Ultrasonic assisted extraction of natural products

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Ultrasound assisted extraction (USAE) is an interesting process to obtain high valuable compounds and could contribute to the increase the value of some food by-products when used as sources of natural compounds. The main benefits will be a more effective extraction, thus saving energy, and also to the use of moderate temperatures, which is beneficial for heat sensitive compounds. For a successful application of the USAE, it is necessary to consider the influence of several process variables, the main ones being the applied ultrasonic power, the frequency, the extraction temperature, the reactor characteristics and the solvent-sample interaction. The highest extraction rate is usually achieved in the first few minutes, which is the most profitable period. To optimize the process, rate equations and unambiguous process characterization are needed, aspects that have often been lacking.

Key words: ultrasound, mass transfer, food by-product, quality

Abbreviations:

Π : ultrasonic power density

f : applied frequency

USAE: ultrasound assisted extraction

1. Introduction.

In the last few years, ultrasound technology has been revealed as valuable tool in food engineering processes (Bhaskaracharya et al. 2009), and this field of research has become a very active one. Two very different approaches to the application of ultrasound have been explored mainly related to the frequency and the power of the ultrasonic vibration. One of them consists of using high frequency-low intensity ultrasound and it has specifically focused on the quality monitoring of products or processes, such as the assessment of the cheese maturation time (Benedito et al. 2000) or compositional analysis (Benedito et al. 2001). The applications are mainly related to the measurement of ultrasound velocity, the attenuation of the signal or the analysis of frequency spectra. In these applications there is no influence on the process or the product.

Another approach, the low frequency-high power ultrasound, has been successfully applied to improve the process and/or the products. This was the case for brining processes (Cárcel et al. 2007a), maceration (Cárcel et al. 2007b), microbial and enzyme inactivation (Vercet et al. 2001), freezing processes (Zheng and Sun 2006), the modification of ingredients (Kardos and Luche 2001), the extraction of natural products (Vilkhu et al. 2008), food cutting operations (Arnold et al. 2009), improving the quality of emulsions (Wulff-Pérez et al. 2009) or slurry preparation (Montalbo-Lomboy et al. 2010), sugar substitution processes (Garcia-Noguera et al. 2010) and fermentations processes (Riener et al. 2010) among others.

Ultrasound is usually applied in solid/fluid media, being the fluid either gas or liquid. The applications in solid/gas systems are not frequent because the impedance mismatch and the air absorption make the transmission of ultrasound difficult. However, advances in transducer technology are allowing a more thorough understanding of power ultrasound assisted drying. The use of ultrasonic systems both with contact or not contact between samples and vibrating elements has been reported such as in vibrating chambers. In these applications, the power ultrasound increases the surface moisture evaporation rate and causes oscillating velocities and microstreaming at the interfaces which may affect the diffusion boundary layer and generate rapid series of alternative contractions and expansions of the material, affecting mass transfer (García-Pérez et al. 2006).

In solid/liquid systems, the applications are more common. The enhancement of the mass transfer brought about by acoustic induced cavitation in a liquid medium is one of the beneficial effects. When mechanical waves are transmitted through a fluid, the average distance within molecules is modified, oscillating around their equilibrium position. During the compression cycle, the intermolecular distance shortens and lengthens again in the rarefaction cycle. When the pressure decrease in the rarefaction cycle is enough to exceed the critical distance between molecules, cavities can appear in the bulk liquid. Those incipient bubbles keep on growing until the system reaches its minimal pressure and the subsequent compression cycle starts. Then, the cavities can start another rarefaction cycle or collapse adiabatically resulting in a violent implosion at the end of a compression cycle, yielding shock waves of several hundred atmospheres and around 5000 K of temperature (Leighton 2007). Cavitation bubbles exist for few acoustic cycles before collapsing, giving rise to smaller bubbles which could act as new cavitation nuclei or simply get dissolved.

The mechanical effects induced by cavitation bubbles in the solid-liquid interface of a heterogeneous medium include micro jet impacts and shockwave induced damages. Thus, the potential energy of the expanded bubble is converted into kinetic energy of a liquid jet that extends inside the bubble and penetrates the opposite bubble wall, reaching velocities of hundreds of meters per second (Suslick 2001). Moreover, sonochemical processes led chemical reactions induced by the formation of radical species, mainly $^{\cdot}OH$,

from the scission of water when it acts as a solvent (Fischer et al. 1986). The kind of radicals formed depends on the kind of gas dissolved (Adewuyi 2001). Furthermore, cavitation modifies the chemical processes in the system, mainly enhancing the reaction rates of existing processes or starting new reaction mechanisms, by the formation of reactive radical species (Ince at al. 2001). Those statements could suggest dramatic changes in the parameters as temperature or the pressure of the bulk surrounding but this is not the case because the time scale for these micro-reactors is really small to affect the macroscopic system. However, they could affect cellular structures and enhance mass transport processes, like extraction.

From the effects so far mentioned, it appears that the use of ultrasound could be a promising way to introduce innovation into extraction processes.

2. Extraction processes of natural products.

In food engineering, the extraction of natural compounds appears to be of quite considerable interest mainly due to the properties of some natural extracts. Moreover, the extraction of bioactive compounds can increase the value of some food industry by-products, one example being the extraction of flavonoids from citrus peel that could be further exploited by both the pharmaceutical and food industries (Sun et al. 2011), another being the obtainment of natural extracts from marine sources (Ferraro et al. 2010), from the residues of the distillation of essential oils (Velickovic et al. 2008) or from apple pomace (Virot et al. 2010).

The extraction processes have been mainly focused on vegetal compounds. Plants contain a broad range of bioactive compounds such as lipids, phytochemicals, flavours, fragrances or pigments that are widely used in the food, pharmaceutical and cosmetic industries. The interest in those compounds has led to an increased need for better extraction methods, which could obtain the greatest possible amount of bioactive constituents in a shorter processing time and at a low cost. The extraction of antioxidants such as anthocyanins, flavonols, or phenolic acids has been specially addressed. The properties exhibited by polyphenols are of interest in the production of functional foods increasing their antioxidant activity and enhancing their biological benefits (Liazid et al. 2010). The extraction has also focused on natural additives, such as flavour from soy (Yang et al. 2011) or capsacinoids (Barbero et al. 2008) and colorants (Sivakumar et al. 2009). Furthermore, the extraction can also be used for the elimination of undesirable components in foods, for example, some aroma compounds (Abad Romero et al. 2010).

There are many extraction techniques, such as maceration, digestion, infusion, decoction, percolation, hot continuous extraction, counter-current extraction, supercritical fluid extraction, microwave assisted extraction, phytonic processes or ultrasound assisted extraction (Handa et al. 2008). The main differences among these techniques are related to the design of the reactors, the solvents used, the time and temperature of the

processes or the use of new technologies (microwave, ultrasound, supercritical fluids or the use of enzymes).

The conventional liquid–solid extraction techniques are laborious, time-consuming and often require large volumes of organic solvents (Wang and Weller 2006). Nowadays, the tendency is to use more environmentally friendly solvents such as alcohol-water mixtures, thus increasing the costs and lowering the extraction yield. Then, there is great interest in the development of efficient extraction methods.

The supercritical phase can be attained by increasing the pressure and temperature, reaching a state of aggregation at which no distinction between the gas and liquid can be observed (Starmans and Nijhuis 1996). The density of supercritical fluids is intermediate between gas and liquid and, therefore, its solubilising power is higher than gases. Their transport properties, as the lower viscosity and the higher diffusivity than liquid solvents, favor higher extraction yields by penetrating into porous solid materials more effectively than liquid solvents (Riera et al. 2004). The most common fluid used for supercritical fluid extractions is carbon dioxide, due to its low supercritical temperature and pressure and its quasi inert character (Sahena et al. 2009). Indeed, the extracted organic compounds are easily separated because carbon dioxide is a gas at atmospheric pressure and can, therefore, be recycled.

Ultrasound assisted extraction (USAE) has been used extensively in the last two decades as an efficient extraction method both in the food and pharmaceutical industries. The number of papers published in the last three decades related with this topic has suffered an exponential increase (Figure 1). According to the applied power, different effects may be sought. At low intensities, the external and, possibly, the internal mass transfer resistances are affected. Nevertheless, the product structure remains mainly unaffected. Intermediate intensities may affect the product structure thus increasing the effects on the internal mass transfer resistance. If ultrasonic power is further increased, cell disintegration can take place.

Nowadays, it is a powerful tool in extraction processes, even being the reference point for some extractive technologies in development (Chena et al. 2009). USAE has been used, for example, in the extraction of polyphenols from vegetal tissues (Ma et al. 2009), protein, sugar (Karki et al. 2010) and starch (Naguleswaran and Vasanthan 2010) from cereals and legumes, oil (Zhang et al. 2009), flavour compounds (Da Porto and Decorti 2009; Da Porto et al. 2009) from spearmint and lavanda. Sonication improves the extraction efficiency and rate, reduces the temperature needed, allows solvents to be saved and favours the solubilisation of the targeted compounds (Luque de Castro et al. 2007). The marked increase in the very local temperature enhances the solubility of the analytes (as in the case of lipids) in the solvent and eases their diffusion from the sample matrix to the outer region. On the other hand, the local pressure increase facilitates both the penetration of the solvent into the sample matrix and the transfer of compounds (Abad Romero et al. 2010). Moreover, the implosion of cavitation bubbles can hit the

surface of the solid matrix and disintegrate the cells (Figure 2) (Veillet et al. 2010). As a consequence of these effects, less extraction time is required than in conventional extraction processes. Thus, Roldán-Gutiérrez et al. (2008) showed that for the extraction of valuable compounds from aromatic plants and flowers, the USAE was faster than conventional steam distillation extraction in a range from 45 to 12 and from 9 to 2 times faster than supercritical water extraction. One of the main drawbacks of USAE, compared with carbon dioxide supercritical extraction, is the unavoidable use of organic solvents in some cases, but the equipment is simpler and the overall cost is lower (Abad Romero et al. 2010).

3. Main variables to be considered in USAE.

Besides innovation, the reliability and reproducibility of results, are among the main goals in any scalable process. In the case of USAE, it is necessary to consider the influence of process variables, such as ultrasonic power, frequency, temperature, reactor design, solvents, solvent-sample ratio or particle size and structure. Those variables may allow the identification of the scale factors which are necessary to be able to transfer the experimental conditions found in a laboratory to an industrial context. Moreover, it is necessary to consider that in extraction processes, the target of the process is not always to achieve the largest extraction yield (i.e. in maceration processes), but the lowest consumption of monetary and energy resources. Thus, optimization is an important step in the USAE processes. This has been extensively addressed in the literature, as can be seen in Table 1, where a collection of research work dealing with different USAE for natural compounds is summarized.

In addition to the previously mentioned variables, the pre-treatment, conservation and storage (Romdhan and Gourdon 2002) of the sample influence the extraction yield to a high extent and should also be carefully controlled. Domínguez et al. (1994) reviewed the beneficial effects of the enzymatic pre-treatment of fruits and oilseeds prior to conventional solvent extraction, concluding that shorter times can be achieved and the capacity of conventional equipment increased. In the same way, García-Pérez et al. (2010) pointed to the influence of the drying method used on grape stalk before the extraction of antioxidants. Thus, the extracts obtained from freeze dried samples presented the highest antioxidant capacity and, the extraction process involved, a higher effective diffusivity and mass transfer coefficient than conventionally dried samples. Extracts from hot air drying involved a lower antioxidant concentration and a slower extraction process.

3.1 Ultrasonic power.

The measurement of the actual acoustic energy applied in a sonochemical process is quite difficult and is not very often reported. Sometimes, considering the different power levels of the device, authors show the values of power applied as, for

example, “20 % of the total electric power capacity” and this is not an accurate measurement at all. In fact, in most of the ultrasound devices, the power measured is not proportional to the power step shown (Figure 3), leading to wrong conclusions or irreproducible results.

Several methods can be found in literature for the estimation of the acoustic energy transferred by measuring the physical or chemical changes occurring in solution due to ultrasound. Among the physical methods the direct measurement of the acoustic pressure using hydrophones (Martin and Law 1983) or optical microscopes, the aluminium foil method (Chivate and Pandit 1995) or the calorimetric method (Margulis and Margulis 2003) can be highlighted. The application of chemical methods is based on the indirect estimation of the $^{\cdot}OH$ radical formed by cavitation using measurements of the sonoluminiscence related to cavitation processes (Archley and Crum 1998) or the chemical dosimeters able to react with the radicals (Makino et al. 1982). The products formed (or reacting products) can be determined easily (i.e. by UV-Vis, fluorescence), as, for instance, in the case of luminol (Trabelsi et al. 1996), iodide (Entezari and Kruus 1994), phenolphtaleine (Rong et al. 2008), terephthalate (Mason et al. 1994) or 4-nitrophenol (Kotronarou et al. 1991), among others. Even knowing the ultrasonic power actually applied, it is difficult to compare the effects because often, the results are not only reported on a different basis, but are also influenced by the geometry of the reactor. For instance, to report data indicating only the power applied is not enough. Indicating the power density (Π; W / cm^3) is more appropriate, especially for the case of ultrasonic baths, where the whole bath volume should be considered, but the bath volume is usually a missing data in research papers, making it difficult to achieve reproducible results. In this paper, the value of Π will be given if it is possible to calculate it from the reported data, assuming anyway, that there is no homogeneity in the pieces of work found on the measurement of the applied ultrasonic power.

As previously stated, the effects of the applied power are different according to the applied power density. It is possible that the power density applied will not be enough to affect the external/internal resistance thus, a threshold will be observed. It should also be noticed that the power density is not the same for the whole volume, being the power density distribution in the stationary field an important factor to be considered. A different power distribution may be a source of disagreement among authors. A power density limit may also be observed once the cells have been disrupted and the ultrasonic effects will no longer increase. This could also be the case when it is only the external resistance that is affected. For instance, Cárcel et al. (2007b) observed an increase in solute gain and water losses for the osmotic treatment of apple in aqueous sucrose solutions at Π: 0.076 W / cm^3 (20 kHz), thus indicating a decrease of internal/external resistance due to ultrasound. On the other hand, when using Π: 0.107 W / cm^3 (20 kHz) in meat brining processes, Cárcel et al. (2007a) found that the amount of salt in the meat increased, but so did the moisture. That points to a different influence of the ultrasound in the mass

transfer process. In this case, the microinjection of brine inside the meat could explain the observed increase in both salt and moisture content.

The extraction yield usually increases in line with the power intensity applied, sometimes linearly. This was observed by Zou et al. (2010) working on the extraction of melanin from *Auricularia auricula* applying ultrasonic power density from 3.33 to 8.33 W / cm^3 (frequency: 40 kHz; solvent: water pH 12; extraction temperature: 60 ºC; extraction time: 30 min; ratio raw material/solvent: 1g / 30 mL). In the case of the USAE of geniposide from gardenia fruit (frequency: 18 kHz; water as solvent; extraction temperature: 20 ºC; extraction time: 160 min; ratio raw material/solvent: 1g / 40 mL) Ji et al. (2006) demonstrated that stirring had no effect on the total extraction, but ultrasound intensified both the mass transfer in the liquid film around fruit particles and intraparticle diffusion. The external mass transfer coefficient and the intraparticle diffusion coefficient increased in line with an increase in ultrasonic intensity. Stirring could intensify the external mass transfer, but had no effect on the intraparticle diffusion.

However, some systems could present a power plateau, as the results obtained by Zhao et al. (2007) indicate. In this work, it was observed that for the extraction of saikosaponins from *Radix Bupleuri (*frequency: 20 kHz; solvent composition: 70/30 v/v ethanol-water; extraction temperature: 80 ºC; extraction time: 30 min; ratio raw material/solvent: 1g / 25 mL), at Π of above 0.28 W / cm^3, no increase of the yield of extraction was found. Less usual was the effect found by Ma et al. (2008) for the extraction yields of hesperidin from Penggan peels (frequency: 100, 20 and 40 kHz; methanol as solvent; extraction temperature: 40 ºC; extraction time: 5 min; ratio raw material/solvent: 1g / 40 mL) where the applied ultrasound power had only a slight effect on the yield of hesperidin, achieving similar results for the different acoustic power intensities applied (3.2, 8, 30 and 56 W). These results point to the existence of thresholds depending on the material treated.

In some cases, the proper use of the pulse mode of ultrasound can replace continuous irradiation by ultrasound in order to obtain better extraction yields, as in the case of the extraction of colorants from beetroot (Sivakumar et al, 2009), or to reduce the electrical energy consumption (Sun et al. 2011).

The applied power not only greatly influences the total amount of compounds extracted, but can also affect the proportion of species extracted because there is an effect on the extraction rate. In this sense, Wei et al. (2010) (frequency not shown; water as solvent; extraction temperature: 25 ºC; 50 g / 400 mL; 5 min followed re-sonication in 300 mL, 5 min), observed that the percentage of neutral polysaccharides obtained from tea flower decreased while increasing the applied power, rising from 100 to 300 W, but no influence was found on the total amount of polysaccharides or the acidic ones.

Therefore, considering all the parameters mentioned, it is apparent that the applied ultrasonic power can have a great influence on the extraction, not only increasing the extraction yield at shorter times, but also modifying, in some cases, the proportion of final

products. Researchers/processors should carefully evaluate the kind of characterization control that should be carried out in their system in order to achieve reproducible results in different devices for every single extraction problem, and check the ultrasonic power applied.

3.2 Ultrasonic frequency.

It is known that the lower the frequency, the larger the cavitation bubble. So, the lower frequencies of high power ultrasound (around 20 kHz) achieve more violent bubble implosions, and consequently, are more efficient in extraction processes. As far as the extractive system is a heterogeneous and complex porous media, the effect the bubble size has on the efficiency of the extraction should be addressed. The frequency effect may be linked not only to the cavitation bubble size, but also to its influence on the external and internal resistances to mass transfer. Although the subject has not been addressed in extraction studies, it has been found in drying. In that process the solid structure/porosity plays a key role on the effects derived from ultrasonic application.

There are few comparative studies related to the frequency effects in extraction processes, but Ma et al. (2008) observed that for the same applied power, the best frequency for the extraction of hesperidin from peengan peel was 60 kHz, instead of 20 or 100 kHz. Dong et al. (2010) observed the extraction yields of salvianolic acid B from *Salvia miltiorrhiza* root (solvent composition: 60/40 v/v ethanol-water; extraction temperature: 30ºC; ratio raw material/solvent: 1g / 20 ml; extraction time: 25 min; power applied: 100 W) under different ultrasound frequencies (28, 45 and 100 kHz), in a cleaning bath. The extraction yield under the highest frequency was lower than those under lower frequencies. So, there could exist an optimal frequency for the extraction related to the specific textural properties of any complex matrix.

2.3. Temperature.

Since temperature affects the physical and chemical characteristics of a product and the effects of ultrasound are linked to product characteristics, temperature appears to be a key variable. This is especially true if some compounds are temperature sensitive or volatile. For the simultaneous extraction of phenolic compounds from citrus peel (frequency: 60 kHz; solvent: methanol; extraction time: 60 min; ratio raw material/solvent: 2g / 40mL; Π: 0.2 W / cm^3) using USAE, Ma et al. (2009) observed a reduction in the extraction yield of phenolic compounds and long extraction time at high temperatures. This is probably due to thermal degradation or polymerization reactions of phenols themselves. It was found that the maximum extraction yield was achieved at significantly different temperatures for each compound in the mixture.

In general, the increase of the extraction temperature enhances the mass transfer. Nevertheless, the temperature increase produces less cavitational energy conversion due to the decrease in surface tension and the increase in vapour pressure

(Kuijpers et al. 2002). However, usually, the observed increase in the extraction yield may be linked to the increase of the solvent diffusivity into the cells and the enhancement of desorption and solubility. Hemwimol et al. (2006) observed this behaviour in the USAE extraction of anthraquinones from roots of *Morinda citrifolia* (frequency: 38.5 kHz; solvent: ethanol; extraction time: 90 min; ratio raw material/solvent: 0.1 g / 10 mL; Π: 0.007 W / cm^3). At 45ºC and 60 ºC, the initial extraction rate was so high that the extraction yield remained almost constant after 30 minutes of USAE. This yield value could not be reached when working at 25 ºC, even in USAE periods of 90 minutes, and a slow extraction rate was evidenced.

It is also common to observe a decrease in the yield as the temperature rises, especially in the case of unstable or volatile compounds. During the USAE of epimedin C from fresh leaves of *Epimedium* (frequency: 24 kHz; solvent: methanol; extraction time: 25 min; ratio raw material/solvent: 1g / 30 mL; Π: 0.44 W / cm^3) the extraction yield rises as the extraction temperature goes up from 15 to 45 °C, at this temperature reaching the peak value (Zhang et al. 2009). However, when the extraction temperature was above this threshold temperature (45 °C), the extraction yield decreased. Furthermore, the use of higher temperatures above the threshold temperature might result in the acceleration of solvent volatilization, higher energy costs and the enhancement of the extraction of impurities.

As it could be infer from the previous comments, the optimum values of the operational variables are interrelated. Therefore the higher boiling point of some solvents permits the use of higher temperatures (limited by the product stability) and so, a greater efficiency could be achieved. Thus, an optimum extraction temperature value exists at which the extraction yield can reach its maximum level, and this temperature value may be different if other working parameters change, i.e. the applied power, the kind or the amount of solvent. Thus, a multivariate optimization of the process is recommended.

3.4 Reactor characteristics.

The design of the reactor is an important factor to be taken into account. Thus, in the early years of sonochemistry, experiments were performed in open flasks immersed in ultrasonic cleaning baths and it could be observed how important the accuracy of the geometry of the reactor is for the reproducibility of the results (Weissler et al. 1950). Advances in the construction of acoustic generators allowed the use of transducers that were dipped directly in the bulk solution. This technique allowed higher energy to be transmitted into the medium, but it increases the chance that the samples may be contaminated with undesired materials (mainly from the degradation of the ultrasonic probes). In this approach, the study of the chemical and physical compatibility of all the materials and chemicals involved is mandatory. Further advances have been made by taking into account the lack of homogeneity of the pressure field in the reactor in order to optimize the process efficiency. It is necessary to calculate the optimum reactor dimensions and the position of the elements inside in relation to the transducer to attain

the maximum energy transferred to the fluid (Esclapez et al. 2010). For that purpose, it is necessary to test different dimensions of the reactor and the relative position of the transducers. Mapping techniques that allow the identification of the position where cavitational effects are at their maximum can be used (Kanthale et al. 2003).

Some authors have optimized their designs by taking into account the effect of tip immersion in extraction flasks, obtaining substantial differences in the results. During the extraction of all-trans-β-carotene from citrus peels, Sun et al. (2011) observed that the extraction yield decreased significantly with an increase in the liquid height. For this purpose, an ultrasonic tip was immersed 1 mm in a tube containing the sample liquid (3 cm diameter, 10-20 cm of height). Under USAE, the extraction yield at heights of 2 cm and 12 cm were, respectively, 84.5% and 12.3% higher than the extraction yield for conventional extraction (2.51 µg / g). However, for those kinds of experiments, the power density should remain constant for valid results just related to geometry, maintaining the applied power/volume ratio, changing the geometry of the flask, or alternatively, the total applied power. The same happens in ultrasonic baths, where it is known that the acoustic stationary field is inhomogeneous and affected by the liquid height (Mulet et al. 2003).

Nowadays, the most widely used extraction systems on laboratory scale are ultrasonic baths or probes working in batch or in flow mode (Figure 4). Efforts have been made to systematically characterize sonoreactors (Sáez et al. 2005a; Sáez et al. 2005b), even developing several numerical simulation models for the behaviour of systems with different geometries (Louisnard et al. 2009). Some research groups use continuous, specifically designed, devices for leaching with an optimized alternating solvent flow direction like the one used by Roldán-Gutiérrez et al. (2008) for the extraction of polyphenols from vegetal tissues. In that case, the sample was placed in a leaching chamber connected to the manifold flow and immersed in a transmitting fluid where the ultrasonic probe is dipped. Other groups have adapted this same idea, but by immersing the cell in an ultrasonic bath (Lou et al. 2010). That approach has focused mainly on the improvement of analytical procedures, but is an interesting first step for the scale-up. For the next few years expect to witness further research in this area, bearing in mind that the interaction between the pressure map inside a reactor and a coupled hydrodynamic flow is now under research with the aim of building more efficient sonoreactors (Esclapez et al. 2010). In any case, the reactors must be carefully characterized in order to provide useful and reproducible results.

3.5 Solvent-sample interaction.

Careful consideration should be given to the choice of an appropriate solvent because the optimum solvent for traditional extractions may not be the best for USAE. Solvent selection is usually based on achieving high molecular affinity between the solvent and solute, but factors affecting cavitation, such as solvent vapour pressure or surface tension, need to be considered as well (Li et al. 2004). At high vapour pressures, the volatilized solvent will penetrate the cavitation bubbles more easily, cushioning their

collapse (Price 1990). In this sense, cheaper solvents such as water mixtures could work better than traditional volatile pure solvents used for conventional extraction.

For a fixed amount of solid matrix, the more solvent used, the greater concentration gradient effect is achieved between the vegetal issue and the solvent, thus obtaining a faster extraction rate (Stanisavljevic et al 2007). However, for large solvent/solid ratios the improvement in extraction is negligible because the increase in the gradient is also negligible (Yang and Zhang 2008) and more time and energy consumption are needed for post-treatment concentration. Nevertheless, Barbero et al. (2008) found no influence of the solvent/solid ratio in the USAE of caspsacinoids from pepper (frequency: not shown; extraction temperature: 50ºC; solvent: methanol; extraction time: 10 min; raw material: 1 g; power applied: 360 W in ultrasonic bath). For that purpose, extractions were carried out with different volumes (15, 25, 40 and 50 mL). No statistical differences in the extraction yield were found for the extraction volumes tested. Those results may be linked to fast extraction kinetics or long observation times that did not permit distinguish among treatments. Nevertheless, in this case, the lower solvent ratio should be chosen.

The extraction yield can be influenced by the particle size too, because extraction is linked to the surface exposed and the length of the path that the molecules should move along. In the extraction of oil from tobacco seeds (frequency: 40 kHz; extraction temperature: 25 ºC; solvents: hexane or petroleum ether; extraction time: 60 min; raw material/solvent volume ratio: 1g / 3 mL; power applied: 150 W in an ultrasonic bath), it was observed that the highest extraction yield was achieved for particle size 0.4 - 0.5 mm (Stanisavljevic et al. 2007). The oil yield from the largest particles (>0.5 mm) class was lower than that from the small ones for the same period of time. The authors concluded that a smaller amount of oil could be transported from the interior of larger seed particles to the bulk of liquid extract compared to the smaller ones, due to a greater resistance to the oil transport, linked to longer paths. Other authors (Zhao et al. 2007) found the same behaviour in their system, also suggesting that when the particle is small enough, most of the cell walls are broken by the application of ultrasound, and diffusion would not be a significant step in the extraction of such small particles. A further decrease in the size would not result in a corresponding increase in the extraction rate.

4. Extraction optimization.

For any extraction process there is an optimum extraction time. Beyond this time, the extractable compounds of interest can be degraded or the achieved yield does not compensate the energy and processing costs. The intention behind the use of ultrasound is that it achieves very high extraction efficiency at the beginning of the process (Orozco-Solano et al. 2010). An example of this approach was described by Wang et al (2008) when studying, in the optimization of the USAE of phenolic compounds from wheat bran (frequency: 40 kHz; extraction temperature: 50 ºC; solvent: 70% (v/v) ethanol; raw

material/solvent volume ratio: 5 g / 100 mL; Π: 0.025 W / cm^3), different extraction experiments with 5.0 g of wheat bran macerated and sonicated for times ranging from 10 to 50 min. A marked increase of the total phenolic content was observed up to 30 min, then remaining constant until 50 min. Then, the use of ultrasound could be a good way to increase the extraction yield in the first stage of the process, which is quite appealing for industrial applications. Despite the great amount of interest in optimizing the operation for industrial purposes, few USAE kinetics for natural products can be found in the literature, this being a field of research that, in the future, should be paid attention.

5. Industrial approaches.

Soria and Villamiel (2010), considered that, of all the applications of high power-low frequency ultrasound in the food industry, ultrasound assisted extraction is the most feasible and economically profitable in the large scale. It is easy to install, has competitive energy costs and is low maintenance, mainly due to the absence of moving pieces as in the mechanical stirring methods. However, as was previously shown, it is not a standard technology and the optimisation of all the considering variables implied in the process is necessary. For that purpose, it is important to analyse and to optimize the laboratory scale extraction process as a first step and consider the research and development for every single application because the processes are case sensitive. For this reason, the particular scale-up studies could be a profitable source of patents. Scale-up effects were reported by Boonkird et al. (2008). They found an important decrease in the process yield for the extraction of capsaicinoids from *Capsicum frutescens* when moving from laboratory to pilot plant scale. This was a consequence of important changes in the operational parameters of particle size, power, frequency, geometry and mixing efficiency, although the kind of solvent, the solvent to material ratio and temperature were the same.

There are not many reports on industrial applications for reasons of confidentiality, but Patist and Bates (2008) described an example of the industrial application of the USAE technology. They reported that the initial investment of 700 k$ was paid back in only four months and represented a 2,000 k$ gain per year, just for increasing the extraction yield of a natural product. However, the process was not specified. Another Australian company reported payback for the implementation of the USAE extraction of grape colour and flavour for must after two years, not only increasing the extraction yield by 30 %, but also the quality of the organoleptic properties of the final product (Cavitus 2009). Another example of an industrial ultrasonic reactor was designed and built in Romania for the extraction and preparation of tinctures from various herbs (Vinatoru 2001). Using this reactor, the solvent extraction time of medicinal compounds from various plant sources could be shortened from 28 days to around 10 h (Leonelli

2010). Ultrasound equipment manufacturers offer a wide range of devices for different applications, sometimes on an industrial scale (Hielscher 2011, Meinhardt 2011).

6. Future prospects.

As has happened in other fields of ultrasound applications, research is expected into the new possibilities of hybrid ultrasonic technologies in the extraction of natural products. Some successful attempts have been made, such as the combination of ultrasound assisted extraction with supercritical carbon dioxide extraction. Riera et al. (2004) implemented this technology for the extraction of almond oil using an ultrasonic transducer working at 20 kHz located inside a high-pressure extractor operating with CO_2 at 280 bar and 55 ºC (Figure 5). The results showed that not only was the kinetics faster, but the extraction yield of the oil was enhanced by 20% to 30%. These improvements may be attributed to an increase in the mass transfer coefficient.

This attempt was later scaled up (Riera et al. 2010) to a pilot-plant scale, tested and validated for cocoa cake oil extraction. The power ultrasonic system operated automatically during the extraction process, meaning that no manual intervention by an external operator is required and the performance, reliability and stability of the process are good. The encouraging results support the need for further experimental and theoretical research into this new, promising field.

Microwave has also been used in combination with ultrasound in extraction processes, either applied simultaneously or in serial disposition. Lianfu and Zelong (2008) optimised an ultrasound-microwave extraction method for the extraction of lycopene from tomatoes. A microwave oven with a maximum power of 800 W at a frequency of 2450 MHz, and an ultrasonic transducer with a fixed power of 50 W at a frequency of 40 kHz were used simultaneously, the solvent being ethyl acetate. Under the optimum conditions for the hybrid method they achieved a recovery of 97.4 % in 6.1 min, improving the best result for USAE, which was 89.4 % in 29.1 min. For the extraction and drying of isoflavonoids from *Pueraria,* a serial disposition was used (USAE followed by microwave drying) (Hu et al. 2008). The time required for the extraction was 20 times shorter than the conventional reflux extraction methods were used. Although it cannot be considered as a hybrid approach for the serial design, it is remarkable that the combination of these emerging technologies is leading to significant advances in the attainment of processes that are safer and less time and energy consuming.

7. Final remarks.

It has become more and more commonplace to use USAE in the food industry as the technique for extracting natural valuable compounds thanks to its easy installation and maintenance costs which can be paid back in a short time. It requires less energy and solvent usage and is easier to handle.

The variables of the process have a strong influence on the extraction yield and may be first optimized in a laboratory step for any process. One of the key points for the scale up and development of the technique is the establishment of a valid method for the characterization of the power applied and the design of a well-defined reactor. The research in the scale-up, the design of improved sonoreactors and the combination with other techniques is expected to significantly enhance the development and commercialization of this technique.

Although this article is mainly focused on food products, they could be easy extrapolated to the pharmaceutical industry.

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Figure Captions

Fig. 1 Number of peer reviewed articles published in the last 30 years dealing about ultrasound assisted extraction in food science (www.sciencedirect.com 2011).

Fig. 2 Schematic representation of the rarefaction (A) and compression cycle (B) of a cavitating bubble that eventually collapses near the solution/biological tissue interface generating shock waves and micro-jets (C) that can disrupt the cell wall releasing the intra cellular material into the solution (D).

Fig. 3. Relationship between the percentage of electrical input to the ultrasonic generator and ultrasonic intensity measured using a calorimetric method in a sucrose solution of 30 Brix at 30 ºC. From (Cárcel et al. 2007b)

Fig. 4 Most typical reactor configurations: ultrasonic bath (a), transducer dipped in batch configuration (b), transducer immersed in a flow reactor (c). From González-García et al. (2010).

Fig. 5 Scheme of the supercritical fluid extractor coupled with an ultrasonic transducer. Adapted from Riera et al. (2004).

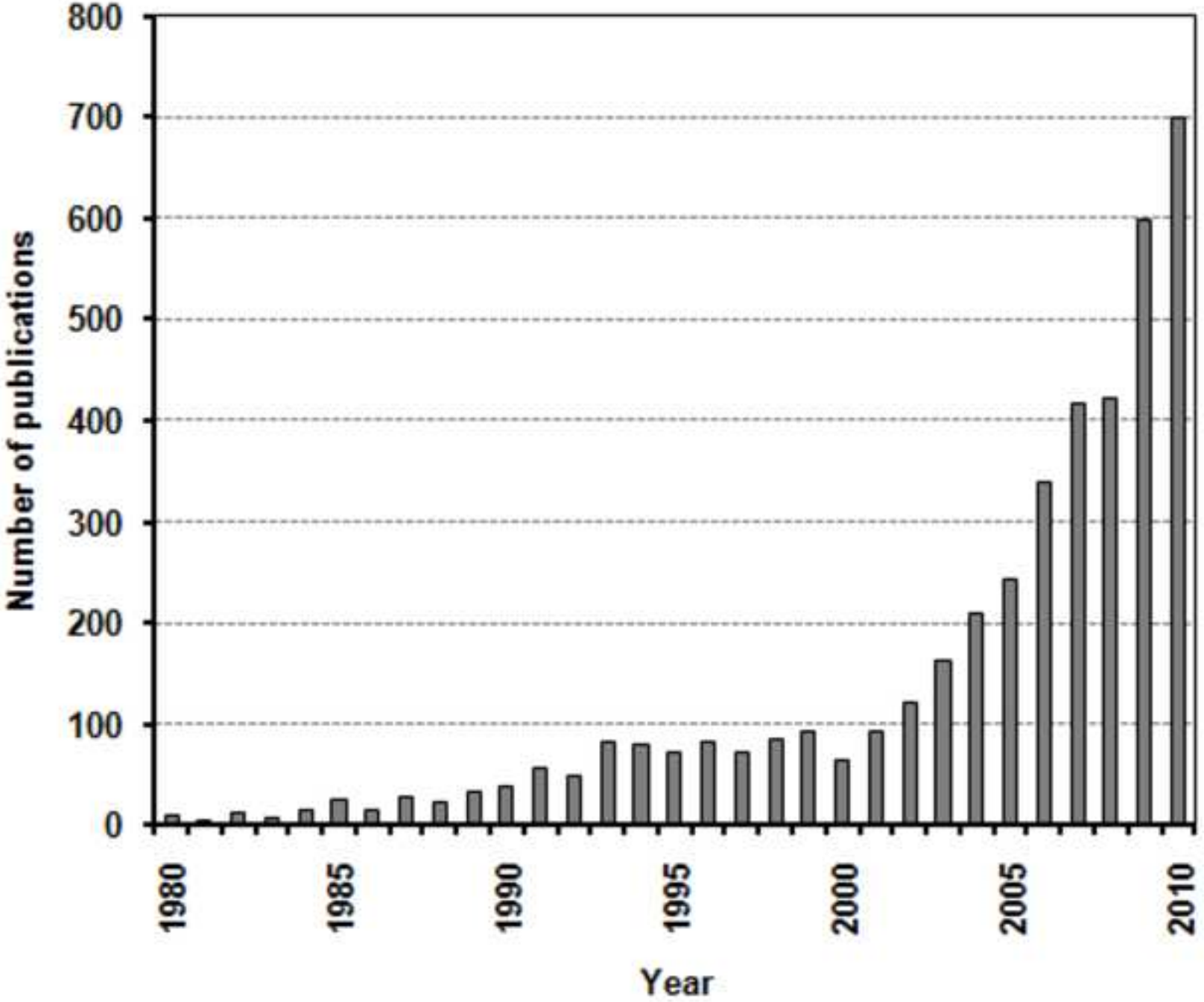
Table

Table 1. Operating conditions for the extraction of some natural compounds.

Extract	Raw material	Freq. (kHz)	Π (W/cm^3)[b]	t (min)	T (ºC)	Raw material/total solvent ratio	Solvent	Equipment	Extraction yield	Reference
Total carbohydrates	Stevia	20[a]	0.06	32	68	100g dry/1 L[a]	Water, pH 7[a]	2	17 g/100g	Liu et al. 2010
Flavonoids	Citrus peel	60	**	30	40	1 g dry/10 mL	basified water	1	40 mg/g	Londoño-Londoño et al. 2010
Oil	Chickpea	40[a]	250 W	20	50	1 g/8.5 mL	3:1 hexane-isopranol	3 (5mL/min flow)	81% of soxhlet leaching	Lou et al. 2010
Salvianolic acid B	Salvia miltiorrhiza root	45[a]	100 W[a]	28	30	1 g/20 mL	60:40 EtOH-H_2O	1	33.9 mg/g[1]	Dong et al. 2010
Equiv. catequin	Apple pomace	24[a]	0.142 W/g	45	40.1	15 g/100 mL	1:1 EtOH-H_2O	1	964 mg/100 g	Virot et al. 2010
Dye	Beetroot	20[a]	1.6	180	45 [a]	1 g/50 mL[a]	1:1 EtOH-H_2O	1	0.19 g/g	Sivakumar et al. 2009
Cinnamic acids	Citrus peel	60[a]	0.02	40	30	2 g/40 mL[a]	4:1 EtOH-H_2O	1	Depending on compound	Ma et al. 2009
Benzoic acids	Citrus peel	60[a]	0.02	10	40	2 g/40 mL[a]	4:1 EtOH-H_2O	1	Depending on compound	Ma et al. 2009
Proteins	Defatted wheat germ flour	20[a]	7.26	24	Ice bath[a]	0.5 g/50 mL[a]	Reverse micellar solution	2 (pulsed 2.4s:2s)	57 %	Zhu et al. 2009[1]
Phosphatidylethanolamine	Palm-pressed fiber	24[a]	1.53	30	25[a]	15 g/60 mL	1:3 $HCCl_3$-MeOH[a]	2 (pulsed 0.2 W / s)	12570 mg/kg	Chea Chua et al. 2009
Phosphatidylcholine	Palm-pressed fiber	24[a]	1.53	30	25[a]	15 g/60 mL	1:3 $HCCl_3$-MeOH[a]	2 (pulsed 0.2 W s^{-1})	5426 mg/kg	Chea Chua et al, 2009
Vainillin	Vanilla pods	22.4[a]	2.40	60	Water bath[a]	0.5 g/100 mL	1:1 EtOH-H_2O	2 (pulsed 5 s:5 s [a])	140 ppm in leachant	Jadhav et al. 2009
Phenolic compounds	Wheat bran	40[a]	0.025	25	60	5 g/100 mL	64:36 EtOH-H_2O	1	3.12 mg gallic ac. equiv/g	Wang et al. 2008
Oil	Flaxseed	20[a]	50 W	30	30	16.7 g/100 mL	n-hexane	2	85 % of soxhlet leaching	Zhang et al. 2008
Nordihydrocapsaicin	Cayenne	**[a]	360 W[a]	10	50	1 g/25 mL	MeOH	1	94 μmol/kg	Barbero et al. 2008

Extract	Raw material	Freq. (kHz)	Π (W/cm^3)[b]	t (min)	T (ºC)	Raw material/total solvent ratio	Solvent	Equipment	Extraction yield	Reference
Nordihydrocapsaicin	Bolilla Redondo pepper	**[a]	360W[a]	10	50	1 g/25 mL	MeOH	1	40 μmol/kg	Barbero et a.l 2008
Nordihydrocapsaicin	Bolilla Largo Pepper	**[a]	360 W[a]	10	50	1 g/25 mL	MeOH	1	25 μmol/kg	Barbero et al. 2008
Capsaicin	Cayenne	**[a]	360 W[a]	10	50	1 g/25 mL	MeOH	1	448 μmol/kg	Barbero et al. 2008
Capsaicin	Bolilla Redondo pepper	**[a]	360 W[a]	10	50	1 g/25 mL	MeOH	1	370 μmol/kg	Barbero et al. 2008
Capsaicin	Bolilla Largo pepper	**[a]	360 W[a]	10	50	1 g/25 mL	MeOH	1	275 μmol/kg	Barbero et al. 2008
Dihydrocapsaicin	Cayenne	**[a]	360 W[a]	10	50	1 g/25 mL	MeOH	1	265 μmol/kg	Barbero et al. 2008
Dihydrocapsaicin	Bolilla Redondo pepper	**[a]	360 W[a]	10	50	1 g/25 mL	MeOH	1	190 μmol/kg	Barbero et al. 2008
Dihydrocapsaicin	Bolilla Largo pepper	**[a]	360 W[a]	10	50	1 g/25 mL	MeOH	1	122 μmol/kg	Barbero et al. 2008
Essential oils	Laurel	20[a]	45 W[a]	10	25	1 g/8.5 mL	EtOH	3 (pulsed 30%[a], 4 mL/min),	Depending on compound	Roldan-Gutierrez et al. 2008
Hesperidin	Penggan peel	60	3.2	60	40	1 g/40 mL	MeOH	1	57 mg/g	Ma et al. 2008
Rutin	Euonymus alatus	50[a]	0.05[a]	30(x3)	Amb.[a]	0.5 g/20 mL	70:30 EtOH-H_2O	1	0.299 mg/g	Yang et al. 2008
Quercetin	Euonymus alatus	50[a]	0.05[a]	30(x3)	Amb.[a]	0.5 g/20 mL	70:30 EtOH-H_2O	1	0.013 mg/g	Yang et al, 2008

[a] Non-optimized value.
[b] Π was calculated when possible. In other cases, total power applied is shown, (W).
1 Ultrasonic cleaning bath.
2 Ultrasonic probe.
3 Specifically designed reactor.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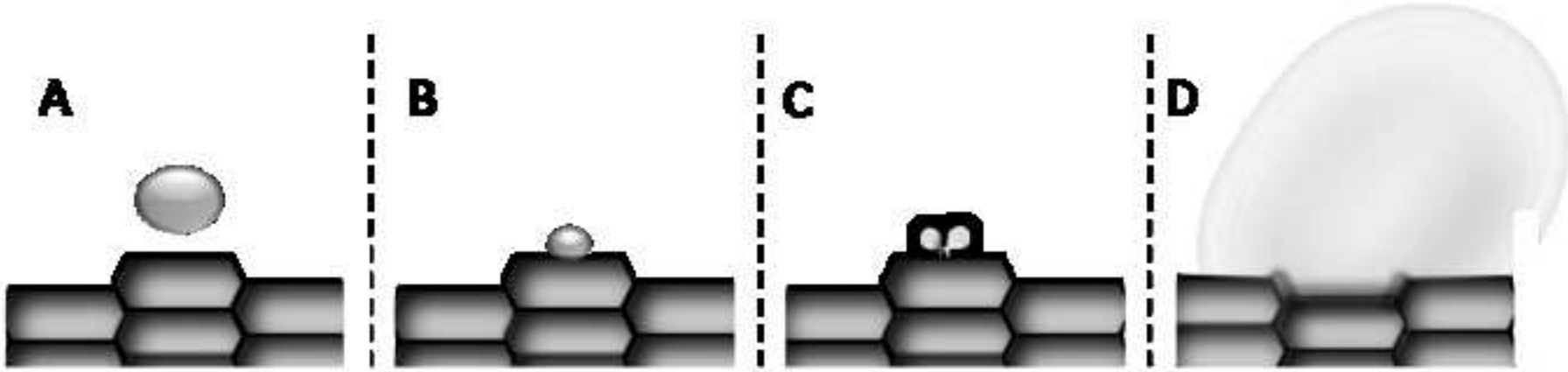
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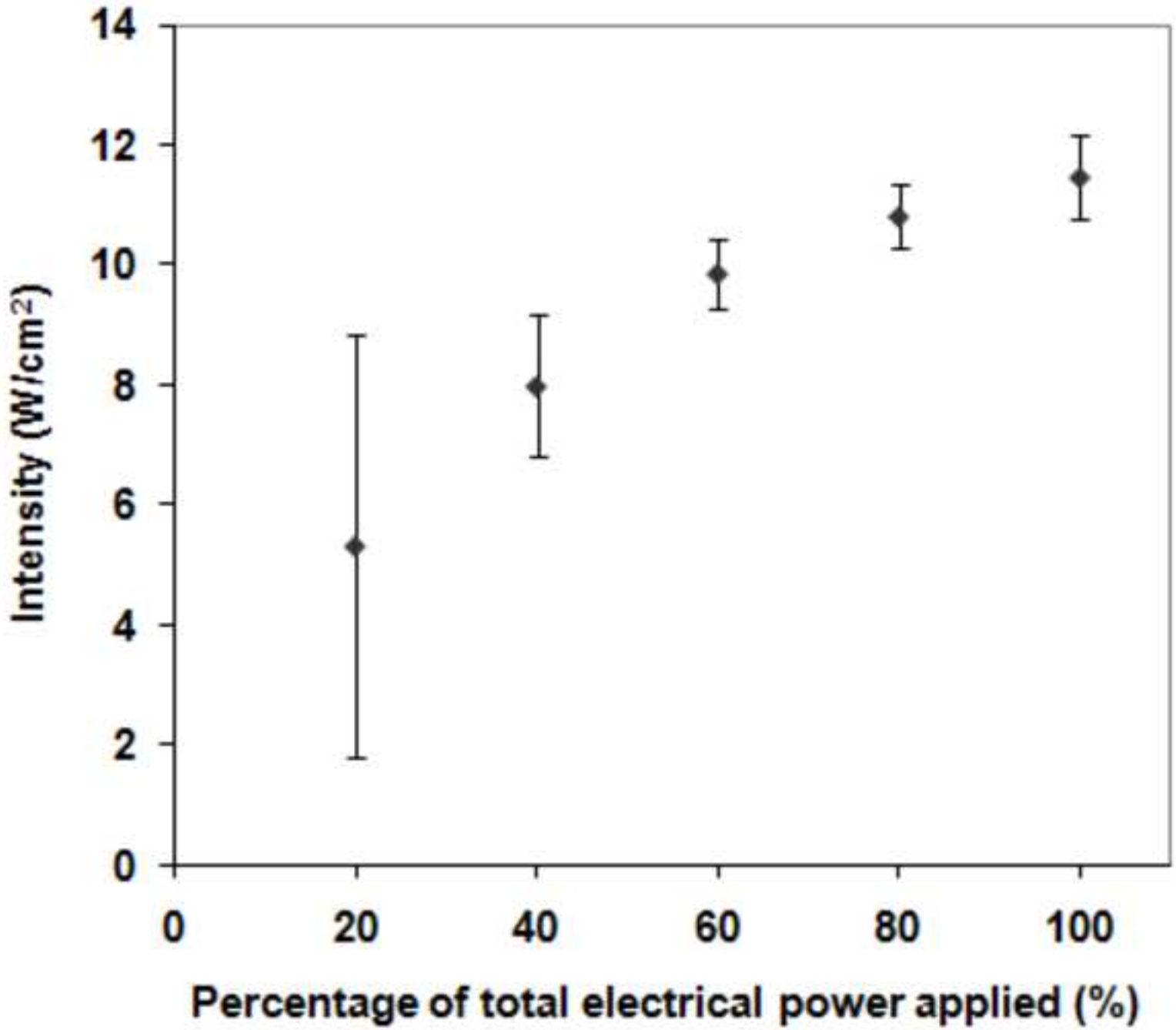
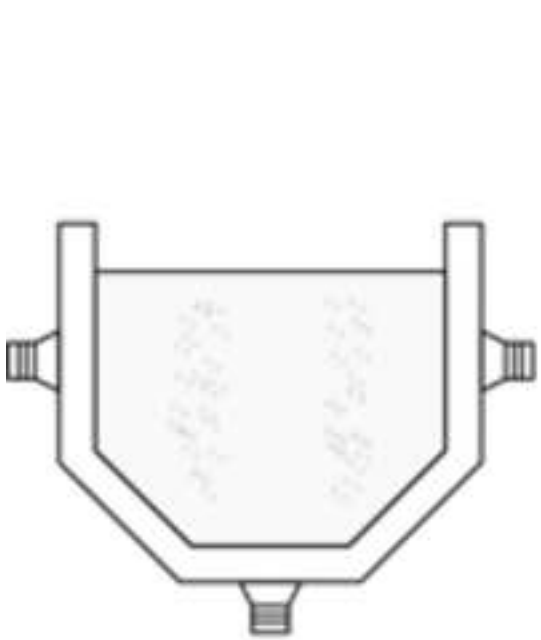
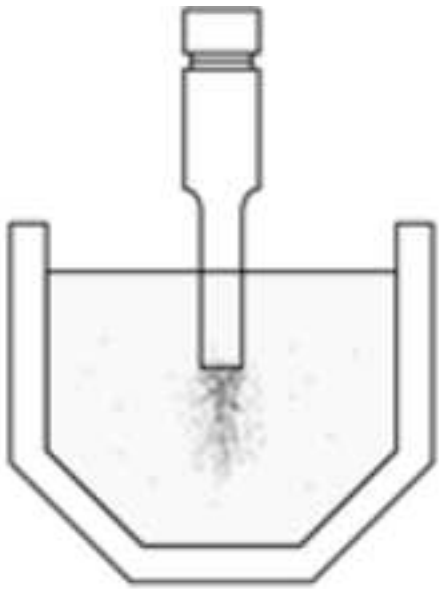
D

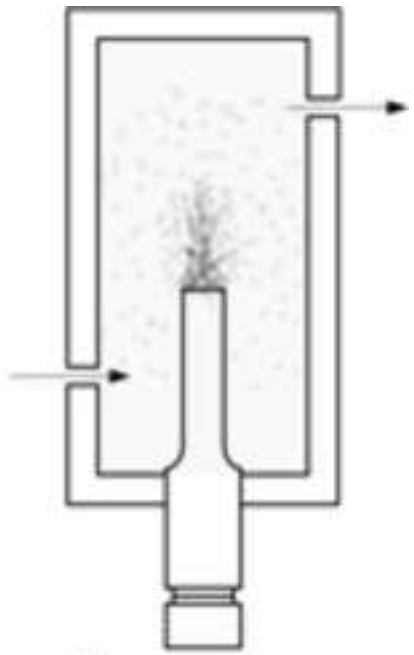

14
12
10
8
6
4
2
0
Intensity (W/cm²)
0
20
40
60
80
100
Percentage of total electrical power applied (%)



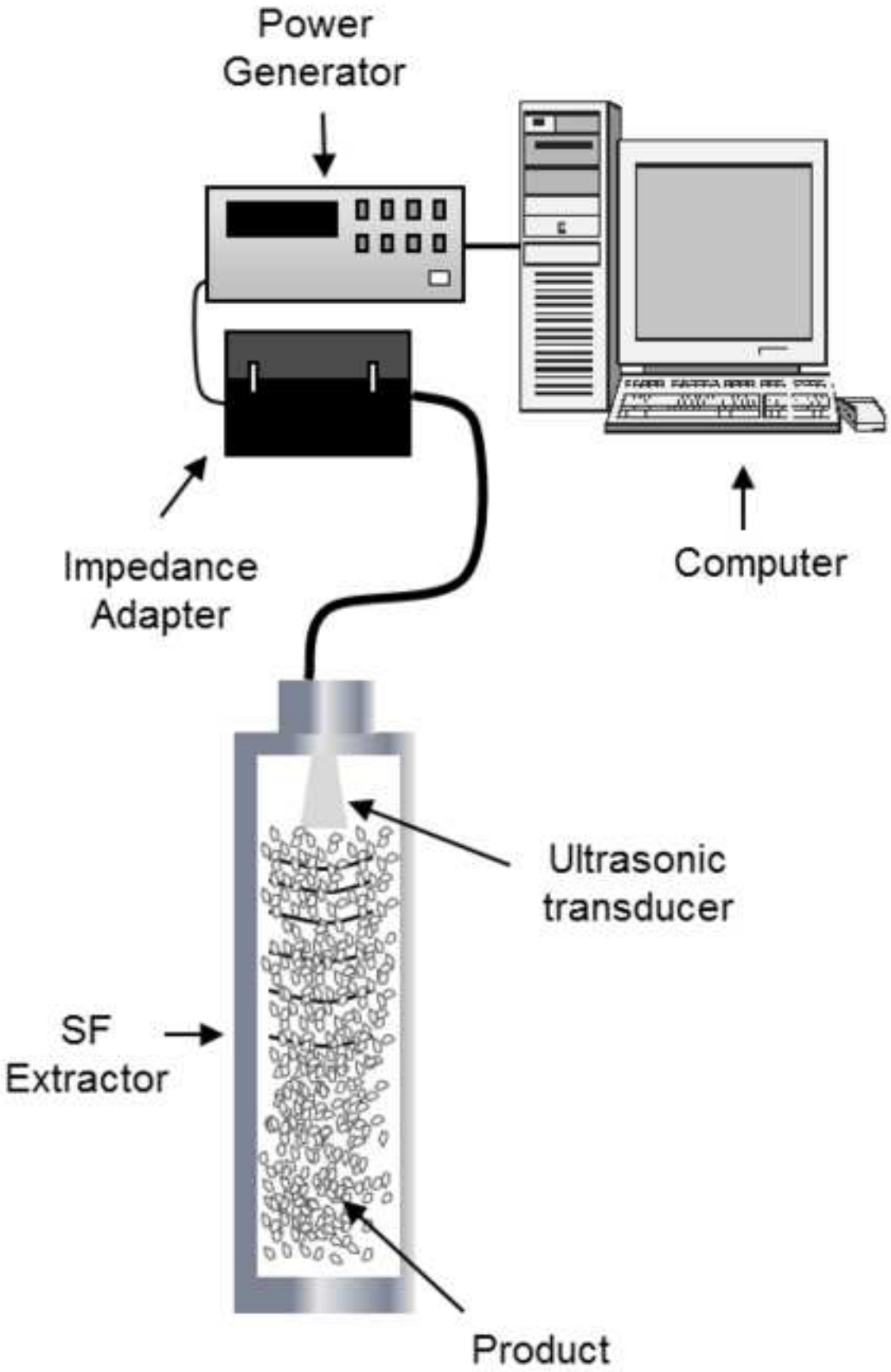
a



b



c


Power
Generator
Impedance
Adapter
Computer
Ultrasonic
transducer
SF
Extractor
Product