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Characterization of electromagnetic freezing in food matrixes and model food

TESIS DOCTORAL

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ABSTRACT

The challenges

Freezing basically consists in reducing the temperature of foodstuffs below the freezing point of water in such a fashion that freezable water changes of state, avoiding that way the growth of microorganisms and decelerating chemical and enzymatic reactions that cause food spoilage. Traditional methods are based on enhancing the heat removal rate. Recently new methods trying to control nucleation has been proposed, one of the more relevant ones being magnetic field (MF) freezing. It is based on the application of a determined MF along with cooling. According with some authors, those fields would increase supercooling degree. It is known that the higher the supercooling degree, the smaller and better distributed the ice crystals. If the effect of MF were proved, it would imply a great advance in freezing technology.

State-of-the-art

The most renowned commercial MF freezer applies static and oscillating MFs during freezing. Besides, several patents presenting MF freezing methods and equipment have been published, as well as papers applying either laboratory prototypes or commercial MF freezers to different freezable materials, namely water and model food substances and foods within the field of Food Technology; and cells, tissues, organs and organisms.

Objectives

The objectives of this thesis are:

- Studying the development of the electromagnetic freezing process in model substances which allow supporting the hypotheses on which the envisaged improvements are based.
- Studying the effect of electromagnetic freezing on the quality of different foods.
- Obtaining electromagnetic field generator prototypes suitable for electromagnetic freezing and other applications.

Our approach

In addition to using laboratory and commercial MF freezers, two new laboratory prototypes were built. The most important one was an electronic inverter for working at various frequencies from 1 Hz to 50 kHz. This inverter supplies the required sinusoidal current to two different solenoids (one proper for low and other for high frequencies) also produced, wherein samples are located during freezing. The obtainment of a sufficiently sinusoidal current in order to discriminate the effect that different frequencies could have on MF freezing was pursued. So an especial interest was devoted for minimizing the harmonics of the output currents.

Finite element method models have been developed to get an accurate insight into the 3D gradient distribution of MF strength and line directions inside the devices.

ABSTRACT

The influence of MF assisted freezing carried out in commercial freezers on the quality of pork and crab sticks was evaluated. Analogously, in the laboratory prototypes, comprehensive studies on the effect of MFs on the freezing of pure water, aqueous solutions, magnetic nanoparticle dispersions, enzymes and fish muscle lodging living parasites were carried out.

Results

On the contrary to what has been reported in some papers, not many relevant effects of MF freezing can be supported from the developed experimental results. Thus, either parameters extracted from the freezing curves of model food; properties affecting the heat transmission rate like ice thermal conductivity; or quality variables like water holding capacity, drip losses and color of food showed no differences in most cases when MF and conventional freezing were compared. However an interesting increment in the precooling rate was observed in the nanoparticle dispersion when oscillating MF was employed.

Original contributions

A range of MF strengths and frequencies have been proved not to have positive effect on the freezing of food and model foods. An interesting finding of this work is the improvement of the cooling rate of magnetic nanoparticle dispersions. This fact could be used for medical uses. Several prototypes for the application of static and sinusoidal MFs at particular frequencies have been designed and built, and modeling of every used MF freezing devices has been carried out.

RESUMEN

Los desafíos

La congelación consiste básicamente en reducir la temperatura de los alimentos por debajo del punto de congelación del agua de tal manera que el agua congelable cambie de estado, evitando así el crecimiento de microorganismos y ralentizando las reacciones químicas y enzimáticas que causan el deterioro de los alimentos. Los métodos tradicionales se basan en aumentar la tasa de retirada de calor. Recientemente se han propuesto nuevos métodos que intentan controlar la nucleación, siendo uno de los más relevantes la congelación con campo magnético (CM). Se basa en la aplicación de un CM junto con la refrigeración. Según algunos autores, esos campos aumentarían el grado de subenfriamiento. Se sabe que cuanto mayor sea el grado de subenfriamiento, más pequeños y mejor distribuidos serán los cristales de hielo. Si se demostrase el supuesto efecto del CM, ello implicaría un gran avance en la tecnología de congelación.

Estado de la técnica

El congelador comercial con CM más conocido aplica CMs estáticos y oscilantes durante la congelación. Además, se han publicado varias patentes que presentan métodos y equipos de congelación con CM, así como trabajos que aplican prototipos de laboratorio o congeladores con CM comerciales a diferentes materiales congelables, a saber, agua, sustancias modelo de alimento y a alimentos dentro del campo de Tecnología de Alimentos; y a células, tejidos, órganos y organismos.

Objetivos

Los objetivos de esta tesis son:

- Estudiar el desarrollo del proceso de congelación electromagnética en sustancias modelo que permitan respaldar las hipótesis en las que se basan las mejoras previstas.
- Estudiar el efecto de la congelación electromagnética en la calidad de diferentes alimentos.
- Obtener prototipos generadores de campos electromagnéticos adecuados para congelación electromagnética y otras aplicaciones.

Nuestro enfoque

Además de usar congeladores con CM de laboratorio y comerciales, se construyeron dos nuevos prototipos de laboratorio. El más importante fue un inversor electrónico para trabajar a varias frecuencias desde 1 Hz hasta 50 kHz. Este inversor suministra la corriente sinusoidal requerida a dos solenoides diferentes (uno adecuado para bajas y otro para altas frecuencias) también producidos, en donde se ubican las muestras durante la congelación. Se persiguió la obtención de una corriente suficientemente sinusoidal para discriminar el efecto que las

RESUMEN

diferentes frecuencias podrían tener sobre la congelación con CM. Por lo tanto, se dedicó un interés especial a minimizar los armónicos de las corrientes de salida.

Se han desarrollado modelos de métodos de elementos finitos para obtener una visión precisa de la distribución 3D del gradiente de la intensidad y líneas de CM dentro de los dispositivos.

Se ha evaluado la influencia de la congelación asistida por CM llevada a cabo en congeladores comerciales sobre la calidad de cerdo y palitos de cangrejo. Análogamente, en los prototipos de laboratorio, se han llevado a cabo estudios exhaustivos sobre el efecto de los CMs en la congelación de agua pura, disoluciones acuosas, dispersiones de nanopartículas magnéticas, enzimas y músculo de pescado que albergando parásitos vivos.

Resultados

Al contrario de lo que se ha informado en algunos artículos, pocos efectos relevantes de la congelación con CM se pueden apoyar en los resultados experimentales desarrollados. Así, ninguno de los parámetros extraídos de las curvas de congelación del modelo de alimento; propiedades que afectan la velocidad de transmisión de calor como la conductividad térmica del hielo; ni variables de calidad como la capacidad de retención de agua, las pérdidas por goteo y el color de los alimentos mostraron diferencias en la mayoría de los casos cuando se compararon la congelación con CM y la convencional. Sin embargo, se ha observado un incremento en la tasa de preenfriamiento de la dispersión de nanopartículas cuando se emplea un CM oscilante.

Contribuciones originales

Se ha demostrado que una gama de intensidades y frecuencias de CM no tiene un efecto positivo en la congelación de alimentos y modelos de alimentos. Un hallazgo interesante de este trabajo es la mejora de la velocidad de enfriamiento de las dispersiones de nanopartículas magnéticas. Este hecho podría ser utilizado para usos médicos. Se han diseñado y construido varios prototipos para la aplicación de CMs estáticos y sinusoidales a frecuencias particulares, y se han llevado a cabo modelos de todos los dispositivos de congelación con CMs utilizados.

1. Introduction

1.1. Overview of the frozen food market

During decades a great attention is being paid, both from scientific and commercial environments, to all issues related to the improvement of biomaterials quality. One of the biggest current challenges is the achievement of a process for its preservation for long periods of time with no or negligible loss of quality, in comparison to the one of the initially fresh product. Traditionally, most of the processes to keep perishable bioproducts in good conditions until they reach its final use are based on heat removal, by refrigeration (short and medium term) or by freezing (long term). However, the ice crystals formed in the process, especially if they are large, can severely damage the frozen material. The size, shape, and distribution of the ice crystals depend on freezing kinetics and, therefore, it is important to optimize the process to minimize injuries. The deterioration of its quality is mainly associated to the formation of relatively big ice crystals during freezing. In addition, freezing is not suitable for all foods and biomaterials, and freezing can cause physical and chemical changes in some foods that are perceived as reducing the quality of either the thawed material or the final product. For that reason, there is a great interest in methods of improving the freezing process. The demand for frozen food is huge. For example, the global frozen food market size exceeded USD 250 billion in 2015 (<http://www.grandviewresearch.com/industry-analysis/frozen-food-market>). Busy lifestyle coupled with shifting preferences among consumers towards ready to cook meals owing to conveniences and hygiene is expected to remain a key driving factor for the overall industry. In this connection, freezing preserves the products for extended periods without any preservatives and deters against any microbial growth that causes food spoilage. Those facts are appreciated by consumers. Increasing online purchase of staple food is gaining popularity across developed nations. This, in turn, is also expected to have a positive influence on the overall industry over the next eight years. They also help in increasing the shelf life of fruits and vegetables. Also, availability of refrigeration media for commercial and industrial freezing is further expected to benefit the industry growth. Analysts predict the global frozen food market to grow steadily at a Compound Annual Growth Rate of 4% during the 2015-2019 period. The rise in disposable income and the growing desire for convenience is driving the growth of this market. Consumers prefer ready to eat meals that can reduce their cooking and clean up time. Moreover, the ease of use associated with the packaging technique and the microwave cooking support for frozen food is also making frozen food a popular choice for consumers. For instance, nearly 8 out of every ten consumers across Europe consider frozen or prepared meals an excellent option when they are too busy to cook from scratch.

Europa Press agency in 26/01/2017 on the site <http://www.europapress.es/economia/noticia-mercado-alimentos-congelados-confirma-recuperacion-20170126104709.html>) published information of 26/01/establishing that Spanish frozen food market in Spain surpassed € 4600 · 10⁶ by growing 2% in 2016 respecting 2015. The fish segment accounts for about 60% of the market, with a value of € 2740 · 10⁶ in 2016 and an increase of 1.3% compared to the previous year, while that of frozen prepared dishes, which had a figure close to € 1000 · 10⁶, grew by 3.2%. Sales in the domestic market of frozen pre-frozen vegetables, meat and potato also

Introduction

experienced a positive evolution in 2016, showing a joint variation rate of 2.2% and a turnover close to € 875 · 10⁶. The report says that in recent years companies in the sector have strengthened export activity. In 2015, the total value of sales abroad has already exceeded € 3000 · 10⁶, after increasing 10.7% compared to 2014. Forecasts for market developments point to a continuation of the smooth growth trend observed in the 2015-2016 biennium, with rates between 1% and 2% expected in the 2017-2018 biennium. At the end of 2015, about 325 companies operated in the sector, a figure that fell slightly compared to previous years as a result of the purchase and merger processes. On the other hand, the volume of employment was around 16000 workers.

1.2.The nucleation temperature on the freezing curve

A specific freezing process has to fulfill the objective for which it has been designed. To verify this provision, one can profit from analyzing the obtained freezing curve. Among the existing tools to be aware about the quality of a biological or food sample subjected to a specific freezing process it is noted that the analysis of its corresponding freezing curve [1] is a good choice. Its monitoring can also be used to know about the viability of biological materials [2, 3] at nanoscale (molecular) and at microscale (cellular) levels. The cell membrane surrounding the intracellular solution should be the site most affected by freezing. The composition of the phospholipids contained in the membrane, their chain length and their degree of saturation, could have influence on the freezing curve of the sample. Ice crystal characteristics and distribution throughout the product will be a function of the number of nuclei (or seeds) formed from the nucleation temperature, T_n [4] and the growing rate of the subsequent crystals. Due to freezing, additional effects on freezing curve could come from denaturation of proteins in the dehydrated cells as a consequence of hypertonic concentrations and from the mechanical damage of cells due to the formation of intracellular ice. Although no apparent differences could be appreciated, deviations in the freezing temperature appear when comparing the temperature-time curves corresponding to several foods frozen from fresh materials with the ones corresponding to foods which are obtained from pre-frozen materials [5]. Among the parameters defining a freezing curve, Figure 1.2, T_n is the most important one and represents the temperature at which ice nucleation occurs (which is the minimum temperature before liquid-water phase change).

Figure 1-1: The freezing curve parameters. V_p and V_t : precooling and tempering rates, respectively; T_f : phase change temperature; T_n : nucleation temperature; t_{pt} : phase transition time; T_a : ambient temperature

Nucleation implicates two events [6] and the first one is to initiate the transformation from liquid to solid matter. This fact involves a variation of free energy, ΔG_1 , being negative for temperatures below the equilibrium freezing temperature (phase change temperature) T_f . The second important event is the formation of the liquid–solid interface which involves a positive variation of free energy, ΔG_2 . In order to achieve spontaneous crystallization, the sum of both terms of free energy has to be negative. This is only possible when the size of crystal nucleus is large enough.

The final size, shape, and distribution of the ice crystals formed throughout a product depend on the rates of ice nucleation and subsequent crystal growth. The larger these rates, the smaller, the rounder, and the more homogeneously distributed the ice crystals. Ice nucleation is an activated process driven by supercooling and, according to [7], the rate of ice nucleation increases roughly tenfold for every degree of supercooling. Crystal growth takes place only once nucleation has occurred, through addition of water molecules to the nuclei already formed, and its rate mainly depends on the efficiency of latent heat removal [8-10]. Because supercooling is an important parameter of a specific freezing process, it is necessary to know the influence of processing variables on the obtained supercooling temperature. Decreasing nucleation temperature (to increase ΔT) or the related reduction of phase change duration [4]

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of the sample being frozen are the most pursued aspects when adopting a specific freezing procedure. Only after T_n the freezing period purely starts (nevertheless, it must also be noted that by performing molecular simulations at very high cooling rates (10Kns^{-1} - 1Kns^{-1}) in water confined in a 3-nm-diameter cylindrical nanopore, [11] conclude that the freezing temperature of water is controlled by the structural transformation of the liquid and not merely by the degree of supercooling). T_f is a colligative property of a material and corresponds to the highest temperature on the freezing curve after T_n . In pure substances temperature remains at a constant value T_f (0°C for pure water) during the phase change, while latent heat is released, and it does not depend on the process. For food and biological products this temperature depends on composition and its determination can be performed both by experimental methods (by temperature-time curve or by Differential Scanning Calorimetry) and by empirical equations [12, 13]. Accurate determinations of T_f can be used to calculate or to determine other important colligative properties of food such as its effective molecular weight, water activity or bound and free water and frozen water [14, 15]. Related with t_{pt} and with V_t , and calculated in different ways, derivative parameters are given in a non-standardized way in the literature, as the “characteristic freezing time”, the “completion of freezing rate” [16], etc., as also occurs, for example, with the “characteristic freezing times”, calculated in [17] as the time to cool the thermal centre of the samples from the initial freezing point temperature to -7°C and with the “completion of freezing rate” which is calculated as the rate of cooling at the thermal centre of the samples cooled from -10 to -15°C .

In bioscience and food technology areas and looking for safety, quality, economy or other reasons, important endeavors have been performed during last decades to improve freezing processes, by the analysis of the freezing curve.

1.3.Current food freezing technologies

The interest expressed in Section 1.1 is to promote the developing of new methods that improve the final quality of the obtained product [8, 18-20]. A determining factor in the organoleptic quality of the frozen product is the size of the ice crystals formed. This depends on the nucleation rate and the heat extraction rate of the system [9]. If the nucleation rate is low, few ice nuclei are formed. Those nuclei give rise, during the stage of phase change, to few ice crystals but of large size. These large crystals damage the structure of the food, causing alterations in its texture and important loss of water during thawing. Conversely, if the nucleation rate is high, a large number of ice nuclei are formed. These ones give rise to many ice crystals which, if the heat extraction rate of the system is adequate, will be small in size and will cause little loss of quality in food. Therefore, it is generally recommended the freezing process to be carried out as quickly as possible, not only to produce small ice crystals, but also to rapidly inhibit processes of food deterioration. For those reasons it is admitted that the two main factors on which the freezing process can be improved are the heat extraction rate of the system and the nucleation rate [8]. Traditional strategies to improve the freezing process consist in increasing the speed of extraction of heat from the system. Usual practices in the industry to accelerate the freezing process are the chopping of products (potatoes, cauliflower,

carrot, etc.), the application of pre-cooling treatments (forced air, cold water, ice or vacuum) or the partial dehydration of the food. Regarding strategies related to the freezing system, cryogenic freezing systems, cryomechanical freezing or ultra-fast individual freezing systems are currently used [18].

In the meanwhile, the most recent research focus on the nucleation phase to try to produce a high number of ice nuclei evenly distributed throughout the product volume [8]. In this case, the parameter of interest is the nucleation rate that defines the number of nuclei formed. At present, there are three different physical technologies that allow acting on the phenomenon of nucleation: ultrasound, high pressure and electromagnetic fields.

1.4. Control of nucleation. Innovative technologies

Much of the recent advances in freezing systems are occurring in the nucleation control procedures. However, there are notable differences in their development. [21] carry out a review on the ice nucleation control by using innovative methods during freezing. While there is a remarkable scientific production for high pressure and ultrasonic assisted freezing, this is not the case for electromagnetic freezing. Nevertheless, for the latter case, the number of patents (see Appendix 0) is higher than in the other two cases. In addition, only commercial equipment has been developed for the use of electromagnetic freezing, remaining freezing assisted by ultrasonic, high pressure and electrically disturbed freezing systems in the study phase at the laboratory level. In spite the mentioned number of patents and the existence of some scientific publications, there is no unanimity on the potential goodness of this new technology.

1.4.1. The action of ultrasound and high pressure.

Power ultrasound can be defined as a low frequency acoustic wave type (from about 20 to 100000 Hz) and high intensity (generally greater than 1 W / cm^2). If ultrasonic power is applied to a product being frozen, they produce cavitation on the liquid phase which has not yet been frozen. These bubbles act as nucleating agents favoring the formation of ice nuclei throughout the sample volume [22, 23]. The oscillatory movement of the bubbles induces, in addition, strong micro currents that facilitate the heat and mass transfer accelerating, in this way, the freezing process. On the other hand, the stresses exerted by the ultrasounds cause fractures in the ice crystals, which results in the frozen final product having smaller ice crystal size. Another method to control nucleation is to apply high pressures. The technology is based on Pascal's principle that pressure is transmitted instantly and evenly through a liquid. By means of a hydraulic pump and a pressure intensifier, the fluid is subjected to high pressure (200 MPa) and low temperature. The fluid transmits the pressure integrally to all points of the food, regardless of its size and geometry. There are some ways to freeze the food with the help of high pressures [24]. Among them, freezing by sudden change of pressure appears as the most

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interesting from the point of view of the control of the nucleation stage. The foods suffer, with the change of pressure, an additional cooling of about 2-3 °C per 100 MPa. Under these conditions, the ice nucleation probability is large, due to the high degree of supercooling attained and, almost immediately, ice crystal nuclei appear throughout the food volume. Thanks to the high initial nucleation rate it can reach 30% of the water present, compared to less than 10% in a traditional freezing - the formed ice crystals, being more numerous, are also smaller ice crystals [22, 25, 26].

1.4.2. The action of electromagnetic fields

The third innovative system focused on the control of the nucleation phase is the electromagnetic (EM) freezing. This latter system can be classified, in turn, into two different subsystems: electrically and magnetically disturbed freezing systems. In the first one, high voltage has also been utilized to increase ice nucleation temperature and improve the quality and microstructure of frozen foods. Its effect is based on taking benefit of the fact that the dipole polarization of water can be rearranged and water molecules move in the direction of the electric field (EF) [27]. Magnetic freezing, in turn, can be classified as static magnetic field (SMF) and oscillating magnetic field (OMF). In this latter case an induced oscillating electric field also appears. SMFs can visibly affect water. Thus, water droplets can levitate in air when they are in a magnetic field (MF) of 10 T or higher [28, 29]. Weaker SMFs of the order of one third of a tesla can still produce a 0.25- μ m depression in the water surface [30]. At these conditions, some water properties such as the viscosity, the surface tension force, or the refractive index, among others, seem to be affected [31-35] but the experimental data published in the literature generally have low reproducibility and little consistency. The mechanisms explaining the effects of SMFs on water properties are not clear [36]. Most theories conclude that SMFs affect the hydrogen-bond networks, but there is no agreement on how they are affected. Some authors claim that SMFs cause the weakening of hydrogen bonds [37, 38] whereas other researchers consider that SMFs enhance the bonding among water molecules [39]. Rearrangements in hydrogen bonding can substantially affect the interactions between water molecules and, consequently, kinetics of some processes such as freezing or vaporization, for example, could be significantly affected [35, 40].

1.4.2.1. State of the art

In recent years, the ability of SMF and/or OMF to improve food freezing has been dealt in several patents, see Appendix 0, and some of them have been developed and commercially implemented, see in particular [41-43]. Besides it has been also investigated by many research groups [44-47], see Appendix 0. It is generally assumed that the application of magnetic fields during freezing inhibits ice nucleation and allows the product to remain largely supercooled, that is, unfrozen at a temperature well below its freezing point. It is well-known that the

greater the extent of supercooling attained before nucleation, the larger the amount of ice instantaneously formed when nucleation occurs and, consequently, the shorter the phase transition time and the smaller the size of the ice crystals [48]. Small ice crystals reduce cellular damage and quality losses in frozen food [48, 49]. Therefore, if the application of SMFs and/or OMFs during freezing were effective in increasing supercooling, it could be an interesting strategy for improving food freezing.

The generally used MF conditions in food freezing are summarized in Figure 1-2:

Figure 1-2: Static and oscillating magnetic field strengths and frequencies employed in scientific works on magnetic freezing of foods. The works which showed positive results are encircled by green lines. References by colors: red [46]; purple [50, 51]; yellow [45, 52]; dark blue [53]; green [51]; light blue [54]; maroon [55]

Since the earlier 2000s, some companies have patented and marketed electromagnetic freezers (see Appendix 0) that apply different types of magnetic fields to theoretically improve the quality of frozen food. Thus, ABI Co., Ltd. (Chiba, Japan) sells 'CAS (Cells Alive System) freezers' that combine static and oscillating magnetic fields, while Ryoho Freeze Systems Co., Ltd. (Nara, Japan) commercializes 'Proton freezers' that use static magnetic fields and electromagnetic waves [56, 57]. According to commercial advertisements, both CAS and Proton freezers are able to generate tiny ice crystals throughout the frozen product, prevent cell destruction, and preserve the quality of the fresh product intact after thawing [56, 58]. Since that date, many magnetic freezers have been sold to food processors, restaurants, hotels, hospitals, and research centers in and outside Japan [45, 59]. Magnetic freezing has awakened much interest on the Internet and there exist innumerable websites with amazing videos on CAS and Proton freezers [60-65]. These videos usually show delicate products such as fruits, vegetables, seafood and even flowers, magnetically frozen, that retain the fresh appearance and the original taste, flavor, and texture after thawing. If MFs were responsible for all these advantages, magnetic freezing would represent a significant advance in freezing technology, not only for food preservation but also for cryopreservation of biological

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specimens such as cells, tissues, and organs. Surprisingly, scientific studies on the effect of MFs on freezing of water and biological products are very scarce and, to date, clear evidences of the promised effects have not yet been found [66, 67]. The previous reviews are in agreement with [68] where an analysis of the effect of static and oscillating EM fields, focused on their effect on the ice crystal size and their potential repercussion in the quality of frozen food, is carried out. Besides, results published in the literature are often apparently contradictory probably because some factors that play a role in magnetic freezing are not considered. Finally, it is important to note that the existing scientific papers have been written by experts in quite different disciplines (physics, food science, cryobiology, for example) and, therefore, sometimes they are focused on particular aspects of the area of study while important aspects of the process are neglected.

According to the patents, see Appendix 0, oscillating magnetic fields (OMFs) applied during freezing enhance water supercooling, inhibit ice crystallization, and accelerate heat transfer [41-43]. When freezing occurs, either by lowering the temperature well below the freezing point or by ceasing the OMFs, small ice crystals are supposed to be formed throughout the whole volume of the product. In this way, damage produced in frozen foods is hypothetically reduced and, therefore, manufacturers claim that foods frozen in electromagnetic freezers maintain the quality of the fresh product unaltered. However, the extremely low strength of the OMFs commonly applied in commercial freezers (< 2 mT) casts doubt on the effects that these weak OMFs can have on a substance with a low magnetic susceptibility such as water. Nevertheless, the mechanisms adduced in the patents to explain the effects of OMFs on water molecules are vague and they have not been scientifically proved [36].

The MF conditions applied in patents of magnetic freezing are summarized in:

Figure 1-3: Static and oscillating magnetic field strengths and frequencies employed in patents on magnetic freezing. References by colors: red [69]; purple [41]; yellow [70]; blue [71]; dark green [71]; turquoise [42]; olive [72]; maroon [73]

On the other hand, SMFs are also supposed to impact on some water properties that govern freezing kinetics such as the freezing point, the internal energy, or the specific heat of water [33, 38, 74] and, therefore, some effects of SMFs and in principle also of OMFs on freezing times should also be expected.

However, the experimental data reported in the literature do not give clear evidence of the effects of SMFs on either water and model systems supercooling or freezing kinetics, see Appendix 0. Thus, when freezing water under SMFs, [75] observed that supercooling increased with the SMF intensity (up to 5.95 mT); [76] noted the opposite, that is, supercooling decreased when increasing the SMF strength (71-505 mT) whereas [77] did not detect any SMF effect (0-43.5 mT) on either supercooling or the phase transition time. Nevertheless, when freezing 5-mL 0.9% NaCl samples, these latter authors found that SMFs enhanced supercooling and reduced the phase transition time by about 55%. They suggested that an enhanced mobility of Na^+ and Cl^- ions under SMFs could be responsible for a larger thermal diffusion coefficient and, consequently, for a shorter phase transition time. However, their results differ from those reported by [78] who also froze 2-mL 0.9% NaCl samples between two neodymium magnets. Depending on the magnets arrangement, the phase transition time increased by 17% (480 mT, unlike magnet poles faced each other: attractive position) or reduced by 32% (50 mT, like magnet poles faced each other: repulsive position) compared with the control. Therefore, the authors concluded that the direction of the field forces might play a relevant role in the freezing process.

The MF conditions applied in the literature on magnetic freezing of water and model systems are shown below:

Figure 1-4: Static and oscillating magnetic field strengths and frequencies employed in scientific works on magnetic freezing of water and model systems. The works which showed positive results are encircled by green lines. References by colors: red [79]; purple [75]; yellow [76]; blue [78]; dark green [80]; turquoise [73, 81]; olive

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[51]; maroon [82]; black [83]; pink [84]; light brown [77]

When dealing with freezing of biological materials, it is appreciated that on some occasions authors of scientific publications have had to rectify erroneous or incomplete previously reported MF data, as [85] who recognized having made a mistake when specifying the OMF strength value supplied by CAS equipment in three previous papers on freezing of biological material.

The MF conditions applied in the literature on magnetic freezing of biological materials are shown below:

Figure 1-5: Static and oscillating magnetic field strengths and frequencies employed in scientific works on magnetic freezing of biological materials. The works which showed positive results are encircled by green lines. References by colors: red [86-88]; purple [89-92]; yellow [81]; blue [82]

According to some authors, the application of low temperatures and any magnetic field causes a reorientation of the electronic spin and nuclear spin of the water molecules of the object to be frozen [93]. Because of this, small crystals can be produced and in a higher number than with a conventional freezing system [66].

The application of the magnetic field induces forces of magnetic vibration in the water molecules, which prevents the early formation of ice crystals and their growth even at very low temperatures. Thus, water crystallization of the food can be delayed, and a high degree of supercooling can be achieved [18]. Besides, by controlling crystallization by the magnetic field, freezing occurs rapidly and uniformly throughout the product, rather than from the surface to the interior of the food as in traditional methods [94]. Depending on the type of application, the magnetic field may cease during the supercooling stage, inducing freezing of the product,

or it may be maintained throughout the entire process for a better control of the crystallization process [93].

1.4.2.2. Electromagnetism and EM freezing

Matter is constituted by electric charges. They appear mostly in elemental atoms or molecules electrically neutral, i.e. having an equal number of positive and negative charges, although they can gain or lose electrons, giving rise to anions or cations, respectively. Two point electric charges exert forces on each other, whose value is given by Coulomb's law. Those forces will be attractive if charges have different sign, or repulsive if they have equal sign. When in addition charges are in motion, currents appear and these in turn originate attractive or repulsive forces, expressed by Ampère's force law. However when a distribution of charges or currents is present, it is easier to consider their joint effect at any point of space by means of the electric field $\vec{E}$ and magnetic field $\vec{B}$, respectively. Thus the formula of Lorentz force provides the total action of both $\vec{E}$ and $\vec{B}$ on an electric charge, which could be moving at a certain velocity. The relationships describing the physical behavior of electromagnetic field are known as Maxwell's equations:

$$\nabla \cdot \vec{E} = \frac{\rho}{\epsilon_0} \quad (\text{Eq. 1})$$

$$\nabla \cdot \vec{B} = 0 \quad (\text{Eq. 2})$$

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (\text{Eq. 3})$$

$$\nabla \times \vec{B} = \mu_0 \vec{J} + \mu_0 \epsilon_0 \frac{\partial \vec{E}}{\partial t} \quad (\text{Eq. 4})$$

where ρ is the charge density (C/m^3), $\vec{J}$ is the current density (A/m^2), ϵ_0 is the permittivity of the vacuum ($8.854 \cdot 10^{-12} \text{ F} \cdot \text{m}^{-1}$) and μ_0 is the permeability of the vacuum ($4\pi \cdot 10^{-7} \text{ H} \cdot \text{m}^{-1}$). For a given material, its absolute permittivity, ϵ , and permeability, μ , are related to those of the vacuum by means of its relative permittivity, ϵ_r , and relative permeability, μ_r , through equations:

$$\epsilon = \epsilon_0 \cdot \epsilon_r \quad (\text{Eq. 5})$$

$$\mu = \mu_0 \cdot \mu_r \quad (\text{Eq. 6})$$

When considering the application of an EM field in food processing, it is convenient to review the different nature of the field involved in it. The first step is to know about the state of that field: static or variable field. It would depend on whether their strengths and directions remain constant or not with time. In the first case electric or magnetic fields may appear independently. However, the application of a time-varying electric or magnetic field gives rise

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to the corresponding induced magnetic or electric field, respectively, in accordance with what is formulated in Ampère-Maxwell law or in Faraday's law, two of the Maxwell's equations. In the case of variable EM fields, the ratio of electric field E to magnetic field H modules is referred to as the wave inductance. The region of far field is defined as the one placed further than a distance from the field source of around $\lambda/2\pi$, where λ is the wavelength. In this far field region the wave inductance E/H corresponds to the characteristic impedance of the medium, which is approximately $377 \, \Omega$ for vacuum. Up to that distance, i.e. in the near field region, there is normally one dominant field depending on the type of source. Then, if the source generates an alternating electric field, $E/H > 377 \, \Omega$, whereas if it is an alternating magnetic field source, $E/H < 377 \, \Omega$. In the first case, E attenuates at a rate of $1/r^3$ and H attenuates at a rate of $1/r^2$. Analogously, these attenuation rates are exchanged for both fields in the second case [95]. Therefore for a low frequency field, samples subjected to this would be in the near field region and there will be either a magnetic or an electric field (which must be considered separately), whereas for a sufficiently high frequency, in the far field region there will be an EM wave formed by an electric and a magnetic field perpendicular to each other, and propagating perpendicularly to both fields, as shown in Figure 1-6.

Figure 1-6: Schematic representation of an electromagnetic wave

Frequently EM field is present in food studies aside from freezing. Very often it is used as an analytical tool to look inside products for the effects produced by processing but having no interaction with the material.

In that sense, among the different possibilities offered by the EM spectrum, Nuclear Magnetic Resonance (NMR) is a non-invasive technique frequently used as an analytical tool to know about what happens inside a food. Is it based on applying to the sample a strong static field $\vec{B}$ combined with an EM wave (RF pulse). Isotopes of elements with a net nonzero nuclear spin, present, from a classical mechanics point of view, a rotation which gives rise to an angular momentum $\vec{L}$, proportional to the spin magnetic moment $\vec{\mu}$:

$$\vec{\mu} = \gamma \vec{L} \quad (\text{Eq. 7})$$

with γ being the gyromagnetic ratio, constant for each particular nucleus. Given the azimuthal quantum number l , there are $2l+1$ different values that can have the magnetic quantum number m_l . In particular, for hydrogen ^1H nucleus $l = 1/2$, and those nuclei have two possible values for m_l : $\pm 1/2$. In the absence of an external magnetic field, both levels are degenerated, having the same energy, but when a SMF $\vec{B}$ is present, the magnetic moments will show a precession movement around $\vec{B}$ at an angular velocity f_L called Larmor frequency, as shown in Figure 1-7, verifying:

$$f_L = \frac{\gamma}{2\pi} |\vec{B}| \quad (\text{Eq. 8})$$

Figure 1-7: Precession movement of nuclear angular momentum around uniform magnetic field

Those magnetic moments have two possible orientations: one of less energy (parallel to $\vec{B}$), with magnetic quantum number $m_l = +1/2$ (state α); and other of more energy (antiparallel to $\vec{B}$), with $m_l = -1/2$ (state β), as depicted in Figure 1-8, increasing the proportion of these latter at higher temperatures according to a Boltzmann probability distribution.

Figure 1-8: Energy levels of a nucleus with azimuthal quantum number $l = 1/2$ with or without SMF applied

The energy of one state, E , is given by:

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$$E = -\frac{\gamma h}{2\pi} \cdot m_l \cdot |\vec{B}| \quad (\text{Eq. 9})$$

where h is the Planck constant. On applying an external EM wave of a determined frequency, nuclei go into resonance, being able to pass from the state α to the state β , through an absorption of energy:

$$\Delta E = \frac{\gamma h}{2\pi} |\vec{B}| \quad (\text{Eq. 10})$$

being able to detect the radiation emitted when the excited nuclei return to the lowest energy state [96-98]. This is besides the basis of Magnetic Resonance Imaging (MRI), which needs also a gradient in the magnetic field along a given direction, giving rise to different resonance frequencies for different positions. By varying the orthogonal direction of the field $\vec{B}$ during the decay of the excited state, a two-dimensional picture can be obtained. When varying $\vec{B}$ as a function of time during the decay, three-dimensional MRI can be produced.

1.4.2.3. The water molecule

Here it is also necessary to review the action of MF on water as it is the main component of foods.

Water is a small molecule composed of two hydrogen atoms covalently bonded to one atom of oxygen. Water bonding and geometry can be roughly explained according to the valence bond theory, the hybridization of atomic orbitals, and the Valence-Shell Electron-Pair Repulsion (VSEPR) model. Figure 1-9a shows the electron configuration of the constituent atoms of the water molecule. Hydrogen atom has one electron ($Z = 1$) while oxygen has 8 electrons ($Z = 8$). Two of them are core electrons located in the first s atomic orbital, immediately adjacent to the nucleus, while the other six are valence electrons. The Lewis formula for water (Figure 1-9b) shows that oxygen, the central atom of water, is surrounded by four separate regions of high electron density: two of them correspond to two lone pairs of electrons and the other two correspond to two σ -bonding pairs of electrons. For this configuration, the VSEPR model predicts a tetrahedral distribution of electron clouds with an ideal bond angle of 109.5° that results in a V-shaped water molecule. This geometry can be explained by sp^3 hybrid orbitals (Figure 1-9c). Thus, $2s$ and $2p$ orbitals in oxygen would hybridize to form four sp^3 orbitals oriented at a bond angle of 109.5° . The valence electrons in oxygen would fill two of these sp^3 hybrid orbitals (two lone pairs of electrons) while each of the other two sp^3 hybrid orbitals would be occupied with one unpaired electron. Bonding of water would occur through the overlap of these latter two sp^3 hybrid orbitals on oxygen with $1s$ orbitals on the two hydrogen atoms. As bonding pairs of electrons experience less repulsive force than lone pairs, the perfectly symmetrical shape ideally adopted by the electron pairs would be distorted. Thus, the water geometry shown in Figure 1-9d, with an angle of 104.5° between the hydrogen atoms, could be explained.

To understand water properties, it is also important to note that the oxygen in the water molecule attracts electrons more strongly than hydrogen due to its large electronegativity. Therefore, shared electrons in the covalent bond will be closer to oxygen and, thus, its region

in the water molecule has a slightly negative charge while each hydrogen atom has a slightly positive charge. This fact, joined to its V-shape geometry, makes water, therefore, a polar molecule. This permanent dipole behavior of the water molecules allows them to be oriented toward the direction of an external electric field. Another effect of that charge displacement has to do with the electrostatic attraction between the partial positive charge near the hydrogen atoms and the partial negative charge near the oxygen, which makes water molecules interact with each other and form intermolecular hydrogen bonds. Hydrogen bonds in water are much weaker than covalent bonds (about $23 \text{ kJ} \cdot \text{mol}^{-1}$ compared to the O–H covalent bond strength of $492 \text{ kJ} \cdot \text{mol}^{-1}$), but they are the strongest kind of dipole-dipole interaction. Thus, these H-bonding forces allow a strong interaction between water molecules and this intermolecular interaction is responsible for most of the anomalous properties of water: volume expansion on freezing, high freezing point, high specific and latent heats, high surface tension, among others. Each water molecule can form up to four hydrogen bonds and, thus, the structure of liquid water is usually represented either as a continuous three-dimensional network of hydrogen bonds or as a mixture of clusters of molecules with different degrees of hydrogen bonding in an equilibrium. Water clusters can have different number of molecules (dimers, trimers, tetramers, and so on up to hundreds of molecules) and adopt different structures: linear, rings, prisms, or cages, among others [99-101]. However, rotation and other thermal motions in water molecules cause individual hydrogen bonds to break and re-form on a 10^{-12} - 10^{-9} s time scale. Therefore, the lifetime of any specific structure in liquid water is continuously changing.

Figure 1-9: a) Electron configuration of the constituent atoms of the water molecule; b) Lewis formula for water; c) sp³ hybridization and water bonding; d) water geometry.

Concerning the potential effects of EM freezing on water, it must be considered that hydrogen bonds are favored by low temperature until frozen water is obtained. The crystal structure of this frozen water depends on its hydrogen-bonded lattice. It means that weakening in some way those hydrogen bonds would favor the objective of obtaining a great supercooling [102] as pursued with EM freezing. Looking at the magnetic nature of water molecule, it can also be

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considered that its electrons have orbital and spin movements producing magnetic moments. The orbital movements are related to diamagnetism whereas the spin motions give rise to a paramagnetic behavior [103]. Water has all the electrons paired so, by the Pauli exclusion principle, the spins of each pair of electrons are opposite and as a result there is no paramagnetic action, since its resultant magnetic moment is zero in the absence of an external MF. This fact confers a diamagnetic character to water molecule. By using a classical simplification, without entering into a more detailed quantum analysis, orbital motion of electrons would produce magnetic moments randomly oriented and, consequently, there would not be any net magnetic moment. Accordingly the magnetic susceptibility of water is very small and negative ($\chi_m = -9.046 \cdot 10^{-6}$, at 0 °C and at a pressure of 1 atm) [104, 105]. This circumstance implies that when an external MF, $\vec{H}$, is applied to water, the individual magnetic moments of this diamagnetic material will tend to align against the applied $\vec{H}$, as depicted in Figure 1-10, generating a small induced magnetic induction $\vec{B}$ opposed to that field (as stated in Lenz's law) and the final outcome would be a resulting field strength in the water sample slightly minor than in its surrounding air and thus water tends to repel very slightly the applied external MF. This small counteraction barely cause macroscopic effect with low MFs and therefore, only when using very high magnetic field intensities, i.e., 10 T or higher, levitation of water has been observed [28].

Figure 1-10: Diamagnetic behavior of water in the absence (left) and in the presence of an external magnetic field

1.4.2.4. Effects of magnetic fields on water

First of all, it is important to note that a real understanding of the magnetic properties of matter cannot be achieved by classic physics, but only by quantum electrodynamics. However, this is out of the scope of this thesis and, therefore, in this review, very simplified concepts are used to explain water magnetization.

As outlined before, the magnetic properties of a substance arise from the orbital motion and spin of electrons in the atoms. Nuclei also possess spin, but electron-field interactions are thousands of times stronger than nuclear ones. Therefore, electrons, not nuclei, primarily determine magnetic susceptibility. The orbital motion of electrons around the nucleus creates tiny atomic current loops that induce a magnetic moment along the axis of rotation. In the

same way, the spinning of the electrons also produces a magnetic moment. The net magnetic moment of an atom is the vector sum of both orbital and spin moments of all the electrons in the atom.

In water, all the orbitals are fully occupied by pairs of electrons (Figure 1-9c). Paired electrons orbit in opposite directions and, therefore, orbital moments are cancelled. The same occurs with the spin moments of paired electrons. Thus, water has no net magnetic moment in the absence of an externally imposed MF. When an external MF is applied, the orbital motion of electrons is altered in such a way that the induced MFs oppose to the external field. This may be viewed as an atomic version of the Lenz's law, which is a direct consequence of the energy conservation law. Thus, the effect is to 'repel' the external field and water is, therefore, a diamagnetic substance.

The magnetic force exerted on a substance is proportional to the square of the strength of the external magnetic field and the magnetic susceptibility. Magnetic susceptibility of water is rather low ($\chi_m = -9.046 \cdot 10^{-6}$) and, therefore, weak MFs will have little effect on water while strong MFs can exert considerable force. The effects of strong MFs (≥ 10 T) can be macroscopically visualized by levitating water droplets in air, that is the magneto-Archimedes levitation [28, 29] or by visibly deforming the water surface [106]. Weaker MFs also produce effects on water, although not so evident. For example, magnetic fields of the order of one third of a tesla can still create a microscopic depression of about 25 μm in the water surface [30]. Moreover, some properties such as the surface tension force, the viscosity, the refractive index, the electric conductivity, and the enthalpy of vaporization, among others, seem to be affected after exposing water to magnetic fields, even at intensities as low as 1 mT [31, 32, 80, 107-111]. In recent years, analyses of magnetized and non-magnetized water by spectroscopic techniques confirm that MF exposition produces changes (shifts of some peaks and appearance of new bands) in infrared, Raman, visible, ultraviolet, and X-ray spectra [107, 108, 112]. Some authors attribute these modifications to changes in water structure by displacement and polarization of molecules and atoms and modification of hydrogen bonding [107, 108, 112, 113] while others identify in the spectra of magnetized water some similarities with the spectra of ozone and hydrogen peroxide [114]. Thus, [114] suggest that Lorentz forces can produce small currents in water, producing the same effect as electrolysis.

The magnitude of the changes observed in water after MF exposition depends on the magnetic field strength and frequency, the exposition time, and the temperature, but no linear relationship between these factors has been found. A saturation effect is also observed, that is, after a given exposition time, the effects of the magnetic field reach a maximum. Moreover, the MF effects do not disappear immediately, but maintain for a time, that is, the memory effect of magnetized water [80, 107, 108].

However, the results reported in the literature have low reproducibility and little consistence. For example, Pang and Deng [107] observed that the exposition of water to a 440 mT SMF for 30 min significantly decreased the surface tension force and viscosity. By contrast, Toledo, et al. [109] reported an increase in the surface tension and the viscosity of water after exposition to a 45-75 mT magnetic field for 3 hours while [31] detected a decrease in the surface tension and an increase in the viscosity of purified water circulated at a constant flow rate in a 500 mT

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magnetic field. The reproducibility of experiments with magnetized water is hampered by many factors related to the sample, the magnetic field applied, and the measurements performed. Some factors related to the sample, such as magnetic impurities and quantity of dissolved oxygen, are difficult to control [109]. The reproducibility of the MFs applied is not trivial and special care must be taken to guarantee that the MF can penetrate over the whole water sample [115]. Moreover, it is important to note that when time-varying MFs are applied, EFs are induced. EFs have been proved to efficiently reorient water molecules due to the intrinsic electric dipole moment that water has [100]. Therefore, discerning the effects of time-varying MFs and EFs on water is not simple. On the other hand, the MF effects observed in water are usually very weak and effective methods and sensitive instruments must be employed to detect them. Moreover, these effects should be measured during magnetic field application [32] or, at least, immediately after it because, as previously mentioned, they are not permanent, but they fade away after some time [107, 108, 115]. Furthermore, it is important to note that impurities can be dissolved or suspended from the sample containers or from the measurement instruments and they can affect the results [116, 117]. Therefore, caution is needed in the interpretation of the phenomena observed.

The precise mechanisms that produce these effects in water exposed to MFs are not clear, although many hypotheses have been proposed [37, 101, 114, 118, 119]. For example, taking into account the polar nature of the water molecule, Wang, et al. [37] assumed that the thermal motion of the partially charged atoms of water under the MF gives rise to Lorentz forces. The direction of these forces on the positive charge center of the water molecule is opposite to that on the negative charge center and, therefore, both centers will be relocated, the distance between them will become larger and these changes will weaken the hydrogen bonds. Based on the existence of linear and ring hydrogen bonded chains of molecules in water, [101, 115] hypothesized that closed hydrogen-bonded chains become 'ring electric-current' elements when submitted to a magnetic field due to the proton transfer in them under the action of Lorentz forces. The magnetic interactions of these 'ring electric-current' elements with each other or with the externally applied magnetic field would result in the reorientation and formation/breaking of hydrogen bonds. Consequently, the distribution of water molecules would be modified and, therefore, also the physical and chemical properties of the magnetized water. By contrast, experiments by Colic and Morse [114] and by [119, 120] suggest that the gas bubble/water interface is the primary target of the MF action because, when water is degassed, no MF effects are observed. According to these authors, MF exposition leads to the destabilization of the air nanobubbles, naturally present in non-degassed water, by disturbing the ionic balance between the negative ions adsorbed on the bubbles and the shell of counter ions. These changes at the gas/water interface can modify the water cluster size and the reactivity of bulk and interfacial water.

Computational techniques, such as Monte Carlo and Molecular Dynamics (MD) simulations, have also been employed to elucidate the effects of magnetic fields on water systems at the molecular level [38, 39, 109]. These studies show that hydrogen bonds can be affected by magnetic fields and, consequently, also the interactions between water molecules [38, 39]. Therefore, new clusters arrangements can be formed that, obviously, can affect water properties. Again, the conclusions by different authors are, in some way, divergent. For example, Zhou, et al. [38], using Monte Carlo computer simulation, found that 100-200 mT

MFs increased the mean distance between water molecules while field strengths smaller than 50 mT did not produce appreciable effects. Thus, the external field can cause a weakening of the hydrogen bonds and the diminishing of the hydrogen bond average number between water molecules. However, using MD simulation, Chang and Weng [39] found that the number of hydrogen bonds increased by approximately 0.34% when the magnetic field strength increased from 1 to 10 T. Thus, according to these authors, magnetic fields enhance the bonding between water molecules and stabilize the structure of liquid water. At this point, it is interesting to note that hydrogen bonds can be inter- and intra-cluster. In this sense, the results obtained by Toledo, et al. [109] suggest that MFs weakens the intra-cluster hydrogen bonds, breaking larger water clusters, and forming smaller clusters with stronger inter-cluster hydrogen bonds.

Despite the low reproducibility of the experimental data and the controversial theories explaining water behavior in a MF, all the studies conclude that MFs affect the hydrogen bond networks. Rearrangements in hydrogen bonding can substantially impact on some water properties that govern freezing kinetics such as the freezing point, the specific heat capacity, or the thermal conductivity. However, data about the effect of MFs on these water properties are especially scarce. Inaba, et al. [74] measured the MF effect on the freezing point of water by using a high resolution and supersensitive differential scanning calorimeter working in a magnetic bore. They found that exposition to SMFs increased the freezing temperature of water and the temperature shift was proportional to the square of the MF intensity. At 6 T, the freezing point increased by $5.6 \cdot 10^{-3}$ °C and they concluded that MFs strengthen hydrogen bonding and make the solid phase more stable than the liquid state. Moreover, Monte Carlo simulations by Zhou, et al. [38] predicted significant changes in the internal energy and specific heat when water is exposed to 100 mT MFs and larger. These predictions were later confirmed by Pang, et al. [111] who observed a decrease in the specific heat of water when exposed to 440 mT SMFs for 30 min. Some MD simulations of ice growth from water exposed to magnetic fields have been recently published [121, 122]. Thus, Zhang, et al. [121] investigated freezing of confined water in a 10 T SMF. According to the authors, confinement induced a bilayer crystalline ice which resembled none of the structures of existing ice polymorphs while MF exposition significantly increased the freezing temperature of the confined water. Thus, at 10 T, an anomalously high freezing temperature of 67 °C was found. Hu, et al. [122] studied the microscopic mechanism for ice growth from supercooled water when external electric (0-10⁹ V/m) and magnetic (0-10 T) fields were applied simultaneously. They found that ice growth on the primary prismatic plane could be accelerated when fairly low electric (10⁶ V/m) and magnetic (10 mT) fields were applied. By contrast, growth on the basal plane was hardly affected unless the fields increased up to 10⁹ V/m and 10 T. Moreover, when studying electric and magnetic fields separately, they found that EFs could play a significant role in the hydrogen-bonding structures of liquid water, but the effect of MFs, even at 10 T, was only marginal.

1.4.3. The ice produced by a process and its resulting thermal conductivity

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In spite of the controversial theories explaining water behavior in a MF (see Section 1.4.2.4) all the studies conclude that MFs affect the hydrogen bond networks. Rearrangements in hydrogen bonding can substantially impact on some water properties that govern freezing kinetics such as the freezing point, the specific heat capacity, or the thermal conductivity. Besides, thermal conductivity, k , is crucial in food engineering in order to calculate heat transfer in heating/cooling processes. Given the fact that water is commonly accepted as the major component in food products, its thermal conductivity is extensively used. Even so, although thermal conductivity of liquid water is a well-known parameter, high discrepancies can be found in the literature regarding the corresponding value of ice, as recognized by [123]. The discrepancies in the thermal conductivity data might be due to differences in the i) freezing procedures, ii) complex measurement protocols, and iii) concentrations of impurities, such as salts, trace elements or dissolved gas, in the water before freezing. All of these factors might affect the thermal properties of the resulting ice [124]. The particular procedure used to freeze water in food science is important because of the previously described relevant freezing processes currently available.

1.4.4. Electromagnetic field modelling in food

EM field is frequently present in many food studies. Very often it is used as an analytical tool to look inside products for the effects produced by processing but having no interaction with the material. The quality of the provided information often allows it to be used to generate mathematical models. Besides, EM field by itself or in combination with some other parameter is used as an interactive force able to act during food processing. In order to optimize those processes, this interaction is also frequently modeled.

In that regard, among the possibilities given by the EM spectrum, Nuclear Magnetic Resonance (NMR) is a non-invasive technique frequently used as an analytical tool to know about what happens inside a food (as stated in Section 1.4.2.2). It is based on applying to the sample a strong static field $\vec{B}$ combined with an EM wave (RF pulse). This is besides the basis of MRI. A general characteristic of works that use NMR or MRI in food research as an analytical tool is that they do not solve the mathematical equations involved in the MF distribution in the product. Very often NMR and MRI are used as powerful techniques for monitoring the composition and structural changes in foods after or during processing and frequently allowing researchers to perform modeling works, making a profit from those results. Thus in [125] the NMR technique was used to determine the amount of each different water state (ice, freezable water and bound or unfreezable water) in frozen or unfrozen food gels. This information was used by the authors to proceed with the modeling of the heat capacity and the thermal conductivity of the same gels. [126] carried out a review about the studies performed by using NMR in the characterization of droplet sizes of emulsions, analyzing its ability to be used as a bench-top 'routine' measurement of complex industrial emulsions and to provide unique insight into emulsion science. Also [127] dealt with the characterization of droplet sizing in food emulsions, with emerging novel NMR measurement and data modeling approaches standing out. In a similar way [128] reviewed applications of low field NMR and

MRI in food colloids dealing with the relaxation of solid and liquid fat, ice, biopolymer and water.[129] were concerned with water vapor transport through food powder packaging defects, analyzing it by using modeling, gravimetric measurement and MRI, concluding that this last technique shows how the absorption through a pore into the powder is carried out. The modeling of moisture in rice during drying, mapped with MRI taking into consideration the shrinkage during drying was carried out by [130]. From it a diffusive model obtained from the NMR data collected during drying is also developed. A set of MRIs were acquired from a series of potatoes in [131]. By performing a sensory image analysis, reliable and informative data about the unique effects of varieties, storage time and dry matter content on the MR-images of potatoes were collected. Those data were compared to the ones obtained by predictive modeling of sensory image description from computer-assisted image analysis.

But modeling studies referred to EM fields applied to food processing have not limited themselves to cases of NMR and MRI, but also to situations where EMF fields act as a driving force. The majority of works modeling the performance of magnetic fields acting as a driving force in food processing were carried out with microwaves. When referring to “microwave” action it means that an EM radiation in the frequency range of 300 MHz–300 GHz is used [132]. Due to the complexity of the equations describing an EM field distribution, Finite Element Method (FEM) software has been generally used. Authors in [133] use analytical solutions and commercial software (TWOPEPEP, ANSYS) to model heat and mass transfer in food materials during microwave heating. By using a fluoroptic temperature measurement system and a near infrared technique, temperature and moisture distributions are determined in order to check the validity of the performed modeling. The coupling between EM field and heat transfer through changes in dielectric properties during heating is carried out in [134], where also experimentally measured temperature profiles are compared with the numerical predictions. Dealing with thawing, in [135] and considering that the microwave power absorbed by materials is given by Lambert’s law, a mathematical model is developed by solving the involved unsteady-state heat and mass transfer differential equations by finite difference methods and validating those results with the experimental ones. By using the Maxwell’s equations to describe the interaction between EM radiation and food, and with the employment of a FEM software (COMSOL Multiphysics), a simulation model is obtained in [136] for heating of foods in microwave ovens taking into account different food heating strategies. Microwave drying is reviewed in [137], showing the development of computer simulation techniques to predict temperature and moisture history and distribution in the product to be dried, stating that the heat and mass transport in microwave drying can be simulated with both simplified and comprehensive mathematical models and that more investigations into simulation of microwave drying processes, will stimulate the adoption of this relatively new drying method in the food industry. In [138] modeling and model validation of a domestic microwave oven is performed by solving coupled Maxwell’s EM equations and Fourier equations to obtain optimal design parameters. A similar study was carried out by [139] to model a combined convective-microwave assisted drying system. It is always desirable to know the connection among the physical magnitudes playing a role in different processes. In this sense two commercial FEM software packages (FEMAP & Photo-Series) are applied in [140] to simulate the coupling of the EM field and heat transfer phenomena in a microwave oven with a complex configuration. Also a complex case relating to the simulation of

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microwave heating of frozen mashed potato is covered in [141], where a rotating turntable is used for this purpose. To simulate the process, the authors use a FEM model and take advantage of COMSOL software taking into account Maxwell's EM heating, energy conservation, Darcy's velocity, mass conservations of water and gas, and phase change of melting and evaporation of water. COMSOL is also used in [142] to solve the FEM model about the heating of fluid foods in a specially designed continuous-flow microwave heating unit. The results of this model are compared with the experimental temperature distribution measured by thermocouples.

Apart from microwave, other driving EM fields are modeled in food processes. Regarding the magnetocaloric effect, the work carried out by [143] reports on the modeling of the MF distribution generated by magnets and its interaction with a magnetocaloric material. In [144] a mathematical modeling is developed to simulate an ohmic heating in a static heater, remarking that to avoid an inaccurate verification of results by measuring only a certain number of selected points of the device, it is worth mentioning the interest of having a modeling tool to provide important data, such as choosing different working conditions for the process design.

1.4.5. Modeling freezing processes based on heat extraction rate.

It is generally admitted that performing modeling studies of food freezing processes allows a comprehensive insight into the effect of the different variables involved in them. In the recent review [145] the interest of food researchers and engineers to investigate on parameters as freezing time and refrigeration requirements, to know about changes in food products as well as desirable temperature reduction is pointed out. When the problem is treated with mathematical rigor, its complexity is enormous. This is due to several factors mainly due the non-linear behavior of the involved thermophysical properties during the liquid-solid phase change process and because this is not a pure heat transfer process but a heat and mass transfer process. This fact jeopardizes to find analytical solutions. Approaches to analytical solutions have been frequently used to predict freezing time based on Plank equation for simple geometries obtaining good approaches for practical use. However numerical methods based on FEM are the generally used when irregular geometries, thermophysical properties depending on temperature or any other more realistic approach is considered. This is stated by [146] when analyzing freezing of foods models for predictions in freezing processes including heat and mass transfer analysis.

1.4.6. Modeling nucleation-controlling freezing processes

As it has been established, this mathematical tool is more important in the case of the innovative freezing processes which try to control ice crystal nucleation because apart from the above depicted, some other physical parameter, playing a singular role, is also implicated

in the freezing process. In this regard, [147] carried out numerical simulations of Pressure Shift Freezing processes in a tubular reactor for semi-continuous operation, using tylose as a model food. By employing two different FEM software packages (Cosmos and FEMLAB®) and depending on the sample velocity and initial temperature, they predict the vessel length needed to completely freeze the sample, through a simpler 1D only conductive model and a 2D model which added also convective effects, being interesting for design purposes. Also for High Pressure Shift Freezing processes, [148] developed a numerical model of the growth and coarsening of ice crystals, programmed in Fortran language, for estimating both the evolution and distribution of ice crystal sizes with regard to storage time. This model was successfully compared with experimental results extracted from the literature for salty water model foods, for which the model was intended, and for a more complex model food like ice cream. On the other hand, [149] applied ultrasound pulses irradiated during the freezing of potato spheres, analyzing the effect of different duty cycles on freezing time. With the aid of the software OpenFOAM®, they generate a numerical model based on enthalpy, whose results are compared with those obtained by experimental and analytical methods, achieving more accuracy for the numerical results than for the analytical ones. In addition the modeling solution allows knowing profiles of temperature and water fraction, improving the control of the freezing process.

It results evident that modeling and simulation of innovative freezing processes, whose effects are frequently not well defined or known, appear as fundamental tools to get a better understanding of the actual interaction among the involved parameters. The only paper published until now [150] elaborates a model considering the dielectric and thermophysical properties during the freezing of methylcellulose gel subjected to microwaves. These authors solve the Maxwell's equations (see Section 1.4.2.2) in combination with the heat transfer equations, by using a FEM model and COMSOL to obtain the distribution of the electric field, the generated heat and the displacement of hot spots and freezing front inside the sample during freezing. Nevertheless to our knowledge, there is no publication about the distribution of MF vector in the sample and surrounding medium during EM freezing.

1.5.Magnetic field freezing at laboratory scale.

Freezers can be found both at the laboratory and at the commercial level, characterized because the range of the applied MF magnitudes during freezing is not completely fixed. In fact noticeable alternative possibilities could be found when analyzing data given in literature for each application [36, 151, 152].

When looking at the MF effects on freezing processes, it has been reported in [153] the cryoprotective effects of SMFs on human dental pulp stem cells during cryopreservation on frozen cells in a lab-made freezer with 0.4 T and 0.8 T and then stored at -196 °C for 24 h. The authors found that the exposure to those SMFs improves its preservation when the sample is free of Dimethyl Sulfoxide. Reviewing the use of SMF for assisting and accelerating foods freezing processes [27] paid attention to the work performed by [76] in water. The latter observed a decrease of the critical degree of supercooling with the increase of SMF in the

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range of 0–0.5 T. Also that the supercooling could be negligible and the solidification occurred once the MF intensity is higher than 0.5 T. [78] analyzed the effect of using SMF on the freezing time of a 0.9% NaCl solution. Those authors combine low temperature with different MF strengths by using an experimental cell with two different setups for the magnets: parallel or antiparallel polarity. This gives rise to a repulsive ($|\vec{B}| = 50$ mT) or attractive ($|\vec{B}| = 480$ mT) field for acting on a sample situated in an equidistant position with regard to the magnet surfaces. They found that the repulsive arrangement produced the highest reduction of the freezing time of the sample, being in this case 32.1% and 42% lower than the corresponding one to the control (without magnets) and to the attractive arrangement, respectively. Those results would indicate that some different effect could be attributed to the distribution of MF strength and direction in the sample when the magnets are disposed either with equal or with different parallel faced surface polarities, i.e., in a repulsive or in an attractive way, respectively. By using also a 0.9% NaCl solution, deionized water and a 5% ethylene glycol solution, in [77] an experimental study on their freezing under SMF is carried out. In each case the nucleation temperature and the phase transition obtained from the freezing curves when applying or not SMF are analyzed. Applying SMFs ($|\vec{B}| < 50$ mT), they find that nucleation temperature and phase transition time of deionized water are not significantly influenced by MF, but they are for the 0.9% NaCl and the 5% ethylene glycol solutions. Besides, they find the nucleation temperature of 0.9% NaCl with MF is lower than that without MF, while its phase transition time is 55.4% shorter than that without MF. However the nucleation temperature of 5% ethylene glycol with MF is higher than without MF. [54] study the effects of magnetic field on the phase change of carrots. They work both with SMF and with OMF by using 0, 0.46, 0.9, 1.8, 3.6, and 7.2 mT at 50 Hz obtaining that both the SMF and OMF can delay the time of phase change and that the higher the MF intensity the larger the delay of the phase change time and the shorter the phase transition duration. Those authors cannot have an answer to which is better between the SMF and OMF, giving just that in different intervals of field intensity, the effect will be different and suggesting that in practical application, it can be chosen for the actual situation, as appropriate.

1.6. Magnetic field freezing at industrial scale

1.6.1. Patents

The existing patents are summarized in 9 Appendix A.2.

In recent years, many patents have been developed that try to take advantage of MF effects on water properties to improve freezing of foods, ice cubes, feedstuffs, living cells (blood, animal tissues and organs, for example), flowers, chemical and pharmaceutical products, among others [41, 154-160]. All these patents claim that the application of MFs during freezing inhibits water crystallization and allows large supercooling. When freezing occurs, either by lowering temperature well below the freezing point or by ceasing MFs, small ice crystals are formed throughout the whole volume of the product. In this way, damage produced is

supposed to be substantially reduced. However, the extremely low strength of the frequently applied MFs casts doubt on the effects that these weak MFs can have on a substance with a low magnetic susceptibility such as water. Moreover, the mechanisms adduced in the patents to explain the expected improvements are frequently vague, not scientifically proved and, according to Kobayashi and Kirschvink [161], 'do not agree with basic biophysics'.

Most of the inventors state that MFs act by aligning the electronic and nuclear spins of the atoms in the direction of the magnetic field. As stated in Section 1.4.2.4, the magnetic moments of the hydrogen nuclei of water molecules, when a magnetic field is applied, will behave like mini-bar magnets and will align opposing to the external magnetic field. Moreover, the spinning nuclei will precess around the direction of the field. According to the patents, this will enhance thermal vibration of the hydrogen nuclei, supercooling, and heat transfer throughout the product [41, 154, 158, 159, 162]. Moreover, hydrogen bonds of water molecules will be also affected (as seen in Section 1.4.2.4) and some authors consider that the cluster size of free water will tend to decrease [41, 154, 156, 159]. According to Sato and Fujita [156], when water clusters are fragmented in this way, the quality (appearance, flavor, and fragrance) of the products to be frozen is hardly deteriorated and small ice crystals are formed. On the other hand, some authors claim that decreasing the cluster size of free water makes possible to increase the amount of non-freezable bound water and this involves better preservation of the product freshness [41, 154, 159]. They consider that small water clusters are capable to form hydrogen bonds with the polar groups of the tertiary structures of proteins and carbohydrates and attach compactly to them. Thus, MFs would reduce the amount of freezable water and, therefore, the amount of ice crystals. Moreover, MFs would also prevent tertiary structures from being oxidized by promoting a hydration structure on them.

Published patents make use of both SMFs and OMFs (Table 8-1), either separately or combined [41, 154, 158, 159, 162]. Moreover, these fields can be continuous [73, 158] or pulsed [70, 156]. SMFs can be generated by permanent magnets or by electromagnets, although the former is preferred because operating costs are lower. OMFs are generated by coils supplied with alternating current. When SMFs and OMFs are combined, overlapped in the same direction or not, the expected effects on freezing are enhanced and operating costs can be reduced [41, 154, 158, 159]. When used separately, OMFs are preferred to SMFs due to their versatility [156]. Moreover, as previously mentioned, OMFs induce oscillating electric fields (OEFs). These induced OEFs can also enhance the impediments for ice formation. Thus, water molecules, that have an electric dipole, will be orientated in the oscillating direction of the induced electric field. The vibration and friction of water molecules will generate minute heat that also inhibits water crystallization. According to Hirasawa, et al. [158], the combined action of oscillating magnetic and induced electric fields allows reaching large supercooling. Moreover, Owada and Kurita [159] claimed that this electric field will generate free electrons that are gained by the water and oxygen molecules in the freezing device. According to the authors, hydroxyl-radicals are then produced that destroy the cell membrane of microbes and, therefore, reduce the microbial load in the frozen product. Owada and Saito [154] also remarked that free electrons will avoid the oxidation of the product to be frozen.

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The existing patents on magnetic freezing are not especially strict on the selection of the optimal values of the process parameters. Thus, the MF strength and frequency ranges included in the demands are particularly wide (Figure 1-3 and Table 8-1). The MF strength can vary between 0.1 mT and 2 T while the MF frequency ranges between 50 Hz and 10 MHz. However, the conditions tested by the inventors are considerably more limited: MF strengths between 0.1 mT [73] and 800 mT [156] and MF frequencies between 50 Hz [41] and 200 kHz [73]. Most of authors claim that the MF strength and frequency are not particularly restricted, but according to Mihara, et al. [73] and Ino, et al. [162], the optimal values should be selected based on the specific characteristics of the product to be frozen (size, type, impedance). The wave shape (sinusoidal, square, or triangular, for example) in OMFs is not frequently described, but some inventors prefer rectangular waves obtained by superimposing several OMFs [162]. Other parameters of the freezing process such as the cooling rate or the freezer temperature are even less limited and can range between 0.1 and 1 °C/min and between -2 °C and -100 °C, respectively (Table 8-1).

The uniformity of the magnetic fields applied during freezing is a relevant issue. According to Owada [41], if MFs are not uniformly applied, their effects are not evenly exerted on the frozen product and, therefore, the product quality can be affected. Owada [41] found that the uniformity of OMFs increases by disposing a plurality of coils in parallel, in series, or crosswise along the sample holder. Sato and Fujita [156] also designed a number of feasible embodiments that allow a uniform application of the magnetic fields on the product.

In most of the published patents, the preferred embodiments combine permanent magnets and/or electromagnetic coils with other devices to improve the freezing process. Thus, the combination of MFs with EFs [41, 154, 158, 159] and/or other energy imparting devices that irradiate ultrasonic waves, microwaves, far infrared rays, ultraviolet light, α -rays, and negative ions, among others, is frequently described [41, 72, 154, 156, 157, 159, 160, 163].

Oscillating electric fields are, generally, applied to produce the vibration of water dipoles and, in this way, to inhibit crystallization [158]. According to the revised patents, the electric field strength and frequency range between 10-1000 kV and 50 Hz-5 MHz, respectively [41, 154, 159]. Owada [41] claimed that growing of ice crystals can be substantially reduced by applying an electric field of variable frequency in stages. Thus, in the temperature range between -2 °C and -10 °C, a frequency of 250 kHz is particularly effective in decreasing ice crystals size while, in the temperature range between -30 °C and -60 °C, the optimal frequency is 3 MHz. Moreover, as previously mentioned, Owada and Kurita [159] remarked that OEFs also enhance the production of hydroxyl-radicals that have an anti-microbial effect on the product.

The effect of other energy imparting devices is more ambiguous. According to Sato and Fujita [156], the use of negative ions, α -rays, ultrasonic waves, microwaves, far infrared rays, and ultraviolet light allows better fragmentation of water clusters by MFs. Moreover, Owada [41] stated that the addition of ionic air (negative ions) to the cold wind also improves heat transfer. However, evidences of such statements are not provided.

Especially interesting is the combination of SMFs with EM waves to induce NMR in the hydrogen atoms of water molecules and, in this way, achieve large supercooling [157, 160, 163]. Hirasawa, et al. [157] designed a freezing device with a SMF in its inner space and an EM

wave generator. When the product to be frozen is located inside the freezer, the hydrogen nuclei of water molecules exhibit a precessional motion around the direction of the SMF as mentioned. The precession frequency, ω , depends on the MF strength, B , and the gyromagnetic ratio, γ ($\gamma = 42.6 \text{ MHz/T}$ for the hydrogen nucleus) and, according to the Larmor equation, is $\omega = B \cdot \gamma$. When the product is irradiated with electromagnetic waves, either continuously or intermittently, at this same frequency, nuclear magnetic resonance is induced in the hydrogen nucleus of water molecules. According to the inventors, the energy of electromagnetic waves absorbed by the hydrogen nucleus avoids water freezing at temperatures as low as -40°C . Unfortunately, the authors don't provide experimental evidences of this statement. Moreover, it is important to note that it is difficult to obtain a uniform magnetic field inside the freezer and, therefore, the resonance frequency would not be constant in the whole volume of the device. Later patents in the literature tried to overcome this problem. Thus, Kino [160] presented different solutions based on either varying MFs or applying broadband EM waves to generate NMR in wide regions inside the freezer.

Apart from these energy-imparting devices, some patents also include other elements to improve the freezing process such as sound-waves generators, far-infrared-ray absorbers, and pressure regulators. Owada and Kurita [159] proposed to superimpose sound waves, in the audio-frequency range, to the cold wind in contact with the product to stir up the boundary layer of air that inhibits heat transmission. Moreover, far-infrared-ray absorbers can be arranged on the inner walls of the freezer to absorb the radiant heat of the product, and thus, accelerate the cooling rate [41, 72, 154, 159]. Pressure regulators are employed to adjust gas pressure (above or below the atmospheric pressure) inside the freezer [154, 156]. By decreasing pressure with a suction pump, it is possible to reduce temperature inside the freezer and also to eliminate oxygen, and thus, avoid product oxidation. Once temperature is low enough, increasing pressure limits water evaporation and prevents drying of the product. Moreover, increasing pressure with gases with low or no oxygen content contributes to avoid product deterioration.

Other common devices and elements, usually employed in conventional freezers to improve heat transfer, are also included in the preferred embodiments described in most of the patents: heat insulators to maintain the freezer temperature [41, 159, 162, 163], ventilators to circulate cold air in the freezer [41, 156, 159, 162], air sanitizers to avoid product contamination [154, 157], honeycombs to promote a uniform flow of cold air [41], and air dehumidifying devices to avoid frost formation both on the freezer and on the frozen product [156].

Patented equipment includes solutions for both batch and continuous freezing. Continuous freezers can be straight belt, multi-pass belt, or spiral type and the product to be frozen is continuously conveyed through them. Therefore, continuous freezers require more complex embodiments to apply uniform MFs, either static or time varying, during the complete freezing process [41, 72, 156, 162].

On the other hand, it is important to note that MFs can be applied not only during freezing, but also during frozen storage and subsequent thawing. Thus, Ino, et al. [162] patented a

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system in which OMFs are applied during the complete freezing-storage-thawing process. According to the authors, this method allows better preservation of the food quality.

1.7. The lack of scientific research, motivation and objectives of this doctoral thesis

In an attempt to make the effects of weak OMFs on food freezing clear, [50] and [51] froze several food products, both with and without OMF application (0.5 mT/50 Hz). They did not find any effect of the oscillating magnetic field on the degree of supercooling and the freezing times recorded. Moreover, the ice crystals (size and shape), microstructure, drip losses, color, texture, and sensory evaluation were similar in all the frozen products. It is important to note that [50] and [51] performed all their experiments in a lab prototype and, therefore, this brings up the question of whether the characteristics of the OMF applied were exactly the same as those employed in commercial freezers. This is not easy to know because manufacturers usually do not provide these technical data (presence of static, oscillating, or both MFs; strength and frequency values; combination with EFs, EM waves, etc.).

To avoid this inconvenience, some authors have compared the quality of several foods frozen in both commercial electromagnetic freezers and conventional devices [44, 53, 164, 165]. Unfortunately, the few existing studies provide little or no information about the characteristics of the magnetic fields applied. Moreover, most of the experiments have been performed at very low temperatures, that is, at $-45\text{ }^{\circ}\text{C}$ and lower. At these conditions, the quality of frozen foods is usually well preserved with conventional methods and, therefore, observing improvements due to the OMF application could be difficult. Furthermore, an added obstacle is the inherent variability of food products (size, shape, structure, and composition) that can also contribute to diffuse the OMF effects. Thus, [53] compared the quality of chicken breasts frozen, at $-45\text{ }^{\circ}\text{C}$, in both a conventional rapid freezer and a CAS freezer. After one week of storage at $-30\text{ }^{\circ}\text{C}$, no differences were detected between the samples. However after six months of storage the rupture stress values for the CAS-frozen samples remained almost the same as those of the samples stored for one week, whereas the stress values for the conventional-frozen and rapid-frozen samples were significantly increased. Likewise, [44] compared the quality of gutted Atlantic cod frozen either in a CAS freezer at $-45\text{ }^{\circ}\text{C}$, in an air-blast freezer at $-35\text{ }^{\circ}\text{C}$, or in a cold storage room at $-30\text{ }^{\circ}\text{C}$. Even though the freezing rates achieved in each device were very different, the authors only found minor differences among the samples. By contrast, [164-167] froze beef, pork, and chicken samples in both a CAS freezer at $-55\text{ }^{\circ}\text{C}$ and an air-blast freezer at $-45\text{ }^{\circ}\text{C}$. They concluded that EM freezing reduced the total freezing times and preserved the quality attributes of the samples better than air-blast freezing. However, the temperatures of the EM and the conventional freezer were too different to attribute these improvements exclusively to the OMF application.

To correctly discern the effect of OMFs, freezing experiments, with and without OMF application, should be performed in the same device. This is the only way to exclude the effect of other variables than the OMF application (freezing temperature, air convection, sample

location in the freezer, etc.) on the results. In this sense, [45] compared the freezing curves of garlic bulbs frozen with (0.1-0.4 mT) and without OMF application in a CAS freezer. They did not find any effect of the OMFs on the supercooling reached in the samples or on the freezing kinetics. The same CAS equipment is used in [52] to freeze apple and potato samples at different CAS settings (0%, 25%, 50%, 75%, 100% CAS and control without CAS, according to the OMF values shown in Figure 1-2), and two different freezer air temperatures: -30 °C and -45 °C. They analyzed freezing times, freezing plateau times and nucleation temperatures from the freezing registered temperatures, as well as texture, weight and dimensional changes after freezing, after immediately thawing and after storing samples during a month at -19 ± 1 °C and subsequently thawing. Despite of the fact that for some specific combinations of influencing factors (CAS settings, freezer temperatures, food product) there were significant differences in some measured parameters with regard to those extracted from no CAS freezing trials, the finding of no significant effect for all CAS settings and/or temperatures leads to think that differences could be due to inherent variations in samples and conditions. Lamentably, to the best of our knowledge, no other studies exist in the literature that analyzes the effect of OMFs on food quality in such a way in commercial electromagnetic freezers.

Concerning SMFs, the comparison of the results obtained by different laboratories is often difficult due to two major reasons. On the one hand, the SMFs actually applied in the experiments are frequently not reported rigorously and the spatial magnetic gradients established throughout the sample are completely ignored. On the other hand, the number of replicated experiments sometimes is insufficient to capture the stochastic nature of ice nucleation and the statistics are unclear. Therefore, there is an urgent need to perform well-defined experiments that can be replicated and confirmed by different laboratories. To do so, the SMFs applied to the sample should be characterized accurately and carefully controlled. When assessing the effects of SMFs on supercooling, enough number of freezing experiments with and without SMF application should be replicated to characterize the probability functions correctly. Furthermore, when comparing freezing kinetics, the sample size and the cooling rate should be adjusted so that differences in the duration of the characteristic steps of the freezing process can be easily detected. Moreover, when assessing the efficacy of SMFs in improving food freezing, the sample size should be appropriate to exhibit the spatial magnetic and thermal gradients established in real foods during freezing. In this case, the temperature evolution should be recorded not only at the sample center, as is usual in the literature, but also at the surface. Otherwise, the detection of the exact time at which nucleation occurs is difficult due to the thermal gradients that are established throughout the sample.

In a recent review about the subject, [36] suggested that the extremely low strength of the frequently applied OMFs in the commercial freezers casts doubt on the effects that these weak OMFs can have on a substance with a low magnetic susceptibility such as water. MF characteristics corresponding to each selection are not provided by the manufacturers. Hence the employment of proper measurement instruments and sensors, like teslameters or oscilloscopes, very often unavailable in freezing laboratories, is required in order to correctly describe the MF. That may be one of the reasons why MF strength and/or frequency are not detailed in several scientific papers on magnetic freezing carried out in freezers produced by ABI Co. Ltd. [164-171]. Despite the fact that some authors claim positive results when applying

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OMF, in cryopreservation of human periodontal ligament (PDL) [89, 90], rat incisors [90] and human teeth [91], the above reported errors (Section **¡Error! No se encuentra el origen de la referencia.**) could reduce scientific rigor. An additional circumstance is that there are slight differences in the MF features among installed commercial freezers. Accounting that naturally MF received at Madrid (Spain) is about 0.044 mT, most of MF strengths of equipment reported in literature are rather low, ranging from 0.098 mT [45] up to 2 mT [53], with OMF frequencies between 1.8 Hz [47] and 60 Hz [85]. The potential direct effect of such weak MFs on water which is claimed in patents of ABI Co., Ltd. [42, 69], has been called into question due to the diamagnetic character and small magnetic susceptibility of this substance [36, 161, 172].

In an attempt to propose a possible mechanism of actuation of the MFs existing at CAS freezers, [161] formulate two hypotheses based on the presence of ferrimagnetic materials, like magnetite (Fe_3O_4) or maghemite ($\gamma\text{-Fe}_2\text{O}_3$) particles, precipitated in many animal tissues [173-175], in parts of human body [176, 177] and even in some vegetal species [178]. These magnetic particles could be related to the capacity of magnetoreception, i.e. the sensorial ability of some living beings to feel the geomagnetic field, used mainly for orientation purposes. In that sense, the action of Earth's magnetic field, present in our lives, can affect some species of birds and fishes' migration as well as other series of phenomena occurring in nature. Thus, some authors are committed themselves to the fact that SMFs could also affect biological tissue freezing, although the dependence of magnetoreception on such particles remains unproved [179]. Apart from these cases of biological origin, magnetic pollutant particles present in the environment are also likely to be incorporated into biological tissues [180]. Therefore these particles, whatever their origin, may be the receptors of MF direct action and provoke in turn the positive effects pursued on the products to be frozen. The first hypothesis put forward by [161] states that the vibration of ferrimagnetic particles, which have been proved to be nucleating agents [181] as expected, induced by the OMF would prevent water molecules from aggregating around them. On the other hand the second hypothesis points out that the waves due to magnetic particle vibrations would dissipate around the cells containing such particles through spatially large gradients, which would break aggregates of water molecules which form ice crystal structures. Both hypotheses would result in an increment of supercooling degree.

Although, from a physical point of view, magnetic particle inducing vibrations may involve a plausible mechanism to improve freezing process, it is not clear that the presence of magnetite and/or maghemite is a generalized fact in the products usually frozen, in the light of the studies available in literature, because many of them are only directed towards animals liable to possessing magnetoreception and within specific areas of their bodies. There are also studies which could not give evidence of the presence of magnetic materials in some animals [182, 183]. Then, if an effect of the MFs of CAS on the freezing of materials containing magnetic particles was proved, it would be necessary for these to exist in a considerable number of foodstuffs or biological tissues destined to freezing, in order to find a practical utility in this field.

To use food grade structures at nanoscale levels have been showing interesting features and has been proposed as a new way to not only improve safety and quality of foods, but also for the development of new and innovative food products with unique properties. Applications

are being envisaged [184] on food ingredients for color, texture and flavor; food production and packaging; nutrients and dietary supplements; antimicrobial nanomaterials for food storage; food nanosensors. In addition, magnetic nanoparticles have been widely used in scientific research, principally for medical applications, playing different roles. Those nanoparticles have been used as contrast agents in magnetic resonance imaging [185]. Besides they have been also used in cryopreservation studies to obtain uniform and rapid rewarming in both physical and biological systems including human dermal fibroblast cells, porcine arteries and porcine aortic heart valve leaflet tissues [186]. Other applications correspond to its use as heating centers for destruction of cancerous cells in hyperthermia [187, 188]. The widespread use of superparamagnetic iron oxide nanoparticles for these purposes is due, among other reasons, to their biocompatibility and low toxicity found even at doses much higher than those normally employed. Another advantage is the fact that, due to their superparamagnetic character, magnetism disappears in the absence of an external magnetic field, which avoids aggregation of nanoparticles [187]. Thus the possibility of adding this kind of particles to food or biological tissues, in order to improve their freezing in the presence of MFs such as those employed in CAS, would suppose a new tool for the enhancement of frozen products quality after thawing, as long as their effectiveness is verified. In spite of that, further studies about magnetic nanoparticles toxicity, accumulation and excretion may be necessary [189].

In a parallel way, it is necessary to evaluate also the magnetic effects, not only in water, but also in other models, molecules and systems that could potentially be benefited by this technology. Magnetic iron solutions can be considered as a model as it used as source of iron in dietary supplements and because of ionic liquids containing a transition metal (such as Fe, Ni, Co) ions that exhibit a magnetic response [190].

One of the areas where OMF freezing could be of particular interest is the application for improving the storage of proteins. Protein instability in aqueous solution is a major difficulty in producing pharmaceutical formulations. Lactate Dehydrogenase (LDH) is a thermolabile enzyme which undergoes significant deterioration during freezing-thawing processes [191, 192]. The combination of this enzyme with other cryoprotectant proteins such as serum albumin is frequently used but with moderate results. So the challenge of searching for a suitable freezing procedure still remains alive. The effects due to freezing and thawing on the denaturation of LDH and other enzymes were analyzed in [192] and authors concluded that the characteristics of the freezing and thawing process had significant influence on protein denaturation so that in order to reduce the freezing damage of proteins a relatively slow freezing and fast thawing processes were recommended. Because no data are found when the frequency of the EM field is low enough, here the study of the unexplored behavior of the activity of LDH after being frozen-thawed in comparison with conventional freezing without OMF was performed.

Another potential area of interest for EM freezing would be the application of this method to fish infected with *Anisakis* larvae in the third stage (L3), a parasite nematode that can infect humans when they consume raw or undercooked parasitized fish or cephalopods, since one of the most effective ways to avoid *Anisakis* L3 infection by humans is by freezing. EU Regulation [193] obliges food business operators to freezing fish that is to be consumed raw or by light

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culinary treatments, for at least 24h at a maximum temperature of -20 °C, or for 15h at -35 °C or below. This in practice covers a wide range of conditions in terms of i.e. freezing rate, time, or temperature which can have an impact on the characteristics of fish muscle, and therefore on their quality as food [194, 195]. Therefore, applications of effective methods to inactivate parasites in conditions that preserve the characteristics of the muscle are of high interest so that both quality and safety are fulfilled with the subsequent beneficial effects for the consumer.

On the other hand *Anisakis* L3 are moderately freezing tolerant [196] which involves the survival to intra and/or extracellular ice crystal formation under certain freezing circumstances. This could pose a problem on the application of OMF freezing for inactivation of these nematodes, since there are examples such as freezing living cells (i.e. erythrocytes or stem cells [92, 197]) which render better survival results as compared to conventional freezing. [82] examined the effect of a OMF with a 0.5 mT and 30 Hz on *Drosophila* under supercooled conditions at 0 °C for 72 hours, 24 °C for 24 hours and 28 °C for 1 hour, the *Drosophila* all survived, while all conversely died under the supercooled conditions without the magnetic field. However, until now it has not been proven whether OMF would increase survival of *Anisakis* L3 during freezing which, irrespective of the potential beneficial effects on the quality of the muscle, would preclude the use of this technology in the particular application of [193]. The objective of this work is to contribute to the current discussion on the potential effect of the application of OMFs during freezing by studying the effect of OMF during freezing in systems of different complexity. For that we performed a thermodynamic, an *in vitro* and an *in vivo* studies: a) the freezing profiles of a ferric chloride solution, b) Lactate Dehydrogenase (LDH) activity, and c) the viability of *Anisakis simplex* larvae and the water-holding capacity of hake muscle experimentally infected with *Anisakis*, respectively.

Besides, studies on real food are necessary. In this work, myosystems based on fish and meat origin products are being frozen in commercial electromagnetic system and conventional freezers in order to know its behavior during freezing as well as its quality characteristics after being thawed. For this purpose, crab sticks have been used which have been stored in its frozen state for different periods of time and then analyzed the freezing curve, the drip loss, water-holding capacity, toughness, and whiteness. In addition, the characteristics of the freezing curve and drip losses, texture and colour of samples extracted from pork loin are analysed.

Summarizing, the published experimental data existing in the literature, failed to back up the claims reported in patents on magnetic freezing with evidence. Some papers reveal positive results, but others show no effect of MF application. Many difficulties, associated to both MFs and freezing, hamper the reproducibility and replicability of the results. Moreover, it is important to note that, although there exist a number of reports on the effects of magnetic freezing, most of them have not been peer-reviewed and, in consequence, the quality of these papers is sometimes questionable. Therefore, there exists an urgent need to perform high-quality scientific research to prove whether magnetic freezing is effective in enhancing supercooling and/or improving the quality of frozen products or it is only a commercial fraud. If some effect is confirmed, the following step would be to investigate on the mechanisms that produce such effect.

To perform this research with success, it is essential to carry out well-defined experiments that can be replicated and confirmed by different laboratories. The effects of magnetic fields on freezing should be first evaluated in the simplest matrix, that is, in pure water and, then, more complex samples (saline solutions, model foods, real foods, and biological specimens) could be studied. Thus, the impact of added components and their possible interactions can be differentiated. When designing the experiments, special care must be taken to correctly characterize the sample and the freezing equipment and, also, to identify all the factors that can have an influence on the observed results. It is necessary to study both static and time varying MFs. The low strength of the MFs applied in ABI freezers (usually lower than 1 mT) casts doubt on the effects that these extremely weak MFs can have on freezing of water and biological products. Therefore, a wide range of MF intensities and frequencies should be tested to verify or discard MF effects on freezing.

To compare magnetic and conventional freezing, magnetic field exposition should be isolated as an independent factor while maintaining all the other factors (target temperature, freezing rate, air convection, etc.) fixed in the experiments. Moreover, the experiments should be carefully replicated to take into account the variability of response due to the sample and the process variations. Only a mathematical modeling and the adequate experimental design and correct sampling will allow a rigorous statistical analysis of the data to draw valid conclusions.

If real effects of magnetic fields on either supercooling, freezing kinetics, quality, or viability of the frozen products were confirmed, the mechanisms involved in the improvements observed should be investigated. To do so, it is necessary to evaluate magnetic effects not only in water, but also in other molecules that could be affected by magnetic fields. [86-88] have already pointed out the role that phospholipids could play in the cryoprotective effect of SMFs. Two more hypothesis have been published and both of them have been put forward by [161]. The first one states that the vibration of ferrimagnetic particles induced by the OMF would prevent water molecules from aggregating around them. The second hypothesis points out that the waves due to magnetic particle vibrations would break aggregates of water molecules which form ice crystal structures. Both hypotheses would result in an increment of supercooling degree.

Finally, experiments should not be limited to study the effects immediately after freezing, but also after prolonged storage time. It is well known that recrystallization phenomena occur during frozen storage and they can produce detrimental effects on food quality and viability of biological specimens. Depending on the rate and extent, recrystallization can nullify all the benefits derived from rapid ice nucleation. To date, only Yamamoto, et al. [198] and Choi, et al. [164] have published some data about the effect of storage time on the quality of magnetically frozen foods. More information is needed to evaluate the stability of ice crystals after magnetic freezing.

Therefore, it is necessary to provide a series of contrasted scientific data allowing to support, or not those hypotheses or to look for any others. In this connection it is essential to fully characterize the process. This work intends to study in depth the nature of the process, its effects on the food quality and to create devices to generate new OMF devices to further research in this area. All of that allowing advancing in the knowledge of the effects of magnetic

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fields on food and other products of biological origin during freezing or just submitted to any other MF treatment. To achieve these goals, three fundamental objectives have been defined.

Objective 1: Studying the development of the electromagnetic freezing process in model substances which allow supporting the hypotheses on which the envisaged improvements are based.

Hypothesis: The analysis of the freezing curve should provide the knowledge of how the physical process of electromagnetic freezing occurs and how they affect the parameters involved in it is essential for the optimization of this technology and its full implementation in the industry.

Objective 2: Studying the effect of electromagnetic freezing on the quality of different foods.

Hypothesis: Knowledge of the effects of electromagnetic freezing on the quality of different types of food should render to know about food freezing applications that can be commercialized successfully according the accepted quality parameters.

Objective 3: Obtaining electromagnetic field generator prototypes suitable for electromagnetic freezes and other applications.

Hypothesis: To own such generators at a laboratory level, working on the MF strengths and frequency ranges used in industrial devices, or in any other being potentially efficient should facilitate the development of systematic scientific studies and must be extrapolated at the industrial level.

By pursuing these objectives, it is intended to acquire a complete scientific base allowing to be conscious on the possibilities that this emerging freezing technology can offer. This is, of course, necessary for its possible future implantation in the industry.

2. Materials and Methods

2.1. Description of the equipment

The starting point being taken for the development of this thesis has been the analysis of the industrial facilities of electromagnetic freezing to which it has been possible to access. From this stage and accounting the described in literature, new equipment have been obtained that, at the laboratory level, allow addressing partial but complementary aspects of the effects produced by the application of electromagnetic fields during the freezing of food.

2.1.1. Determination of electromagnetic and thermal parameters on the electromagnetic freezers.

It is noteworthy to mention that the commercial freezers available during the experimental phase, all of them being CAS models from ABI, presented several unspecified magnitudes, despite being important for the final product quality. Such is the case of CAS setting or fan speed, both appearing as a percentage from 0 to 100, but without making clear the meaning of those values. It was therefore needed to measure the value corresponding to each percentage. Likewise it is necessary to define the MF and refrigerant flow speed in the other magnetic freezer prototypes employed in laboratory. For that reason airflow velocity was sensed with an anemometer (VT100, Kimo S.A., Montpon, France) at the centers and the middle points of the edges of trays 1, 5 and 10 (Figure 2-2) in one of the CAS freezers and at the center and representative points of the rest of the used equipment. The evolution of the temperature versus time at the center of the sample, on the surface of the sample holder (if pertinent) and in the surrounding environment of the freezer was obtained by using: type T (copper-constantan) thermocouples recording every 30 s using a datalogger (Diligence N2014, Comark Instruments, Norwich, UK) or every second by means of other data acquisition unit (DAQMaster MW100, Yokogawa Electric Corp., Tokyo, Japan). In some of the experiments carried out in CAS freezers, measurements were affected by electromagnetic interference (EMI) at certain OMF conditions. This could be due to the fact that the used thermocouples were parallel-pair thermocouple cables instead of twisted-pair cables. Consequently the area of the measurement loop is higher, increasing that way susceptibility to differential mode noise induced by MF [199]. In order to avoid this issue, when interaction with MF was detected, fiber optic probes (T1S, Neoptix Inc., Ville de Québec, QC, Canada) were used, connected to a signal conditioner (Reflex-4 Neoptix Inc.) which in turn recorded data in a PC every 5 seconds, allowing its monitoring via the manufacturer software (Optilink-II, Neoptix Inc.). The root mean square (RMS) strengths of SMFs and OMFs were characterized for different CAS percentages by means of a teslameter (GM07, Hirst Magnetic Instruments Ltd., Falmouth, UK) with a transverse Hall probe, at interesting points in order to get a comprehensive view of MF distribution in the useful volume. This instrument was also used for MF determination in all the used magnetic freezers. In the commercial equipment (Section 2.1.2) and in the laboratory air core OMF generator freezing equipment constructed within this

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thesis (Section 2.1.5), the field frequency varies also with the selection of “CAS energy” or with the chosen frequency in the built prototype. Therefore, in the case of the commercial freezer, due to the difficulty of measuring the current in a small gauge wire, it was determined measuring as well the frequency of the current induced by that field in a 7-turn coil acting as a loop antenna (frequency probe). For that purpose a current probe (TCP202A, Tektronix Inc., Beaverton, OR, USA) connected to an oscilloscope (TDS3012B, Tektronix Inc., Beaverton, OR, USA) were employed. Additionally, the current flowing through the coils in CAS equipment is unknown. The accessibility for sensing current is not easy due to dimensions of the coil and a Rogowski current probe (model CWT 3N, Power Electronic Measurements Ltd, Nottingham, UK) with a proper coil length was used. This measured current was monitored in an oscilloscope, implying also an indirect measurement of MF frequency. On the other hand, in the built prototype a current clamp (TA189, Pico Technology Ltd., Saint Neots, UK) connected to an oscilloscope (TDS5032B, Tektronix, Inc., Beaverton, OR, USA) was employed to measure the OMF frequency. To check the correct operation of the inverter, a voltage probe associated to the oscilloscope allows the monitoring of switching pulses.

2.1.2. The commercial equipment

Regarding magnetic freezing, it is remarkable a development of patents (see Appendix 0) previous to the emergence of scientific works that could serve as a basis for the potential effectiveness of this technology. Some of these patents gave rise to the implementation of commercial magnetic freezing equipment. There are at least two companies marketing different type of magnetic freezers: Ryoho Freeze Systems Co., Ltd.(Nara, Japan) which sells the model ‘Proton freezer’, and ABI Co., Ltd. (Chiba, Japan) which put onto the market ‘CAS (Cells Alive System) freezers’. The former freezer combines SMFs with electromagnetic waves of a determined frequency so as to generate nuclear magnetic resonance in hydrogen nuclei of water molecules, whereas CAS technology makes use of SMFs and OMFs. Although with some differences in their way of operation, advertising of CAS [56] and Proton freezers [57, 58] as well as patents on CAS [41, 42, 200] and on NMR freezing [72, 157] claim that the application of those electromagnetic fields is able to rise supercooling degree, delaying the start of nucleation by means of inhibition of crystal formation. When nucleation is finally triggered (either by a higher reduction of temperature or by a removal of the action of OMF), a higher amount of crystal embryos appear in the product, provoking a reduction in the ice crystal sizes and a better spreading of those throughout the entire food, which decreases cell damages and contributes to enhance quality. It is even stated that fresh food quality is maintained after thawing the MF-assisted frozen products.

Despite there are these two possible marketed solutions available, only ABI freezers have been used in scientific works employing commercial equipment with MF freezing, as seen in Section 1.7. Furthermore CAS technology have received attention also outside Japan [59, 201], having equipment sold to food processing and catering companies, hotels, hospitals or research centers [36]. In this work it has been dealt with three similar ABI freezers. In one of them, owned by the technology center AZTI-Tecnalia [202] the preliminary work was performed. It is formed by a conventional refrigeration system, a freezing cabinet with a tray rack and 2 fans to

direct the cold air towards the cabinet. In addition to these normal elements of traditional freezers, there is a MF generator system, which comprises two parts: thus the SMF is generated by means of a set of permanent magnets embedded in the rear and left walls, the front doors and walls, and the ceiling. The OMF in turn is induced by currents circulating through 4 rectangular coils (outer dimensions: 1.6 m height x 1.4 m length) which enclose the tray rack and the freezing circuit. Each of these coils is hidden inside a tubular metallic structure (4 cm square cross section) shaping the coils in the said rectangular fashion. Such coils are separated by 18 cm each.

On the other side, the Food Refrigeration and Process Engineering Research Centre [203] at the Grimsby Institute of Further and Higher Education (GIFHE) has an experimental batch air-blast freezer equipped with CAS, intended for research [45]. It was used for the studies related with the pork loin freezing. On this occasion the MF generator consists of 3 coils encompassing only the usable volume of the freezer, where products could be located. There are a series of rectangular permanent magnets bolted at least to the left and back walls of the freezing cabinet. Therefore these are not built-in and seem to be removable. As regards the rest of elements of the freezer, the most remarkable differences are the presence of only one grid fastened to an aluminum structure instead of a rack with trays and of an extra fan at the back of the cabinet, oriented toward the door, as well as two fans between the refrigerating system and the freezing compartment, similar to the ones of AZTI.

Figure 2-1: Schematic drawing of the main components of the CAS freezer in the FRPERC-GIFHE

Another example of ABI freezer (model CAS-30B, ABI Co., Ltd., Chiba, Japan) is used by the catering service company Kotobuki, belonging to the Kabuki Group, which delivers Japanese cuisine specialties of high standing to supermarkets, events and its own restaurants [204, 205]. In this work this freezer was used for the crab sticks freezing. This freezer is composed of a refrigeration circuit, a freezing cabinet and two fans to direct the cold air towards the cabinet

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[47]. This latter can hold up to ten trays for food, equidistantly distributed in a rack. As for the MF generator system, it comprises two parts as the previously seen models. Accordingly the SMF is generated by means of a set of permanent magnets embedded in the floor, the back and left walls, the front door and the ceiling. The OMF in turn is induced by currents circulating through 4 rectangular coils (outer dimensions: 1.6 m height x 0.7 m length) which enclose the tray rack. Each of these coils is hidden inside a tubular metallic structure (4 cm square cross section) shaping the coils in the said rectangular fashion. The distance between pairs of coils was 18 cm. Apart from that, trays were 40 cm x 60 cm, giving rise to approximately a useful freezing space of 152 cm x 40 cm x 60.

Figure 2-2: Schematic drawing of the main components of the CAS freezer in Kotobuki. a) Main components; b) Points at which magnetic field measurements were performed in freezing trays 1, 5, and 10.

This latter freezer, as the two previous ones, has a control screen (on the front of the freezer in this instance) whereby some operation parameters can be chosen, among them the freezing chamber temperature (down to $-50\text{ }^{\circ}\text{C}$), air-blast speed (0 – 100 %) and “CAS energy” (0 – 100% CAS), exerting the corresponding action on the compressor, the fans and the coils, respectively.

Therefore, although with some differences in their layouts, due to the fact that ABI supplied and commissioned the MF generators and the control system, just giving guidelines for the rest of the freezer, it is clear that CAS is installed in an air-blast freezer which is good in itself, which makes more difficult to appreciate additional contributions of CAS to quality. It is noteworthy also that some of the additional attributes claimed in ABI patents [41, 42, 200] (see Appendix 0) has not been seen in these three freezers, as happens with: internal surfaces capable of absorbing far-infrared rays, sound wave generators, honeycomb structures for guiding the airflow. The most remarkable absence is that of electric field electrodes, which seemed to be a fundamental part in the effect of electromagnetic fields on freezing.

2.1.3. The static magnetic field generator

Considering a representative example, the device here employed to generate static magnetic field (SMF) is represented in Figure 2-3. The SMF was produced by using two cylindrical

permanent magnets of neodymium ($\text{Nd}_2\text{Fe}_{14}\text{B}$), axially magnetized, 20 mm high and 35 mm diameter, having a nominal remanent MF (the $\vec{B}$ present in the absence of an external MF) $|\vec{B}_r| = 1.32 \text{ T}$ in the axial direction (S-35-20-N, Webcraft GmbH, Gottmadingen, Germany), equally separated from the geometric center where the sample to be frozen is disposed, Figure 2-3b. The structure of the device was built by using two square-prism shaped pieces of polymethyl methacrylate (PMMA) with dimensions 80 x 80 x 28 mm and 80 x 80 x 33 mm. A blind hole (20 mm high and 36 mm in diameter) was drilled, in the center of each piece, to lodge each magnet with a slight clearance, without protruding above the block. Another two PMMA square lids (80 x 80 x 3 mm) were used to block the magnets inside their cavities, yet permitting to extract them and change their relative position and polarity. A number of Teflon® nuts and four Teflon® bolts can be employed to fasten the stoppers and to vary the distance between magnets. Such non-magnetic materials (PMMA and Teflon®) were chosen for constructing the structure so that they do not disturb the MF in a sensible way. A 12 mL glass vial (outer diameter $\phi = 23.2 \text{ mm}$) was used as a sample holder. The center of the liquid sample volume was always placed at the same position, i.e., equidistant and aligned with the geometric centers of both magnets.

Figure 2-3 The laboratory SMF generator used for freezing. a) Device to produce magnetic field by using two parallel magnets; b) Disposition of the sample holder between the PMMA blocks

2.1.4. The iron core oscillating magnetic field generator

In order to make a more comprehensive analysis of MF action on food freezing and thus complement the previous device, the construction and assembly of an oscillating magnetic field (OMF) system has been addressed. It basically consists of a custom-made C-shaped laminated iron core (Figure 2-4b) with external dimensions 35.2 x 25.5 x 10 cm³. Around three of their legs there are windings in series with the rest of the circuit, acting as an inductor. An autotransformer, whereby the circuit is connected to the power supply, and thus operates at the electricity grid frequency, i.e. 50 Hz, allowed for the selection of the output voltage in a range between 8 and 250 V and the generated electric current up to a maximum of 3.5 A. So the strength of the OMF to be applied to the sample situated in the air gap of the iron core, which is directly proportional to the inductor current as the Biot-Savart law states, could also be varied. The equivalent circuit of the winding around the iron core is an inductor (1.23 H) in

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series with a resistor ($28\ \Omega$). Given the inductive character of the used iron core device, in order to correct the power factor, it was necessary to add a battery of capacitors (with equivalent capacitance of $10\ \mu\text{F}$) able to support $2480\ \text{V}$, in series with the circuit. A resistor of $680\ \Omega$ was also disposed in series, in order to reduce the current going through the circuit (Figure 2-4a) to get small OMF and achieve a higher selectivity through the autotransformer knob. In this way, four OMF strengths: 0.33 , 0.8 , 1.5 and $7\ \text{mT}$ were generated. In addition to these OMF strengths, $31.3\ \text{mT}$ were also used in some of the trials by removing the added series resistor. The device was designed in order to obtain a uniform OMF in the middle of the iron core volume ($10 \times 10 \times 4.2\ \text{cm}^3$, Figure 2-4b, just in the place where the sample holder could be disposed during freezing, Figure 2-4c. This device was located into a 308-liter domestic freezer (Koxka, Pamplona, Spain) and also into a 100-liter domestic freezer (AFG 050 MAP, Whirlpool Corp., Benton Harbor, MI, USA), both of them modified with the presence of a fan (5958, ebm-papst Inc, Mulfingen, Germany). The temperature evolution at the center and surface of the sample as well as the temperature in the freezer was registered every 5 seconds with a fiber optic temperature sensor or alternatively by thermocouples, employing the respective data acquisition units of Section 2.1.1 in each case.

Figure 2-4: The laboratory iron core OMF generator used for freezing. a) Electric circuit. b) Volume to place the sample. c) Potential location of the sample

To correctly discriminate between measurements with and without OMF, it was necessary to keep constant the ambient temperature in the freezer [36]. In this relation, it is necessary to take into account that the used OMF was produced by an electric current which provoked an increase in temperature around due to the Joule effect. The cable which formed the inductor had an equivalent resistance of $28\ \Omega$ (measured previously) and as the current circulating to generate the field was $1\ \text{A}$ it gave rise to a dissipated power of $28\ \text{W}$. It must be mentioned

that this current corresponds to the 31.3-mT field strength, because the other fields were generated by smaller currents which gave rise to negligible heat dissipation. Taking that power into account, a similar amount of power was added to the freezing chamber during non-MF experiments to get the same experimental conditions in both cases. This requirement was achieved by introducing inside the freezer a set of three electric heating wires, connected in parallel, whose total resistance was 56 Ω . Thus applying a 40 V DC voltage by means of a power supply (FAC-662B, PROMAX Electronica S. L., L'Hospitalet de Llobregat, Spain), a power of 28.6 W was obtained, very similar to the sought one. To corroborate this theoretical calculation, stationary state freezer temperatures were registered and compared between the case with MF and the control case with the heating wires, verifying that both were sufficiently near. Besides, the air speed was fixed by programing the fan to work at a constant velocity. However, in this case, its corresponding fan power dissipation caused a temperature increase in the freezer which was equal both in OMF and control experiments.

2.1.5. The air core OMF generator of electromagnetic field for wide range low frequencies.

2.1.5.1. Motivation of the design

Electromagnetic waves can move in any material medium, as in foodstuffs, at a determined velocity v given by:

$$v = \frac{1}{\sqrt{\epsilon\mu}} = \frac{1}{\sqrt{\epsilon_0\epsilon_r\mu_0\mu_r}} \quad (\text{Eq. 11})$$

ϵ , ϵ_0 , ϵ_r , μ , μ_0 and μ_r being the constants previously seen in (Eq. 5) and (Eq. 6). The refractive index n is then defined as the speed of light in vacuum c divided by the speed of light in medium v :

$$n = \frac{c}{v} = \frac{\sqrt{\epsilon_0\epsilon_r\mu_0\mu_r}}{\sqrt{\epsilon_0\mu_0}} = \sqrt{\epsilon_r\mu_r} \quad (\text{Eq. 12})$$

For non-magnetic materials $\mu_r \approx 1$ and then:

$$n = \sqrt{\epsilon_r} \quad (\text{Eq. 13})$$

In the presence of a variable electric field, the dielectric response of materials, i.e. the way in which they are affected by and, likewise, affects that electric field, depends on the field frequency, existing phenomena of dipole relaxation and resonance. This behavior can be expressed in terms of complex frequency dependent refractive index n^* and relative permittivity ϵ_r^* :

$$\epsilon_r^* = \epsilon_r' - j\epsilon_r'' \quad (\text{Eq. 14})$$

$$n^* = n' + j\kappa' \quad (\text{Eq. 15})$$

where ϵ_r' is the relative dielectric constant and ϵ_r'' is the loss factor, representing the capacity of the material for storing or dissipating energy, respectively. In turn, n' is the refractive index and κ' is the extinction coefficient, this latter expressing the attenuation of the wave when

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traversing the material [206, 207]. When (Eq. 13) is fulfilled, the relation between the real and imaginary parts of ϵ_r^* and those of n^* is easily deduced:

$$\epsilon_r' = n'^2 - \kappa'^2 \quad (\text{Eq. 16})$$

$$\epsilon_r'' = 2 \cdot n' \cdot \kappa' \quad (\text{Eq. 17})$$

In polar substances of small molecular sizes, as water, it can be demonstrated [208] that ϵ_r' and ϵ_r'' satisfy the Debye-type expressions:

$$\epsilon_r'(\omega) = \epsilon_\infty + \frac{(\epsilon_s - \epsilon_\infty)}{1 + \omega^2 \tau^2} \quad (\text{Eq. 18})$$

$$\epsilon_r''(\omega) = \frac{(\epsilon_s - \epsilon_\infty) \omega \tau}{1 + \omega^2 \tau^2} \quad (\text{Eq. 19})$$

where ϵ_s and ϵ_∞ are the permittivity values at low and high frequencies, respectively, τ is the characteristic relaxation time and ω is the angular frequency (measured in rad/s in contrast to the electromagnetic frequency f which is measured in Hz, i.e. cycles/s). An approximate representation of the complex permittivity values for water at 25 °C and 1 bar is shown in Figure 2-5, from the available values of τ [100], ϵ_s [209] and ϵ_∞ [210].

Figure 2-5: Debye's model of the complex relative permittivity of water

This reduction of the real part of ϵ_r on reaching high frequencies, is due to the fact that polar molecules become unable to follow electric field variations and therefore there is a lag between them which increases losses. Then the maximum of ϵ_r'' , and consequently the maximum losses, appear at the frequency in which ϵ_r' decreases down to the middle value between ϵ_s and ϵ_∞ . The angular frequency at this point is equal to the inverse of the relaxation time ($\omega = 1/\tau$). For a given material, temperature is one of the main factors that causes variations in the relaxation angular frequency, the maximum of ϵ_r'' and ϵ_s , but the drastic reduction in the mobility of molecules produced by freezing, originates a big reduction in the appearance of maximum losses. In that sense [210] compare the angular frequencies of the peak of ϵ_r'' for water and ice at 0 °C, whose respective relaxation times are $1.7 \cdot 10^{-11}$ and $2.2 \cdot 10^{-5}$ seconds, presenting very similar graphs but shifted six decades. This provokes for instance

a much higher absorption of energy by liquid water than by ice in microwave ovens (usually working at 2.45 GHz). Thus the ratio of water to ice EM wave absorptions per unit length is 71.4 at that frequency [13]. So given the displacement of 6 decades in the graph of dielectric response versus frequency, it could be reasonable to think that if interesting effects of electromagnetic freezing are sought, the range of kHz frequencies should be explored.

[211] studied the freezing process of a 0.9% K_2MnO_4 solution in the presence of an OEF of strength 5 V/cm and at several frequencies between 1 and 200 kHz. From the lowest frequency on, they observed a gradual reduction of ice crystal sizes and of complete freezing time, reaching a minimum at 50 kHz. For higher frequencies both ice crystal sizes and freezing times rise again (Figure 2-6a). The authors remarked that this frequency is almost the same as 48 kHz, where the dielectric relaxation peak of ice appears. It should be noted that this value differs from the one provided by [210] which turned out to be 7.23 kHz at 0 °C. Similarly [212], collecting the data of [213], report a frequency of relaxation peak around 5.31 kHz at 272 K. This lower frequency may be due to the well-known increase of the dielectric relaxation time of water and ice, when decreasing temperatures [214, 215]. Other interesting result is obtained by [78] who apply pulsed electric fields of 1.78 V/cm and 50% duty cycle at different frequencies between 1 and 20 kHz, getting a reduction of phase transition times with increasing frequencies (Figure 2-6b). At 20 kHz ice crystal were smaller and rounder than without applying electric fields. It must be mentioned that [216] carried out a study of ice grain sizes and their associated ice crystallization fraction for 0.9 wt % NaCl solutions frozen in the presence of several OEF of strengths between 12.5 and 100 kV/m and frequencies ranging from 100 kHz to 10 MHz. These authors obtained a reduction of the studied parameters when sample is subjected to OEFs, reaching an optimum behavior at 100 kV/m and 1 MHz. They state that this frequency is in the region where the complex electric modulus M^* (the inverse of ϵ_r^*) of the solution at -5 °C undergoes dielectric relaxation, which could be related to the reduction of ice crystal size. However these positive results may be due to the higher OEF strength with regard to that of the other considered works, which seem to indicate that much weaker OEFs, and therefore less energy-consuming, are able to obtain an improvement of freezing characteristics by using lower frequency ranges.

Figure 2-6: a) Complete freezing time of 0.9% K_2MnO_4 solutions under 5 V/cm alternating electric field at different frequencies (extracted from [211]); b) Phase transition time during freezing of 0.9% NaCl solutions under 1.78 V/cm pulsed electric field at different frequencies (extracted from [78])

The frequencies of several of the previously referred scientific papers, as well as that of microwave ovens and 50 Hz (one of the frequencies of CAS freezers and the one used in the

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iron core inductor) have been marked (Figure 2-7) on the spectrum of the complex index of refraction for ice at 0 and -20 °C supplied by [217]. This could give an idea of the area of interest to be covered by a new device:

Figure 2-7: Model of the complex index of refraction (extracted from [217]) and representative frequencies

At this point it must be necessary to consider that the predominant trend of commercial freezers is to employ MFs instead of EFs, either alone as in CAS freezers or in conjunction with EM waves as in Proton freezers. In turn, EF assisted freezing is used basically only in the research area. There is a notable difference in the way those EFs affect the freezing process, depending on their static or oscillating nature [21, 66]. Thus static electric fields (SEFs) tend to align water molecules in the direction of the field due to their dipolar character and this would strengthen hydrogen bonds parallel to the SEF [218], inducing ice nucleation at a lower degree of supercooling than in conventional freezing and consequently increasing phase transition times. In that sense [219] obtained a rise of 1.6 °C in the nucleation temperature of water with 10^5 V/m SEF although they recognize that SEF is lower than the *critical value* found by molecular dynamics simulation ($1.5 \cdot 10^7$ V/m) below which SEF effects on freezing should not be significant. A decrease of supercooling was also observed by [220, 221] upon applying $1.7 \cdot 10^5$ and $4 \cdot 10^5$ V/m SEFs to pure water freezing, also smaller the *critical value*. On the contrary [222] does not found any significant effect on the nucleation temperature caused by a SEF of strength $1.6 \cdot 10^5$ V/m. Hence the real effect of SEF strength on supercooling degree is not clear. Another puzzling discovery is reported by [223] who froze pork tenderloin subjected to $6 \cdot 10^6$ V/m SEF and as well as resulting in a reduction of supercooling, ice crystal sizes were significantly lower than those without SEF. In the same way [224] with a weaker SEF ($5.8 \cdot 10^4$ V/m) obtained an improvement in the quality of frozen lamb meat. This could indicate an increase in the number of nuclei appeared. Therefore the actual mechanism of freezing under the action of SEF, and the need for higher or lower field strengths have not been clarified yet.

Some consideration must be given to the difficulties of using EFs in freezing processes. Among them the dielectric breakdown strength of air, $3 \cdot 10^6$ V/m at atmospheric pressure, and of pure water, 10^7 V/m in millimeter-scale samples [222] should not be attained in order not to produce sparks. For the same reason electrodes should have sufficiently polished, preferably parallel surfaces preventing the rise of charge density which appears at protruding parts. These could give rise to the appearance of corona wind, i.e. the ionization around the electrode surfaces which can enhance heat transfer but should also be avoided [21]. These authors state as well that the distance between electrodes should be smaller than their diameter. Thus in EF freezing scientific works, electrode separation distances between 0.3 mm [221] and 20 mm [219] have been observed, which limits the dimensions of food products to be frozen. Apart from the small distance, sample should not be in contact with both electrodes in order not to let current go across food, so the practical distance is more reduced. In many cases voltages in the order of kV are employed and in a moist environment it could cause safety problems. The electrical circuit generating the field must be provided with a switching device which avoids any electrical risk for users, cutting off the high voltage when they open the freezer door as in the patent [225].

The previously explained works of [78, 211] open, however, an alternative way of employing EFs for freezing application. The employment of relatively weaker fields and the variation of the measured effects with frequency suggest that this parameter could play a role in the improvement of freezing. Considering this fact and the interest which could have the region of kHz in the electromagnetic spectrum, as explained before, here an alternative method is proposed for applying OEFs in the range of kHz by means of OMFs as announced in [68], because according to Faraday's law (Eq. 3) any variable MF will induce a variable EF whose orientation is such that if there were a conductor, the induced current would generate a MF which would tend to oppose the variation of MF flux (Lenz's law). This is a non-conservative EF. To quantify the strength of this EF, a variable MF $\vec{B}$ confined in a circular region of radius R is supposed (Figure 2-8):

Figure 2-8: Electric field induced by a variation of magnetic flux

Then from the circulation of the induced EF $\vec{E}$ along a circular concentric path of radius r, the value of the EF strength is easily calculated, being:

$$|\vec{E}| = \frac{r}{2} \frac{d|\vec{B}|}{dt} \quad (\text{Eq. 20})$$

when $r \leq R$, whereas for $r > R$ it is:

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$$|\vec{E}| = \frac{R^2}{2r} \frac{d|\vec{B}|}{dt} \quad (\text{Eq. 21})$$

Supposing that the MF is uniform on the circle surface and it only varies in a sinusoidal fashion at a constant frequency f :

$$|\vec{B}| = B_{pk} \cdot \sin(2\pi ft) \quad (\text{Eq. 22})$$

then, taking into account that in this case there is a maximum of the induced EF strength for $r = R$, this is:

$$|\vec{E}| = \frac{R}{2} \cdot B_{pk} \cdot 2\pi f \cdot \cos(2\pi ft) \quad (\text{Eq. 23})$$

To give an idea of the order of magnitude of the EF, supposing $f = 50$ kHz (optimal value in [211]), $B_{pk} = 21.5$ mT (around the maximum OMF of the commercial freezer in [47]) and radius $R = 4$ cm, then the RMS value of the OEF equals 9.55 V/m, i.e. 5.4% of the strength employed in [78]. Whether this is a sufficiently strong field or not to make a difference to freezing, it should be determined experimentally. What is clear is that if improvements were found in freezing assisted by these weak EFs and the determinant factor turned out to be their frequency, the employment of much more manageable OMF generators instead of electrodes generating OEFs, would result in an important technological advance.

Other reason for the utilization of OMFs is that although the physical foundations of their action are not clear [161, 172], it is MFs and not EFs on which the potential beneficial effects of CAS freezers are based. As previously seen in Section 1.5, there are a number of works using CAS equipment, with OMFs of frequencies ≤ 60 Hz, which claim to improve cell cryopreservation. Such is the case of [89] who found higher survival rate of human PDL cells than with conventional freezing and cell proliferation close to that in fresh teeth. Also in CAS-frozen human PDL cells, results comparable to those of fresh ones were obtained in [91] and [90], this latter showing high viability in replanted rat incisors. In turn [92] found better results when freezing human embryonic stem cells with a CAS freezer than in an isopropanol-jacketed freezing container at -80 °C. Likewise some other scientific papers obtained promising results when applying OMFs with lab prototypes. Thus [80] observed a higher supercooling in bidistilled water with OMF strength up to 0.88 mT and ranged at frequencies between 10^{-2} and 200 Hz. An increment in supercooling appeared also in the freezing of physiological saline solutions under OMF of 1.2 ± 0.2 mT with frequencies between 200 Hz and 200 kHz [81]. This work shows also an improved preservation of swine liver at 2 kHz (the only proved frequency) compared with that of conventional freezing. Therefore it becomes clear that OMF should not only be seen as a means for generating OEFs, but they may themselves be interesting. If positive effects on freezing were finally identified, the corresponding OMF strength and frequency in which those experiments have been carried out, should also be investigated.

The previously seen iron core inductor (Section 2.1.4) allows applying OMFs of different strengths but always at the mains frequency (50 Hz in Europe). It is consequently valuable to have an electronic device able to apply OMFs of at least the strength of the commercial CAS freezers in a wide range of frequencies, covering from 1 Hz (minimum CAS OMF frequency registered) up to 50 kHz.

2.1.5.2. Design of the inductor of electromagnetic field for a wide range of low frequencies

For the application to samples of OMFs in a wide range of frequencies during freezing, an air core inductor has been selected. This not only provides with a bigger space for placement of samples than in the previous air gap but also eliminates the core losses which for the highest selected frequencies could be significant, as well as avoiding the chance of core saturation. One major drawback however, is the reduction of generated MF strength because of the much smaller magnetic permeability of air with regard to that of iron.

As the Maxwell–Ampère equation (Eq. 4) states, any current generates a MF $\vec{B}$ around itself. Supposing a current I going through a wire, the infinitesimal MF $d\vec{B}$ generated at a point by the passage of that current through an infinitesimal length $d\vec{l}$ can be expressed by the Biot-Savart law:

$$d\vec{B} = \frac{\mu_0}{4\pi} \frac{Id\vec{l} \times \vec{u}_r}{r^2} \quad (\text{Eq. 24})$$

in which r and $\vec{u}_r$ are respectively the distance and the corresponding unit vector from the differential current-carrying element $d\vec{l}$ to the point where the field is calculated. Letting apart possible simplifications by symmetry, the integration of this equation is in most cases not simple. In our particular situation of a finite solenoidal coil of N turns, with current I , assuming magnetic permeability of the medium similar to that of vacuum and given the geometrical parameters represented in Figure 2-9:

Figure 2-9: Scheme of a solenoidal coil

the value of the field at any point P of the coil axis, which only has component along that axis is given by:

$$|\vec{B}| = \frac{\mu_0 NI}{2L} \left[\frac{(L/2) - z}{\sqrt{(L/2 - z)^2 + R^2}} + \frac{(L/2) + z}{\sqrt{(L/2 + z)^2 + R^2}} \right] \quad (\text{Eq. 25})$$

However at points out of the axis, the mathematical study becomes more complicated. Then in order to acquire a thorough knowledge of the distribution of the MF in the space inside the

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coil where samples are going to be placed during freezing, and in this way to assist in the design process, a FEM program, ANSYS Maxwell (v. 16, ANSYS Inc., Canonsburg, PA, USA) was employed. In a preliminary calculation a rectangle rotating around a vertical axis was considered (Figure 2-10a). The objective is to generate a determined sinusoidal field $\vec{B}$, as uniform as possible, inside the coil. Hence for a determined coil geometry, the MF module, B, is proportional to the magnetomotive force (mmf), measured in Ampère-turns, whereas the energy stored in the coil, W, is proportional to the square of B and thus to the square of mmf. It must be taken into account that the solver employed for these simulations (Eddy current solver) uses peak values of the concerned magnitudes (represented below with a circumflex on them). For an initial mmf, $\widehat{AT}_1 = 1$ ampere-turn, the simulated field $\widehat{B}_1$ and energy W_1 are converted to the peak value corresponding to the desired RMS value $B = 0.8$ mT, around the MF measured in the coil axial direction at the center of the useful space in the commercial CAS equipment of Kotobuki (see Table 3-9), by scaling through a factor k:

$$\begin{aligned}\widehat{B} &= k\widehat{B}_1 \\ \widehat{AT} &= k\widehat{AT}_1 \\ W &= k^2W_1\end{aligned}\tag{Eq. 26}$$

The peak current can be expressed as:

$$\widehat{I} = \frac{\widehat{AT}}{N} = \frac{k\widehat{AT}_1}{N} = \sqrt{2} \cdot I\tag{Eq. 27}$$

where the square root of two is because of the sinusoidal waveform. Then, from the equation of the energy in an inductor with inductance L, this can be calculated as:

$$L = \frac{4W}{\widehat{I}^2} = \frac{4k^2W_1}{\left(\frac{k\widehat{AT}_1}{N}\right)^2} = \frac{4W_1}{\widehat{AT}_1^2}N^2 = \frac{N^2}{\mathcal{R}}\tag{Eq. 28}$$

with $\mathcal{R}$ being the magnetic reluctance.

Figure 2-10: a) Rectangular coil copper cross section for selection of height and width; b) Hexagonal winding patter; c) Square winding pattern

The equivalent circuit of an air core coil will be given by an inductor in series with a resistor. The current flow through this equivalent resistance gives rise to an active power P dissipated along the coil as expressed in:

$$P = RI^2 = \rho_{Cu} \cdot \frac{l_m N}{A_c} \cdot \left(\frac{k \widehat{AT}_1}{\sqrt{2} N} \right)^2 = \frac{1}{2} \rho_{Cu} \cdot \frac{l_m}{A_c} \cdot \frac{k^2 \widehat{AT}_1^2}{N} \quad (\text{Eq. 29})$$

in which ρ_{Cu} is copper resistivity, A_c is the cross section of the conductor and l_m is the average length of one turn. Copper resistivity increases with temperature, as it is well-known, and here has been chosen the value at 0 °C, $1.543 \cdot 10^{-8} \Omega \cdot m$ [226].

Figure 2-11: ANSYS Maxwell simulated MF: low frequency range inductor

By changing the height and width of the copper cross section (Figure 2-10a), with a chosen wire of 0.8 mm diameter (for the low frequency inductor), it gives rise to a number of turns which are used to calculate the values of current, inductance, resistance, active power, impedance and voltage, according to (Eq. 27 to (Eq. 29). It is worth to mention that if dimensions are not too different, a constant MF strength can be achieved by keeping constant the number of ampere-turns, so a reduction in the current, which tends to decrease the power, would imply an increase in the number of turns and accordingly a rise of both inductance and resistance, involving a trade-off. Once chosen an option, two different patterns of multilayer winding were assessed: hexagonal with a fill factor of 0.907 (Figure 2-10b) and square winding pattern, having a fill factor of 0.785 (Figure 2-10c) [227]. Although ideally the hexagonal pattern is more compact and it means less copper employed than the square pattern, a manual or semimanual winding, as the one used in the construction of this coil, will likely produce a coil pattern mixture of both. Here for the calculation of the design parameters, the square pattern and 100 Hz have been considered (Figure 2-11), resulting in the values shown in Table 2-1, from which a coil with 500 turns (5x100) was selected, mainly considering the geometry providing the smaller impedance.

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Width (mm)	Height (mm)	Scale factor, k	Layers	Turns/layer	Total turns, N	L (H)	R (Ω)	I _{RMS} (A)	P (W)	Z (Ω)	U _{RMS} (V)
4	80	117	5	100	500	0.014	4.05	0.17	0.11	9.73	1.61
6	80	116	7	100	700	0.028	5.81	0.12	0.08	18.60	2.18
8	80	116	10	100	1000	0.058	8.49	0.08	0.06	37.67	3.09
4	100	140	5	125	625	0.019	5.06	0.16	0.13	12.91	2.05
6	100	139	7	125	875	0.038	7.26	0.11	0.09	24.85	2.79
8	100	139	10	125	1250	0.079	10.61	0.08	0.07	50.60	3.98
4	120	150	5	150	750	0.024	6.08	0.14	0.12	16.15	2.28
6	120	150	7	150	1050	0.048	8.71	0.10	0.09	31.25	3.16
8	120	140	10	150	1500	0.100	12.73	0.07	0.06	63.92	4.22
20	20	119	25	25	625	0.045	6.03	0.13	0.11	28.80	3.88
30	30	139	37	37	1369	0.199	14.52	0.07	0.07	125.71	9.03
40	30	138	50	37	1850	0.380	21.41	0.05	0.06	239.61	12.64
30	40	125	37	50	1850	0.330	19.63	0.05	0.04	208.42	9.96
40	40	124	50	50	2500	0.637	28.93	0.04	0.04	401.39	14.08
50	40	135	62	50	3100	1.035	38.86	0.03	0.04	651.20	20.05
40	50	124	50	62	3100	0.905	35.87	0.03	0.03	569.95	16.12
50	50	134	62	62	3844	1.479	48.19	0.02	0.03	930.49	22.94
80	4	150	100	5	500	0.040	7.72	0.21	0.35	26.24	5.57
100	4	174	125	5	625	0.067	10.85	0.20	0.42	43.18	8.50
120	4	175	150	5	750	0.102	14.47	0.16	0.39	65.86	10.87
80	6	160	100	7	700	0.077	10.80	0.16	0.28	49.61	8.02
100	6	185	125	7	875	0.129	15.19	0.15	0.34	82.30	12.30
120	6	186	150	7	1050	0.198	20.25	0.13	0.32	126.13	15.80
80	8	169	100	10	1000	0.155	15.43	0.12	0.22	98.59	11.78
100	8	173	125	10	1250	0.259	21.70	0.10	0.21	164.40	16.09
120	8	173	150	10	1500	0.400	28.93	0.08	0.19	252.95	20.63

Table 2-1: Low frequency range inductor: comparison of electrical parameters for different coil geometries; green intensity indicates order from lower to higher values; the red borders indicate the final selection

A section of PVC pipe with a standardized outer diameter of 90 mm, between two square wood plates was used as a bobbin around which the copper wire was wound with the aid of a coil winding machine. Some inaccuracies happened due to the manual winding and eventually some of the turns were arranged in a sixth layer until completing 500 turns (Figure 2-14a). This fact, together with the use of a different diameter to that employed in the selection stage produces alterations in the estimated parameters. The impedance was subsequently measured by means of an impedance analyzer (4294A, Agilent Technologies, Santa Clara, CA, USA) with an adapter (16093B, Hewlett-Packard, Palo Alto, CA, USA) for connection of the device to be measured, resulting in $R = 5.16 \Omega$ and $L = 0.017 \text{ H}$, similar to the calculated ones (this resistance must not be compared with that appearing in Table 2-1, but with 4.41Ω , corresponding to copper resistivity of $1.679 \cdot 10^{-8} \Omega \cdot \text{m}$ at 20°C [226], much closer to the temperature of measurement).

An analogous procedure was performed to design the inductor for high frequencies, but in this case the effect of higher frequencies was considered in the calculations. It is well-known that any variable current flowing through a conductor produces a variable MF in the wire itself that induces eddy currents opposed to the main current. This is the cause of the skin effect which makes current density higher on the outer surface of the wire, decreasing exponentially towards its center, which in turns means an increase in the AC resistance. The skin depth δ , depending on the frequency and the copper conductivity (here selected the value at 0 °C, i.e. the inverse of the previously given resistivity) (Eq. 30), is defined as the distance from the region at which the current density reaches $1/e$ ($\approx 37\%$) of its value to the surface, and the external ring of this width is considered as the useful section of wire. Then for a given frequency, the diameter of the cross section area of the conductor should be lower than 2δ for a proper utilization of the wire section.

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \quad (\text{Eq. 30})$$

For 50 kHz and approximating the magnetic permeability of copper to that of vacuum, the resulting skin depth is 0.28 mm, this being lower than the radius of the wire used for low frequencies (0.4 mm). Other detrimental effect for the current conduction at high frequencies is proximity effect. This takes into account the magnetic field induced in a wire cross section by the flow of current through neighbor cross sections, tending also to increase the (alternating current) AC resistance. In order to make up for these effects, Litz wire has been used in the design and construction of the inductor for the high frequency range. This type of wire consists of multiple copper isolated strands twisted and interwoven in a particular way so that each one alternates positions between the center and the surface of the wire, reaching an equal use of all the strands [228]. A Litz wire of 135 strands, 0.07 mm diameter each was employed, having an external diameter of 0.97 mm. Due to the configuration of the wire, the relation between copper and insulation or gaps must be considered. With illustrative purposes, the sum of areas of all of the copper strands would be equal to the area of a circle of 0.81 mm diameter. However for the simulations carried out in the design of the inductor, a previous calculation was considered to substitute the stranded wire by an equivalent solid circular conductor. Instead of changing the diameter of the equivalent circle, resistivity was appropriately varied to contemplate the ratio of copper with regard to the total cross section. Then with the external diameter d of the Litz wire with N_{Litz} strands and the diameter of each strand d_1 , previously given (Figure 2-12), and doing the calculations for a temperature of 0 °C, (direct current) DC resistance can be expressed according to (Eq. 31):

Figure 2-12: Cross sections of: a) Litz wire; b) Equivalent solid wire

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$$R_{DC} = \rho_{Cu,0^\circ C} \cdot \frac{l}{N_{Litz} \pi \frac{d_1^2}{4}} = \rho_{eq,0^\circ C} \cdot \frac{l}{\pi \frac{d^2}{4}} \quad (\text{Eq. 31})$$

from where the equivalent resistivity $\rho_{eq,0^\circ C}$ can be extracted:

$$\rho_{eq,0^\circ C} = \rho_{Cu,0^\circ C} \cdot \frac{d^2}{N_{Litz} d_1^2} = 2.19 \cdot 10^{-8} \Omega \cdot m \quad (\text{Eq. 32})$$

This resistivity has been utilized in the design process, allowing the substitution of a Litz wire by its equivalent round solid wire. It is worth to mention there is no need to consider the AC resistance because the employment of Litz wire is supposed to cancel it out. This time the bobbin has been built with polylactic acid by means of a 3D printer (BQ Witbox, Mundo Reader S.L., Las Rozas de Madrid, Spain), thereby allowing a more precise design. An inner diameter of 115 mm, in such a way that it can hold the SMF generator device of Section 2.1.3, and an outer diameter of 119 mm were selected. The latter logically coincides with the inner diameter of the coil. Then an analysis of different geometries, similar to the said before for the low frequency inductor, was carried out. On this occasion the highest frequency considered (50 kHz) led to bigger inductive impedances which produce voltages higher than 1 kV for 4 or more layers. For that very reason, in order to reduce the DC resistance and above all the inductance, a one-layer arrangement was chosen. Finally 5 cases were compared in Table 2-2, where the maximum operating frequency (50 kHz) has been used. An option with 77 turns (1 x 77) was chosen, showing intermediate values for RMS voltage and dissipated power.

Width (mm)	Height (mm)	Scale factor, k	Layers	Total turns, N	L (μH)	R (Ω)	I _{RMS} (A)	P (W)	Z (Ω)	U _{RMS} (V)
1	70	2.16	1	72	555	0.81	1.53	1.88	174.25	266.14
1	75	2.03	1	77	610	0.86	1.44	1.78	191.49	274.87
1	80	1.95	1	82	665	0.92	1.38	1.75	209.02	288.21
1	100	1.62	1	103	907	1.15	1.15	1.51	285.06	326.54
1	120	1.43	1	123	1146	1.38	1.01	1.41	360.15	364.18

Table 2-2: High frequency range inductor: comparison of electrical parameters for different coil geometries; green intensity indicates order from lower to higher values; the red borders indicate the final selection

According to the calculated inductor, the support bobbin was designed by means of a 3D CAD design tool (Tinkercad, Autodesk, Inc., Mill Valley, CA, USA), obtaining the corresponding file with extension .STL. Afterwards it was converted, with the help of a software package (Cura v. 15.04, Ultimaker, Geldermalsen, Netherlands) into another file with extension .gcode, readable by the 3D printer (Figure 2-13).

Figure 2-13: Construction of the bobbin for the high frequency range inductor: a) Design with Tinkercad software; b) Translation into an readable archive for 3D printing with Cura

The bobbin was printed in two halves and glued together to form an only piece. Its total height was 94 mm (including bases 4 mm high) with 86 mm for winding the wire. Again due to imprecisions during the operation which reduced the filling factor, only 75 turns could be completed (Figure 2-14b). In this case it was decided not to wind the two remaining turns in a second layer because 75 turns yields also proper electrical parameters as can be interpolated from Table 2-2. The inductance and equivalent series resistance (ESR) of the coil for high frequencies was evaluated by the impedance analyzer, resulting in $R = 990 \text{ m}\Omega$ and $L = 562 \text{ }\mu\text{H}$, similar to those interpolated from table 2 which were $910 \text{ m}\Omega$ (corrected value at $20 \text{ }^\circ\text{C}$) and $590 \text{ }\mu\text{H}$ respectively. Also by interpolation a target RMS current of 1.47 A, to generate the required MF strength of 0.8 mT, has been found. For design of the rest of the circuit, the values provided by the impedance analyzer have been used, since are considered closer to the real impedance.

Figure 2-14: a) Low frequency range inductor; b) High frequency range inductor

Despite having thought initially the utilization of both air core inductors, each within its own frequency range, only the one for high frequencies was employed henceforth. Several reasons can be argued to explain this option. First of all the high-frequency inductor is totally valid in the whole range of interest (1 Hz to 50 kHz) without adding skin effects and, the use of an only coil contributes to simplify circuit operation. As previously mentioned, its higher bobbin internal diameter allows the insertion of the SMF generator device, facilitating the jointly study of both types of fields and their possible synergetic effects during freezing. It is true that the dissipated power is higher in the selected coil, 2.14 W compared with 0.15 W in the low-

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frequency coil (calculated from the FEM modelled current and the measured resistance), but it remains within a reasonable value, although an experimental assessment of the increase of temperature within the freezing equipment would be desirable. However, the bigger current which causes this inconvenience allows in turn an increase in the resolution of MF strength so as to change its value with higher accuracy.

2.1.5.3. Setting in motion the OMF air core freezing system

The solenoid for the higher frequency range, shown in Figure 2-14b was disposed in an embedded fixed position inside the Whirlpool freezer mentioned in Section 2.1.4 (Figure 2-15):

Figure 2-15: Air core OMF inductor and sample placed inside the laboratory magnetic freezer

In the same way as it is described in Section 2.1.4 for the case of the iron core OMF generator, the heat dissipated as a consequence of the Joule effect must be considered. As mentioned in the previous Section 2.1.5.2, this active power is 2.14 W (in the nominal conditions of 1.47 A flowing through the ESR of 990 m Ω of the solenoid). An equivalent power has to be dissipated in the control experiments without OMF in order to get the same temperature conditions inside the freezer. For that reason, as previously done in the case with the iron core inductor (Section 2.1.4), the set of three electric heating wires presented in that Section, whose resistance was 56 Ω , was in this case put at a 10.8 V DC voltage.

2.1.5.4. Initial prototyping of the inverter for EM field in a wide range of low frequencies

At this point it should be necessary to take into account that part of the work here presented corresponds to the works, carried out as the Final Projects to obtain the Engineering Degree in Industrial Technologies [229, 230] and the Engineering Degree in Energy [231], all of which were co-tutored by the author of this thesis.

Once the air core inductor for generating the OMF in a wide range of frequencies (1 Hz to 50 kHz) has been created, it must be supplied with a sinusoidal current $I_{load, RMS} = 1.47$ A, as explained in section 2.1.5.2. For this purpose a frequency-variable single-phase inverter device was planned, converting the voltage supplied by a DC power source into OMF current.

For the achievement of a sinusoidal current, a series of pulses will be applied to the load through the inverter. These pulses, possessing a certain periodicity, can be decomposed into Fourier series formed by an infinite sum of sines and cosines. The fundamental frequency of the applied pulsed waveform must correspond to the frequency of the target sinusoidal current, which will be obtain by doing in some way a low-pass filtering to remove high-frequency harmonics. In addition the magnitude of the RMS voltage between the terminals of the inductor, $U_{load, RMS}$ can be calculated by applying Ohm's law to the impedance of the inductor:

$$U_{load, RMS} = \sqrt{R^2 + (2\pi f \cdot L)^2} \cdot I_{load, RMS} \quad (\text{Eq. 33})$$

and this is displayed in the following Table 2-3 [231] for the whole range of frequencies. Analyzing those results and taking into account the values of resistance (0.99Ω) and current (1.47 A), it is patent the resistive behavior of the coil at the lowest frequencies. After the cutoff frequency of the resistive and reactance impedances in the coil, i.e. the frequency at which R equals ωL , which is 280 Hz for the high-frequency inductor coil, its response has basically inductive character. This is the reason for the change in apparent power, whose value is equal to the active power (2.14 W) at low frequency but achieves a maximum of 382 VA at 50 kHz.

Frequency, f (Hz)	Voltage across inductor, $U_{load, RMS}$ (V)	Apparent power, S (VA)
1	1.46	2.14
2	1.46	2.14
5	1.46	2.14
10	1.46	2.14
20	1.46	2.14
50	1.48	2.17
100	1.55	2.27
200	1.79	2.63
500	2.98	4.37
1000	5.39	7.92
2000	10.48	15.41
5000	25.99	38.21
10000	51.93	76.33
20000	103.83	152.62
40000	207.64	305.23
50000	259.54	381.53

Table 2-3: RMS voltage and apparent power at inductor terminals for different frequencies

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In order to attain inverter functionality, only those topologies allowing bidirectional current through the load can be used, like the classical push-pull, half-bridge or full-bridge. Within these, a full-bridge topology (also known as H-bridge) was selected for this application, which produces lower switch voltage stresses than those of push-pull and half-bridge inverter topologies, assuming the same current flow through the load. For the present design, instead of the transformer and the output circuit (at the secondary side of the transformer) usually placed between the bridge and the load, this latter, i.e. the built inductor has been directly put at the bridge terminals (Figure 2-16). Albeit the elimination of the transformer implies a loss of electric isolation between input and output as well as loss of the possibility to advantageously use turns ratio to adjust output voltage and current, it is not present in this design because apart from saving space and transformer core losses, the relatively large frequency bandwidth which must be covered (full-bridge transformer operates at switching frequencies, which in principle could be thought as proportional or related to the range of interest, i.e. 1 – 50000 Hz) would complicate the design of this transformer.

Figure 2-16: Schematic diagram of the full-bridge inverter with inductor as load

In the full-bridge topology, the opening and closing of switches are adequately controlled so that the required load voltage or current are obtained. As can be appreciated in Figure 2-16, the four selected switches (S_1 to S_4) were N-Channel MOSFETs (their source-to-drain body diodes and output stray capacitors have also been depicted) instead of IGBTs, mainly because the latter are not suitable for high switching frequencies and would only be interesting for higher powers [232] than those employed. For this experimentation-focused application, Silicon-based MOSFETs fulfilled sufficiently requirements and more expensive SiC or GaN switches were not considered [233].

In full-bridge converters, independently of the algorithm of switching, there are some common features, the main one being that both switches of a same leg cannot be simultaneously on, to avoid the short circuit of the DC power supply by shoot-through. Then, given the notation polarity references used in Figure 2-16, three basic states can be considered: when switches S_1 and S_4 are on, the coil terminals are positively biased with practically all the input voltage U_{in}

and, consequently, current I_{load} through it increases; analogously, when switches S_2 and S_3 are on, a negative voltage $-U_{in}$ drops across the load and current decreases; on the other hand if S_1 and S_3 or S_2 and S_4 are on, then the coil is short circuited and the absolute value of I_{load} , which ideally would remain constant, tends to diminish exponentially by discharging the inductor through the ESR of coil and MOSFETs, with a time constant equal to the division of inductance by that sum of resistances. It is important to mention that when some MOSFET is off and the other of the same leg is on, the drain-to-source voltage V_{DS} of the former will be equal to the input voltage U_{in} and, therefore this is the voltage that its drain-to-source intrinsic capacitor needs to discharge completely before being turned on if zero voltage switching (ZVS) is pursued. This discharge can be produced in a resonant manner by the current circulating through the inductor [234].

For the generation of the sinusoidal current at the inverter output, it is necessary to apply a series of control signals to adequately turn on and off the four MOSFETs of the bridge. The obtainment of control signals for driving MOSFETs would be performed by pulse width modulation (PWM) for the initial prototype. Thus the opening and closing of each MOSFET is carried out by comparison of two control signals: a triangular (or a saw tooth) signal at a about the switching frequency $f_{carrier}$, also called the carrier signal; and a sinusoidal signal, known as reference or modulating signal, whose frequency f_{ref} coincides with that wished at the output. When the reference signal exceeds the carrier signal, then one switch is turned on and the other one of that leg is turned off, switching again when the reference becomes lower than the carrier. In that way the variable-width (variable duty cycle) control pulses, able to produce a sinusoidal current through the inductor, are generated, as can be appreciated in Figure 2-17 for the particular case of bipolar control which is explained in Section 2.1.5.5. Two parameters are defined from this sinusoidal PWM (SPWM) procedure, namely amplitude modulation index m_A (Eq. 34), which is the ratio between peak voltages of reference and carrier signals, and frequency modulation index m_F (Eq. 35), which corresponds to the carrier frequency divided by the reference frequency:

$$m_A = \frac{\hat{U}_{ref}}{\hat{U}_{carrier}} \quad (\text{Eq. 34})$$

$$m_F = \frac{f_{carrier}}{f_{ref}} \quad (\text{Eq. 35})$$

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Figure 2-17: Bipolar switching waveforms for SPWM: a) Triangular carrier signal (blue), sinusoidal reference (red); b) Output voltage (green) and its fundamental harmonic (orange dashed)

Depending on the magnitude of m_A , three different operation regions can be described (Figure 2-18):

- Linear region: for $m_A \leq 1$, where the amplitude of the output voltage first harmonic varies linearly with m_A . Harmonics of this signal appear at frequencies multiple of the switching frequency.
- Overmodulation region: for $m_A > 1$ there is an initial part where first harmonic amplitude continues growing but nonlinearly. Many more harmonics appear in the sidebands, compared with the linear region. Now there are odd harmonics multiple of the fundamental frequency and filtering is more complicated, requiring larger reactive components.
- Saturation region: from a certain m_A onwards, PWM degenerates in square wave (harmonic content with odd multiples of the fundamental frequency). The amplitude of this square signal remains constant and therefore the output voltage cannot be regulated. The number of switchings per cycle and hence switching losses, however, are clearly reduced.

Figure 2-18: RMS voltage at the inverter output with regard to amplitude modulation index

For the present inverter it was decided to work in the linear region because of linearity and lower spectral content although an assessment of the acceptable total harmonic distortion (THD) (Eq. 40) introduced for $m_A > 1$ would have allowed applying to the load voltages over the input RMS voltage, reducing that way the needed input voltage [235]. Thus, (Eq. 36) applies to the calculation of the input DC voltage needed in the inverter:

$$U_{in} = \frac{\sqrt{2} \cdot U_{load,RMS}}{m_A} \quad (\text{Eq. 36})$$

and for the maximum RMS voltage given in Table 2-3 at 50 kHz, multiplying by $\sqrt{2}$ as it is a sinusoidal waveform, a minimum input voltage of 367 V (at the limit of the linear zone, i.e. $m_A = 1$) would be necessary. However, around the maximum and minimum of the sine waveform, as it is the narrowest part of the carrier signal, SPWM will give rise to duty cycles upper or lower than a certain value which may cause that the narrowest pulses do not get the opening or closing of MOSFETs because of, among other reasons, dynamic characteristics of components which cause signal propagation delays, and then the actual m_A limit for linear behavior must be < 1 , involving an increase of U_{in} . But this circumstance has not been considered in the calculations and the previous voltage (367 V) has been taken as maximum input voltage.

Regarding m_F , it must be taken into account that, when working in the linear zone, the harmonic spectrum shows only content at $f_{carrier}$ and at their multiples, i.e. m_F , $2m_F$, $3m_F$, etc. of the fundamental frequency, as well as sidebands centered at each of these baseband harmonics [236]. Then, with regard to m_F , the bigger its value, the higher the frequency of harmonic appearance which makes it easier to cancel them out. However a too high m_F will redound to higher switching losses and consequently a trade-off should be made. The intention in this particular case was to apply different m_F values adapted to each output frequency, such that at lower frequencies a value m_F of 100 would generate a sinewave smooth enough. On the other hand, for 10 kHz or higher, keeping that m_F would imply switching frequencies above 1 MHz, with increased switching losses and EMI issues. This problem aggravates enormously in this design where voltage rises proportionally with output frequency. Hence a maximum switching frequency of 500 kHz (corresponding to $m_F = 100$ for 5 kHz sine frequency) was thought for the output frequency range from 5 to 50 kHz, calculating in each case the integer m_F whose equivalent switching frequency was closest and below that limit. In order to appreciate qualitatively the distortion introduced in the sinusoidal current for the smallest m_F values, simulator software PSIM (v. 9.1.1, Powersim Inc., Rockville, MD, USA) was employed. Simulation results for three different frequencies and m_F are shown in Figure 2-19:

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Figure 2-19: Output current at the selected conditions for switching frequency = 500 kHz: a) Output frequency = 5 kHz, $m_f = 100$; b) Output frequency = 20 kHz, $m_f = 25$; c) Output frequency = 50 kHz, $m_f = 10$

In order to proceed with the design of the inverter, the followed step was selection of components. An analysis of the voltage and current conditions at which they will be working is needed for this purpose. Thus the maximum voltage applied to each MOSFET is that of the DC power source U_{in} , when the other MOSFET of the same leg is on. Then the needed input voltage in the most demanding case (50 kHz) was employed in the calculation, applying as well a safety factor of 80 %:

$$V_{DS} \cdot 0.8 \geq U_{in,max} \quad (\text{Eq. 37})$$

resulting in a maximum admissible V_{DS} of 458.75 V. It must be pointed out that although the V_{DS} indicated in MOSFET datasheets is RMS value, it is compared with the voltage peak value (coincident with the input supply DC voltage) to add an extra safety margin. Analogously the

maximum peak current $\hat{I}_{load,max}$ passing through the MOSFET, i.e. 2.08 A ($1.47A \cdot \sqrt{2}$) has been used to calculate the drain current I_D that the chosen MOSFETs must be able to withstand, whose value was 2.6 A, worked out from:

$$I_D \cdot 0.8 \geq \hat{I}_{load,max} \quad (\text{Eq. 38})$$

Consequently for the initial prototype, four MOSFETs (STP5NB60, STMicroelectronics, Geneva, Switzerland) with $V_{DS} = 600$ V, and $I_D = 5$ A at 25 °C and 3.1 A at 100 °C, this latter being expected to be closer to the actual working temperature. With regard to power losses, as these MOSFETs are not the finally employed ones, their calculation is described in Section 2.1.5.5.1.

As it is well-known, the operation of the full-bridge inverter requires the flow of current from source to drain in switches. When both MOSFETs of a leg are going to change states (between turned-on and turned-off), started by the opening of the conducting MOSFET, a resonant charge and discharge of their respective drain-to-source parasitic capacitances is produced, through the inductor current (see Section 2.1.5.5.1). Once the initially charged MOSFET drain-to-source parasitic capacitor is discharged, its MOSFET body diode (represented in Figure 2-16) starts conducting [237], clamping in this way the voltage across MOSFET. A problem which could arise during MOSFET opening is related to the reverse recovery characteristics of its body diode. When a conducting diode is oppositely biased current does not go immediately to zero but there is a time (reverse recovery time, t_{rr}) in which current goes from cathode to anode, instead of being blocked. The interval in which both anode-to-cathode voltage and current have the same polarity gives rise to power losses. In this design, four external parallel ultrafast diodes (HFA08TB60, Vishay Intertechnology, Inc., Malvern, PA, USA) between source and drain have been included to reduce this problem. This model can block 600 V from cathode to anode and allow for up to 8 A forward current. [238] reported some efficiency enhancement by adding external SiC Schottky diodes in parallel to the MOSFETs of a bidirectional inverter topology, though maybe not so high as to justify the increase of volume, cost and complexity. The addition of parallel diodes needs a lower forward voltage V_F (from anode to cathode) in the external diodes than in the body diodes, forcing current going through the former, although impedances of PCB tracks connecting MOSFET and external parallel diode have to be low enough so that current found less resistance through the external diode path. It could be interesting to consider parallel diode integrated in the MOSFET package for this purpose [239, 240].

Selection of inverter input capacitors is explained in Section 2.1.5.5 which deals with the description of MOSFET driving SPWM algorithm (bipolar or unipolar). Several input capacitors in parallel are used in the design, whose equivalent capacitance is represented in Figure 2-16. They are mainly intended for the filtering of the harmonic content of the current going into the H-bridge, in such a way that the current coming from the power supply has principally DC component, reducing the voltage ripple at the power supply. In this first prototype, an aluminum electrolytic capacitor of 470 μ F and 4 ceramic capacitors of 33 nF were selected. The former is a bulk capacitor able to manage low frequency components. It is well-known that real capacitors can be modelled by an ideal capacitor in series with an ESR and equivalent series inductance (ESL). Both impedances have high values in the case of electrolytic capacitors. Then the pass of high frequency harmonics of current through this type of

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capacitors brings about an increase in the ripple voltage as well as the subsequent dissipated heat. The addition of ceramic capacitors allows handling those high frequency issues.

These MOSFETs, antiparallel diodes and capacitors, together with the DC power source and junction elements (wires, connectors, printed circuit board (PCB) tracks, etc.) constitute the basic power stage. It is necessary to add the logic for driving those MOSFETs, which will be carried out through a digital signal processor (DSP). Signals governing MOSFETs coming from the corresponding DSP output ports have to be adapted before reaching MOSFET gates. That is the mission of drivers, which receive low power input signals from DSP and provide at their output a high-current gate drive for a fast turning-on and turning-off of transistors, by rapid charge and discharge of their input parasitic capacitances. For the present application, two drivers (IR2110, Infineon Technologies AG, Neubiberg, Germany) were selected, each one controlling the two switches of the same leg.

Any driver controlling both MOSFETs of a leg has to provide them with a proper gate-to-source voltage V_{GS} (e.g. between 10 and 20 V) which is not problematic for the low side switches because they are referenced to ground (as happens with their respective drivers), but at the high-side MOSFET of each leg, wherein its source is a floating point, the voltage at its gate would have to be higher than the inverter input voltage U_{in} . To solve this problem, one of the typical methods for N-channel MOSFETs is bootstrap [241, 242]. It has been used in the inverter design, as IR2110 drivers integrate part of the circuitry needed for implementation of this technique, being necessary to connect externally a capacitor (C_{boot}) and a diode (D_{boot}) as shown in Figure 2-20. Bootstrap is based on a floating channel connected to the source of the high-side MOSFET. This channel swings between ground and U_{in} . When the lower-side MOSFET is on, the floating channel is connected to ground, allowing the charge of C_{boot} at V_{CC} supplied by the driver. This voltage which is referenced to the floating channel can be afterwards employed to drive the high-side MOSFET. On turning on the high-side MOSFET, C_{boot} is discharged via pin V_B (internally connected to high-side output pin H_O) and not through V_{CC} thanks to the blocking action of D_{boot} . This discharge, which implies a reduction of V_{GS} , has to be slow enough not to bring MOSFET to a turn-off condition during on-time of that high-side MOSFET, t_{on} . That way the minimum bootstrap capacitance $C_{boot,min}$ has been obtained as the total charge supplied by the bootstrap capacitor Q_{total} divided by the maximum allowable voltage drop ΔV_{boot} . Both numerator and denominator can be worked out by using, for instance, the application note [241]:

$$C_{boot,min} = \frac{Q_{total}}{\Delta V_{boot}} = \frac{Q_G + (I_{LKcap} + I_{LKGS} + I_{QBS} + I_{LK} + I_{LKdiode}) \cdot t_{on} + Q_{LS}}{V_{CC} - V_{diode} - V_{GS,min}} \quad (\text{Eq. 39})$$

where Q_G and Q_{LS} are the charges at the transistor gate and at the level shifter inside the driver, respectively; I_{QBS} is the quiescent V_{BS} supply current in the driver; I_{LKcap} , I_{LKGS} , I_{LK} and $I_{LKdiode}$ are a series of leakage currents at different parts of the discharge circuit (defined in [241]); V_{diode} is the forward voltage of D_{boot} and $V_{GS,min}$ is the minimum gate-to-source voltage for the MOSFET to remain in on-state. Nonetheless bootstrap capacitance should not be too high in order not to increase time needed to refresh C_{boot} , which always limits the available duty cycle.

Figure 2-20: IR2110 driver and basic connections including bootstrap circuit for the excitation of high-side N-channel MOSFET (extracted from [229])

As can be seen in Figure 2-20 a gate resistor R_{gate} , has been added. This component contributes to reduce switching speed, decreasing that way the EM noise and ringing which appears due to resonance between stray inductances along the switching path and parasitic capacitors of MOSFETs. Another benefit is protection of driver's integrated circuit (IC) by reducing peak current and power dissipation inside. However a very high resistance should not be chosen so as not to increase switching losses because of a rise of switching time. An additional downside of higher gate resistors comes from an increment of gate voltage due to the current returning to the driver through the gate-to-drain parasitic capacitance by a high rise of MOSFET's V_{DS} . This V_{GS} increase may give rise to hazardous parasitic turn-ons which could cause full-bridge shoot-throughs [243]. Consequently a gate resistor of less than 20Ω will be selected.

Once all components were chosen, a first design of the printed circuit board (PCB) on which they were going to be located was carried out. For this purpose, the PCB design software package Altium Designer (v. 13.2.5, Altium Ltd., San Diego, CA, USA) was used. Inside a PCB project file, Altium Designer allows dealing with schematic sheets (file .SchDoc) where the different components which configure our circuit, extracted from libraries, and their electrical connections are placed. One important feature of Altium Designer is that symbols which appear in the schematic diagram allow the attachment of several models: SPICE model for simulation, signal integrity description, 3D model and footprint. However simulation functionality of Altium Designer has not been used here. The parts of the schematic diagram corresponding to the power stage and to the drivers of the preliminary prototype are shown in Figure 2-21:

[illegible]

plane has been split into two different planes, one for the return of low voltage noisy digital control signals and the other one for higher voltage, less noisy, power stage currents. Both ground planes were connected at one point by a $0\ \Omega$ resistor, so that they did not constitute a dipole antenna, but had the same voltage reference [246, 247]. The eventual PCB layout, after applying several design rules such as those regarding trace clearance, as well as the physical implementation of the first prototype are shown in Figure 2-22 and Figure 2-23, respectively:

Figure 2-22: PCB layout of the first prototype: a) Top layer with power planes; b) Bottom layer with ground planes (extracted from [231])

As the PCB was constructed before the implementation of the algorithm to govern drive signals, a preliminary test as a DC-DC converter was intended. However due to the break of some components and mostly to the necessity of correcting some aspects of the design, a second prototype was required. Thus one of the greatest concerns in PCB design is the reduction of current loop areas which act as a source of EMI. In that regard it is well known that return currents tend to flow along the least impedance path, so at low frequencies it will look for the least resistive path (the shortest route within the ground plane) whereas at high frequencies it will look for the least inductance one. Consequently, return currents show a trend to flow under their corresponding signal traces, which reduces loop current sizes. Then the presence of those long traces in the ground planes hinders the returning of current through the least impedance routes and produces as well bigger EMC problems. As can be seen in Figure 2-22, the position of power supply connectors and input capacitors originate some imbalance of lengths for the different signals which may produce undesired asynchronies.

Figure 2-23: View of the preliminary prototype of inverter (extracted from [231])

Therefore with the goal of improving inverter's operation, the second prototype offered a more symmetric distribution, as seen in Figure 2-24. On this occasion power planes were removed although the width of the traces of the power stage, which have to carry the highest currents, was increased from 0.9 to 2 mm, instead. Another enhancement of this design came by a higher removal of ground plane slots, facilitating the return of currents.

Figure 2-24: PCB layout of the second prototype: a) Top layer; b) Bottom layer with ground planes (extracted from [229])

However posterior considerations made it necessary to redesign the PCB in order to fulfill new introduced specifications.

2.1.5.5. Process of adaptation of the initial inverter to achieve sinusoidal magnetic fields suitable for electromagnetic freezing of foods

In this particular application it is important to obtain an essentially sinusoidal waveform in order to be able to discriminate between the effects that different frequencies could have on magnetic freezing of foodstuffs. For the consecution of this objective, some filtering of the output current must be carried out. However, the selection of an adequate switching approach is necessary in order to facilitate this purpose. Before starting the improvement of the initial

prototype (see Section 2.1.5.4), an evaluation of two possible switching strategies has been carried out. Our interest was focused on either applying PWM within the linear region of Figure 2-18 or alternatively on applying a square wave of voltage at the output frequency across the load. This latter option contributes as well to reach an advantageous reduction of switching losses and a much simpler switching drive algorithm. But on the other hand, as mentioned in section 2.1.5.4, applying the fast Fourier transform (FFT) to obtain the frequency spectrum, higher harmonic content appears at odd multiples of the output desired frequency. An approximate solution of less harmonic content could be contemplated by the utilization of a trapezoidal or even a triangular current waveform, by means of phase-shift [248], even though these lower harmonics appear at the same odd multiples. This method applies also square waves of 50% duty cycle at switches but introducing a displacement of phases between the two legs of the bridge. This phase shift creates regions where the voltage applied to the load cancels out.

For the filtering of the square wave output signal in order to obtain a sinusoidal current, a low-pass filter could be used, but instead of this, a resonance filter was proposed here, taking advantage of the inductive load. This way, the addition of the pertinent capacitors in series, which resonate with the coil inductor at the desired target frequencies, generates a band-pass filter which rejects quite well frequencies different to that one, obtaining the pursued sinusoidal current. Taking advantage of this fact, simply a square wave will be applied here, instead of introducing phase-shift algorithms whose control is more complex. An extra benefit of resonant inverters derives from the fact that in a LC series resonance circuit, both impedances cancel each other out, reaching the desired current for lower values of voltage across the load since this latter is proportional only to the ESR of the solenoid, considered constant in all the frequency range if skin and proximity effects have been sufficiently counteracted.

Therefore, apart from getting the main purpose of applying a quite sinusoidal OMF, this configuration of series resonant inverter could additionally give rise to an inferior required voltage, to a reduction of switching frequency, as it coincides with output frequency, and to a consequent simplification of MOSFET driving signals and reduction of switching losses. One of the drawbacks of this solution, however, is due to the fact that for the inductive load, the tuning of each frequency needs a different capacitance. Then, in order to encompass a sufficient number of frequencies along the whole range (1 Hz to 50 kHz) it could be thought about the utilization of a fix connector, e.g. socket headers or screw terminals, allowing for an easy change of capacitors. Nonetheless it is necessary to evaluate the capacitance needed within that range. With that purpose, the capacitors required to produce resonance at a number of frequencies with the two constructed coils, the one for low frequency range (higher L) and the one for high frequency range (lower L) can be seen in Table 2-4.

Frequency (Hz)	1	10	100	200	500	1000	2000	5000	10000	20000	30000	40000	50000
Low L resonant capacitance (F)	45.07	0.45	4.5E-03	1.1E-03	1.8E-04	4.5E-05	1.1E-05	1.8E-06	4.5E-07	1.1E-07	5.0E-08	2.8E-08	1.8E-08
High L resonant capacitance (F)	1.49	1.5E-02	1.5E-04	3.7E-05	6.0E-06	1.5E-06	3.7E-07	6.0E-08	1.5E-08	3.7E-09	1.7E-09	9.3E-10	6.0E-10

Table 2-4: Capacitances for resonance of the low inductance and the high inductance coils at several frequencies

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The highest problems appear at the lowest frequencies, as might be expected, where too big capacitors are required even using the inductor designed for the smallest frequencies of the range. It is therefore unfeasible to employ the square wave solution in the entire range but it has been profitably used at the highest frequencies, namely from 10 to 50 kHz.

Consequently a modulated control technique was used in the low frequency range, whereas square wave with resonant capacitor was applied for the highest frequencies. As mentioned in Section 2.1.5.4, there are typically two switching strategies in PWM inverters: unipolar and bipolar. The explanation of both mechanisms is made below, using the notation of Figure 2-16:

- Bipolar modulation: there is one reference signal compared to the triangular or saw tooth carrier signal. This governs the simultaneous opening or closing of MOSFETs placed at each of the two diagonals of the H-bridge. Hence when $U_{ref} > U_{carrier}$ (Figure 2-17) MOSFETs S_1 and S_4 are on (S_2 and S_3 are off) and the voltage drop across load terminals is basically U_{in} . On the contrary when $U_{ref} < U_{carrier}$, S_2 and S_3 are on (S_1 and S_4 off), applying $-U_{in}$ across the coil terminals.
- Unipolar modulation: the control of switching is carried out by means of two sinusoidal reference signals (ref_1 and ref_2), each one being the inverse of the other. Both are compared to the same carrier signal, but instead of controlling the opening and closing of MOSFETs placed in each diagonal, each reference is aimed at providing the drive signal for both MOSFETs of one leg. When $U_{ref1} > U_{carrier}$, then S_1 is on and S_2 is off, putting point 'a' at U_{in} voltage, while this point is connected to ground if $U_{ref1} < U_{carrier}$. The other leg is analogously controlled through ref_2 , i.e. when $U_{ref2} > U_{carrier}$, S_3 is on and S_4 is off, turning off and on, respectively, when $U_{ref2} < U_{carrier}$. It must be highlighted that during the positive half cycle of ref_1 (negative half cycle of ref_2) the voltage at the load terminals oscillates only between $+U_{in}$ and 0, whereas in the negative half cycle of ref_2 it changes between $-U_{in}$ and 0 Figure 2-25:

Figure 2-25: Unipolar switching waveforms for SPWM: a) Triangular carrier signal (dark blue), sinusoidal references ref1 (red) and ref2 (magenta); b) Voltage from a to ground; c) Voltage from b to ground; d) Output voltage (green) and its fundamental harmonic (orange dashed)

One of the advantages of unipolar versus bipolar switching is the fact that in the former, output voltage leaps are halved, which is why those algorithms receive their respective names. Considering that our goal is to get essentially sinusoidal currents, bipolar and unipolar PWM methods have been evaluated with the assistance of the corresponding simulation models, improved from those given in [230] with PSIM, Figure 2-26 and Figure 2-27, respectively:

Figure 2-26: Schematic circuit for simulation of bipolar PWM full-bridge inverter

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Figure 2-27: Schematic circuit for simulation of unipolar PWM full-bridge inverter

Concerning the parity of the frequency modulation index m_F , and under the assumption of $m_A < 1$, the utilization of an integer odd m_F in bipolar modulation brings about an output voltage waveform (Figure 2-17b) with half-wave symmetry, i.e. at every instant t , it can be seen as a function f verifying $f(t) = -f(t + T/2)$, where T is the period of the reference signal. Then it only contains odd harmonics, although the sidebands of even harmonics remain, so an even m_F is not advised, above all for small m_F values if an optimization of the sinusoidal waveform is pursued [249]. On the contrary, in unipolar modulation only an even m_F gives rise to half-wave symmetry in the output voltage waveform (Figure 2-25d), because the voltages from points a and b to ground (Figure 2-25b and Figure 2-25c) are 180° out of phase and with an even m_F , the different of phases $\Phi_{ab} = 180^\circ \cdot m_F = 0^\circ$. But on this occasion there is an extra benefit because the switching frequency is “effectively” doubled and the harmonic content amounts only to sidebands around harmonics at even multiples of m_F ($2m_F$, $4m_F$, etc.) [236, 250]. A quantitative evaluation of the harmonics present in the output current waveforms for both PWM techniques has been carried out with the help of PSIM simulator which supplies the THD (in %):

$$THD = \frac{\sqrt{I_{2,RMS}^2 + I_{3,RMS}^2 + I_{4,RMS}^2 + \dots}}{I_{1,RMS}} \cdot 100 \quad (\text{Eq. 40})$$

where $I_{1,RMS}$, $I_{2,RMS}$, etc. are the first, second, etc. harmonics of the output current. The closer this THD is to zero, the better the sinusoidal approach. The simulations of bipolar and unipolar mechanisms were performed, applying the proper input DC voltage U_{in} for the obtainment of 1.47 A in the low impedance coil, and frequencies of 5, 50, 500 and 1000 Hz. Amplitude and frequency modulation indexes, m_A and m_F , were respectively chosen as 0.8 and 49 in bipolar modulation and 0.8 and 50 in unipolar modulation. A triangular carrier signal waveform was also employed. Under those conditions the THD of output current is shown in Table 2-5:

THD (%)

Frequency (Hz)	Bipolar PWM	Unipolar PWM
5	94.4	33.1
50	14.5	4
500	2.8	1
1000	2.4	0.7

Table 2-5: Total harmonic distortion of bipolar and unipolar modulations in a range of frequencies for the low impedance coil

As well as THD values, plots of those simulations both in the time domain and the frequency spectrum with the harmonic content of the output RMS current, through the application of the FFT, have been depicted in Figure 2-28 (5 Hz), Figure 2-29 (50 Hz), Figure 2-30 (500 Hz) and Figure 2-31 (1 kHz). It is clear that unipolar modulation is the option which presents a more sinusoidal behavior due to its reduced harmonic content, although the lower the frequencies the lesser the accuracy of sine waveforms. This is due to the fact that in the widest pulses, current through the coil even reaches steady state. This is appreciable in the exponential waveform it takes within those pulses in Figure 2-28a. A more detailed analysis could be done comparing the pulses width with the time when steady state is considered reached (5τ , with τ the time constant of the load, i.e. L_i/R_i). It can be checked that $\tau = 3.3$ ms for the coil built for low frequencies and $\tau = 0.57$ ms for the high frequency coil. The distortion introduced may lead to reconsider the use of the coil designed for low frequency operation if interesting results were obtained under 10 Hz, although for the sake of simplicity the design process has been continued with the coil for the highest frequencies. As for the carrier waveform, as far as harmonic content is concerned, a triangular waveform has been preferred to a saw tooth (up or down) waveform, since the even character of the former eliminates odd harmonics of the fundamental frequency, contributing that way to a better consecution of our goals.

Figure 2-28: Simulations at 5 Hz: a) Bipolar modulation in time domain; b) Bipolar modulation current harmonic spectrum; c) Unipolar modulation in time domain; d) Unipolar modulation current harmonic spectrum

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Figure 2-29: Simulations at 50 Hz: a) Bipolar modulation in time domain; b) Bipolar modulation current harmonic spectrum; c) Unipolar modulation in time domain; d) Unipolar modulation current harmonic spectrum

Figure 2-30: Simulations at 500 Hz: a) Bipolar modulation in time domain; b) Bipolar modulation current harmonic spectrum; c) Unipolar modulation in time domain; d) Unipolar modulation current harmonic spectrum

Figure 2-31: Simulations at 1 kHz: a) Bipolar modulation in time domain; b) Bipolar modulation current harmonic spectrum; c) Unipolar modulation in time domain; d) Unipolar modulation current harmonic spectrum

2.1.5.5.1. Minimization of the power losses in the switches of the inverter for electromagnetic freezing of foods

Although for this particular application, the consumed power is pretty low, it should be considered also the approach providing the lowest power losses, as long as it is the solution which yields the above referred highly sinusoidal current waveform. The switching transitions differ between both methods. According to the notation of Figure 2-16 those transitions in the bipolar PWM are:

- MOSFETs S_1, S_4 on $\rightarrow$ off / S_2, S_3 off $\rightarrow$ on, and $I_{load} > 0$: stray drain-to-source capacitors of S_2 and S_3 initially charged at U_{in} , tend to discharge in a resonant way via the inductive load. When totally discharged, the parallel diodes D_2 and D_3 get forward biased and start to conduct before the closing of S_2 and S_3 , having ZVS. For this purpose, the energy stored in the inductor L has to be greater than that stored in both MOSFET output capacitances C_{ds} :

$$\frac{1}{2} \cdot L \cdot I_{load}^2 > \frac{4}{3} \cdot C_{ds} \cdot U_{in}^2 \quad (\text{Eq. 41})$$

where the term on the right is the double of the energy stored in the output capacitor, which is nonlinear, depending on the inverse of the square root of the voltage [237, 251]. The MOSFETs chosen for the final design were SPW47N60C3 (Infineon Technologies AG, Neubiberg, Germany). Estimating C_{ds} as $C_{oss} - C_{rss}$ from that MOSFET datasheet (data at 25 V), the minimum current I_{load} able to discharge those capacitances (achieving ZVS) for the case of 5 kHz ($U_{in} = 36.76$ V) would be 0.11 A. For a RMS current of 1.47 A, it means that only during 3.52 % time of each output current cycle these transitions are not getting ZVS. For lower frequencies, i.e. lower voltages, this percentage reduces even more, so the closing of S_2 and S_3 has been simplified as a soft switching transition in all cases. As for the dead times between the closing of S_1 and S_4 and the opening of S_2 and S_3 , to ensure ZVS at the above obtained limit, the dead time t_d should be $\geq$ a quarter of the resonant period, which for this design is:

$$t_d = \frac{2\pi\sqrt{L \cdot 2C_{ds}}}{4} = 2.4 \mu s \quad (\text{Eq. 42})$$

In the time intervals where the energy stored in the coil is higher than that stored in drain-to-source capacitors, smaller t_d could be selected without any detriment in ZVS. However a fixed t_d value has been selected for simplicity.

This transition is equivalent to S_2, S_3 on $\rightarrow$ off / S_1, S_4 off $\rightarrow$ on, and $I_{load} < 0$.

- MOSFETs S_1, S_4 on $\rightarrow$ off / S_2, S_3 off $\rightarrow$ on, and $I_{load} < 0$. When S_2 and S_3 turn on, their output stray capacitors discharge through their respective channel $R_{ds(on)}$ (hard switching).

This case is equivalent to the transition S_2, S_3 on $\rightarrow$ off / S_1, S_4 off $\rightarrow$ on, and $I_{load} > 0$.

On the other hand, in unipolar PWM, switching transitions happen separately in each leg, having these types of change:

- MOSFET S_4 on $\rightarrow$ off / S_3 off $\rightarrow$ on, and $I_{load} > 0$. Output parasitic capacitance of S_3 may be totally discharged by resonance with the coil, analogously to the bipolar case, but the energy balance condition will be less restrictive because involves an only MOSFET:

$$\frac{1}{2} \cdot L \cdot I_{load}^2 > \frac{2}{3} \cdot C_{ds} \cdot U_{in}^2 \quad (\text{Eq. 43})$$

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Substituting in this equation the values mentioned in the bipolar modulation instance for 5 kHz, the minimum current able to produce ZVS would be 0.08 A, which implies a limit of 2.49 % of the period of the output current in which ZVS cannot be achieved.

This case is equivalent to the transition S_2 on $\rightarrow$ off / S_1 off $\rightarrow$ on, and $I_{load} < 0$, and also equivalent to the transitions: S_3 on $\rightarrow$ off / S_4 off $\rightarrow$ on, and $I_{load} > 0$; and S_1 on $\rightarrow$ off / S_2 off $\rightarrow$ on, and $I_{load} < 0$.

- MOSFET S_3 on $\rightarrow$ off / S_4 off $\rightarrow$ on, and $I_{load} > 0$. The output capacitance of S_4 discharges through the resistance of its n-channel ($R_{ds(on)}$), as occurs with the equivalent transitions: S_1 on $\rightarrow$ off / S_2 off $\rightarrow$ on, and $I_{load} < 0$; S_4 on $\rightarrow$ off / S_3 off $\rightarrow$ on, and $I_{load} < 0$; and to S_2 on $\rightarrow$ off / S_1 off $\rightarrow$ on, and $I_{load} > 0$.

The fact that switching frequency is practically doubled in the unipolar modulation, which would imply double switching losses, is partially compensated for the appearance of switching losses only in one MOSFET in each lossy transition instead of two as occurs in bipolar PWM. It is interesting to mention that in both PWM methods, any transition in which ZVS is likely achieved is normally followed by a transition in which not. So for an estimation of turn-on losses, P_{sw-on} , switching frequency $f_{carrier}$ has been divided by 4:

$$P_{sw-on} = 4 \left(\frac{2}{3} \cdot C_{ds} \cdot U_{in}^2 + \frac{1}{2} \cdot t_{sw,on} \cdot U_{in} \cdot \overline{|I_{load}|} \right) \cdot \frac{f_{carrier}}{4} \quad (\text{Eq. 44})$$

where $t_{sw,on}$ is the time when drain current and drain-to-source voltage are present at once during turning-on as shown in Figure 2-32, and $\overline{|I_{load}|}$ is the average of the module of the output current, which is the average of the current sine rectified wave, i.e. $2\sqrt{2}I_{load,RMS}/\pi$.

Figure 2-32: MOSFET drain-to-source voltage, drain current and power losses with hard-switching

Some turn-on transitions achieve ZVS, however all of the turn-off transitions in this topology are lossy, without getting zero current switching (ZCS). As before, in bipolar turn-off transitions two MOSFETs are involved whereas in each unipolar turn-off transition there is an only affected MOSFET, but as switching frequency doubles, and turn-off losses P_{sw-off} are equal in both cases:

$$P_{sw-off} = 4 \left(\frac{1}{2} \cdot t_{sw,off} \cdot U_{in} \cdot \overline{|I_{load}|} \right) \cdot \frac{f_{carrier}}{2} \quad (\text{Eq. 45})$$

$t_{sw,off}$ being analogous to the previous turn-on time, as defined in Figure 2-32.

Regarding conduction losses P_{cond} , there are two MOSFET conducting any time, resulting in:

$$P_{cond} = 2(R_{ds(on)} \cdot I_{load,RMS}^2) \quad (\text{Eq. 46})$$

Any losses related to the diodes parallel to MOSFETs has been neglected, both conduction losses, as current is essentially flowing through MOSFET channel, and switching losses because of the use of fast diodes, with lower reverse recovery charge.

So both modulation methods, unipolar and bipolar can be considered equivalents as far as power losses are concerned. It is noteworthy to show MOSFET power losses in the square wave case. In that sense, conduction losses are equal to that in the analyzed PWM methods. However switching losses appear in every switching transition, because they coincide with the points where current cancels out and this cannot be employed to get ZVS. Nevertheless, this circumstance makes turn-off transitions happen without current traversing MOSFETs, achieving ZCS. Then only turn-on losses P_{sw-on} appear. It must be taken into account that switching frequency matches that of the output current, f_{ref} , and that only two switches are turning on in each switching transition, therefore being:

$$P_{sw-on} = 2 \left(\frac{2}{3} \cdot C_{ds} \cdot U_{in}^2 \right) \cdot f_{ref} \quad (\text{Eq. 47})$$

Power losses were used in a thermal model, as presented in [229], in which thermal resistances (in °C/W) and differences of temperatures are respectively modelled as electrical resistances and voltage drops, and from this result, four heatsinks (SW25-2G, Aavid Thermalloy LLC, Laconia, NH, USA) of 13 °C/W each, adequate for the assembling of MOSFETs with TO-247 package as those employed, were selected.

2.1.5.5.2. Selection of input and resonant capacitors

Once the two possible PWM methods have been presented, the calculation of the input capacitors filtering the current going into the full-bridge, so as to reduce the ripple of the input voltage (as stated in Section 2.1.5.4), has also been carried out. That input current before filtering is different for bipolar or unipolar modulations, so they will be independently analyzed and compared afterwards. In the analysis, a sufficiently high value of m_F has been supposed as to consider that output current does not vary much between consecutive switching periods:

- Bipolar modulation: the unfiltered current, $I_{unfiltered}$, which enters into the full-bridge swings between positive and negative values as the MOSFETs of the diagonal S_1 - S_4 or the diagonal S_2 - S_3 are turned-on, respectively, as depicted:

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Figure 2-33: Bipolar modulation: load voltage (V_{load}) and current (I_{load}), and current going into full-bridge after filtering capacitors ($I_{unfiltered}$)

Although the unfiltered current waveform could seem symmetrical with regard to the time axis, it is not indeed, having a DC component, $I_{unfiltered,DC}$ given by [236] under the assumption that input and output instantaneous power were equal:

$$I_{unfiltered,DC} = \frac{V_{load,1,RMS} \cdot I_{load,RMS}}{U_{in}} \cdot \cos(\theta) \quad (\text{Eq. 48})$$

where $V_{load,1,RMS}$ is the RMS value of the output voltage fundamental harmonic and θ is the angle which I_{load} lags V_{load} , as corresponds to an inductive load. But only AC components to be filtered by input capacitors were considered in this study. In a PWM inverter, current and duty cycle D , are continuously varying, but if m_F is sufficiently high, the ampere-second balance could be applied to two consecutive pulses of the current through the input capacitor (the equivalent to the capacitors in parallel at the input). This implies that the shaded areas above and below the time axis in Figure 2-34 are equal:

Figure 2-34: Bipolar modulation: current through input capacitor and ampere-second balance

Therefore the expression for the minimum input capacitor C_{in} to get a maximum input voltage ripple ΔU_{in} is:

$$C_{in} \geq \frac{(1-D) \cdot 2i_{load} \cdot D \cdot T}{\Delta U_{in}} \quad (\text{Eq. 49})$$

- Unipolar modulation: in contrast to the bipolar case, now the current going into the H-bridge only oscillates between positive values and zero when output voltage pulses and output current have the same polarities, or negative ones and zero, during the time when they have equal polarities, as shown in Figure 2-35:

Figure 2-35: Unipolar modulation: load voltage (V_{load}) and current (I_{load}), and current going into full-bridge after filtering capacitors ($I_{unfiltered}$)

This $I_{unfiltered}$ waveform implies a reduction in the amplitude to be filtered by input capacitors. In addition, the duplication of frequency leads to an easier filtering. Doing an ampere-second balance for the unipolar PWM similar to the previously done for bipolar modulation, with the same assumption of m_F high enough to consider current constant in two consecutive pulses, the current traversing input capacitors verifies the equality of shaded areas in Figure 2-36:

Figure 2-36: Unipolar modulation: current through input capacitor and ampere-second balance

Whereby the expression for the minimum required input capacitor C_{in} which guaranties a maximum input voltage ripple ΔU_{in} can be deduced:

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$$C_{in} \geq \frac{(1 - D) \cdot i_{load} \cdot D \cdot T}{2 \Delta U_{in}} \quad (\text{Eq. 50})$$

resulting in one fourth of the capacitance for the bipolar case. This fact agrees with the previously done harmonic content study of the output current, since the more harmonics the more difficult to filter also the input signal, affected by MOSFET switching, and a less accurate sinusoidal current would be obtained.

For a numerical determination of the needed capacitance in both PWM techniques, for introduce a safety margin, the worst case has been selected, which would appear for 50 % duty cycle. Likewise calculations have been made applying the maximum output current. The admissible maximum ΔU_{in} has been selected as the 1 % of the input voltage U_{in} although this margin has not been so rigid for the lower frequencies because it would require a too high capacitance. All in all, an aluminum electrolytic capacitor of 2200 μF and able to support 63 V has been finally selected in parallel to 4 ceramic capacitors of 27 nF each.

Considering all the previous analysis of modulation methods, the unipolar PWM in the lower frequencies (1 Hz to 5 kHz) has been selected for implementing the driving algorithm in the final design, because of the reduction in the switching harmonic content, trying to provide the solution closer to a pure sine waveform, with the subsequent improvement of EMC and size reduction of the filtering elements. For the attainment of resonance in the square wave method applied at higher frequencies, and with the coil constructed for those frequencies, four capacitances have been selected at 10, 20, 40 and 50 kHz, according to the closest commercially available values to the theoretical ones of Table 2-4. Film capacitors were employed for that purpose. Thus for 10 kHz a commercial capacitor of 470 nF (theoretical resonance at 9.79 kHz) was chosen. Analogously, for 20 kHz: two capacitors, one of 100 and other of 15 nF in parallel, i.e. total capacitance of 115 nF (resonance at 19.80 kHz); for 40 kHz: 33 nF (resonance at 36.96 kHz); and for 50 kHz: 15 nF (resonance at 54.82 kHz). Regarding the voltage these capacitors have to withstand, it has been taken into account that the flow of the nominal current (RMS value of 1.47 A) across the impedance of the resonance capacitors, obtaining the following AC RMS voltages: 50.8 V for 9.79 kHz, 102.8 V for 19.80 kHz, 191.8 V for 36.96 kHz and 284.5 V for 54.82 kHz, as we made in [229]. But for an adequate selection, due to the fact that they have to work in relatively high frequencies, graphs with the permissible AC voltage vs frequency supplied by datasheets have been considered as it is known an attenuation from a cutoff frequency onwards as shown in Figure 2-37 for the particular case of the 33 nF capacitor, intended for 36.96 kHz and 191.8 V. Then the marked permissible value (over 300 V) at that frequency is appropriate.

Figure 2-37: Permissible AC voltage V_{RMS} versus frequency f (for sinusoidal waveforms) for the resonance capacitor of 33 nF (extracted from [252])

2.1.5.5.3. Simulation and quality factor of the square wave method

Considering as starting point the simulation model developed in PSIM [230], the necessary modifications were carried out to get the adequate response for the inverter controlled by square wave pulses at the highest frequencies. Its schematic circuit is shown below:

Figure 2-38: Schematic circuit for simulation of square wave controlled resonant full-bridge inverter

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MOSFETs of each leg are governed with complementary signals having 50 % duty cycle in such a way that the same signal drives the MOSFETs of each diagonal. The gate drive signals of one leg (V_{gs1} and V_{gs2}) together with the voltage across and current through the RLC series impedance of the resonant circuit, are shown in Figure 2-39:

Figure 2-39: Simulations at 54.8 kHz: Square wave modulation. Pulses V_{gs1} and V_{gs2} driving MOSFETs S_1 and S_2 ; voltage and current in the RLC output circuit, V_{out} and I_{load}

This plot shows a great accuracy of the sinusoidal current obtained by means of resonance. The quality factor Q of a series RLC circuit gives a ratio of reactive (stored) power to active (dissipated) power, through the division of any of the reactive impedances (equal if there is resonance) at the resonance frequency, f_r , between the resistance, expressed by:

$$Q = \frac{\omega L}{R} = \frac{1}{\omega C R} = \frac{1}{R} \sqrt{\frac{L}{C}} = \frac{f_r}{BW} \quad (\text{Eq. 51})$$

A high Q implies a very selective bandpass filter, with a narrow bandwidth BW . This BW is defined here as the frequency range where current is attenuated 3 dB with regard to its value at f_r , i.e. where it takes 70.7 % of its central value and power is halved. A high Q could be good in principle but care must be taken because the higher the Q , the higher the voltage drop between terminals of any of the reactive impedances, for the same current. Another drawback of a lesser BW is due to the available capacitances in the market which determine the f_r , maybe not as close to the desired ones as desirable, but in this case differences have been rated as acceptable. Then for the high-frequency coil ($R = 0.99 \Omega$, $L = 562 \mu\text{H}$) the quality factor for the four considered frequencies is:

Desired frequency (Hz)	Capacitance (nF)	Resonance frequency (Hz)	Q factor	BW (Hz)
10000	470	9793	34.9	280.4
20000	115	19797	70.6	
40000	33	36957	131.8	
50000	15	54816	195.5	

Table 2-6: Quality factor Q and bandwidth BW for the highest frequencies in the high-frequency coil

2.1.5.5.4. Implementation of the control algorithms

With regard to the DSP for implementing the unipolar PWM algorithm in the low-frequency range (1 Hz – 5 kHz) and the 50 % duty cycle square wave algorithm (created in [230]) in the high frequency range (10, 20, 40 and 50 kHz) a development board (LAUNCHXL-F28069M, Texas Instruments Inc., Dallas, TX, USA) was employed (Figure 2-40). It includes the microcontroller unit (MCU) TMS320F28069M which integrates a series of modules with different functionalities. Among them there are 8 enhanced pulse width modulators (ePWM) modules which have been used in this application. Each of them represents one channel with two outputs: EPWMxA and EPWMxB (x varies between 1 and 8). The used MCU has two internal oscillators of 10 MHz. This frequency can be changed by means of a phase-locked loop (PLL) module which allows multiplying it by any integer between 1 and 18 or dividing it by 1, 2 or 4. The output period of the PLL, $T_{SYSCLKOUT}$, can be used to supply the clock signal of other modules in the MCU, the ePWM modules among them. This input clock frequency, $F_{SYSCLKOUT} = 1 / T_{SYSCLKOUT}$, is divided down through the values introduced in two registers, CLKDIV and HSPCLKDIV, in the Time-Base submodule (within the ePWM modules). That way, with a prescaling operation, the counter inside the ePWM modules slows down and consequently it improves the calculation capacity of the MCU (which works at 90 MHz) to carry out the subroutine associated to interrupts. However prescaling produces as well a proportional reduction of the period of the Time-Base counter, TBPRD (Eq. 52), which is related to the number of points used to calculate the reference and carrier signals. This will create a trouble at the highest frequencies, f_{ref} , for unipolar modulation, and the minimum prescaling needed for performing the calculation algorithms will be high enough to force a reduction of m_f , instead of the intended value of 100.

$$TBPRD = \frac{F_{SYSCLKOUT}}{f_{ref} \cdot (CLKDIV \cdot HSPCLKDIV)} \quad (\text{Eq. 52})$$

Taking all the previous issues into consideration, the programming of the MCU must include a number of initializations like those synchronizing and changing the phase, if necessary, of the ePWM modules taking part in the process, establishing the pertinent master/slave relations between these modules. All programming was carried out in the integrated development environment Code Composer Studio (v. 7.1.0, Texas Instruments Inc., Dallas, TX, USA).

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Figure 2-40: Upper view of the LAUNCHXL-F28069M development board of Texas Instruments

Two different source codes, one for unipolar PWM and the other for square wave, were developed by [230] (see Appendixes 0 and 0, respectively). Up counter was selected in ePWM modules, from 0 to TBPRD. So the performed actions, i.e. set (force output to logic 1) or clear (force output to 0) were associated a two events in the case of square wave algorithm: when the counter is zero and when it reaches $D \cdot TBPRD$, with D a duty cycle of 50 %.

On the contrary, the unipolar PWM technique requires a series of numerous periodic interrupts in which a subroutine of comparison of the sinusoidal reference signals with the triangular carrier is executed, activating the corresponding set or clear actions. The points of the triangular waveform are calculated during program initialization and stored in a vector. The calculation of both sinusoidal signals is much more complicated. Any trigonometric waveform requires the calculation of several terms of its Taylor series to be accurate enough. This task means a great computational load difficult to complete in the time between two interrupt events. A faster solution could be given with the employment of lookup tables, interpolating between two consecutive values if needed. However this could not be valid due to for example memory limitations. Some enhancement of memory availability can be obtained taking advantage of the quarter-wave symmetry of trigonometric functions, storing in the lookup table only points corresponding to angles from 0 to $\pi/2$ radians. But this method needs of an extra computational consumption to calculate the rest of the wave [253]. Here is proposed [230] a recursive algorithm to calculate sine function, based on the fixed discrete steps $\Delta\alpha$ at which is calculated, as shown in Figure 2-41:

Figure 2-41: Discrete steps for the calculation of the sinusoidal waveform by recursive algorithm (extracted from [230])

The mechanism of formation of the sine waveform consists in working out $\sin(n \cdot \Delta\alpha)$ with n a positive integer. This can be expressed as:

$$\sin(n \cdot \Delta\alpha) = \sin([n - 1] \cdot \Delta\alpha + \Delta\alpha) \quad (\text{Eq. 53})$$

and applying the expression for the sum of two angles:

$$\begin{aligned} \sin([n - 1] \cdot \Delta\alpha + \Delta\alpha) \\ = \sin([n - 1] \cdot \Delta\alpha) \cos(\Delta\alpha) + \cos([n - 1] \cdot \Delta\alpha) \sin(\Delta\alpha) \end{aligned} \quad (\text{Eq. 54})$$

This is only constituted by products and sum of two constant values (cosine and sine of $\Delta\alpha$) calculated during the program initialization and the sine and cosine found in the previous

interrupt event. It turns out to be necessary to calculate also the cosine and hence the analogous equation is applied:

$$\begin{aligned}\cos([n - 1] \cdot \Delta\alpha + \Delta\alpha) &= \cos([n - 1] \cdot \Delta\alpha) \cos(\Delta\alpha) \\ &- \sin([n - 1] \cdot \Delta\alpha) \sin(\Delta\alpha)\end{aligned}\tag{Eq. 55}$$

For the second reference, 180 ° out of phase, the formula of minus sine is used. With this recursive algorithm, computational resources are improved respecting the Taylor series solution.

As it is known, interrupt events occur periodically. Nevertheless, the existence of conditional jumps in the source code may cause a variable number of cycles since the time when interrupt routine starts until the updating of outputs. This could give rise to a jitter problem and a certain wave distortion. In order to reduce this malfunction, instead of directly updating the outputs (Figure 2-42a), the partial result is stored in Boolean variables and it will be passed to the outputs at the beginning of the following interrupt routine, i.e. at specific moments of the period (Figure 2-42b).

Figure 2-42: Flowcharts of subroutine for management of interrupt event: a) Updating of variables after calculations; b) Updating of variables at the beginning of the subroutine to reduce jitter (extracted from [230])

2.1.5.5.5. Optimization of the PCB design

In addition to the programmed source codes for both unipolar PWM and square wave with resonance, some advances were applied to the final designed PCB [229]:

- In order to incorporate the resonance at the highest frequencies, the through-holes for the connection of capacitors were added, having 5 alternative routes in series to the load (one of them without capacitor, for the PWM implementation) selectable by means of a jumper socket.

- Two different supply voltages for the IR2110 drivers were added, one for the logic supply voltage V_{DD} and other for the low side fixed supply voltage V_{CC} . Their corresponding power and ground planes were accordingly separated.
- Through-hole gate resistors were substituted for surface-mount ones. That way both size and parasitic inductance are reduced.
- A four-layer PCB was employed instead of the previous two-layer prototype. That way, the two external layers (1st and 4th) were devoted to tracks connecting components. In fact, the traces carrying the current traversing the load were duplicated in both layers in order to reduce resistance. The two internal layers have ground planes (2nd) and power planes (3rd). Thanks to the overlapping of these power and ground planes and to the smaller distance between them, capacitance was increased, aiding in the task performed by decoupling capacitors. The distribution in four layers has helped also to reduce PCB size, and has reduced loop lengths, thus decreasing EMI susceptibility.
- Socket strips were placed to interface PCB and the initially thought microcontroller board (F28069 Piccolo controlSTICK, Texas Instruments Inc., Dallas, TX, USA) header pins. This interface was not finally fit because of the different distribution of pins in the ultimately used MCU board and they were connected via jumper wires.
- A highest finish was obtained, having the PCB built by an external supplier instead of etching it in the lab as the previous prototypes. Hence the final one has a solder mask, silkscreen and gold-plated pads and holes.

The final prototype PCB layout and real aspect before mounting of components can be seen in Figure 2-43, whereas in Figure 2-44 the final inverter aspect can be appreciated:

b

Figure 2-43: Inverter final prototype: a) PCB layout view in Altium; b) physical PCB upper view (extracted from [229])

Figure 2-44: Upper view of the inverter final prototype

2.1.6. Model Food

Due to its well-known thermophysical properties and because water can be used as a reference for many studies related to heat transfer in food [254], deionized water (pure water type I, Milli-Q system, Millipore Corp., Billerica, MA, USA) was used to carry out the determination of its freezing curve parameters. In addition, 0.9% NaCl (Sigma-Aldrich Corp., St. Louis, MO, USA) solutions in ultrapure water were used in the SMF study. For each experimental freezing, a calibrated pipette (Transferpette® S D-5000, Brand GmbH, Wertheim, Germany).

Before each experiment, 10 mL of sample was located in a 12-mL glass vial (outer diameter: 23.2 mm, height: 38.1 mm) and tempered in a thermostatic bath for, at least, 60 min to achieve a uniform temperature of 25 ± 0.5 °C. Freezing experiments were performed by immersing the sample in a thermostatic bath (model Haake K, Fisons Instruments, Inc., Saddle Brook, NJ, USA) filled with ethanol and maintained at -25 ± 0.2 °C. The samples were frozen at different conditions, both with and without SMF application. In SMF experiments, two neodymium magnets (diameter: 35 mm, height: 20 mm) axially magnetized were employed to generate different SMFs, as exposed in Section 2.1.3. As described in that Section, a device consisted of two PMMA blocks and four Teflon® bolts was specially designed and fabricated for holding both the sample and the magnets at fixed positions and, thus, ensuring identical SMFs in repeated experiments (Figure 2-45).

Figure 2-45: Schematic draw of the device fabricated for holding the sample and the magnets during the SMF freezing experiments. (1): PMMA block, (2) Neodymium magnet, (3) Removable PMMA lid, (4): Teflon® bolt, (5): Teflon® nut, and (6): Sample vial. (a-g): Positions at which the magnetic field strength was experimentally measured

Two removable PMMA lids allowed the magnet manipulation to change the relative position of their poles. The sample was located on a glass support between the magnets in such a way that the sample center was equidistant and aligned with the geometric center of both

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magnets. In all the freezing experiments, the distance between the PMMA blocks was set at 32 mm; that is, the distance that allowed obtaining the maximum field intensity at the conditions tested. To test any hypothetical effect of the direction of the field forces, the magnet poles were placed in attractive or repulsive positions; that is, with unlike or like poles faced each other, in SMF-A and SMF-R experiments, respectively. The characteristics of both fields are defined in Section 3.1.1. A similar device, but with solid PMMA blocks (that is, with no holes and lids to lodge magnets), was employed to hold the sample in control experiments with no SMF application.

Before the experiments, the sample holder was immersed in the cooling medium at $-25\text{ }^{\circ}\text{C}$ for, at least, 30 min. Once the system was tempered, the sample was placed on the glass support between the PMMA blocks and the freezing experiment started. During the experiments, the evolution of temperature versus time in the sample was measured by two T-type thermocouples located at both the geometric center and the surface to obtain the freezing curves for each tested condition. Moreover, another T-type thermocouple was immersed in the cooling medium to verify that the temperature remained constant during the experiment. All thermocouple measurements were recorded every second by the DAQMaster MW100 data acquisition system (Section 2.1.1) linked to a computer.

For the OMF experiments, 6 mL of water sample was inserted in a vial and tempered for 5 min in the above mentioned Haake K thermostatic bath filled with water, to achieve a uniform temperature of $25 \pm 0.2\text{ }^{\circ}\text{C}$. Each sample was placed afterwards at the central position of the solenoid, where the OMF strength was considered sufficiently uniform, as shown in Figure 3-31, and which was located inside the Whirlpool freezer, Figure 2-15. The RMS current through the coil was adjusted at 1.47 A, inducing an OMF RMS strength of around 0.8 mT, as the design requirements presented in Section 2.1.5.2. This set of water freezing experiments was carried out at three different frequencies: 5 Hz, 50 Hz, 50 kHz and without OMF. Sample containers were designed to make up for the volume increase of the sample due to the liquid-solid phase change during freezing, drilling a hole in the vial cap to allow the evacuation of air. In a similar fashion to that employed in the SMF freezing experiments, the sample temperature was sensed by two fiber optic probes (one at the center and the other at the vial surface) and registered with its corresponding data acquisition unit of Neoptix (Section 2.1.1). The freezer ambient temperature was equally measured by another fiber optic probe. Those measurements were registered every five seconds.

Both in the cases of water and NaCl solutions studied with SMFs and in the case of water in the presence or absence of OMFs, all the freezing experiments were considered finished when the sample center reached $-20\text{ }^{\circ}\text{C}$. All the mentioned trials were independently repeated thirty times in the SMFs experimental conditions and fifteen times for the trials analyzing the effect of OMFs.

2.1.7. The nanoparticles dispersion

The starting material was a very concentrated dispersion of superparamagnetic maghemite (γ - Fe_2O_3) nanoparticles, which was split into aliquots to perform the different freezing experiments. To obtain this colloidal dispersion, a two steps process was carried out: firstly magnetite (Fe_3O_4) nanoparticles were synthesized by means of standard coprecipitation [255]. Briefly, 75 mL of a NH_4OH solution (25 %) were rapidly added to a mixture of distilled water (400 mL), FeCl_3 27 % (43 mL) and FeCl_2 0.175 M (45 mL). After 5 minutes, the sample was washed three times with distilled water. Secondly, particles were oxidized to maghemite to increase their stability and improve their colloidal behaviour [256]. Thus, the previous sample was treated with 300 mL of HNO_3 (2M) and stirred for 15 min. After this time, the supernatant HNO_3 was removed and 75 mL of a solution of $\text{Fe}(\text{NO}_3)_3$ (1M) and 130 mL of water was added. The mixture was boiled for 30 minutes. After the sample were cooled down to room temperature, the supernatant was extracted and 300 mL of HNO_3 (2M) were added, stirring for another 15 min. Finally, particles were washed three times with acetone to remove acid wastes and dispersed in water. A rotary evaporator was used to remove acetone and concentrate the so denoted SAMN sample. The named SAM sample corresponded to the HNO_3 (2M) sample without nanoparticles.

2.1.7.1. The nanoparticles characterization

The crystal structure of the samples was identified by X-ray powder diffraction (XRD) performed in a Bruker D8 Advance powder diffractometer using $\text{Cu K}\alpha$ radiation. The patterns were collected between 10° and 70° in 2θ . The average crystallite size was calculated with the half-width of the (311) X-ray diffraction peak by means of the diffraction computer program (APD) utilities from Phillips. Particle size and shape were determined by transmission electron microscopy (TEM) micrographs using a JEOL 2000FXII (200 kV) microscope. TEM samples were prepared by placing one drop of an aqueous dilute suspension of magnetic nanoparticles on a copper grid covered with a perforated carbon film and allowing the solvent to evaporate slowly at room temperature. The mean particle size and distribution were evaluated by measuring the largest internal dimension of at least 100 particles. Afterward, data were fitted to a gauss distribution to obtain the mean size and standard deviation (σ). Colloidal properties of the samples were studied in a Zetasizer Nano S, from Malvern Instruments. The hydrodynamic size of the particles in suspensions was measured by dynamic light scattering (DLS), and the zeta potential was measured as a function of pH at 25°C , using $10\text{--}2\text{ M KNO}_3$ as background electrolyte and HNO_3 and KOH to change the pH of the suspensions. The Fe concentration was measured with an inductively coupled plasma optical emission spectrometer (ICP-OES) Perkin-Elmer Optima 2100 DV. For this purpose samples were digested with hydrochloric acid for 24 h.

Magnetic characterization of the sample was carried out in a vibrating sample magnetometer MagLabVSM, Oxford Instrument with a maximum field of 50 kOe. Samples were dried in an inox-coated oven at 50°C for 24 h before measurements. Afterwards samples were accurately weighed and fitted into the sample holder. Temperature dependent zero field cooling (ZFC) and field cooling (FC) magnetization measurements were taken by initially cooling the samples

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to 5 K in zero and 200 Oe fields, respectively. Then, the magnetization was measured during the heating cycle ($3 \text{ K} \cdot \text{min}^{-1}$) from 5 to 250 K under a 200 Oe field. Hysteresis loops of the powder samples were measured at different temperatures at a rate of $5 \text{ kOe} \cdot \text{min}^{-1}$.

2.1.7.2. Freezing nanoparticles experiments

For each experimental freezing, a calibrated pipette (Transferpette® S D-5000, Brand, Wertheim, Germany) was used to drop 6 mL of sample in a cylindrical glass sample holder with a holed plastic cap permitting the air to go out after the ice expansion. Before freezing, each sample was sonicated for 5 min and then thermostated by immersion in a water bath at 25 °C for another 5 min. Then they were located at the center of the air gap volume of the iron core generator situated in the freezer as represented in Figure 2-4c. A sufficiently big sample holder was prepared to deal with the volume increase of the sample due to the liquid-solid phase change. During freezing, the evolution of the temperature versus time in the center of the sample, at the surface of the sample holder and on the surrounding ambient media of the freezer were obtained by using the respective Neoptix fiber optic probes connected to the Reflex-4 optic fiber temperature thermometer (seen in Section 2.1.1), recording data each five seconds. Samples were subsequently extracted from the freezer and then thawed at room temperature for further use. A set composed of fifteen freezing experiments assisted with an OMF of 31.3 mT at 50 Hz and fifteen without MF were executed.

The corresponding freezing curves were subsequently analysed.

2.1.8. Crab sticks

Fresh crab sticks, all produced in the same batch, were acquired to a Spanish manufacturer. According to the product label, the main ingredients of the crab sticks were surimi (44%), water, starch, modified starch, sunflower oil, salt, and egg albumen. After reception, all the sticks were unpacked and cut in half. The portions obtained (about 38 mm length, 15 mm width, and 15 mm height) were packed in plastic bags and stored at 4 °C before freezing.

Magnetic freezing experiments were carried out in the commercial CAS freezer (ABI Co., Ltd., Chiba, Japan) of Kotobuki described in Section 2.1.2.

Crab sticks were frozen at different conditions, both with (10%, 50%, and 100% CAS) and without (0% CAS) OMF application. In all these experiments, the crab sticks were located on tray 5 in the freezing cabinet (Figure 2-2a), that is, the tray situated approximately at the center of the magnetic coils, and the MF strength and frequency values for the tested conditions are shown in Table 3-9. The air temperature and air flow were fixed at -25 °C and 100%, respectively.

In parallel, air-blast and static-air freezing experiments were carried out at $-25\text{ }^{\circ}\text{C}$ in a conventional freezer (model 0-6373, AGA-Frigoscandia, Helsingborg, Sweden) by setting the air speed to the maximum value (4.8 m/s) and to 0 m/s. In all these experiments, the crab sticks were located approximately at the center of the freezing cabinet.

During the freezing process, the temperature evolution (every second) in the samples was measured by 2 T-type thermocouples located at the thermal center of 2 of the crab sticks. Moreover, air temperature was also monitored at 2 different locations in the freezer. The freezing process was considered completed when the thermal center of the samples reached $-20\text{ }^{\circ}\text{C}$. Then, the crab sticks were taken out of the freezer and transferred to a cold storage warehouse at $-20\text{ }^{\circ}\text{C}$.

All the freezing experiments were performed in triplicate.

2.1.9. Pork loin

Fresh pork loin was obtained from a local supermarket and stored in chilled conditions, at a mean (standard deviation) temperature of $-1.4\text{ (}1.0\text{)}\text{ }^{\circ}\text{C}$, for a period between 1 and 5 days. When required, several cylindrical samples were extracted from each pork loin using a cork borer with an inner diameter of approximately 30 mm. The longitudinal axis of the cylinder followed the fibre direction to minimise damage to fibres and potentially reduce drip losses. After cutting, each meat cylinder was wrapped in plastic film to minimise evaporation of water from the surfaces. The wrapped pork samples were then equalised for 24 h prior to freezing, in a catering refrigerator running at a mean (standard deviation) temperature of $-0.9\text{ (}0.8\text{)}\text{ }^{\circ}\text{C}$ and then cut to a length of approximately 22 mm. A total of 40 cylinder-shaped pork samples were used throughout the trials. The mean (standard deviation) diameter, length, and mass of the samples were 30.3 (1.0) mm, 21.8 (0.9) mm, and 13.6 (1.3) g, respectively.

The experimental batch air-blast-freezer at the FRPERC-GIFHE, with and without CAS being applied was used (as in [45]). The freezer had been designed and constructed in consultation with the referred ABI Corporation and the magnetic coils and control system supplied and commissioned by ABI. The CAS freezer was equipped with both static and oscillating magnetic field generators to assist the freezing process in a similar way as described in Figure 2-1a. The air temperature was set to $-30\text{ }^{\circ}\text{C}$ (providing a mean (standard deviation) air temperature of $-29.2\text{ (}0.6\text{)}\text{ }^{\circ}\text{C}$ across the product) with CAS settings of: off (control), 10%, 50%, and 100%. Two samples, placed at two different fixed positions on a grid, were used in each trial. These positions were those with the highest and the lowest magnetic field strengths at the different CAS settings (see Section 3.3.4.1). The RMS of OMF strength at the different CAS settings were measured for the positions of highest field and the lowest field. The surface heat transfer coefficient at the two positions was also determined using the method described by [257]. Temperature was registered until temperature readings at the centre of both samples were below $-27\text{ }^{\circ}\text{C}$. All the freezing experiments, with two samples in each, were performed in quintuplicate.

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2.1.10. Magnetic iron solutions, in vivo and in vitro experiments

2.1.10.1. Magnetic iron solution

The concentration of iron in the solution was taken based on the amount of iron in blood and used in excess (about four times higher). Experiments were performed in triplicate for each MF condition, by freezing 20 mL of freshly made up FeCl_3 solutions (0.58 g in 0.1 M HCl) held in a glass vial (diameter = 2.3 cm, height = 5.1 cm). The samples were frozen in the Koxka freezer, with the iron core OMF generator prototype, in the presence of OMFs with strengths of 0.33, 0.8, 1.5 and 7 mT at 50 Hz, and without OMF as control condition.

2.1.10.2. In vitro experiments

The potential in vitro cryoprotective activity of OMF was determined after freezing-thawing a freeze-labile enzyme. For this purpose, lactate dehydrogenase (LDH, EC 1.1.1.23, Type V-S from rabbit muscle, Sigma, St. Louis, MO, USA) was used as control in the cryoprotective activity assay since it is known its marked lability, practically null after freezing with liquid nitrogen (-196°C for 30 s). The freezing of 6 small plastic tubes (1.5 mL eppendorfs) containing 100 μL of stock enzyme solution (8 $\mu\text{g}/\text{mL}$ in 20 mM potassium phosphate buffer, pH 7.5) was performed, placing them at the center of the referred air gap of the iron core OMF generator by hanging the eppendorfs from a timber bar, inside the Koxka freezer without and with OMF (7 mT / 50 Hz). Immediately after freezing, thawing was carried out at room temperature for 5 min. Two cycles of freezing-thawing were performed before measuring the enzymatic activity.

Following the method of [258], the residual enzyme activity was measured based on the conversion of pyruvate to lactate with concomitant conversion of equimolar amounts of NADH to NAD^+ . LDH enzymatic activity was determined in aliquots of 4 μL in a final volume of 250 μL of the reaction assay buffer (80 mM Tris-HCl pH 7.5, 100 mM KCl, 2 mM pyruvate and 0.15 mM NADH). NAD^+ production was monitored as the decrease of absorbance at 340 nm for 3.5 min at 25°C using a plate reader spectrophotometer (Synergy Mx, BioTek Instruments Inc., Winooski, VT, USA). The activity was measured in triplicate and the data are presented as the percentage of the LDH activity relative to the unfrozen controls.

2.1.10.3. In vivo experiments

Two batches of hake (*Merluccius merluccius* L.) captured in North-East Atlantic Ocean, FAO fishing area 27 division VIIj were purchased from a local fishmonger in February 2015 and June 2016 and arrived at the laboratory 7 and 9 days after catch respectively. For each trial, five individuals were inspected and any visible *Anisakis* larva was taken out from the muscle before grinding it in the meat mincer machine (diameter hole of 3 mm). The mince was packaged and stored at 4 °C until needed. Two batches of live *Anisakis* L3 from heavily infected ovaries and viscera of hake were obtained from the central market in Madrid (Mercamadrid) (February 2015 and June 2016). Once in the laboratory the larvae were taken out from the tissues, cleaned with 0.85% NaCl solution, pooled in groups of 50, and stored in 10 ml 0.85% NaCl at 4 °C until use.

Ten alive *Anisakis* L3 larvae dispersed in 77g minced hake were disposed in triplicate into Petri dishes ($\varphi=9\text{cm}$, height=1.2cm). Each dish was sequentially hung from a timber bar and located at the center of the referred air gap of the iron core OMF generator of the experimental freezer. The closure of the sample holders was previously drilled and a T-type thermocouple was disposed crossing it to be located and fixed at the center of the sample during freezing experiments. The OMFs applied were 0 and 7 mT at 50 Hz at around -23 °C. After reaching -20 °C, which was the selected end point of freezing (see Section 2.2.1), the samples were taken out of the freezer and allowed them to thaw at 4°C. Frozen and thawed larvae were recovered from the mince with tweezers under UV light (366 nm) [259] since *Anisakis* L3 emit a bluish-white fluorescence after treatments such as freezing.

2.1.10.3.1. Viability of *Anisakis*

In each experiment recovered larvae were placed in 0.85% NaCl and checked for mobility according to [260] and those larvae which did not show any movement spontaneously or by stimulation with tweezers, either just after thawing or after incubation at 37 °C for 4 h in 0.85% NaCl, were considered dead.

2.2. Thermophysical properties and Analytical determinations

2.2.1. The freezing curve parameters

All experiments were carried out by comparing freezing curves obtained in the same conditions but with the application or not of the corresponding MF. Depending on the cases, when only one thermocouple was located at the center or two thermocouples were located both at the center and at the surface, the parameters of the experiments analyzed for each MF strength were different although similar.

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In fact, Figure 1-1 represents the case where only one thermocouple is located at the center. Here, in the precooling period (AB) the precooling rate, V_p ($^{\circ}\text{C/s}$) was calculated as the ratio between 12°C and the elapsed time registered in the sample to pass from 20°C to 8°C . The first temperature was chosen to consider the region of steady cooling after the beginning of the process. The second one was chosen in order to avoid potential disturbances due to the heat convection near the temperature of the maximum density of water [261]. From the supercooling temperature measured at the center of the sample (B), T_c^{nuc} ($^{\circ}\text{C}$) and the phase change temperature, or in other words the freezing point (C), T_f ($^{\circ}\text{C}$), the supercooling degree $\Delta T_c = |T_c^{nuc} - T_f|$ was obtained. If no supercooling appeared in the freezing curve at the center of the sample, ΔT_c was considered 0. The phase change time was determined in two alternative ways, except for the cases of crab sticks and pork loin, whose respective methods of obtainment of their 'characteristic freezing times' (the analogous parameter to phase change time) are explained in Sections 3.3.3.2 and 3.3.4.1. On the other hand, in the experiments carried out with ferric chloride solutions, Section 2.1.10.1, t_{p0} was obtained as the elapsed period since the moment when T_f appeared (just after T_n) until $T_f - 0.5^{\circ}\text{C}$ was registered. Other way to obtain the phase change time in the same experiments was performed, calling it t_{pd} . This value was calculated from the appearance of T_f until the derivative of the freezing curve near the beginning of the tempering region was below -0.005°C/s . By comparison with t_{p0} , t_{pd} can give more realistic information concerning the final release of the latent heat of the sample. For the rest of experiments with model foods, Section 2.1.6, the phase transition time, t_{pt} (s), was defined in this thesis as the time span between nucleation and the end point of freezing. The end point of freezing was identified from the slope of the freezing curve recorded at the sample center [262]. To do so, the first derivative of the freezing curve was obtained by using the software Matlab (v. 7.11.0.584 (R2010b), MathWorks Inc., Natick, MA, USA) and analyzed (Figure 2-46b). During the freezing plateau, the slope is zero because temperature remains constant at the initial freezing point due to the release of latent heat. When ice formation starts to decrease, the slope starts to increase up to a maximum that indicates the phase change is completed [262]. In this work, this maximum is considered to be the end point of freezing.

In the tempering region (DE in Figure 1-1), the tempering rate V_t ($^{\circ}\text{C/s}$) was calculated as the ratio between 2 and the elapsed time registered in the sample to pass from -8°C to -10°C . The first temperature was selected in order to avoid the potential disturbances near the completion of the phase change time. As before, the analogous 'completion of freezing rate' in the pork loin experiments is explained in Section 3.3.4.1. The freezing time t_{tot} was determined as the elapsed time from the starting of the freezing process (A), i.e., 25°C in the sample, until the registered temperature at the center of the sample was -18°C (E) for the particular case of the magnetic nanoparticle freezing experiments. In the rest of cases, the total freezing time, t_{tot} (s), was the time required to lower the sample temperature from 25°C (initial sample temperature) to -20°C .

The case where two thermocouples were located both at the center and at the surface is represented in Figure 2-46a. Freezing curves were analyzed mainly to obtain: the time at which nucleation occurred, the temperature at the sample center when nucleation was triggered, the extent of supercooling attained at the sample center, and the phase transition and total freezing times (Figure 2-46a).

Figure 2-46: a) Characteristic parameters of the freezing process (t_{nuc} : Nucleation time, T_c^{nuc} : Temperature at the sample center when nucleation occurred, ΔT_c : Extent of supercooling at the sample center, t_{pt} : Phase transition time, and t_{tot} : Total freezing time) obtained from the freezing curves. (---): Temperature at the sample surface. (—): Temperature at the sample center. b): Slope of the freezing curve at the sample center.

The second thermocouple, placed at the surface of the sample vessel in water, NaCl and nanoparticle dispersions, permitted the determination of the moment when the nucleation was triggered, t_{nuc} (s). Thus, this time at which nucleation occurred, was recognized in the freezing curves by a sudden temperature increase at the sample surface (Figure 2-46a) due to the release of latent heat. At that moment, T_c^{nuc} (°C) was the temperature at the sample center. When T_c^{nuc} was lower than the freezing point of the sample, the extent of supercooling

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attained at the sample center, ΔT_c (°C), was calculated as the difference between T_f and T_c^{nuc} , as explained above. In other cases, no supercooling existed at the sample center and ΔT_c was considered to be zero.

2.2.2. Thermal conductivity of ice

To study the effects of different freezing processes on the thermal conductivity of ice, the k values were determined for ice prepared: i) at different freezing rates, ii) from aerated and non-aerated water and iii) in the presence of a magnetic field. The TR-1 probe of the KD2 Pro thermal properties analyzer (Decagon Devices, Inc., Pullman, WA, USA) was used to measure the thermal conductivity k of ice. The main components of this device, which is based on the hot-wire probe method, are a needle probe with a hot wire and a temperature sensor. The sensor can measure temperatures in the range of -50°C to $+150^\circ\text{C}$ with a precision of 0.001°C . The probe is a single needle designed primarily for use with soils and other granular or porous materials. It consists of a $100\text{ mm} \times 2.5\text{ mm}$ tube containing a current hot wire. Its large size minimizes the errors due to the contact resistance in granular or solid samples. The measurement range of this device is $0.2\text{--}4.0 \pm 0.02\text{ W/(m}\cdot\text{K)}$. It should be noted that the TR-1 sensor dimensions comply with the lab probe specifications in [263] and [264]. Detailed description of the procedure is given in [124].

2.2.2.1. Ice prepared at different freezing rates

To study the effect of the freezing rate on the thermal conductivity of the resulting ice, water was frozen by both slow and fast traditional freezing processes. For the slow freezing method, a $40 \times 40 \times 15\text{ cm}^3$ thermostatic bath (HAAKE, Germany) controlled by a classical mechanical compression system was used. For the fast freezing method, liquid N_2 was poured directly onto the sample in a Dewar flask. The liquid N_2 volume was more than three times the sample volume. In both cases, when the sample temperature reached the working temperature, the sample was transferred to another identical thermostatic bath that was also thermoregulated. The obtained ice was maintained at a given temperature overnight before the conductivity measurements. The sample temperature was monitored during the heating process using a T-type thermocouple.

2.2.2.2. Ice prepared from aerated and non-aerated water

To obtain the aerated/non-aerated ice samples, gas was added to/removed from the samples before slow freezing. The fact that the gas solubility decreases with increasing temperature was exploited to degas the water sample. Specifically, water was boiled under stirring for

approximately 5 h. Likewise, gas was dissolved in the water by decreasing the temperature to increase its solubility. Accordingly, an air current flowed through the sample for 10 h at 5.5°C and a pressure of approximately 1.2 atm. In both cases, the sample was kept in a closed container until it reached room temperature. Then, the sample was transferred to a thermoregulated bath and kept at the desired temperature overnight before the conductivity measurements.

2.2.2.3. Ice prepared in the presence of a magnetic field

The air-blast freezer from ABI Co., Ltd. (Chiba, Japan) located in Kotobuki and described in Section 2.1.2 was used to freeze water in the presence of a SMF and an OMF. The sample was placed in the center of a tray situated in turn at the geometrical center of the usable freezer volume. The chamber and final freezing temperatures were −50°C and −29°C, respectively. The MF strength inside the freezer, as well as the frequency of the applied OMF was determined by using a teslameter and an oscilloscope, respectively, according to Section 2.1.1. Two different freezing processes were used: i) application of a SMF in the 0% CAS setting condition and ii) simultaneous application of an OMF at the 50% CAS setting condition and the same SMF. The values corresponding to these CAS energy conditions can be seen in Table 3-9. For each condition, the thermal conductivity was determined in quintuplicate at the final freezing temperature.

2.2.3. Quality parameters in food and bio-samples

2.2.3.1. Drip loss

In the study of crab sticks, the term ‘drip’ was used to describe the exudates from both fresh and frozen samples after 24 h of storage at 4 °C. Obviously, the frozen samples were thawed during this storage period. For each determination, 6 crab sticks were weighed, packed in a plastic bag, and stored at 4 °C. After 24 h of storage, the surface of the crab sticks was dried with soft paper and, then, the samples were weighed again.

Drip loss (DL) was expressed as the percent of mass loss according to (Eq. 56):

$$DL(\%) = \frac{(M_{bs} - M_{as})}{M_{bs}} \times 100 \quad (\text{Eq. 56})$$

where M_{bs} and M_{as} are the masses (g) of the sticks before and after the storage period, respectively. For each experiment, the drip loss determinations were performed in duplicate.

In the case of pork loin studies, the frozen samples were wrapped in food grade polyethylene film to prevent evaporation and stored in a chest freezer for between 21 and 27 days. After storage samples were taken out of the chest freezer, the polyethylene film removed, and the

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sample wrapped in a piece of absorbent paper, before placing then in a zipped plastic bag to prevent evaporation losses. Both the bag and paper were weighed together prior to use and again together with the pork sample and the inserted thermocouple using a calibrated scale (RC2022, Sauter GmbH, Balingen, Germany). Samples were then thawed in a domestic refrigerator at a mean (standard deviation) temperature of 2.6 (0.9) °C. The samples remained in the refrigerator until their centre temperatures were above 0 °C, which took between 17 and 21 hours, after which they were removed. Immediately after removal the bags, pieces of absorbent paper, meat sample, and thermocouples were weighed. Each thermocouple was then removed from the sample and the weight of the sample and thermocouple weighed individually. The drip loss was expressed as the percentage of mass loss according to (Eq. 56).

2.2.3.2. Water-Holding Capacity

The water-holding capacity (WHC) of the crab sticks was measured by using centrifugal force to remove the free and loosely bound water from the samples. For each determination, 3 crab sticks were coarsely chopped. Then, about 8 g of the chopped sticks was weighed and put into a centrifuge tube. The tube had a perforated disc, covered with 2 filter papers, and located approximately half way down the tube. The sample was placed on this perforated disc and centrifuged at 2200xg and 4 °C for 10 min (Sorvall Evolution RC centrifuge, model 728311, Thermo Electron Corporation, Asheville, NC, USA). After centrifugation, the chopped sticks were weighed again. WHC was expressed as the percent of water retained per 100 g of water present in the sample prior to centrifuging according to:

$$WHC (\%) = \left(1 - \frac{(M_{bc} - M_{ac})}{M_{bc} \times m_{tw}} \right) \times 100 \quad (\text{Eq. 57})$$

where M_{bc} and M_{ac} are the masses (g) of the chopped sticks before and after centrifugation, respectively, and m_{tw} is the mass fraction of total water present in the sample prior to centrifuging. m_{tw} was evaluated in the samples by determining the mass loss in chopped crab sticks after oven drying at 105 °C until a constant weight was reached. All WHC and m_{tw} measurements were performed in triplicate.

In the case of minced fish muscle, WHC was measured in the second experiment (June 2016) according to [265]. Three repetitions in each triplicate were performed. Unfrozen mince stored for the same period at 4 °C was used as control per each respective freezing condition, i.e. 0 and 7 mT.

2.2.3.3. Texture analysis

The toughness of the crab sticks was evaluated by a Warner-Bratzler test to determine the force needed to shear the sample. A Texture Analyzer (TA-XTPplus, Stable Micro System Ltd., Surrey, UK), equipped with a V-shaped Warner-Bratzler blade and controlled by the Texture Exponent 32 software (v. 6.1.5.0), was employed. For each experiment, 6 crab sticks were

sheared (2 mm/s crosshead speed, 5 kg load cell) perpendicular to the fibers and the maximum force (N) was recorded.

In turn, after the thawing and the color measurements, the texture of each pork loin sample was determined using a texture meter (TVT-150, TEXVOL Instruments, Stockholm, Sweden). The texture test consisted of a compression trial performed using a 25 mm-diameter piston, applying a compression rate of 40% and a hold time of 30 s.

For each trial, a series of values were obtained: density (g/ml), hardness (g), force A (g), force B (g), and elasticity (%). Force A was the maximum force exerted during compression and force B the force exerted at the end of the 30 s period, just before the withdrawal of the piston. Elasticity was calculated by dividing force B by force A and expressing it as a percentage.

2.2.3.4. Color analysis

The whiteness and color of the crab sticks and pork loin were characterized objectively according to the L^* , a^* , and b^* color parameters in the CIELab uniform color space defined by the Commission Internationale de l'Éclairage. To do so, a CM-3500d spectrophotometer managed by the color data software CM-S100w SpectraMagic™ (Konica Minolta, Tokyo, Japan) and a chroma meter (CR-400, Konica Minolta Corp, Tokyo, Japan) for the crab sticks and pork loin, respectively, were employed. The illuminating and viewing configurations of the instrument complied with the CIE diffuse/8° geometry. The spectrophotometer operated in the reflectance specular included mode and the measuring aperture was 8 mm in diameter. Measurements were made with the D65 standard illuminant and a ten-degree observer angle. The instrument was calibrated with black and white standards before each series of analysis. For each crab sticks experiment, whiteness was evaluated in 3 crab sticks. Before the measurements, the orange outer layer of the crab sticks was carefully removed. Two measurements were performed in each sample (one at the center of the upper side of the crab stick and the other at the center of its lower side) and the obtained L^* , a^* , and b^* values were averaged. From these mean values, the whiteness index of each sample was calculated according to:

$$\text{Whiteness} = 100 - \sqrt{(100 - L^*)^2 + a^{*2} + b^{*2}} \quad (\text{Eq. 58})$$

For the pork loin, values were initially measured on the bases of each cylindrical sample immediately before being frozen in the CAS freezer. The measurements were repeated on each sample after freezing and thawing. Values measured after freezing/thawing were subtracted from the values measured before freezing to calculate the variations in value ΔL^* , Δa^* and Δb^* .

2.3. Mathematical equations governing the laboratory freezer assisted by a SMF generator

According to the well-known physical bases and in order to model and simulate the SMF generated by the SMF system of Section 2.1.3, the corresponding mathematical differential

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equation system must be solved. This model makes use of the fact that with two magnets there is no current present and no variable EF either, being only a magnetostatic problem. Hence, from the Maxwell-Ampère's law (Eq. 4), it can be deduced that MF intensity $\vec{H}$ is conservative (its curl is zero, $\nabla \times \vec{H} = \vec{0}$) and a scalar magnetic potential V_m could be defined, verifying:

$$\vec{H} = -\nabla V_m \quad (\text{Eq. 59})$$

Taking into account that MF $\vec{B}$ is solenoidal (its divergence is zero, $\nabla \cdot \vec{B} = 0$), as stated in the magnetic form of Gauss's law (Eq. 2), and the constitutive equation which relates $\vec{B}$, $\vec{H}$ and magnetization $\vec{M}$:

$$\vec{B} = \mu_0(\vec{H} + \vec{M}) \quad (\text{Eq. 60})$$

the following equation for V_m can be derived:

$$-\nabla \cdot (\mu_0 \nabla V_m - \mu_0 \vec{M}_0) = 0 \quad (\text{Eq. 61})$$

Given the fact that $\nabla \cdot \vec{B} = 0$, a magnetic vector potential $\vec{A}$ could be calculated, so that $\vec{B} = \nabla \times \vec{A}$ (since the divergence of a curl is always zero).

For linear response materials, magnetization is proportional to magnetic field intensity ($\vec{M} = \chi_m \cdot \vec{H}$) and from (Eq. 60):

$$\vec{B} = \mu_0(1 + \chi_m)\vec{H} = \mu_0\mu_r\vec{H} = \mu\vec{H} \quad (\text{Eq. 62})$$

where μ_r is the relative permeability, μ_0 is the permeability of vacuum and μ is the permeability of the material. This is applicable to the air and sample placed between the magnets.

For 0.9% NaCl samples, χ_m was calculated according to the Wiedemann's additivity law:

$$X_{m,0.9\% \text{ NaCl}} = \frac{V_{\text{water}} \cdot X_{\text{water}} + V_{\text{NaCl}} \cdot X_{\text{NaCl}}}{V_{\text{water}} + V_{\text{NaCl}}} \quad (\text{Eq. 63})$$

where V_{water} and V_{NaCl} are the volume of pure water and NaCl in the solution, while X_{water} and X_{NaCl} are the magnetic susceptibility of pure water and NaCl, respectively [105].

Nevertheless, for a nonlinear response material such as the one forming magnets, this constitutive relation (Eq. 62) can be replaced by:

$$\vec{B} = \mu_0\mu_r\vec{H} + \vec{B}_r \quad (\text{Eq. 64})$$

Two different boundary conditions must be imposed to solve the FEM problem. The first one uses the symmetry of SMF with respect to any plane containing the magnet axes, which means that MF lines intersect none of those planes, expressed by the scalar product:

$$\vec{n} \cdot \vec{B} = 0 \quad (\text{Eq. 65})$$

in which $\vec{n}$ is the normal vector to the corresponding plane. On the other hand the second boundary condition establishes that MF lines are perpendicular to the symmetry plane of both

Mathematical equations governing the laboratory freezers assisted by an iron core and by a commercial inductor coil OMF generators

magnets parallel to their circular bases. Thus, V_m would be constant on that plane, selecting a value of zero in our model:

$$V_m = 0 \quad (\text{Eq. 66})$$

In the case of only one magnet homogeneously magnetized, this plane would correspond to the central one located at the middle between the north and south faces. However, with two magnets in the mentioned arrangement, the plane satisfying this condition is the one equidistant from both magnets and not the central plane of each. This is due to the fact that the resultant MF is the composition of the MFs generated by each magnet. Nevertheless, in our particular case, the condition of MF lines perpendicularity has been applied to the central plane of each magnet in order not to make the modeling very complex (see Section 3.1.1). This simplification could be considered valid, without introducing a great error, if the MF created on each of these two planes just by the other magnet is negligible compared to the MF generated by the magnet itself, so the more separated the magnets are, the smaller the error introduced.

The full analytical set of equations governing this problem is given in the Appendix 0.

2.4. Mathematical equations governing the laboratory freezers assisted by an iron core and by a commercial inductor coil OMF generators

As it is well known, the OMF generation is indefectibly joined to the employment of either variable currents or variable EFs. This fact implies a change in the Maxwell's equations with regard to those employed previously. Because both systems work at low frequencies, the analysis is carried out in the near field region and therefore the induced OEF $\vec{E}$ can be neglected. Therefore the Maxwell-Ampère's law (Eq. 4), considering also that no conductor part is moving, is expressed as:

$$\nabla \times \vec{H} = \vec{J} \quad (\text{Eq. 67})$$

where $\vec{J}$ is the current density. As happens in Section 2.3, MF $\vec{B}$ can be derived from a vector potential $\vec{A}$, so that $\vec{B} = \nabla \times \vec{A}$.

The constitutive (Eq. 62) is used as well on this occasion for all the materials. It is necessary to mention that for the iron constituting the core this equation is not fulfilled but instead there is a relation $\vec{H} = f(\vec{B})$ through a hysteresis loop. However, with the aim of showing a numerical simulation, a series of simplifications have been introduced, supposing that the iron core works in the linear part of the B-H curve (given the relatively small MF strengths) and thus allowing the use of such (Eq. 62). A value of relative permeability 1814 for the iron core was added to the model from an electric steel 2412 with the data extracted from [266].

As excitation conditions, the measured value of currents in each of the four coils in the commercial OMF generator and the current going through the coil in the case of the iron core

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inductor has been introduced in a cross section of each individual conductor. These currents I_{coil} provide the value of the previously mentioned current density through the equation:

$$I_{coil} = \iint \vec{J} \cdot \vec{n} \cdot dS \quad (\text{Eq. 68})$$

in which $\vec{n}$ is the vector normal to the cross section where the current is introduced and dS is a differential element of this section where the integral is calculated.

No boundary conditions were imposed in the OMF cases except for the outer medium surfaces which behave as magnetic insulators. This would not have a great influence in the iron core inductor given the fact that MF lines are very confined, without reaching these surfaces, whereas in the case of the inductor coils such surfaces are far enough from the region of interest where trays are located, not affecting MF simulated values in it.

2.5. Modeling of the MF freezers

Knowing the distribution of a MF through the volume of a freezing cell should be very useful in order to analyze and discuss the effects produced by the interaction between (i) the MF (generated by using a specific device), (ii) the election of a suitable device to be used for a specific freezing process and (iii) the components of food subjected to this process in which an adequate interaction is desired. Besides, and as occurs in other cases, it is neither easy nor convenient to carry out direct determinations of the MF involved in a process in order to optimize performances or to avoid perturbations or undesired interactions. So getting a reliable model of the MF-generating device containing the sample to be frozen is a valuable tool.

Because of the lack of data existing in the scientific world, numerical modeling and experimental determinations are shown in this work in order to appreciate the MF strength and MF vector direction produced by a SMF generator, by an iron core OMF generator, by a solenoidal OMF generator and by an OMF generator formed by four coils, the latter being a simplified model of the OMF-generating part of the commercial EM freezer of Kotobuki [47].

In a similar way as performed in the literature when dealing with modeling freezing processes, it is peremptory to seek about the MF distribution inside the sample to be frozen and then to be able to characterized possible effects of MF strength and direction during freezing. In this relation, the modeling of the above described magnetic freezers is shown here. In the case of the two permanent magnets and in addition to the direct solving of the above described mathematical equations, the FEM program COMSOL Multiphysics® (v. 4.2, COMSOL AB, Stockholm, Sweden), was used in order to determine the characteristics of MF in each point of the sample. This software, based on the resolution of the above mathematical (Eq. 59) to (Eq. 62) and (Eq. 64) to (Eq. 68), allows simulating the behavior of any system in which the effects of one or several different physical phenomena want to be studied. In the present work, it was used to evaluate the MF strength and the direction of MF lines created by the mentioned two permanent magnets as well as by the OMF generator of the commercial freezer of Kotobuki

(Figure 2-2). On the other hand, ANSYS Maxwell (v 16, ANSYS Inc., Canonsburg, PA, USA) was used to model the iron core and the air core OMF generators, applying in each case the specific boundary conditions.

2.6. Statistical analysis

In order to do an adequate analysis of the possible effects that the different MF conditions employed in this thesis have had on the freezing behavior and measured quality parameters, the different results have been compared by means of a software package of Statistics (IBM SPSS Statistics v. 24.0.0.1, IBM Corp., Armonk, NY, USA). Although the followed steps have been basically the same in all the set of experiments, the approach has been very different depending on the number of assessed treatments. Therefore when only two experimental conditions were studied, a general linear model was used. Such is the case of the freezing experiments performed with magnetic nanoparticle dispersions. In this case, after the pertinent normality and homoscedasticity tests, if the hypothesis of normality was not rejected (only happened for V_t) then a Student-t test was carried out. Otherwise the Mann-Whitney U test was applied for analyzing possible significant differences between both groups. On the contrary, when three or more set of conditions are studied, the comparison of means is carried out through a one-way analysis of variance (ANOVA) in those cases in which the data conformed a normal distribution, whereas when the assumption of normality was not confirmed, the non-parametric Kruskal-Wallis test was employed. This latter is the procedure followed in the rest of experiments of this thesis. Regarding the methods used for the verification of normality and homoscedasticity, they were in all the cases the Shapiro-Wilk's and Levene's tests, respectively. If the test of comparison between means in the ANOVA or Kruskal-Wallis's tests resulted in the appearance of any significant difference, the subsequent post-hoc test Tukey b or Tamhane were done. A significance level of 0.05 was employed in all the experiments.

For the magnetic nanoparticle dispersion freezing cases, two series of freezing experiments, with not less than fifteen repetitions each, were executed for the cases with MF and without MF, respectively. The potential effect of OMF and freezer temperatures on the freezing curve parameters considered in Section 2.2.1 and through a general linear model was analyzed. It could be seen that such parameters did not vary significantly with the freezer temperature, so the only effect of the OMF was analyzed.

In the experiments of SMF freezing of water and NaCl solutions, thirty independent repetitions were conducted, and the statistical analysis of different parameters extracted from the freezing curve (t_{nuc} , T_c^{nuc} , ΔT_c , t_{ptr} and t_{tot}) was completed. Likewise the same analysis was carried out in OMF freezing experiments of pure water, with not less than fifteen independent trials.

Analogously in the freezing experiments carried out in commercial equipment, the corresponding statistical analysis was performed. Such is the case of the magnetic freezing of pork loin samples, where independent variables (characteristic freezing time, completion of

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freezing rate, percentage of drip loss, variation of color parameters (ΔL^* , Δa^* , Δb^*), density, hardness, force A, force B and elasticity) were compared. On the other hand, for the experiments on crab sticks, at month 0, a multivariate step-wise linear discriminant analysis was carried out to determine whether the fresh samples and those frozen by different methods can be distinguished and, in this case, which quality attributes are the best to explain the differences among them. To test the main effects of the freezing conditions and the storage time on the quality attributes of the thawed crab sticks, a two-way analysis of variance (ANOVA) was performed on the data by using the General Linear Model procedure of the statistical software.

3. Results

3.1. Effects of SMF generator in the freezing of water and solutions of NaCl

3.1.1. Modeling of the laboratory freezer assisted by a SMF generator

Since the validity of the model should be checked, the agreement among the experimental results, the ones obtained by solving the set of analytical equations given in the Appendix 0 and the results found by using the modeling procedure was assessed. For this aim, the device represented in Figure 2-3a was used and attention was paid to determining the SMF $\vec{B}$ (mT) produced at several particular locations. While it could be easy to geometrically determine MF at any interesting point by using mathematical or modeling procedures, some inaccuracies are produced on situating the experimental probe at a certain position, mainly due to two reasons: (i) the sample occupies a space which interferes with the placement of the probe, and (ii) even though this problem was eluded, it would be difficult to precisely control the position and orientation of the probe. Keeping in mind these limitations, one of the specifically chosen locations was the central axis which connects the centers of both magnets. To make a broader study, two different situations, i.e. repelling and attracting setups were analyzed depending on the relative position of the parallel faces of the magnets. The MF strength distribution along the central axis of the repelling magnets is shown in Figure 3-1a

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Figure 3-1: The laboratory SMF generator used for freezing. Comparison of the values of magnetic field distribution: a) Along the central axis of the repelling magnets, $\blacksquare$: measured by a teslameter, $\bullet$: extracted by the COMSOL model, and $\blacktriangle$: extracted by solving (Eq. A5) of the Appendix 0; b) Along the central axis of the attracting magnets, $\blacksquare$: measured by a teslameter, $\bullet$: extracted by the COMSOL model, and $\blacktriangle$: extracted by solving (Eq. A5) of the Appendix 0; c) Along a line perpendicular to the axis of both repelling magnets at its middle point, $\blacksquare$: measured by a teslameter, $\bullet$: extracted by the COMSOL model, and $\blacktriangle$: extracted by solving (Eq. A6), (Eq. A7) and (Eq. A10) of the Appendix 0

while the corresponding to the attractive setup is depicted in Figure 3-1b for a separation distance of 42 mm between magnets. It is well known that on that axis MF has only axial component. Analogously, the MF radial component at several points along a line perpendicular to that longitudinal axis and crossing it at its central point was also determined, only in the case of magnets repelling (Figure 3-1c), because in the attracting arrangement the MF does not have any radial component just on the central plane between magnets. It must be taken into account that in the repelling setup, the axial components of MF on the plane placed in the middle of magnets cancel each other out by symmetry, so the radial component represented in Figure 3-1c coincides with the total MF strength as well. The MF values obtained by using the direct resolution of mathematical equations given in the Appendix 0 and the results achieved through the modeling software fit quite properly the corresponding experimental results, as depicted in those Figures. For the first two cases, the MF presents higher intensity values than the experimental ones near the magnet surfaces, although the difference tends to

vanish towards the middle point. Nevertheless some interesting differences can be appreciated when analyzing not only the strength but also the orientation of the MF vector produced in the sample, depending on the relative positions of the magnet poles. Thus when the magnets are arranged in a position attracting each other, the MFs created by both magnets have the same direction along the axis, whereas they have opposite directions if magnets are disposed in a repulsive way, which leads to a total cancelation of MF just in the middle point between magnets. Concerning the behavior of MF along a line parallel to the magnet bases on the plane shown in Figure 3-1c, as stated previously, there will be only radial component with MF directed outwards the center. In this latter case, MF strength initially increases as the point considered goes further from the center (Figure 3-1c). Although it has not been shown in this Figure, at a certain distance the MF reaches a maximum, decreasing for further distances due to the rotational nature of the field. This maximum appears when MF lines generated by both magnets become tangential to the considered line.

Figure 3-2: The laboratory SMF generator used for freezing: a) Geometrical disposal of elements for modeling and b) volume used for its modeling

When dealing with the MF vector, in Figure 3-2a, the schematic disposal used for modeling the above described MF generator (Figure 2-3a) with the sample inside is shown (Figure 2-3b). The vial in the model is placed horizontally just to make the magnet axes coincide with the vertical direction in cylindrical coordinates, but in the experiments all the set was actually rotated 90 °, with the vial in vertical position. Taking into account the non-magnetic character of the materials used for the structure to hold the magnets (PMMA and Teflon®, as seen in Section 2.1.3), the glass from the vial and the microscope slide, and also the vial plastic caps to hold up and to close the vial, a simplification in the FEM model was made by selecting only air as the material between magnets and sample. The model for the sample was designed as a cylinder of water with $\phi=23.2$ mm in diameter and height of $h=34.2$ mm which is the value measured from the vial base to the meniscus of the liquid sample. Taking symmetries into account, using the quadrant represented in Figure 3-2b allows optimizing the simulation, reducing unnecessary time and processing resources consumption. The qualitative distribution of MF

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strength and direction when magnets are disposed either with equal or with different polarity positions of the parallel faced surfaces, i.e. in a repulsive or in an attractive way, are shown in Figure 3-3a and Figure 3-3b, respectively.

Figure 3-3: The laboratory SMF generator used for freezing. Color: normalized magnetic field strength (T). Curves and vectors: directions of magnetic field lines. a) Repulsion due to like faced polar surfaces; b) Attraction due to opposite faced polar surfaces

In the first case, the repulsive one in Figure 3-3a, MF lines go out from each magnet and tend to return to its own opposite pole without crossing the central surface situated in the middle of the volume between magnets, whereas in Figure 3-3b many of those lines go out from one magnet pole to the opposite pole of the other magnet, crossing always perpendicularly the mentioned central surface. In addition, MF strength behaves in a different way depending on the relative orientation of magnetic poles. In the space between magnets, when oriented in a repulsive way, MF tends to be stronger upon moving away from the central point. On the contrary, when oriented in an attractive way, MF tends to be stronger towards the centers of the faced surfaces of each magnet. Besides MF strengths are in both cases higher towards the periphery lateral surface, inside and in the adjoining zones of each magnet [267, 268]. This can

be explained by considering a magnet uniformly magnetized in which magnetic moments are represented as small current loops which occupy all the volume of the magnet. As in all these loops their current rotates in the same direction, then for the inner elements, current would compensate with that of their neighboring current loops and only the current in magnet lateral surface would not be cancelled out [269], being a model similar to that employed here to calculate the MF on the axis of the magnet by means of Biot-Savart's law (see Figure 8-1 in Appendix O).

Due to its practical interest, the MF produced for the minimal distance between magnets in the employed device (38 mm), and depending on the polarity of its relative orientation, was obtained: in attractive (Figure 3-4a and Figure 3-4b) and repulsive (Figure 3-4c and Figure 3-4d) ways.

Figure 3-4: The laboratory SMF generator used for freezing: Distribution of magnetic field in the sample when magnets are oriented in an attractive way: a) MF vectors. b) MF strength (in mT); and in a repulsive way: c) MF vectors. d) MF strength (in mT)

In these cases both MF strength and MF vectors depicting magnitude and orientation are given. Only the central section of the generator, corresponding to a representative quarter of the volume of the sample holder, Figure 3-2b, has been selected for modeling purposes. MF vectors and strength for the attractive case are depicted in Figure 3-4a and in Figure 3-4b, respectively. Here, it can be appreciated that this MF strength reaches its maximum value

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(359.6 mT) on the parts of the sample near the external surfaces of the sample holder which face both magnets, exactly at the points where the axis crosses these surfaces. This strength progressively decreases in the volume along the axis separating the geometric centers of the magnets, reaching a value of 245 mT at the geometric center between magnets. The experimental measured MF strength turns out to be 237 mT, very close to that of the model. As the distance to this axis increases, MF strength vanishes on any of the surfaces parallel to those of the magnet poles and to a greater extent on those which are situated in the middle volume of the sample holder. MF reaches here its minimum value at the points in the middle of the base and the meniscus of the liquid sample (106.2 mT), i.e. the points furthest from both magnets, as expectable. In turn, Figure 3-4c and Figure 3-4d represent the MF vectors and the MF strength, respectively, when the magnets are oriented in a repulsive way. It can be appreciated that the MF line orientations loss perpendicularity with regard to the attracting magnet setup. In this case, the MF strength at the center of the sample holder vanishes. The value obtained through the model (0.7 mT) is close to zero as theoretically should be obtained. This fact should be in agreement with [78] who found a minimal value of MF strength for this case. However the value provided in that work (50 mT) is further from the theoretical one than in our model, maybe due to some imprecision in the point of measurement, as explained previously. In that sense our experimental measurements gave 7 mT, lacking also the accuracy obtained by means of modeling. When having a FEM model with a smaller element size this discrepancy should be reduced. Going away from this center, MF strength increases up to 242.7 mT, in an opposite way to what happens when separating from the axis connecting the geometric centers of magnets in the attractive disposition (Figure 3-4b).

It becomes interesting to realize that an attractive or repulsive disposal of the polarities of magnets in the SMF freezer matters concerning the MF strengths produced in a position. Although MF strength being in both cases higher towards the periphery inside each magnet, MF lines behave in a very different way, crossing or not the central plane of the volume between magnets. This fact could be important when trying to correlate MF effects in combination with other processing phenomena as occurs in food freezing. When looking for actions produced by the MF in a sample, it is necessary to be aware that MF strength significantly decreases at short distances from the magnets. This fact could produce inhomogeneity in the corresponding effects on the exposed sample. The MF strength vanishes at the center of the cell for the repulsive disposal of magnets. As it could be expected, due to the fact that magnetic susceptibilities are so small in the air (paramagnetic medium) and both in pure water and in 0.9% NaCl aqueous solution (diamagnetic mediums), MF strength differences are negligible and in this particular case, some additional simplification could have been done.

3.1.2. Evaluation of the modeling and the analytical solutions for the laboratory freezer assisted by a SMF generator

As a general rule, it is convenient to contrast significant discrepancies between the results provided by the FEM model and by the mathematical equations. For this purpose, comparisons

with the analytical equations given in the Appendix 0 have been made in eight representative points (I to VIII in Figure 3-4a and Figure 3-4c), under the conditions of magnets placed in an attractive and a repulsive way and at the minimum possible distance. By using cylindrical components (ρ , φ , z), the average of MF relative errors for these eight points, B_{error} (%), calculated between the values of MF given by the FEM model, B_{FEM} (mT), and those obtained from the analytical solution, B_{an} (mT), expressed by the equation:

$$B_{error} = \left(\frac{B_{FEM} - B_{an}}{B_{an}} \right) \cdot 100 \quad (\text{Eq. 69})$$

have been exposed in Table 3-1 for the error components $B_{p,error}$ (radial) and $B_{z,error}$ (vertical) and for their total sum, $B_{total,error}$, having a maximum error value of 5.75 %. In this case, both the FEM modeling and the analytical approaches have been proved as good methods for defining the MF applied to a volume of water or aqueous solutions (such as the ones presented here) during a process of magnetic freezing, characterizing both the MF strength and the line directions.

	$B_{p,error}$ (%)	$B_{z,error}$ (%)	$B_{total,error}$ (%)
Attractive disposal	1.12	5.75	5.09
Repulsive disposal	4.47	5.23	4,71

Table 3-1: Error average of B_p (radial) and B_z (vertical) components and total error between the MF strength calculated by FEM or analytical models in the SMF generator

With a practical purpose, a simplified model considering macroscopic magnetic properties can be extended to model foods different from water. Thus contemplating a 0.9% NaCl solution as the one used by [78], it is necessary to find its magnetic susceptibility, $\chi_{mixture}$. Wiedemann's additivity law has been used for this goal (Eq. 63).

Although this law may have some limitations [270], it turns out to be a valid calculation for the susceptibility in alkali and alkaline earth halide solutions [271]. Thus obtaining the susceptibility $-1.40 \cdot 10^{-5}$ for NaCl from the value of molar susceptibility provided in [272], and with the volumetric proportions of solvent and solute for a solution of 0.9% NaCl, **¡Error! No se encuentra el origen de la referencia.** results in a susceptibility of $-9.067 \cdot 10^{-6}$, very close to that of water and it produces a negligible effect on the behavior of MF strength and lines with regard to that of pure water [273]. Nevertheless, there may be a non-considered effect due to a higher mobility of ions Na^+ and Cl^- in the presence of a MF because of the Lorentz force, tending to reduce the number of hydrogen bonds [274] when the concentration reaches a certain level, which may give rise to an increase in supercooling [21]. This fact would not explain the differences encountered by [78] when magnets are placed in an attractive or a repulsive way, because the rotation in the direction of MF lines, easily appreciated macroscopically by comparing Figure 3-4a and Figure 3-4c, would be negligible however at a

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molecular level in the range of the hydrogen bond network, and in any zone at this level MF lines could be considered mainly parallel. As exposed by [274], an increase in MF strength would be the cause of an enhancement in the hydrogen bond network both in pure water and in a low concentration NaCl solution (1 M). This may be the factor, and not the outward direction of MF lines, which provokes an increase in the phase transition time during the freezing of a 0.9% NaCl solution (1.5 M) when the magnets are attracting each other in [78], i.e. when MF strength is higher, producing a growth in the number of hydrogen bonds and a subsequent decay of supercooling. The reduction on phase transition time when magnets are in a repulsive position, regarding the phase transition time without MF, would however remain unexplained. It may happen that the relative orientation between crystal growing direction and MF lines which depends on each particular experimental setup could explain the results encountered by [78] better than the “sequential rotary effect” of water molecules.

As occurs in common situations, several materials with different magnetic characteristics are present in MF freezing. Consequently, it is also important to notice that the relative permeability shown in the analytical equations given in the Appendix 0 is valid if only one material is present between magnets. By contrast, the FEM model allows a higher versatility, with models being valid also when several materials with different relative permeabilities between magnets are employed.

3.1.3. Effect of SMFs on water freezing

Following the experimental procedure explained in Section 2.1.6, typical time-temperature plots at the sample center and on the external surface of the vial containing it, obtained during conventional freezing experiments of pure water are shown in Figure 3-5a and Figure 3-5b.

Figure 3-5: Temperature evolution at the sample surface (---) and center (—) during freezing experiments in (a-b): pure water and (c-d): 0.9% NaCl solutions with no SMF application. (a and c): Typical experiments with partial supercooling of the sample ($\Delta T_c = 0$ °C) and (b and d): Typical experiments with complete supercooling of the whole sample ($\Delta T_c > 0$ °C). ΔT_c : Extent of supercooling reached at the sample center just before nucleation. Key steps of the process: (1): precooling, (2): phase transition, and (3): tempering

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During the freezing process, thermal gradients were established along the samples. Thus, the temperature at the sample surface, which is in contact with the cooling medium, was always lower than that at the sample center. The SMFs applied in this work, whose characteristics are studied in Section 3.1.1, did not affect the shape or the appearance of the freezing curves and the time-temperature plots obtained in SMF freezing experiments were similar to those depicted in Figure 3-5 (plots not shown).

The freezing curves clearly exhibited the three key stages of the process: precooling, phase transition, and tempering, Figure 1-1. In the precooling step, the cooling of the sample implied the removal of only sensible heat. Although the real temperature at the sample surface was not measured, but the temperature at the external surface in contact with the coolant, some facts were inferred from it. Thus it was observed that once the freezing point of pure water ($T_f = 0\text{ }^{\circ}\text{C}$) was reached at the sample surface, ice nucleation did not occur immediately in any case, but all the samples supercooled to a temperature well below T_f . Then, after reaching a certain extent of supercooling, ice nucleation suddenly occurred.

Figure 3-6a certainly shows the stochastic nature of ice nucleation. Thus, and according to the literature [10, 275], we found that ice nucleation did not occur at the same time or after reaching the same extent of supercooling in repeated experiments. At the conditions tested in this paper, ice nucleation was triggered between 67 s and 175 s after immersing the sample in the cooling medium, when the temperature at the sample center ranged between $10.4\text{ }^{\circ}\text{C}$ and $-11.1\text{ }^{\circ}\text{C}$.

Figure 3-6: Temperature (°C) and extent of supercooling (°C) at the sample center when nucleation occurred in (+): control, (○): SMF-A, and (Δ): SMF-R experiments. a) Pure water samples; b) 0.9% NaCl solutions

Figure 3-6a revealed no effect of the SMF application on both variables presented in Section 2.2.1, t_{nuc} and T_c^{nuc} ($p > 0.05$, Table 3-2). Due to the established thermal gradients, T_c^{nuc} is the temperature at the hottest point in the sample when nucleation occurred and, therefore, ΔT_c represents the minimum supercooling reached throughout the sample. Obviously, the later the nucleation occurred, the lower T_c^{nuc} , the larger the extent of supercooling reached throughout

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the sample and, consequently, the larger ΔT_c (Figure 3-6a). For example, in Figure 3-5a, ice nucleation was triggered early, namely 75 s after the onset of the freezing experiment.

	Shapiro-Wilk			ANOVA	Kruskal-Wallis
	No SMF	SMF-A	SMF-R		
Pure water samples					
t_{nuc}	0.003	0.002	0.014	--	0.408
T_c^{nuc}	0.000	0.000	0.004	--	0.440
ΔT_c	0.191	0.063	0.170	0.996	--
t_{pt}	0.001	0.015	0.113	--	0.619
t_{tot}	0.079	0.126	0.097	0.068	--
0.9% NaCl solutions					
t_{nuc}	0.005	0.067	0.415	--	0.830
T_c^{nuc}	0.000	0.001	0.008	--	0.742
ΔT_c	0.073	0.611	0.730	0.577	--
t_{pt}	0.027	0.042	0.022	--	0.827
t_{tot}	0.917	0.576	0.814	0.837	--

Table 3-2: p-values obtained after applying the Shapiro-Wilk test to check the normality of the data and the Kruskal-Wallis and ANOVA tests to compare the characteristic parameters of control (no SMF application), SMF-A, and SMF-R freezing experiments. t_{nuc} : Time at which nucleation occurred, T_c^{nuc} : Temperature at the sample center when nucleation occurred, ΔT_c : Extent of supercooling at the sample center if exists ($\Delta T_c > 0$), t_{pt} : Phase transition time, and t_{tot} : Total freezing time

At that moment, the sample surface was supercooled ($\Delta T_s = 10.6$ °C), but the temperature at the sample center was still above T_f ($T_c^{nuc} = 10.1$ °C), that means, $\Delta T_c = 0$. Therefore, ice nuclei were formed only at the sample surface where enough extent of supercooling had been reached. By contrast, in Figure 3-5b, ice nucleation was triggered much later, namely, 132 s after immersing the sample in the cooling medium. At this time, the sample was completely supercooled ($\Delta T_s = 19.5$ °C and $\Delta T_c = 6.6$ °C) and, therefore, ice nucleation took place throughout the whole sample and not only at the surface. When no SMFs were applied, complete supercooling of the whole sample before nucleation or, in other words, $\Delta T_c > 0$ °C, occurred in 14 of 30 experiments. This proportion was similar to that observed when the magnets were arranged either in attractive or in repulsive positions (16 of 30 experiments and 18 of 30 experiments, respectively). Moreover, in these experiments in which supercooling occurred at the sample center, $\Delta T_c (> 0)$ was not significantly affected by the SMF application ($p > 0.05$, Table 3-2) and, thus, mean ΔT_c values were close to 5 °C in all cases (Table 3-3). Therefore, in contrast to some results reported in the literature [75, 76] and according to [77], we did not find any effect of SMFs on water supercooling.

	No SMF	SMF-A	SMF-R
Pure water samples			
t_{nuc}	99 ± 4	103 ± 4	106 ± 5
T_c^{nuc}	2.6 ± 1.3	1.5 ± 1.3	0.5 ± 1.3
ΔT_c	4.8 ± 0.7	4.8 ± 0.6	4.8 ± 0.7
t_{pt}	430 ± 4	430 ± 4	425 ± 4
t_{tot}	605 ± 2	611 ± 2	605 ± 2
0.9% NaCl solutions			
t_{nuc}	115 ± 4	110 ± 4	110 ± 3
T_c^{nuc}	-0.9 ± 1.2	0.2 ± 1.2	-0.5 ± 1.0

Effects of SMF generator in the freezing of water and solutions of NaCl

ΔT_c	5.6 ± 0.5	5.4 ± 0.7	4.3 ± 0.5
t_{pt}	437 ± 3	440 ± 4	440 ± 3
t_{tot}	637 ± 3	635 ± 2	636 ± 2

Table 3-3: Mean $\pm$ standard error values of the characteristic parameters of control (no SMF application), SMF-A, and SMF-R freezing experiments. t_{nuc} : Time at which nucleation occurred, T_c^{nuc} : Temperature at the sample center when nucleation occurred, ΔT_c : Extent of supercooling at the sample center if it exists ($\Delta T_c > 0$), t_{pt} : Phase transition time, and t_{tot} : Total freezing time

After nucleation, crystal growth occurs by the addition of water molecules to the formed nuclei. During the phase transition step, the temperature at the center of the sample remained constant at T_f until all the water was converted into ice and the latent heat of crystallization was removed (Figure 3-5a and Figure 3-5b). Figure 3-7a confirms previous data in the literature [4, 276, 277] that show that the larger the extent of supercooling attained throughout the sample (or, in other words, the longer the nucleation time), the larger the amount of ice instantaneously formed at nucleation and, therefore, the shorter the phase transition step. In this paper, the phase transition time ranged between 381 s and 462 s in repeated experiments and no effect of SMFs was detected ($p > 0.05$, Table 3-2).

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Figure 3-7: Phase transition time (s) in (+): control, (O): SMF-A, and (Δ): SMF-R experiments. a) Pure water samples; b) 0.9% NaCl solutions

Once all water was transformed into ice, the sample temperature decreased while sensible heat was removed during the tempering step (Figure 3-5a and Figure 3-5b). No effect of SMFs on the rate of heat removal during the freezing process was observed and, thus, the total freezing times did not differ significantly in control, SMF-A, and SMF-R experiments ($p > 0.05$, Table 3-2).

3.1.4. Effect of SMFs on freezing of 0.9% NaCl solutions

The time-temperature plots obtained during control experiments in 0.9% NaCl solutions (Figure 3-5c and Figure 3-5d) were similar in shape and appearance to those recorded for pure water except for the temperature at the freezing plateau ($T_f = -0.6\text{ }^{\circ}\text{C}$). When the SMFs were applied, the freezing curves were not visually affected and the SMF freezing plots seem to be identical to the control ones (plots not shown).

As occurred in pure water, no effect of the applied SMFs was detected, whichever the direction of the field forces, on supercooling. In 0.9% NaCl solutions, ice nucleation occurred between 77 s and 154 s after immersing the sample in the cooling medium (Figure 3-6b) and t_{nuc} distributions were similar in control, SMF-A, and SMF-R experiments ($p > 0.05$, Table 3-2). Depending on nucleation time, the samples were supercooled in a greater or lesser extent (Figure 3-5c and Figure 3-5d) and, thus, T_c^{nuc} ranged between $8.3\text{ }^{\circ}\text{C}$ and $-9.8\text{ }^{\circ}\text{C}$ (Figure 3-6b). When no SMFs were applied, complete supercooling of the entire sample, that is, $\Delta T_c > 0$, occurred in 18 of 30 experiments. Similar proportions, 15/30 and 17/30, were observed in the SMF-A and SMF-R experiments, respectively. ΔT_c , when existed, ranged between $0.5\text{ }^{\circ}\text{C}$ and $9.2\text{ }^{\circ}\text{C}$ and no effect of SMFs on either T_c^{nuc} or ΔT_c was detected ($p > 0.05$, Table 3-2).

The phase transition time, negative correlated to the nucleation time (Figure 3-7b), and the total freezing time distributions were similar in control, SMF-A, and SMF-R experiments (Table 3-3). Thus, in contrast to the results reported by [78] and [77], no effect of SMFs was found, whichever the direction of the field forces, on the freezing kinetics of 0.9% NaCl solutions ($p > 0.05$, Table 3-2).

3.2. Effects of an iron core OMF generator in the freezing of iron solution, enzymes, larvae and magnetic nanoparticle colloid

3.2.1. Modeling the laboratory freezer assisted by an iron core OMF generator

Paying attention to the possibilities to build a simple OMF generator, the iron core device explained in Section 2.1.4 was chosen. As mentioned there, a variable OMF is generated in the iron core inductor by modulating the current flowing with a variable autotransformer, Figure 2-4a. By using the Teslameter referenced in Section 2.1.1, the selected OMFs proved to be 0.33, 0.8, 1.5 and 7.0 mT at 50 Hz by varying the supplied current source. Using the results obtained by means of 3D modeling, Figure 3-8 contains three different but complementary sections of the distribution of MF strength for the case of 7.0 mT selected at the position occupied by the sample in the air gap of the core, Figure 2-4b, namely, a) Front view,

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corresponding to a perpendicular section to x axis, b) Right view, corresponding to a perpendicular section to y axis, and c) Top view, corresponding to a perpendicular section to z axis. The legends on the left show the corresponding relation between colors and MF peak intensities, therefore considering their sinusoidal character, the given values should be divided by $\sqrt{2}$ to get the RMS MF strength. It can be appreciated that this magnitude is very homogeneous around the middle of the volume, just where the sample to be frozen should be disposed. As occurs for 0.33, 0.8 and 1.5 mT (graphics not shown), in Figure 3-8, for the case of 7.0 mT, it can be seen that MF is more homogeneously distributed at the center than in the periphery due to boundary effects because MF lines are not so perpendicularly directed here as at the center, appearing a fringing flux around the air gap, where MF is not confined as it is in the ferromagnetic core. This is the reason for the dispersion of a certain amount of MF around the air core volume.

Figure 3-8: The laboratory iron core OMF generator used for freezing. Distribution of magnetic field in the volume occupied by the sample. a) Front view, b) Right view, c) Top view

In order to show a more detailed graph of MF gradient variation in the air gap, all MF strengths higher than 14.13 mT are represented in red (inside the core) whereas those lower than 2.87 mT are depicted in the darkest blue (in the air around the core and far from the air gap), independently of the values of 2 and 15 mT showed in the legends of Figure 3-8 which would erroneously seem to be the limits.

3.2.2. Effects of an iron core OMF in the freezing of magnetic iron solution

In the case of tetrachloroferrate anion $[\text{FeCl}_4]^-$, the magnetic susceptibility of the iron solution has evidenced an antiferromagnetic character, displaying a transition to a paramagnetic behavior for temperatures higher than the Néel temperature, which turns out to be of 9.75 K [278] for FeCl_3 .

The maximum air speed, measured by the hot-wire anemometer of Section 2.1.1 and the cooling air temperature inside the Koxka freezer were 0.24 m/s and $-22.74\text{ }^\circ\text{C} \pm 0.12$, respectively.

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	No OMF (control)	0.33 mT	0.8 mT	1.5 mT	7.0 mT
Precooling rate V_p (°C/min)	-1.8 ± 0.1	-1.8 ± 0.1	-1.8 ± 0.1	-1.9 ± 0.1	-1.8 ± 0.0
Supercooling degree ΔT (°C)	3.5 ± 1.6	1.2 ± 0.3	5.6 ± 1.9	3.3 ± 2.0	1.7 ± 1.7
Phase change time t_{p0} (min)	51.1 ± 1.3	48.6 ± 2.7	50.0 ± 2.4	48.6 ± 1.9	50.5 ± 1.2
Phase change time t_{pd} (min)	49.2 ± 1.6	48.6 ± 1.2	48.1 ± 3.7	45.9 ± 2.0	48.0 ± 1.5
Tempering rate V_t (°C/min)	-0.9 ± 0.1	-0.9 ± 0.1	-0.9 ± 0.0	-1.0 ± 0.0	-1.0 ± 0.0
Total freezing time t_{tot} (min)	92.5 ± 3.0	89.5 ± 2.0	93.1 ± 2.5	87.3 ± 1.5	89.0 ± 0.8

Table 3-4: Averages $\pm$ standard errors for each OMF treatment for FeCl₃ solution: Precooling rates, V_p (°C/min); Supercooling degree, ΔT (°C); Phase change times, t_{p0} (minutes); Phase change times, t_{pd} (minutes); Tempering rates, V_t (°C/min); Total freezing times, t_{tot} (minutes). No letters indicate no significant differences between means for each row

When analyzing the main freezing curve parameters of the ferric chloride solution subjected or not to those weak OMFs (Table 3-4), it is appreciated that no significant deviations are found among them and respecting the non-application of OMF. In the literature, high attention is paid to look for the effect of processing parameters on the appearance of ΔT or on its correlated T_n . In this respect, important endeavors are being carried out to control T_n in freezing processes [21]. Before appearing T_n in Figure 1-1, more and more formation of hydrogen bonds and more ordered structures in liquid water will happen [279]. But with regard to the non-application of OMF, the action of applying those four weak OMF freezing could have no significant influence on V_p and on the appearance of T_n . Respecting a purely diamagnetic material as water [280] a major contribution of the magnetic moment of the FeCl_3 solution should be expected regarding alterations on the T_n appearance in the freezing curve when the sample was subjected to those OMFs. The magnetic behavior of the used ferric solution subjected to those OMFs during freezing could not bring on the appearance of nucleation sites (then decreasing T_n) whose aggregation should be inhibited (and no ice crystals produced) by the action of the oscillations of those OMF. This argument should remain even in the case that a potential precipitation of ferric particles had happened [161]. Those authors suggested that the presence of ferromagnetic materials in biological tissues, principally biologically precipitated magnetite (Fe_3O_4), could be relevant to inhibit ice nucleation. By using a commercial OMF freezer in [45], its potential thermal effects in freezing garlic are analyzed. They find that the measured MF near the sample (0- 0.418 mT) has little significant additional effect on the freezing curve characteristics or on T_n in comparison with freezing under the same environment without OMF. Also working on the OMF (0.5 mT/50 Hz) freezing of w/o emulsions and food materials, [50] do not detect any apparent difference in temperature history aspects of the freezing curve caused by applying OMF respecting its non-application. This is in agreement to the obtained t_{p0} , t_{pd} , V_t and t_{tot} freezing curve parameters where just a pure heat transfer phenomenon should mainly govern those parts of the freezing curve.

Considering the analyzed parameters of the freezing curve of FeCl_3 , there is therefore no clear evidence about the claimed potential effects of OMF in the studied strength and frequency ranges. However further studies would be interesting with other ranges of OMFs.

3.2.3. Effect of OMF on the lactate dehydrogenase (LDH) activity

As control of the cryoprotective activity assay, the freeze-thaw protocol with liquid nitrogen was checked, resulting in a 98 % loss of LDH activity relative to the unfrozen control. However, as expected, lower loss of LDH activity (72 %) was obtained when slow freezing was applied (at a temperature of -23 °C in the Koxka freezer). This fact can be explained since fast cooling provides much more stress to proteins than a low cooling rate [192, 281]. Probably, protein denaturation occurs at the ice-water interface, therefore rapid cooling leads to formation of many small ice crystals, with larger surface area than the crystals produced by slow cooling.

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Regarding the potential cryoprotective effect of OMFs (7 mT/50 Hz/-23 °C and the same air velocity as in Section 3.2.2), no cryoprotective activity was found since the remnant relative activity was in the same range ($28.2 \% \pm 3.3$ vs $29.5 \% \pm 1.7$), probably due to the low frequency applied in combination with the slow freezing process. In that regard [282] found out that high frequency EM fields, in the microwave frequency region, affected to LDH activity. It was theoretically demonstrated in [283] that below a limit of frequencies it is not possible to get a modification of proteins depending on the number of their amino acids. Therefore, it would be interesting in further studies the combination of high range of frequencies with the freezing process to determine the potential cryoprotective effect.

3.2.4. Effects of an iron core OMF on viability of *Anisakis* and water-holding capacity in experimentally infected minced hake muscle

Freezing profiles of minced fish muscle (Figure 3-9), in the same temperature and air speed conditions as indicated in Sections 3.2.3 and 3.2.2, respectively, showed that a smooth variation of temperature with time was obtained in the freezing curves before the plateau with a similar behavior for both cases; no significant decrease of the supercooling temperature T_n when applying OMF was found either, thus the potential decrease in T_n , associated with a supercooling degree increase and faster ice nucleation was not appreciated [21, 47]. This result is in agreement with [16] where the absence or the presence of OMF (0.04 to 0.53 mT) in pork loin freezing did not show a significant degree of supercooling.

Figure 3-9: Freezing curves of the minced hake muscle during freezing by applying or not OMF (7 mT)

Effects of an iron core OMF generator in the freezing of iron solution, enzymes, larvae and magnetic nanoparticle colloid

In both trials performed with hake mince infected with *Anisakis* L3, 100% of the larvae were inactivated by OMF freezing and, as expected, conventional freezing also rendered 100% mortality under the tested conditions. These results suggest that OMF would be safe in terms of *Anisakis* inactivation and any possible reported beneficial effects of those OMFs on the membrane fluidity or stability to resist dehydration damage caused by freezing, if present, was not able to counteract the damage produced by the increasing volume of water due the liquid-solid phase change inherent to freezing [92].

Changes in muscle characteristics were studied by means of WHC, a well-known indicator that has been reported to correlate with sensory attributes of fish muscle [284]. Depending on the processing conditions, this property decreases during freezing and mainly during frozen storage [194]. Since the freezing experiments (i.e. without and with OMF) had to be done sequentially in the same freezer, the comparison of the WHC of the frozen thawed samples with the unfrozen ones was performed with hake mince stored for the same period at 4 °C (Table 3-5):

Sample	9 days <i>post-mortem</i>		12 days <i>post-mortem</i>	
	Fresh	frozen (0 mT)	fresh	frozen (7 mT)
WHC (%)	62.29 ± 2.34	61.03 ± 1.83	68.31 ± 3.76	68.29 ± 1.04

Table 3-5: Water-holding capacity (%) of minced hake muscle. No letters indicate no significant differences between means for each day of analysis

There was an increase of WHC of unfrozen hake mince with storage days at 4 °C, which was attributed to the changes occurring in *post-mortem* muscle such as raise of pH [285]. The hake mince frozen in a conventional freezer lost some ability to retain water as compared to the unfrozen control (Table 3-5). This slight decrease but with no statistical significant difference was in agreement with previous data in cod mince [286]. No changes were observed in WHC between minced hake frozen with OMF as compared to their corresponding control (Table 3-5). Similarly, [44] did not find significant differences in WHC between cod frozen in a commercial CAS magnetic freezer and air-blast freezers. Likewise, in [16] there were no significant differences in drip losses, after thawing pork loin regardless of if it was frozen in the presence or the absence of OMF (0.04 to 0.53 mT). These results were also consistent with those of [47] in commercial crab sticks frozen by different OMF freezing conditions. It cannot be discarded that the absence of improvement in muscle quality by OMF as compared to conventional freezing might be due to the fact that no major differences were observed between fresh and conventionally frozen fish. However, data from freezing curves did not show any differences in any parameter either, including T_n . Taking both results into account, the possible beneficial effects of using this technology has not been demonstrated for this particular application.

3.2.5. Effects of an iron core OMF in the freezing on the nanoparticles emulsion

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Maghemite nanoparticles used in this work have nearly spherical morphology and an average size of 8 nm ($\sigma=2$), measured from the set of TEM images (Figure 3-10).

Figure 3-10: a) TEM micrograph (x200k) of maghemite nanoparticles; b) Gaussian fit of the particle size distribution.

The X-ray diffraction spectra of the magnetic nanoparticles (data not shown) were indexed to an inverse spinel structure (CPDS 39-1346). The average crystallite size, calculated by Scherrer's formula, was close to 8 nm within the experimental error, in agreement with TEM observations. Z-potential of the sample at pH = 3 and 25 °C is close to 40 mV, which demonstrates the colloidal stability of the magnetic nanoparticle dispersion in these conditions.

High field magnetization (M_{50kOe}) at 295 K was 74 emu/g with no coercivity, confirming the superparamagnetic behavior of the sample at this temperature. The maximum of the ZFC curve (TM) is close to 100 K, so at the temperature used in this study, the sample is far from its blocking temperature. The final concentration of the obtained SAMN sample was 50 mg Fe/mL.

In the Whirlpool freezer described in Section 2.1.4, where experiments took place, average temperatures were worked out from the values registered from two minutes after setting the sample into the freezer until the end of the experiment. First two minutes were discarded in order not to consider the rise in the freezer temperature which is produced when the freezer door is opened to place the sample. Freezer ambient temperatures T_a (Figure 1-1) calculated that way were (mean $\pm$ standard error) -18.17 ± 0.17 °C and -17.62 ± 0.13 °C for the cases without and with MF, respectively, whereas the air speed was determined by the hot wire thermo-anemometer of Section 2.1.1 remaining at 0.51 m/s.

A preliminary study was carried out by freezing the SAM sample submitted or not to OMF, and no statistical significant differences were obtained among their corresponding freezing curve parameters (data no shown).

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Representative experimental freezing curves of the SAMN dispersion parameters with and without OMF are shown in Figure 3-11. Numerical results of the main parameters are given in Table 3-6.

Figure 3-11: Representative freezing time-temperature curves of maghemite dispersion. Blue: conventional freezing; Red: OMF-assisted freezing. The discontinuity of slopes is eliminated in the OMF freezing

	No OMF (control)	31.3 mT
Precooling rate V_p (°C/s)	0.06884 ± 0.00123^a	0.07736 ± 0.00128^b
Supercooling degree ΔT (°C)	3.5 ± 0.8^a	4.6 ± 0.8^a
Phase transition time t_{pt} (min)	24.2 ± 0.5^a	24.5 ± 0.4^a
Tempering rate V_t (°C/s)	0.04828 ± 0.00198^a	0.04671 ± 0.00138^a
Total freezing time t_{tot} (min)	35.8 ± 0.9^a	37.2 ± 0.8^a

Table 3-6: Averages $\pm$ standard errors for the main parts of the freezing curve for SAMN without OMF and SAMN with OMF ($B = 31.3$ mT and frequency = 50 Hz): precooling rates, V_p (°C/s), supercooling degree, ΔT (°C), phase transition times, t_{pt} (minutes), tempering rates, V_t (°C/s), total freezing times, t_{tot} (minutes). Different letters indicate significant differences between means for each row

In the precooling phase of the freezing curves of the SAMN dispersion parameters without OMF of Figure 3-11, the existence of a discontinuity can be appreciated. This behavior, which implies a change in the curve slope, is also common in experiments carried out with water. [261] perform a detailed study of this fact which is attributed to the interaction of heat transfer during cooling with the appearance of the maximum density of water, as mentioned in

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Section 2.2.1, at around 3.98 °C [287], as can be seen in Figure 3-12a. According to all these authors, the knee of the cooling curve is due to the fact that initially density is increasing as temperature decreases, which tends to move the coldest molecules downwards, but upon passing this maximum, density of colder water diminishes, and the convective movements change direction with regard to their normal behavior. These two opposite convective rotations would cooperate or hinder the heat removal which explains the change of slopes.

Figure 3-12: a) Discontinuities in the time-temperature curve slopes, during cooling and heating, near the maximum density of water (extracted from [100] and [287]); b) The same discontinuity in still water during cooling. It disappears in stirred water (extracted from [261])

[261] perform a set of experiments with both still and stirred water and they conclude that, stirred water minimizes a lot the named discontinuity (as shown in Figure 3-12b). This last phenomenon is also appreciated in this work where in the freezing curves of the SAMN dispersion with OMF this discontinuity also disappears. This fact, in turn, has a significant incidence on the precooling rate (Table 3-6). So regarding V_p and comparing the behavior of SAMN samples which have been frozen with OMF versus the ones without OMF it is found that the first case represents an increase of 12.4 % in the speed of precooling respecting the second one, despite the fact that the freezer temperature was slightly higher in the OMF-assisted experiments. This fact indicates that an aqueous dispersion of maghemite nanoparticles undergoing a freezing process speeds up significantly its precooling step ($p < 0.05$), before the start of nucleation, when subjected to the OMF. It is probable that an increase of the thermal conductivity also appears on this kind of samples when subjected to OMFs. In the absence of an external magnetic field, the magnetic moments of the nuclear spins are oriented in random directions. Nevertheless by supplying to the sample a magnetic field, the moments of the magnetic particles begin to align themselves parallel to the direction of the applied magnetic field. This fact is pointed out by [288] where the thermal conductivity of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanofluids is determined as a function of the volumetric particle concentration. Thus, the thermal conductivity enhancement observed by the authors is attributed to the effective heat transport through the chain-like aggregates of the nanoparticles. By applying OMF strengths of up to 30 mT they find that the bigger the maghemite nanofluids volumetric particle concentration and the higher the applied OMF, the higher the thermal conductivity. In this work this behavior is found when the applied magnetic field is perpendicular to the temperature gradient. [289] apply magnetic field to Fe_3O_4 nanofluids to study the thermal conductivity of magnetite dispersions, both using water and heptane as liquid phases, in the

presence of SMFs ranging from 50 to 200 mT. They observe a thermal conductivity change when the applied magnetic field was perpendicular to the hot wire measuring thermal conductivity, obtaining an enhancement of thermal conductivity with regard to the case in which no MF is employed. Besides in [290] it is established that values of the thermal conductivity of the Fe_3O_4 ferrofluid become higher when a magnetic field is applied due to the development of further chains in the base fluid. Furthermore the heat transfer enhancement is higher by applying OMF than by applying SMF [291]. Also [292] find significant enhancements of heat transfer properties dealing with Fe_3O_4 nanofluids assigning this fact either to external rotations (Brownian mechanism) of the magnetic nanoparticles within the carrier fluid or to the internal rotations of the magnetic moments with respect to the crystal lattice (Néel mechanism).

Concerning supercooling degree ΔT , the statistical analysis showed no significant differences ($p > 0.05$) in this parameter due to the application or not of OMF during freezing. This would not be surprising, given the fact that magnetic nanoparticles can act as nucleating agents [181] which is also fulfilled by other non-magnetic nanoparticles [293, 294]. On the other hand, from the results it cannot be drawn that an OMF applied to a sample with magnetic nanoparticles tends to enhance supercooling when freezing as assumed in [161], at least in an aqueous medium as the one employed in these experiments. This could be in agreement with that exposed in the patent [295] where magnetite particles are used as nucleating agents in the presence of a MF, although it does not seem to be a OMF but a SMF.

In the rest of the analyzed freezing curve parameters, the statistical analysis showed no significant differences either ($p > 0.05$, Table 3-6) when comparing the application or not of OMF during freezing.

3.3. Effects of commercial OMF generators in the freezing of water and food

3.3.1. Modeling the commercial freezer assisted by an inductor coil OMF generator

As stated in [36], available commercial freezer manufacturers often lack to provide MF values. It would be therefore valuable to have a model able to describe the distribution of MF in their useful space. For that reason, the sensing of current going through the coils of one of the available CAS pieces of equipment presented in Section 2.1.2, specifically the one owned by Kotobuki (Figure 2-2) was achieved by means of the Rogowski current probe (Section 2.1.1). The RMS value of the currents circulating in the four inductor coils turned out to be: 190.4, 207.8, 232.2 and 173.5 A, from the front coil to the back one respectively. Figure 3-13 represents the MF line distribution in an air volume simulating the freezing cabinet inner room and the MF strength on the planes where trays 1, 5 and 10 of Figure 2-2 are located, when the instantaneous electrical current is flowing for all the four coils in the same direction (case A).

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Figure 3-13: The inductor coil OMF generator used in the commercial freezer. MF lines distribution and MF strength on the planes of trays 1, 5 and 10 of Figure 2-2

Besides this study, another simulation has been performed supposing that the instantaneous electrical currents flowing through coils 2 and 4 have opposite direction to currents through coils 1 and 3 (case B). Figure 3-14a shows the tray 5 (central) with MF strength and line distribution in case A. Analogously Figure 3-14b depicts the same aspects but for case B.

Figure 3-14: Commercial freezer: MF line distribution and MF strength on the planes of tray 5 (central). White rectangle shows the tray edges: a) Instantaneous currents in the same direction in the four coils; b) Instantaneous currents in coils 2 and 4 in opposite direction to currents in coils 1 and 3

In Figure 3-15a and Figure 3-15b, graphs analogous to those of Figure 3-14a and Figure 3-14b, respectively, represent the MF strength and lines on the plane of tray number 1 (upper).

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Figure 3-15: Commercial freezer: MF line distribution and MF strength on the planes of tray 1 (upper). White rectangle shows the tray edges: a) Instantaneous currents in the same direction in the four coils; b) Instantaneous currents in coils 2 and 4 in opposite direction to currents in coils 1 and 3

Similarly, Figure 3-16a and Figure 3-16b show the MF strength and lines for the plane of tray number 10 (lower). Taking the trays depicted in Figure 3-14 to Figure 3-16, corresponding to trays 5, 1 and 10 respectively, as a reference, the MF strength at three points of their horizontal central axes (left, central and right positions, which are also the respective points d, a and e of Figure 2-2b) is indicated in Table 3-7.

Figure 3-16: Commercial freezer: MF line distribution and MF strength on the planes of tray 10 (lower). White rectangle shows the tray edges: a) Instantaneous currents in the same direction in the four coils; b) Instantaneous currents in coils 2 and 4 in opposite direction to currents in coils 1 and 3

Tray	Case	Left	Central	Right
1	A	0.48	0.51	0.46
1	B	0.27	0.28	0.24
5	A	0.22	0.39	0.22
5	B	0.02	0.02	0
10	A	0.49	0.53	0.48
10	B	0.27	0.28	0.24

Table 3-7: MF strength (mT) for the central axis of trays 1, 5 and 10, with the corresponding values for left, central and right positions

It can be appreciated that all the distribution of MF lines is similar within each case, regardless of the position of each tray. However the distribution of case A is very different to the distribution of case B. Whereas in case A the composition of MF lines generated by each coil act in a parallel way to the longitudinal axis of each tray, this fact is not obtained for the case B. This is due to the fact that the MF produced by the coil with instantaneous current in a certain direction is compensated by the corresponding one produced by its neighboring coil in the opposite direction. Regarding the MF strength, as can be seen in Figure 3-14, Figure 3-15 and Figure 3-16 as well as in Table 3-7, this magnitude reaches higher values on trays 1 and 10 than on tray 5. This is explained by the nearness to the horizontal superior and inferior sections of the coils, creating therefore a higher MF in those areas. When comparing case A to B, higher MF strengths are also appreciated in the former case, because MF lines going in the same direction tends to increase MF strengths while in case B, on the contrary, those lines tend to counteract each other. Figure 3-14b, Figure 3-15b and Figure 3-16b also show a non-negligible MF component in transversal direction to that of the longitudinal axis of trays. This

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same circumstance can be appreciated also in Figure 3-17, where MF lines and strength on a vertical cross section at the center of the freezing chamber is represented for cases A and B. Then there is a quite uniform distribution of MF lines in parallel to the coil axis in case A (Figure 3-17a), while case B (Figure 3-17b) has also a non-negligible vertical component. The fact that in this latter case current is passing through each coil in opposite direction to that of their adjacent coils, makes MF strengths reduce down to zero in one point between every couple of coils (located ideally at the geometric center between each pair of neighboring coils, if current values were equal in all coils).

Figure 3-17: Commercial freezer: MF line distribution and MF strength on a vertical central cross section of the freezing cabinet. White segments show the positions of trays 1, 5 and 10: a) Instantaneous currents in the four coils; b) Instantaneous currents in coils 2 and 4 in opposite direction to currents in coils 1 and 3

The amount of information obtained by means of this modeling is much higher than the one coming from experimental procedure. Although the values registered in this simplified model are similar to the ones extracted from direct measurements in a real commercial MF freezer [47], the possibilities that modeling offers are much higher than performing direct experimental measurements. The main difficulty in this latter case is the inaccuracy coming from the uncertainty in the location and orientation of the experimental probe. Maybe in those cases where MF strength is very low, this circumstance can be more important. For instance, the provided values on Table 3-7 for case B on the tray 5 are very low due to the previously explained. It is worthy to note that this field is lower than the Earth's MF, having in Madrid (Spain) an estimated value of 0.04478 mT (according to the calculator from the National Centers for Environmental Information (NCEI, USA) website [296]).

3.3.2. Thermal conductivity of ice obtained in a commercial electromagnetic freezer

3.3.2.1. Previous determinations

The thermal conductivity was measured by applying heat to the TR-1 probe for a fixed defined as a heating time, and then leaving the sample to cool for the same amount of time (t_h in total). All details can be found in our article [124]. The needle temperature was monitored during the heating and tempering processes. The change in the temperature over time was then analyzed. To determine the effect of t_h on the thermal conductivity of ice, different values of that magnitude were used during the measurements for the ice produced by slow freezing. The obtained temperature vs time data were fitted by two different methods. The temperature during the heating time was modelled by the following equation:

$$T = m_0 + m_2 \cdot t + m_3 \cdot \ln(t) \quad (\text{Eq. 70})$$

where m_0 is the ambient temperature during heating, which could be influenced by the contact resistance and heating elements adjacent to the temperature sensor inside the needle; m_2 is the background temperature drift rate; m_3 is the slope of the linear relationship between the temperature and the logarithm of time; and t is the time. The following model was applied to the tempering process:

$$T = m_1 + m_2 \cdot t + m_3 \cdot \ln\left(\frac{t}{t - t_h}\right) \quad (\text{Eq. 71})$$

The thermal conductivity was calculated by using the following equation:

$$k = \frac{q}{4\pi m_3} \quad (\text{Eq. 72})$$

q being the power input per unit length. As an example, the temperature versus time plot for $t_h = 1$ min and $q = 3.56$ W/m starting at $T_i = -10^\circ\text{C}$ is shown in Figure 3-18a. In that Figure, solid red and blue lines represent the best non-linear least squares analysis (NLLSA) for (Eq. 70 and

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(Eq. 71, respectively, whereas lines in Figure 3-18b show the linear least squares analysis (LLSA) obtained for (Eq. 70) as $\Delta T = T_i - T$ versus $\ln(t)$, with $\Delta T = A + B \ln(t)$; and those in Figure 3-18c, the ones acquired for (Eq. 71) as T versus $\ln(t/(t - t_h))$, with $T = A + B \ln(t/(t - t_h))$).

Figure 3-18: Analysis of: a) Temperature vs time; b) ΔT vs $\ln(t)$; c) T vs $\ln(t/(t-t_h))$ for a sample of ice at -10°C for $t_h = 1\text{min}$

Because LLSA generally gives reliable results, whereas NLLSA can give a wide range of results depending on the initial estimates used to solve (Eq. 70) and (Eq. 71), the thermal conductivities were calculated using the LLSA method in the following sections.

For each ice temperature, different heating times were employed in the following order: $t_h = 1, 2, 3, 5, 10, 5, 2$, and 1 min. It was discovered that over the entire temperature range studied, the thermal conductivity increases as t_h is increased from 1 to 5 min and then remains nearly constant within the error as t_h is increased from 5 min to 10 min. Furthermore, a significant hysteresis between the k values obtained before and after heating for 10 min is observed, i.e., the k values determined after the $t_h = 10$ min measurement are always higher than those determined before that measurement. Those results together with the error for each measurement are shown in Table 3-8. After the analysis of errors, it was assessed that a heating time of 5 min was the optimal heating time to minimize that error.

Heating time t_h (min)	Thermal conductivity k (W/(m·K))	Measurement k -error (W/(m·K))
-5 °C		
1	1.932	0.0096
2	2.076	0.107
5	2.25	0.0077
10	2.197	0.0044
5	2.198	0.0051
2	2.077	0.0051
-10 °C		
1	1.962	0.0046
2	2.077	0.0036
5	2.222	0.0037
10	2.217	0.0027

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5	2.219	0.0031
2	2.091	0.0043
1	1.973	0.0043
-30 °C		
1	1.514	0.12
2	2.278	0.0089
5	2.606	0.0079
10	2.578	0.0073
5	2.537	0.0096
2	2.291	0.0089
1	2.038	0.0573
-40 °C		
1	1.919	0.013
2	2.412	0.0688
5	2.754	0.0388
10	2.591	0.0388
5	2.663	0.359
2	2.469	0.219
1	2.342	0.0573

Table 3-8: Thermal conductivity, k , of ice at temperatures ranging from -40 to -5 °C obtained by using different heating time applied sequentially

3.3.2.2. Thermal conductivity of ice prepared by different freezing processes as a function of temperature

Figure 3-19 shows the thermal conductivities of the ice prepared by slow freezing at -5 °C, -10 °C, -20 °C, -30 °C, and -40 °C obtained using a heating time of 5 min and LLSA to solve both (Eq. 70) and (Eq. 71).

Figure 3-19: Experimental thermal conductivity of ice obtained from the literature and from the different studied freezing processes

The results show that k decreases with increasing temperature, in agreement with the findings of [297] study of frozen food. In this work, k depends linearly on the temperature, increasing by approximately 24% as the temperature is lowered from $-10\text{ }^{\circ}\text{C}$ to $-40\text{ }^{\circ}\text{C}$. The data can be fitted by the following equation: $k = -0.0176 + 2.0526 T$, which is consistent with the results of [298], although it is significantly different from those shown by other researchers, as in [123, 299]. Figure 3-19 also compares the thermal conductivities of the ice prepared by fast and slow freezing measured at $-20\text{ }^{\circ}\text{C}$ ($2.64 \pm 0.06\text{ W/(m}\cdot\text{K)}$) versus $2.41 \pm 0.03\text{ W/(m}\cdot\text{K)}$, respectively). Clearly, as the freezing rate increases, the k value increases significantly, by approximately 10%. To understand the magnitude of this difference in the thermal conductivity, it should be noted that it is equivalent to the difference observed when the thermal conductivity is measured at temperatures varying by nearly $15\text{ }^{\circ}\text{C}$, as can be seen in Figure 3-19.

3.3.2.3. Ice prepared from aerated and non-aerated water.

The thermal conductivities of the ice samples prepared from aerated and non-aerated water measured at $-20\text{ }^{\circ}\text{C}$ ($2.39 \pm 0.08\text{ W/(m}\cdot\text{K)}$) versus $2.48 \pm 0.06\text{ W/(m}\cdot\text{K)}$, respectively) are the same within the error (see Figure 3-19), indicating that the thermal conductivity of ice is not affected by the dissolved gas concentration of the water.

3.3.2.4. Ice prepared in the presence of a magnetic field

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The thermal conductivities of the ice samples prepared by the air-blast CAS equipment of Kotobuki (see Section 2.1.2) at 0% CAS and 50% CAS settings, measured at $-29\text{ }^{\circ}\text{C}$ are both $2.75 \pm 0.03\text{ W}/(\text{m}\cdot\text{K})$ (see Figure 3-19). These results reveal that freezing water in the presence of an OMF as those employed in commercial MF freezers does not affect the thermal conductivity of the resulting ice. It should be noted that the k values of the ice prepared in the CAS freezer are higher than those of the samples prepared by slow freezing. These results, which could in principle be attributed to the SMF, i.e. the only field present both in 0% and 50% CAS, can be explained by the fact that the freezing rate was higher in the CAS experiments because the temperature of the air-blast freezer was $-50\text{ }^{\circ}\text{C}$ during the freezing process. To our knowledge, the thermal conductivity of ice prepared in the presence of an OMF had not been previously reported. Instead, other related thermal properties of ice or other systems have been measured and used to validate the results, leading to conflicting reports of the effects of OMF freezing in the literature. [77] measured the freezing curves of deionized water under a SMF and found that applying a low field intensity ($|\vec{B}| < 50\text{ mT}$) did not significantly affect the nucleation temperature and phase transition time. [51] used differential thermal analysis to demonstrate that a weak OMF did not influence the temperature history during pure water freezing. Similar results were reported in studies of several food products [50, 51] that were frozen in the presence or absence of an OMF (0.5 mT/50 Hz) or under NMR conditions (SMF of 20 mT combined with an OMF of frequency 1 MHz and strength 0.12 mT). In these studies, no significant effects of the applied OMFs on the degree of supercooling or the freezing times were observed. Furthermore, [45] found that applying different OMFs ($|\vec{B}| < 0.418\text{ mT}$) or not applying anyone had little effect on the freezing curve characteristics for garlic bulbs. These results are consistent with those presented in this work. In contrast, [55] treated chicken breast samples with a combination of pulsed electric fields and an OMF to achieve a supercooled state at -6.5°C , in contrast to the partially frozen state of the control samples at this temperature.

3.3.3. Effects of OMF in the freezing of crab sticks

3.3.3.1. Magnetic freezer characterization

Air velocity (m/s) and MF strength (mT) and frequency (Hz) values were measured at several locations in trays 1, 5, and 10 of the freezing cabinet in the CAS freezer of Kotobuki, Figure 2-2a, after programming 100% air flow and different 'CAS energy' conditions (0-100%).

Air velocity at different locations strongly depended on their relative positions with regard to the fans of the freezer. Thus, the maximum air velocity was measured at the center of tray 5, while the minimum value was registered for tray 10. At the center of tray 5, air velocity increased from 0 m/s for 0% air flow up to 3.8 m/s for 100% air flow.

On the other hand, MF strength values at different locations depend on the distance to the permanent magnets and to the magnetic coils as expected. Thus, for a given tray, the X-

component of the SMF (according to the coordinate axes shown in Figure 2-2a) was larger at the centers of the front and back edges of the tray (positions d and e in Figure 2-2b, respectively) because of the front-door and rear-wall magnets, while the Y-component was larger at the left edge because no permanent magnets exist on the right side of the freezing cabinet (Figure 2-2a). Moreover, the Z-component of the static field was larger on trays 1 and 10 than on tray 5 due to the ceiling and floor magnets. In a similar way, the OMF was not uniform throughout the freezing cabinet, but it depended on the relative location with respect to the magnetic coils. In general, the X- and Z- components of the OMF were larger than the Y-component at the positions measured in each tray (points 'a' to 'e' in Figure 2-2b). For all considered trays, the X-component was maximum at the front edge (position 'd' in Figure 2-2b), while both the Y- and Z- components presented a minimum at this location. The lowest X-values were measured at the middle of the tray (positions 'b', 'a', and 'c' in Figure 2-2b). At the center (position 'a' in Figure 2-2b), the Z-component of the OMF was maximum, whereas the maximum Y-values were found at the left and right edges of each tray (positions 'b' and 'c' in Figure 2-2b, respectively). From the sensed SMF and OMF components in the XYZ Cartesian directions, the total field strength at each of the 15 measured positions was calculated by vector sum. These values were represented as in Figure 3-20 (depicting only the cases of SMF and 100% CAS OMF) to show graphically the distribution of the measured MF values:

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Figure 3-20: Magnetic field strength measured values at different points of trays 1, 5 and 10 in the magnetic freezer (ABI Co., Ltd., Chiba, Japan) of Kotobuki: a) Total SMF strength; b) Total OMF strength for 100% 'CAS energy'

It must be mentioned that this characterization carried out by means of a teslameter, is subject to inaccuracies in the placement of the Hall probe, both in the location of the point and in the orientation of the plane of the probe with regard to XYZ axes, as well as unwanted displacements of the trays with regard to the ideal central position on the shelves. Then what figures in the present Section could be valuably complemented with the modeling exposed in Section 3.3.1.

Furthermore, it is important to note that the OMF also depended on the 'CAS energy' conditions programmed at the control panel. Thus, at 0% CAS, no OMF was applied in the freezer owned by Kotobuki and only the SMF acted. For other CAS conditions, different OMFs were produced. Thus Figure 3-21 shows the X-component of the OMF measured at the center of tray 5 (point 'a') for different 'CAS energy' conditions. It clearly shows that the magnetic field strength increased in the range from 0% up to 10% CAS and, then, slightly decreased for growing 'CAS energy' values, while frequency increased linearly in the range from 0% to 100% CAS.

Figure 3-21: Characteristics of the oscillating magnetic field for different 'CAS energy' settings in the magnetic freezer (ABI Co., Ltd., Chiba, Japan) of Kotobuki: a) X-component of the magnetic field strength; b) Magnetic field frequency. Measurements performed at the center of tray 5 in the freezing cabinet

The freezing experiments described in Section 2.1.8 in the CAS equipment from Kotobuki, were performed at different conditions, both with (10%, 50%, and 100% CAS) and without (0% CAS) OMF application, to evaluate the effect of OMFs on the quality of the frozen crab sticks.

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	MAGNETIC FIELD STRENGTH (mT)								MAGNETIC FIELD FREQUENCY (Hz)
	Static magnetic field				Oscillating magnetic field				Oscillating magnetic field
	X	Y	Z	Total	X	Y	Z	Total	
0% CAS	0.07 (0.00-0.15)	0.12 (0.02-0.22)	0.04 (0.02-0.04)	0.14 (0.12-0.22)	0 (0-0)	0 (0-0)	0 (0-0)	0 (0-0)	0
10% CAS					0.92 (0.92-1.81)	0.70 (0.60-1.25)	0.99 (0.42-0.99)	1.52 (1.51-1.95)	6
50% CAS					0.79 (0.79-1.71)	0.69 (0.58-1.20)	0.93 (0.41-0.93)	1.40 (1.40-1.85)	30
100% CAS					0.74 (0.74-1.69)	0.71 (0.59-1.18)	0.92 (0.43-0.92)	1.38 (1.38-1.84)	59

Table 3-9: Magnetic field strength and frequency values measured at the center of tray 5 after programming different 'CAS energy' conditions in the CAS freezer of Kotobuki. Values between parentheses represent minimum and maximum field measured all over the tray

Table 3-9 shows the corresponding OMF strength and frequency values measured at the center of tray 5 and the maximum and minimum values registered in this tray. This Table also includes the strength of the SMF induced by the permanent magnets in this same tray. Unfortunately, the effects of the SMF alone on the quality of crab sticks could not be assessed in these experiments because the permanent magnets were embedded in the freezer walls and, therefore, they could not be removed to make comparisons.

3.3.3.2. Effectiveness of oscillating magnetic fields in retaining the quality of fresh crab sticks

Four representative freezing curves of conventionally (static air and air-blast) and CAS-assisted (0% and 100%) frozen crab sticks are depicted in Figure 3-22.

Figure 3-22: Representative freezing curves of crab sticks frozen at -25°C and under different conditions: (---): 0% CAS; (—): 100% CAS; (—): Air-blast; and (···): Static air

The curves clearly show the 3 key steps of a freezing process: precooling, phase transition, and tempering. During the phase transition step, the temperature remained constant at about -3°C , that is, at the initial freezing point of the crab sticks while the latent heat of crystallization was removed. In this phase, most of the ice crystals are formed in the product and, therefore, the rate of heat removal is crucial for the quality of the frozen food. Thus, the slower the heat removal, the larger the ice crystals formed and, therefore, the poorer the quality of the

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product [8]. Figure 3-22 reveals that the rate of heat removal was significantly slower in the static-air freezing experiments, as expected. Thus, the characteristic freezing time (time needed to change the temperature at the center of the sample from the initial freezing point to a temperature 10 °C lower) was (mean $\pm$ standard error) 74.9 ± 4.5 min, which turned out to be about 5 times longer than those corresponding to the rest of methods. By contrast, no significant differences were found among CAS and air-blast experiments (14.4 ± 0.7 , 13.0 ± 0.5 , and 16.0 ± 0.8 min in 0% CAS, 100% CAS, and air-blast freezing experiments, respectively).

To evaluate the effectiveness of OMFs in retaining the quality of fresh product, drip loss, water-holding capacity, toughness, and whiteness were measured in fresh and frozen-thawed samples after 24 h of frozen storage (month 0 in Figure 3-23).

a

b

c

d

Results

Figure 3-23: (a) Drip loss, (b) water-holding capacity, (c) toughness, and (d) whiteness of fresh crab sticks (Δ) and of those frozen at different freezing conditions ($\square$: 0% CAS, $\square$: 10% CAS, $\blacksquare$: 50% CAS, $\blacksquare$: 100% CAS, $\diamond$: air-blast, and $\bullet$: static air) during storage at $-20\text{ }^{\circ}\text{C}$. Vertical bars represent standard error. For a given storage time, different letters indicate significant differences among means ($p < 0.05$) due to the freezing conditions. No letters indicate no significant differences among means.

The data clearly proved that all the frozen and thawed samples, whichever the employed freezing method, significantly differed ($p < 0.05$) from the fresh crab sticks. The multivariate stepwise linear discriminant analysis of the data revealed that the water-holding capacity (F value = 76.13) and drip loss (F value = 24.67) were the properties that best discriminated among the different samples (fresh, CAS, air-blast, and static-air frozen) at month 0. Figure 3-24 illustrates how the water-holding capacity allowed a perfect discrimination between fresh and frozen samples, while the drip loss discriminated among samples frozen at different conditions to a lesser extent.

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was the only quality attribute that remained unaltered after thawing, but it is interesting to note that the same occurred for all the freezing methods tested.

3.3.3.3. Effect of freezing conditions on quality attributes during frozen storage

Drip loss, water-holding capacity, toughness, and whiteness were measured in frozen-thawed samples after 24 h and 1, 3, 6, 9, and 12 months of storage to evaluate the effect of the freezing conditions (0% CAS, 10% CAS, 50% CAS, 100% CAS, air-blast, and static-air freezing) on the quality of the crab sticks (Figure 3-23).

The statistical analysis of the data showed that both the freezing conditions (FC) and the storage time (t) significantly affected all the quality attributes ($p < 0.05$, Table 3-10).

	Sources of variation	Degrees of freedom	F	Sig
Drip loss	Freezing conditions (FC)	5	399.93	0.00
	Storage time (t)	5	4.76	0.00
	FC x t	25	13.13	0.00
Water-holding capacity	Freezing conditions (FC)	5	31.64	0.00
	Storage time (t)	5	747.54	0.00
	FC x t	25	2.10	0.01
Toughness	Freezing conditions (FC)	5	37.33	0.00
	Storage time (t)	5	1233.81	0.00
	FC x t	25	3.47	0.00
Whiteness	Freezing conditions (FC)	5	17.76	0.00
	Storage time (t)	5	93.73	0.00
	FC x t	25	1.23	0.22

Table 3-10: Results of the two-way ANOVA for the effect of the freezing conditions (0% CAS, 10% CAS, 50% CAS, 100% CAS, air-blast, and static-air freezing) and the storage time (0-12 months) on the quality of crab sticks ($p < 0.05$)

The effect of the freezing conditions was especially important for the drip loss (F value = 399.93), while the effect of the storage time was more relevant for all the other quality attributes. Moreover, a significant interaction between the freezing conditions and the storage time (FC x t) was found for drip loss, WHC, and toughness. Therefore, the evolution of these quality attributes during storage was different in samples frozen by different methods.

No effect of the OMFs applied, whichever their strength or frequency, was found in any of the quality attributes of the crab sticks. Thus, post-hoc comparisons after the two-way ANOVA did not detect significant differences between the crab sticks frozen with or without OMFs in the CAS freezer. Similar results were reported by [50] and [51] who did not find any effect of OMFs on the microstructure, drip losses, color, texture, and sensory evaluation of frozen radish, sweet potato, spinach, yellow tail fish and tuna. Likewise, [53] did not detect apparent effects of the OMF conditions (1.5-2 mT at 20, 30, and 40 Hz) on the drip and cooking losses and the

rupture stress and strain of chicken breasts frozen in a CAS freezer, after one week although after six months of storage texture parameters, the CAS-frozen samples remained almost the same by rapport to the samples stored for one week, contrasting the increased stress values for the conventional-frozen and rapid-frozen samples. In this sense, [201] declared they had not found clear and repeatable effects of the CAS conditions on the quality (dimensions, weights, drip loss, color, moisture content, sugar content, and texture) of magnetically frozen fruit, vegetables, meat, and fish products.

The statistical analysis of the results revealed significant differences between the crab sticks frozen in the CAS freezer and those frozen by conventional methods. Thus, the samples frozen in static air presented the largest drip loss and toughness and the lowest water-holding capacity and whiteness. By contrast, air-blast frozen samples released the lowest drip after thawing and exhibited the largest WHC. Toughness and whiteness in these samples were similar to those observed in CAS frozen crab sticks. Therefore, we did not find any advantageous effect of CAS freezing over conventional air-blast freezing at the conditions tested.

3.3.4. Effects of OMF in the freezing of pork loin

3.3.4.1. Magnetic freezer characterization

As mention in Section 2.1.2 the ABI CAS freezer available at the FRPERC-GIFHE (Figure 2-1) has a grid off-centered with regard to the three inducting coils, as can be seen in Figure 3-25. This, together with the fact that OMF strength is not uniform in all the volume of the freezing cabinet, causes an asymmetric distribution of MF strength in the grid, with higher values in the areas closest to each of the coils.

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Figure 3-25: View of the freezing chamber of the CAS freezer at FRPERC-GIFHE showing the position of the grid with regard to the coils. Samples placed at positions 'd' and 'g'

In order to acquire a knowledge of the distribution of the OMF on the grid where products to be frozen are placed, measurements were performed with the handheld teslameter explained in Section 2.1.1. For this purpose, the probe was situated in 9 different positions of the grid (letters 'a' to 'i' in Figure 3-25). Only the field in the axial direction of the coils, i.e. its X-component according to the axes shown in Figure 2-1, was measured, assuming that currents flowing through the coils have the same instantaneous direction (case A seen in Section 3.3.1), which would give rise to MF lines mainly oriented in that axial direction, as seen in that Section. Different 'CAS energy' settings from 0 to 100% were programmed and the X-component of the OMF strengths was registered with the teslameter and is depicted in Figure 3-26a. As can be seen, OMF is highest at position 'd' whereas it is lowest at position 'g'. This happens because point 'd' is located next to one of the coils on the right, and a strong X-component of MF appears. However, for position 'g', in addition to being out of the space covered by the coils, where the field is weaker, is almost aligned with the vertical section of the coil but in the X direction, which makes MF lines be quite parallel to the Y direction and tends to cancel out the OMF X-component. The frequency of the OMF for the different CAS settings is also shown in Figure 3-26b, according to the corresponding graphic of [52].

Figure 3-26: Characteristics of the oscillating magnetic field for different 'CAS energy' settings in the magnetic freezer (ABI Co., Ltd., Chiba, Japan) of FRPERC-GIFHE: a) X-component of the magnetic field strength at points 'a' to 'i' (referenced in Figure 3-25); b) Magnetic field frequency (extracted from [52])

Although the MF values of Figure 3-26a are subjected to errors introduced by a misplacement of the Hall probe of the teslameter as mentioned in Section 3.3.3.1, for any given position there seems to be a constant value of OMF strength between 0 and 20% CAS, decreasing for growing percentages of the 'CAS energy' setting. Analogously, the frequency of the OMF keeps constant at 10 Hz from 0 to 20% CAS, increasing linearly from that percentage on, until it reaches almost 60 Hz at 100% CAS. It must be emphasized that apart from the differences in

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the magnitude of OMF strengths between this equipment and that of Kotobuki (Section 3.3.3.1) that could be attributed to the different number of coils, this constant values of strength and frequency from 0 to 20% CAS implies differences in the programmed conditions by ABI manufacturers, and consequently each ABI CAS freezer should be thoroughly characterized before drawing mistaken conclusions.

The OMF strength measured in the ABI equipment of the FRPERC-GIFHE were 0, 0.53, 0.29, and 0.15 mT for the highest field point (position d), and 0, 0.18, 0.09, and 0.04 mT for the lowest field point (position g), respectively. The mean (standard deviation) values of surface heat transfer coefficients calculated by means of the cooling curve of copper blocks for position d and position g were $22.3 (1.0) \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ and $16.1 (1.1) \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, respectively. These surface heat transfer coefficients are quite low for an air-blast freezer and were likely to be due to how the magnetic coils in the chamber deflected the air flow.

Figure 3-27: Typical freezing curve for pork loin samples frozen in air at ca. -30 °C and 1-2 m/s. Position d (highest OMF strength): blue; Position g (lowest OMF strength): red

From each freezing curve, a typical example being shown Figure 3-27, no significant degree of super-cooling was observed in any of the samples irrespective of the application or absence of OMF during the freezing process.

Figure 3-28: Plot of characteristic freezing time (min) against magnetic field intensity (mT). Position d (highest OMF strength): red circles; Position g (lowest OMF strength): blue diamonds

The characteristic freezing time, calculated from the initial freezing point temperature down to -7°C , and the completion of freezing rate, calculated as the rate of cooling when the sample temperatures went from -10 to -15°C , are shown plotted against the MF strength in Figure 3-28 and Figure 3-29 respectively, and the mean and standard deviation of these variables are shown in Table 3-11.

Figure 3-29: Plot of completion of freezing rate ($^{\circ}\text{C/s}$) against magnetic field intensity (mT). Position d (highest OMF strength): red circles; Position g (lowest OMF strength): blue diamonds

There appeared to be no relationship between magnetic field strength and characteristic freezing time or completion of freezing rate.

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CAS condition	Position	n	Characteristic freezing time (min)	Completion of freezing rate (°C/s)
Control	d	5	14.8 (0.9) ^A	-0.0351 (0.007) ^A
	g	5	18.2 (3.1) ^a	-0.0272 (0.005) ^a
0.04 mT	g	5	18.1 (2.3) ^a	-0.0301 (0.002) ^a
0.09 mT	g	5	19.8 (2.1) ^a	-0.0288 (0.001) ^a
0.15 mT	d	5	15.9 (1.9) ^A	-0.037 (0.004) ^A
0.18 mT	g	5	19.1 (1.6) ^a	-0.0253 (0.005) ^a
0.29 mT	d	5	17.6 (3.4) ^A	-0.0362 (0.004) ^A
0.53 mT	d	5	16.7 (2.2) ^A	-0.0345 (0.004) ^A

Table 3-11: Mean (standard deviation) characteristic freezing time (min) and completion of freezing rate (°C/s) at different magnetic field intensities. Different letters in the same column indicate significant differences. Position d (highest OMF strength): capital letters; Position g (lowest OMF strength): lower-case letters

The OMF did not appear to have any significant effect ($p>0.05$) on the characteristic freezing time or the completion of freezing rate. In all cases, as would be expected given the differences in surface heat transfer coefficients, samples in position d cooled and froze faster than those in position g, irrespective of MF strength. Mean characteristic freezing times were 16.3 and 18.8 minutes at positions d and g, respectively, and completion of freezing rates were -0.036 and -0.028 °C s⁻¹, respectively.

3.3.4.2. Drip loss analysis

An increase in the drip from meat after freezing and thawing compared with that in chilled meat is the most common quality deterioration associated with the freezing of meat. One of the most important claims of the CAS patents [41, 301] is that OMF prevents cells from being damaged, due to the generation of smaller ice crystals, and thus reduces drip.

Figure 3-30: Drip loss (%) after thawing as a function of magnetic field intensity (mT). Position d (highest OMF strength): red circles; Position g (lowest OMF strength): blue diamonds

Drip losses in the present work ranged from 1.7 to 4.6 % (Figure 3-30), which is within the usual range reported for pork [302]. The results indicated no clear effect of OMF on drip loss or any effect of different field strengths on the amount of drip loss (Figure 3-30). No significant difference ($p > 0.05$) between OMF strengths for each of the positions was shown. The average drip loss from samples frozen in position g was slightly higher than that from samples frozen in position d, indicating that there was a slight effect of freezing rate on drip loss. It should be noted that although drip loss is of great monetary importance and can make meat less attractive, it has not been shown to influence the final eating quality after cooking, except in extreme cases [302].

3.3.4.3. Color analysis

Pork can naturally be rather variable in color and color changes during freezing can affect perceived meat quality. To check for any bias in the color of samples prior to freezing, the values of L^* , a^* , and b^* were plotted (data not shown in this paper) against magnetic field intensity and no bias was observed. Means (standard deviations) for these color parameters, before freezing and after thawing, are shown in Table 3-12. The application of the different OMF strengths during freezing did not cause any significant ($p > 0.05$) effect on the variation of color characteristics.

Results

CAS condition	Position	n	L*		ΔL^*	a*		Δa^*	b*		Δb^*
			Before	After		Before	After		Before	After	
Control	d	5	48.0 (2.8)	46.9 (3.4)	-1.1 (1.6) ^A	7.2 (1.1)	7.6 (1)	0.5 (1.2) ^A	0.8 (2.2)	1.7 (0.8)	1.0 (2.1) ^A
	g	5	50.7 (4.1)	48.7 (4.3)	-2.0 (0.5) ^a	7.0 (0.9)	7.2 (1.3)	0.2 (0.7) ^a	2.3 (1.7)	2.5 (1)	0.2 (0.8) ^a
0.04 mT	g	5	55.4 (2.7)	52.8 (2.6)	-2.6 (1.2) ^a	6.6 (1.3)	6.3 (1.4)	-0.3 (0.4) ^a	3.2 (0.7)	3 (0.5)	-0.2 (0.7) ^a
0.09 mT	g	5	53.9 (5)	51.3 (4.5)	-2.6 (1.2) ^a	6.1 (0.9)	6.6 (1.3)	0.5 (0.4) ^a	2.3 (1.5)	2.7 (0.6)	0.5 (1.0) ^a
0.15 mT	d	5	55.2 (2.6)	51.7 (2.5)	-3.5 (1.0) ^A	6.7 (1.5)	7 (1.6)	0.2 (0.2) ^A	3.3 (0.9)	3.1 (0.7)	-0.2 (0.2) ^A
0.18 mT	g	5	55.3 (3.2)	52.9 (3.5)	-2.5 (2.1) ^a	6.5 (1.6)	6.4 (1.6)	-0.1 (0.6) ^a	3.1 (1.0)	3 (0.8)	-0.1 (0.4) ^a
0.29 mT	d	5	53.6 (5.9)	50.3 (4)	-3.3 (2.3) ^A	5.9 (0.9)	6.7 (1.1)	0.8 (1.0) ^A	2.1 (1.9)	2.6 (0.5)	0.6 (1.4) ^A
0.53 mT	d	5	55 (2.6)	52.9 (2.3)	-2.0 (1.7) ^A	6.1 (1.1)	6.2 (0.8)	1.0 (0.6) ^A	3.1 (0.5)	3.1 (0.5)	0.0 (0.6) ^A

Table 3-12: Mean (standard deviation) L*, a* and b* color values of samples prior to freezing and after freezing-thawing, and incremental values ΔL^* , Δa^* and Δb^* . Different letters in the same column indicate significant differences. Position d (highest OMF strength): capital letters; Position g (lowest OMF strength): lower-case letters

3.3.4.4. Texture analysis

If the application of OMF resulted in less cell damage it could be expected to affect the texture of the thawed samples. The mean (standard deviation) values of density, hardness, force A, force B, and elasticity against MF strength are shown in Table 3-13. No significant difference ($p>0.05$) showing a clear relationship between magnetic field intensity and any of the texture parameters was found.

CAS condition	Position	n	Density (g/mL)	Hardness (g)	Force A (g)	Force B (g)	Elasticity (%)
Control	d	5	1.29 (0.21) ^A	2195 (1466) ^A	3615 (2405) ^A	1748 (1386) ^A	45 (9) ^A
	g	5	1.3 (0.18) ^a	2132 (1417) ^a	3179 (1595) ^a	1489 (911) ^a	46 (10) ^a
0.04 mT	g	5	1.24 (0.22) ^a	1424 (389) ^a	2267 (630) ^a	883 (253) ^a	39 (6) ^a
0.09 mT	g	5	1.28 (0.1) ^a	2135 (1278) ^a	3574 (2154) ^a	1993 (1480) ^a	51 (12) ^a
0.15 mT	d	5	1.27 (0.08) ^A	2079 (591) ^A	3471 (1163) ^A	1659 (825) ^A	46 (8) ^A
0.18 mT	g	5	1.25 (0.07) ^a	1921 (779) ^a	3112 (1241) ^a	1459 (737) ^a	45 (7) ^a
0.29 mT	d	5	1.29 (0.11) ^A	2784 (1089) ^A	4496 (1898) ^A	2333 (1283) ^A	49 (8) ^A
0.53 mT	d	5	1.18 (0.05) ^A	1970 (433) ^A	3413 (781) ^A	1547 (403) ^A	45 (6) ^A

Table 3-13: Mean (standard deviation) of density, hardness, force A, force B and elasticity for different magnetic field intensities and positions. Different letters in the same column indicate significant differences. Position d (highest OMF strength): capital letters; Position g (lowest OMF strength): lower-case letters

3.4. Running of air core OMF generator of electromagnetic field for wide range of low frequencies

Before starting the freezing experiments assisted by the air core OMF generator, a verification of the correct operation of the built inverter is required. For this purpose, once all the connections have been correctly carried out, it is necessary to supply the pertinent input voltages to the PCB as follows:

- Logic supply voltage V_{DD} between 3.3 and 5 V. For V_{DD} higher than 5 V a problem has been found, not recognizing high level of pulses coming from the MCU as a logic “1”, because V_{DD} affects the minimum required V_{IH} (see IR2110 datasheet) to be considered as logic high level.
- Low side fixed supply voltage V_{CC} between 15 and 20 V. This coincides with the output voltage of the drivers when turning on the corresponding low side MOSFETs and also the high side MOSFETs thanks to the bootstrap circuit (Figure 2-20).

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- Input voltage U_{in} . It is raised manually increasing the output voltage of the power source.

All the results presented in the following Sections 3.4.2 and 3.4.3 were acquired by means of an oscilloscope (TDS5032B, Tektronix, Inc., Beaverton, OR, USA), measuring the gate-to-source voltage of one of the MOSFETs and the current through the coil designed for higher frequencies. The DC voltages V_{CC} and V_{DD} were supplied by a power supply with two independent outputs (FAC-662B, PROMAX Electronica S.L., L'Hospitalet de Llobregat, Spain) while for the input of the power stage, other power supply (N8762A, Keysight Technologies Inc., Santa Rosa, CA, USA) was used. The MCU, in turn, was powered by means of a mini-USB connector through which program source codes were also loaded after its compilation in a PC with Code Composer Studio installed in it.

3.4.1. Modeling the laboratory freezer assisted by an air core OMF generator

As in the previous used devices, it is convenient to have a model of the MF distribution inside the solenoid where the sample to be frozen is going to be placed. In this case the starting point was not an earlier existing device as in the modeling of Sections 3.1.1, 3.2.1 and 3.3.1, but this coil was designed based on the requirements of the desired OMF. For this purpose, the methodology of FEM exposed in Section 2.1.5.2 was used. The target was to reproduce the OMF strength conditions previously measured at the center of the commercial device of Kotobuki, described in Section 2.1.2. The objective was to get that the entire sample placed at the center of the air core OMF generator were subjected to the experimentally measured MF strength given in Table 3-9. To achieve that OMF strength, an iterative procedure based on the trial-and-error method was carried out. Two different coils were designed and constructed for low (1 to 100 Hz) and high (up to 50 kHz) frequency ranges, selecting internal radii of 40 and 59.5 mm respectively. With those fixed radii, a number of simulations were carried out, changing the dimensions of the copper rectangle representing the transversal section of the coil, which in turn depends on the number of turns and their distribution. Therefore, by keeping constant the current flowing through the solenoid, its geometry was varied each iteration. After finding the field values by means of simulation, the scale factor k (Eq. 26) to (Eq. 29) which must multiply that current in order to get the desired value of the OMF strength was determined. That k has to be included in the pertinent formulas in order to get the electrical parameters of the coil. The followed criteria to select a proper geometry were based on trying to optimize these parameters. Thus the impedance should be low in order to get a lower voltage for the same current. Besides, the reduction of the heat dissipation due to the Joule effect would be given by a low resistance value, but taking into account that a too low inductance would need to apply a higher current, which could originate higher losses in the coil.

The finally chosen geometry was simulated with the real current to obtain the OMF strength distribution inside the solenoid. Taking advantage of the symmetry around the coil axis, only

one planar half section was needed to simulate and represent. It must be considered that the used FEM software, ANSYS Maxwell (v 16, ANSYS Inc., Canonsburg, PA, USA), operates only with peak values. Due to the fact that the measured field, given in Table 3-9 are expressed in RMS values, it is necessary to transform the MF strength values of the model into RMS ones, i.e. dividing them by $\sqrt{2}$.

Figure 3-31: The laboratory air core OMF generator used for freezing. Distribution of peak MF values in a half section of the solenoid

3.4.2. Inverter operation in the low-frequency range

The inverter system was operated in a series of frequencies when the program implementing the unipolar PWM control was executed. The input voltage was manually increased up to the point in which a RMS current of 1.47 A was measured through the air core inductor. The theoretical input voltages for a perfectly sinusoidal current waveform applied to the equivalent RL load, in agreement with Table 2-3 (bear in mind that in that table only the RMS voltage values applied to the coil terminals appear), have been compared with the actually applied ones in Table 3-14:

Frequency (Hz)	Theoretical input voltage (V)	Applied input voltage (V)
1	2.1	3
2	2.1	3.2
5	2.1	3.2
10	2.1	3.4
20	2.1	3.6
50	2.1	3.4
100	2.2	3.7
200	2.5	4.6
500	4.2	5.8

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1000	7.6	10
2000	14.8	18

Table 3-14: Theoretical and applied input voltages in the low-frequency range

As can be seen, for every frequency the real applied voltage is higher than the calculated one in the ideal theoretical case. There is always a fixed factor due to the passing of current through the resistive part of the circuit that has not been considered in the ideal case. For example when current flows through two of the employed MOSFETs, each one has a $R_{ds(on)}$ of 0.07Ω and the voltage drop across two MOSFETs in series would be $2 \cdot 0.07 \cdot 1.47 = 0.2 \text{ V}$. Other voltage drops in PCB traces, connectors and wires could be considered, taking into account also that the stray inductances of the circuit will highly hamper current flow whenever frequency is increasing. However the harmonic content of the output current and the switching losses are maybe more determinant factors affecting these voltage differences, which are related to efficiency.

In Figure 3-32 to Figure 3-35, at the same frequencies as those of simulations of Section 2.1.5.5, i.e. for 5 Hz, 50 Hz, 500 Hz and 1 kHz (from Figure 2-28 to Figure 2-31), respectively, the current waveform flowing through the inductor and the drain-to-source voltage in the MOSFET T4 of Figure 2-43a, are represented. These plots have been extracted by means of the oscilloscope TDS5032B (Tektronix) presented in Section 2.1.1 and corresponding current and voltage probes. On the right side, the numerical data corresponding to the measured magnitudes can be seen. The most important ones are the frequency (Freq(C1) in Hz) and RMS values (RMS(C1) in A) of the current through the coil.

Figure 3-32: Waveforms measured in the oscilloscope with the inverter working at 5 Hz: Current through the coil (brown); Drain-to-source voltage in one of the MOSFETs (blue)

Figure 3-33: Waveforms measured in the oscilloscope with the inverter working at 50 Hz: Current through the coil (brown); Drain-to-source voltage in one of the MOSFETs (blue)

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Figure 3-34: Waveforms measured in the oscilloscope with the inverter working at 500 Hz: Current through the coil (brown); Drain-to-source voltage in one of the MOSFETs (blue)

Figure 3-35: Waveforms measured in the oscilloscope with the inverter working at 1 kHz: Current through the coil (brown); Drain-to-source voltage in one of the MOSFETs (blue)

A clear reduction in the harmonic content of the current sinusoidal waveform for frequencies higher than 50 Hz can be seen in the three latter graphs, with regard to the waveform at 5 Hz. Even so, the outcome at this frequency has also been considered satisfactory. However, a higher distortion can be observed in the oscilloscope outputs for 1 and 2 Hz (Figure 3-36 and Figure 3-37, respectively), being advisable to substitute the higher-frequency solenoid by that of lower-frequency in these cases. On these two plots, the magnitudes Freq(C1) and RMS(C1) appear at the bottom, but due to oscillations in the frequency value, it was preferably measured by the inverse of the period (parameter $1/\Delta t$ on the right of the plots) calculated through the positioning of two vertical cursors, as shown below:

Figure 3-36: Waveforms measured in the oscilloscope with the inverter working at 1 Hz: Current through the coil (brown); Drain-to-source voltage in one of the MOSFETs (blue)

Figure 3-37: Waveforms measured in the oscilloscope with the inverter working at 2 Hz: Current through the coil (brown); Drain-to-source voltage in one of the MOSFETs (blue)

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3.4.3. Inverter operation in the high-frequency range

Since the chosen current (1.47 A for the high-frequency solenoid) is constant, in an ideal resonant case, the input voltage should be constant and equal to $\pi/4$ of the peak current multiplied by the resistance of the coil. Then, for the value of 990 m Ω (given in Section 2.1.5.2) a theoretical input voltage U_{in} of 1.6 V is worked out. However, the actual U_{in} applied values turned out to be: 2 V (at 10 kHz), 2.2 V (at 20 kHz), 2.3 V (at 40 kHz) and 2.4 V (at 50 kHz). That value rising with frequency seems to indicate the effect of stray inductances in the circuit.

Analogously to the figures depicted in Section 3.4.2, the current waveform flowing through the inductor and the drain-to-source voltage in the MOSFET T4 of Figure 2-43a, are shown in Figure 3-38 to Figure 3-41, for expected frequencies of 9.79 kHz, 19.80 kHz, 36.96 kHz and 54.82 kHz, respectively (as seen in Section 2.1.5.5.2). As can be appreciated, these frequencies are very close to those indicated on the oscilloscope screenshots by Freq(C1).

Figure 3-38: Waveforms measured in the oscilloscope with the inverter working at 10 kHz: Current through the coil (brown); Drain-to-source voltage in one of the MOSFETs (blue)

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Figure 3-41: Waveforms measured in the oscilloscope with the inverter working at 50 kHz: Current through the coil (brown); Drain-to-source voltage in one of the MOSFETs (blue)

3.4.4. Effects of an air core OMF generator in the freezing of water

All the experiments were carried out when the ambient temperature T_a (mean $\pm$ standard error) of the Whirlpool freezer (described in Section 2.1.4) was -28.30 ± 0.02 °C. After the perturbation in the ambient temperature at the freezer due to the setting of the sample into the freezer (opening of its door and placing of the sample), the ambient temperature was fast stabilized at -27.28 ± 0.03 °C (Figure 3-42). In turn, the air speed was determined by the hot wire thermo-anemometer of Section 2.1.1 remaining at 0.25 m/s. The experimental MF conditions were specified in Section 2.1.6.

As previously said, that coil is the load of the inverter. In order to facilitate its use in a food freezing technology, a protocol (Appendix 0) was elaborated to make it user-friendly to non-electronic-specialized technician. In this protocol the required connections among the computer, the inverter PCB, the microcontroller and the solenoid are thoroughly specified. The main sections of this protocol are related with: the upload of the program source codes in a computer, explained in Section 3.4, for the low frequency and high frequency algorithms, given in Appendixes 0 and 0, respectively, and the running of each of the codes, after selecting the corresponding parameters for the programming of the frequency. That load is carried out only once in the computer, before the first execution of the algorithms. Besides, the setting of the sensing elements, to measure and monitor the current and the voltage, as well as the

measurement of temperature at the centre and on the surface of the sample were performed as stated in Section 2.1.1.

According to what has been stated in Section 1.4.2.3, as temperature decreases in the precooling stage, more formation of hydrogen bonds and more ordered structures in liquid water will happen [279]. It is necessary to analyze the potential action of the OMFs generated by this device on this hydrogen bonding network, via the parameters related with nucleation on the freezing curves, as well as other parameters of interest on the curves. When, in addition to low temperature, an OMF is also applied, it is necessary to take into account the diamagnetic character of water. This involves, as mentioned in Section 1.4.2.3, that their magnetic moments will show a small induced magnetic field opposed to the applied OMF and as this latter changes direction and module with time, magnetic moments would tend to turn around, always opposing this OMF. However this fact has not significantly influenced the V_p variation when using those OMFs ($p > 0.05$, Table 3-15). In that regard, although the ANOVA test significant index has turned out to be very close but lower than 0.05, the subsequently performed post-hoc tests have not shown any differences among groups which allow confirming any possible effect.

In [45] a commercial freezer with weak OMFs is used to analyze its potential thermal effects on freezing of garlic. They find that the measured MF near the sample (0 - 0.418 mT) has little significant additional effect on the freezing curve characteristics or on the nucleation temperature T_n , in comparison with freezing under the same environment without OMF. These OMF strengths and frequencies are similar to the ones used in another commercial EM device when freezing crab sticks [47]. Because of its influence on the freezing rate, a remarkable attention is paid in the literature to evaluate the effect of traditional freezing processing parameters on the appearance of T_n . It is commonly admitted that when the supercooling degree ΔT_c (defined in Section 2.2.1) increases, the probability of nucleation also increases. The number of nuclei formed at T_n is directly proportional to the extent of supercooling reached in the sample before nucleation [6, 84]. For that reason important endeavors have been carried out to control T_n in freezing processes. By using traditional ones, [303] worked with an ectotherm and found that at high cooling rates (e.g. 1.0 °C/min) there was little evidence of supercooling appearance. By contrast, when they used lower cooling rates (e.g. 0.1°C/min) supercooling occurred. This is in disagreement with [304] where, working with peeled garlic, they analyze several parameters of the freezing curve and find that supercooling is independent on freezing rates and cooling media temperature. Besides they perform an interesting review of the variation and incidence of supercooling when freezing several fruits and vegetables. For a specific freezing process, it is commonly admitted that depending on its programmed freezing rate, important differences in the freezing curve and the corresponding quality of the obtained frozen sample appear. For example in [219] several freezing rates (-10, -15, -20, and -40 °C/min) were used for cryopreservation of striped bass sperm and it was found that -40 °C/min was the optimal one. By using innovative freezing methods, a high pressure shift freezing (PSF) process was used in [305] to control T_n in order to produce small-sized ice crystals in big food samples at their surface and center by comparison with the ones obtained by other classical technologies as air-blast and liquid N₂ freezing. In [306] it is shown that for a given sample, the larger the observed ΔT_c , the earlier nucleation occurs in PSF. In

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[307] it is suggested that power ultrasound can be used in freezing as a potential tool to decrease the size of ice crystals in frozen food. In [308] and [1] the effect of ultrasound irradiation temperature and ultrasound intensity on the freezing and the nucleation in strawberry and mushroom samples respectively were studied. The authors found that the application of ultrasounds was able to induce nucleation at lower degree of supercooling compared to the non-irradiated samples. They found also that the time to pass from 0 to -6°C of the ultrasound-treated samples was significantly shorter than that of the one of the control process. In our particular case, although most of the curves have shown a certain supercooling degree, there have been some cases where nucleation started in the surface of the liquid, as exposed in Section 3.1.3 for the SMF experiments. That way, typical time-temperature plots at the sample center and on the external surface of the vial for two freezing trials of pure water are shown in Figure 3-42a and Figure 3-42b:

Figure 3-42: Temperature evolution at the sample surface (red dashed line) and center (dark blue solid line) during freezing experiments in pure water: a) Typical experiments with partial supercooling of the sample ($\Delta T_c = 0^{\circ}\text{C}$); b): Typical experiments with complete supercooling of the whole sample ($\Delta T_c > 0^{\circ}\text{C}$). Freezer ambient

temperature (light blue solid line)

As expected, the temperature at the surface is always lower than that of the center of the sample, because the probe is in contact with the cooling medium. Apart from the logic differences introduced by the stochastic nature of the freezing process, all curves are rather similar and no apparent variation can be observed when comparing the different OMF conditions. However, in contrast to the SMF freezing experiments of pure water (Section 3.1.3), the probe placed on the vial surface showed little or no supercooling in the cases where no supercooling was observed at the sample center, as in the example depicted in Figure 3-42a. This fact happened in every frequency and it could be attributable to the lower heat transfer rate of the cooling medium on this occasion. Since the removal of heat and the sample volume are lower, the temperature gradient in the sample is reduced (as could be seen also by the lesser difference between both probe temperatures), and this homogeneity of temperatures facilitates the appearance or not of supercooling in all the points of the liquid.

In a similar way as stated in Section 3.1.3, the stochastic nature of nucleation can be seen in Figure 3-43. Thus in this work the ice nucleation was triggered between 6.75 and 12.75 min after plunging the sample in the cooling medium, whereas the temperature at the center ranged between 2.26 °C and -11.5 °C.

As it is logic, a relation between the time to nucleate and the nucleation temperature is established (Figure 3-43), as the more it takes to start, the lower the reached temperature without initiating nucleation. However, that plot and the statistical study ($p > 0.05$, Table 3-15) evidence that none of the OMF frequencies or the control without OMF application produce any significant effect on the obtained supercooling degree ΔT_c . Specifically, all the 15 experiments without OMF applied had supercooling. For the freezing experiments carried out at 5 Hz, 15 of 17 showed supercooling. In turn, the corresponding proportions of experiments in which nucleation was preceded by supercooling were of 17 of 18 experiments for 50 Hz, and 19 of 20 for the case at 50 kHz. As can be seen, supercooling was very likely to occur, much more than in the water freezing experiments exposed in Section 3.1.3, probably due to the lower temperature gradient in the sample, as explained above.

Other parameter of interest to improve the quality of the final products after freezing is the phase transition time, t_{pt} , as it is in that stage when the ice crystal growing happens. As it is known by the scientific literature [4, 276, 277], the highest the supercooling degree, the shortest the value of t_{pt} , giving rise to a higher number of smaller ice crystals, as desired. Dealing with OMF in [50], working in food materials (Japanese radish and sweet potato) and using field intensities of 0.5 mT at 50Hz, they did not detect any apparent difference in temperature history caused by the applied magnetic field, considering e.g., aspects of the freezing curve such as T_n , t_{pt} and t_{tot} . In [51] different OMFs were applied to w/o emulsions, using Differential Thermal Analysis to look for T_n of supercooled water. As here, they concluded that the T_n of water was not affected by these fields. When dealing with food, they analyzed the surface and center temperature-time curves by applying a unidirectional OMF or NMR during freezing. As before, no differences were found on T_n , t_{pt} and t_{tot} when comparing the effects of applying or not magnetic fields during freezing of the studied samples. From T_n

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onwards ice crystals are being formed and they start also its evolution. In [262], the derivative of the temperature-time curve was used to determine the final freezing point when working with solutions. Following this method, the values of t_{pt} were calculated from the nucleation starting point up to the final freezing point. The existing correlation between T_n and t_{pt} can be appreciated in Figure 3-44 for the set of performed experiments, and as happened with ΔT_c , no significant difference in the t_{pt} was detected for any of the proved field conditions ($p > 0.05$, Table 3-15).

	Shapiro-Wilk				ANOVA	Kruskal-Wallis
	No OMF	5 Hz	50 Hz	50 kHz		
Pure water samples						
ΔT_c	0.701	0.500	0.381	0.163	0.965	--
t_{pt}	0.435	0.886	0.174	0.517	0.946	--
V_p	0.352	0.100	0.064	0.263	0.049	--
V_t	0.059	0.059	0.361	0.006	--	0.331
t_{tot}	0.634	0.751	0.950	0.225	0.174	--

Table 3-15: p-values obtained after applying the Shapiro-Wilk test to check the normality of the data and the Kruskal-Wallis and ANOVA tests to compare the characteristic parameters of control (no OMF application), OMF at 5 Hz, 50 Hz and 50 kHz. ΔT_c : Extent of supercooling at the sample center if exists ($\Delta T_c > 0$); t_{pt} : Phase transition time; V_p : Precooling rate; V_t : Tempering rate; t_{tot} : Total freezing time

	No OMF	5 Hz	50 Hz	50 kHz
Pure water samples				
ΔT_c	4.8 ± 0.7	5.0 ± 0.8	4.5 ± 0.7	4.8 ± 0.6
t_{pt}	24.66 ± 0.28	24.66 ± 0.30	24.71 ± 0.26	24.78 ± 0.21
V_p	0.0629 ± 0.0003	0.0638 ± 0.0003	0.0635 ± 0.0004	0.0625 ± 0.0004
V_t	0.0482 ± 0.0009	0.0460 ± 0.0008	0.0465 ± 0.0010	0.0482 ± 0.0011
t_{tot}	38.37 ± 0.13	38.64 ± 0.10	38.83 ± 0.22	38.78 ± 0.13

Table 3-16: Mean $\pm$ standard error values of the characteristic parameters of control (no OMF application), OMF at 5 Hz, 50 Hz and 50 kHz freezing experiments. ΔT_c : Extent of supercooling at the sample center if exists ($\Delta T_c > 0$); t_{pt} : Phase transition time; V_p : Precooling rate; V_t : Tempering rate; t_{tot} : Total freezing time

After phase change period, the freezing process correspond to a pure energy, mass and moment transfer phenomenon mainly governed by the applied refrigeration power (and design characteristics) at the equilibrium freezing temperature (or below) of the used refrigeration equipment. No additional effects due to the applied OMF should be expected. The results corresponding to the tempering rate, V_t do not present statistical significant differences among any of the studied conditions with and without the OMF action during freezing ($p > 0.05$, Table 3-15). The total freezing time t_{tot} summarizes the behavior of the previously described parameters of the freezing curve from a practical point of view. By using t_{tot} , practical information about handling frozen foods along its cold chain can be obtained [309]. In this work no significant differences have been found in this parameter in the freezing curves of water obtained with and without the applied OMFs ($p > 0.05$, Table 3-15). This result does not agree with the given one in [53] where the effect of an OMF freezer using weak magnetic fields (1.5 - 2 mT) and low frequencies (20, 30, 40Hz) was compared with the effect of a conventional rapid freezer (CRF). When weighing up the corresponding temperature change during freezing, it was obtained that all the three studied freezing cases took more time to pass from -1°C to -4°C than for the CRF. This fact is justified by the authors arguing that the total electric power of both the CRF and OMF equipment was at the same level and OMF required an extra power for generating the magnetic field within the freezer.

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Figure 3-43: Temperature (°C) and extent of supercooling (°C) at the pure water sample center when nucleation occurred in (◇): control; (□): 5 Hz; (△): 50 Hz; and (X): 50 kHz experiments

Figure 3-44: Phase transition time (min) of pure water in (◇): control; (□): 5 Hz; (△): 50 Hz; and (X): 50 kHz experiments

Comparative results of all the studied parameters of the freezing curve, when freezing without or with different OMF frequencies, are summarized in Table 3-16.

4. Discussion and original contributions

Within the infinite number of EM field frequencies and strengths, which are potentially available, and that have been applied in the different fields of Science and Technology, a lot of instances can be found where certain combinations of these magnitudes originate interactions with matter which can be used in a beneficial manner. Besides, many of these interactions and the observed effects have been proved properly and scientifically explained. In the case of the process of EM-field-assisted freezing, this cannot be stated yet. The first objective of this thesis is to get either to corroborate, or to question, the hypotheses that have been posed, until now, to explain the potential improvements in freezing which are announced in some scientific publications with the employment of certain commercial devices and by means of some laboratory equipment. In this thesis, those pieces of equipment have been employed and the study has been tackled by coping with the problem from two complementary points of view: by means of the analysis of freezing curves and through the study of the effects produced in samples treated by similar fields to those of the said devices. The study of water freezing curve in the presence of SMFs and OMFs of different characteristics has not provided any significant differences with regard to the non-application of these fields. The lack of remarkable effects has also been evidenced upon having confirmed, by this thesis that the thermal conductivity of ice produced by a MF freezing commercial equipment, is not significantly different from that achieved through other methods of obtainment which simulate different traditional food freezing modes. However, it has been collaterally proved that the thermal conductivity measured at a given temperature depends on the freezing rate. For that reason this property could be used to distinguish between high-quality (fast) and low-quality (slow) traditional freezing processes. Therefore, thermal conductivity measurements might be a promising method for ascertaining how quickly a food product was frozen, although this property must be evaluated for each food to extend its application.

In order to indicate the reasons which could influence the consecution of notable effects on the freezing curve, such as the achievement of remarkable supercooling, it was necessary to work with nanoparticle dispersions. Its aim was to confirm, or not, the posed hypotheses [161]. In this respect, the results obtained with this thesis have been demonstrated not to support their hypotheses. Nevertheless, some results here obtained could have a practical interest in several areas. In fact it has been obtained that in the precooling process, prior to nucleation, an increment in the cooling rate, i.e. a significant reduction in the time before starting crystallization, do appear. This increment seems to be due to the combination of two factors. On the one hand the OMF should inhibit the effect produced by the change in the convection movements around the point of maximum density of water. This action is reflected in the elimination of the discontinuity in the slope of the precooling curve (see Figure 3-11). On the other hand the application of OMF should improve the thermal conductivity of the used magnetic nanoparticles dispersion (see Section 3.2.5). As this fact brings as a consequence a fast precooling rate, this phenomenon could be exploited for energy saving in large-scale commercial freezing, for medicine and for cryotherapy in sportspersons and other population. In this relation, pertinent works should be carried out in order to determine if these savings will be rather higher than the costs brought about by this technology. As previously said, one

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of the therapeutic treatments for which magnetic nanoparticles are being used is magnetic hyperthermia. It consists in increasing the temperature of the area of the body in which malignant cells are located. On the contrary, the treatment of therapeutic hypothermia, recommended by the International Liaison Committee on Resuscitation in patients who have suffered a cardiac arrest (under certain requirements) in order to minimize neurological injuries [310], seeks for reduction of the body temperature to values between 32 and 34°C during 24 hours. Bearing in mind that therapeutic hypothermia should be initiated as soon as possible [311, 312], the results obtained here could open up the possibility of inserting magnetic nanoparticles in the zones of interest in the body and reaching then the pursued lower temperature in a shorter time interval. Besides, this potential faster precooling rate could be obtained when using magnetic nanoparticles in the tissue cryopreservation domain, complementing the promising results obtained when using a later inductive heating of the frozen samples [186].

Another potential application could be in the whole-body cryotherapy treatments. As stated in [313], the old cold therapy practice consisting in remaining for four minutes in highly negative temperatures in a small cold chamber is very appreciated by athletes and more and more by other populations. Taking into account its interest, the International Institute of Refrigeration is supporting the creation of a working group dedicated to “Cryobiology, Cryomedicine and Health Products” to foster research in this area where the faster precooling rate here obtained could have interest.

Upon analyzing the effect that MF freezing has on foodstuffs, second objective of this thesis work, it has been observed that the quality of foods after processing in commercial MF freezing equipment has not been better than that achieved without the application of such fields. The obtained results are rather explained by the incidence of freezing speed than by the presence of the MF of those devices. The results concerning the crab sticks are consistent with the thermal kinetics observed in the obtained freezing curves. Thus, the slow freezing rates achieved in the static-air freezing experiments allowed water molecules to migrate and agglomerate, forming large ice crystals. By contrast, when much quicker freezing rates were used, as occurred also in the commercial MF freezing, the water migration was reduced and, thus, smaller ice crystals were formed that produced significantly lower quality losses on thawing. So it is remarkable that no differences among fast freezing methods were obtained. During frozen storage, recrystallization phenomena occurred that increased ice damage. It is well-known that, in fish gels, large ice crystals produce the dehydration of the gel network, affect protein interactions, and induce starch retrogradation. All these phenomena greatly affect the physical attributes of crab sticks and produce quality losses in agreement with [314-316]. Besides, in this thesis no effect of OMFs has been found (<2 mT, 6-59 Hz) on freezing time, drip loss, water-holding capacity, toughness, or whiteness of crab sticks. Very similar results were obtained with pork loin in a different commercial MF freezing device. Overall this study found that the application of OMFs during air-blast freezing had no effect, whichever their strength or frequency, on the freezing time or quality attributes of pork loin. Similar results were reported by [50] and [51] who did not find any effect of OMFs on the microstructure, drip losses, color, texture, and sensory evaluation of frozen radish, sweet potato, spinach, yellowtail fish, and tuna. [53] also found that the application of OMF (1.5-2

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mT at 20, 30, and 40 Hz) during freezing had no effect on the drip and cooking losses, or the rupture stress and strain of chicken breasts frozen in a ABI CAS freezer.

Nevertheless, not all published studies on OMF have been negative. Studies at the Korea Food Research Institute have reported benefits for OMF frozen meats. [165, 166] reported reduced total freezing times and improved quality attributes in beef, pork, and chicken, and [167], and [164] reported similar findings for pork and beef, respectively. However, unfortunately, none of these studies compared like with like. The air blast freezer used for the magnetic resonance freezing was different to the air blast freezer used to freeze the control samples, as were the operating air temperatures. The commercial equipment freezer used was operated at -55 °C, while the conventional air blast freezer used as the control was operated at -45 °C (although in the case of the experiments carried out by [165] the published temperature curves indicate that actual temperatures in the conventional air blast were nearer -40 °C than -45 °C). In this relation it seems that the established thing by us in [36] is in agreement on this results; in addition, since the air temperatures used in the two compared systems were very different, and no details of the air speeds or surface heat transfer coefficient used in the different systems were given, it is not possible to deduce whether the improvements detected by these authors were produced by the OMF or by the different freezing applied conditions.

Although we have yet to see any clear advantages of OMF assisted freezing, we do not believe that studies to date completely invalidate the commercial EM system as a method of enhancing the overall freezing of foods; however, they do suggest that weak OMF may not affect all foods. As we establish in [317] it is possible that any effect will depend on a complex combination of food, freezing rate and MF frequency. Such is the case of [52], who found interesting aspects at some specific conditions when freezing potato and apple samples, but no explanation could be provided. Similar observations have been made in published studies using commercial equipment to freeze human tissues [318].

Regarding the third objective proposed in this thesis, it is remarkable the great potential usefulness which the air core OMF generator constructed here offers. It is convenient to remember that the application of an OMF implies the appearance of an associated OEF. This circumstance would provide a less problematic way to apply those OEFs for EM freezing applications [68]. Besides its use in expanding the experimental conditions employed until now to perform EM freezing it is also remarkable its potential use in other topics. A current research field is being conducted towards the study of the protein instability in aqueous solution, as it presents a major interest in producing pharmaceutical formulations. Without performing freezing, several works demonstrate that non-thermal effects can be obtained when applying EM fields to macromolecules, proteins and enzymes [283, 319-322]. Those phenomena should be in relation with the observations of [282, 319] where it is considered that the protein activation is electromagnetic in nature.

Other interesting research field to be covered by the obtained air core OMF generator is to investigate the impact of those OMFs on the cells and small living beings as microorganisms, its action, actuating as a harmful destroying factor or, on the contrary, as a stimulating effect, depending on conditions [323]. Concerning bacteria, a reduction load was obtained in [324] by means of subjecting food samples to OMF ranging from 5 to 50 T and between 5 and 500 kHz.

5. Conclusions and future work

Conclusions and future work

5.1.Conclusions

- I. The differences found in the distribution of the MF vector, both inside and around the sample, made for the pieces of equipment containing each of the generators used here, are very remarkable. Whereas in the iron core and air core generators, there exists a homogeneous distribution of MF vector in the measurement area, that distribution is more irregular in the one employing permanent magnets and in the commercial equipment.
Since the verification of the existence of interactions between foodstuffs and fields must be the basis for the development of theories supporting the potential effects achieved upon applying EM fields during their freezing, it becomes relevant the mathematical modeling in the design stage of a magnetic freezing system. This consideration would be important both at laboratory and industrial level. Unlike to what has been published until now in this area, that MF vector distribution should be provided before going on to interpret the results obtained through EM freezing.
- II. In opposition to the direct experimental determination, mathematical modeling can be very useful to know the MF vector in many of the situations at laboratory level and at industrial level. The reason lies in the uncertainty which arises when positioning the measurement point at the planned place. This is due to several factors, namely: the difficult accessibility and the unwanted interactions, both with other elements of the equipment and with other process parameters such as the speed air distribution or the system temperature.
- III. The analysis of the main parts of the freezing curve has allowed corroborating that the application of MFs of similar characteristics to those of the commercial MF freezing equipment, and as well at frequencies above those, does not originate significant differences in relation to what has been obtained in the same experimental conditions.
- IV. The hypothesis formulated by some authors, attributing improvements in biomaterial freezing to the presence of magnetic particles in them which would promote the consecution of larger supercoolings, has not turned out to be valid. This has been proved by the freezing of a concentrated dispersion of superparamagnetic maghemite in the presence of an OMF.
- V. The observed loss of symmetry in the MF vector distribution, when changing the relative position of the magnetic poles in a device with permanent magnets makes also required to develop a mathematical modeling of such distribution. This becomes necessary if the up-to-date hypothesis, based on the hydrogen nucleus spin orientation, is tried to be employed in order to support the theory of supercooling obtainment by means of magnetic freezing.
- VI. The air core OMF generator, designed and built by means of this thesis, supplies, on a small scale, the operating conditions present in most of the commercial systems. It provides also those employed by a large part of the scientific community in their experiments on EM food freezing, protein modification and biomaterial cryopreservation. Furthermore, it facilitates to extend such studies to frequency

ranges above and below a large proportion of those conditions, with or without freezing. Its design has permitted achieving the required MF uniformity in the region of measurement.

- VII. The OEFs induced by the application of these OMFs offer a lot of advantages over the direct application of EFs to the sample to be treated. Depending on the strength of those fields, important drawbacks would be left aside, such as the potential appearance of sparks, protruding “corona wind”, damages due to use high voltages in moist environments, the necessity of a switching device to avoid any electrical risk for users, the requirement that samples should not be in contact with both electrodes or the use of small distances between electrodes.
- VIII. The methodology designed here to determine the thermal conductivity of ice by applying the hot wire technique, has been used to evaluate this property in the ice produced in a similar fashion to that obtained upon freezing water by means of different processing, carried out in the frozen food industry. It has been corroborated that there are no significant differences among several of these ice types and the one obtained by means of a commercial EM food freezing system. In parallel, it has been proved that freezing speed does have a significant influence on the value of the thermal conductivity of the produced ice. This would allow using that magnitude as a tool for the traceability of ice samples.
- IX. Each of the studies carried out in commercial EM freezing systems, in food of meat origin and in fish, has not yielded significantly different results with regard to the corresponding freezing experiments performed without the application of EM fields, both in freshly frozen foods and in those which have been stored in a frozen state for several months.
- X. Both in the case of the ice thermal conductivity value and in the case of the quality parameters of the analyzed food, freezing velocity has had a greater influence than the presence of EM fields during their freezing. The quality parameters of that food and the thermal conductivity of ice are affected by freezing speed and not by the presence of the EM fields of those systems.
- XI. Further research into OMF should investigate a wider range of OMF strength and frequency than those currently employed in commercial CAS freezers. The inverter and solenoid constructed here can be a tool of great interest for that. Its adaptation to get nonsinusoidal waveforms would not offer great technical difficulties. In addition to this, the employment of electrostatic fields and combined pulsed electric field and static magnetic field technology, may also show great promise.

5.2.Future work

- I. The use of emulsion nanoparticles produces a fast precooling rate. Among others, this phenomenon could be exploited for energy saving in large-scale commercial freezing, for medicine and for cryotherapy in sports and other population.
- II. Further research into OMF should investigate a wider range of OMF strength and frequency than those currently employed in commercial CAS freezers. The inverter and

Conclusions and future work

solenoid constructed here can be a tool of great interest for that. Its adaptation to get nonsinusoidal waveforms would not offer great technical difficulties. In addition to this, the employment of electrostatic fields and combined pulsed electric field and static magnetic field technology, may also show great promise.

6. List of publications

Articles in JCR indexed journals

- Bonales, L. J., Rodríguez, A. C., & Sanz, P. D. (2017). Thermal conductivity of ice prepared under different conditions. *International journal of food properties*, 1-10.
- Otero, L., Pérez-Mateos, M., Rodríguez, A. C., & Sanz, P. D. (2017). Electromagnetic freezing: Effects of weak oscillating magnetic fields on crab sticks. *Journal of Food Engineering*, 200, 87-94.
- Otero, L., Rodríguez, A., & Sanz, P. (2018). Effects of static magnetic fields on supercooling and freezing kinetics of pure water and 0.9% NaCl solutions. *Journal of Food Engineering*, 217, 34-42.
- Otero, L., Rodríguez, A. C., Pérez Mateos, M., & Sanz, P. D. (2016). Effects of Magnetic Fields on Freezing: Application to Biological Products. *Comprehensive Reviews in Food Science and Food Safety*, 15(3), 646-667.
- Rodríguez, A. C., James, C., & James, S. J. (2017). Effects of Weak Oscillating Magnetic Fields on the Freezing of Pork Loin. *Food and Bioprocess Technology*.
- Rodríguez, A. C., Sánchez Benítez, J., & Sanz, P. D. (2017). Simulation of the Magnetic Freezing Process Applied to Foods. *Food Engineering Reviews*, 1-24.

International Congress

- Rodríguez, A. C., Otero, L., Pérez-Mateos, M., Sánchez-Benítez, J., Puértolas, E., Martínez de Marañón, I., Cobos, J. A., Sanz, P. D. *Congelación electromagnética: estado actual*. VII Congreso Ibérico de Ciencias y Técnicas del Frío. V Congreso Iberoamericano de Ciencias y Técnicas del Frío. 18-20 de junio de 2014. Tarragona.

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8. Appendix A.1 Analytical description of the stationary MF in the laboratory freezer

In order to assess the respective accuracies of the proposed FEM model and the experimental measurements, a comparison with the results provided by an analytical method is employed in this work. By analyzing the different analytical approaches exposed in the literature to calculate the MF generated by permanent magnets, they can be typically divided into two groups [325, 326]: one is the coulombian model in which two fictitious charge densities (positive and negative), distributed on the north and south faces of the magnet, would be responsible for generating a magnetic scalar potential V_m , of which $\vec{B}$ could be extracted by applying (Eq. 59) and (Eq. 62) [327, 328]; the other group is the amperian model which makes use of fictitious currents generating a MF equivalent to that of the magnet. In this case $\vec{B}$ is calculated as the curl of the magnetic vector potential $\vec{A}$ or based on Biot-Savart's law [329]. Based on the later model, we have obtained an expression for the MF $\vec{B}$ on the axis passing through the centers of both cylindrical magnets. Starting from a cylindrical magnet with radius R and height L , as represented in Figure 8-1, a current uniformly distributed throughout its lateral surface is supposed in such a way that the induced MF is equivalent to that of the magnet. This is accepted as a valid model for a cylindrical magnet, considering that its magnetization is sufficiently uniform [330]. In this model, the currents must flow in the pertinent direction so that the lines of induced $\vec{B}$ follow a trajectory going from the north to the south poles of the magnet.

Figure 8-1: Derivation of MF $\vec{B}$ on the axis of a cylindrical magnet by using Biot-Savart's law.

The total equivalent current would be given by:

$$I_{eq} = \frac{p}{\pi R^2} \quad (\text{Eq. A1})$$

where p is the net magnetic moment of the magnet. Taking a differential element of surface as a circular loop of height dz and radius R , the differential current circulating through this loop would be:

$$di = \frac{I_{eq} dz}{L} = \frac{p}{\pi R^2 L} dz \quad (\text{Eq. A2})$$

Given a point P on the axis of the cylindrical magnet, this differential current would contribute to MF with a $d\vec{B}$ only in the direction of that axis, since MF components parallel to the magnet basis are cancelled out by symmetry. By applying the Biot-Savart's law, the expression for the differential MF in a material medium is:

$$d\vec{B} = \frac{\mu R^2 di}{2 \left(\sqrt{R^2 + z_p^2} \right)^3} \vec{k} = \frac{\mu p dz}{2\pi L \left(\sqrt{R^2 + z_p^2} \right)^3} \vec{k} \quad (\text{Eq. A3})$$

in which z_p is the distance from the point P to the differential current loop and $\vec{k}$ is the unit vector in the direction of axis going out from the magnet north pole. Considering the angle θ formed by the relative position vector from the differential current loop to P and the magnet axis, the change of variable $R = z_p \cdot \tan(\theta)$ allows to work out the integral on the lateral surface:

$$\vec{B} = -\frac{\mu p}{2\pi L R^2} \int_{\theta_1}^{\theta_2} \sin(\theta) d\theta \vec{k} = \frac{\mu p}{2\pi L R^2} (\cos(\theta_2) - \cos(\theta_1)) \vec{k} \quad (\text{Eq. A4})$$

Magnetization $\vec{M}$ is defined in terms of the net magnetic moment of the magnet divided by its volume, and multiplied by μ_0 , thus resulting in the magnetic remanence $\vec{B}_r$. Thus MF on the axis of a cylindrical magnet can be expressed as a function of $\vec{B}_r$, μ_r of the material medium, distance to the magnet and dimensions of the cylinder by applying the known equation [331] to a medium different from vacuum:

$$\vec{B} = \mu_r \frac{\vec{B}_r}{2} \left(\frac{z + L}{\sqrt{(z + L)^2 + R^2}} - \frac{z}{\sqrt{z^2 + R^2}} \right) \quad (\text{Eq. A5})$$

Nevertheless, looking for an expression of MF off the axis of the magnet, there is not such a simple solution to this problem, requiring, in general terms, the use of elliptic integrals as shown in [330, 332-334]. In the present work the MF out of the magnet axis has been determined by using the equations given in [335] for the case of a ring-shaped magnet with axial magnetic polarization, conveniently adapted to a material medium. In order to calculate the MF created by a solid cylinder, the inner radius of the ring needs to be zero. Those authors used a coulombian approach to find the field, introducing fictitious positive and negative magnetic charge densities ($+\sigma^*$ and $-\sigma^*$) in both superior and inferior bases, respectively. The total field at any point can be calculated as a sum of two terms depending on each charge distribution. The equations given in terms of the MF intensity $\vec{H}$ have been expressed here in terms of the MF $\vec{B}$, considering only the volume out of magnets, i.e. without the magnetization term in the constitutive equation, to simplify those formulas. So according to Babic and Akyel manuscript, in cylindrical coordinates (ρ, ϕ, z_0) , taking the center of the south pole circular base as the origin of coordinates, there are two terms for the radial component:

$$B_\rho^+(\rho, \varphi, z_0) = \mu_r \frac{\sigma^*}{\pi} \sum_{n=1}^2 (-1)^{n-1} \frac{1}{k_n^+} \sqrt{\frac{r_n}{\rho}} \left[E(k_n^+) - \left(1 - \frac{k_n^{+2}}{2} \right) K(k_n^+) \right] \quad (\text{Eq. A6})$$

$$B_\rho^-(\rho, \varphi, z_0) = \mu_r \frac{-\sigma^*}{\pi} \sum_{n=1}^2 (-1)^{n-1} \frac{1}{k_n^-} \sqrt{\frac{r_n}{\rho}} \left[E(k_n^-) - \left(1 - \frac{k_n^{-2}}{2} \right) K(k_n^-) \right] \quad (\text{Eq. A7})$$

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where the functions K() and E() are the complete elliptic integrals of the first and second kinds, respectively. And the two terms for the vertical component are:

$$B_{z_0}^+(\rho, \varphi, z_0) = \mu_r \frac{\sigma^*}{4\pi(z_0 - L)} \sum_{n=1}^2 (-1)^{n-1} \frac{k_n^+}{\sqrt{\rho r_n}} \left(\left[\sqrt{\rho^2 + (z_0 - L)^2} - \rho \right] \left[\sqrt{\rho^2 + (z_0 - L)^2} - r_n \right] \Pi(h_1^+, k_n^+) + \left[\sqrt{\rho^2 + (z_0 - L)^2} + \rho \right] \left[\sqrt{\rho^2 + (z_0 - L)^2} + r_n \right] \Pi(h_2^+, k_n^+) \right) \quad (\text{Eq. A8})$$

$$B_{z_0}^-(\rho, \varphi, z_0) = \mu_r \frac{-\sigma^*}{4\pi z_0} \sum_{n=1}^2 (-1)^{n-1} \frac{k_n^-}{\sqrt{\rho r_n}} \left(\left[\sqrt{\rho^2 + z_0^2} - \rho \right] \left[\sqrt{\rho^2 + z_0^2} - r_n \right] \Pi(h_1^-, k_n^-) + \left[\sqrt{\rho^2 + z_0^2} + \rho \right] \left[\sqrt{\rho^2 + z_0^2} + r_n \right] \Pi(h_2^-, k_n^-) \right) \quad (\text{Eq. A9})$$

where $\Pi()$ is the complete elliptic integral of the third kind. There is neither azimuthal component of $\vec{B}$, in accordance with (Eq. 65), nor dependence on this azimuthal coordinate because of axial symmetry of MF, and its cylindrical components at any point off the magnets result in:

$$B_\rho(\rho, \varphi, z_0) = B_\rho^+(\rho, \varphi, z_0) + B_\rho^-(\rho, \varphi, z_0) \quad (\text{Eq. A10})$$

$$B_\varphi(\rho, \varphi, z_0) = 0 \quad (\text{Eq. A11})$$

$$B_{z_0}(\rho, \varphi, z_0) = B_{z_0}^+(\rho, \varphi, z_0) + B_{z_0}^-(\rho, \varphi, z_0) \quad (\text{Eq. A12})$$

It can be easily proved [328] that the sum of the magnetic charge densities of both magnet poles has to be equal to the magnetization of the magnet. Then the value of σ^* which appears in (Eq. A6) to (Eq. A9) is half that of the magnet remanence $\vec{B}_r$. Some other parameters were introduced in those equations to shorten them, namely:

$$\begin{aligned} k_n^+ &= \sqrt{\frac{4\rho r_n}{(\rho + r_n)^2 + (z_0 - L)^2}} & k_n^- &= \sqrt{\frac{4\rho r_n}{(\rho + r_n)^2 + z_0^2}} \\ h_1^+ &= \frac{2\rho}{\rho + \sqrt{\rho^2 + (z_0 - L)^2}} & h_2^+ &= \frac{2\rho}{\rho - \sqrt{\rho^2 + (z_0 - L)^2}} \\ h_1^- &= \frac{2\rho}{\rho + \sqrt{\rho^2 + z_0^2}} & h_2^- &= \frac{2\rho}{\rho - \sqrt{\rho^2 + z_0^2}} \\ r_1 &= r_{in} = 0 & r_2 &= r_{out} = R \end{aligned}$$

It is worth noting that on doing $r_1 = 0$, as this would be the diameter of the cylindrical hollow of ring-shaped magnets (not present in these solid cylindrical magnets), the first terms of the summations in (Eq. A6) to (Eq. A9) are cancelled. These equations result in indeterminations for any point on the axis, that is when $\rho=0$. In this case (Eq. A5) is adequate for the purpose of determining the MF.

The formulas presented in this analytical approach are referred to only one cylindrical magnet, so the superposition principle will be applied to obtain the solution for the case with two magnets, calculating the MF $\vec{B}$ at any point as the vector addition of the fields created by both

magnets. In this particular case, given the arrangement of the magnets with their axes coinciding, there will not be any azimuthal component of the MF either.

9. Appendix A.2 Patents on magnetic freezing

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INVENTORS	MAGNETIC FIELD			COMBINATIONS			FREEZING TEMPERATURE	PRODUCTS TO FREEZE
	STATIC B	OSCILLATING B; ω	PULSED B; ω ; pw	ELECTRIC FIELDS E; ω	ELECTRO MAGNETIC WAVES ω	OTHERS		
Hirasawa et al. (2000)	Patented	ω/γ	-	-	10 kHz-100 MHz	Air sanitizer	-40 °C	Food
Hirasawa et al. (2001)	Patented	X	X	-	-	Air sanitizer	-20 °C	Food
Owada & Kurita (2001)	Patented	0.1 mT-2 T	0.1-10 mT; 50-60 Hz	-	100-1000 kV/m	-	-30 °C to -100 °C	Food and food ingredients
	Tested	10 mT	0.5 mT; 50-60 Hz	-	600 kV/m	-	-50 °C	Tuna, sardines, pork, juices, wine, oranges, and cakes
Kino (2002)	Patented	X	X	-	-	γ -B	X	Food
Toyoshima (2005)	Patented	X	-	-	-	X	Ventilators Heat insulators	-40 °C Food
Ino et al. (2005)	Patented	-	≤ 100 mT; ≤ 10 MHz	-	-	-	Ventilators Heat insulators	X Food
	Tested	-	X	-	-	-	-35 °C	Sweet potatoes
Miura et al. (2005)	Patented	-	-	0.1-10 T; 0.1 Hz-1kHz; 10-100 μ s	-	-	-10 °C to -60 °C	Starch-containing food
	Tested	-	-	5 T; 1 Hz; 55 μ s	-	-	-20 °C	Potato starch gels
Owada (2007)	Patented	0.1 mT-1 T	0.1-100 mT; 50-60 Hz	-	10-500 kV/m; 50 Hz-5 MHz (0.25-3 MHz) ^r	-	20 °C to -40 °C	Foodstuffs, food products, organisms, and other materials

	Tested	1 mT	0.5-0.7 mT; 50 Hz	-	15 kV/m; 250 kHz, 3 MHz, - 50 Hz-5 MHz	Heat insulators	-20 °C, -40 °C	Chicken and tuna
Sato & Fujita (2008)	Patented	-	10 mT-1.2 T (30-700 mT) ^f ; 20 Hz- 25 kHz (40 Hz-1.2 kHz) ^f	-	-	Ionic air Ultrasonic waves, microwaves, far infrared rays, ultraviolet light, α- rays	-20 °C to -60 °C	Food
	Patented	10 mT-1.2 T (30-700 mT) ^f	10 mT-1.2 T (30-700 mT) ^f ; 20 Hz- 25 kHz (40 Hz-1.2 kHz) ^f	-	-		-20 °C to -60 °C	Food
	Tested	-	80 mT, 200 mT, 300 mT; 60 Hz, 100 Hz	-	-	Air dehumidifier Air pressure regulator Ventilators	-40 °C, -50 °C	Chinese noodles, spinaches, packed pasta, pork lumps, and tofu blocks
	Tested	800 mT	300 mT; 100 Hz	-	-			
	Tested	800 mT	300 mT; 100 Hz	-	-			
Kim et al. (2009)	Patented	-	X	-	-	Not described	X	Ice cubes
Owada & Saito (2010))	Patented	0.1 mT-2 T (10 mT) ^f	0.1-10 mT (0.5 mT) ^f ; 50-60 Hz	-	100-1000 kV/m (2-60 kV/m) ^f	Air pressure regulator Air sanitizer Oxygen absorber Sound wave generator Ventilators Far-infrared-ray absorber Heat insulators	-30 °C to -100 °C	Food products, food ingredients, medical products, medicines, living tissues, and living cells
	Tested	X	X	-	X		X	Mackerel and lobster
Fujisaki & Amano (2012)	Patented	1-200 mT (10-15) mT ^f	-	-	-	0.3-2 MHz (0.6-1 MHz) ^f	X	Food products, cooking ingredients, living bodies, and biological samples
Mihara et al. (2012)	Patented	-	0.01-0.4 mT (0.2 mT) ^f ; 200 Hz-200 kHz (2 kHz) ^f	-	-		-2 °C to -40 °C (-20 °C to -40 °C) ^f	Foods, organs, and the like
	Tested	-	0.12 mT 0 Hz-200 kHz	-	-	Not described	X	Physiological saline solution
	Tested	-	0.1-0.2 mT 2 kHz	-	-		-30 °C	Rats

	0.8 mT 2 kHz	-	-	-	-40 °C	Alkaline phosphatase, green fluorescent protein
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Table 8-1: Patents on magnetic freezing. B: magnetic field strength; ω : frequency; pw: pulse width; E: electric field strength; γ : gyromagnetic ratio for hydrogen (42.58 MHz/T); -: not employed; X: not reported value; ()^r: recommended conditions

10. Appendix A.3 Scientific works on magnetic freezing of foods

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FIELDS APPLIED	INTENSITY (mT)	FREQUENCY (Hz)	DEVICE	SAMPLE	EFFECTS OF THE FIELDS APPLIED				AUTHOR/ DOCUMENT
					ΔT	FREEZING KINETICS	ICE CRYSTALS	QUALITY	
STATIC MAGNETIC FIELD	0.36 0.72 1.08		Lab prototype	Carps	No effect	No effect on precooling time Shorter freezing plateau Shorter tempering and total freezing times	-	-	Lou, et al. [46] Research paper
OSCILLATING MAGNETIC FIELD	≤ 100	$\leq 10^7$	Patented by Kansho Riyo Gijutsu Kenkyusho: KK	Sweet potatoes	-	-	Smaller	Color, taste, aroma, smoothness, and hardness similar to those of raw potato	Ino, et al. [162] Patent
	0.5-0.7	50	Patented by ABI Co., Ltd.	Chicken and tuna	-	Time for lowering the core temperature from 0 °C to -20 °C was 20-50% reduced	-	Cells were hardly destroyed. Color, flavor, and taste similar to those of the original raw food	Owada [41] Patent
	200-300	60-100	Patented by Shounan Jitsugyou Co.	Packed Chinese noodles, spinaches, packed pasta, lumps of pork, and tofu blocks	-	-	-	Quality satisfactory after thawing	Sato and Fujita [156] Patent

	0.5	50	Lab prototype	Radish, tuna, sweet potato, yellow tail fish, and agar gel	No effect	No effect	No effect	No effect	Suzuki, et al. [336]; Watanabe, et al. [337]
									Research papers
PULSED MAGNETIC FIELD (55 μ s)	500	1	Lab prototype	Potato starch gels	-	-	-	Larger exudates Lower rupture stress	Miura, et al. [70]
									Patent
STATIC MAGNETIC FIELD + OSCILLATING MAGNETIC FIELD	1.5-2	20, 30, and 40	Commercial freezer designed by ABI Co., Ltd.	Chicken breasts	-	Longer plateau	freezing	No effect on drip and cooking losses Softer texture after 6 months of frozen storage	Yamamoto, et al. [198]
									Research paper
	1 $\pm$ 0.6	50	Patented by ABI Co., Ltd.	Chicken tuna and	-	Time for lowering the core temperature from 0 °C to -20 °C was 20-50% reduced	-	Cells were hardly destroyed. Color, flavor, and taste similar to those of the original raw food	Owada [41]
									Patent
	20 $\pm$ 0.12	1·10 ⁶	Lab prototype	Tuna and agar gel	No effect	No effect	No effect	No effect	Suzuki and others [336]; Watanabe and others [337]
									Research papers

	n.r.	n.r.	Commercial freezer designed by ABI Co., Ltd.	Beef (loin and round), pork (belly and ham), and chicken (breast and leg)	-	Shorter total freezing time	-	Effects on drip and cooking losses, water holding capacity, and composition depend on the product	Kim, et al. [165] Research paper
	n.r.	n.r.	Commercial freezer designed by ABI Co., Ltd.	Beef (loin and round)	-	-	-	Lower drip losses Larger water holding capacity. No effect on sensory evaluation	Kim, et al. [166] Research paper
	n.r.	n.r.	Commercial freezer designed by ABI Co., Ltd.	Pork (belly and ham)	-	-	-	Effects on drip and cooking losses, water holding capacity, and moisture content depend on the pork cut. No effect on sensory evaluation	Ku, et al. [167] Research paper
	0.098 0.155 0.418	≤ 50	Commercial freezer designed by ABI Co., Ltd.	Garlic bulbs	No effect	-	-	-	James, et al. [45] Research paper
	n.r.	n.r.	Commercial freezer designed by ABI Co., Ltd.	Beef (loin and round)	-	-	Smaller	Larger water holding capacity Better overall acceptability after sensory evaluation. Better flavor and taste	Choi, et al. [164] Research paper

	0.1-0.32	n.r.	Commercial freezer designed by ABI Co., Ltd.	Atlantic Cod	No effect	No effect	Smaller thickness of extracellular spaces	No effect on external appearance. No detected effect although the authors admit that effects cannot be excluded	[44] Research paper
	0, 0.46, 0.9, 1.8, 3.6, and 7.2	50	Lab prototype	Carrot	Increased	Delay of the phase change time. Shorter freezing plateau.	Smaller and more flocculent		[54] Research paper
	< 0.4	≤ 50	Commercial freezer designed by ABI Co., Ltd	Apple and potato	Unsure effect		Unsure effect	Unsure effect	[52] Research paper
OSCILLATING MAGNETIC FIELD + ELECTRIC FIELD	0.5	50	Patented by ABI Co., Ltd.	Chicken and tuna	-	Time for lowering the core temperature from 0 °C to -20 °C was 50% or more reduced	-	Cells were not ruptured. Color, flavor, and taste are the same as the original raw food	Owada [41] Patent
	50-100	1 Hz (only during 0.2 duty cycle EF) *EF:20 kHz. Three consecutive pulses: 300 s (duty cycle 0.8) 120 s (duty cycle 0.5) 90 s (duty cycle 0.2)	Lab prototype	Chicken breast	At -6.5 °C remains unfrozen		Microstructure maintains the original aspect	Drip loss, pH, color and texture maintain the original qualities	[55] paper

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STATIC MF + OSCILLATING MF + ELECTRIC FIELD	10 ± 0.5	50	Patented by ABI Co., Ltd.	Tuna, sardine, pork, juices, - wines, oranges, cakes	No effect on precooling time Shorter freezing - plateau Shorter total freezing time	Lower drip losses, color and odor changes, and microbial counts No phase separations	Owada and Kurita [159] Patent
	*EF: 600 kV/m	*EF: n.r.					
	1 ± 0.5	50	Patented by ABI Co., Ltd.	Chicken and - tuna	Time for lowering the core temperature from 0 °C to -20 °C - was 50% or more reduced	Cells were not ruptured Color, flavor, and taste are the same as the original raw food	Owada [41] Patent
	*EF: 15 kV/m	*EF: 50 Hz-5 MHz					
	1 ± 0.5	50	Patented by ABI Co., Ltd.	Mackerel and - lobster	-	Improved microstructure after thawing	Owada and Saito [154] Patent
	*EF: 100-1000 kV/m	*EF: n. r.					

Table 10-1: Experimental data about the effects of magnetic fields on freezing of food products. -: not studied; n.r.: not reported; *EF: electric field

11. Appendix A.4 Scientific works on magnetic freezing of water and model foods

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FIELD APPLIED	INTENSITY (mT)	FREQUENCY (Hz)	DEVICE	SAMPLE	EFFECTS OF THE FIELDS APPLIED			AUTHOR/ DOCUMENT
					ΔT	FREEZING KINETICS	ICE CRYSTAL	
STATIC MAGNETIC FIELD	100-5000		Lab prototype	2.8-14.9% NaCl	-	-	Effects on ice nucleation, but not on crystal growth	Rohatgi, et al. [338] Research paper
	Up to $23 \cdot 10^3$		Lab prototype	Water globules	-	-	Levitating	Tagami, et al. [79] Research paper
	71-505		Lab prototype	Drops of distilled water	Lower	Shorter precooling time Longer freezing plateau No effect on total freezing time	-	[76] Research paper
	Up to 5.95		Lab prototype	Tap water	Larger	Longer precooling time Longer total freezing time	-	Zhou, et al. [339] Research paper
	480 Unidirectional field forces		Lab prototype	0.9% NaCl	-	Longer freezing plateau	Irregular shapes dependent on the direction of the field forces	Mok, et al. [78] Research paper
	50 Outward field forces		Lab prototype	0.9% NaCl	-	Shorter plateau freezing	Irregular shapes dependent on the direction of the field forces	Mok, et al. [78] Research paper

	< 50		Lab prototype	Deionized water 0.9% NaCl solution 5% ethylene glycol	No effect on deionized water Larger in 0.9% NaCl solution Lower in 5% ethylene glycol	No effect on deionized water and 5% ethylene glycol Shorter freezing plateau in 0.9% NaCl solution		[77] Research paper
OSCILLATING MAGNETIC FIELD	Up to 600	60	Lab prototype	2.8-14.9% NaCl	-	-	Effects on ice nucleation, but not on crystal growth	Rohatgi, et al. [338] Research paper
	Up to 0.88	10 ⁻² -200	Lab prototype	Bidistilled water	Larger	-	-	Semikhina and Kiselev [80] Research paper
	0.5-10	50	Lab prototype	Pure water and 1-mol/kg NaCl aqueous solution	No effect	-	-	Watanabe, et al. [337] Research paper
	0.12 ± 0.02	50-2·10 ⁵	Lab prototype	Physiological saline solution	Larger at frequencies of 200 Hz and higher No effect at 50 Hz	-	-	Mihara, et al. [73] Patent Niino, et al. [81] Research paper
	0.5	30	Lab prototype	Distilled and saline water	No effect	No effect	-	Naito, et al. [82] Research paper
PULSED MAGNETIC FIELD	6.5 (325 T/s) 3 (150 T/s)	10 18	ABI Co. Ltd	D-MEM culture medium 0.1 M NaCl	-	-	Enhanced movement of ice crystals: more uniform crystals. Effects on light transmission	Iwasaka, et al. [84] Research paper

Table 11-1: Experimental data about the effects of magnetic fields on freezing of water and aqueous solutions. -: not studied

12.Appendix A.5 Scientific works on magnetic freezing of biomaterials

FIELDS APPLIED	INTENSITY (mT)	FREQUENCY (Hz)	DEVICE	SAMPLE	CONTROL COMPARISONS	FOR	EFFECTS OF THE FIELDS APPLIED	AUTHORS
STATIC MAGNETIC FIELD	200 400		Lab prototype	Human erythrocytes	Samples frozen in the same device with no MF application		Higher survival rate No effects on cell morphology or function Reduced membrane fluidity at 400 mT	Lin, et al. [86]
	400 800		Lab prototype	Human erythrocytes	Samples frozen in the same device with no MF application		Higher survival rate No effects on cell morphology and metabolite levels Reduced membrane fluidity	Lin, et al. [87]
	400 800		Lab prototype	Human dental pulp stem cells	Samples frozen in the same device with no MF application		Higher survival rate	Lin, et al. [88]
	300	n.r.	n.r.	Entire ovaries porcine	Samples frozen in the same device with no MF application		More primordial follicles remained intact after thawing	[340]
OSCILLATING MAGNETIC FIELD	n.r.	n.r.	ABI Ltd. Co.	Entire ovaries of cynomolgus monkeys	No controls All samples are exposed to MFs during freezing		After frozen-thawed ovarian autotransplantation, 4 of the 5 monkeys recovered their ovarian functions with hormone production and the menstrual cycle	[168]
	0.1-0.2	n.r.	ABI Ltd. Co.	One entire rat	One rat frozen in an ultracold freezer at -80 °C		Magnetic freezing reduced tissue breakdown, especially in the brain, pancreas, small intestine, and ovary	Mihara, et al. [170]
	0.1-0.2	n.r.	ABI Ltd. Co.	Mouse testes	Mouse testes frozen in an ultracold freezer at -80 °C		Magnetic freezing reduced tissue destruction	Samanpachin, et al. [171]

	n.r.	n.r.	ABI Ltd.	Co.	Entire ovaries of cynomolgus monkeys and rabbits	No controls All samples are exposed to MFs	Cell structure of frozen ovaries well preserved Viable oocytes immediately after thawing	Kyono, et al. [169]
	0-0.15 ^a	60 ^a	ABI Ltd.	Co.	Human PDL cells	No controls All samples are exposed to MFs	Survival rate: Up to 96% depending on the MF strength and freezing temperature	Kawata, et al. [341]
	0.005,0.1 ^a , 0.15	60 ^a	ABI Ltd.	Co.	Human PDL cells	Cells frozen in the same freezer with no MF application	Higher survival rate immediately after thawing Higher cell viability after 48 h	Kaku, et al. [89]
	0.1 ^a	60 ^a	ABI Ltd	Co.	Human teeth	Teeth frozen in the same freezer with no MF application Fresh teeth Dried teeth	PDL cells from magnetically frozen teeth could proliferate as much as those from fresh teeth. In conventionally frozen tooth, cells did not appear	Kaku and others [89]
	n.r.	n.r.	ABI Ltd	Co.	Human premolars	Nonfrozen premolars	After culture for 5 generations, no significant difference in cell viability between DPSCs isolated from magnetically frozen teeth and those from fresh teeth No differences in morphology, expression of stem cell markers, or osteogenic and adipogenic differentiations	Lee, et al. [342]
	0.1 ^a	60 ^a	ABI Ltd	Co.	Human PDL cells	Noncryopreserved cells	No difference between the expression of collagen type I messenger RNA in magnetically and non-frozen cells The expression of alkaline phosphatase messenger RNA was slightly decreased after magnetic freezing	Kamada, et al. [90]
	0.1 ^a	60 ^a	ABI Ltd	Co.	Rat incisors	Freshly extracted incisors Dried incisors	No progressive root resorption in the teeth that were replanted immediately (fresh incisors) or cryopreserved Widespread root resorption and ankylosis in the dried teeth	Kamada and others [90]

	0.1 ^a	60 ^a	ABI Ltd	Co.	Human teeth	Freshly extracted teeth	Magnetic freezing did not affect the growth rate and characteristics of PDL cells Proper PDL regeneration and appropriate apexogenesis after transplanting magnetically frozen teeth	Abedini, et al. [91]
	0.01	n.r.	ABI Ltd	Co.	Rat teeth Dental pulp tissue	Rat teeth and dental pulp tissue frozen in an isopropanol-jacketed freezing container at -80 °C	Lower concentration of cryoprotectant and shorter pre-equilibration time are required for magnetic freezing Fewer cracks in magnetically frozen samples	[343]
	0.01	n.r.	ABI Ltd	Co.	Human DPSCs	Non-frozen cells Cells frozen in an isopropanol-jacketed freezing container at -80 °C	Lower concentration of cryoprotectant is required for magnetic freezing Larger cell viability, proliferation rate, expression of some stem cell markers, and induced osteogenic differentiation and more viable adherent cells after magnetic freezing	[344]
	0.1-0.2	Broad frequency component	ABI Ltd	Co.	3-5 mm sections from mouse brain and rat brain and pancreas	Samples frozen in an ultracold freezer at -80 °C	Lower damage in magnetically frozen samples	Nakagawa, et al. [318]
	1.2 ± 0.2	2000	Lab prototype		Portions of swine ovaries and liver	Samples frozen in the same device with no MF application	No effect of MFs on ovarian tissue destruction MFs improved liver cryopreservation	Niino and others [81]
	0.5	30	Lab prototype		Drosophila flies	Flies maintained in the same device with no magnetic field application	Higher survival when MFs were applied	Naito, et al. [82]
	0.1	60	ABI Ltd	Co.	Human embryonic stem cells	Cells frozen in an isopropanol-jacketed freezing container at -80 °C	Higher attachment efficiency after magnetic freezing Magnetically frozen cells can be subcultured while expressing pluripotent markers, differentiate into 3 germ layers, and maintain a normal karyotype	Lin, et al. [92]

	0.005, 0.2	0.1, n.r.	ABI Ltd	Co.	Mouse osteoblasts	Osteoblasts frozen in the same device at 0 mT	Larger cell survival and proliferation rate after magnetic freezing at 0.1 mT	[345]
	0.1	n.r.	ABI Ltd	Co.	Mouse osteoblasts	Nonfrozen osteoblasts	No significant difference in alkaline phosphatase, osteopontin, bone sialoprotein mRNA and protein expression between magnetically frozen and control cells	[345]
	0.005, 0.2	0.1, n.r.	ABI Ltd	Co.	Rat mesenchymal stem cells	Cells frozen in the same device at 0 mT	Larger cell survival and proliferation rate after magnetic freezing at 0.1 mT	[346]
	0.1	n.r.	ABI Ltd	Co.	Rat mesenchymal stem cells	Nonfrozen cells and cells frozen in a conventional programmed freezer	The ability of adipogenic and osteogenic differentiation is better preserved after magnetic freezing	[346]
	0.1	n.r.	ABI Ltd	Co.	Rat parietal bones	Nonfrozen bones and bones frozen with no MF	Larger osteoblast survival and proliferation rate after magnetic freezing	[347]
	0.1	n.r.	ABI Ltd	Co.	Rat parietal bones	Nonfrozen bones and dried bones	New bone formation after transplantation when magnetically frozen and nonfrozen bones were used	[347]

	0.1-0.8	n.r.	ABI Ltd	Co.	Subseafloor sediments <i>Escherichia coli</i> cells	Samples preserved at 4, -20, -80, and -196 °C	conventionally frozen samples	Larger microbial counts in magnetically frozen samples	Morono, et al. [348]
	0.1	n.r.	ABI Ltd	Co.	Rat mesenchymal stem cells	Cells conventionally frozen at -150 °C		Larger cell survival and proliferation rate after magnetic freezing	[346]
	0.1	n.r.	ABI Ltd	Co.	Rat mesenchymal stem cells	Nonfrozen cells and cells conventionally frozen at -150 °C		Better bone regeneration after transplantation when nonfrozen and magnetically frozen cells were used	[346]

Table 12-1: Experimental data about the effects of magnetic fields on cryopreservation of cells, tissues, organs, and organisms. n.r.: not reported; PDL: periodontal ligament; DPSCs: dental pulp stem cells; ^a: data provided in [85]

13.Appendix A.6 Source code for the PWM control algorithm intended for operation of the inverter in the lower frequency range

[Escriba el título del documento]

Main_3.c

```
1
2
3 #include "Lab.h" // Main include file
4 #include "DSP2802x_Device.h" // Peripheral address definitions
5 #include <math.h>
6 #include <stdbool.h>
7
8                                     // #include
9 <C:\ti\controlSUITE\libs\math\FPUfastRTS\V100\include\C28x_FPU_FastRTS
10 .h>
11 // Control Variables
12 #define Ma 0.8 // Modulo de amplitud
13 #define PI 3.1415926536
14 // CHANGE
15 THIS //
16 //-----
17 -----//
18 //-----
19 -----//
20 #define Fo 200 // frecuencia de salida [Hz]
21 #define Mf 100 // Modulo de frecuencia
22
23 float triangular[36]; // 2Hz -> 168; 20Hz -> 28; 100Hz -> 20; 200Hz -
24 >36
25 //-----
26 -----//
27 //-----
28 -----//
29
30 //--- Global Variables
31 Uint16 AdcBuf[ADC_BUF_LEN]; // ADC buffer allocation
32 Uint16 DEBUG_TOGGLE = 1; // Used for realtime mode investigation
33 test
34
35 Uint16 N=1; // multiplica la resolución de la triangular
36 Uint16 preescalado=1; // preescalado del ePWM
37 Uint16 freq_PLL=10; // Frecuencia PLL
38
39 float DeltaT=0; //
40 float C_DeltaT=0; // cos(DeltaT)
41 float S_DeltaT=0; // sin(DeltaT)
42 float C_Ant=Ma; // Anterior valor de Cos en algoritmo recursivo
43 (valor
44 inicial Cos(0)=1)
45 float S_Ant=0; // Anterior valor de Sin en algoritmo recursivo
46 (valor
47 inicial Sin(0)=0)
48 float AuxS=0;
49 float AuxC=0;
50
51 float Salto=0;
```

```
43 float T_Ant=0; //Anterior valor de Triangular en algoritmo
recursivo
(Valor inicial 0)
44
45
46 bool Salida1=0;
47 bool Salida2=0;
48
49 int i=0;
50 int flag=0;
51
52 void InitPLL(Uint16 conf_frec){
53
54 Uint16 aux_DIVSEL=0;
55 Uint16 aux_DIV=0;
56
57 asm(" EALLOW"); // Enable EALLOW protected register access
58
59
60 /*
61 switch (conf_frec){
62
63 //completar frecuencias
64
65 case 60:
66 aux_DIVSEL=3;
67 aux_DIV=6;
68 break;
69 case 80:
70 aux_DIVSEL=3;
71 aux_DIV=8;
72 break;
73 case 100:
74 aux_DIVSEL=3;
75 aux_DIV=10;
76 break;
77 case 140:
78 aux_DIVSEL=3;
79 aux_DIV=14;
80 break;
81 case 170:
82 aux_DIVSEL=3;
83 aux_DIV=17;
84 break;
85 case 180:
86 aux_DIVSEL=3;
87 aux_DIV=18;
88 break;
89
90
91 //mientras solo utilice DIVSEL=3
92
93
94 }*/
95
96 aux_DIVSEL=3;
97 aux_DIV=conf_frec/10;
98
99 if (SysCtrlRegs.PLLSTS.bit.MCLKSTS != 1)
100 { // PLL is not running in
limp mode
```

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```
101 SysCtrlRegs.PLLSTS.bit.MCLKOFF = 1; // Turn off missing
clock detect before changing PLLCR
102 SysCtrlRegs.PLLSTS.bit.DIVSEL = 0; // DIVSEL must be 0 or 1
(/4 CLKIN mode) before changing PLLCR
103 SysCtrlRegs.PLLCR.bit.DIV = 0x5; // PLLx5/4 (because
DIVSEL is /4)
104
105 // Wait for PLL to lock.
106 // During this time the CPU will run at OSCCLK/4 until the PLL is
stable.
107 // Once the PLL is stable the CPU will automatically switch to the
new
PLL value.
108 // Code is not required to sit and wait for the PLL to lock.
However,
109 // if the code does anything that is timing critical (e.g.
something that
110 // relies on the CPU clock frequency to be at speed), then it is
best to
wait
111 // until PLL lock is complete. The watchdog should be disabled
before
this loop
112 // (e.g., as was done above), or fed within the loop.
113 while(SysCtrlRegs.PLLSTS.bit.PLLLOCKS != 1) // Wait for PLLLOCKS
bit
to set
114 {
115 SysCtrlRegs.WDKEY = 0x0055; // Service the watchdog
while waiting
116 SysCtrlRegs.WDKEY = 0x00AA; // in case the user
enabled it.
117 }
118
119 SysCtrlRegs.PLLCR.bit.DIV = aux_DIV;
120 SysCtrlRegs.PLLSTS.bit.DIVSEL = aux_DIVSEL;
121 }
122 else
123 { // PLL is running in
limp mode
124 // User should replace the below with a call to an appropriate
function,
125 // for example shutdown the system (since something is very
wrong!).
126 asm(" ESTOP0");
127 }
128
129 asm(" EDIS"); // Disable EALLOW protected register access
130
131 //--- Enable global interrupts
132 asm(" CLRC INTM, DBGM");
133 // Enable global interrupts and realtime debug
134 }
135
136
137
138
139
/*****
*
140 * Function: main()
```

```
141 *
142 * Description: Main function for C28x workshop labs
143
144 *****
145 /
146 void main(void) {
147
148
149
150 //--- CPU Initialization
151 InitSysCtrl(); // Initialize the CPU (FILE: SysCtrl.c)
152 InitGpio(); // Initialize the shared GPIO pins (FILE: Gpio.c)
153 InitPieCtrl(); // Initialize and enable the PIE (FILE: PieCtrl.c)
154 InitWatchdog(); // Initialize the Watchdog Timer (FILE:
WatchDog.c)
155
156 //--- Peripheral Initialization
157 InitAdc(); // Initialize the ADC (FILE: Adc.c)
158
159
160 //calcular_parametros();
161
162 switch (Fo){
163 case 1:
164     preescalado=1792;
165     frec_PLL=60;
166     N=84;
167     break;
168
169 case 2:
170     preescalado=1792;
171     frec_PLL=60;
172     N=42;
173     break;
174
175 case 5:
176     preescalado=1792;
177     frec_PLL=140;
178     N=39;
179     break;
180
181 case 10:
182     preescalado=1792;
183     frec_PLL=100;
184     N=14;
185     break;
186
187 case 20:
188     preescalado=1792;
189     frec_PLL=100;
190     N=7;
191     break;
192
193 case 50:
194     preescalado=640;
195     frec_PLL=180;
196     N=14;
197     break;
198
```

```
199 case 100:
200   preescalado=640;
201   frec_PLL=180;
202   N=7;
203   break;
204
205 case 200:
206   preescalado=320;
207   frec_PLL=180;
208   N=7;
209   break;
210
211 case 500:
212   preescalado=256;
213   frec_PLL=150;
214   N=4;
215   break;
216
217 case 1000:
218   preescalado=320;
219   frec_PLL=180;
220   N=4;
221   break;
222
223 case 2000:
224   preescalado=256;
225   frec_PLL=180;
226   N=6;
227   break;
228
229 }
230
231
232
233 DeltaT=2*PI/(4*Mf*N);
234 Salto=1.0/N;
235
236 C_DeltaT=cos(DeltaT);
237 S_DeltaT=sin(DeltaT);
238
239 triangular[0]=0;
240 for (i=1;i<=N;i++) triangular[i]=triangular[i-1]+Salto;
241 for (i=N+1;i<=3*N;i++) triangular[i]=triangular[i-1]-Salto;
242 for (i=3*N+1;i<4*N;i++) triangular[i]=triangular[i-1]+Salto;
243 i=0;
244
245
246 i=0;
247 InitEPwm(4*Mf*N,preescalado,frec_PLL); // Initialize the EPwm
(FILE: EPwm.c)
248 InitPLL(frec_PLL);
249
250
251 //--- Enable global interrupts
252 // asm(" CLRC INTM, DBGm");
253 // Enable global interrupts and realtime debug
254
255 //--- Main Loop
256 while (1) // endless loop - wait for an interrupt
257 {
258   asm(" NOP");
```



```
259 }
260
261 } //end of main()
262
263
264 interrupt void EPWM1_INT_ISR(void) // PIE3.1 @ 0x000D60 EPWM1_INT
(EPWM1)
265 {
266
267 PieCtrlRegs.PIEACK.all = PIEACK_GROUP3; // Must acknowledge the
PIE group
268
269 //-----medir tiempos-----//
270 /*
271 EPwm3Regs.TBCTL.bit.CTRMODE = 0x3; // Disable the timer
272 EPwm3Regs.TBCTR = 0x0000; // Clear timer counter
273 EPwm3Regs.TBCTL.bit.CLKDIV=0;
274 EPwm3Regs.TBCTL.bit.HSPCLKDIV = 0;
275 EPwm3Regs.TBPRD=0xFFFF;
276 EPwm3Regs.TBCTL.bit.CTRMODE = 0x0; // Enable the timer in count up
mode
277 */
278
279 //-----subrutina de interrupción-----//
280
281 //poner salidas ciclo anterior
282 if(Salida1) EPwm1Regs.AQCSFRC.bit.CSFA=10; else
EPwm1Regs.AQCSFRC.bit.CSFA=01;
283 if(Salida2) EPwm2Regs.AQCSFRC.bit.CSFA=10; else
EPwm2Regs.AQCSFRC.bit.CSFA=01;
284
285 // EPwm1Regs.AQCSFRC.bit.CSFA=01; //force continuous low
286 // EPwm1Regs.AQCSFRC.bit.CSFA=10; //force continuous high
287
288 //actualizar variables
289 i++;
290
291 if(i==4*N)i=0;
292
293 if(EPwm1Regs.TBCTR==EPwm1Regs.TBPRD) //una vez por ciclo reiniciar
parámetros para
evitar error acumulado
294 {
295 EPwm1Regs.CMPA.half.CMPA = 0;
296 C_Ant=Ma;
297 S_Ant=0;
298 T_Ant=0;
299 }
300 else
301 {
302 EPwm1Regs.CMPA.half.CMPA++;
303
304 AuxS=(S_Ant*C_DeltaT+C_Ant*S_DeltaT);
305 C_Ant=(C_Ant*C_DeltaT-S_Ant*S_DeltaT);
306 S_Ant=AuxS;
307
308 }
309
310
311
312 if(S_Ant<triangular[i]) Salida1=1; else Salida1=0;
```

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```
313 if(-S_Ant<triangular[i]) Salida2=1; else Salida2=0;
314
315
316
317 //-----end subrutina de interrupción-----//
318
319 //medir tiempos
320 //EPwm3Regs.TBCTL.bit.CTRMODE = 0x3; // Disable the timer
321 //EPwm1Regs.ETSEL.bit.INTEN = 0; //disable ePWM interrupt
322
323 //clear flags
324 EPwm1Regs.ETCLR.bit.INT=1;
325 PieCtrlRegs.PIEACK.bit.ACK3=1;
326
327 }
328
329          /**          end          of          file
*****/
330
```

EPwm.c

```
1
2 #include "DSP2802x_Device.h" // Peripheral address definitions
3 #include "Lab.h" // Main include file
4
5
6 #define DELAY 2
//-----|AJUSTAR!!!!!!-----//
7
8
/*****
*
9 * Function: InitEPwm()
10 *
11 * Description: Initializes the Enhanced PWM modules on the F2802x
12
*****
/
13
14 void InitEPwm(Uint16 CuentaMax, Uint16 preescalado, Uint16
frec_PLL)
15 {
16
17 asm(" EALLOW"); // Enable EALLOW protected register access
18 SysCtrlRegs.PCLKCR0.bit.TBCLKSYNC = 0;
19 asm(" EDIS"); // Disable EALLOW protected register access
20
21 //enable EPWM1 y 2
22 GpioCtrlRegs.GPAMUX1.bit.GPIO0 = 1; // 0=GPIO 1=EPWM1A
2=rsvd 3=rsvd (used in Lab 3)
23 GpioCtrlRegs.GPAMUX1.bit.GPIO1 = 1; // 0=GPIO 1=EPWM1B
2=rsvd 3=COMPL0UT
24 GpioCtrlRegs.GPAMUX1.bit.GPIO2 = 1; // 0=GPIO 1=EPWM2A
2=rsvd 3=rsvd
25 GpioCtrlRegs.GPAMUX1.bit.GPIO3 = 1; // 0=GPIO 1=EPWM2B
```

```
2=rsvd 3=COMP2OUT
26
27
28
29
30 //-----
31 //--- Configure ePWM1 PWM on EPWM1A pin
32 //-----
33
34 //-----
35 //--- Must disable the clock to the ePWM modules if you
36 //--- want all ePMW modules synchronized.
37 //-----
38 EPwm1Regs.TBCTL.bit.CTRMODE = 0x3; // Disable the timer
39 EPwm1Regs.TBCTR = 0x0000; // Clear timer counter
40
41
42 //-----//
43 //configuration Time-Base Control Register//
44 //-----//
45
46 EPwm1Regs.TBCTL.all = 0xC033; //Muchos de estos valores serán
modificados posteriormente.
47 // bit 15-14 11: FREE/SOFT, 11 = ignore emulation suspend
48 // bit 13 0: PHSDIR, 0 = count down after sync event
49 // bit 12-10 000: CLKDIV, 000 => TBCLK = HSPCLK/1
50 // bit 9-7 000: HSPCLKDIV, 000 => HSPCLK = SYSCLKOUT/1
51 // bit 6 0: SWFSYNC, 0 = no software sync produced
52 // bit 5-4 11: SYNCOSSEL, 11 = sync-out disabled
53 // bit 3 0: PRDL, 0 = reload PRD on counter=0
54 // bit 2 0: PHSEN, 0 = phase control disabled
55 // bit 1-0 11: CTRMODE, 11 = timer stopped (disabled)
56
57
58 EPwm1Regs.TBPRD = CuentaMax; // Set timer period
59
60
61
62 EPwm1Regs.CMPCTL.all = 0x0002; // Compare control register
63 // bit 15-10 0's: reserved
64 // bit 9 0: SHDWBFULL, read-only
65 // bit 8 0: SHDWAFULL, read-only
66 // bit 7 0: reserved
67 // bit 6 0: SHDWBMODE, don't care
68 // bit 5 0: reserved
69 // bit 4 0: SHDWAMODE, 0 = shadow mode
70 // bit 3-2 00: LOADBMODE, don't care
71 // bit 1-0 10: LOADAMODE, 10 = load on zero or PRD match
72
73
74 EPwm1Regs.CMPCTL.bit.SHDWAMODE=1; //disable shadow mode.
75
76
77 //-----//
78 //Action-qualifier control register A//
79 //-----//
80 EPwm1Regs.CMPA.half.CMPA = 1; //Set CMPA
```

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```
81 EPwm1Regs.AQCTLA.bit.CAU=01; //Action when the counter equals
the active CMPA register and the counter is incrementing. Clear
82 EPwm1Regs.AQCTLA.bit.ZRO=10; //Action when counter equals
zero. Set
83 // EPwm1Regs.AQCTLA.bit.PRD=01; //Action when counter equals
TBPRD. Set
84
85
86 //-----//
87 //-----Software forced events-----//
88 //-----//
89
90 EPwm1Regs.AQSFRC.bit.RLDCSF=11; //immediate mode
91
92 // EPwm1Regs.AQCSFRC.bit.CSFA=01; //force continuous low
93 // EPwm1Regs.AQCSFRC.bit.CSFA=10; //force continuous high
94
95 //-----//
96 // Sincronización con otros PWM //
97 //-----//
98
99 EPwm1Regs.TBCTL.bit.PHSEN=0; //disable
100 // EPwm1Regs.TBPHS.half.TBPHS = 0x0000; // Set timer phase
101 // EPwm1Regs.TBCTL.bit.PHSEN=0; //MASTER
102 // EPwm1Regs.TBCTL.bit.SYNCOSEL=1; //select CTR=ZERO as source of
EPWMxSYNCO signal
103
104 //-----//
105 // Interrupciones //
106 //-----//
107
108 // EPwm1Regs.ETSEL.bit.INTEN = 0; //disable ePWM interrupt
109
110 PieCtrlRegs.PIEIER3.bit.INTx1=1; //enable PIE
111 IER |= 0x0004; //enable IER
112
113 EPwm1Regs.ETPS.bit.INTPRD=1; //N° events required= 1
114 EPwm1Regs.ETSEL.bit.INTEN = 1; //enable ePWM interrupt
115 EPwm1Regs.ETSEL.bit.INTSEL=100; //interrupt event = CMPA
incrementing
116 // EPwm1Regs.ETSEL.bit.INTSEL=101; //interrupt event = CMPA
decrementing
117
118 // EPwm1Regs.ETPS.bit.INTCNT=01; //read N° events
119
120
121
122 //-----//
123 // DEAD_BAND CONFIGURATION //
124 //-----//
125
126 // EPwm1Regs.DBCTL.bit.OUT_MODE = 0; // Deadband disabled
127 EPwm1Regs.DBCTL.bit.HALFCYCLE=0; //half-cytle disabled
128 EPwm1Regs.DBCTL.bit.IN_MODE=00; //source EPWM1A
129 EPwm1Regs.DBCTL.bit.POLSEL=10; //
130 EPwm1Regs.DBCTL.bit.OUT_MODE=11; //ACTIVE HIGH COMPLEMENTARY
131 EPwm1Regs.DBRED=frec_PLL*DELAY/preescalado;
132 EPwm1Regs.DBFED=frec_PLL*DELAY/preescalado;
133
134
135
```

```
136 EPwm1Regs.PCCTL.bit.CHPEN = 0; // PWM chopper unit disabled
137 EPwm1Regs.TZCTL.bit.TZA = 0x3; // Trip action disabled for output
A
138
139
140 //-----//
141 //--- Configure ePWM2---//
142 //-----//
143
144
145 EPwm2Regs.TBCTL.bit.CTRMODE = 0x3; // Disable the timer
146 EPwm2Regs.TBCTR = 0x0000; // Clear timer counter
147
148
149 //-----//
150 //configuration Time-Base Control Register//
151 //-----//
152
153 EPwm2Regs.TBCTL.all = 0xC033; //Muchos de estos valores serán
modificados posteriormente.
154 // bit 15-14 11: FREE/SOFT, 11 = ignore emulation suspend
155 // bit 13 0: PHSDIR, 0 = count down after sync event
156 // bit 12-10 000: CLKDIV, 000 => TBCLK = HSPCLK/1
157 // bit 9-7 000: HSPCLKDIV, 000 => HSPCLK = SYSCLKOUT/1
158 // bit 6 0: SWFSYNC, 0 = no software sync produced
159 // bit 5-4 11: SYNCOSSEL, 11 = sync-out disabled
160 // bit 3 0: PRDL, 0 = reload PRD on counter=0
161 // bit 2 0: PHSEN, 0 = phase control disabled
162 // bit 1-0 11: CTRMODE, 11 = timer stopped (disabled)
163
164
165 EPwm2Regs.TBPRD = CuentaMax; // Set timer period
166
167
168
169 EPwm2Regs.CMPCTL.all = 0x0002; // Compare control register
170 // bit 15-10 0's: reserved
171 // bit 9 0: SHDWBFULL, read-only
172 // bit 8 0: SHDWAFULL, read-only
173 // bit 7 0: reserved
174 // bit 6 0: SHDWBMODE, don't care
175 // bit 5 0: reserved
176 // bit 4 0: SHDWAMODE, 0 = shadow mode
177 // bit 3-2 00: LOADBMODE, don't care
178 // bit 1-0 10: LOADAMODE, 10 = load on zero or PRD match
179
180
181 EPwm2Regs.CMPCTL.bit.SHDWAMODE=1; //disable shadow mode.
182
183
184 //-----//
185 //Action-qualifier control register A//
186 //-----//
187 EPwm2Regs.CMPA.half.CMPA = 1; //Set CMPA
188 EPwm2Regs.AQCTLA.bit.CAU=01; //Action when the counter equals
the active CMPA register and the counter is incrementing. Clear
189 EPwm2Regs.AQCTLA.bit.ZRO=10; //Action when counter equals
zero. Set
190 // EPwm2Regs.AQCTLA.bit.PR=01; //Action when counter equals
TBPRD. Set
191
```

```
192
193 //-----//
194 //-----Software forced events-----//
195 //-----//
196
197 EPwm2Regs.AQSFRC.bit.RLDCSF=11; //immediate mode
198
199 // EPwm2Regs.AQCSFRC.bit.CSFA=01; //force continuous low
200 // EPwm2Regs.AQCSFRC.bit.CSFA=10; //force continuous high
201
202 //-----//
203 // Sincronización con otros PWM //
204 //-----//
205
206 EPwm2Regs.TBCTL.bit.PHSEN=0; //disable
207 // EPwm2Regs.TBPHS.half.TBPHS = 0x0000; // Set timer phase
208 // EPwm2Regs.TBCTL.bit.PHSEN=0; //MASTER
209 // EPwm2Regs.TBCTL.bit.SYNCOSEL=1; //select CTR=ZERO as source of
EPWMxSYNCO signal
210
211 //-----//
212 // Interrupciones //
213 //-----//
214
215 EPwm2Regs.ETSEL.bit.INTEN = 0; //disable ePWM interrupt
216 /*
217 PieCtrlRegs.PIEIER3.bit.INTx1=1; //enable PIE
218 IER |= 0x0004; //enable IER
219
220 EPwm2Regs.ETPS.bit.INTPRD=1; //N° events required= 1
221 EPwm2Regs.ETSEL.bit.INTEN = 1; //enable ePWM interrupt
222 EPwm2Regs.ETSEL.bit.INTSEL=100; //interrupt event = CMPA
incrementing
223 // EPwm2Regs.ETSEL.bit.INTSEL=101; //interrupt event = CMPA
decrementing
224
225 // EPwm2Regs.ETPS.bit.INTCNT=01; //read N° events
226 */
227
228
229 //-----//
230 // DEAD_BAND CONFIGURATION //
231 //-----//
232
233 // EPwm2Regs.DBCTL.bit.OUT_MODE = 0; // Deadband disabled
234 EPwm2Regs.DBCTL.bit.HALFCYCLE=0; //half-cytle disabled
235 EPwm2Regs.DBCTL.bit.IN_MODE=00; //source EPWM1A
236 EPwm2Regs.DBCTL.bit.POLSEL=10; //
237 EPwm2Regs.DBCTL.bit.OUT_MODE=11; //ACTIVE HIGH COMPLEMENTARY
238 EPwm2Regs.DBRED=frec_PLL*DELAY/preescalado;
239 EPwm2Regs.DBFED=frec_PLL*DELAY/preescalado;
240
241
242
243 EPwm2Regs.PCCTL.bit.CHPEN = 0; // PWM chopper unit disabled
244 EPwm2Regs.TZCTL.bit.TZA = 0x3; // Trip action disabled for output
A
245
246 /*
247 //-----//
248 //--- Configure ePWM4---//
```

```
249 //-----//
250
251 EPwm4Regs.TBCTL.bit.CTRMODE = 0x3; // Disable the timer
252 EPwm4Regs.TBCTR = 0x0000; // Clear timer counter
253
254 EPwm4Regs.TBCTL.all = 0xC033;
255
256 EPwm4Regs.TBPRD = CuentaMax; // Set timer period
257
258 EPwm4Regs.CMPCTL.all = 0x0002; // Compare control register
259
260 //-----//
261 // Sincronización con otros PWM //
262 //-----//
263
264 EPwm4Regs.TBCTL.bit.PHSEN=0; //disable
265 // EPwm4Regs.TBPHS.half.TBPHS = 0x0000; // Set timer phase
266 // EPwm4Regs.TBCTL.bit.PHSEN=0; //MASTER
267 // EPwm4Regs.TBCTL.bit.SYNCOSEL=1; //select CTR=ZERO as source of
EPWMxSYNCO signal
268
269 //-----//
270 // Interrupciones //
271 //-----//
272
273 EPwm4Regs.ETSEL.bit.INTEN = 0; //disable ePWM interrupt
274
275 // PieCtrlRegs.PIEIER3.bit.INTx1=1; //enable PIE
276 // IER |= 0x0004; //enable IER
277
278 // EPwm4Regs.ETPS.bit.INTPRD=1; //N° events required= 1
279 // EPwm4Regs.ETSEL.bit.INTEN = 1; //enable ePWM interrupt
280 // EPwm4Regs.ETSEL.bit.INTSEL=100; //interrupt event = CMPA
incrementing
281 // EPwm4Regs.ETSEL.bit.INTSEL=101; //interrupt event = CMPA
decrementing
282
283 // EPwm4Regs.ETPS.bit.INTCNT=01; //read N° events
284
285
286
287 //-----//
288 // DEAD_BAND CONFIGURATION //
289 //-----//
290
291 EPwm4Regs.DBCTL.bit.OUT_MODE = 0; // Deadband disabled
292 // EPwm4Regs.DBCTL.bit.HALFCYCLE=0; //half-cytle disabled
293 // EPwm4Regs.DBCTL.bit.IN_MODE=00; //source EPWM1A
294 // EPwm4Regs.DBCTL.bit.POLSEL=10; //
295 // EPwm4Regs.DBCTL.bit.OUT_MODE=11; //ACTIVE HIGH COMPLEMENTARY
296 // EPwm4Regs.DBRED=DELAY;
297 // EPwm4Regs.DBFED=DELAY;
298
299
300
301 EPwm4Regs.PCCTL.bit.CHPEN = 0; // PWM chopper unit disabled
302 EPwm4Regs.TZCTL.bit.TZA = 0x3; // Trip action disabled for output
A
303
304
305
```

```
306 */
307
308
309 //-----//
310 // Preescalado //
311 //-----//
312
313 switch (preescalado){ //completar frecuencias
314 case 1:
315 EPwm1Regs.TBCTL.bit.CLKDIV=0;
316 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
317 EPwm2Regs.TBCTL.bit.CLKDIV=0;
318 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
319 break;
320 case 2:
321 EPwm1Regs.TBCTL.bit.CLKDIV=1;
322 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
323 EPwm2Regs.TBCTL.bit.CLKDIV=1;
324 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
325 break;
326 case 4:
327 EPwm1Regs.TBCTL.bit.CLKDIV=2;
328 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
329 EPwm2Regs.TBCTL.bit.CLKDIV=2;
330 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
331 break;
332 case 8:
333 EPwm1Regs.TBCTL.bit.CLKDIV=3;
334 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
335 EPwm2Regs.TBCTL.bit.CLKDIV=3;
336 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
337 break;
338 case 16:
339 EPwm1Regs.TBCTL.bit.CLKDIV=4;
340 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
341 EPwm2Regs.TBCTL.bit.CLKDIV=4;
342 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
343 break;
344 case 32:
345 EPwm1Regs.TBCTL.bit.CLKDIV=5;
346 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
347 EPwm2Regs.TBCTL.bit.CLKDIV=5;
348 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
349 break;
350 case 64:
351 EPwm1Regs.TBCTL.bit.CLKDIV=6;
352 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
353 EPwm2Regs.TBCTL.bit.CLKDIV=6;
354 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
355 break;
356 case 112:
357 EPwm1Regs.TBCTL.bit.CLKDIV=3;
358 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 7;
359 EPwm2Regs.TBCTL.bit.CLKDIV=3;
360 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 7;
361 break;
362 case 128:
363 EPwm1Regs.TBCTL.bit.CLKDIV=7;
364 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
365 EPwm2Regs.TBCTL.bit.CLKDIV=7;
366 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
```



```
367 break;
368 case 256:
369 EPwm1Regs.TBCTL.bit.CLKDIV=7;
370 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 1;
371 EPwm2Regs.TBCTL.bit.CLKDIV=7;
372 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 1;
373 break;
374 case 320:
375 EPwm1Regs.TBCTL.bit.CLKDIV=5;
376 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 5;
377 EPwm2Regs.TBCTL.bit.CLKDIV=5;
378 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 5;
379 break;
380
381 case 512:
382 EPwm1Regs.TBCTL.bit.CLKDIV=7;
383 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 2;
384 EPwm2Regs.TBCTL.bit.CLKDIV=7;
385 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 2;
386 break;
387
388 case 640:
389 EPwm1Regs.TBCTL.bit.CLKDIV=6;
390 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 5;
391 EPwm2Regs.TBCTL.bit.CLKDIV=6;
392 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 5;
393 break;
394
395 case 1024:
396 EPwm1Regs.TBCTL.bit.CLKDIV=7;
397 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 4;
398 EPwm2Regs.TBCTL.bit.CLKDIV=7;
399 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 4;
400 break;
401
402 case 1792:
403 EPwm1Regs.TBCTL.bit.CLKDIV=7;
404 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 7;
405 EPwm2Regs.TBCTL.bit.CLKDIV=7;
406 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 7;
407 break;
408
409 }
410
411
412 //Enable EPwms clocks//
413
414 EPwm1Regs.TBCTL.bit.CTRMODE = 0x0; // Enable the timer in count up
415 EPwm2Regs.TBCTL.bit.CTRMODE = 0x0; // Enable the timer in count up
416
417
418
419 asm(" EALLOW"); // Enable EALLOW protected register access
420 SysCtrlRegs.PCLKCR0.bit.TBCLKSYNC = 1; // TBCLK to ePWM modules
421 asm(" EDIS"); // Disable EALLOW protected register
422 access
423 } // end InitEPwm()
424
425
```

[Escriba el título del documento]

```
426 //--- end of file -----  
-----  
427
```

14. Appendix A.7 Source codes for the square wave control algorithm intended for resonant operation of the inverter in the higher frequency range

Main_3.c

```
1
2
3 #include "DSP2802x_Device.h" // Peripheral address definitions
4 #include "Lab.h" // Main include file
5 #include <math.h>
6 #include <stdbool.h>
7                                     // #include
8 <C:\ti\controlSUITE\libs\math\FPUfastRTS\V100\include\C28x_FPU_FastRTS
9 .h>
10
11 // CHANGE
12 THIS //
13 //-----
14 -----//
15 //-----
16 -----//
17
18 #define Fo 10 //frecuencia de salida [kHz]
19
20 //-----
21 -----//
22 //-----
23 -----//
24
25 //--- Global Variables
26
27 Uint16 AdcBuf[ADC_BUF_LEN]; // ADC buffer allocation
28 Uint16 DEBUG_TOGGLE = 1; // Used for realtime mode investigation
29 test
30
31 Uint16 preescalado=1; //preescalado del ePWM
32 Uint16 freq_PLL=10; //Frecuencia PLL
33 Uint16 TBPRDvalue=1;
34
35
36
37 int i=0;
38 int flag=0;
39
40 void InitPLL(Uint16 conf_freq){
41
42 Uint16 aux_DIVSEL=0;
43 Uint16 aux_DIV=0;
44
45 asm(" EALLOW"); // Enable EALLOW protected register access
46
47
48
49 switch (conf_freq){
50
51 //completar frecuencias
52 case 100:
53 aux_DIVSEL=3;
54 aux_DIV=10;
55 break;
```

```
48 case 50:
49 aux_DIVSEL=3;
50 aux_DIV=5;
51 break;
52 }
53 if (SysCtrlRegs.PLLSTS.bit.MCLKSTS != 1)
54 { // PLL is not running in
limp mode
55 SysCtrlRegs.PLLSTS.bit.MCLKOFF = 1; // Turn off missing
clock detect before changing PLLCR
56 SysCtrlRegs.PLLSTS.bit.DIVSEL = 0; // DIVSEL must be 0 or 1
(//4 CLKIN mode) before changing PLLCR
57 SysCtrlRegs.PLLCR.bit.DIV = 0x5; // PLLx5/4 (because
DIVSEL is /4)
58
59 // Wait for PLL to lock.
60 // During this time the CPU will run at OSCCLK/4 until the PLL is
stable.
61 // Once the PLL is stable the CPU will automatically switch to the
new
PLL value.
62 // Code is not required to sit and wait for the PLL to lock.
However,
63 // if the code does anything that is timing critical (e.g.
something that
64 // relies on the CPU clock frequency to be at speed), then it is
best to
wait
65 // until PLL lock is complete. The watchdog should be disabled
before
this loop
66 // (e.g., as was done above), or fed within the loop.
67 while(SysCtrlRegs.PLLSTS.bit.PLLLOCKS != 1) // Wait for PLLLOCKS
bit
to set
68 {
69 SysCtrlRegs.WDKEY = 0x0055; // Service the watchdog
while waiting
70 SysCtrlRegs.WDKEY = 0x00AA; // in case the user
enabled it.
71 }
72
73 SysCtrlRegs.PLLCR.bit.DIV = aux_DIV;
74 SysCtrlRegs.PLLSTS.bit.DIVSEL = aux_DIVSEL;
75 }
76 else
77 { // PLL is running in
limp mode
78 // User should replace the below with a call to an appropriate
function,
79 // for example shutdown the system (since something is very
wrong!).
80 asm(" ESTOP0");
81 }
82
83 asm(" EDIS"); // Disable EALLOW protected register access
84
85 //--- Enable global interrupts
86 asm(" CLRC INTM, DBGM");
87 // Enable global interrupts and realtime debug
88 }
```

```
89
90
91
92
93
/*****
*
94 * Function: main()
95 *
96 * Description: Main function for C28x workshop labs
97
*****/
/
98
void main(void) {
99  /--- CPU Initialization
100  InitSysCtrl(); // Initialize the CPU (FILE: SysCtrl.c)
101  InitGpio(); // Initialize the shared GPIO pins (FILE: Gpio.c)
102  InitPieCtrl(); // Initialize and enable the PIE (FILE: PieCtrl.c)
103  InitWatchdog(); // Initialize the Watchdog Timer (FILE:
WatchDog.c)
104
105  /--- Peripheral Initialization
106  InitAdc(); // Initialize the ADC (FILE: Adc.c)
107
108  TBPRDvalue=50000/(2*Fo);
109
110  InitEPwm(TBPRDvalue,preescalado); // Initialize the EPwm (FILE:
EPwm.c)
111  InitPLL(frec_PLL);
112
113
114  /--- Enable global interrupts
115  // asm(" CLRC INTM, DBGM");
116  // Enable global interrupts and realtime debug
117
118  /--- Main Loop
119  while (1) // endless loop - wait for an interrupt
120  {
121  asm(" NOP");
122  }
123
124  } //end of main
125
126  interrupt void EPWM1_INT_ISR(void) // 0x000D1A TINT1 - CPU Timer1
127  {
128  // Next two lines for debug only - remove after inserting your ISR
129  asm (" ESTOP0"); // Emulator Halt instruction
130  while(1);
131  }
132
```

```
1
2 #include "DSP2802x_Device.h" // Peripheral address definitions
3 #include "Lab.h" // Main include file
4
5
6 #define DELAY 2
//-----|!!!!!!AJUSTAR!!!!!!-----//
7
8
/*****
*
9 * Function: InitEPwm()
10 *
11 * Description: Initializes the Enhanced PWM modules on the F2802x
12 *****/
/
13
14 void InitEPwm(Uint16 CuentaMax, Uint16 preescalado)
15 {
16
17     asm(" EALLOW"); // Enable EALLOW protected register access
18     SysCtrlRegs.PCLKCR0.bit.TBCLKSYNC = 0;
19     asm(" EDIS"); // Disable EALLOW protected register access
20
21     //enable EPWM1 y 2
22     GpioCtrlRegs.GPAMUX1.bit.GPIO0 = 1; // 0=GPIO 1=EPWM1A
23     // 2=rsvd 3=rsvd (used in Lab 3)
24     GpioCtrlRegs.GPAMUX1.bit.GPIO1 = 1; // 0=GPIO 1=EPWM1B
25     // 2=rsvd 3=COMP1OUT
26     GpioCtrlRegs.GPAMUX1.bit.GPIO2 = 0; // 0=GPIO 1=EPWM2A
27     // 2=rsvd 3=rsvd
28     GpioCtrlRegs.GPAMUX1.bit.GPIO3 = 0; // 0=GPIO 1=EPWM2B
29     // 2=rsvd 3=COMP2OUT
30
31     //-----
32     //--- Configure ePWM1 PWM on EPWM1A pin
33     //-----
34
35     //-----
36     //--- Must disable the clock to the ePWM modules if you
37     //--- want all ePMW modules synchronized.
38     //-----
39
40     EPwm1Regs.TBCTL.bit.CTRMODE = 0x3; // Disable the timer
41     EPwm1Regs.TBCTR = 0x0000; // Clear timer counter
42
43     EPwm2Regs.TBCTL.bit.CTRMODE = 0x3; // Disable the timer
44     EPwm2Regs.TBCTR = 0x0000; // Clear timer counter
45
46     //-----//
47     //configuration Time-Base Control Register//
48     //-----//
49
50     EPwm1Regs.TBCTL.all = 0xC033; //Muchos de estos valores serán
51     modificados posteriormente.
52     // bit 15-14 11: FREE/SOFT, 11 = ignore emulation suspend
```

```
48 // bit 13 0: PHSDIR, 0 = count down after sync event
49 // bit 12-10 000: CLKDIV, 000 => TBCLK = HSPCLK/1
50 // bit 9-7 000: HSPCLKDIV, 000 => HSPCLK = SYSCLKOUT/1
51 // bit 6 0: SWFSYNC, 0 = no software sync produced
52 // bit 5-4 11: SYNCOSSEL, 11 = sync-out disabled
53 // bit 3 0: PRDL, 0 = reload PRD on counter=0
54 // bit 2 0: PHSEN, 0 = phase control disabled
55 // bit 1-0 11: CTRMODE, 11 = timer stopped (disabled)
56
57
58 EPwm1Regs.TBPRD = CuentaMax; // Set timer period
59
60
61
62 EPwm1Regs.CMPCTL.all = 0x0002; // Compare control register
63 // bit 15-10 0's: reserved
64 // bit 9 0: SHDWBFULL, read-only
65 // bit 8 0: SHDWAFULL, read-only
66 // bit 7 0: reserved
67 // bit 6 0: SHDWBMODE, don't care
68 // bit 5 0: reserved
69 // bit 4 0: SHDWAMODE, 0 = shadow mode
70 // bit 3-2 00: LOADEBMODE, don't care
71 // bit 1-0 10: LOADAMODE, 10 = load on zero or PRD match
72
73
74 //-----//
75 //Action-qualifier control register A//
76 //-----//
77 EPwm1Regs.CMPA.half.CMPA = CuentaMax; // Set PWM duty cycle
78 EPwm1Regs.AQCTLA.bit.PRD=01; //Action when the counter
equals the active CMPA register and the counter is incrementing. Clear
79 EPwm1Regs.AQCTLA.bit.ZRO=10; //Action when counter equals
zero. Set
80
81 //-----//
82 // Sincronización con otros PWM //
83 //-----//
84
85 // EPwm1Regs.TBCTL.bit.PHSEN=0; //disable
86 EPwm1Regs.TBPHS.half.TBPHS = 0x0000; // Set timer phase
87 EPwm1Regs.TBCTL.bit.PHSEN=0; //MASTER
88 EPwm1Regs.TBCTL.bit.SYNCOSSEL=1; //select CTR=ZERO as source of
EPWMxSYNCO signal
89
90 //-----//
91 // Interrupciones //
92 //-----//
93
94 EPwm1Regs.ETSEL.bit.INTEN = 0; //disable ePWM interrupt
95 // EPwm1Regs.ETSEL.bit.INTEN = 1; //enable ePWM interrupt
96 // EPwm1Regs.ETPS.bit.INTCNT=01; //interrupt when 1 event
97 // EPwm1Regs.ETSEL.bit.INTSEL=100; //interrupt event = CMPA
incrementing
98
99 //-----//
100 // DEAD_BAND CONFIGURATION //
101 //-----//
102
103 // EPwm1Regs.DBCTL.bit.OUT_MODE = 0; // Deadband disabled
104 EPwm1Regs.DBCTL.bit.HALFCYCLE=0; //half-cytle disabled
```



```
105 EPwm1Regs.DBCTL.bit.IN_MODE=00; //source EPWM1A
106 EPwm1Regs.DBCTL.bit.POLSEL=10; //
107 EPwm1Regs.DBCTL.bit.OUT_MODE=11; //ACTIVE HIGH COMPLEMENTARY
108 EPwm1Regs.DBRED=50*DELAY/preescalado;
109 EPwm1Regs.DBFED=50*DELAY/preescalado;
110
111
112
113 EPwm1Regs.PCCTL.bit.CHPEN = 0; // PWM chopper unit disabled
114 EPwm1Regs.TZCTL.bit.TZA = 0x3; // Trip action disabled for output
A
115
116
117 //-----
-----
118 //--- Configure ePWM1 PWM on EPWM1A pin
119 //-----
-----
120
121
122 //-----//
123 //configuration Time-Base Control Register//
124 //-----//
125
126 EPwm2Regs.TBCTL.all = 0xC033; //Muchos de estos valores serán
modificados posteriormente.
127 // bit 15-14 11: FREE/SOFT, 11 = ignore emulation suspend
128 // bit 13 0: PHSDIR, 0 = count down after sync event
129 // bit 12-10 000: CLKDIV, 000 => TBCLK = HSPCLK/1
130 // bit 9-7 000: HSPCLKDIV, 000 => HSPCLK = SYSCLKOUT/1
131 // bit 6 0: SWFSYNC, 0 = no software sync produced
132 // bit 5-4 11: SYNCSEL, 11 = sync-out disabled
133 // bit 3 0: PRDLD, 0 = reload PRD on counter=0
134 // bit 2 0: PHSEN, 0 = phase control disabled
135 // bit 1-0 11: CTRMODE, 11 = timer stopped (disabled)
136
137
138 EPwm2Regs.TBPRD = CuentaMax; // Set timer period
139
140
141
142 EPwm2Regs.CMPCTL.all = 0x0002; // Compare control register
143 // bit 15-10 0's: reserved
144 // bit 9 0: SHDWBFULL, read-only
145 // bit 8 0: SHDWAFULL, read-only
146 // bit 7 0: reserved
147 // bit 6 0: SHDWBMODE, don't care
148 // bit 5 0: reserved
149 // bit 4 0: SHDWAMODE, 0 = shadow mode
150 // bit 3-2 00: LOADBMODE, don't care
151 // bit 1-0 10: LOADAMODE, 10 = load on zero or PRD match
152
153
154 //-----//
155 //Action-qualifier control register A//
156 //-----//
157 EPwm2Regs.CMPA.half.CMPA = CuentaMax; // Set PWM duty cycle
158 EPwm2Regs.AQCTLA.bit.PRDL=01; //Action when the counter
equals the active CMPA register and the counter is incrementing. Clear
159 EPwm2Regs.AQCTLA.bit.ZRO=10; //Action when counter equals
zero. Set
```

```
160
161 //-----//
162 // Sincronización con otros PWM //
163 //-----//
164
165 // EPwm2Regs.TBCTL.bit.PHSEN=0; //disable
166 EPwm2Regs.TBPHS.half.TBPHS = CuentaMax; // Set timer phase
167 EPwm2Regs.TBCTL.bit.PHSEN=1; //MASTER
168 EPwm2Regs.TBCTL.bit.SYNCOSEL=1; //select CTR=ZERO as source of
EPWMxSYNCO signal
169
170 //-----//
171 // Interrupciones //
172 //-----//
173
174 EPwm2Regs.ETSEL.bit.INTEN = 0; //disable ePWM interrupt
175 // EPwm2Regs.ETSEL.bit.INTEN = 1; //enable ePWM interrupt
176 // EPwm2Regs.ETPS.bit.INTCNT=01; //interrupt when 1 event
177 // EPwm2Regs.ETSEL.bit.INTSEL=100; //interrupt event = CMPA
incrementing
178
179 //-----//
180 // DEAD_BAND CONFIGURATION //
181 //-----//
182
183 // EPwm2Regs.DBCTL.bit.OUT_MODE = 0; // Deadband disabled
184 EPwm2Regs.DBCTL.bit.HALFCYCLE=0; //half-cytle disabled
185 EPwm2Regs.DBCTL.bit.IN_MODE=00; //source EPWM1A
186 EPwm2Regs.DBCTL.bit.POLSEL=10; //
187 EPwm2Regs.DBCTL.bit.OUT_MODE=11; //ACTIVE HIGH COMPLEMENTARY
188 EPwm2Regs.DBRED=50*DELAY/preescalado;
189 EPwm2Regs.DBFED=50*DELAY/preescalado;
190
191
192
193 EPwm2Regs.PCCTL.bit.CHPEN = 0; // PWM chopper unit disabled
194 EPwm2Regs.TZCTL.bit.TZA = 0x3; // Trip action disabled for output
A
195
196 //-----//
197 // Preescalado //
198 //-----//
199
200 switch (preescalado){ //completar frecuencias
201 case 1:
202 EPwm1Regs.TBCTL.bit.CLKDIV=0;
203 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
204 EPwm2Regs.TBCTL.bit.CLKDIV=0;
205 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
206 break;
207 case 2:
208 EPwm1Regs.TBCTL.bit.CLKDIV=1;
209 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
210 EPwm2Regs.TBCTL.bit.CLKDIV=1;
211 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
212 break;
213 case 4:
214 EPwm1Regs.TBCTL.bit.CLKDIV=2;
215 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
216 EPwm2Regs.TBCTL.bit.CLKDIV=2;
217 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
```

```
218 break;
219 case 8:
220 EPwm1Regs.TBCTL.bit.CLKDIV=3;
221 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
222 EPwm2Regs.TBCTL.bit.CLKDIV=3;
223 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
224 break;
225 case 16:
226 EPwm1Regs.TBCTL.bit.CLKDIV=4;
227 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
228 EPwm2Regs.TBCTL.bit.CLKDIV=4;
229 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
230 break;
231 case 32:
232 EPwm1Regs.TBCTL.bit.CLKDIV=5;
233 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
234 EPwm2Regs.TBCTL.bit.CLKDIV=5;
235 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
236 break;
237 case 64:
238 EPwm1Regs.TBCTL.bit.CLKDIV=6;
239 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
240 EPwm2Regs.TBCTL.bit.CLKDIV=6;
241 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
242 break;
243 case 112:
244 EPwm1Regs.TBCTL.bit.CLKDIV=4;
245 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 7;
246 break;
247 case 128:
248 EPwm1Regs.TBCTL.bit.CLKDIV=7;
249 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 0;
250 EPwm2Regs.TBCTL.bit.CLKDIV=7;
251 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 0;
252 break;
253 case 256:
254 EPwm1Regs.TBCTL.bit.CLKDIV=7;
255 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 1;
256 EPwm2Regs.TBCTL.bit.CLKDIV=7;
257 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 1;
258 break;
259 case 512:
260 EPwm1Regs.TBCTL.bit.CLKDIV=7;
261 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 2;
262 EPwm2Regs.TBCTL.bit.CLKDIV=7;
263 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 2;
264 break;
265 case 1024:
266 EPwm1Regs.TBCTL.bit.CLKDIV=7;
267 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 4;
268 EPwm2Regs.TBCTL.bit.CLKDIV=7;
269 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 4;
270 break;
271
272 case 1792:
273 EPwm1Regs.TBCTL.bit.CLKDIV=7;
274 EPwm1Regs.TBCTL.bit.HSPCLKDIV = 7;
275 EPwm2Regs.TBCTL.bit.CLKDIV=7;
276 EPwm2Regs.TBCTL.bit.HSPCLKDIV = 7;
277 break;
278
```

```
279 }
280
281
282 //Enable EPwms clocks//
283
284 EPwm1Regs.TBCTL.bit.CTRMODE = 0x2; // Enable the timer in count
up-down
285 EPwm2Regs.TBCTL.bit.CTRMODE = 0x2; // Enable the timer in count
up-down
286
287
288
289 asm(" EALLOW"); // Enable EALLOW protected register access
290 SysCtrlRegs.PCLKCR0.bit.TBCLKSYNC = 1; // TBCLK to ePWM modules
enabled
291 asm(" EDIS"); // Disable EALLOW protected register
access
292
293 } // end InitEPwm()
294
295
296 //--- end of file -----
-----
297
```

15.Appendix A.8 Protocol of operation of the air coil OMF generator

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CONTROL DE LAS MODIFICACIONES		
Revisión	Fecha	Descripción de los cambios

MATERIALES y EQUIPOS A UTILIZAR

MATERIAL	LABORAT. / CAMARA/TEMPERATURA	EQUIPOS
	L0-L04	Osciloscopio Tektronix TDS5032B
		Ordenador portátil Lenovo T60 Think Pad
		Fuente de Alimentación Keysight N8762A
		Pinza Amperimétrica Pico TA189
		Sonda Osciloscopio Tektronix P5050
		Microcontrolador Launch XL-F 2806919 Texas Instruments
		Placa Inversora de Corriente (Prototipo)
		Fuente de Alimentación Promax FAC-662B
		Bobina Inductora (Prototipo)
4 cables con conectores tipo banana		
7 cablecitos de puenteado (cables de

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jumper)		
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TÉCNICA A LLEVAR A CABO

DESCRIPCIÓN

Se pretende generar campos magnéticos alternos en un rango de frecuencias variable entre 1 Hz y 50 KHz con el fin de poder estudiar el efecto de estos campos en la congelación de cualquier alimento.

Conviene aclarar que todos los pasos iniciales que figuran a continuación, en el apartado **INSTALACIÓN**, sólo se realizarán por primera vez cuando se ejecutan los archivos en un ordenador nuevo.

INSTALACIÓN

Para la generación y cuantificación de los campos magnéticos es necesario aplicar un programa informático llamado Code Composer Studio versión 7.1.0 de la empresa Texas Instruments.

Para ello se descarga el programa de la página web de Texas Instruments. En el mismo ordenador donde se ha descargado el programa, se copian dos carpetas llamadas “**Altas frecuencias**” y “**Bajas frecuencias**” situadas en la carpeta Compartido Pedro Sanz (M:)\TESIS DE ANTONIO\Código fuente control del inversor. A continuación se crean dos nuevas carpetas llamadas “**Workspace altas frecuencias**” y “**Workspace bajas frecuencias**”. Se da doble clic en el icono del programa en el escritorio. Se pincha en el botón “**Browse**” y se selecciona la carpeta “**Workspace altas frecuencias**” ó “**Workspace bajas frecuencias**” según las frecuencias que se quieran estudiar en el ensayo. Se pulsa en “**Aceptar**” y luego en “**Ok**”.

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Se selecciona la pestaña “File”, luego “Import” y en la pantalla emergente se selecciona la carpeta “Code Composer Studio” y luego la subcarpeta “CCS Projects”. Se pulsa el botón “Next” apareciendo otra ventana emergente. En ésta se pulsa el botón “Browse” y se selecciona la carpeta “Altas frecuencias” ó “Bajas frecuencias” según corresponda. En el caso de “Altas frecuencias” se elige la subcarpeta “pwm_inv01” y en el caso de “Bajas frecuencias” se elige la subcarpeta “pwm_inv02”. Luego se pulsa en “Aceptar”.

Se marca con un clic en el apartado “Automatically import referenced project found in same search-directory” y en el apartado “Copy projects into workspace”. Para finalizar se pulsa el botón “Finish”.

Se minimiza el programa y se selecciona la carpeta “Altas frecuencias” ó “Bajas frecuencias” según corresponda. Se copia la carpeta “DSP2802x_headers” en la carpeta “Workspace altas frecuencias” ó “Workspace bajas frecuencias” que corresponda y se regresa al programa.

Dentro de la banda izquierda (FOTO 1) del Project Explorer, se despliega la carpeta “pwm_inv01” en el caso de “Altas frecuencias” ó se despliega la carpeta “pwm_inv02” en el caso de “Bajas frecuencias” pulsando el triángulo de la izquierda.

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FOTO 1

Con el botón derecho del ratón, se pulsa en la carpeta “pwm_inv01” ó “pwm_inv02” y se selecciona “properties”. En la parte izquierda de la ventana emergente se selecciona el directorio según la ruta “Build/C2000 Compiler/Include options”.

A continuación se borra la primera fila seleccionada por defecto (FOTO 2) con el icono de la cruz roja. No borrar la segunda fila.

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FOTO 2

Se pulsa el icono con la cruz verde y en la pantalla emergente se pulsa el botón “Browse” y se busca la carpeta “Workspace altas frecuencias” ó “Workspace bajas frecuencias” que corresponda. Dentro de la carpeta se selecciona la subcarpeta “DSP2802x_headers” copiada anteriormente. Dentro de ella se selecciona la subcarpeta “include”. Se pulsa en “Aceptar” y luego en “OK”. Ahora acaba de aparecer la nueva línea que se ha incorporado (FOTO 3). Por último se pulsaría en el botón “OK”. Con este proceso estaría listo para su funcionamiento.

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FOTO 3

FUNCIONAMIENTO

Cuando se tengan instalados y cargados los procesos de altas frecuencias y de bajas frecuencias, a la hora de trabajar sólo se pulsará el icono del programa, en la ventana emergente se pulsa el botón “Browse” y se busca la carpeta “Workspace altas frecuencias” ó “Workspace bajas frecuencias” que se quiera utilizar. Luego se pulsará el botón “Ok”. Aparece la ventana que se refleja en la FOTO 4.

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FOTO 4

Dentro del directorio de archivos que se ve en la imagen se realiza doble clic en el archivo “Main_3.c” apareciendo la imagen que se ve en la **FOTO 5**.

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FOTO 5

A partir de aquí se procede al ajuste de los equipos para su posterior conexión y medición. Es imprescindible comprobar el ajuste antes de la conexión.

IMPORTANTE: CUANDO SE REALICE ALGÚN AJUSTE A CUALQUIER EQUIPO ES IMPRESCINDIBLE DESCONECTAR TODOS LOS CABLES DEL SISTEMA. FOTO 6.

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FOTO 6

Se enciende la fuente de alimentación PROMAX con el interruptor LINE situado en el centro del cuadro de mandos. Se procede a seleccionar la corriente que se emplea en la medición. Para ello, desconectando previamente todos los cables, se pulsa el botón INDEP de la izquierda de los cuatro centrales para seleccionar de manera independiente cada una de las dos fuentes

FOTO 7.

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FOTO 7

EL siguiente paso es seleccionar el voltaje de la fuente de la izquierda, para ello en el lado izquierdo que representa el voltaje V se pulsa el botón de la izquierda S1. Aquí se trabaja con voltaje de 17,8 V. Para ello, con la rueda COARSE se llega hasta 17 V aproximadamente. Con la rueda FINE se ajusta hasta llegar a 17,8 - 17,9 V. Cabe resaltar que la intensidad correspondiente permanecerá en cero hasta que no se realice la conexión del cableado.

Para la fuente de la derecha, se pulsa el botón derecho S2 del lado izquierdo del voltaje V. Aquí se trabaja con 3,9 - 4 V procediendo del mismo modo que el ajuste anterior utilizando las dos ruedas COARSE y FINE de la parte derecha. Una vez procedido el ajuste del voltaje, se apaga la fuente con el interruptor LINE.

A continuación, se procede al conexionado de la fuente de alimentación con la placa inversora. Se incluye una foto de la placa inversora previa al montaje de componentes electrónicos (FOTO 8).

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FOTO 8

Se conecta el cable A desde la toma A de la fuente de alimentación hasta la toma A “Driver Power” de la placa inversora. Se conecta el cable B desde la toma B de la fuente de alimentación hasta la toma B “GND Driver” de la placa inversora (FOTOS 9 y 10).

DETERMINACIÓN: Generación de campos magnéticos alternos en rango de frecuencias variable

FOTO 9

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FOTO 10

Se conecta el cable C desde la toma C de la fuente de alimentación hasta la toma C “Logic power” de la placa inversora. Se conecta el cable D desde la toma D de la fuente de alimentación hasta la toma D “GND Control” de la placa inversora (FOTOS 11 y 12).

DETERMINACIÓN: Generación de campos magnéticos alternos en rango de frecuencias variable

FOTO 11

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FOTO 12

A continuación se procede al conexionado de la placa inversora con la bobina inductora. Se conecta el cable E desde la toma E “OUT2” de la placa inversora hasta el conector E de la bobina. Se conecta el cable F desde la toma F “OUT 1” de la placa inversora hasta el conector F de la bobina (**FOTOS 13 y 14**).

Aquí es importante resaltar que las partes metálicas de las conexiones de las bobinas tienen que estar aisladas de manera independiente, por ejemplo con cinta aislante como en la **FOTO 14**, para no tocarse entre sí ni con las paredes del congelador.

FOTO 13

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FOTO 14

Ahora se procede al ajuste y posterior conexionado de la fuente de alimentación KEYSIGHT (FOTO 15).

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FOTO 15

Asegurándose que los terminales de los 2 cables que salen de detrás de dicha fuente de alimentación (rojo y negro) están desconectados y separados entre sí, se enciende la fuente de alimentación. Cuando aparezca “OFF” en la pantalla (**FOTO 16**), se pulsa el botón LIMIT y con la rueda CURRENT de la derecha se ajusta a 2 Amperios. Se presiona el botón FINE y con el equipo apagado (display en “OFF”) se procede a su conexión a la placa inversora.

FOTO 16

Se conecta el cable G desde la toma G “GND POWER” de la placa inversora hasta el conector G de la fuente de alimentación. Se conecta el cable H desde la toma H “Vin” de la placa inversora hasta el conector H de la fuente de alimentación (**FOTO 17**).

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FOTO 17

Una vez hechas las conexiones entre la placa inversora y la fuente de alimentación, se enciende el osciloscopio dejando los botones como aparecen en la **FOTO 18**.

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FOTO 18

Se conecta la sonda de tensión de la salida CH2 del osciloscopio a la placa inversora tal como aparece en las **FOTOS 19 y 20**. De las tres patillas grandes, se coloca la pinza de cocodrilo roja (tierra) en la patilla de la derecha y el gancho negro en la patilla grande de la izquierda.

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FOTO 19

FOTO 20

Se coloca la pinza amperimétrica desde el canal CH1 del osciloscopio hasta el cable F ó el cable E (sólo uno de ellos) rodeándolo como se muestra en la FOTO 21.

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FOTO 21

Los canales de salida del osciloscopio se muestran en la FOTO 22.

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FOTO 22

Una vez finalizadas las conexiones del osciloscopio a la placa inversora, se procede al conexionado mediante cables de puentear del microcontrolador con la placa inversora. Para ello, se conecta el cable número 1 desde el pin número 22 del microcontrolador al quinto pin de la placa inversora (**FOTO 23, FOTO 24 y FOTO 25**).

FOTO 23

DETERMINACIÓN: Generación de campos magnéticos alternos en rango de frecuencias variable

FOTO 24

FOTO 25

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Se conecta el cable 3 desde el pin número 40 del microcontrolador al agujero 4 de la placa inversora (**FOTO 26 y FOTO 27**).

FOTO 26

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FOTO 27

Se conecta el cable 2 desde el pin número 39 del microcontrolador al agujero 3 de la placa inversora (FOTO 28 y FOTO 29).

FOTO 28

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FOTO 29

Hasta aquí el conexionado sería igual tanto si se quiere trabajar con altas frecuencias como si se quiere trabajar a bajas frecuencias.

A continuación se indica el conexionado específico empleado para altas frecuencias que se realizará junto con el conexionado general y posteriormente se indica el conexionado específico para bajas frecuencias que se realizará también con el conexionado general.

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Conexionado específico para altas frecuencias:

Se conecta el cable 4 desde el segundo pin al tercer pin de la placa inversora. (FOTO 30).

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FOTO 30

Se conecta el cable 5 desde el primer pin al cuarto pin de la placa inversora (FOTO 31).

FOTO 31

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Se colocará el jumper color azul en la posición JMP1, JMP2, JMP3 ó JMP4 según se trabaje a 10 KHz, 20 KHz, 40 KHz ó 50 KHz respectivamente (**FOTO 32**).

FOTO 32

Con este paso finalizaría el conexionado específico relativo a las altas frecuencias.

A partir de aquí se procedería a seguir las instrucciones para realizar la medición.

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Conexionado específico para bajas frecuencias:

Se conecta el cable 6 desde el pin número 38 del microcontrolador al agujero 18 de la placa inversora (FOTO 33 y FOTO 34).

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FOTO 33

FOTO 34

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Se conecta el cable 7 desde el pin número 37 del microcontrolador al agujero 19 de la placa inversora (**FOTO 35 y FOTO 36**).

FOTO 35

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FOTO 36

Se coloca el jumper color azul en la posición JMP5 (**FOTO 37**).

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FOTO 37

Con este paso finalizaría el conexionado específico relativo a las bajas frecuencias.

A partir de aquí se procedería a seguir las instrucciones para realizar la medición.

Así se acabaría tanto el conexionado general como el conexionado específico para altas frecuencias o bajas frecuencias comenzando el esquema para realizar la medición correspondiente.

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Medición en bajas frecuencias:

Con el programa Code Composer cerrado, se pincha el icono del programa en el ordenador, en la ventana emergente se pulsa el botón **"Browse"**, se selecciona la carpeta **"Workspace bajas frecuencias"** y se pulsa el botón **"Ok"**. Aparece la pantalla **"Main_3.c"** y se despliega la carpeta **"pwm_inv02"**.

Dentro de la carpeta, se selecciona el archivo **"EPwm.c"** haciendo doble clic. Aparece como segunda pestaña tras **"Main_3.c"**.

En el siguiente paso se procederá a cambiar los valores de medida por aquellos que son específicos para la frecuencia a la que se quiera trabajar. Para ello, al final del protocolo se adjunta una tabla con los valores a cambiar para cada frecuencia.

Dentro de la pestaña de **"Main_3.c"**, se cambia la **"frecuencia de salida"** definida en la línea 17 por aquella que esté definida en la tabla que se adjunta al final del protocolo para la frecuencia específica a ensayar. De la misma manera se modificará el **"módulo de frecuencia"** de la línea 18 y el valor de **"float triangular"** de la línea 22.

En la pestaña **"EPwm.c"**, se cambia el **"define DELAY"** definido en la línea 6 por aquella que esté definida en la tabla que se adjunta al final del protocolo para la frecuencia específica a ensayar.

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Una vez realizadas estas modificaciones, se pulsa en el botón del “martillo” (FOTO 38).

FOTO 38

Al pulsarlo, se empiezan a compilar los datos modificados apareciendo al final la frase “Build Finished” en la parte inferior de la pantalla (FOTO 39).

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FOTO 39

Antes de seguir, si no estuviera conectado, se debe realizar la conexión de la tarjeta microcontroladora al ordenador donde está instalado el Code Composer, mediante el cable mini USB. Posteriormente se pulsa el botón “Bicho” para cargar el programa compilado en el microcontrolador (FOTO 40).

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FOTO 40

A continuación se pulsa el botón Play (triángulo verde) y se ejecutan los cambios en el microcontrolador (FOTO 41).

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FOTO 41

Luego se enciende la fuente de alimentación PROMAX (previamente ajustada al principio con los cables desconexionados), se enciende la pinza amperimétrica con el botón ON / OFF y se enciende la fuente de alimentación KEYSIGHT. Se pulsa el botón LIMIT y con la rueda CURRENT de la derecha se ajusta a 2 Amperios. Se presiona el botón FINE, luego el botón OUT ON y con la rueda VOLTAGE de la izquierda se selecciona el voltaje requerido, para conseguir el valor deseado de corriente circulando por la bobina. Los valores a la temperatura de -28 aparecen en la tabla que se adjunta al final del protocolo, para cada frecuencia específica a ensayar, pudiendo modificarse según la tabla del Excel que acompaña al protocolo.

Es importante resaltar que las correcciones de los valores reflejados en la tabla tienen que ser correctas cuando se alcanza un valor de tensión en la pinza amperimétrica de 147 mV aproximadamente. Si no es así habría que modificar el voltaje para llegar a ese valor (FOTO 42).

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FOTO 42

Una vez realizadas las mediciones con el campo establecido, se baja el voltaje de la fuente KEYSIGHT a 0,4V (se da alguna vuelta más hasta que se pueda suponer que el voltaje es realmente cero) y se pulsa el botón OUT ON para apagar el voltaje (si no se llega a bajar, al volver a conectarlo aparece el último voltaje seleccionado). A continuación se pulsa el botón negro del microcontrolador para parar la ejecución del programa (FOTO 43) y se pulsa el botón de STOP (icono de cuadrado rojo) en el programa del ordenador (FOTO 44). Se apaga la fuente de alimentación PROMAX, se desconecta el puerto USB del microcontrolador que conecta al ordenador y se cierra el programa en el ordenador.

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FOTO 43

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FOTO 44

Es importante resaltar que dentro del apartado de las bajas frecuencias puede ocurrir que el osciloscopio no registre la frecuencia deseada para el ensayo; para solucionarlo se baja el voltaje de la fuente KEYSIGHT a 0,4V (se da alguna vuelta más hasta que se pueda suponer que el voltaje es realmente cero), se pulsa el botón OUT ON para apagar el voltaje, a continuación se pulsa el botón negro del microcontrolador para parar la ejecución del programa, se pulsa el botón de STOP (icono de cuadrado rojo) en el programa del ordenador y se apaga la fuente de alimentación PROMAX . Posteriormente se pulsa el botón “Bicho” para cargar el programa compilado en el microcontrolador, se pulsa el botón Play (triángulo verde) y se comienza otra vez el protocolo establecido anteriormente.

Si estando en bajas frecuencias se requiere realizar más ensayos a lo largo del tiempo dentro de las bajas frecuencias ó si estando en altas frecuencias se requiere realizar más ensayos a lo largo del tiempo dentro de las altas frecuencias, no es necesario desconexionar nada en los equipos para cada medición.

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Medición en altas frecuencias:

Se procede a conexionar todos los equipos como anteriormente se ha descrito para altas frecuencias y, con el programa cerrado se pincha el icono del programa en el ordenador, en la ventana emergente se pulsa el botón “Browse”, se selecciona la carpeta “Workspace altas frecuencias” y se pulsa el botón “Ok”. Aparece la pantalla “Main_3.c” y se despliega la carpeta “pwm_inv01”.

Dentro de la carpeta, se selecciona el archivo “EPwm.c” haciendo doble clic. Aparece como segunda pestaña tras “Main_3.c”.

En el siguiente paso se procederá a cambiar los valores de medida por aquellos que son específicos para la frecuencia a la que se quiera trabajar. Para ello, al final del protocolo se adjunta una tabla con los valores a cambiar para cada frecuencia.

Dentro de la pestaña de “Main_3.c”, se cambia la “frecuencia de salida” definida en la línea 13 por aquella que esté definida en la tabla que se adjunta al final del protocolo para la frecuencia específica a ensayar.

Una vez realizadas estas modificaciones, se pulsa en el botón del “martillo”. Al pulsarlo, se empiezan a compilar los datos modificados apareciendo al final la frase “Build Finished” en la parte inferior de la pantalla. Antes de seguir, si no estuviera conectado, se debe realizar la conexión de la tarjeta microcontroladora al ordenador donde está instalado el Code Composer, mediante el cable mini USB. Posteriormente se pulsa el botón “Bicho” para cargar el programa compilado en el microcontrolador. A continuación se pulsa el botón Play (triángulo verde) y se ejecutan los cambios en el microcontrolador.

Luego se enciende la fuente de alimentación PROMAX (previamente ajustada al principio con los cables desconexiónados), se enciende la pinza amperimétrica con el botón ON / OFF y se enciende la fuente de alimentación KEYSIGHT. Se pulsa el botón LIMIT y con la rueda CURRENT de la derecha se ajusta a 2 Amperios. Se presiona el botón FINE, luego el botón OUT ON y con la rueda VOLTAGE de la izquierda se selecciona el voltaje requerido, para conseguir el valor deseado de corriente circulando por la bobina. Los valores a la temperatura de -28 aparecen en la tabla que se adjunta al final del protocolo, para cada frecuencia específica a ensayar, pudiendo modificarse según la tabla del Excel que acompaña al protocolo.

También se indica que las correcciones de los valores reflejados en la tabla tienen que ser correctas cuando se alcanza un valor de tensión en la pinza amperimétrica de 147 mV aproximadamente. Si no es así habría que modificar el voltaje para llegar a ese valor.

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Una vez realizadas las mediciones con el campo establecido, se baja el voltaje de la fuente KEYSIGHT a 0,4V (se da alguna vuelta más hasta que se pueda suponer que el voltaje es realmente cero) y se pulsa el botón OUT ON para apagar el voltaje (si no se llega a bajar, al volver a conectarlo aparece el último voltaje seleccionado). A continuación se pulsa el botón negro del microcontrolador para parar la ejecución del programa (FOTO 43) y se pulsa el botón de STOP (icono de cuadrado rojo) en el programa del ordenador (FOTO 44). Se apaga la fuente de alimentación PROMAX, se desconecta el puerto USB del microcontrolador que conecta al ordenador y se cierra el programa en el ordenador.

A veces la senoide que aparece en el osciloscopio se distorsiona y se debe de poner en OFF y luego en ON la pinza amperimétrica. En funcionamiento habitual, tras haber ajustado el campo a su valor, mejor dejarla apagada y encenderla puntualmente sólo cuando se vaya a cambiar algún valor de la corriente (intensidad o frecuencia) o para comprobar su valor.

Si estando en bajas frecuencias se requiere realizar más ensayos a lo largo del tiempo dentro de las bajas frecuencias ó si estando en altas frecuencias se requiere realizar más ensayos a lo largo del tiempo dentro de las altas frecuencias, no es necesario desconexión nada en los equipos para cada medición.

Tabla de modificación de valores para cada frecuencia establecida.

Los valores de tensión e intensidad son para conseguir una corriente eficaz (RMS) de 1.47 A en la bobina (indicado en el osciloscopio como tensión eficaz (RMS) de 147 mV por la razón de conversión de la pinza amperimétrica). Este valor es el que se debe conseguir para el campo deseado.

BAJAS FRECUENCIAS

triangular[x]

Frecuencia objetivo (Hz)	Código Main_3.c			Código EPwm.c	Fuente de Keysight	
	F ₀	Mf	x		DELAY	Tensión de entrada (V)* Corriente de entrada (A)**
1	1	100	336	30	2,5	1,4
2	2	100	168	30	2,5	1,31
5	5	100	156	15	2,6	1,13
10	10	100	56	20	2,7	1,07
20	20	100	28	20	2,9	0,75
50	50	100	56	4	2,8	0,83
100	100	100	28	5	3,1	0,79
200	200	100	28	4	3,8	0,71
500	500	75	16	2	4,8	0,58
1000	1000	35	16	2	8,5	0,4
2000	2000	15	24	2	15,4	0,24

* Tensiones medidas a -28. Para cada temperatura del congelador, la resistencia del cobre puede variar. Calcularla con la fórmula de abajo a la derecha

** Éstas corrientes no siempre son medibles en el display de la fuente de Keysight (demasiada oscilación). En todo caso mirar siempre el valor de 1,47 A por la bobina (147 mV en el osciloscopio)

ALTAS FRECUENCIAS

Frecuencia objetivo (Hz)	Fuente de Keysight	
	Tensión de entrada (V)	Corriente de entrada (A)
10000	12,3	2
20000	24,8	2,2
40000	46,9	2,3
50000	68,5	2,4

Tabla auxiliar para cálculo

2
2,2
2,3
2,4

Tabla auxiliar para cálculo

3,1
3,1
3,2
3,3
3,6
3,5
3,8
4,7
5,9
10,5
19,1

Temperatura del congelador	Resistencia bobina a la T del congelador
-28	0,79797168

Baja Frecuencia (Hz)	Tensión de entrada correspondiente a la T del congelador
1	2,5
2	2,5
5	2,6
10	2,7
20	2,9
50	2,8
100	3,1
200	3,8
500	4,8
1000	8,5
2000	15,4
Alta Frecuencia (Hz)	Tensión de entrada correspondiente a la T del congelador
10000	1,6
20000	1,8
40000	1,9
50000	1,9

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GESTIÓN DE RESIDUOS

No se generan residuos.

TIPO DE MEZCLA. COMPATIBILIDADES:

RETIRADA EN EL CONTENEDOR:

Fecha: 01/08/2017

Revisado por:

GESTIÓN DE RESIDUOS

MEDIDAS DE SEGURIDAD

<p>CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS INSTITUTO DE CIENCIA Y TECNOLOGÍA DE ALIMENTOS Y NUTRICIÓN (ICTAN)</p>	<p>PROTOCOLO DE TRABAJO</p>	<p>PT-DPROC-PSM-72 Rev. Nº: 0 Elaborado por: Ignacio Rodríguez Pág. 318 de 347</p>
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- Bata.

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