1
The Power of Ultrasound

Hugo Miguel Santos, Carlos Lodeiro, and José-Luis Capelo-Martínez

1.1
Introduction

During the last 20 years we have witnessed an amazing increase in the application of ultrasonic energy in different fields of science. This is especially true for analytical chemistry. The number of manuscripts devoted to almost all kinds of analysis dealing with the uses of ultrasonic energy continues to grow year by year. As the uses of ultrasonication have become increasingly important in analytical chemistry so to has the importance of the type of ultrasonic device chosen to work with. Figure 1.1 shows the most common ultrasonic devices used nowadays in analytical applications. Not all devices perform equally and neither are all intended for the same applications. Therefore, the first thing to acquire when developing analytical chemistry with the aid of ultrasonication is a knowledge of the differences among the ultrasonic apparatus available, especially of the advantages and disadvantages expected for each one. Therefore, this chapter explains the state-of-the-art of ultrasonic technology as applied to analytical chemistry.

1.2
Cavitation

Sound, including ultrasound, is transmitted through any physical medium by waves that compress and stretch the molecular spacing of the medium through which it passes. As the ultrasound cross the medium (Figure 1.2) the average distance between the molecules will vary as they oscillate about their mean position. When the negative pressure caused for an ultrasonic wave crossing a liquid is large enough, the distance between the molecules of the liquid exceeds the minimum molecular distance required to hold the liquid intact, and then the liquid breaks down and voids are created. Those voids are the so-called cavitation bubbles [1–3].
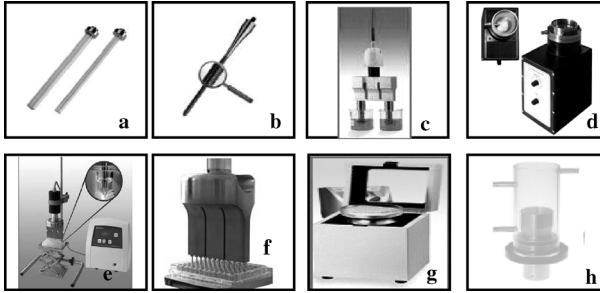
Figure 1.1 Advances in ultrasonic technology: (a) silica glass probe; (b) spiral probe; (c) dual probe; (d) sonoreactor; (e) and (f) multi probe; (g) microplate horns; (h) cup horns. Parts (a,b,e,f and h) are reproduced with permission of the Bandelin company; part (d) is reproduced with permission of the Dr Hielscher company; (c) and (g) are reproduced with permission of Misonix company. Adapted from Ref. [13].

As the liquid compresses and stretches, the cavitation bubbles can behave in two ways [1]. In the first, called stable cavitation, bubbles formed at fairly low ultrasonic intensities (1–3 W cm^{-2}) oscillate about some equilibrium size for many acoustic cycles. In the second, called transient cavitation, bubbles are formed using sound intensities in excess of 10 W cm^{-2}. Transient bubbles expand through a few acoustic cycles to a radius of at least twice their initial size, before collapsing violently on compression (Figure 1.2).
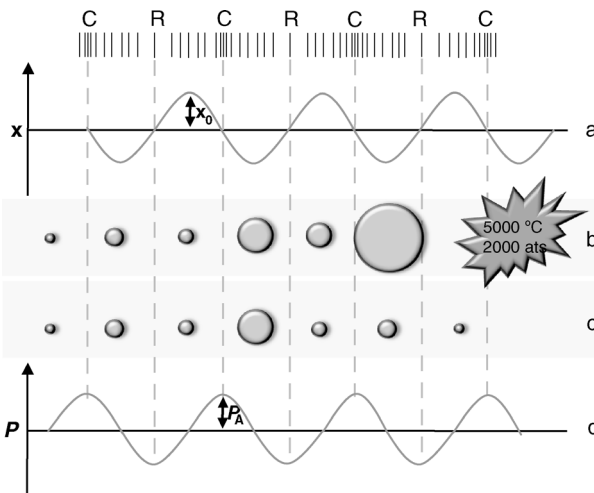
Figure 1.2 Creation of stable cavitation bubbles and creation and collapse of transient and stable cavitation bubbles. (a) Displacement (x) graph; (b) transient cavitation; (c) stable cavitation; (d) pressure (P) graph.

Transient bubble collapsing is considered to be the main source of the chemical and mechanical effects of ultrasonic energy. Each collapsing bubble can be considered as a microreactor in which temperatures of several thousands degrees and pressures higher than one thousand atmospheres are created instantaneously [4].

From an analytical chemistry point of view, most of the effects of interest regarding ultrasonication are related to cavitation. Cavitation causes solute thermolysis along with the formation of highly reactive radicals and reagents, such as hydroxyl radicals and hydrogen peroxide, which induce drastic reactive conditions in the liquid media [3]. In addition, if a solid is present in solution, the sample size of the particles is diminished by solid disruption, thereby increasing the total solid surface in contact with the solvent. In this way, ultrasonication remains unique, since no other method of sample treatment can produce such effects [5, 6].

Generally, ultrasonication aids chemical analysis by:

- enhancing solid–liquid elemental extraction;
- shortening sequential extraction schemes for elemental determination;
- shortening elemental speciation schemes;
- speeding up solid–liquid extraction of organic species;
- accelerating electroanalytical measurements by enhancing mass transport efficiency;
- speeding up enzymatic reactions;
- accelerating liquid–liquid extraction techniques;
- enhancing the performance in solid-phase extraction and microextraction;
- incrementing accuracy in the solid-matrix dispersion technique.

1.2.1
Parameters Affecting Ultrasonic Cavitation

Ultrasonic cavitation is a physical phenomenon whose performance depends upon the parameters described below.

1.2.1.1 Frequency

At high sonic frequencies, on the order of the MHz, the production of cavitation bubbles becomes more difficult than at low sonic frequencies, of the order of the kHz. To achieve cavitation, as the sonic frequency increases, so the intensity of the applied sound must be increased, to ensure that the cohesive forces of the liquid media are overcome and voids are created. This phenomenon can be easily understood by looking at Figure 1.3, which shows the variation in threshold frequency versus intensity for aerated water and air-free water. As can be seen, ten times more power is required to induce cavitation in water at 400 kHz than at 10 kHz. The physical explanation for this lies in the fact that, at very high frequencies, the cycle of compression and decompression caused by the ultrasonic waves becomes so short that the molecules of the liquid can not be separated to form a void and, thus, cavitation is no longer obtained.

Recent literature suggests that ultrasonic frequencies can be of paramount importance for some analytical applications. For instance, Rial-Otero *et al.* have shown that
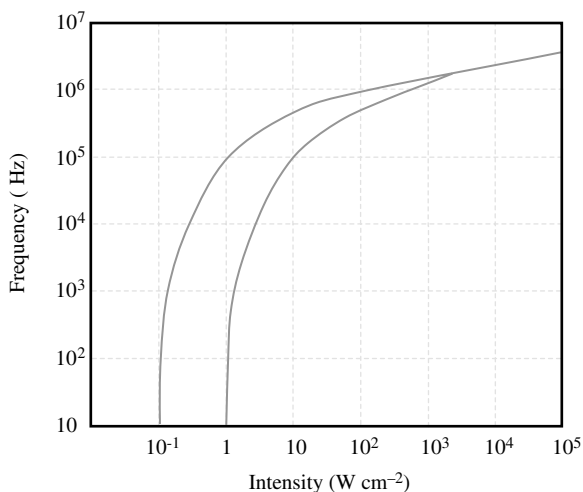
Figure 1.3 Variation of intensity of sonication versus the threshold frequency for aerated water (left-hand graph) and air-free water. Adapted from Ref. [1].

some pesticides can be determined in honey through a fast solid phase microextraction procedure using an ultrasonic bath operating at 130 kHz, whilst poor pesticides recoveries were obtained at an operating frequency of 35 kHz [7]. As another example, Pena-Farfal *et al.* have found that the frequency of the ultrasonic bath is critical for the enhancement of the enzymatic extraction of metals from mussel tissue [8].

1.2.1.2 Intensity

The intensity of sonication is proportional to the amplitude of vibration of the ultrasonic source and, as such, an increment in the amplitude of vibration will lead to an increase in the intensity of vibration and to an increase in the sonochemical effects. To achieve the cavitation threshold a minimum intensity is required. This means that higher amplitudes are not always necessary to obtain the desired results. In addition, high amplitudes of sonication can lead to rapid deterioration of the ultrasonic transducer, resulting in liquid agitation instead of cavitation and in poor transmission of the ultrasound through the liquid media. However, the amplitude should be increased when working with samples of high viscosity, such as blood. This is because as the viscosity of the sample increases so does the resistance of the sample to the movement of the ultrasonic device, for instance the tip of an ultrasonic probe. Therefore, a high intensity (i.e., high amplitude) is needed to set the ultrasonic device to obtain the necessary mechanical vibrations so as to promote cavitation in the sample.

Different authors have studied extensively the effect of sonication amplitude on the efficiency of the solid–liquid extraction of metals. There is agreement in the published data on this subject and, as a general rule, the higher the amplitude the more analyte is extracted, for given conditions of solution acidity and sonication time. Thus, the analyte extraction increases continuously with amplitude until an optimum is reached [9–11]. This effect of amplitude on the solid–liquid extraction of metals can

be extended to the other ultrasonic applications. However, equilibrium should be attained between the intended effects and sonication amplitude since, as explained above, high amplitudes lead to high sonication intensities and high sonication intensities can promote some undesired effects, such as analyte degradation. Finally, the use of high amplitudes does not always lead to good results. For example, chromium is difficult to extract from biological samples using ultrasonication, whatever the amplitude used for an ultrasonic probe with a frequency of 20 kHz and a potency of 100 W [12].

1.2.1.3 Solvent
The solvent used to perform sample treatment with ultrasonication must be carefully chosen. As a general rule, most applications are performed in water. However, other less polar liquids, such as some organics, can be also used, depending on the intended purpose. Both solvent viscosity and surface tension are expected to inhibit cavitation. The higher the natural cohesive forces acting within a liquid (e.g., high viscosity and high surface tension) the more difficult it is to attain cavitation [2].

1.2.1.4 Temperature
Solvent temperature plays two roles in ultrasonication. On the one hand, the use of high temperatures helps to disrupt strong solute–matrix interactions, which involve Van der Waals forces, hydrogen bonding and dipole attractions between the solute molecules and active sites on the matrix. Moreover, faster diffusion rates occur at higher temperatures. On the other hand, cavitation is better attained at lower temperatures when the ultrasonic power of the generator is constant (Ref. [3], p. 68). This is because as the temperature of the solvent rises so to does its vapor pressure and so more solvent vapor fills the cavitation bubbles, which then tend to collapse less violently, that is, the sonication effects are less intense than expected. Hence a compromise between temperature and cavitation must be achieved. For example, the extraction ratios of polycyclic aromatic hydrocarbons from sediments were increased by between 6% and 14% when ultrasonic extraction with a probe was carried out under non-cooling conditions [13]. In contrast, when we tried to accelerate the enzymatic digestion of proteins in acetonitrile using an ultrasonic probe at room temperature, the enhancement in temperature caused by ultrasonication led to rapid evaporation of the solvent, making sample treatment impossible (J.L. Capelo *et al.*, unpublished data).

1.2.1.5 External Pressure and Bubbled Gas
If the external pressure is increased, then a greater ultrasonic energy is required to induce cavitation, that is, to break the solvent molecular forces. In addition, there is an increment in the intensity of the cavitational bubble collapse and, consequently, an enhancement in sonochemical effects is obtained. For a specific frequency there is a particular external pressure that will provide an optimum sonochemical reaction [2]. It must be stressed that most ultrasonic applications in analytical chemistry are performed under atmospheric pressure.

Dissolved gas bubbles in a fluid can act as nuclei for cavitation, favoring the ultrasonication process. However, ultrasonication can be used to degas a liquid. For

this reason, if gas is used to increase cavitation effects it must be bubbled continuously into the solvent to maintain the effect. Monoatomic gases such as He, Ar and Ne should be used [1–3].

1.2.1.6 Direct and Indirect Ultrasonic Application

Ultrasonication can be applied in analytical chemistry in two ways: directly to the sample or indirectly through the walls of the sample container. Direct application is achieved through ultrasonic probes, which are immersed into sample, performing ultrasonication directly over the solution without any barrier to be crossed by the ultrasonication wave other than the solution itself. This approach has several drawbacks. For instance, sample contamination with metals detaching from the probe can be expected. Although modern ultrasonic probes are made from high purity titanium, contamination by metals such as Cr or Al has been reported [14]. Modern ultrasonic probes made from glass greatly reduce this problem [15]. Another disadvantage arises from the fact that most ultrasonic probes are used in open approaches, that is, the sample container is not sealed during sample treatment. Consequently, some volatile analytes can be lost. As an example, when the content of the 16 polycyclic aromatic hydrocarbons in the Environmental Protection Agency (USEPA) priority list was studied in sediments, a significant fraction of the most volatile compounds was lost due to the heating produced by the sonication probe used for the solid–liquid extraction process [13].

Indirect application is performed, generally, using an ultrasonication bath, although modern approaches take advantage of the powerful sonoreactor [15]. In both cases the ultrasonic wave needs first to cross the liquid inside the ultrasonic device and then to cross the wall of the sample container. Therefore, ultrasonication intensity inside the sample container is lower than expected. As ultrasonic baths are not powerful devices, their applications are greatly limited by the lack of ultrasonic intensity. In fact, many ultrasonic applications related to baths can be linked to the heating produced in the liquid that the bath contains – heat that is transmitted to the sample – rather than to actual ultrasonic effects, that is, cavitation [16]. However, as mentioned above, nowadays, a sonoreactor can be used instead of an ultrasonic bath in some regular applications [15]. A sonoreactor works like a powerful, small ultrasonic bath; it has been shown to be a reliable approach for speeding up chemical reactions in modern areas of analytical chemistry, such as protein identification and metal speciation [17, 18].

1.3
Common Ultrasonic Devices Used in Analytical Chemistry

1.3.1
Ultrasonic Bath

Figure 1.4 shows a modern ultrasonic bath equipped with the most advanced tools that are nowadays incorporated to improve performance, and which are commented on in the sections below.
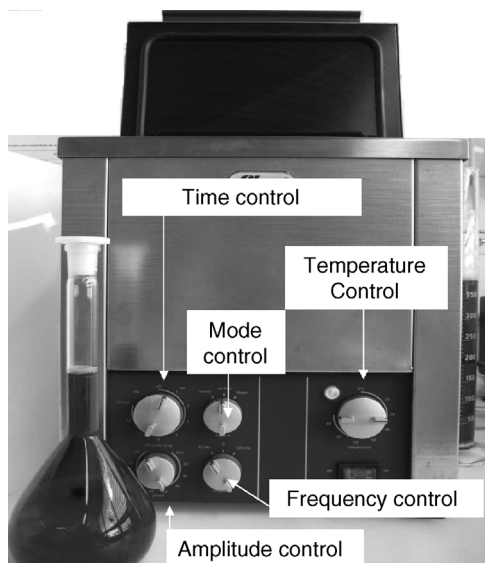
Figure 1.4 A modern ultrasonic bath incorporating the following advances: dual frequency of sonication, variable amplitude of sonication and three different modes of sonication.

1.3.1.1 Types of Ultrasonic Baths

At present there are three classes of ultrasonic baths [15]. The classic one is the common ultrasonic bath, which is found in most laboratories. This bath works with only one frequency, generally 40 kHz, and can be supplied with temperature control. A second type is provided as a multifrequency unit, which operates using, simultaneously, ultrasonic transducers with different frequencies, for instance 25 and 40 kHz, on the bottom and the side, respectively. The benefit of this is a uniform ultrasonic power distribution [19]. The third model corresponds to the most advanced in terms of technology, including the following features [20]:

1. Dual frequency of sonication.
2. A choice of 25/45 or 35/130 kHz. The baths are designed to work with one of the two frequencies at a time.
3. Power regulation.
4. The intensity of sonication can be controlled through amplitude control (10–100%).
5. Three operation modes:
   (a) Sweep: in this mode the frequency varies within a defined range. In this manner the ultrasonic efficiency is more homogeneously distributed in the bath than during standard operation.
   (b) Standard
   (c) Degas: the power is interrupted for a short period so that the bubbles are not retained by the ultrasonic forces.
6. Heating and timer.

1.3.1.2 How to Locate the Most Efficient Place Inside an Ultrasonic Bath

The ultrasonic intensity distribution inside an ultrasonic bath is not homogeneous. However, simple, rapid methods have been developed to locate the position that has the highest intensity of sonication (Ref. [3], p. 44). The aluminium foil test is, perhaps, the easiest method to apply in the laboratory. Using a series of aluminium foil sheets the most intense zones of sonication inside the bath can be quite accurately identified. As consequence of cavitation the aluminium foils are perforated (Figure 1.5). The maximum perforations occur at maximum intensity. Obviously, the reaction vessel should be located at the point where the maximum sonochemical effect is achieved.

1.3.1.3 Temperature Control

Most ultrasonic bath applications are performed for longer than 30 min and, as consequence of continuous ultrasonication, the bulk liquid warms up. Endothermic reactions can take advantage of this warming. In addition, the kinetics of many
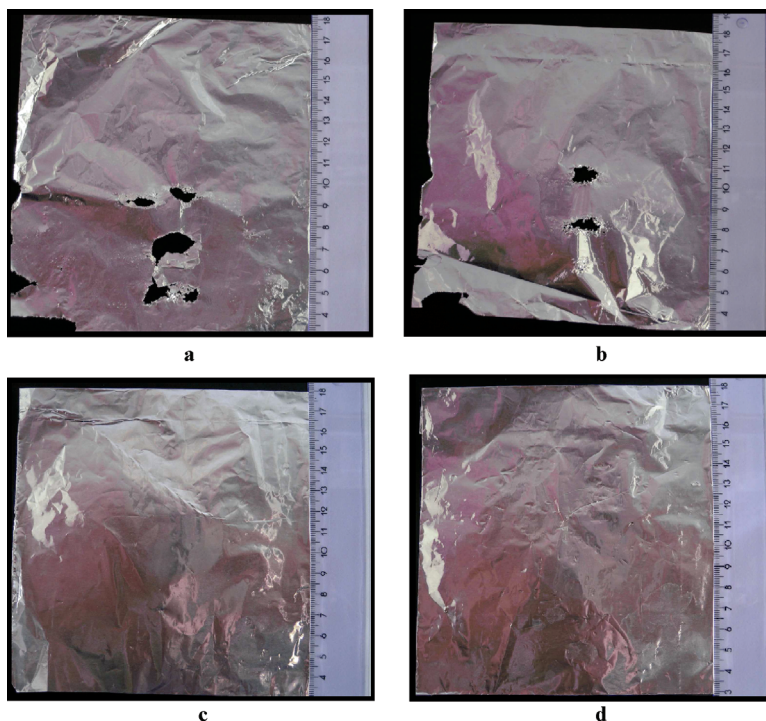

Figure 1.5 Aluminium foil test. Sonication time used for all experiments: 5 min. (a) 35 kHz sonication frequency and 100% sonication amplitude; (b) 35 kHz sonication frequency and 50% sonication amplitude; (c) 130 kHz sonication frequency and 100% sonication amplitude; and (d) 130 kHz sonication frequency and 50% sonication amplitude.

reactions are accelerated when the temperature is increased. However, some problems can arise regarding effectiveness and reproducibility of the sonochemical results obtained. Most ultrasonic baths are used without temperature control, and since bulk liquid warming is a slow process the final temperature achieved for a given time of sonication depends on the temperature of the laboratory (i.e., summer or winter). Thus, it is generally accepted that it is necessary to determine the maximum temperature the bath reaches and maintains, the so-called equilibrium temperature, when operating continuously under ambient conditions. Most reactions can be performed under the equilibrium temperature simply by filling the bath with water heated to that temperature previously. Alternatively, the problem can be solved by acquiring an ultrasonic bath with heater. However, before performing an ultrasonic treatment, it is recommended to wait until the working temperature is achieved.

When operation at room temperature is mandatory, control can be achieved with a simple water cooling recirculation system attached to the ultrasonic bath.

1.3.1.4 Shape and Material of Reaction Container

The shape of the reaction vessel is critical for the correct application of ultrasonication with a bath [2, 3]. This is because, as with any other wave, when the ultrasonic wave impinges against any solid surface some energy is reflected. If the base of the container is flat, such as in a conical flask, the ultrasound reflected is a minimum. Conversely, when the base of the container is spherical the ultrasonic wave hits the container at an angle, and a huge proportion of the ultrasonic wave is reflected away. For example, the amount of iodine liberated from KI in a solution of tetrachloride after 10 min ultrasonication, in a 100 mL flask, was three times higher when the flask had a flat base than when it had a round-bottom base [21].

The intensity of ultrasound is attenuated as it progress through a medium. The extent of attenuation is inversely related to the frequency. Therefore, the thickness of the wall of the vessel container should be kept to a minimum to avoid intense attenuation. This problem must be also borne in mind when the objective is to favor the solid–liquid extraction of analytes from solids deposited on a column: inside the column the effectiveness of the ultrasonic wave diminishes as it passes through the solid to the inner part of the column. Consequently, large-thin columns are preferred to short-wide ones for in-column ultrasonic bath applications.

1.3.2
The Ultrasonic Probe

Whilst the vessel container is immersed in an ultrasonic bath, an ultrasonic probe is immersed directly into the sample container. This is the main difference between the ultrasonic systems. The second difference is that the ultrasonic probe can deliver much higher ultrasonication intensity than the ultrasonic bath (100 times greater). These differences make each system appropriate for a different set of applications. The probe is generally used to attain effects that can not be achieved with the ultrasonic bath, for instance the mercury and arsenic speciation in human urine or seafood samples, respectively [22, 23].

1.3.2.1 **Parts of an Ultrasonic Probe**

Figure 1.6 shows the different parts of an ultrasonic probe. The generator converts mains voltage into high frequency electrical energy (generally, 20 kHz). The ultrasonic converter transforms electrical energy into mechanical vibrations of fixed frequency. The standard and booster horns increase the sonication amplitude. The probes or detachable horns transmit ultrasonic energy into the sample. The detachable horn design is crucial for a good performance. There are dedicated probes for a given range of volumes, and therefore mistakes such as using small probes for high volumes or high probes for small volumes must be avoided. The most important part of the whole system is the probe or detachable horn, which allows the vibration of the booster horn to be transmitted through a further length of metal in such a way that the power delivered is magnified.

Power magnification depends on the shape of the probe (Figure 1.7). The stepped probe gives the highest amplitude magnification [i.e., power, amplitude gain $(D/d)^2$] of the shapes shown. Nevertheless, the exponential probe shape, although difficult to manufacture, offers small diameters at its working end, which makes it particularly suited to micro-applications.

1.3.2.2 **Types of Ultrasonic Probes**

Ultrasonic probes are usually made of titanium alloy (titanium probes) and are thermoresistant, can be treated in autoclaves and are resistant to corrosive media. The sample volume to be treated along with the sample type is crucial in determining
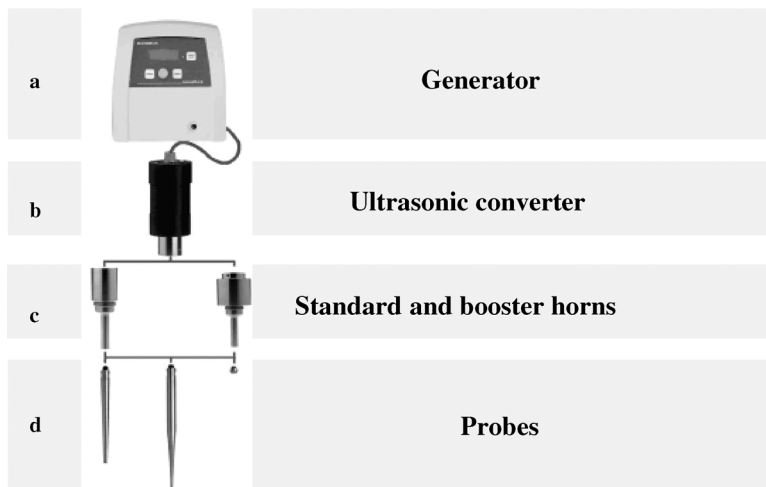

a	**Generator**
b	**Ultrasonic converter**
c	**Standard and booster horns**
d	**Probes**

Figure 1.6 An ultrasonic probe. (a) Generator: the generator converts mains voltage into high frequency (20 kHz) electrical energy (most likely, although other frequencies are also available); (b) the converter transforms electrical energy into mechanical vibrations of fixed frequency, normally 20 kHz; (c) standard and booster horns: the horns increase the sonication amplitude; (d) probes: (also called detachable horns) probes transmit ultrasonic energy into the sample. The design is crucial for a good performance. Adapted from the Bandelin company with its kind permission.
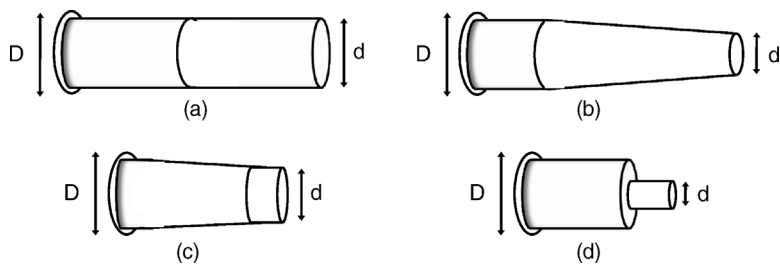
Figure 1.7 Probe shapes: (a) uniform cylinder; (b) exponential taper; (c) linear taper or cone; (d) stepped.

the selection of unit and the type of probe. It must be always borne in mind that the higher the amplitude provided by the probe the more intense is the sonication. Probes made of titanium alloy can contaminate the solutions in which they are used with metals such as Al or Cr [14]. For this reason, researchers working in trace metal analysis have long demanded the development of ultrasonic probes made from a non-contaminant material. Thus, the so-called silica ultrasonic probe made, as its name indicates, from silica has been developed [19]. This kind of probe has the advantage of non-particle metal intrusion in the sample. In addition, the typical metal contamination from titanium probes is avoided. Silica probes have high chemical and temperature shock resistance. Moreover, they do not exhibit electrical conductivity. However, several drawbacks must be addressed. For instance, the cavitation strength of silica glass is relatively low and, consequently, the amplitude must be limited. All silica glass probes are designed to be used with a maximum power setting of 50%, which corresponds to maximum amplitude of 12 μm. In addition, such probes are especially fragile during operation, and so they must not be placed on a solid surface or allowed to make contact with the vessel.

Spiral probes [19], made of Ti, Al and V, provide gentle ultrasonic treatment of aqueous media in test tubes or other long, thin laboratory containers. In contrast to traditional probes, the ultrasonic power is distributed across the entire surface of the spiral probe, thus making the distribution of the sonication intensity more homogeneous throughout the probe length. The drawbacks are related to metal contamination, like all probes made of titanium.

Multiple probes (Figure 1.1e and f) are manufactured to allow the use of two or more probes at the same time. The main advantage of this type of sonicator is throughput, which is greatly increased. Such sonicators meet the United States Environmental Protection Agency, USEPA, requirements specified in Method SW846-3550, which is referenced by the USEPA analytical test methods 8040, 8060, 8080, 8090, 8100, 8120, 8140, 8250, 8270, 413.2 and 418.1.

1.3.2.3 Dead Zones

The ultrasonic intensity rapidly decreases both radially and axially from the ultrasonic probe. For this reason the space between the ultrasonic probe and the wall of the container must be kept to a minimum, while ensuring that the probe does not touch the container – otherwise the probe might break. Keeping dead zones to a minimum
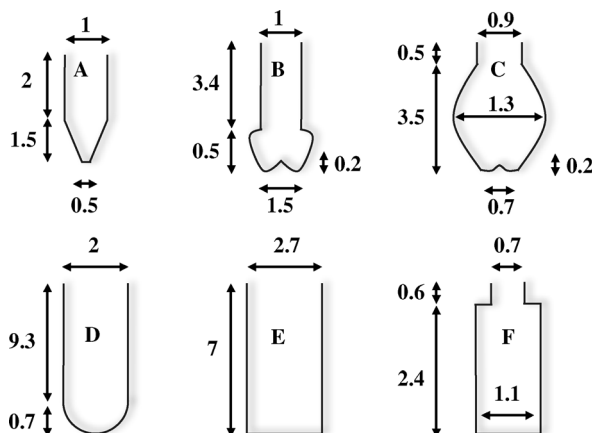
Figure 1.8 The shape of the vessel influences ultrasonic performance. The best forms are those that minimize "dead zones," namely, forms A–C. Adapted from Ref. [13].

ensures a maximum contact between the sample and the cavitation zones, and also among the sample particles, which helps to diminish their size by collisions and hence increases the total area in contact with the solution. The final result will be an increment in desired effects, such as, for example, in the solid–liquid extraction efficiency. Figure 1.8 shows different types of vessels. The influence of their shape on the extraction of PAHs from sediments under an ultrasonic field has been studied. The distance between the probe and the wall container in the case of design D is 8.5 mm and for desing E it is 12 mm, whereas the distances for containers A, B, C and F are 3.5, 3.5, 3 and 2 mm, respectively. Sample treatments carried out with containers D and E led to recoveries below 70%. This low extraction efficiency may be linked to the "dead cavitation zones", due to the distance between the probe and the wall container.

1.3.2.4 How to Choose the Correct Ultrasonic Probe

Two main issues determine the type of ultrasonic probe chosen for laboratory work. The type of application is the primary concern. As an example, if we are going to work with elemental extraction from soft tissues, then the probe has only one requirement: to be made of silica to avoid metal contamination. If the metal contamination introduced in solution by titanium probes is not a problem, and the elemental extraction is to be carried out in samples with low solid–liquid elemental extractability under the effects of an ultrasonic field, such as sediments or soils, then the most powerful ultrasonic probe made from titanium should be chosen. The high intensity will ensure both stronger and a higher number of collisions among particles, thus increasing the total area of contact between the solid and the solvent, and raising the ratio of elemental extraction. The second concern is related to the sample volume to be sonicated. The lowest volume that can be sonicated with an ultrasonic probe is 10 µL, but to date only the Dr Hielscher company offers a dedicated ultrasonic probe for such a volume [24].

1.3.2.5 **Temperature Control**

The utilization of an ultrasonic probe leads to an increase in bulk temperature. The higher the amplitude the faster the temperature increases. If the temperature is not controlled some undesired effects can occur. The most obvious is the degradation of compounds of interest, but also the volatilization of low volatile analytes can occur [13]. In addition, as the temperature is increased, the physical characteristics of the liquid media change in such a way that the ultrasonic transmission can be affected and no cavitation is achieved. This phenomenon is known as "decoupling" [2, 3]. It is not easy to control the temperature when ultrasonication is applied with an ultrasonic probe. However, three strategies can be followed. The first and simplest consists in using an ice bath. The vessel is inserted in an ice bath and sonication is performed. This ensures a rapid dissipation of heating. This strategy can be applied for short sonication times, otherwise care is needed to replace the ice. The second strategy entails the use of dedicated vessels, such as those shown in Figure 1.9, which are specially designed to dissipate warming. The third strategy is to use the "pulse" mode of ultrasonic application, which is available in all modern
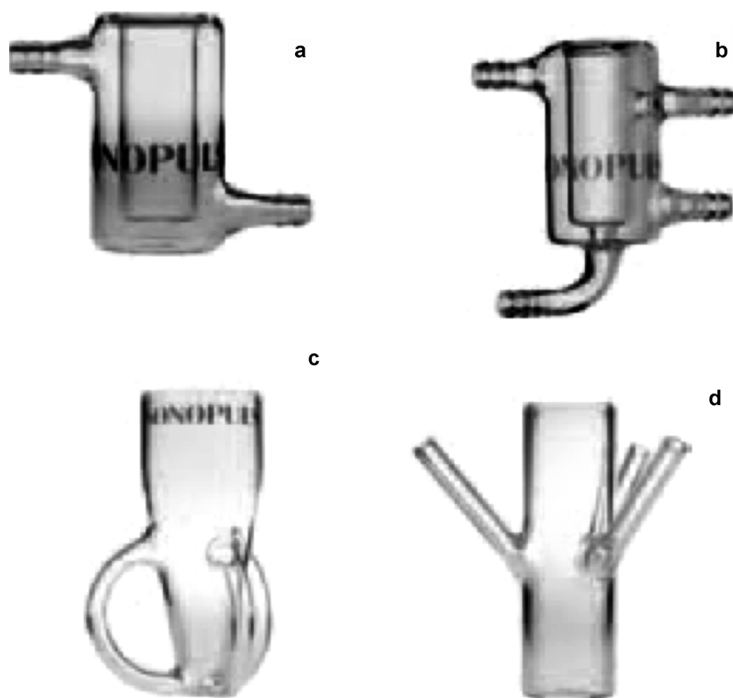

Figure 1.9 Vessels specially designed for applications with an ultrasonic probe. The design allows rapid refrigeration (Reproduced with the kind permission of Bandelin). (a) Cooling vessel KG for sonication of temperature-sensitive samples; (b) flow-through vessel with cooling jacket for irradiation of large volumes; (c) Rosett cell RZ for homogenous and intense recirculation of sample; (d) Suslick cell SZ with three sidearms for the introduction of gas or measuring probes.

sonication probes. In this mode the amplifier switches the power of the probe on and off repeatedly, thus avoiding the build up of reaction temperature. The three strategies can be combined.

1.3.2.6 Shape and Material of Reaction Container

A critical factor to be considered, for a correct ultrasonic probe application, is the shape of the reaction vessel, which must be conical [7] and with a diameter as small as possible so as to raise the liquid level for a given volume. When the concept of analytical minimalism is applied to any analysis, the low sample amount and solution volume used require a dedicated shaped vessel. The influence of vessel shape on the extraction of PAHs (Figure 1.8) from sediments using an ultrasonic probe has been studied [13]. Design A in Figure 1.8 corresponds to a classical Eppendorf cup made from polypropylene, while designs B and C each have a bump in the base and were laboratory-made from glass. These latter designs assist sonic mixing by dispersing the sonic waves as they impinge upon the bump and are reflected from the base. Design D has a spherical bottom whilst designs E and F each have a flat-bottom. Receptacles A, B, C and F were specially designed to work with low volumes, to reduce the dead zones during sonication. Moreover, the distance from the probe sonicator to the wall container was minimized to maintain the particles inside the area under the effects of cavitation. Cavitation phenomena rapidly decrease axially and radially. The low sonication volume allows to induce more collisions among particles and, hence, increase the total area exposed to solvent extraction. Receptacle C was used with a volume of 4 mL, whereas D was used with larger volumes (5 mL and 18 mL). Vessels A, B and C were found to be appropriate to achieve total extractions, whereas the extraction efficiency using design F was the lowest of all attempts made with containers with a total volume lower than 2 mL. In the latter case, due to the flat bottom, the particles climbed up the ultrasonic tip, leading to poor particle–solution contact and, hence, to lower extraction efficiencies.

Regarding the material of the reaction container, the particular analytical application will dictate the best one. Thus, if the analyte under investigation is a phthalate, then plastic containers should be avoided.

1.4
Current Ultrasonic Devices for New Analytical Applications

Cup horns (Figure 1.1h) are available from almost all ultrasonic companies. The sonoreactor (Figure 1.1d) is available from the Dr Hielscher Company. Such ultrasonic devices offer indirect sonication. This means that the ultrasonic waves need to cross the wall of the sample container. This does not occur with the ultrasonic probe, which is immersed directly into the sample, giving direct sonication. Cup horns, the sonoreactor and microplate horns can be compared to high intensity ultrasonic water baths. For example, the sonoreactor is 50 times more intense for a 2 mL volume of sonication than an ultrasonic bath. Using the above-mentioned devices, samples can be processed in sealed tubes or vials, eliminating aerosols, cross-contamination or the

Table 1.1 Important ultrasonic companies along with the main parameters of the most common ultrasonic devices.

Variable	Sonoreactor	Ultrasonic probe	Ultrasonic bath
Sonication time (s)	Up to 300	Up to 120	Up to several hours
Thermostat	No	No	Yes
Intensity of sonication at 1.5 mL vial (W)	0.5	15	0.01
Amplitude (%)	20–100	10–100	10–100
Sample handling	Low	High	Low
Sample throughput (1 mL vials at once)	Up to 6	Up to 96 (multiple probes)	100 to 500 (depending on size)
Direct application	No	Yes	No
Solid–liquid extraction yield	Medium	High	Low
On-line applications	Yes	Yes	Yes
Degradation of organics	Medium	High	Low
Ultrasonic companies	www.bandelin.com; www.hielscher.com; www.equilabcanada.com; www.bransonultrasonics.com; www.misonix.com; www.elmaultrasonic.com		

loss of volatile compounds. Such devices are ideal for samples such as those that are sterile or dangerously pathogenic. In the cup horn, the titanium probe is held within an acrylic cup filled with water. Samples are placed within the cup, above the probe. The cavitation produced in the immersed samples is higher than that given by an ultrasonic bath but it is lower than the cavitation produced by direct immersion of the ultrasonic probe into the solution. All the systems allow refrigeration. The microplate horn is similar to the cup horn, but it allows high-throughput applications, especially for the 96-well plate. Different versions of the same concept can be found for several of the ultrasonic companies cited in Table 1.1.

References

1 Mason, T.J. and Lorimer, J.P. (1989) *Sonochemistry: Theory, Applications and uses of Ultrasound in Chemistry*, Wiley-Interscience, New York.

2 Mason, T.J. (1992) *Practical Sonochemistry: User's Guide to Applications in Chemistry and Chemical Engineering*, Ellis Horwood Ltd, New York.

3 Mason, T.J. (2000) *Sonochemistry, Oxford Chemistry Primers*, Oxford, UK.

4 Suslick, K.S., Cline, R.E. and Hammerton, D.A. (1986) *Journal of the American Chemical Society*, **108**, 5641.

5 Wibetoe, G., Takuwa, D.T., Lund, W.D. and Sawula, G. (1999) *Fresenius' Journal of Analytical Chemistry*, **363**, 46.

6 Capelo-Martínez, J.L., Ximenez-Embun, P., Madrid, Y. and Camara, C. (2004) *Trends in Analytical Chemistry*, **23**, 331.

7 Rial-Otero, R., Gaspar, E.M., Moura, I. and Capelo, J.L. (2007) *Talanta*, **71**, 1906.

8 Pena-Farfal, C., Moreda-Pineiro, A., Bermejo-Barrera, A. *et al.* (2004) *Analytical Chemistry*, **549**, 3541–3547.

9 Amoedo, L., Capelo, J.L., Lavilla, I. and Bendicho, C. (1999) *Journal of*

Analytical Atomic Spectrometry, **14**, 1221–1226.

10 Lima, E.C., Barbosa, F., Krug, F.J. *et al.* (2000) *Journal of Analytical Atomic Spectrometry*, **15**, 995–1000.

11 Capelo, J.L., Lavilla, I. and Bendicho, C. (1998) *Journal of Analytical Atomic Spectrometry*, **13**, 1285–1290.

12 Amoedo, L., Capelo, J.L., Lavilla, I. and Bendicho, C. (1999) *Journal of Analytical Atomic Spectrometry*, **14**, 1221–1226.

13 Capelo, J.L., Galesio, M.M., Felisberto, G.M. *et al.* (2005) *Talanta*, **66**, 1272–1280.

14 Wibetoe, G., Takuwa, D.T., Lund, W. and Sawula, G. (1999) *Fresenius' Journal of Analytical Chemistry*, **363**, 46–54.

15 Santos, H.M. and Capelo, J.L. (2007) *Talanta*, **73**, 795–802.

16 Patrício, A., Fernández, C., Mota, A.M. and Capelo, J.L. (2006) *Talanta*, **69**, 769–775.

17 Rial-Otero, R., Carreira, R.J., Cordeiro, F.M. *et al.* (2007) *Journal of Proteome Research*, **6**, 909.

18 Vale, G., Rial-Otero, R., Mota, A. *et al.* (2008), *Talanta*, **75**, 872–884.

19 BANDELIN electronic, GmbH & Co. KG, Heinrichstraße 3-4, D-12207, Germany BerlinTwinSonic® series, www.bandelin. com, last accessed 7 November 2007.

20 Elma Hans Schmidbauer GmbH & Co, KG Postfach 280 D-78202. Singen Kolpingstr. 1-7, D-78224 Singen, Germany; www. elma-ultrasonic.com, last accessed 21 November 2007.

21 Mason, T.J., Lorimer, J.P., Cuesta, F. and Paniwnyk, L. (1989) Ultrasonics International 89, Conference Proceeedings, p. 1253.

22 Capelo, J.L., Lavilla, I. and Bendicho, C. (2000) *Analytical Chemistry*, **72**, 4979.

23 Capelo, J.L., Lavilla, I. and Bendicho, C. (2001) *Analytical Chemistry*, **73**, 3732.

24 Hielscher Ultrasonics GmbH, Am Dobelbach, 19 D-70184 Stuttgart, Germany; www.hielscher.com, last accessed 21 November 2007.