



Evaluation of aroma release of gummy candies added with strawberry flavours by gas-chromatography/mass-spectrometry and gas sensors arrays



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ABSTRACT

Aroma release of two strawberry flavourings (one natural-NS and one nature-identical-NIS) at different concentration (0.15%, 0.30%) added to gummy candies made of pectin, gum arabic and gelatine as structuring agents was studied by gas chromatography/mass-spectrometry (GC–MS) and electronic nose (e-nose) equipped with two different sets of sensors to characterise and differentiate the products. By using GC–MS, different aroma patterns of the pure NS and NIS flavouring were obtained. The effect on the presence and amount of the volatile compounds of the strawberry flavours in the vapour phase was studied and discussed as a function of the candies formulation; the products were partly differentiated, in agreement also with the sensory analysis. The innovative e-nose instrument has differentiated candies based on flavour origin and concentration for both gelatine and gum arabic independently on the sensor array type; for the pectin-based products porphyrines and GNP showed lower and different performances in the discrimination ability.

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1. Introduction

Gummy candies are confectionery products and their texture is achieved by using various gelling agents such as gelatin, starch, gums and pectin. However, the most important ingredients from a quantitative point of view are the sweetener agents (i.e. sucrose, glucose and corn syrups) while colouring agents and aromas are specifically added to give the peculiar sensory attributes to this food commodity (Edwards, 2000; Lubbers and Guichard, 2003).

The release of volatile compounds from food matrices is governed by kinetic and thermodynamic phenomena (Voilley and Souchon, 2006; Fabre et al., 2002). Thermodynamic factors determine the partitioning of volatiles between the food and air phases under equilibrium while the kinetic phenomena influence the rate at which equilibrium is achieved (de Roos, 1994) and may affect the rate of perception. Intrinsic properties of the food matrix and

extrinsic factors (e.g. temperature, pressure) are involved in both the release rate and the aroma concentration under equilibrium.

Interactions of different nature could be established between matrix compounds and aroma molecules, reducing their concentration in the vapour phase. As a consequence, the same aroma can generate totally different odour sensations when used in different foods or even result in an imbalance in the aroma profile (de Roos, 2006; Guyot et al., 1996).

Several studies have been carried out to study and/or to characterise the aroma release of gelled candies taken in most of the cases as model systems in the attempt to understand the effect of the gelling agent on the retention of the volatile compounds and their release and perception upon mastication (Jangchud, 2013; Déléris et al., 2011; Boland et al., 2006; Lubbers and Guichard, 2003; Kalviainen et al., 2000; Baek et al., 1999).

Increasing amount of hydrocolloids in a food matrix has been shown to increase the thickness of the product associated to a reduction of the perception of flavour. This effect could be due to both specific interactions between the aroma compounds and the matrix, that decrease the partitioning in the vapour phase, and to an increased resistance to the mass transport and diffusion of the volatiles from the food into the air phase that, in turn, depends

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on the structural properties and viscosity of the system (Renard et al., 2006).

Sweeteners and, in particular, small saccharides play also a main role in affecting not only the sensory properties of the product but also the textural properties of the hydrocolloids matrix, the viscosity of the aqueous phase and the water activity (a_w). These physical and physico-chemical properties may influence the release and partitioning of aroma compounds, even if they have been scarcely investigated.

In confectionery, flavour properties are due to the addition of different type of aromas that, according to the European Union (EU) legislation, are classified as natural, nature-identical (chemically identical to natural substances but obtained by chemical processes) and artificial (Demyttenaere, 2012). Besides compulsory regulations and labelling, in recent times there is an increasing interest in the use of natural flavourings. In fact, they meet the expectations of the consumers continuously looking for products made of raw and fresh-like materials, ingredients and additives. However this arises some issues for the producers as they are more costly and their stability over time may be lower.

The formulation of a complex formulated products to meet consumer acceptability is a main challenge for the confectionery industry and any change occurring in the recipe, including that of an aroma mixture has to be evaluated as it may affect the release of the volatile odorous compounds thus affecting their perception and the overall sensory quality. The optimisation of the flavour quality of foods requires, in general, a deep knowledge and understanding of the of the nature and intensity of the interactions between aroma compounds and no volatile compounds that may occur at molecular level during formulation and processing as well as of the other intrinsic factors and phenomena affecting the aroma release. However, more recently in the candies sector, modern research approaches have pointed out the importance of the evaluation of the aroma profile by innovative 'in nose' instrumental techniques, because of the unique physiological factors of the consumers (e.g. chewing rate, saliva flow, swallowing frequency) affect the release of flavours during eating and thus their perception (Yang et al., 2011).

Besides overall quality and acceptability, aroma compounds and pattern of foods are relevant aspects in relation to the origin of raw materials and ingredients and thus, their authenticity. This is a main issue for food producers even if consumers may not be able to discriminate among food products produced with ingredients and additives, flavouring agents included, of different type and origin.

A number of instrumental methods are used for the determination of single volatile aroma compounds and/or the overall aroma compounds pattern of food products. The known procedures used for the identification and determination of the authenticity of food products and more specifically the individual aroma volatile compounds employ high performance liquid chromatography, gas chromatography with mass selective detection, mass spectrometry, chromatography-mass spectrometry (Reynecius, 2006), and other methods that require complex equipment and highly skilled personnel. The development of simple test methods based on the qualitative/quantitative estimation of aroma pattern using sensors is of particular importance for establishing the authenticity of food products and/or discriminate them on the basis of the flavouring origin and related composition. In these last years electronic noses have proved to be very useful tools for food and aromas analysis: applications were proposed both for quality control and study on aroma release in a wide range of food products such as cheese, wine, coffee, tomato and meat (Drake et al., 2003; Michishita et al., 2010; Miettinen et al., 2002; Pinheiro et al., 2002; Sinesio et al., 2000; Vestergaard et al., 2007).

Different kind of sensors can be used to built an electronic nose (e.g. in the cited works MOS, MOSFET, Quartz crystal and optical sensors were used). In this study a Quartz crystal microbalance (QCM) sensors array was used. In literature, QCMs sensors surface have been modified in different ways using porphyrins, peptides or molecular imprinted polymers (Dai et al., 2014; Di Natale et al., 1997; Pizzoni et al., 2014).

The objective of this study was to investigate the influence of the composition (i.e. gelling agents – gelatin, pectin- and sugars) on the release and sensory perception of aroma compounds from candy model systems added with two strawberry flavours, one nature-identical and one natural added in two different concentrations. Strawberry flavoured candies head-spaces were characterised and studied with both GC-MS and electronic nose; sensory analysis was used to test human abilities to discriminate products added with the two different aromas.

For this specific application, both a porphyrin and a peptide based QCMs sensors array were used. In previous studies these kind of modified sensors showed the ability to discriminate different aroma patterns (both in model and complex system) in a large field of application (food included) (Pennazza et al., 2013; Pizzoni et al., 2013; Piccone et al., 2011).

2. Material and methods

2.1. Materials

All reagents and standards were purchased from Sigma-Aldrich (Milan, Italy). The natural and nature-identical strawberry aromas were from Symrise srl (Milan, Italy) that did not provide their composition. 20 MHz QCM sensors, were from Elbatech (Marciana, Italy).

2.2. Samples preparation

Model gummy candies (average weight of $6.3 \text{ g} \pm 0.1 \text{ g}$) of different formulation were kindly provided by Gelco srl (Castelnuovo Vomano, TE, Italy) that prepared them at laboratory scale by using ingredients and additives and by applying process conditions reproducing the industrial manufacturing procedures. Three different gelling agents were used: gelatin (Gel), gum arabic (GAR) and pectin (Pec). For each structuring gelling agent, two types of strawberry flavours (a natural – NS and a nature-identical – NIS one) at two different concentrations ($0.15\%_{w/w}$ and $0.30\%_{w/w}$, coded as "1" and "2", respectively) were used. In Table 1 the initial formulation of the model candies is reported. The aroma quantity to be added was computed on the total initial weight of the candy initial formulation. Thus, in total 12 type of samples were prepared, four for each gelling agent. To avoid any interference on the evaluations, candies were formulated and manufactured without the addition of colouring agents.

The model candies were named as follows: NS- $0.15\%_{w/w}$: A1; NS- $0.30\%_{w/w}$: A2; NIS- $0.15\%_{w/w}$: B1; NIS- $0.30\%_{w/w}$: B2. Aroma was added to the candy mixture after the cooking step and following cooling at a temperature of 45°C . After flavour addition and mixing, the candies were poured in moulds and dried to set the gel at different conditions according to the structuring agent: GAR at 55°C for 41 h followed by a further equilibration step at 20°C for 31 h; Pec and Gel at $22\text{--}24^\circ\text{C}$ for 48 h.

2.3. Mechanical properties analysis

Mechanical properties of the candies were determined by creep test by using a dynamometer (mod. 5542 Instron Universal Testing

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