Innovative Food Science and Emerging Technologies 48 (2018) 122–130

Contents lists available at ScienceDirect

Innovative Food Science and Emerging Technologies

journal homepage: www.elsevier.com/locate/ifset

Headspace fingerprint as a potential multivariate intrinsic indicator to monitor temperature variation of thermal in-pack processes: A case-study on broccoli puree

Tara Grauwet[a], Avi Shpigelman[b,*]

[a] Laboratory of Food Technology, Leuven Food Science and Nutrition Research Center (LFoRCe), Department of Microbial and Molecular Systems (M2S), KU Leuven, Kasteelpark Arenberg 22 box 2457, 3001 Leuven, Belgium

[b] Laboratory of Novel Food and Bioprocessing, Faculty of Biotechnology and Food Engineering, Technion Israel Institute of Technology, Technion City, Haifa 3200003, Israel

ARTICLE INFO

Keywords:
Indicator
Thermal processing
Temperature non-uniformity
Multivariate
Headspace fingerprint

ABSTRACT

The aim of the presented study was to evaluate the potential of a headspace fingerprint as a multivariate intrinsic indicator for monitoring temperature history variation that can occur, for example, during in-pack food processing at the product level. Using solid-phase micro-extraction gas chromatography mass spectrometry (SPME-GC–MS), we monitored the extracted volatile fraction of a series of 8 well-defined thermally processed broccoli purees, differing only in the maximal process temperature reached. Our results showed that the relative composition of the extracted volatile fraction clearly depended on the processing intensity (as a measure for thermal variation) applied. In addition, this headspace fingerprinting approach, including multivariate data analytical approaches, allowed a swift selection of specific intrinsic fingerprint markers. The evaluation of the concentration of each of these markers allows to discriminate between the different processing intensities. However, we suggest to perform a linear combination of the information from relevant identified intrinsic fingerprint markers given the increased reliability of a multiple response indicator. The presented approaches are a promising proof-of-principle that has potential to be exploited for monitoring other processing non-uniformities as well.

Industrial relevance: Thermal treatment is by far still the most commonly used preservation method for food with a high water content. In-pack retort treatment commonly results in some temperature non-uniformity occurring during the treatment at both the reactor and/or the product level. While the use of thermocouples for acquiring time-temperature history is often an excellent solution, the use of intrinsic food components as indicators can be of great advantage for process monitoring. So far usually pre-selected single component intrinsic indicators were suggested. In this work, we are presenting the utilization of the headspace fingerprint as a multivariate intrinsic indicator instead of using a single compound. From the industrial point of view, we present an innovative concept of monitoring product specific extracted volatile fraction, followed by selection of specific intrinsic fingerprint markers and linearly combining the information from those markers. While the advanced data analysis for selection of the fingerprint markers will have to be done per specific product, only the linear combination of the specific data from the markers can be used for routine analysis. Such concept can provide increased reliability due to the utilization of a non-pre-selected multiple response indicator with a relatively feasible monitoring of the markers using gas chromatography mass spectrometry (GC–MS).

1. Introduction

Nowadays, thermal treatment is by far still the most commonly used preservation method for food with a high water content. The main objective of thermal treatment is, in most cases, the destruction of potentially harmful micro-organisms by the achievement of a targeted and theoretically defined sterilization (F_0) or pasteurization (P) value. At the same time, in the context of process optimization, it is aimed to minimize the concomitant reduction in quality (Baucour, Cronin, & Stynes, 2003). High temperature in-pack sterilization (usually in a retort) is a commonly used batch treatment designed to provide shelf-stable, nutritious and high-quality food products (Baucour et al., 2003).

* Corresponding author.
E-mail address: avis@bfe.technion.ac.il (A. Shpigelman).

https://doi.org/10.1016/j.ifset.2018.06.001
Received 30 January 2018; Received in revised form 30 May 2018; Accepted 1 June 2018
Available online 03 June 2018
1466-8564/

However, during every conventional in-pack thermal processing, there are inevitable temperature non-uniformity issues that can be due to:

(*i*) variability in heat delivery to the food surface in the processing equipment (heat distribution); (*ii*) variability in the internal (in the product) heat delivery from the surface to the coldest spot (heat penetration) (Smout, Van Loey, & Hendrickx, 2000); and (*iii*) variability of product initial temperature (Baucour et al., 2003). Consequently, the in-pack retort treatment commonly results in some temperature non-uniformity occurring during the treatment at both the reactor and/or the product level. Assan, Watanabe, and Mihori (2000) reported a 30% difference in sterilization value between different canned tuna fish in a commercial-sized static retort (i.e. non-uniformity at retort level). While in recent years efforts were made to equip retort systems with sophisticated temperature control systems, there is still a need to document such differences on the product level. Almonacid and Amézquita (2009), reported that in-pack variability occurs in creamy white sauce due to temperature profiles resulting in F_0-values ranging from 5.4–28.2 min during sterilization at 121.1 °C. While in most cases in the coldest spot of a packed food product we aim at sterilization values F_0 lower than 15 min (Holdsworth & Simpson, 2007), significantly higher values can be reached at the outer regions of packed food. As the kinetics of the safety or quality attributes are frequently sensitive to temperature history differences, process impact variation can occur. Of course, temperature differences resulting in under-processing are, from a consumer-safety point of view, hazardous and completely unacceptable. Consequently, in practical applications, to ensure complete safety over the whole volume of the product, as well as over the whole volume of the reactor, products may be potentially over-processed, resulting in reduced product quality in terms of nutritional aspects (e.g. vitamin concentration) as well as sensorial properties (Mehauden, Bakalis, Cox, Fryer, & Simmons, 2008). It is clear that monitoring and accurate evaluation of temperature for designing, controlling and optimizing thermal treatments is crucial for providing safety with minimum unnecessary thermal quality degradation effects.

In order to avoid erroneous treatments, correct determination of the thermal history perceived in the food reactor as well as inside the food product is of primary importance in thermal processing. The time-temperature history can be obtained from thermocouples or any type of sensor which records temperature as a function of time (in situ approach; (Hendrickx et al., 1993)). Such history can be further translated into an equivalent processing time at a reference temperature using the *P*- or F_0-values for safety targets as well as cook values (*C*-value) for quality attributes (Mehauden et al., 2008). While such measurement technique is easy to apply and provides valuable data and simple analysis, the utilization of thermocouples is not always convenient, reliable nor practical. A major limitation is an indispensable need for a large number of thermocouples to fully represent possible 'cold' or 'hot' spots in the treatment vessel and/or product (Mehauden et al., 2008). Additionally, the size of the thermocouples can limit their applicability to small products, or limit the possibility of revealing the in-pack variability.

As direct measurements of temperature in samples can be problematic, the utilization of temperature-time-integrators (TTI) has been described in literature (Van Loey, Hendrickx, De Cordt, Haentjens, & Tobback, 1996). A TTI can be defined as 'a small device that shows a temperature-time-dependent, easily and correctly measurable irreversible change that mimics the change of a target quality parameter undergoing the same dynamic temperature exposure' (Taoukis & Labuza, 1989). A reliable integrator must present a kinetic equivalence to the target attribute under consideration and should guarantee a measurable response within the processing parameters of interest (Claeys, Van Loey, & Hendrickx, 2003). When the aim is not necessarily predicting the impact of a temperature history on a *specific* food safety or quality attribute, but is to obtain insight in the temperature distribution within the process reactor and/or food product, 'indicators for temperature non-uniformity' mapping have been described in literature (Grauwet et al., 2012; Grauwet, Van der Plancken, Vervoort, Hendrickx, & Van Loey, 2009, 2010). In this context, the prerequisites are less strict as for an integrator (no kinetic equivalence needed, since no attribute is selected from the start): the kinetics of change of the indicator's response should be clearly sensitive for occurring temperature history differences as a function of space in the product/process reactor. Consequently, evaluation of the indicator's response as a function of the different coordinates can document the observed temperature distribution (Grauwet et al., 2012, 2010, 2009). Integrators/indicators have been classified in terms of working principle (biological, chemical, physical), type of response (single, multiple), origin (intrinsic, extrinsic), application (dispersed, permeable, isolated) in the food material and location (volume average, single point) in the food (Hendrickx et al., 1993; Van Loey et al., 1996).

Using an intrinsic food component as an indicator/integrator is advantageous as the indicator/integrator is more or less homogeneously dispersed in the food, which eliminates the limitations of heat transfer into the indicator/integrator and allows evaluation of the volume-average impact of the thermal process. In practice, intrinsic markers have the advantages that no monitoring compound or device has to be added and/or placed in position before the processing step, and that problems related to the selection of an appropriate carrier system, are avoided. However, to the best of our knowledge, in literature only single-component (i.e. only one attribute/chemical compound is monitored as a response) intrinsic integrators have been suggested (Claeys, Van Loey, & Hendrickx, 2002; Vanderhaegen et al., 2004).

With the development of high-throughput analytical equipment capable of monitoring simultaneously many compounds (i.e. multiple variables) in a single analytical run combined with the progress made in multivariate data analysis tools, the idea of an intrinsic indicator based on multiple compounds can be put forward. Indeed, recently several projects used headspace fingerprinting as an untargeted approach to differentiate and compare novel and traditional processing procedures and to study the kinetics of complex food reactions (e.g. during shelf-life) (Grauwet, Vervoort, Colle, Van Loey, & Hendrickx, 2014; Kebede et al., 2013, 2015; Koutidou, Grauwet, & Acharya, 2016; Vervoort et al., 2013). The objective of the current project was to extend the potential of this methodology towards its utilization for the evaluation and documentation of temperature variation in in-pack thermally treated food systems. As far as we are aware, there is no open literature on the evaluation of the potential of a fingerprint (i.e. multivariate) indicator for the detection of temperature history differences. As a multivariate intrinsic indicator, the headspace fingerprint of a food product was analyzed with headspace solid-phase micro-extraction gas-chromatography mass-spectrometry (HS-SPME-GC–MS). Broccoli puree was selected for this work as a case-study. In order to obtain insight in the potential of the multivariate indicator to document temperature history differences, broccoli purees were thermally processed at a range of thermal processing intensities that differ only at the maximal treatment temperatures (while total process time was constant) resulting in a range of perceived and distinct F_0-values. The headspace of the treated broccoli purees were fingerprinted by HS-SPME-GC–MS. Fingerprints were analyzed by multivariate data analysis in order to find specific fingerprint markers, i.e. compounds detected which concentration was clearly correlated to changes in F_0-values.In addition, we present the concept of integrating the information from the identified specific fingerprint markers by linear regression to obtain a multiple response intrinsic indicator, that can combine the advantages of increased reliability of multiple responses.

2. Materials and methods

2.1. Materials

A single batch of freshly harvested broccoli (*Brassica oleracea* var. *italica*) was purchased at a local shop. The broccoli was carefully