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Expert assessment for clarification of scientific terminology and evaluation of the Red Arrow process for the smoking of foodstuffs

A smoking process for foodstuffs that differs from conventional, traditional processing has been developed by the company Red Arrow. This expert assessment answers the following questions related to the new method:

(1.) Are the materials produced by the Red Arrow process "smoke" in a rigorous sense of the scientific terminology?

(2.) What are the differences of the substances originating from the Red Arrow process with respect to those from regular, uncontrolled incineration of wood materials?

(3.) Does the treatment of foodstuffs with the substances created by the Red Arrow process meet the common expectations regarding a "smoking process" (also in comparison with friction smoke and steam smoke treatments)?

For reference a glossary is appended below which provides a list of definitions together with the underlying explanations for clarification of the relevant terms. This terminology is used throughout the expert assessment with direct reference to the Red Arrow process in several parts. Those technical terms listed below which are not explicitly used in the text are provided for better understanding of the physical and chemical backgrounds. Since the definitions of some terms are more generally used in the public, their application in the context of the Red Arrow process could be perceived as diffuse despite their scientific foundation. For this reason the definitions themselves are categorized as "stringent definitions", "operational definitions" and "heuristic definitions". Clarity, precision, and delineation of terms are the highest with stringent definitions and lowest for heuristic definitions. The inherent lack of precision - particularly with terms like “smoke” or “fog” and “mist” – needs to be taken into account for the assessment of the nature of the Red Arrow process.

(ad 1.) In my opinion the Red Arrow process is a real smoking process based on the following line of reasoning:

- The generation of the aerosol particles that transport the flavoring is performed by a combustion process as is the case for traditional smoking processes.

- Like for conventional smoking the combustion material for the Red Arrow process comprises biomass, wood logs, needles from trees, wood/sawdust or shavings. During the Red Arrow process untreated, dried sawdust is incinerated in a controlled burning process.

- The size distributions of the aerosol particles sampled and measured during the Red Arrow process have a maximum at particle size diameters of 0.7 micrometers, and 97% of the particles are smaller than 1.5 micrometers. Considering particle size and peak of the size distributions these values correspond precisely with our laboratory measurements for smoke aerosols from the combustion of oak and beech wood, grass and other biogenic materials (see Schneider et al., 2006, in the references below).

- After the combustion step in the Red Arrow process the original solid smoke particles are subjected to subsequent additional processing in the liquid phase. For this the aerosol particles are dispersed in the liquid (water) as "cleaned smoke condensate" and thus the aerosol is converted into a hydrosol. The smoke particles are not at all or at most only partially dissolved in the liquid. Subsequently the hydrosol is transformed back into an airborne aerosol implying that the particles are no longer suspended in the liquid bulk. The aerosol particles generated this way are the cleaned combustion particles having the abovementioned size distribution. The individual particles are coated with a liquid layer made of water and the dissolved substances. Consequently, the original aerosol particles originating from the wood incineration are administered to the foodstuffs in cleaned form together with the flavorings contained within.

- The relative humidity in the smoke chamber containing the foodstuffs to be treated during the Red Arrow process[1] varies between 90% and 100 % at temperatures around 25 °C. In such an environment, the aerosol particles can quickly grow to sizes above 10 micrometers due to the condensation of gaseous water vapor. The growing particles form an optically thick fog inside the smoking chamber. Strictly speaking, pure water droplets only grow in size at relative humidities above 100%. For the acidity of the SMOKEZ primary smoke aerosol products from Red Arrow pH values between 2.5 to 3.0 were specified. From this it can be concluded that the aqueous liquid contains dissolved materials which lead to droplet growth at humidity levels below 100% as a result of the so-called physical/chemical Raoult effect of solutions. The small droplets, which contain the insoluble solid portion of the smoke particles, thus grow to a certain equilibrium size in the humid environment due to enhanced condensation of gaseous water vapor onto their surfaces.

From a scientific perspective and within the context of the terminology in my estimation it is indeed “smoke” which is the central and eponymous constituent part of the overall Red Arrow process for the reasons provided above. This is corroborated by the fact that the foodstuffs have to be exposed for similar periods of time inside the respective smoking chambers during the conventional and the Red Arrow smoking procedures, which also proves that the different smoking procedures correspond to each other.

(ad 2.) During the combustion of wood fresh, dry, and hot smoke is directly generated. This smoke consists of solid aerosol particles, microscopic droplets (e.g. made of non-volatile organic compounds like oils and acids), vapors, and gases. Health endangering or hazardous substances could be contained in each of these components. If dry, pure, fresh combustion particles are directly exhausted from the chimney of the combustion furnace into a smoking chamber (without prior treatment through the Red Arrow liquid phase process), a dense fog would result in any case because the air humidity is high inside the smoking chamber and the temperatures are low in comparison to the combustion temperature. This equally applies to the conventional treatments with combustion smoke or friction smoke, as well as to the procedure from Red Arrow. In all cases condensational growth of the droplets and aerosol particles occurs (quickly) until they reach their final, stable, equilibrium sizes. According to my calculations (following Gutacker, 2004; see literature references below) the particles of the population reach this equilibrium size within seconds or minutes. Given such short growth times, the differences inherent in the various smoking processes only can be small. Since the exposure times of the foodstuffs range from days to weeks for all of the different smoking processes, there is hardly any difference between the resulting fogs/mists in their final equilibrium states. (If the exposure times were significantly shorter – say of the order of minutes - this would be quite different.)

[1]Detailed inspection of a corresponding smoking facility showed that the cold smoking process was similar. The following information, however, also is valid for warm smoking processes [30 to 50 °C, 50 -100 % r.h.] as well as hot smoking processes [50 to 90 °C, 50 – 100 % r.h.].

In my opinion it does not constitute a significant difference for the treated foodstuffs whether this fog/mist in the smoking chamber arises (1) from the combustion directly followed by water vapor condensation, or (2) through combustion plus liquid phase treatment per the Red Arrow process with subsequent water vapor condensation. Certainly, the Red Arrow process permits the convenient removal of hazardous materials, which result from the inital combustion, as well as a constant process sequence with repetitious accuracy.

(ad 3.) During friction smoke processes the smoke is generated by mechanical friction of large wood pieces or logs on fast rotating machine parts where temperatures above 300 degrees Celsius are reached. By means of steam smoke processes the smoke is not created from wood in open fires but rather through exposure of the combustible material in hot water steam (at 300 to 600 degrees Celsius). Due to the high temperatures of both processes many hazardous substances (e.g. tar, polycyclic aromatics) are directly decomposed so that the exhaust gas contains fewer detrimental emissions. If the "common expectation" regarding the smoking of foodstuffs is that these are to be treated by direct exposure to smoke over an open flame, then neither the friction smoke process, nor the steam smoke process, or the Red Arrow process concur with such an expectation. By their nature the modern techniques originate from smoking processes, because these methods also expose the foodstuffs to the aromatic flavors coming from smoke particles and also because the smoked flavor solely arises from wood combustion or from the exposure of wood to heat.

Glossary of terminology and detailed explanations:

Definition, stringent: The definition of a term or a parameter based on proven physical or scientific principles, most often based on quantitative relationships and therefore precisely delineable. Terms or parameters can be determined by these definitions so that divergent understanding of the terms is excluded. **Examples:** Natural number, sphere in geometry, strength of an electrical current, heat, force.

Definition, operational: Definition of a parameter or a term based on one or several measurement processes. As such definitions are procedure-dependent they can be imprecise. Contrary to physical/technical definitions operational definitions can change with time, if new and/or better measurement techniques are developed, or if an improved method permits more precise delineation. **Examples:** Carbon/soot per Euro standard IV "Black carbon", gross domestic product.

Definition, heuristic: Attempt to define a term or parameter through verbal, non-quantitative or insufficiently precise quantitative descriptions. Heuristic definitions, which can be imprecise or colloquial, are based on reasoning (or on arguments which at least appear reasonable), assumptions, or working hypotheses. They should be considered at least conditional, so long as no stringent definitions can be formulated based on new knowledge.
Examples: Sustainability, cloud, smoke. However, the lack of precision for heuristic definitions also can result from differing opinions within the community of natural scientists on a particular term or on what is subsumed with the term. For example many scientists refer to a volcanic eruption plume as "cloud", whilst others consider a cloud as population of hydrometeors which are created solely by atmospheric processes.

Gas: An ensemble of freely moving atoms or molecules that are not bound to one another by strong forces and which completely and homogenously fills an empty space. (Stringent definition as derived from molecular physics and thermodynamics).

Vapor, steam: A gaseous, pure chemical substance mixed with a carrier gas (most often air), that arises through vaporisation/evaporation from its chemically identical liquid and which can be returned to its liquid form through condensation. (In case of water this vapor also is referred to as **"steam"**) Also, solids (e.g. ice) can be the source of the vapor, which then is termed sublimation or resublimation. Evaporation is the process whereby molecules from a liquid are spontaneously transferred into the gas phase this way forming the vapor/steam that is specific for the liquid material. By condensation the vapor molecules return back to the chemically identical liquid. Water molecules evaporate/vaporize from a liquid water surface into the air and form invisible water vapor there. Such gaseous water vapor molecules return to the liquid through condensation. Water molecules also transit into the gas phase (i.e. sublimation) from solid ice surfaces. Conversely, water vapor molecules can be deposited on the surface of the ice again being integrated into in the molecular lattice of the solid ice becoming a constituent part of the ice this way by resublimation. Besides microscopic droplets the vapors are important constituents of fog, mist, and clouds.

Aerosol particles: An aerosol particle is a small piece of matter consisting of an assembly of atoms or molecules (or both), that are bound together with sufficiently strong forces. The forces prevent the assembly from immediate disintegration by which its constituents would return back to the gas phase (i.e. mostly the air). The physical state of an aerosol particle can be solid, liquid, "fluffy" (an amorphous form), or a mixed phase. Mixed phase particles contain liquid **and** solid components, whereby for the most part a fine, insoluble particle is surrounded by a liquid layer. This is the case for the aerosol created by the Red Arrow process.

Aerosol: An assembly of discrete aerosol particles suspended in a gas as a carrier medium. The scientific community considers the term aerosol to be the entirety of the particles ***together with*** the carrier gas in which they are suspended. An aerosol must be stable for at least a few seconds. This is not a stringent definition, albeit close enough as the particle sizes are not precisely and quantitatively defined. The dimensional size diameters of the aerosol particles range (imprecisely delineated) from approximately 1 nanometer and 100 micrometers.

Hydrosol: Similar to the aerosol except that the carrier medium here is a liquid. If the hydrosol has been created from particles that were previously airborne, soluble portions of the original aerosol particles can enter the liquid. In ultimate cases the aerosol particles can be completely dissolved after entering the liquid. This is the case, for example, with an aerosol of sodium chloride particles, once the particles are deposited onto a water surface. The crystalline, solid, but easily soluble salt of the particles then entirely dissolves in the water. During the Red Arrow process the aerosol particles from the original combustion smoke do not completely dissolve when being transferred to the hydrosol (and thus to the smoke condensate). The chemical substances on the surface of the combustion particles can transfer to the liquid, if they are soluble. This is also the basis for the cleaning of smoke particles, whereby the hazardous chemical substances can be separated from the smoke particles and subsequently removed. Aromatic substances that are present on or within the smoke particles transfer to the liquid either completely, partially or not at all - depending on their solubility.

Dust: An aerosol of solid particles that are created through mechanical disintegration, destruction or demolition of macroscopic pieces of solid material. (Examples for this type of mechanical processes are milling, machine-chipping, sand-blasting, sawing and cutting with fast-rotating machinery, grinding, sanding, pulverizing, breaking, re-suspension - as with desert dust, etc.). Wood particles also arise as dust from the generation of friction smoke. The particles are not generally round in shape and lie within a size (diameter) range of a few micrometers to approximately 100 micrometers. This largely constitutes an operational definition.

Smoke: In the strictest sense defined as a visible aerosol resulting from incomplete combustion, and consisting only of solid particles suspended in the carrier gas. The aerosol particle sizes are generally below one micrometer. The smoke particles originate from incomplete combustion of solid or liquid fuels under conditions where the combustible material is not completely converted into carbon monoxide, carbon dioxide, water vapor, light, and heat. The incompletely burned residual materials then appear in form of exhaust gases together with particulate matter like soot particles or fly ash. This is a heuristic definition.

[**Soot:** Microscopic, airborne particles (or deposits thereof), primarily solid and strongly light absorbing - from the carbon atoms of the original combustible material that had no contact with oxygen in an (incomplete) combustion process and thus were not fully converted into carbon monoxide or carbon dioxide.]

Smoke: A broadened definition of “smoke” includes the presence of purely liquid droplets besides the solid aerosol particles. Droplets of oil or organic acids in the sub-micrometer to micrometer size range are subsumed here as well as solid particles with liquid surface coatings. This clearly is the case for the aerosols generated by the Red Arrow process for SMOKEZ primary smoke products to which the foodstuffs ultimately are exposed.

Smoke flavoring: See also the definitions in Art. 3 Ordinance (EC) No. 2065/2003: "Primary smoke condensate" is the cleaned, aqueous part of a condensate smoke. This term also is included in the definition of "smoke flavorings". The "primary tar fraction" is the cleaned fraction of the water-insoluble tar. It can be considered as separate thermodynamic phase which in its physical characteristics differs from the "liquid", "solid" and "gaseous" phases. Such a separate tar fraction phase originates from the condensed smoke and is of high material density. This term likewise falls under the definition of "smoke flavorings". Furthermore, the "primary smoke condensate" and the "primary tar fraction" also are designated as "primary products". The smoke flavorings based on these condensates are therefore flavorings obtained from further processing of the original, primary products. Flavorings are administered to foodstuffs to give them the desired smoky flavor.

Smoke condensate: If smoke is transferred into a hydrosol through contact with water, this hydrosol is termed as “smoke condensate”. A smoke condensate made from the smoke of wood combustion can contain solid smoke particles, water-insoluble liquid oil droplets, tar and other non- soluble constituents. Numerous methods are adopted to process and clean a smoke condensate in order to remove hazardous substances to a large extent. If tobacco smoke is deposited in the liquid surface lining the interior of the lungs, a smoke condensate which also contains tar arises. The SMOKEZ primary smoke products created by Red Arrow are such a cleaned smoke condensate.

Fumes, dense smoke, smolder: Visually very dense, dark, optically opaque smoke. (Heuristic definition)

Fog, mist: Visible aerosol of finely dispersed liquid droplets with sizes ranging from below 1 micrometer to approximately 200 micrometers. As molecules of the liquid material are constantly evaporating into the gas phase and gaseous molecules of the liquid substance are simultaneously re-condensing onto the droplets, the vapor is a significant constituent part of the mist, alongside the liquid droplets. If there is no or not enough vapor present in the immediate environment of the mist droplets, the mist will dissipate. Physically this means that the mist droplets will vaporize completely, which implies that all molecules of the liquid are converted to the gas. This also constitutes the fundamental difference between a mist and a combustion derived smoke. A smoke of solid aerosol particles can exist independently of vapors as the solid particles cannot be converted into to a gas through evaporation (unless the temperatures are extremely high). The droplets of a mist do not necessarily need to exclusively consist of liquid materials. Indeed, they may also contain inclusions of solid particles in their interior made of materials that are insoluble in the liquid. Technical mists are created through spraying/atomization or by induced condensation of some vapour onto an existing aerosol made from other –usually solid- materials. (This process is referred to as “heterogeneous condensation”.)

The latter is the case with the Red Arrow process, whereby the a priori existing aerosol is that of the combustion smoke containing the flavorings. If the mist which contains the original smoke particles and which was generated from the liquid droplets of the SMOKEZ material is mixed with sufficiently dry air, then the liquid components of the mist droplets would evaporate and a dry aerosol of smoke particles would remain as residue. These residual particles additionally could be coated with a layer of non-volatile, liquid organic material.

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Note: The statements in this expert report represent the views and assessments of the author and are not to be considered as official statements from the Max Planck Institute for Chemistry or the Max Planck Society.

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