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On the effects of freeze-drying processes on the nutritional properties of foodstuff: A review

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Abstract

The aim of this paper is to review the effects of several different types of freeze-drying processes on some nutritional properties of foodstuff. Both the vacuum freeze-drying (VFD) process and the atmospheric freeze-drying (AFD) process have been considered, as well as the possibility of accelerating both using ultrasound (US), microwave (MWD), infrared (IR) heating and other techniques. The effects of these processes on ascorbic acid, phenolic compounds and total antioxidant capacity has been extensively reviewed in this paper, as these molecules were widely investigated in the literature. Finally, a summary of effects on other less recurrent studied compounds is also presented. It appears that for vitamin C, VFD most of the time gives the best results; MWD and IR combined processes with VFD seem to be able to decrease processing time, while having a mild effect on product quality. With respect to phenolic compounds and total antioxidant capacity, VFD and AFD seem to have fairly similar effects, with a mild effect of IR and US.

Keywords

Vacuum freeze-drying; atmospheric freeze-drying; nutritional properties; ascorbic acid; phenolic compounds; total antioxidant capacity.

1. Introduction

Nowadays, an important issue in the food industry is the consumers' increased perception of food quality properties. Consumers demand high nutritional, sensorial and functional attributes, hence, attention has to be given to processing in order to meet these requirements [1,2]. Fresh fruits, vegetables, spices and other perishable food products have to be dehydrated to prevent the growth of microorganisms, and reduce or inactivate moisture-mediated deteriorative reactions [3,4]. On the other hand, conventional drying techniques usually cause a decrease on product quality as a result of the high temperatures used [5].

Freeze-drying (FD), also known as lyophilization, is characterized by its low operating temperatures. Water removal in a FD process differs from most dehydration technologies since it is based on solvent sublimation, rather than evaporation. In freeze-drying processes, the driving force for water removal is the vapor pressure difference between the ice front and the surrounding environment. Regarding the water physical states, at 0°C and 6.1 mbar ice, liquid and vapor water coexist in equilibrium. Below this point, the water in the system can be whether in the solid or in the vapor state, thus, water removal is only through sublimation [6,7]. D'Arsonval and Bordas (1906) [8] were the first ones to demonstrate that water removal from frozen products was possible under low pressure. Withal, this technique was actually already in use for many years by the Incas to preserve food, taking advantage of the low pressure and temperature conditions of the Andes.

Initially, the freeze-drying process was considered costly and, as such, it was limited to pharmaceutical applications. Food products that have an appraisal above average can be considered as high-value foods. Some examples of such products are: baby food, nutraceuticals, distinguished organoleptic products like spices, highly perishable products, and special use foods like camping meals and military rations [9]. Since freeze-drying is carried out under low temperatures, better

color, aroma and nutritional compounds retention is observed in products dried by this process [10,11]. Recently, freeze-drying has been widely used for preservation of high-valued materials, achieving superior overall quality compared to other drying methods [2,7,11–13]. Due to the improved final product quality, vacuum freeze-drying is commonly used as a benchmark process to evaluate drying effects of other methods on targeted product traits [14]. Studies involving freeze-drying of several distinct food products can be found in the literature, such as onions [15], barley grass [16], pineapples [17], acerola berries [18], sea cucumber [19], apples [20], cabbage [21], okra [22], tomatoes and ginger [23], banana [7], shiitake [24] and cod fish [25], to list some examples.

Different food products may have different intrinsic characteristics which will affect their suitability for freeze-drying processing. To list some, fruits and vegetables have a cell structure consisting of walls enveloping a membrane, cemented together with pectic substances. The most common preparation steps for such vegetables are washing, peeling, cutting, and blanching. Cutting the plant tissues causes ruptures of the abovementioned cell structures, leading to the release of enzymes and other compounds, and this can result in an impairment of some quality attributes. In addition, fruit peels are sometimes removed to facilitate water transport during dehydration processes, which could make the product more susceptible to degradation.

For meat and fish, the connective tissue thin fibers (fibrils) and the sarcolemma are important factors for the water diffusion during drying. The sample cut has to be done according to the direction of the muscle fibers. High fat tissue differs drastically in comparison to the lean part of meat and bones, which makes it unpractical to freeze-dry all these parts together. The fatty tissue contains from 10 to 50% of water, while lean meat contains approximately 70 to 75%. The concurrent drying of both these parts could lead to high surface temperatures of the fatty portions, which could melt, blocking the matrix pores and compromising water diffusion.

Liquid food products like milk, eggs, juices and extracts have a different behavior since they do not have a structured matrix to support the shape of dried product. In addition, since they have a high water content, it is necessary to concentrate them before freeze-drying.

The freeze-drying process can be carried out under vacuum (VFD) or under atmospheric pressure (AFD), as it will be later explained. Still, both processes share a common first step, which is the freezing step. To understand the impact of the freezing process on the final product quality, and on the drying step, it is necessary to take a deeper look into how freezing occurs.

The intrinsic characteristics of each product will play an important role in all steps, including freezing. For instance, a certain portion of water in a food system is bounded to certain solutes through strong intramolecular interactions and never freezes. In the other hand, the remaining unbounded portion is called “free water”, which freezes and undergoes phase transition during the primary drying step [6,26].

Product freezing can be achieved within the FD equipment or using other devices, before placing the product in the drying chamber [26]. This way, different freezing processes could be used like blast chilling, liquid nitrogen, or even a household freezer. Each process is characterized by a different cooling rate: immersing a product in liquid nitrogen results in a very fast cooling process, while a household freezer would result in a slower one, for instance [27,28].

The first event in the freezing stage is ice nucleation, which is the combining of water molecules into an ordered particle that will serve as a site for crystal growth. Sometimes, suspended particles may act as nuclei for ice crystallization (heterogeneous nucleation). Nucleation can also be promoted by cold surfaces and thermocouples, when they are used to monitor product temperature. Crystal growth is the enlargement of an ice nucleus by the arranged addition of water

molecules. The freezing process is stochastic, which makes hard to predict it, and depends on the food matrix characteristics. To illustrate that, pure water can be used as an example. First the water is cooled and reaches a temperature slightly below its actual freezing point (supercooling), up till ice nucleation starts. From this point on, the heat transfer consists in latent heat removal for the ice crystals formation and the temperature remains constant at 0°C until all water is frozen.

For a food product, the behavior is different. The product is cooled and some supercooling behavior can be also observed, but it is milder. Then, ice nucleation starts, but the product temperature actually keeps decreasing as ice crystals are formed. This happens because as the free water crystalizes, solute concentration on the remaining liquid water increases, depressing the freezing point [29]. Below -30°C the ice content increase achieved is minimal for most food products [30]. This freezing concentration of solutes leads to important changes in the food matrix: solutes may interact with each other leading to alterations and pH may drastically change, also affecting product quality.

The crystallization process is what mostly affects the quality of food products. Crystallization starts outside the cell, which generally has higher freezing points. The rate of water diffusion from the cell to the intracellular space and the heat removal rate determine the crystallization rate [30]. The freezing rate depends on the heat flux exchanged between the product and the cooling surface, which means it depends on the temperature difference between the product and the surface and on the resistances to the heat transfer. When the freezing rate is slower than the crystal growth rate, it leads to the formation of few ice nuclei, resulting in a small number of crystals relatively large in size. On the other hand, when the freezing rate is fast, a larger number of small crystals tends to be formed [6].

Food matrixes are complex, thus freezing may result in intricate mixtures of crystals, hydrates and glass [6]. The size of the ice crystals will have an effect on the food matrix texture, which furthermore will impact product quality [23]. In any case, smaller crystals would be preferred for food products since it is known that the formation of large crystals can damage cell walls and membrane structures, altering texture and favoring biochemical degradation reactions [30]. However, the resulting frozen structure of the product will influence the water diffusion process during the drying stage. Since the cooling rate influences the frozen structure crystal sizes, it will also have an effect on the drying rate [28].

Electric and magnetic fields can be used to assist and control freezing. In fact, due to its structure, water consists of dipole molecules and when a DC electric field is applied, water molecules tend to realign, breaking up the existing hydrogen network and making the water less structured and more polarized. This culminates in stronger bonds in the direction of the applied electric field and can be used to cause spontaneous nucleation of ice at a given supercooling degree. The degree of supercooling from which spontaneous nucleation occurs tends to be reduced when DC is applied. On the other hand, water as a diamagnetic material and it becomes magnetized when subjected to a magnetic field. This makes the hydrogen bonds stronger and the overall structure more stable. A unidirectional magnetic field might imbalance electron spin, granting a slight thermal vibration, which prevents freezing. This could allow maintaining water in a metastable state under very low temperatures, having a higher degree of supecooling. With a potential similar effect, AC may have an effect promoting the vibration of the dipole water molecules, which could prevent water solidification [31]. Freezing of foods can be assisted by magnetic fields, fluctuating electric field and static electric field [32]. Oscillating magnetic fields were used for freezing apples and potatoes, but the results showed no significant impact across the freezing settings tested.

However, under certain conditions, it seemed to have an effect, suggesting that this technique might affect food systems in different ways, depending on food type, freezing rate, magnetic field and storage [33]. Freezing pork meat under static electric field was reported to reduce ice crystal size significantly leading to lower product texture damage [34]. The application of such methods in freeze-drying processing might be promising to improve efficiency and final product quality since they can help control crystal size during freezing.

This paper aims reviewing the reported effects of different freeze-drying processes on the nutritional properties of food products. It is structured based on most frequently reported targeted compounds: ascorbic acid, phenolic compounds and total antioxidant capacity. Subsequently, a summary of other less recurrent studied compounds is presented.

1.1 Vacuum Freeze-drying

As mentioned, freeze-drying is a dehydration process based on ice sublimation as a mean to remove liquids from a product. Vacuum freeze-drying (VFD) does that by operating under low temperature and very low pressure. This way, the ice formed in the freezing step can be removed through sublimation [35]. The vacuum freeze-drying process consists of three main steps: freezing, primary drying and secondary drying. As described above, freezing is a critical step since it influences many aspects that affect product quality during the next stages.

In the primary drying stage, aiming to allow ice sublimation, the pressure is lowered and heat is supplied since it is an endothermic process. This heat can be supplied in various ways, such as gas convection, radiation by hot surfaces and conduction through a heated shelf or gas [36]. By removing the ice from the frozen product matrix, a porous structure is formed, also called cake.

The water vapor flows through the pores of the product, and is collected in a cold trap, the ice condenser. During drying, a boundary between the frozen layer and the dried portion is formed, this is the sublimation interface. This boundary surface moves from the top to the bottom of the product during primary drying. Additionally, some unfrozen water may volatize through desorption in the dried layer [6].

Primary drying is usually the longest stage in VFD and, therefore, it has a big impact on the overall process. The duration of this step is directly related to the sublimation rate, which is determined by various factors, e.g. chamber pressure and shelf temperature [36]. It is important to have a good control of this stage to maximize the sublimation rate, while maintaining product integrity [6]. It has been reported that operating at temperatures above the glass transition temperature (T_g) affects product quality. T_g is defined as the temperature at which a system changes from glassy to rubbery state. Molecules are rigid in the glassy state, whereas in the rubbery state they are allowed to move. Drying at temperatures above the T_g is reported to cause product shrinking, and even collapse, for liquid solutions. Depending on the product, T_g and the operating conditions may be related to shrinkage [37]. The T_g can be experimentally determined, e.g. through Differential Scanning Calorimetry [6,38].

Finally, after the first stage the secondary drying comes, whose goal is to remove residual bounded water from the dried product. This process generally requires higher temperatures than those used in the previous drying step. To avoid product impairment, product temperature must be controlled during all drying process.

The most common equipment configuration is a batch vacuum freeze-drier. This equipment consists of a chamber where the material is loaded per batch. For some industrial processes continuous equipment can be used: this set is composed of drying zones with specific

characteristics. The product is loaded in the first zone and moves ahead to the next zones until the process is completed [26]. Spray freeze-drying (SD-VFD) is another method used for liquid products. In this process, the liquid material might be first concentrated and then atomized to be frozen and subsequently dried by VFD [39]. For granular materials, pulsed spouted bed (PS) has also been used [40].

The drying chamber is connected to a condenser, which is at extremely low temperatures to condensate the vapor removed from the product. The condenser, or cold trap, is very important since the vacuum pump would not be able to pump out all the volume of vapor formed during sublimation [6]. The vacuum pump creates the low pressure in the chamber which can also be kept by controlled leakage with an inert gas [36].

In order to accelerate the process, while also maintaining product quality attributes, combined methods have been studied. Microwave vacuum heating (MVD) has been proposed as a promising method since its energy can be absorbed mainly by the frozen regions. However, when applied into industrial processes, some technical problems were found, like non-uniform heating leading to product impairment [6]. Still, this method was able to substantially reduce drying time, while having comparable product quality results [11,12].

Other combined methods were proposed such as Ultrasound (US), which is the use of sound waves to increase the system energy and accelerate drying. The sound wave frequencies vary from 16 kHz to up to the MHz magnitude and act as pressure waves, causing alternate regions of high and low local acoustic pressure. Care should be taken to avoid overheating the product in a low pressure environment using this method [41].

Infrared heating (IR) was also proposed as an accelerating method. The radiation emitted by the IR source penetrates through the product surface and propagates as molecular vibrations, providing thermal energy to the product. Usually, these combined processes use wavelengths around 2.7–30 mm which is within the far-infrared radiation range [42].

More recently, electrohydrodynamic (EHD) fields were proposed as a new alternative in drying. They consist of electric fields of high intensity applied to generate ionized air-constituent forms. The movement of the air ions in the strong electric field formed generates an ionic wind. This ionic wind orients the water vapor molecules in the direction of the electric field and assists their removal, thus favoring drying [19,43]. Another novel combined method reported to be used is explosion puffing drying (EPD) using VFD as a pre-drying step. In EPD the pre-dried samples are heated under atmospheric pressure and then subjected to an abrupt pressure drop to a vacuum environment (less than 5 kPa). Hereafter, the drying is done under continuous vacuum [44].

1.2 Atmospheric Freeze-drying

From a historical point of view, Meryman (1959) [45] was the first to show that freeze-drying was feasible under atmospheric pressure. It was observed in those experiments that the water removal is driven by vapor pressure gradient, rather than by the absolute pressure in the system. This permitted the development of an atmospheric freeze-drying process. Regarding energy costs, Wolff and Gibert[46] estimated that the atmospheric freeze-drying (AFD) could save 38% of cold requirements and 34% of heat requirements, thus reducing energy costs compared to VFD. Nonetheless, the process still has some limitations, like the long drying times usually required [47].

Atmospheric freeze drying has the same first step as VFD, which is freezing, with similar implications. Subsequently, the drying step is done by circulating dry cold air (around -3°C to -10°C) over the frozen product to improve the mass transfer for water removal [14,48]. The partial water-vapor pressure around the product must be low enough to ensure the required mass-transfer driving force [48]. It is important to keep the convective drying temperature below the product freezing point to ensure no liquid water formation [14].

Since AFD does not require a vacuum pump, processing becomes simpler. The equipment can be designed for batch or continuous processing, as an AFD tunnel. In addition, an inert gas could also be used to prevent product impairment [14,48]. Other configurations have also been used, such as fluidized bed for granular materials and spray atmospheric freeze-drying (SD-AFD) for liquids, analogous to the SD-VFD described above.

As the pressure gradient is lower in an atmospheric setting, AFD drying times are usually longer than VFD ones [47]. Therefore, combined methods have also been used with AFD in order to reduce drying time. Heat pump is one of the most commonly used methods, which consists of a convective drier for heat transfer, preferably suitable for solid products [47,48]. Combined heat-pump AFD with a fluidized bed setting was used for drying bovine intestines [49]. Other methods have also been used, like ultrasound as a combined process to dry eggplants [50]. As well as microwave assisted AFD was reported for drying green peas in another AFD study [51].

1.3 *Paper structure & objectives*

As discussed above, freeze-drying methods are interesting for a large array of products that demand high quality attributes. Previous freeze-drying reviews have been done on: (i) freeze-drying

applications and recent advances [14,52–55]; (ii) process optimization [56]; (iii) control over a specific step [57]; (iv) novel combined methods [12]; and (v) a comparison between drying methods for foods [9]. Nonetheless, there is not yet a review reporting recent findings on the effects of freeze-drying specifically for the quality properties of foodstuff. This paper aims to review this point, i.e. the effects of freeze-drying processes on the content of targeted nutritional compounds. First, a brief discussion on overall effects of freeze-drying processes on the nutritional properties will be presented. Then, each section will be focused on a targeted nutritional compound, highlighting the results found in several studies. The compounds of each of these sections are: ascorbic acid, phenolic compounds, antioxidant capacity and other compounds. Finally, a conclusion on the general trends observed from the data gathered through this review will be presented.

2. Effect of freeze-drying on nutritional properties

The steps prior to freeze-drying may be responsible for the degradation of nutritional compounds. Slicing fruits disrupts cell walls, thus releasing intracellular compounds that now will have a higher mobility, thus increasing chemical and enzymatic interactions. These steps may have a big impact on the final product quality and, thus, their influence should be also taken into account when evaluating the effect of drying methods on product quality [58]. Some examples of reactions that may take place during low temperature processes are: enzymatic browning, oxidation and hydrolytic reactions, interactions with metals, isomerization, cyclization, protein denaturation & cross-liking and polysaccharide synthesis.

In general, rates of destruction of nutritional compounds increase in higher water activity matrixes due to lower viscosity, which increases compound mobility, favoring chemical reactions

[59]. It is important to note that each compound has its own stability characteristics regarding pH and susceptibility to light, heat and oxygen. For this reason it is important to first identify the compounds of interest in a food product and, then, to choose and design processing according to its characteristics [60]. In addition, food matrixes are complex mediums with a large variety of chemical compounds that may interact in an averse or synergistic way. Herbig and Renard (2017) [61] evaluated Vitamin C stability in different buffer solutions, apple and carrot purée serum. Initial Vitamin C concentration did not influence degradation rates. Under the tested conditions, pH medium alone could not explain the different degradation rates observed, as it changed according to the buffer solution used. In addition, in the food purées, degradation rates might have been affected by other compounds present, which might have protective or antagonistic effects on its degradation.

Some effects of freezing on food matrices were described above, still other events might take place in this step. Flink & Hansen (1972) [62] evaluated the loss of volatile compounds in freeze-dried carbohydrates solutions and found the freezing step to have a strong impact on it. The volatiles used in that study were acetone, *n*-alcohols(C_1-C_5), methyl acetate, 2-propanol and *tert*-butanol, at 0.75% wt./wt. in water. In addition, the carbohydrates used were glucose, maltose, lactose, sucrose and dextran-10, at 18.8% wt./wt. in water. They found that the disruption by water of microregion structures lead to a loss of volatiles. During freezing, the remaining unfrozen portions of the solution become like pools of concentrated carbohydrates and organic volatile solutions. The bulk cake outside these pool microregions is relatively permeable to the flow of volatiles and water. However, once a critical level of moisture is achieved, these microstructures are sealed and only water is able to be removed: this means no more losses of volatiles. This would mean that after freezing there should be minimal volatile loss, which implies that most loss should

occur during the freezing step. Indeed, freezing has been reported to noticeably affect product quality in different studies. A decrease in free radical scavenging activity and an effect on ellagic acid, vitamin C and total phenolic content was found in raspberry cultivars after freezing [63]. Also, papaya frozen under slow and fast freezing rates had 15% and 5% reduction on Vitamin C respectively, showing the potential effect of freezing rate on product quality [58]. However, as it will be further discussed, other studies found representative losses of such compounds attributed to the drying step.

The operating conditions such as shelf temperature, chamber pressure, processing time, gas medium and application of other combined technologies may interfere in different ways on the quality properties of foods during freeze-drying. Therefore, it is important to understand how these factors may influence product quality attributes to choose the best practices according to the desired product characteristics [64,65].

Very little is known regarding the effect of low pressure on nutritional compounds. When FD is done under vacuum, oxygen dependent degradative reactions are limited since its concentration is about zero. This can also take place during AFD if it is done with an inert gas. As for vitamin C, anaerobic degradation pathways have considerably slower rates than aerobic ones [66,67]. This means VFD and AFD with controlled atmosphere should have less oxidative reactions leading to compound loss compared to AFD in air and other drying methods. Regarding enzyme activity, polyphenol oxidases (PPO) and peroxidases (POD) play a major role in phenolic compound loss during processing and storage. Drying with assisted methods can inactivate these enzymes. Microwave, electro field pulses and ultrasound were reported as having this inactivation effect on PPO and POD [68].

2.1 Vitamin C

Depending on the studied vitamin, processing conditions may or may not affect its stability. Niacin, for instance, is stable to oxygen, light and heat exposure, and it is also stable under acidic, neutral and alkaline pH. Meanwhile, ascorbic acid is stable only under acidic pH and it is unstable in presence of oxygen, light and heat [67,69].

In the dark, ascorbic acid (AA) degradation major cause has been found to be chemical oxidation, favored by metal ions in solution [66]. Vitamin C can also be degraded by enzymatic activity in the presence of oxygen by ascorbate oxidase [70].

Expectedly, raising hot-air drying (HAD) temperature decreased Vitamin C content in tomatoes cut into pieces, especially at the beginning of the drying [71]. However, varied degradation ranges were observed in a study when operating under different temperatures, suggesting that different degradation mechanisms might be in place according to the operating conditions [61]. In addition, a correlation between increased exposition to air and increased Vitamin C degradation was found, suggesting the use of inert gas during processing in order to reduce degradation reactions [71]. When FD is carried out under vacuum, oxygen concentration during drying is very low, but it might be present during freezing and could favor these degradation reactions.

Vitamin C degradation can occur through aerobic or anaerobic pathways, even though the last has usually slow rates. On the aerobic pathway, a transfer of one electron forms semidehydroascorbic acid; then, further loss of an additional electron yields dehydroascorbic acid (DHAA), which is highly unstable. This could take place directly with the loss of two electrons, leading to the formation of DHAA without the formation of the intermediate. The DHAA has a high susceptibility to hydrolysis of the lactone bridge, which forms 2,3-diketogulonic acid,

responsible for the loss in vitamin C activity. Anaerobically, the degradation mechanism was not fully stablished yet: it has been suggested that a direct cleavage of the 1,4-lactone bridge without prior oxidation to DHAA could be involved. In acidic (pH ~ 3-4) environment the anaerobic pathway rate is best, perhaps due to the opening of the lactone ring under mildly acidic pH [67]. During freezing, the H+ concentration increases, changing the matrix pH [70], which could favor this reaction pathway under low oxygen partial pressure processes.

As food matrixes are complex, other intrinsic factors may have an influence on ascorbic acid degradation pathways. Marques, Ferreira, & Freire (2007) [18] found the ascorbic acid content after VFD to vary according to the maturation stage of acerola berries. Vitamin C of green (unripen) acerola berry decreased by 69.3% after VFD, in yellow-reddish acerola it decreased by 13.0% and in red acerola (ripe) by 51.6%. This variation of the degradation percentage can be due to ascorbic acid sensibility to moisture content, pH and metallic ions, which varies according to the fruit maturation stage. Interestingly, in other studies with tropical fruits, starfruit, mango, mango milkshake, papaya, muskmelon and watermelon, ascorbic acid content did not vary significantly after VFD [72,73].

Pre-treatments can greatly affect the effect of the chosen drying method. For potatoes without blanching pre-treatment, ascorbic acid was found to decrease by 7% after VFD and MD-VFD, which was not a significant variation. However, a 32% reduction was observed when blanching was used [74].

Comparing different methods, Yi *et al.* (2017) [44] found VFD and VFD-explosion puffing drying (VFD-EPD) to get the best ascorbic acid retention on tropical fruits compared to HAD and HAD-EPD. The AA values for the fresh product were: 177.5, 110.8 and 272.4 g/100g d.m. for mango, pitaya and papaya respectively. The retentions found after FD were: 128.2, 75.6 and 202.6

g/100 d.m.. For VFD-EPD, the values were slightly smaller compared to VFD alone, having contents of 108.2, 66.4 and 178.9 g /100 g d.m., for mango, pitaya and papaya in this order. These results represent reductions from approximately 27 to 40% after drying.

Marques *et al*. (2014) [58] observed similar trends for vacuum freeze-dried tropical fruits. Among the tested ones, guava had the greatest vitamin C content variation, with an approximate reduction of 38% after VFD, followed by pineapple with a reduction of about 14%. Papaya and mango, in the other hand, had very small reductions. Evaluating residual AA values on banana samples, pulsed-spouted MVD samples values were comparable to the VFD ones, with approximately 80% retention. Both methods had higher retention compared to MVD alone, which had a 56% retention [7].

Apples vacuum freeze dried with and without MVD assisted drying were found to have optimal operational conditions at 9.15 kPa of pressure and applying a microwave power of 317.6 W. The nutritional quality in this study was evaluated only by means of ascorbic acid retention which varied from about 58.6% (at 10 kPa & 400 W) to 82.6% (at 10 kPa & 300 W) [20]. In a following AFD study, apple samples were cut into slabs or cylinders and exhibited similar ascorbic acid retentions compared to the previous VFD-MVD results abovementioned. Cylindrically cut samples retained 80% of AA, while slabs retained 90%. It was suggested that it could be due to the higher surface area per volume in the cylindrical pieces, which gives a larger area that can favor oxidation reactions. The US application significantly reduced AA content with similar effect on both geometrical shapes. Their retentions fell by 20% in comparison to the samples treated without US. These US effects might be only inside the samples, since the geometry and different proportions of surface/mass did not affect the AA retention [75]. Still, Vieira *et al*. (2012) [17]studied pineapples quality after VFD and found that thinner slices rendered higher AA retention. This result

was suggested to be due to faster freezing and drying times, leaving less time to degrade the vitamin. The process temperature, under the tested conditions, was considered not significant.

Blueberry's quality was evaluated after VFD and AFD with and without IR, cutting them in half and quarters. From the standardized effects of the experimental factors, IR application showed a positive effect in ascorbic acid content of blueberries under FD processing, while pressure and sample size had a negative effect. From observing the results presented, AFD had a negative effect compared to VFD[76]. Nemzer *et al*. (2018) [77] also observed that smaller sampler sizes retained better the ascorbic acid. In this last study, blueberry, strawberry, cranberry and cherry samples were dried by VFD, HAD and refractance window drying (RWD). RWD consists in a contact drying method in which samples are placed on the top of a UV-transparent film placed on top of a thermal bath with water. Higher contents of ascorbic acid were found in all berry samples after VFD compared to the values found after HAD and refractance window drying.

Iron yam slices were freeze-dried by VFD, MVD and combined VFD-MVD, with and without sample thawing prior to the MVD step. For the combined process, the VFD step was tested using 2, 3.5 and 4.5 h of duration. During the MVD process, product temperature was always kept under 35°C while the VFD sublimation stage was done at 20°C and the desorption stage at 50°C. Regarding the vitamin C content, combining two hours of VFD, without letting the sample melt, and then performing MVD led to best retentions. This was followed by applying 3.5 hours VFD + MVD, then 4.5 hours VFD + MVD and finally by VFD alone. The authors suggested this could be due to faster drying times and lower temperatures used when combining MVD to VFD while, on the other hand, the desorption stage of VFD alone was done under higher temperatures. When thawing was done before the MVD step, retention values were the lowest. Still, the vitamin C content did not vary greatly: it ranged from approximately 6.5 to 8.5 mg/100 g d.m. [78]. Studying

other root vegetables, carrots pre-treated with blanching in 90°C water for 7 minutes, were found to have no significant ascorbic acid loss after VFD under 20°C. It was suggested that this might have been due to the low operational temperature used [79].

Testing different pepper cultivars, their ascorbic acid contents widely varied, ranging from 0.225 g/kg d.m. for PKM-1 cultivar to 0.382 g/kg for Bird's eye cultivars. After drying, the degradation was found significant for all samples, and the values ranged from 0.149 for PKM-1 after MVD to 0.373 g/kg for Bird's eye after VFD. VFD showed the best retentions compared to the other tested drying methods for all pepper cultivars. The vitamin C content variations, while statistically significant, were rather small. Observing the Bird's eye cultivar, the reduction was of about 2.4% [80]. For *dedo-de-moça* pepper, in another study from Veras *et al.* (2012) [81], AA decreased around 43.7% after VFD in comparison to the fresh product. Still, even more degradation (69.1 to 86%) was found for HAD, with a correlation of higher degradation when using higher temperatures. Das *et al.* (2012) [82] found HAD and VFD drying methods to present similar vitamin C content decreases on wheat-grass, compared to the fresh samples. Still, VFD also had a smaller reduction, of approximately 40%.

Colucci *et al*. (2018) [50] investigated the effects of AFD on the nutritional properties of eggplants. For ascorbic acid, the degradation observed ranged from 45.89% for 8.8 mm cube size samples, processed at -10°C without ultrasound application and with a 2 m/s air flow, to 74.53% for 17 mm cube sizes, at -10°C, with 50 W US and 2 m/s air flow. Increasing processing temperature, air velocity, US power and sample size were found to cause a significant increase in AA degradation. Figure 1 shows the variation of the ascorbic acid content in eggplant samples (8.8 mm cube size) processed in a vacuum freeze-drying process. It is possible to see that the ascorbic acid average loss, measured according to Ref. [46], varies from 20% at 0°C to 22% at -30°C under

10 Pa while it varies from 16% at 0°C to 22% at -30°C under 30 Pa. It appears that the AA average percentage reduction found for VFD is less than half of the ones found for AFD, probably due to the anaerobic pathway of AA degradation in a VFD process.

Moreno *et al*. (2017) [75] also found that bigger apple slabs had higher AA content reductions after AFD, probably due to the longer times required to dry these samples. Ultrasound application, on a given sample size, had no significant effect on this measured compound.

In another study using US, but in a VFD process, the ascorbic acid content of VFD bell peppers was smaller, but not statistically different from the content found in the VFD-US ones. The contents were approximately 1532.9 mg/100 g d.m. (VFD) and 1518.2 mg/100 g d.m. (VFD-US). The use of US reduced drying time by approximately 11.5%, which could be a contributing factor for the lower AA degradation observed in this samples [41].

Chang *et al*. (2008) [83] investigated the effects of VFD and air drying (AD) on fresh tomatoes of two varieties, Sheng-Neu (SN) and I-Tieng-Hung (ITH), on the ascorbic acid, total phenols, flavonoids, lycopene, reducing power, ferrous chelating power and DPPH scavenging power. For ascorbic acid, lower temperature remarkably led to lower degradation on tomato varieties. Freeze dried SN tomato had 8.2% reduction of ascorbic acid, while ITH had 10.0% [83]. However, in another study also using tomatoes, significant reduction of ascorbic acid of about 78% was found for vacuum freeze-dried samples [23].

2.2 Phenolic compounds, anthocyanins & flavanols

The degradation of phenolic compounds is influenced by light, oxygen, temperature, viscosity and pH of the medium, and is also catalyzed by metal ions, particularly Cu^{2+}, Fe^{2+}, and Zn^{2+} [66,67].

Phenolic compounds can be degraded by enzymatic activity in the presence of oxygen by polyphenol oxidases, besides other metabolic routes [70,84].

Due to its low processing temperatures, freeze-drying usually implies less bioactive compound degradation. However, in a review for aromatic plants, the overall understanding was that freeze-drying, in most cases, decreased the levels of the main flavanols in plant extracts [85].

Freeze-drying may enhance enzyme-catalyst browning reactions, which involve the oxidation of phenolic compounds by the enzyme activity [72]. However, it has also been suggested that a partial reduction of polyphenol oxidase (PPO) activity may occur due to an increase in H+ concentration during freezing, which changes pH values, turning the enzyme unstable [70]. Common assays to evaluate phenolic compounds are total phenols content (TPC), total anthocyanin content (TAC) and total flavanols content (TFC). Still, specific phenolic compounds might be targeted in some studies.

Chan *et al.* (2009) [86] compared VFD, AD, microwave drying, oven and sun drying (SD) on the antioxidant properties of ginger species leaves and tea. VFD significantly increased TPC for two of the varieties - A. zerumbet, 28% & E. elatior, 26% - but led to a decrease of other two - C. longa, 11% & K. galanga, 16%. They inferred theoretically that, according to VFD operational conditions, neither thermal nor enzymatic degradation should be favored; crystallization prior to VFD could result in higher extraction yields of interest compounds. Additionally, they performed a HPLC chromatogram on the fresh leaves and then on VFD leaves. The major compounds apices remained almost unchanged, while minor compounds had an increase after VFD, which could support the increased extraction inference for those compounds. Further studies on storage of dried samples at room temperature revealed 7% decline on TPC levels after one week, while control samples had 23% reduction.

An *et al*. (2016) [87] compared the outcome of VFD, hot-air drying (HAD), infra-red drying (IR), microwave drying (MD) and intermittent microwave-convection drying (IM&CD) on Chinese ginger. The degree of heating during the process showed impact on the volatile compounds, despite treatment times at milder temperature processes being longer. Vacuum treatments also showed substantial influence on these compounds. The drying process was suggested to result in high or low total phenols content depending on the type of plant material and where in the plant cell they are located and stored. Also, different drying methods yielded different results for Chinese ginger. Freeze-dried ginger samples had a significant increase of TPC compared to fresh ones, while the other thermal processes caused a significant decrease in TPC up to over 29% ($p < 0.05$).

Gümüşay *et al*. (2015) [23] also evaluated the effect of some thermal drying processes (sun, oven and vacuum over drying) and of freeze-drying on the TPC of ginger and tomato samples. A 17% TPC reduction was found not significant for tomato, but found to be significant for ginger, having a reduction of about 32%. Conversely, another study with tomatoes on total phenolic content found increases in TPC for the two tomato varieties evaluated after VFD and HAD, while HAD had higher increments than VFD on the phenolic content. VFD had 2.6% and 5.9% increase in total phenols on Sheng-Neu (SN) and I-Tieng-Hung (ITH) tomato varieties respectively. Expectedly, flavonoid content also increased, having 72.3% and 23.2% increase for SN and ITH tomatoes respectively. The higher temperature process of HAD also lead to slightly higher increases in both total phenolic and flavonoids content than the values found for VFD samples [83].

Onion samples, pre-treated by US or blanched, had their quality attributes measured after VFD and HAD. As a general trend, HAD onion samples had lower TPC retentions (70.94% - 110.65%) compared to VFD (79.61% - 121.41%) samples. For TFC however, the retentions found

for VFD ranged from 76.75% to 108.93%, while the retentions observed after HAD ranged from 80.85% to 130.04% [15]. These results show that the TPC levels on onions had decreases of about one third to even small increases. In another study with onions the total flavonoids and anthocyanin content was measured by HPLC and they were defined based on approximately four compounds that contributed the most to its content. The TFC value found for fresh samples was 305 mg/kg in fresh weight, 284 mg/kg for frozen and 402 mg/kg for VFD samples. The anthocyanin content of fresh onions was 2 mg/kg, after freezing 1.84 mg/kg and after VFD 2.69 mg/kg. These results indicate a small decrease of 7% for TPC and 11% for anthocyanin after freezing, while VFD samples had about 32% and 25% increase for TPC and anthocyanin respectively. The authors suggest that this increase is due to an increased extraction. However, if that is due to crystallization, the frozen samples also should have shown an increase in these values, which was not observed in this study. Therefore, they suggested that VFD may provoke changes in the structure of the product that could make the measured bioactive compounds more available, especially non-polar ones [88].

Pepper cultivars had their TPC levels measured before and after drying: VFD achieved the best retentions for all cultivars. The TPC in fresh samples varied according to the pepper cultivar from 0.155 g of gallic acid equivalent/kg in dry weight for Sannam S4 after MVD to 0.222 g/kg for Bird's eye. After drying it varied from 0.959 g/kg for Sannam S4 after MVD to 0.196 g/kg for bird's eye after VFD. TPC was found to be positively correlated to VFD according to the cultivar [80].

Colucci *et al*. (2018) [50] investigated the effects of AFD on the nutritional properties of eggplants. The TPC degradations found ranged from 58.45% for 8.8 mm cube size samples, processed at -10°C without ultrasound application and with a 2 m/s air flow, to 76.28% for 17 mm cube sizes, at -10°C, with 50 W US and 2 m/s air flow. A significant effect of processing

temperature on the degradation of TPC was observed, while neither ultrasound not air velocity had a significant effect on the measured compounds, for a given sample size. However, sample size had an effect: larger samples had higher reductions on the phenolic content. Figure 2 shows the variation of TPC, given as gallic acid equivalent, measured according to Ref. [46], in eggplant samples (8.8 mm cube size) processed in a vacuum freeze-drying process. In this case the average TPC loss values found at 10 Pa were 64% and 67% at 0°C and -30°C, and 52% and 53%, at 0°C and -30°C respectively under 30 Pa. These values are similar with those obtained in the AFD process

VFD and FD-MVD okra samples had final TPC and TFC contents significantly different from fresh samples. However, the relative reduction was very small. VFD and FD-MVD okra samples had 9% and 14% reduction in TPC after drying. For the okra TFC the reductions found were 6% for VFD and 13% for FD-MVD. These results had all better retentions when compared to the other tested drying methods (HAD, MVD and HAD-MVD). The low-oxygen and temperature environment during VFD and FD-MVD could effectively minimize the losses of phenolic acids and flavonoids. However, during FD-MVD treatment, the exposure of the okra samples to oxygen was higher than that during VFD treatment [22].

Das *et al*. (2012) [82] also found TPC increases after processing seven-day-old fresh wheatgrass (Triticum aestivum L.) samples to make wheatgrass flour. Flavonoids and TPC had enhanced contends higher than 50% after VFD, oven drying had slightly higher, above 70%, increases for both. In a VFD process to make pumpkin flour, the TPC values differed significantly between VFD and HAD samples. VFD samples had in average 0.39 mg of gallic acid equivalent/g d.m. TPC content, while HAD samples were found to have a higher average value of 1.64 mg of

gallic acid equivalent/g. This indicated the formation of phenolic compounds during drying at 70°C [89].

Broccoli sample size was found to have an influence on TPC in a VFD and AFD study by Mahn *et al*. (2014) [90]: smaller particles had better retention than larger particles. This might be attributed to shorter drying times required to smaller samples. The TPC reduction after VFD was about 48.7% while AFD had 41.9% reduction, without significant difference between both [90]. Apple geometry was also found to be impacted by samples geometry for AFD samples. TPC retention for slabs (lower surface/mass ratio) was 61%, while it was 83% for apple cylinders (higher surface/mass ratio): this significant difference may be related to the longer drying times that were required for the slab samples could have favored degradation reactions. The application of ultrasound reduced significantly the TPC retention in apples cut in cylindrical shape (57%) compared to the samples without ultrasound (83%), both AFD with convective air. For the slab samples, the contrary was observed, with US the retention was 75%, while without US the retention was 61%. The stress produced by US can damage the cell structure, but also can induce the formation of phenolic compounds, by combining existing bioactive molecules or inducing new metabolic pathways. The US might even have some effect on the activity of oxidative enzymes [75]. In another study with fuji apples, a 39% decrease was observed in total polyphenols content of the samples after AFD with respect to VFD. The application of convective drying in a tunnel dryer produced a similar decrease to the AFD reduction found [91].

As food matrixes are complex, and many interactions are not well known and understood, different results may be observed in different food products. No significant differences were found in TPC between frozen and VFD corn and marionberries, but significant reduction of approximately 30% was found for strawberries in the same study [92]. In another research,

Saskatoon berries were dehydrated by different methods, VFD, MVD and AD. VFD had the best results for retention of TPC and anthocyanin. Two varieties of the berry were evaluated, thiessen and smoky. The average reductions found for them were respectively 33% loss in TPC and 32% loss in total anthocyanin for thiessen and 10% and 23% loss in TPC and total anthocyanin for smoky [93].

Conversely, other studies, also using berries, found small decreases, or even increases, in the phenolic content. Sablani *et al.* (2011) [94] used two blueberry cultivars (Duke & Reka) and Meeker red raspberries in their research. These berries were harvested by hand and by machine and had their phytochemical content determined at harvest, after blanching, and after HAD & VFD. As a general trend, meeker red raspberries had an increase in anthocyanin and phenolic concentration after VFD, but the increase was, in most cases, not significant. HAD blanched samples showed a less expressive increase, while HAD unblanched showed reductions in the content. Conventional Duke blueberry cultivar showed significant decrease in anthocyanin content, while organically produced did not have a significant decrease. The same study on the other cultivar, Reka, showed different results. Conventionally grown samples had an increase in the anthocyanin content, while the organic samples maintained their content at an almost constant level. For phenolics concentration, all blueberries, duke and Reka, cultivated organically or conventionally, showed a non-significant increase on these compounds after VFD.

Ellagic acid is a natural phenol antioxidant found in numerous fruits and vegetables. Its retention in blueberries after MVD and combined HAD-MVD was significantly higher (232 and 297 mg/100 g respectively) than the retention with only HAD and VFD (37.7 and 25.7 mg / 100 g). Quercetin glycoside retention in blueberries was higher after VFD (332 mg / 100 g), followed by MVD, combined HAD-MVD and HAD (201, 156 and 137 mg / 100 g respectively) [95].

Chlorogenic acid is an ester of caffeic acid and quinic acid it is classified as a polyphenolic compound. Chlorogenic acid values were higher in blueberries after VFD, probably due to lower processing temperature. This organic acid is known to isomerize or degrade when treated under high temperatures [77].

Measuring phenolic compounds differing the type of compound may give some clues on the behavior of these compound after drying processes. Mejia-Meza *et al*. (2008) [95] measured the total polyphenols in blueberries in terms of glycosides and aglycones. Under the tested drying conditions, the aglycones seemed to be more stable, and were even formed. In fresh samples, the initial concentrations were 66.8 and 294.2 g of gallic acid equivalent / 100 grams of sample for glycosides and aglycones, respectively. After VFD glycosides had the highest retention, 34.2 g of gallic acid equivalent / 100 grams of sample, the aglycones content found was 474.0 g of gallic acid equivalent / 100 grams of sample. However, the highest values were found for HAD, 505.4 g of gallic acid equivalent / 100 grams of sample and, in overall, they were not very different for MVD and combined HAD-MVD. The anthocyanins of blueberries were also measured in glycosides and aglycones and their contents increased after any drying process. However, the highest retention values were obtained for VFD samples, 16.3 and 291.8 mg of pelargonidyin-3-glucoside/100 g of sample, for glycosides and aglycones respectively.

Raspberry, strawberry and bilberry phenolic compounds did not vary, or slightly increased, after VFD, maybe due to increased extraction. During storage, the phenolic content decreased dramatically. A similar fall was observed for anthocyanin on samples [96].

Neither IR nor freezing rate had significant effect on the polyphenol content of VFD Murtilla berries. [97] Pressure and sample size where found to have a negative effect, while IR did

not reach significance on polyphenol content of blueberries after FD. AFD samples had a trend to have lower values after drying compared to VFD. [76]

Rosales-Soto *et al.* (2011) [98] studied the effect of a few processing conditions on anthocyanin and antioxidant capacity of raspberry juice during processing of muffins. This study compared a standard muffin formulation to a version having 10% raspberry juice added to replace part of the flour. Part of the batters and baked muffins was freeze-dried (frozen for 4 h at -35°C, then FD at 100 mTorr, heating plate at 20°C and condenser at -60°C for 24 h). Freeze-dried batter had a decrease in the recovery of phenolic compounds, while having an increased recover for baked muffins. Also, FD increased the recovery of total anthocyanin content of all batter and muffin samples.

To understand the effects of freezing, the retention of phenols, anthocyanin and flavonoids was measured in blueberries, cherries, cranberries and strawberries. These measurements were done after individually quick-frozen process (IQF), VFD, HAD and refractance window drying (RWD). The content percent variations were based on the IQF initial values. After VFD, cranberries had a 9% decrease in phenolic content. In the other hand, strawberries, cherries and blueberries had 13, 49 and 52% increase in phenolic concentration respectively. RWD increased the phenols concentration in blueberries and cherries and decreased them in cranberries and strawberries. HAD promoted an increase in phenolic compounds for cherries and strawberries and a decrease for blueberries and cranberries. Regarding anthocyanin, HAD promoted a decrease in all berries, while RWD made slight changes. VFD resulted in 22, 31 and 55% increase in anthocyanin content for cranberry, cherry and blueberry respectively, and 6% decrease for strawberry. For flavanols content, all methods provoked an increase for blueberries, cherries and cranberries, with the highest increases achieved after VFD, from 34 to 52%. Strawberries had

flavanol content decreases from 54 to 71% in anthocyanin for all tested drying methods. Lower operational temperatures of VFD were suggested to have favored better retention of the measured compounds compared to the other drying methods [77].

Freeze drying of kiwis under vacuum resulted in the highest TPC values (361.38 mg gallic acid equivalent/100 g d.m.) while microwave drying at 120 W (193.05 mg gallic acid equivalent /100 g) resulted in the lowest TPC of all the available drying treatments ($p < 0.05$). These results might be explained by thermal effect, since polyphenols can bind to other compounds such as proteins and cannot be extracted with the executed methods. This could lead to the observed decrease in TPC on thermally treated samples [99].

Studies with tropical fruits generally found phenolic content reductions. Mango, pitaya and papaya had their quality measured after VFD-EPD, HAD-EPD, VFD and HAD to evaluate which process would be best suited for making chips. The phenolic compounds values for the fresh product were: 550.1, 225.2 and 317.1 mg /100 g of dry product for mango, pitaya and papaya respectively. For flavonols, the values measured in the fresh product were: 4.75, ND and 2.56 mg /100 g of dry product for mango, pitaya and papaya respectively. VFD and VFD-EPD presented the best retention values. After VFD, the phenolic retentions observed were 352.8, 152.6 and 221.8 mg/100 g of dry product for mango, pitaya and papaya respectively. For flavonols after VFD, the values were 2.81, ND and 1.52 mg/100g of dry product for mango, pitaya and papaya respectively. After FD-EPD the phenol retention values were: 346.9, 142.7 and 193.7 mg/100 g of dry product for mango, pitaya and papaya respectively. For flavonols after FD-EPD, the retentions were 2.34, ND and 1.37 mg/100 g of dry product for mango, pitaya and papaya respectively [44]. These results show retentions above about half of the initial content, with slightly better retentions for VFD alone compared to FD-EPD.

Starfruit, mango, papaya and watermelon TPC were smaller after VFD compared to the fresh sample, while muskmelon TPC did not differ significantly. [72] The apparent phenolic content of starfruit encapsulated samples was measured in simulated gastric and intestinal fluid contents were higher for VFD samples compared to spray-dried ones, and the differences were statistically significant [100].

In a study with fresh cacao pod husks, TPC had an average value of 323.7 mg gallic acid equivalent/100 g dry matter which increased after MD, HAD and VFD (1893 mg gallic acid equivalent/100 g for the last one). The suggested reason for this was due to metabolic pathways under the operating conditions that could result in the accumulation of these kind of compounds. VFD and MD were characterized by the highest accumulations, which could also be due to increased extraction efficiency after the process. TFC also showed trends of increase after the drying. They also performed a phenolic profile chromatogram and they observed that different drying processed produced different TPC and TFC patterns, suggesting that different mechanisms may affect these compounds profiles [70].

As a general observation from the results gathered, the increase or decrease in these compounds seems not to follow a specific trend while different explanations were given by the authors to support their findings. As abovementioned, phenolic compounds can be degraded by enzymes and through other oxidation reactions, which could help explain their decrease when observed. In addition, TPC, phenolic compounds could bind to other molecules making its quantification difficult in some cases, leading to decreases in the measured values [99]. Polyphenols in intermediate oxidation state can exhibit higher antioxidant properties, leading to a higher perceived content trough some analytical methods [101]. A probable conversion of cinnamic acids into their corresponding hexosides by a glucosyltransferase was suggested to be capable of leading

to higher TPC measurements depending on the analytical method used. [84,102] This behavior could lead to different measurements, depending on when the phenolic compounds content was measurement. Many authors above also suggested enhanced extraction due to structural changes during freezing and FD to be responsible for the increases observed and different metabolic pathways may lead to the conversion of other compounds into phenolic compounds and their accumulation [70,75,83,89]. Nayak (2015) [101] proposed that increases in phenolic compounds might also be due to a breakdown of large molecular weight phytochemicals into smaller compounds that can increase the measured values.

2.3 Antioxidant capacity

The term antioxidant is attributed to hundreds of compounds that can delay the onset, or slow the rate, of oxidation of materials, including phenols and vitamins. It was postulated that they inhibit chain reactions as hydrogen donors or acceptor for free radicals. Antioxidants can be sensible to high temperatures and many degradation compounds may arise. As mentioned, the antioxidant capacity can be measured by different methods. Some of the general assays for antioxidant capacity include 2,2-Diphenyl-1-picrylhydrazyl method (DPPH), ferric reducing antioxidant power (FRAP), 2,2-Azino-bis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) method, oxygen radical absorption capacity (ORAC), total radical absorption potentials (TRAP) and cupric ion reducing antioxidant capacity (CUPRAC). The first three methods listed are based on single electron transfer, while the last two on hydrogen atom transfer [103].

Chan *et al*. (2009) [86] evaluated the antioxidant capacity of ginger leaves by the FRAP method and by the DPPH, expressed as ascorbic acid equivalent (AEAC). The FRAP and AEAC

values were measured for the fresh product and then their percent increase or decrease in each ginger leaf cultivar was calculated and reported after drying. After VFD, AEAC and FRAP values for A. zerumbet ginger leaf variety increased by, 16% & 9% and E. elatior, 45% & 36%. Furthermore, E. elatior values after drying remained stable after one-week storage. However, VFD also led to a decrease of other two cultivars: C. longa variety had a 9% & 14% decrease for FRAP and AEAC, while K. galanga had 10% & 14% decreases respectively for FRAP and AEC. The authors reported different behaviors for the different ginger leave species. A. zerumbet and E. elaitor presented higher contents of the abovementioned bioactive compounds in the extract, had thick leaves and were powdery. C. longa and K. galangal varieties presented lower contents of such compounds in the extract, had thin leaves and were papery. Modifications of the leaf matrix can affect extractability of interest compounds, which could help explain the different effects the VFD process had on each species [86].

An *et al.* (2016) [87] evaluated the effect of VFD, HAD, MD and intermittent microwave-convection drying (IM&CD) on Chinese ginger. FRAP was found to have its highest values for samples in this order: IR > IM&CD > VFD > HAD > MD. In addition, FRAP was found to have a high correlation with TPC (R^2 = 0.741) and TFC (R^2 = 0.850). ABTS had its highest value for IM&CD > VFD > IR > HAD > MD in this order. For the antioxidant assays on Chinese ginger, DPPH had its highest value of AEAC on VFD samples, and the lowest on HAD ones. A high correlation factor was found for the DPPH scavenging ability with TPC (R^2= 0.866) but not with TFC (R^2= 0.594).

Further studies evaluated the antioxidant capacity of ginger and tomato samples after VFD by the CUPRAC assay. The AC was found to increase and the authors suggested that it may be due to increased extraction efficiency due to freezing, and reduced losses of components with

antioxidant activity [23]. These results agree with Chang *et al.* (2006) [83] findings. The antioxidant capacity of tomato varieties was measured through different assays and for both VFD and HAD they found slight increase, or no-change, in the values. VFD SN tomatoes had 3.7%, 15.6% and 1% increase in reducing power, Ferrous ion chelating power and DPPH scavenging power, respectively. Similarly, ITH tomatoes had 3.7%, 2.4% and 0 % variations for the same assays in the same order.

The IC50 is also used sometimes to report antioxidant values. It can be expressed as the amount of product needed to inhibit antioxidant response by half. Okra samples dried by VFD exhibited the highest FRAP values compared to the combined process, VFD-MVD. The percentage variations found for the antioxidant capacity of okra after VFD & FD-MVD respectively were: 9% decrease & 18% increase for inhibition concentration (IC50), 2% & 9% decrease (AEAC), 6% & 19% decrease (FRAP), and finally 10% & 15% (ABTS) [22]. Further, for wheat-grass flour, by the FRAP assay, antioxidant activity an increase above 50% was found, probably correlated to the TPC and flavonoids increase also found in this study. In addition, by the DPPH assay, increases of almost 10% were measured [82]. The antioxidant activity of pumpkin flour after VFD and HAD was measured by many methods. The total antioxidant activity compared to BHA levels was higher for VFD samples, while the reducing power compared to BHT was higher for HAD than VFD. Samples dried by HAD also had higher DPPH free radical scavenging activity in different methanol concentrations, compared to BHT. The metal chelating activity of HAD flour was also slightly higher than the activities observed in VFD flour samples. These results suggested that, in some extent, the increase in heating during drying might have contributed to the formation of antioxidant compounds derived from Maillard reactions [89].

US or blanched pre-treatments were applied to onion samples, then dried by VFD. Their FRAP antioxidant capacity retentions ranged from 79.61% to 121.41% and DPPH from 89.56% to 136.59%. Samples dried by HAD had FRAP antioxidant capacity retention levels ranging from 70.94% to 110.95% and DPPH from 80.19% to 116.05% [15]. In another study with fresh red onions, the antioxidant activity was 15.84 g/kg (IC50 value) and these values did not significantly change after freezing neither VFD [88].

Colucci *et al*. (2018) [50] investigated the effects of AFD on the nutritional properties of eggplants and found antioxidant capacity (FRAP) reductions from 33.74% for 8.8 mm cube size samples, processed at -10°C without ultrasound application and with a 2 m/s air flow; to 76.17% for 17 mm cube sizes, at -10°C, with 50 W US and 2 m/s air flow. Significant effect of processing temperature and air velocity on the degradation of AC was observed. Increase in sample size significantly reduced the antioxidant capacity, probably due to increase in drying time, while ultrasound had no significant effect on the measured compounds, even though it was able to reduce drying time considerably [50]. Figure 3 shows the variation of FRAP, given as mg of trolox, in eggplant samples (8.8 mm cube size) processed in a vacuum freeze-drying process. The FRAP percentage reduction values, measured according to Ref. [46] found at 0°C and -30°C respectively were 48% and 66% under 10 Pa and 59% and 61% under 30 Pa. As for the TPC, also in this case similar results are obtained in comparison to the AFD process.

Many studies used berries to evaluate the nutritional quality after drying processes. The antioxidant capacity reductions found for saskatoon berries through different assays were, for the thiessen & smoky varieties, respectively 50% (AAE), 41% (DPPH) and 43% (ABTS); 27% (AAE), 9% (DPPH) and 213% (ABTS) for the second variety [93]. Only freezing rate influenced the antioxidant capacity (DPPH) of VFD Murtilla berries with and without IR, better retention was

observed in fast frozen samples [97]. Peroxyl radical-induced DNA breaking activity assay can also be used to assess antioxidant activity. Evaluating the effects of VFD, MVD, AD-MVD and AD on saskatoon berries, this assay was done by measuring the supercoil DNA relative protection on the frozen product and then comparing to the values found for the dried product. VFD had the highest retention of approximately 85%, followed by MVD, AD-MVD an AD, all but the last two were significantly different from each other ($p < 0.05$) [93]

The ORAC values were measured for blueberry, cherry, cranberry and strawberry after individual quick-frozen process (IQF), VFD, HAD and refractance window drying (RWD). Based on the IQF values, HAD led to reduction in the ORAC value for all berries from 19-48%. RWD lead to an 18% increase in this value for blueberries, but decreases from 6-11% for the other berries. VFD had the best retentions: it increased the ORAC value in blueberries by 31% and by 5% on cherries, while cranberries and strawberries had reductions of 13 and 11% respectively [77].

Blueberries after VFD had higher retention of antioxidant activity in the form of glycoside compared to samples dried by HAD, MVD or combined HAD-MVD. However, the antioxidant activity in the form of aglycone was better retained by HAD-MVD samples compared to the others. The ABTS radial oxidation activity was similar for MVD and HAD samples. Kaempferol glycoside had a slightly higher retention in blueberries after MVD and HAD (84.5 and 26.4 mg / 100 g) than after VFD and combined HAD-MVD, since these last two had almost none of this flavonoid recovered after processing [95].

The total antioxidant capacity measured by means of ABTS had not significant increases after VFD for all samples of blueberries conventionally and organically grown and for the Reka and Duke red raspberry samples [94]. The antioxidant activity (DPPH) decreased for freeze-dried samples of both batter and baked raspberry juice muffin formulations studied [98].

Sample size had a negative significant effect on the antioxidant capacity, measured by DPPH, of FD blueberries. Smaller sample sizes, cut into quarters, had better retention compared to the samples cut in half. IR application and the use of AFD instead of VFD did not significantly affect this quality attribute in this study [76]. In another study with broccoli, air temperature, particle size and IR application produced a reduction of anti-radical power of samples using VFD and AFD. In VFD the average loss was of 65.5%, while in AFD of 80.1%[90]. The opposite was observed for AFD apples regarding the geometry: the antioxidant activity was reduced significantly in cylindrical cut samples after AFD, while no significant reduction was observed in slab cuts. This might be due to the higher surface/mass ratio in cylinders, which gives an exchange surface that can favor some oxidative reactions. The samples treated with air combined with US had similar results for both geometrical shapes [75]. Fuji apples in another study had a 6% decrease in the antioxidant capacity (DPPH), while convective drying in tunnel dryer produced a 22% decrease [91].

Many VFD studies have also included tropical fruits for antioxidant assays. The DPPH values for starfruit and mango were found to decrease after VFD, but no significant variation was found for watermelon, muskmelon and papaya. A good correlation was found for TPC and DPPH (R^2=0.758) and for TPC and FRAP (R^2=0.753), indicating that phenols might have a big contribution to the AC measurements. By the FRAP assay, significant reductions were found for starfruit and mango, while papaya, watermelon and muskmelon had reductions that were not significant. In terms of lipid peroxide inhibition, starfruit and mango had significantly higher values when fresh, while papaya, muskmelon and watermelon had significantly higher values after VFD [72].

The AC of fresh cacao pod husks was 30.6 µMol trolox equivalent (TE)/g (ABTS) and 15.1 µMol TE/g (DPPH). These values increased after the drying treatments were caried out, showing the highest increase after VFD (112.4 µMol TE/g on ABTS and 70.8 µMol TE/g on DPPH), followed by MD and HAD [70].

All thermally processed kiwi samples resulted in a decrease of AC, measured by the DPPH assay, with no significant difference between them. The VFD samples had higher antioxidant capacity when compared to the samples dried by thermal drying methods ($p < 0.05$). These results could be attributed to the TPC reduction, since a positive correlation (R^2=0.7796) between the two attributes was found in this study [99].

An interesting study evaluated the quality properties of porcine placenta hydrolysates (PPH). The highest DPPH, hydroxyl radical and superoxide scavenging activity values were found after VFD and these values were significantly different from the ones found for SD and vacuum drying. The lower DPPH values found for vacuum drying and SD may be due to alterations on the exposure and sequencing or positioning of the hydrophobic amino acids in the PPH peptide structure. Furthermore, the losses in solubility in this study were found to be correlated to the decrease in the DPPH scavenging ability. They observed and inferred that the amount of heat supplied during the drying method significantly affects the electron or proton transferring of PPH [105].

2.4 Other targeted compounds

According to the studied food product, different specific compounds may be of interest since they might contribute to the product main quality attributes.

In fresh ginger, for instance, the amount of fresh 6-gingerol was 5.91 mg/g and decreased significantly after drying. VFD samples had the lowest decrease (3.54 mg/g), followed by IR, IM&CD and HAD (3.44, 3.21 and 2.50 mg/g respectively). Contents of 2, 8-gingerol and 10-gingerol had no significant differences between fresh and VFD samples with contents of 2.52 and 2.62 mg/g in the fresh product and 2.52 and 2.74 mg/g in VFD samples. The content of 6-shogaol increased from 0.09 mg/g in fresh ginger to 0.214, 0.209, 0.221, 0.384 and 0.243 mg/g after HAD, IR, VFD, MD and IM&CD process. These results show that 6-shogaol usually was not present in fresh ginger, but was formed during thermal drying or storage [87].

Capsaicin is an active component of peppers, which are plants belonging to the genus called Capsicum. The capsaicin content also greatly ranged according to the pepper cultivar, PLR-1 had 1.504 g / kg d.m (low relative content), while bird's eye had 3.968 g / kg (high relative content). After processing, the values ranged from 1.504 for CO-4 pepper cultivar after SD and 3.969 for bird's eye cultivar after VFD. In general, the capsaicin content of fresh samples was slightly higher than in dried samples. Still, capsaicin was found to have a positive correlation with VFD samples of all cultivars [80].

For barley grass under VFD chlorophyll increased with the rising of heating input; on the other hand, for microwave freeze drying (MD-FD), rising of heating did not lead to chlorophyll increase. However, a high microwave power input impaired chlorophyll and flavonoids significantly, having the highest reduction at the highest power input [16]. Chlorophyll content of wheat-grass had a small decrease of about 10% for VFD samples, oven-dried samples had a slightly higher decrease [82].

AFD was found to have a lower impact on broccoli selenium content compared to that found in VFD samples. This was attributed to a lower volatilization of seleno-compounds during

AFD process. In this study, air temperature and IR application significantly reduced selenium concentration on broccoli samples [90].

Desobry *et al*. (1997) [106] investigated the effects of VFD, drum-drying and spray drying on content of β-carotene encapsulated in 25 dextrose equivalent maltodextrin. The VFD encapsulation process led to an 8% degradation of β-carotene, measured 24 h after drying, while the other two processes led to higher degradations of 11% and 14% for spray and drum drying in this order. These results were expected due to the higher temperatures used in the last two processes.

β-Carotene content degradation in pepper cultivars was significant for all tested drying methods. The fresh samples content varied from 0.156 g / kg d.m for PKM-1 pepper cultivar to 0.271 g / kg for CO-4 cultivars, after drying the values ranged from 0.075 g / kg PKM-1 (SD) to 0.239 g / kg CO-4 (VFD). The maximum retention of β-carotene after VFD may be due to the low processing temperatures used in this process. β-carotene was found to have a positive correlation with VFD, depending on the cultivar [80].

Fresh mango and papaya had 4.75 and 2.56 grams of total carotenoids per 100 grams of dried sample. Mango retained after processing under VFD &VFD-EPD 2.81 and 2.34 g/100 g while papaya retained 1.52 and 1.37 g/100 g respectively. Under both processes the fruits retained more than when HAD and HAD-EPD were carried out [44]. For mango and watermelon, β-carotene content decreased after VFD. The observed reduction was 26% and 43%, respectively for mango and watermelon as result of drying. Starfruit, muskmelon and papaya did not have significant β-carotene reductions in the same study [72].

In a study on freeze-dried mango milk-shake after 6 months of storage under 37°C, saturated fatty acids like lauric, myristic, palmitic and stearic did not show any significant change ($p > 0.01$) in their levels, while the polyunsaturated fatty acids like linoleic, linolenic and arachidonic showed significant difference ($p < 0.01$). This difference observed between the degradation of polyunsaturated and saturated fatty acids could be due to lipid peroxidation of the former. In fact, thiobarbituric acid content, an oxidative rancidity indicator, was positive correlated with these findings and it increased on samples during storage [73].

Çinar (2004) [107] also investigated the effects of VFD and subsequent storage (25°C light, 25°C dark, 4°C and 40°C after a 45-day period) on carotenoid content in orange peels, carrots and sweet potatoes. For all studied products the losses during storage, under all conditions, after VFD were remarkably lower than the losses of the fresh product, suggesting VFD stabilized the products and prevented further deterioration during storage. The presence of light had no significant effects on the carotenoid content in this study. Drying caused a decrease on α and β-carotene content in carrots, but with VFD the variation was not significant. The loss of carotenes during drying can be attributed to a limited amount of oxidation [79]. Vacuum freeze-dried carrot disk samples had a higher polyacetylene and carotenoid retention compared to hot air-dried samples, this was attributed to carotenoids being sensitive to heat, oxygen, light, and enzymes [108].

The variation of reducing sugars was measured after FD and MD-VFD of potatoes and no significant variations were found for unblanched samples (pre-treatment), while for samples that had blanching, the variation was of about 9% [74].

Glutathione (GSH) contents after VFD were found to decrease by 39.44% for tomato and 72.9% for ginger samples. Cysteine (Cys) contents were found to increase by 2.44% for tomatoes after VFD while they had a 72.58% reduction for ginger [23]. Lycopene content on tomato varieties

had decreases of 33% and 47.8% for freeze-dried SN and ITH varieties, but had expressive increases for AD samples. The authors suggested this increase could be due to isomerization during thermal processing - which would not happen during VFD - transforming trans-lycopene into cis-lycopene, which could represent an increase in the measured values [83].

Measuring the free amino acids of iron yam slices, combining two hours of VFD, letting the sample melt and then performing MVD, lead to the best retention results. VFD alone was found to result in the lowest retentions. In their experiments, MVD had shorter treatment times and the temperature used was lower than the temperature during the desorption stage in VFD. In addition, macromolecular peptides may degrade to amino acids under microwave application [78].

MVD mealworm samples was characterized by a large reduction of vitamin B12 compared to VFD. Fresh samples had 0.82 µg/100 g dry mass, VFD samples had a final content of 0.85 µg/100 g dry mass, while MD samples had only 0.31 µg/100 g dry mass retained after drying. The protein and fat contents of VFD mealworms was comparable to the contents achieved by MD, approximately 60 g of protein and 28 g of fat per 100 grams of dry matter [109].

Measurements of protein content on dried sea cucumbers by the Kjedahl's method showed highest retention on VFD samples compared to electrohydrodynamic dried samples and a by the combined EHD-FD method, showing lower quality impairment using VFD alone [19].

The polyphenol oxidase enzymatic activity after processing was also measured on cacao pod husks. The PPO activity decreased for HAD, MWD and FD, in this order, by 27%, 66%, and 52%, compared to the activity of the fresh product. However, there was no significant difference found between them even though HAD has still around 73% of its initial enzyme activity. The authors proposed that the partial reduction of PPO activity after VFD was attributable to the

increase in the H+ concentration during freezing, which can change the pH value by as much as 3 units leading PPO to become unstable [70].

Spray-FD coffee showed a significant better retention of volatiles compared to VFD and spray drying alone [39]. Similarly, Chin *et al*. (2008) [110] studied the effects of VFD and spray drying on the volatiles of durian fruit, having as targets propanethiol, ethyl propanoate, propyl propanoate, ethyl 2-methylbutaboate and diethyl disulfide. Both processes yielded in reductions of these compounds, but VFD had lower reductions than spray drying. Freeze drying had losses hanging from 71.5% to 97.2%, while spray drying had decreased higher than 97.7% for all compounds. The authors suggested that the volatile compounds could have been removed from the samples during the sublimation stage of the freeze-drying process or in the pre-steps to prepare the samples. Spray dried samples had even higher losses, probably due to the volatiles evaporating together with the water during the process.

Wang *et al.* (2007) [111] evaluated the effects of vacuum belt drying (VBD), VFD and HAD on banana pure to produce banana powder. By gas chromatography–mass spectrometry GC-MS the volatiles were evaluated, and the conclusion was that VFD achieved the best aroma value, followed by VBD and AD. In addition, VFD produced some compound that were unique to this process, while VBD and HAD also had their own characteristic compounds, probably due to their higher processing temperature compared to VFD [111]. In another study, the analysis of shiitake mushroom volatiles after drying indicated that FD(4 h)-mid-IR followed by FD were the preferred methods for this product with the highest aroma retentions [24].

Robayo-Torres *et al.* (2007) [112] investigated the effects of VFD and oven-drying on the volatiles and phenolic compounds of grape skins of Carménère and Cabernet Sauvignon varieties. The skins had a 15% decrease for Carménère and 22% for Cabernet Sauvignon in all measured

compounds after freeze-drying, while oven-dried samples had decreases above 34% for both varieties, showing better retentions for VFD. The compounds were measured through a gas chromatograph plus mass selective detector, so, the variations for Carménère found by compound group were: terpenes +3.5%, sesquiterpenes +2.3%, norisoprenoids -42.5%, C6 alcohols and aldehydes +10.5%, alcohols -1.6%, acids +13%, aldehydes +55.5%, esters +51%, benzene derivatives +28.7%, benzene derivatives +44.5%, antocyanidin +15.3% and flavonols +35%. In another study, freeze-drying of grape marc did no reduce antioxidant power of the extracts [113].

With an electronic nose, barley grass dried under VFD and MD-FD was analyzed and showed some differences between the odor signals. Sulfide (S_3) electric signal showed no difference between the tested conditions. Amine/esters (S_2/S_5) showed a significant difference only for the lowest power level on the heating plate during FD, suggesting that the lower power might facilitate the retention of this kind of odor compounds. Ammonia (S8) showed differences across power levels and between FD and MD-FD [16].

3. Conclusions and research needs

As discussed, food matrixes are complex systems and several interactions between their compounds may take place. These interactions can lead to degradation of existing compounds of interest, and formation of new compounds, as well as alterations in their conformation and activity. Whether their outcomes are beneficial or not, depends on the product.

For vitamin C, vacuum freeze drying most of the time gives the best results for its retention. MVD and IR combined processes with VFD seem to be able to decrease processing time, while having a mild effect on product quality. EPD, when applicable, was also able to retain considerably

vitamin C in the dried product. US technology was many times able to deliver dried products with comparable quality when care was taken to control product heating during processing.

For phenolic compounds, depending on the product and drying conditions, different results were achieved. VFD and AFD seem to have fairly similar effects on the phenolic content retention of food products. Combined processes with IR, US ad RDW seem to have a mild impact on the retention of phenolic compounds. MVD combined processes at times resulted in augmented phenolic content and, at times, diminished contents.

VFD and AFD had in general has similar results for AC. US, IR, RWD and MVD were in general able to be used in combined processes without drastically affecting product quality. In an overall, the trends observed for AC are similar to the overall results for phenolic compounds: many studies report decrease, increase or no significant change in the AC by different analytical assays. Which can be explained, since phenolic compounds also have antioxidant activity and studies have found high correlations between phenolic content and antioxidant activity [72,87]. This quality property seems to also vary according to the product characteristics, processing applied and the stage of the product when the interest compounds were measured.

For the other compounds, FD and combined processes resulted in more desirable volatile profiles most times. For best results, the drying conditions must be chosen according to the targeted attributes for each food product.

Since food matrices are complex, it is hard to fully understand the biochemical pathways and mechanisms involved in nutritional content variation after freeze-drying. Future studies could benefit from deepening the knowledge on the factors affecting these pathways, according to the

product characteristics, process parameters and use of assisting drying methods. This would help better control and optimize final product quality.

In addition, the use of modified atmosphere gases in AFD could also be more deeply explored to check if differences in ascorbic acid retentions between VFD and AFD are more influenced by the oxygen present or by product temperature. The applied extraction methods in future studies should be carefully developed to minimize possible enhanced extraction due to the freezing step, since this might deceive interpretations regarding bioactive compounds increased contents after freeze-drying.

Besides, as the freezing process plays a crucial role, novel freezing assisting methods, such as electric and magnetic fields, might as well be interesting for future research to improve freeze-drying process efficiency, along with product nutritional properties. From a hurdle effect perspective, multiple combinations of novel freezing and drying assisting methods should also be investigated in the future.

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List of Figures

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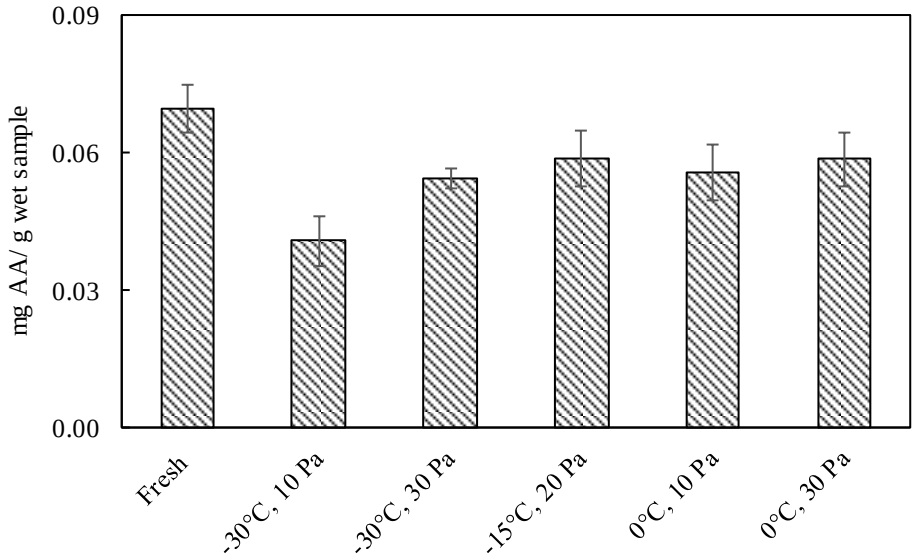
Figure 1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0.06
0.03
0.00
mg AA/ g wet sample
Fresh
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-15°C, 20 Pa
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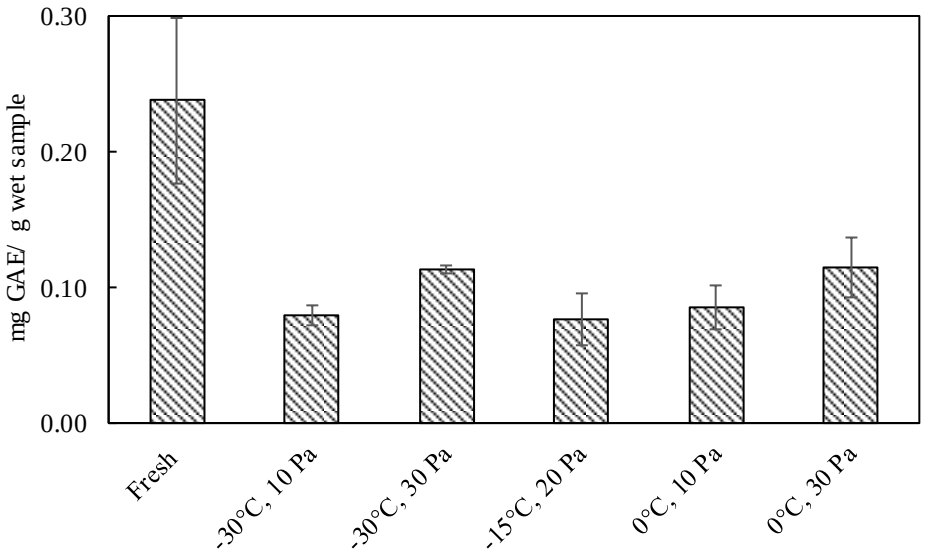
0°C, 30 Pa

Figure 2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0.20
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mg GAE/ g wet sample
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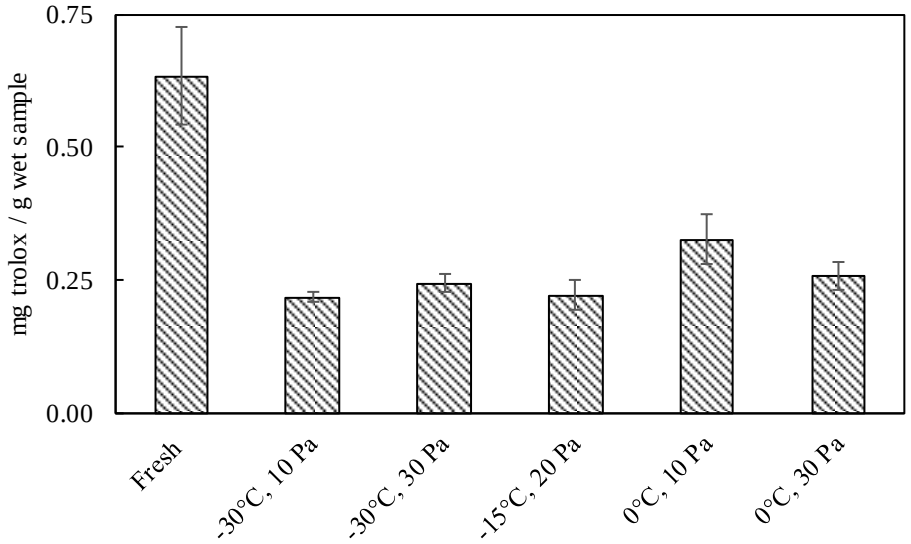
-15°C, 20 Pa
0°C, 10 Pa
0°C, 30 Pa

Figure 3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0°C, 30 Pa