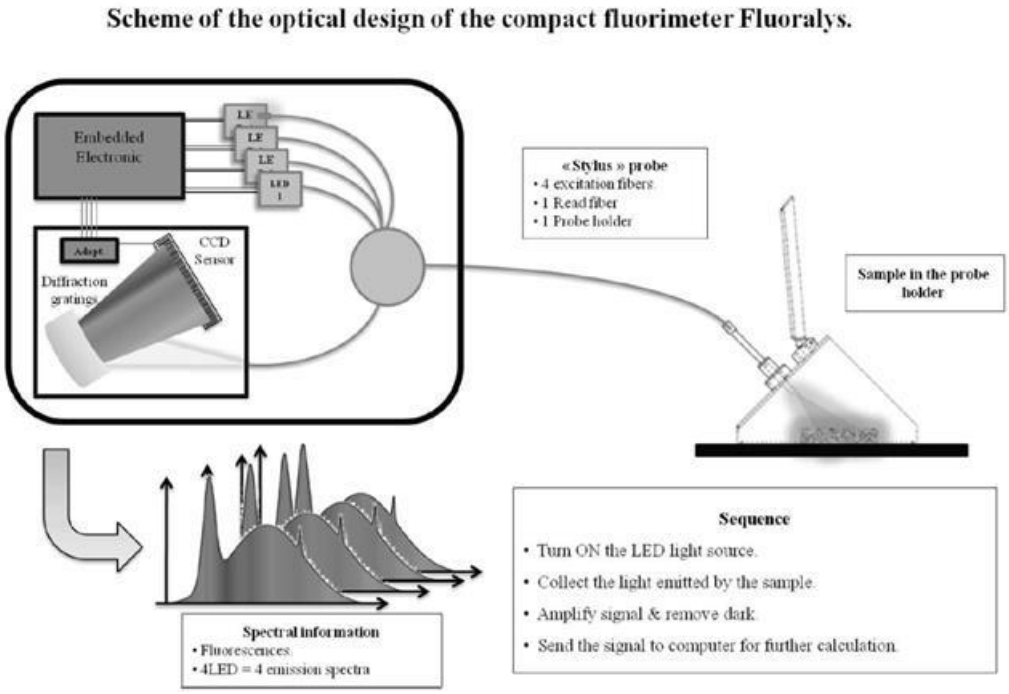

Figure 1. The Fluoralys analyzer: principle.

The Fluoralys analyser allows fast optimization of recipes and process parameters by real-time diagnosis of the impact on final product quality. The analysis can be made at a laboratory by sampling the product and analyzing it in the black chamber or on line (near the production line). The apparatus can also be used in line, using temperature and pressure resistant probes (Figure 2). A control map in real time, allows implementation of corrective actions when necessary to ensure stable product quality.

These various applications are of great advantage to the food industry to help deal with new safety issues such as control of PCs, and more generally to face the high and uncontrolled variability of the ingredients. The simple and real-time analysis of product is an efficient tool for improvement of the

quality, which is not possible when samples have to be sent to external laboratories in an expensive and time-consuming approach.

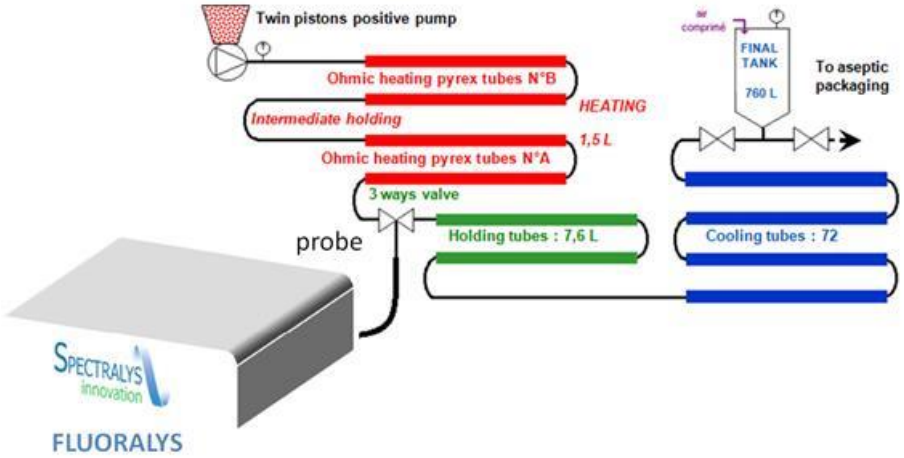

Figure 2. Example of Fluoralys in line implementation on an ohmic heating system for baby food puree sterilization.

1. Application to the objectives

a. A global and rapid diagnosis to compare the efficiencies of different technologies

A simple way to get a rapid view on the efficiency of an alternative technology compared to the conventional one is to calculate the difference between the two fluorescence images of the corresponding products. This difference is calculated on statistical basis as the **Distance from reference index (DFR)**. DFR measures both the degradation of native components such as vitamins, or protein denaturation, and the formation of contaminants including PCs. The method calculates the DFR using the raw product before thermal processing as reference. The DFR index increases proportionally to the severity of the heat charge and damage suffered by the food product. In the Prometheus project, we aimed at selecting alternative technologies able to ensure the microbiological and sensorial qualities of the final product whilst decreasing the negative impacts of the process, including formation of PCs. We show in Figure 3 how the real-time assessment of DFR using Fluoralys provided a reliable diagnosis of the positive impact of ohmic heating compared to retorting on carrot puree quality parameters, as confirmed by furan assessment. The two evolutions are not perfectly similar, because of the global quality assessment of the DFR index. Beyond the specific impact measured on furan as a model PC, many other quality parameters were shown to evolve, but to a different extent. Hence, carotenoids and some phenolic compounds were also increased by ohmic heating compared to retorting, but to a much lesser extent than furan.

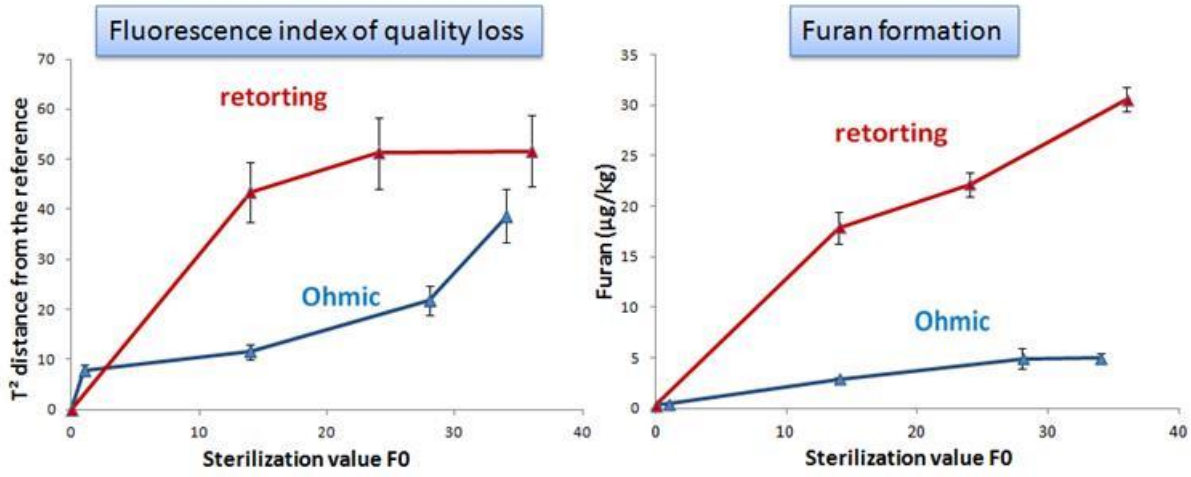

Figure 3. Comparison of retorting and ohmic heating impact at 129 °C on carrot baby food using the fluorescence parameters DFR and the chemical assessment of the PC furan.

b. Assessing product quality parameters including PC in real time

The other aim of Fluoralys was to enable easily real time measurement of several compounds of interest (vitamins, neoformed compounds, moisture, etc.) present in very low amounts. The concentrations of these molecules should be strongly influenced by the heat charge absorbed during the thermal treatment. Other quality parameters, such as texture or colour, evolving under the same conditions could also be assessed in this way.

First, a calibration model is built relating the fluorescence information with quality indicators measured using standard chemical techniques (Figure 4). Based on such calibration models, fluorescence measurement on any food product of the same type as the calibration will allow assessment of the quality parameter of concern. For example, measurement of acrylamide in biscuits can be made without any preparation, by inserting a biscuit in the black chamber and waiting for approximately 30 seconds. The result has an error slightly higher than that of the conventional method due to the additional calibration error. The calibration model must be checked and updated regularly, at least whenever changes in the recipe or process are made. A control map allows monitoring of the data obtained through different batches, and a database including the results together with all sample characteristics for traceability and further analyses can thus be built.

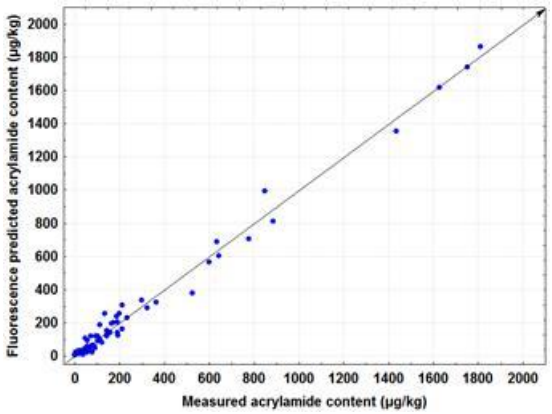

Figure 4. Calibration model for acrylamide (mean relative error 8%).

2. Some major results obtained within the project

We applied the analytical technology with success to the four food products for PC monitoring, or process/recipe comparison regarding their susceptibility to produce PCs.

We show here two examples: detection of the undesirable Maillard product CML in infant formulas (IF) and inline quantification of the impact of ohmic heating time-temperature parameters on the PC, and monitoring of acrylamide in biscuits with other quality parameters.

a. 3.1 CML in infant formulas

A basic IF recipe was chosen and some variations were introduced on the basis of their known impact on Maillard reaction development. For example, docosahexaenoic acid (DHA), a long-chain polyunsaturated fatty acid (LC-PUFA), is a critical ingredient in IF because of its beneficial influence in brain development. However it is very prone to oxidation on heat treatment. A second ingredient of interest is iron, because of its high importance for prevention of anemia, while activating oxidative reaction.

We compared formulas with and without long-chain PUFA in the presence and absence of iron, using Fluoralys in the DFR approach to give a global view on the quality of the product (Figure 5). The DFR evolution during the sterilization treatment was compared with the CML concentration measured by conventional analysis. We observed much faster product damage in presence of LC-PUFA, especially in presence of iron, in agreement with observations based on CML. We confirmed that fluorescence provides a reliable and real-time diagnosis on the recipe impact throughout the heat process. A calibration model was also built to allow CML prediction in the various recipes using Fluoralys. The mean relative error was 8%.

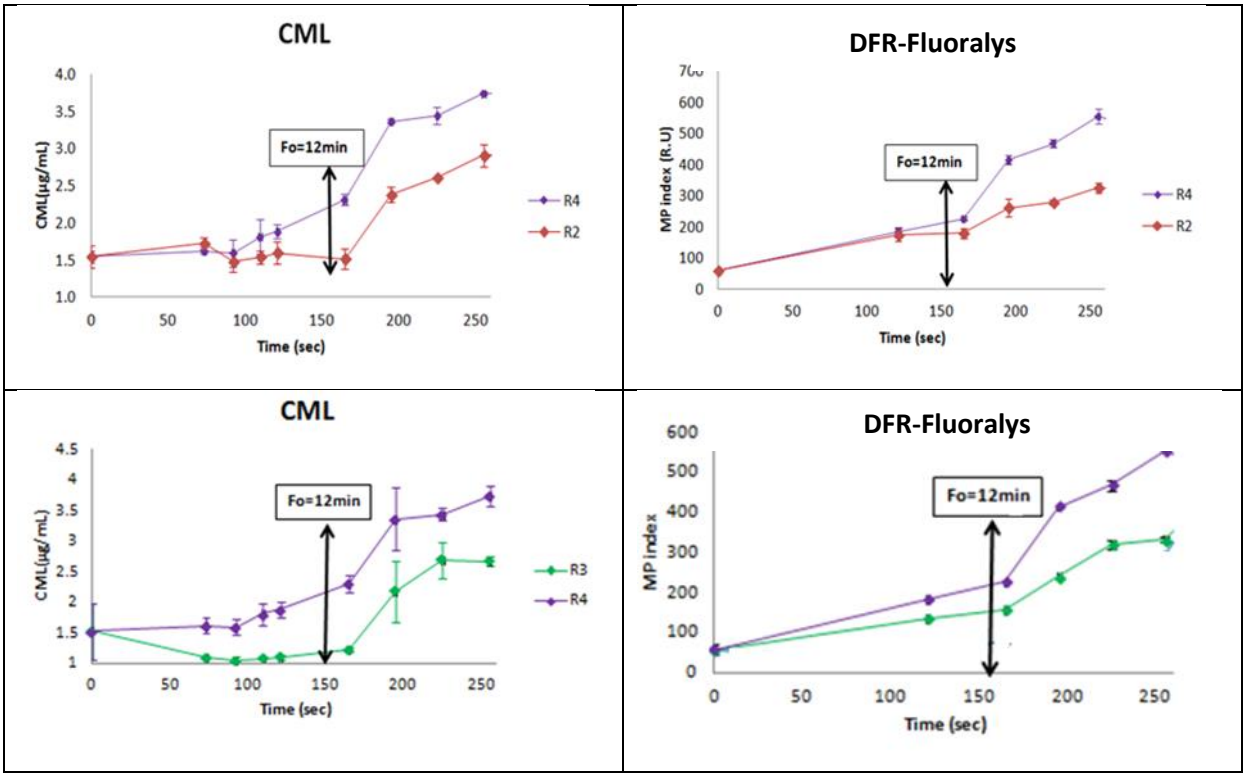

Figure 5. DFR evolution using Fluoralys and CML concentrations of infant formulas including or not LC-PUFA in the presence of iron (R3 without and R4 with) and the effect of iron in the presence of LC-PUFA (R2 without and R4 with 12 mg/L).

b. *A multi-criteria quality assessment of biscuits using Fluoralys*

In partnership with the Spanish company SIRO, a proof of concept was developed at industrial level to demonstrate the potential of Fluoralys to provide a multi-criteria comprehension of the interactions between different batches of dough of two recipes after baking process.

This industrial study was carried out to provide 43 independent batches produced with 2 different recipes of black biscuits (Z and M). The 2 recipes studied were very similar differing only in few ingredients. For the different batches of a same recipe, different ingredients batches and even suppliers were also considered. Samples were taken after baking (final product). The water content is the parameter used to control baking with a target final level of 2-3% depending in the recipe. Baking temperature and ventilation were adapted to reach this standard, the variability on this parameter thus being very low (approx. 10%).

Various calibration models were built, over acrylamide, colour (L ;a ;b), humidity and texture, with a average relative prediction errors of 8%, to provide a multicriteria quality control on the final product in real time. Figure 6 shows batch variability of the different quality criteria. While color (here factor b in Lab assessment) and humidity were relatively stable (less than 10% variation), acrylamide and texture strongly varied, from 71 to 358µg/kg and from 1600 to 2100 g respectively. Such variability is probably due to variation in the ingredients and dough composition and to fluctuations in process parameter intentionally implemented to control the final water content.

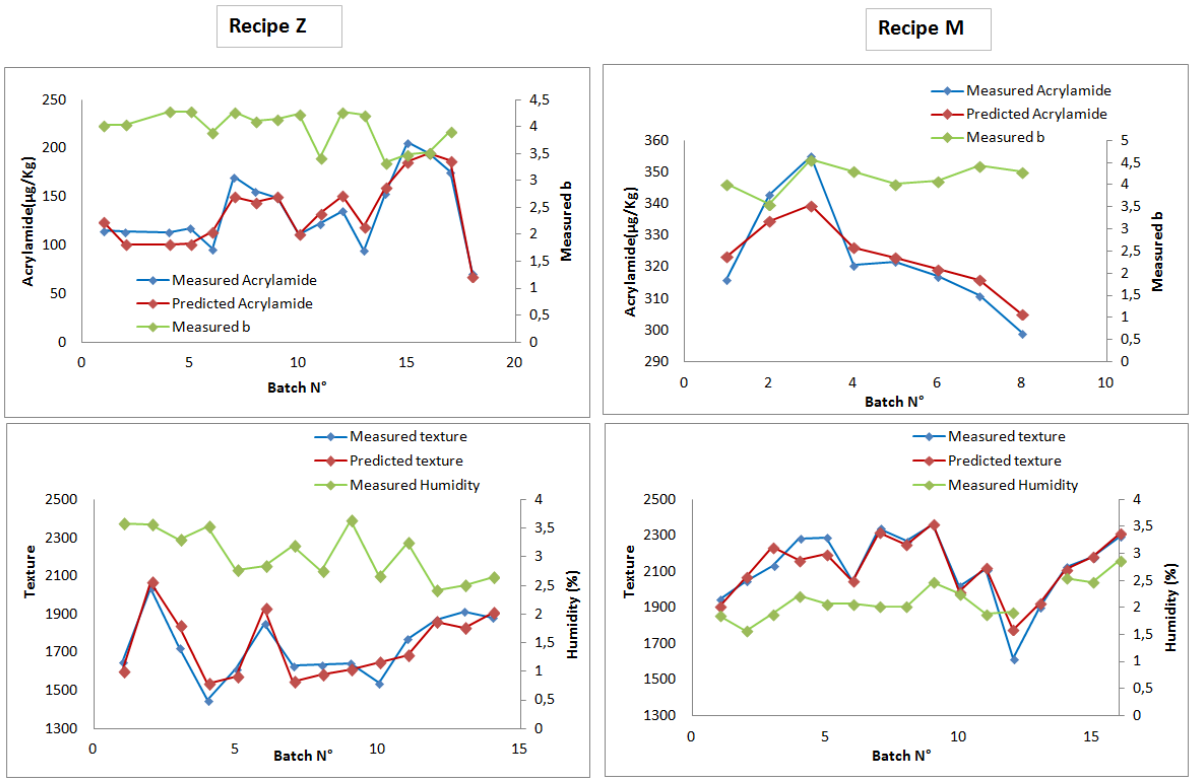

Figure 6. Acrylamide and texture monitoring using Fluoralys in the final biscuits: comparison with conventional analyses. Color (b factor) and humidity are standardized by adaptation of process parameters.

3 Conclusion

- **Front face fluorescence is an accurate, sensitive, and non-destructive real time analytical tool**
    - ✶ To control the raw material variability and impact on the final product quality
    - ✶ To assess the impact of processing steps and storage
    - ✶ To control the compliance of each batch regarding the targeted quality
    - ✶ To compare different technologies

- **Fluoralys can be used with different methods**
    - ✶ **Global quality index** without calibration to get a rapid screening of quality compared to a reference
    - ✶ **Calibration** to monitor in real time a specific quality parameter
    - ✶ Such methods are automated and can be used at line and in line

- Thanks to this innovative tool, it is now possible to get a **rapid diagnosis of the effect of alternative technologies, such as under vacuum baking, ohmic heating, or high pressure**. Not only is the potential to mitigate PC provided but also the possibility to evaluate their impact on other quality parameters, such as water content, colour or texture.
- Furthermore, this multicriteria approach **allows correction of the process parameters in line** to achieve final product standardization at the desired quality level.

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