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New trends in the kitchen: Propellants assessment of edible food aerosol sprays used on food

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ABSTRACT

New products available for food creations include a wide variety of "supposed" food grade aerosol sprays. However, the gas propellants used cannot be considered as safe. The different legislations available did not rule any maximum residue limits, even though these compounds have some limits when used for other food purposes. This study shows a preliminary monitoring of propane, butane and dimethyl ether residues, in cakes and chocolate after spraying, when these gases are used as propellants in food aerosol sprays. Release kinetics of propane, butane and dimethyl ether were measured over one day with sprayed food, left at room temperature or in the fridge after spraying. The alkanes and dimethyl ether analyses were performed by headspace-gas chromatography–mass spectrometry/thermal conductivity detection, using monodeuterated propane and butane generated *in situ* as internal standards. According to the obtained results and regardingthe extrapolations of the maximum residue limits existing for these substances, different delays should be respected according to the storage conditions and the gas propellant to consume safely the sprayed food.

1. Introduction

The recent increase in the various ways of cooking has led to a rise in the number of tools for food creation, including edible food aerosol sprays. These new products have a long shelf-life and are easy to store. Aerosol and non-aerosol sprays must be distinguished and refer to the delivery systems of the spray. Technically, an aerosol is a suspension of fine solid or liquid particles in a gas. An aerosol is packaged in a container under pressure and a release valve is used to emit the pressurised suspension into the air forming a mist propelled by a gas propellant, as long as the gas and/or particles last (Hinds, 1999). Non-aerosol food sprays are packaged as liquid, usually in a bottle with an atomiser attachment (such as a pump-sprayer) (Dolovich, 1999). The pump sprayer uses springs, valves and tubes to mix the liquid with small amount of air and to emitthe liquid as small droplets propelled in short bursts until the liquid inside is finished.

If at the beginning certain food aerosol sprays were designed and ruled for a professional use only (aiming that standardised industrial protocols could be sufficient to evaporate residual propellants), these products are today available in many local markets and on the internet. Therefore, an important variation in their uses can occur and lead to important residual concentrations of propellants.

Food aerosol sprays propellants must be food grade or chemically inert from a toxicological point of view. CO_2 and N_2O are often used as propellants in whipped creams. Even if recreational uses of N_2O as a euphoria-inducing inhalant drug were reported, these gases are not harmful in small amounts, but risks of asphyxia due to a lack of oxygen exist (Gill, Ely, & Zhongxue, 2002). Brain damage due to N_2O has also been reported (Pema, Horak, & Wyatt, 1998; Waclawik, Luzzio, Juhasz-Pocsine, & Hamilton, 2003). However, in their normal uses, these gases are safe even if residual concentrations may be detected. Argon, helium, nitrogen and oxygen complete the list of gases authorised in food processes. Nevertheless, other gases or gaseous mixtures are also used in aerosol foodsprays, such as propane, butane and dimethyl ether. Used alone, propane is not very noxious and acts as an oxygen depletant like CO_2. Ingestion of propane does not seem to cause deleterious effects but the literature available on this subject is scarce. Butane is an oxygen depletant too, and several toxic effects (until death) were already reported when used as recreational drug (sniffing), causing heart arrhythmia for example (Jackowski et al., 2005; Vale, 2007; Williams & Cole, 1998). In aerosol food sprays, these gases are used individually or in liquid petroleum gas (LPG) form as propellant such as in varnish or paints. It is commonly admitted that, taking into account the low boiling point of these gases and the weak eventual residual concentration remaining in food, propane and butane could be safely used in food. However, problems following alkane ingestions, such as gastric perforation,have already been reported and strengthen the fact that alkane ingestion is

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not safe (Cheng, Yeh, & Hsieh, 2010; Mehlman, 1990). For example, butane is listed as harmful by ingestion in many technical data sheets (Butagaz, 2011). These gases are mainly employed in the food industry as defatting agents or extraction solvents. Due to their low boiling point, they should be released very easily leading to a safe final product but residues can be found because limits have been set. DME seems to be a valuable candidate as processing aid because it has a low boiling point (−24.8 °C), high affinity to oily substances, partial miscibility with water and exhibits resistance to autoxidation unlike other alkyl ethers (Kanda, Li & Makino, 2013).

The legislative status of gaseous alkanes is unclear. They can be considered as extraction solvents or propellants. The different international legislations are consensual concerning a maximum residue limit for gaseous alkane as extraction solvents: from 0.1 mg/kg of food in Australia and New-Zealand except for flavouring agents and up to 1 mg/kg of general food in the European Union and Argentina in general food as well as Australia and New Zealand concerning food flavouring agents (Codex Alimentarius Commission, 2012; Scientific Committee on Food, 1999). In this case, the gases are considered as processing aids and are subjected to the legislation on food additives and food contaminants. The maximum value of 1 mg/kg originating as long ago as 1981 (Scientific Committee for Food, 1981), has beenconfirmed in 1992 (Scientific Committee for Food, 1992), and has been the reference value since 1999 (Scientific Committee on Food, 1999). Even if an acceptable daily intake (ADI) seems to be unnecessary considering the low boiling point and the weak residual amount of substances when used as extraction solvents, the necessity to set a maximum residue limit for gases when used as propellants should be considered. Moreover, it is surprising to note the differences among the last European directives (Official Journal of the European Union, 1988; Official Journal of the European Union, 2009), where the maximum residue limit defined in 1981, 1992 and 1999 was not taken in consideration as it was replaced by "use according to Good Manufacturing Practices (GMP)".

The different international legislations are not consensual concerning gaseous alkanes as food aerosol propellants and two cases must be differentiated. In one case, the different international legislations define clearly the use of these products (mainly in vegetable oil pan spray for professional use only and in water-based emulsion sprays) (Food Standards Agency, 2002; Official Journal of the European Communities, 2001) and the maximum residue limit must comply with the GMP, as in Canada, Saint-Martin and Kazakhstan. Other countries have ruled the use of gaseous alkanes as food aerosol propellants according to GMP, but without restriction concerning the nature of the aerosol (not specifically oils for example) as in Russia, China, Australia and New-Zealand. However, only Uzbekistan has defined a maximum residue limit for gaseous alkane (butane) used as food aerosol propellant at 1 g/kg. Otherwise, the different international legislations do not define clearly the use and the nature of these products and ruled a maximum residue limit according to GMP as in the United States (Code of Federal Regulations, 2012) and Japan (Japan External Trade Organization, 2011). They are registered as European food additives (E943a for propane, E943b for isobutane and E944 for propane) and no maximum residue limit is available (use and residual concentrations according to GMP). In 1999, the Scientific Committee on Food (SCF) of the European Commission has not considered volatile alkane as propellants but they have been evaluated in the context of their use as extraction solvents for which the SCF agreed an acceptable residue level per substance of 1 mg/kg in food consumed (Scientific Committee on Food,1999). Moreover, the SCF was provided with residue data of the propellants (vegetable oil-based cooking sprays and water-based emulsion cooking sprays only) after use in cooking representative foods. The data showed that the total hydrocarbons are present in the prepared foods in amounts below 0.1 mg of residual hydrocarbon per kg cooked food. In most cases the amounts are substantially lower than 0.1 mg/kg food. However, nothing is detailed about the use of this kind of aerosol (time of aerosol exposure, time of cooking...). It seems that the acceptable residue level of 1 mg/kg corresponds to the experimental value of 0.1 mg/kg cooked food multiplied by ten giving a safety margin. Therefore, even if this maximum residue limit could be discussed, it seems that 1 mg/kg is the alkane concentration not to be exceeded, considering cooked food as well as consumed food.

Thus, from a toxicological point of view, the hazard of gaseous alkanes has neither been investigated as food processing aid nor as food aerosols propellants. Because of the novelty of these products, the legislation shows some imprecision and loopholes. It could be understood from the past not to rule a maximum residue limit for gaseous alkanes when used as food aerosols propellants, because of their important volatility and their restricted industrial use (followed by thermal industrial processes favouring gas release), but today it becomes crucial to reconsider their residual concentrations. Indeed, the main international legislations are only focused on some products (vegetable oil-based cooking sprays and water-based emulsion cooking sprays only) (Food Standards Agency, 2002; Official Journal of the European Communities, 2001) whereas other products such as dyes, varnishes and cooling agents areavailable and no GMP are defined for them. Moreover, these new food aerosols sprays are not often used before food processing usually after (which could favour gas release), and are sprayed on food which is refrigerated or frozen limiting gas release, and on food such as cakes whose lipidic composition favours the dissolution of these lipophilic gases. Finally, several legislations have defined purity criteria for gaseous alkanes used as extraction solvents but no information concerning these same gases used as food propellants is available (Official Journal of the European Union, 2012).

The present study aims to present the assessment of food aerosol sprays other than vegetable oil-based cooking sprays and water-based emulsion cooking sprays. Firstly, release kinetics of propellants (butane, propane and dimethyl ether) over one hour and one day were presented. Secondly, the remaining gas concentrations found in food were discussed according to the available legislative documents.

2. Material and methods

2.1. Reagents

Madeleines (French butter cakes) and chocolate were purchased in local French (Casino, Pontarlier) and Swiss (Coop, Yverdon-les-Bains) supermarkets. Food aerosol sprays were obtained from a decoration shop and internet retailers. Several propellants were analysed from the four following food aerosols sprays: LPG in dye food aerosol spray – bronze – (Product 1) and in cooling spray for sugar and chocolate (Product 3), butane/isobutane/propane in dye food aerosol spray – silver – (Product 2) and dimethyl ether (DME) in varnish food aerosol spray for marzipan, sugar and chocolate (Product 4). Gas propellants purities and proportions were not indicated in the composition.

Propylmagnesium chloride (C_3H_7MgCl) 2.0 M in diethyl ether and butylmagnesium chloride (C_4H_9MgCl) 2.0 M in tetrahydrofuran (THF) were purchased from Sigma–Aldrich (Saint-Louis, MO). Deuterated water was obtained from Cambridge Isotope Laboratories CIL Inc. (Andover, MA). Dimethyl ether was sampled directly from the varnish food aerosol spray for marzipan, sugar and chocolate. All headspace extractions were carried out in headspace vials of 20 mL.