Ultrasound in materials chemistry

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Ultrasound has applications in materials, organometallic, polymer and synthetic chemistry as well as materials and waste degradation. After a brief description of the fundamentals of sonochemistry, an overview about current uses and future prospects in these fields is given.

The first steps in sonochemistry were taken about 70 years ago, but the extended application of ultrasound as a tool for synthetic and materials chemistry did not begin until the 1980s. Since then, many papers have been published and sonochemistry has become a versatile approach in several areas (for some related reviews see ref. 2–8). The subject is quite large and one had to select from a large number of papers. Thus, this article will focus on applications to materials chemistry (metals, solids, polymers, biological materials), sonochemistry involving metals and non-metallic solids, materials degradation and related industrial and laboratory applications in these fields. Even with such restrictions, a personal choice was unavoidable and some fields are only described in general and not in detail. Therefore, this article attempts to give an overview of the scope and trends in the application of ultrasound in materials science and related fields in chemistry.

Fundamentals

The part of the sonic spectrum which ranges from about 20 kHz to 10 MHz is called ultrasound, and it can be subdivided in three main regions: power ultrasound (20–100 kHz), high-frequency power ultrasound (100 kHz–1 MHz) and diagnostic ultrasound (1–10 MHz). The latter range is also often called high-frequency ultrasound.

Acoustic energy is mechanical energy, i.e. it is not absorbed by molecules. Ultrasound is transmitted through a medium via waves by inducing vibrational motion of the molecules which alternately compress and stretch the molecular structure of the medium. Therefore, the distances between the molecules vary as the molecules oscillate about their mean position. If the intensity of ultrasound in a liquid is increased, a point is reached at which the intramolecular forces are not able to hold the molecular structure intact. Consequently, it breaks down and cavitation bubbles are created. This process is called cavitation and the point at which it starts is known as the cavitation threshold. Two forms of cavitation are known: stable and transient. Stable cavitation means that the bubbles oscillate about their equilibrium position over several refraction–compression cycles, while in transient cavitation, the bubbles grow over one (sometimes two or three) acoustic cycle to double their initial size and finally collapse violently.

There are three different theories about cavitation: the hot-spot, the electrical and the plasma theory. But, according to each theory, there is no doubt that the origin of sonochemical effects is cavitation. Furthermore, it has been shown experimentally that cavitation collapse creates drastic conditions inside the medium: temperatures of 2000–5000 K and pressures up to 1800 atm within the collapsing cavity. Thus, from a practical point of view the parameters which influence cavitation are important (Table 1). However, it should be noted that there is often no simple relationship, and an optimum can generally be found for all parameters. For details of theoretical aspects of ultrasound and cavitation refer to the literature. From a practical point of view, there are three possible reaction sites of a collapsing bubble: the cavity interior, the bubble vicinity and the bulk solution (Fig. 1). The following beneficial sonochemical effects can be observed: (i) ligand–metal bond cleavage in transition-metal complexes to give coordinatively

<table>
<thead>
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<th>parameter</th>
<th>effects</th>
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| frequency       | • low: long cycle, large bubbles, low amplitude required to induce cavitation  
|                 | • high: short cycle, high amplitude necessary, increased attenuation, weak or no cavitation in the MHz range (refraction cycle is too short to create bubbles)  |
| intensity       | • considerably higher intensity at high frequency is necessary to maintain the same cavitation as at low frequency  
|                 | • indefinite increase limited by the material stability of transducer, decoupling with the medium and a large number of bubbles (transmission barrier)  |
| solvent         | • the higher the vapour pressure the less violent the collapse (increased penetration of vapour into the bubbles)  
|                 | • induction of cavitation is more difficult in solvents with low vapour pressure  
|                 | • cavitation is easier in solvents with low viscosity and surface tension  |
| bubbled gas     | • $\gamma = C_2/C_1$ should be high as the collapse temperature is proportional to $(\gamma - 1)$  
|                 | • the smaller the thermal conductivity of the gas the higher the local heating during the collapse  
|                 | • the greater the amount of dissolved gas the smaller the intensity of the shock wave  
|                 | • dissolved gas acts as cavitation nuclei and leads to more facile cavitation  |
| external temperature | • temperature rise increases vapour pressure and collapse is less violent, less intensity necessary to induce cavitation  
|                 | • temperature near the boiling point of the solvent dramatically increases the number of bubbles which can act as sound barrier  
|                 | • pressure rise decreases vapour pressure and collapse is more violent; higher intensity is necessary to induce cavitation  
|                 | • optimum depends on frequency  |

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Metals, Powders and other Particles

Reactions and processes involving metals, powders or other solid particles are probably the most successfully investigated fields in the application of ultrasound in chemistry and materials science. Table 2 gives an overview of such fields.

Deformation of metal carbonyls

The effects of ultrasound on metal carbonyls were investigated initially by Suslick and co-workers in 1981. Upon irradiation of a decane solution of Fe(CO)\(_5\) under argon with ultrasound (20 kHz, 100 W cm\(^{-2}\)), they observed an unusual Fe\(_3\)(CO)\(_9\) cluster formation together with the formation of fine powdered iron (Scheme 1). The unique nature of the ultrasonic treatment can be seen by comparison with the effects of light and heat.

Photolysis of Fe(CO)\(_5\) yields Fe\(_2\)(CO)\(_9\) via Fe(CO)\(_4\) which reacts with unconverted Fe(CO)\(_5\) (Scheme 1). Thermolysis of Fe(CO)\(_5\) results in decomposition to iron clusters and CO. The formation of amorphous iron depends on the sonication parameters influencing cavitational (solvent vapour pressure, gas). The influence of the reaction conditions on the measured properties (e.g. particle size) of sonochemically produced amorphous iron has been described recently.\(^{12}\)

Sonochemically produced iron is an amorphous pyrophoric powder having a surface area of about 150 m\(^2\) g\(^{-1}\). It has a coral-like structure which is built up from nanosized clusters. Amorphous iron has been described recently.\(^{12}\) DSC measurements show an irreversible crystallisation exotherm at 350°C reflecting the formation of normal fully crystallised 

![Scheme 1](image-url)
the coatings and a more uniform microstructure are the benefits of using ultrasound in electroplating. The effects of 1.2 MHz and 20 kHz ultrasound applied at an intensity of 4 W cm\(^{-2}\) have been compared in a study of the electrodeposition of Cu by Drake.\(^2\) Using the high-frequency ultrasound, the diffusion layer is reduced from 200 \(\mu m\) to about 20–30 \(\mu m\), whereas 20 kHz ultrasound reduces it to 3.4 \(\mu m\).

The properties of porous silicon-based films produced by open-circuit stain etching are better under sonication compared to those of samples generated in the absence of ultrasound. The differences induced by ultrasound in surface morphologies (rougther and thicker films) and chemical stability (greater stability on exposure to water and organoamines) proved that ultrasonic irradiation is a useful tool.\(^1\)

Pulsed ultrasound has recently found more interest in chemistry.\(^2\) Reisse and co-workers\(^6\) described the pulsed sonochemistry of metal salts in aqueous solution which resulted in the formation of metals and other solid powders (Cu, Co, Zn, Ni, Cr, Ag, Co/ Ni, MnO\(_2\), CdTe) with particles sizes of about 100 nm. The sonoanode acts as ultrasound emitter and also as the cathode. The 20 kHz high-intensity ultrasound pulse (pulse duration 100 ms followed by a 200 ms switch off) is superseded by an electrical current (pulse duration 300 ms). During sonication, the cathode surface is cleaned, the metal particles are expelled (preventing the growth of large particles) and the double layer is replenished with metal cations. The metals obtained are fine crystalline powders with high surface areas and chemical purity. The electrical yields are about 75–90\%. Using a 1 cm diameter sonoanode, amounts of 1 g h\(^{-1}\) can be produced. Sonoelectrochemically produced Zn has been used as an effective catalyst in the Barbier-type reaction (Scheme 2).

**Sonication of metal powders, solids and supported metals used as catalysts or reagents**

Owing to cavitational collapse, sonication of metals or solids leads to microjet and shock-wave impacts on the surface which can result in particle size reduction, interparticle collisions, depassivation, surface cleaning, defects and erosion. The extent of erosion depends on the type of metal. Sonication of soft metals with hard oxides (e.g. Al, Na, Li) results in metal deformation which will damage the oxide layer. Hard metals are not plasticly deformed by ultrasound but the surface is activated by the above-mentioned cavitation effects owing to the low cohesion of the oxide coating. If the particles are very small and/or in close proximity (e.g. in slurries) they will impinge (interparticle collision), agglomerate and even fusion can occur owing to the high temperatures of the hot spot.\(^6\)

A recent study\(^2\) was devoted to the effects of the particle size morphology of Cu and Pb sonicated in dilute HCl using a 38 kHz cleaning bath. It was found that the cavitational modification of the metals depended on the initial size of the solids. Large copper turnings or lead foil are greatly depassivated by microjets. Small particles (<ca. 100–150 \(\mu m\)) in the study\(^2\) Cu <63 \(\mu m\) and Pb ca. 150 \(\mu m\)) are not subjected to microjet impacts because a collapsing bubble will have an average diameter of about 150 \(\mu m\) at 20 kHz. Consequently, shock-wave impacts and interparticle collisions are dominant and only small differences to a stirred control probe were found.

There are in principle two main groups of applications of ultrasound to metals and solids in sonochemistry, and they are described below.

(1) **Sonochemical preparation of catalysts used in non-sonicated reactions**. Applications include: the preparation of activated metals by reduction of metal salts (e.g. reduction with Li in THF to Rieke-type powders or with formaldehyde to Pt or Pd); the generation of activated metals by sonication; the precipitation of metal (Cr, Mn, Co) oxide catalysts; and the impregnation of metals or metal halides or supports.

The reduction of metal halides with Li in THF in a low-intensity cleaning bath gives rise to active metal powders comparable to Rieke-type powders. Sonication for less than 1 h (the conventional Rieke procedure requires about 8 h and stirring for up to 26 h) yields powders of Mg, Zn, Cu, Ni, Cr, Co, Pt and Pd. Platinum black produced by reduction of platinum halides under ultrasound has increased activity in the hydrogenation of alkenes up to a factor of three.\(^2\) Furthermore, increases in magnetic susceptibility (98\%) and surface area (62\%) has been measured. The most catalytically active platinum and palladium blacks have been obtained at 20 kHz (Pt) and 3 MHz (Pd).\(^2\) Similar activity enhancements have been found for Ni and Co obtained after precipitation of metal oxalates under sonication and subsequent reduction to the metal.\(^5,26\)

The sonication of ordinary commercial Ni (known as a poor catalyst) to obtain highly active metal powder has been investigated extensively.\(^2\)\(^,29\)\(^,29\) Irradiation with ultrasound increases the catalytic activity dramatically, reaching that of Raney nickel. Marked changes in the surface morphology have been observed: the surface is smoothed by removing the crystallitites and the oxide layer. The particle size is hardly reduced. If metal slurries containing different metals are sonicated, melted necks between two different metal particles can be observed. Thus, Suslick\(^6\)\(^,30\) found that, for example, in the cases of Fe and Sn the neck is an alloy between the two metals, i.e. high velocity collisions with sufficient energy to melt the metals have occurred. If the particles experience glancing collisions, smoothing occurs. From investigations of different metals one can estimate the local conditions in the slurry. If Fe and Cr (which melt at 1500°C and 1800°C respectively) are irradiated, tremendous agglomeration is observed. Sonication of Mo (mp ca. 2600°C) still results in agglomeration and practically no smoothing is observed. In the case of W, ultrasound has no effect. Thus, a temperature limit of ca. 3000°C can be estimated. In the cases of Mo and W, the production of metal carbides (e.g. Mo\(_2\)C) has also been reported recently.\(^31\) Sonication of a mixture of MoCl\(_5\)–SiCl\(_4\) and sodium–potassium alloy followed by annealing at 900°C gives nanocrystalline MoSi\(_2\).\(^32\) Sonoechemically obtained MoSi\(_2\) shows 50–70\% higher microhardness and compression strength than the conventional coarse-grained MoSi\(_2\).

Sonoechemically obtained Ni powder is a highly heterogeneous catalyst for hydrocarbon reforming and CO hydrogenation. In the hydrogenation of alkenes, it is comparable with Raney Ni; however, it is more selective as C=O groups are unaffected.\(^21\) Ultrasonic precipitation of chromium molybdenum oxide yields a catalyst with 15–20\% increased dispersity and better activity for the oxidation of methanol to formaldehyde.\(^33\)

In 1973, the sonication of aqueous suspensions of Cr\(_2\)O\(_3\), Co\(_2\)O\(_3\), MnO\(_2\) and alumina giving supported metal oxide catalysts of higher activity and dispersity for \(\text{H}_2\text{O}_2\) decomposition was reported.\(^4\) Thus, the surface area of supported Cr\(_2\)O\(_3\)/Al\(_2\)O\(_3\) is enhanced from 108 m\(^2\) g\(^{-1}\) (normal preparation) to 135 m\(^2\) g\(^{-1}\) (sonochemical preparation). Impregnation of Pt on silica gel produced by sonoreduction.
of ammonium hexachloroplatinate at 440 kHz yields a metal catalyst with an 80% increased surface area compared to that prepared by mechanical stirring.\textsuperscript{35} Ragaglia \textit{et al.}\textsuperscript{36} reported recently on the dispersion of Ru on alumina. RuCl\textsubscript{3} (in water) and Ru(acac\textsubscript{3})\textsubscript{2} (in toluene) absorbed on Al\textsubscript{2}O\textsubscript{3} were subjected to hydrazine reduction under ultrasound. At low Ru content (0.5%) a higher dispersion (66% with RuCl\textsubscript{3}) was found compared to a non-sonicated run (37% with RuCl\textsubscript{3}). With a higher Ru content (5%) the dispersion was relatively low in both runs and was comparable in value (about 20%). The applied power is critical as at high power the alumina support is affected. A further study investigated the promotion of aromatics with CuBr\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{3} Sonication of the reaction mixture with non-impregnated reagents led to a substantial rate improvement for the naphthalene bithermalysis compared to a non-sonicated run. However, even better results were obtained when CuBr\textsubscript{2} was sonoelectrochemically preimpregnated on alumina following by conventional procedures. Sonoechemically supported CuBr\textsubscript{2} on Al\textsubscript{2}O\textsubscript{3} showed reduced particle sizes and pronounced changes in the surface morphology.

Multicomponent catalysts used in chemical technology can also be activated or reactivated: Ziegler-Natta, Ni/Mo cracking, Ti/V oxide or Pd-alumina denitriﬁcation catalysts (see ref. 7 p. 54ff).

(2) Activation of solid reactants (metals and non-metallic solids) in heterogeneous chemical reactions by ultrasound. Applications include: the preparation of activated metal solutions; the preparation of organometallic compounds from main group or transition metals; sonoechemical reactions involving metals \textit{via in situ} generated organoelement species; and reactions involving non-metallic solids.

There are some obstacles to reactions between a solid and a liquid (or in a liquid-dissolved) reactant in a heterogeneous system, e.g. the small surface area of a bulk solid; the solid surface may be coated by oxide layers or impurities; species have to diffuse to and away from the solid surface; and deposition of products may inhibit further reaction.

These difficulties can be overcome by the effects of ultrasound due to cavitation, as has been mentioned already in part: shock waves (causing plastic deformations on soft materials, break-up of coatings), microjets (causing surface erosion, defects and deformations, enhancing the surface area) and microstreaming (improving mass transfer, removing eroded particles and deposited impurities or products). There are excellent reviews on heterogeneous sonochemistry.\textsuperscript{3} Very recently, some papers have been selected as examples to illustrate the wide range of metals and solids used in sonochemistry.

Highly active reducing agents can be prepared by the sonication of Mg in the presence of anthracene.\textsuperscript{41} K in toluene and Na in xylene.\textsuperscript{42} The alkali metals are obtained in colloidal solution. Similarly, highly dispersed Hg emulsions are available.\textsuperscript{43} Organometallic derivatives are useful reagents in organic synthesis. They are either prepared or commercially available or generated \textit{in situ}. Schemes 3–5 show examples of reactions involving different main group and transition metals.

The application of ultrasound to non-metallic solids has recently been reviewed extensively by Ando and Kimura.\textsuperscript{39} Thus, some recent examples will be given. Goh \textit{et al.}\textsuperscript{44} described the effect of ultrasound on sulfur–metal systems. Sonication of Cu, Fe, Zn or Mg with elemental sulfur in the presence of 2 mol dm\textsuperscript{-3} HCl yields the corresponding sulfides (Table 3). The increase of sulfide formation in the order water < hexane < CS\textsubscript{2} corresponds to the solubility of sulfur in these solvents. Surprisingly, iron is an exception, giving the highest yield in water and only poor results in CS\textsubscript{2}. A similar reaction of selenium with alkali metals (Li, K, Na) giving the dimetalselenuides M\textsubscript{2}Se\textsubscript{2} has been published by Thompson and Boudjouk.\textsuperscript{45} Organotin ﬂuorides are insoluble in most solvents owing to their polymeric structures. Therefore, their reactivities are extremely low. Sonication of derivatives R\textsubscript{3}SnF (R = Bu, Ph) with metal salts NaX (X = Cl, Br, OCN, SCN) leads to the rapid formation of monomeric compounds R\textsubscript{2}SnX.\textsuperscript{46}

An interesting effect of sonication on the reaction pathway has been observed in the reaction of solid KCN/Al\textsubscript{2}O\textsubscript{3} with benzoyl bromide (Scheme 6).\textsuperscript{39,47} The course of the sonoechemical reaction is completely changed as under stirring a different product is observed. This so-called sonoechemical switching (see Scheme 6 for examples) is explained by different reaction mechanisms. Under sonication an electron-transfer mechanism (leading in this case to a different product) is preferred, whereas under stirring an ionic pathway dominates.

As this chapter covers mainly synthetic chemistry aspects, some potential future trends and questions will be given. At present, sonochemistry is an established field in laboratory preparations. However, an as yet unsolved problem is the scale-up: on the one hand, the scale-up of a laboratory synthesis to a 20–50 g scale, and on the other hand, chemical synthesis on an industrial scale. There are already examples reported in these two areas, e.g. the preparation of perfluoroalkyl aldehydes was scaled up to 20 g scale\textsuperscript{39} and the introduction of ultrasound in three steps of a complex 14-step steroid synthesis to desogestrel yielding the intermediates on a kg scale.\textsuperscript{69} Thus, the existing sonochemical equipment allows in principle the synthesis on a kg scale, and the realisation of higher bulk amounts should not be a technical problem.\textsuperscript{70} The product of kg amounts of compounds seems to be economical in the preparation of highly valuable compounds, especially drugs in the pharmaceutical industry. Further bulk applications in synthesis are still limited because of cost concerns. In laboratory applications the following trends will be followed: synthesis of complex molecules and natural products; introduction of sonochemical steps in multistep syntheses; increased use of ultrasound for established fields of chemistry, \textit{i.e.}, the combination of sonochemistry with electrochemistry, photochemistry, high-pressure chemistry, polymer chemistry and biotechnology; use of ultrasound in reaction mechanism studies; and study of frequency effects and reactor design, dosimetry of the sound field.

Other applications to metals and non-metallic solids

The use of ultrasound in this field of materials science is already extensive, which can be exemplified by some further selected applications and related recent publications: crystallisation and precipitation of metals, alloys, zeolites and other solids,\textsuperscript{1–7} agglomeration of crystals,\textsuperscript{7} degassing of melts,\textsuperscript{8} spray pyrolysis to form thin films\textsuperscript{9,10} or fine particles;\textsuperscript{9–11} treatment of solid surfaces;\textsuperscript{9,2–5} dispersion of solids;\textsuperscript{9,46} preparation of colloids (Ag, Au, Quoted CdS);\textsuperscript{9,7–99} ultrasonic sieving\textsuperscript{100} and micromanipulation (transportation, concentration, fractionation) of small particles;\textsuperscript{100–102} intercalation of guest molecules into host inorganic layered solids;\textsuperscript{103} ultrasonic-aided development in advanced lithography;\textsuperscript{104} and electroless plating.\textsuperscript{105–109} Some of the items of this list will be described in more detail as the number of papers discussing these aspects has increased significantly over the last decade.

Crystallisation and precipitation. In the treatment of liquid metals or alloys during solidification, and of saturated solutions, the crystallisation process is affected by ultrasound as follows: inhibition of crystal formation; intensiﬁcation of heat transfer; increase in the nucleation and the growth rate; and affecting growth morphology. Thus, ultrasound induces changes in the formation of InSb crystals: altering the crystal diameter, changing the width of the facet region and the inclined angle of non-facet interfaces near the facet region for the (111) plane. For BiSb single crystals a strong decrease in

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the density of growth striations due to ultrasonic-induced convection currents in the melt has been reported.\textsuperscript{73}

Non-ferroelectric but polar-oriented ceramics and films showing excellent piezoelectric or pyroelectric properties (Li\textsubscript{2}B\textsubscript{4}O\textsubscript{7}, Ba\textsubscript{2}TiSi\textsubscript{2}O\textsubscript{8}, Ba\textsubscript{2}TiGe\textsubscript{2}O\textsubscript{8}) have received much attention. These materials can be prepared by surface crystallisation of glasses. However, it is difficult to obtain well oriented crystallites by conventional crystallisation. Enhanced nucleation, precipitation and oriented growth of desired crystals have been found when the glass surface is treated ultrasonically in suspensions of crystalline particles. Thus, surface-crystallised dense thin films of Li\textsubscript{2}B\textsubscript{4}O\textsubscript{7}, Pb-BaB\textsubscript{2}O\textsubscript{4}, Ba\textsubscript{2}TiSi\textsubscript{2}O\textsubscript{8} on glass have been prepared.\textsuperscript{64,74}

Ultrasonic irradiation also improves the precipitation of ceramic powders from solutions (Pb-Zr-Ti oxalate, Pb oxalate, mullite-composition powder) and the hydrolysis of metal (Si, Al) alkoxides. Accelerated precipitation and improvement of the homogeneity in the precipitates were observed.\textsuperscript{74}

**Ultrasonic spray pyrolysis.** One of the most extensively used applications in materials science is ultrasonic spray pyrolysis (USP) which is used to produce either fine particles or thin films. Particles prepared by this ultrasonic method have the following interesting features: spherical shape; uniform size distribution; adjustable particle size from micron to submicron range; and high purity. The process requires a short preparation time and is continuous. Furthermore, the size distribution is controlled easily by changing the solution concentration. In general, aqueous solutions of metal salts (e.g. chlorides, nitrates, alkoxides, carboxylates) are sprayed and hence the products are metal oxide particles.

Studies on oxide ceramic preparations have been intensified since the report of high-$T_c$ superconductors. Examples of sonochemically produced systems are Y-Ba-Cu-O and Bi-Ca-Sr-Cu-O materials (e.g. YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-x}, Bi\textsubscript{2}CaSr\textsubscript{2}Cu\textsubscript{2}O\textsubscript{x}, Bi\textsubscript{2}Ca\textsubscript{2}Sr\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7} having the beneficial properties described above and showing similar characteristics to superconducting particles sintered from the powders by conventional solid-state reactions.\textsuperscript{88}

Other oxide-type examples are the preparation of TiO\textsubscript{2}-SnO\textsubscript{2} powder\textsuperscript{89} used for stable humidity sensors and Pb(Zr,Ti)O\textsubscript{3} (PZT)\textsuperscript{90} which is a widely used piezoelectric and electro-optic material.

Recently, the preparation of non-oxide particles has been reported: fine ZnS particles were produced from Zn(NO\textsubscript{3})\textsubscript{2}, thiourea complexes. Deposition at low temperature (400 $^\circ$C) gave amorphous particles whereas at around 800 $^\circ$C a hexagonal crystalline phase was observed. The latter particles, ranging from 0.5 to 1.3 $\mu$m, are spherical with a smooth surface. ZnS particles which were rough and included a zinc oxide phase were found at high temperatures (900 $^\circ$C).\textsuperscript{91}

Ultrasonic spray pyrolysis to form thin films has many advantages: very small droplets which can be transported without heating of the carrier gas, narrow droplet size

\[ \text{Scheme 3} \text{ Sonochemical reactions involving alkali metals (ref. numbers in square brackets)} \]
distribution; solvent vapourises as it reaches the substrate; deposition under atmospheric pressure, fast deposition rate; easy control of film composition and thickness; pure deposits free of contaminants; and a variety of precursors: inexpensive raw materials (such as nitrates or chlorides), metal-organic compounds, precursors with low volatility or low stability may be used. At present, not only USP-prepared films made from relatively simple compounds (e.g. TiO$_2$, SnO$_2$, ZnO$^{84}$), but also more complex systems such as Y–Fe garnet, calcia-stabilized zirconia, La$_{x}$Sr$_{y}$MnO$_{3}$, La$_{x}$MgCrO$_{4}$ and superconducting Y–Ba–Cu–0 films have been described. Even multilayer films such as PbTiO$_3$(001)/LaNiO$_3$(100)/MgO(100) have been prepared.$^{80}$

Recently, metal-organic chemical vapour deposition (MOCVD) using USP has been used to form ferroelectric BaTiO$_3$ and oriented thin TiO$_2$ films.$^{79}$ For the latter, an improved method using pulsed injection in conjunction with USP and allowing good control over the film deposition rate (growth rate achieved: 2.5 monolayers per pulse) has been developed. The excellent control over film growth and properties is also a key feature in the preparation of SnO$_2$ films. The USP technique allows the fast preparation (2 nm s$^{-1}$) of a film having photoelectrochemical properties and a surface appropriate for a solar cell.$^{82}$

Scheme 4 Sonochemical reactions involving group II, III and IV metals (ref. numbers in square brackets)

Treatment of solid surfaces and particles. Ultrasonic surface treatment (UST) can have different effects on the structures of solids, e.g. increase in hardness of metals, cavitation erosion, enhancement of nucleation sites and generating and affecting crystal defects. Some examples are given below. The impact of ultrasound on a solid depends, amongst other factors, on the irradiation time. As already mentioned in the electrodeposition of metals, sonication can enhance the hardness of metals. Thus, brief irradiation (5 min) of various metals caused a hardness increase of about 27% (Ti, Nb) to 150% (Cu$^{110}$). On the other hand, prolonged sonication leads to erosion of metals and alloys due to cavitation. Data on the resistance of such materials are of interest for applications where hydrodynamic cavitation can occur. Sonication of these materials can easily give such data, as has been shown for aluminium alloys.$^{111}$
nickel:

\[
\text{Me} + \text{C} \xrightarrow{\text{(Ni)}} \text{Me} + \text{OH} + \text{OH}
\]

mercury:

\[
\text{Br} + \text{Me} \xrightarrow{\text{(Hg)}} \text{Me} + \text{OH} + \text{OH}
\]

cadmium:

\[
\text{Ph} \xrightarrow{\text{(Cd/SnCl}_2\text{)}} \text{Ph} + \text{OH} + \text{OH}
\]

copper:

\[
\text{OH} + \text{C} \xrightarrow{\text{(Cu)}} \text{OH} + \text{OH}
\]

**Scheme 5** Sonochemical reactions involving transition metals (ref. numbers in square brackets)

**Table 3** Sonication of elemental sulfur–metal mixtures in different solvents using a cleaning bath

<table>
<thead>
<tr>
<th>metal</th>
<th>(\text{H}_2\text{O})</th>
<th>(\text{n-hexane}^a)</th>
<th>(\text{CS}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8</td>
<td>65 (75)</td>
<td>76</td>
</tr>
<tr>
<td>Fe</td>
<td>68</td>
<td>15 (25)</td>
<td>19</td>
</tr>
<tr>
<td>Zn</td>
<td>9</td>
<td>7 (19)</td>
<td>10</td>
</tr>
<tr>
<td>Mg</td>
<td>3</td>
<td>5 (7)</td>
<td>6</td>
</tr>
</tbody>
</table>

* Yields in parentheses: probe system.

Ultrasonic irradiation effects directly affecting the properties of point and extended defects on semiconductors are due to the stimulation of different processes: generation of Frenkel pairs, dissociation of point defect complexes and enhanced gettering of point defects by sinks such as dislocation, grain boundaries or precipitates. Point defect gettering in silicon-based materials such as silicon wafers and solar-grade polycrystalline silicon are examples. For the latter an improved minority carrier length and enhanced dissociation of Fe–B pairs have been found.92

Carbon nanotubes can be opened selectively and filled with certain metals or metal oxides. Sonication prior to the oxidative opening with nitric acid has been found to enhance the number of Fe–B pairs.

**Scheme 6** Examples of sonochemical switching

\[ \text{PhCH}_2\text{Br} \xrightarrow{\text{(RCN/Al}_2\text{O}_3\text{)}} \text{PhCH}_2\text{CN} \]

\[ \text{PhH} \xrightarrow{\text{[Fe_2(CO)_9]}} \text{PhFe}_{(CO)} + \text{Fe(CO)}_3 \]

\[ \text{RCH}_2\text{OH} \xrightarrow{\text{(HNO}_3\text{)}} \text{RCH}_2\text{ONO}_2 \]

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of acidic groups formed in this oxidation step. These groups on the surface of the carbon nanotubes can bind palladium ions strongly. Thus, the amount of nanosized palladium crystallites deposited on the inner and outer surfaces can be increased by sonication. This effect is due to the creation of small local defects in the tubes such as buckling, bending and lattice dislocations on the surface.96

The dispersion and impregnation of particles by ultrasound is another important application. Thus, metal matrix composites have been prepared by dispersion of ceramic particles in liquid metals. Normally, the poor wettability of the particles by the metal, segregating and clustering are problems in this process. The obtained particle size is > 10 µm. Thus, sonication has been applied successfully in the production of Si₃N₄-Al-Mg. First, Si₃N₄ (1 µm) was presonicated in acetone and then the particles were irradiated directly in the melt. As a result, the particles were well wetted by the Al-Mg matrix, a homogeneous distribution was achieved and no agglomeration was observed, resulting in particle sizes < 5 µm.98

The impregnation of solid particles can be exemplified by dyeing of leather99 and the preparation of dielectric polymer composites by impregnation of dielectric BaTiO₃ gel into pores of microporous polyethylene membranes. In the latter process, a Ba(TiO₂Pr')₃-Pr'OH gel with immersed microporous polyethylene is sonicated for 15 min. The obtained dielectric material has a significantly higher relative permittivity and higher losses than a conventionally produced BaTiO₃-polyethylene film.96

Polymers
The sonochemistry of polymers consists of three main fields: the degradation of polymers, the ultrasonically assisted synthesis of polymers and the determination of the polymer structure (for reviews see ref. 7,8,112–114). The last area has been reviewed recently115 and will not be discussed here.

Polymer degradation
It has long been known that the irradiation of polymer solutions reduces their viscosity, e.g. sonication (960 kHz, 6.8 W cm⁻²) of an air-saturated 1% solution of polystyrene in toluene reduces the flow time from 23.6 s to 18.3 s after 2 h.106 As the early investigators concluded, the decrease in viscosity is due to the degradation of the polymer chains.

In polymer chemistry, not only the rate and the yield of the polymerisation reaction as well as the structure of the polymer, but also particularly the molecular mass and its range and distribution in the polymeric material are of interest. From the experimental data available, some general conclusions concerning the rate and the extent of the ultrasonic degradation process can be made. The rate of depolymerisation decreases with decreasing molecular mass of the polymer, but below a limiting molecular mass there is no further degradation. Furthermore, the degradation is affected by the ultrasonic parameters (frequency, intensity), solution conditions (solvent, gas content, polymer concentration, initial molecular mass) as well as external temperature and pressure (see Table 4). The results of the influence of frequency, intensity, solvent and external temperature are in accord with the effects of experimental parameters on cavitation (see Fundamentals section), i.e. degradation is improved if cavitation is favoured.

The effects of gas and external pressure are somewhat more complicated. There is no doubt that the degradation is higher in the presence of a gas. As would be predicted, polyatomic gases show lower degradation rates than diatomic ones. However, the rates in the presence of monoatomic gases are between those for polyatomic and diatomic gases. Attempts to explain this abnormal behaviour discuss the gas solubility and its thermal conductivity. Contradictory results were found for the effect of pressure (for details refer to ref. 7).

A recent study by Price et al.116 on the ultrasonic degradation of polystyrene clearly showed that by suitable variation of reaction parameters (temperature, solution concentration, solvent vapour pressure, ultrasound intensity), extense control over the molecular mass and the polydispersity of the resulting material is possible.

There have been several attempts to explain the degradation and to outline appropriate reaction mechanisms. The following causes have been considered: frictional forces, shear gradients and impacts due to cavitation collapse; hydrodynamic forces caused by shock waves; and chemical reactions caused by reactive intermediates.

Many of the observed trends in polymer degradation can be explained by these theories. However, why the polymers are broken in the middle of the chains can only partially be explained as reported by Glynn and co-workers,117,118 who found a Gaussian distribution of the scission around the middle of a chain. Direct thermal degradation by the high temperatures of the hot spot seems to play a minor or even infinitely small role, as this is mainly random.

Polymers
There are two basic groups of polymerisation reactions to which ultrasound is applied: (1) sonication of a solution already containing a homopolymer and either a second homopolymer or a monomer; and (2) sonication of a solution containing only monomers (with or without initiator).

The first group is related to the macromolecular radicals formed as a consequence of the polymer chain cleavage. Sonication of a mixture of two polymers or a homopolymer...
Materials degradation

Practically, no solvent is inert under ultrasonic cavitation. Chemical effects are either a consequence of the sonolysis of solvent vapour inside the collapsing bubble due to the harsh reaction conditions (e.g. the elemental sections) or can be carried by secondary reactions (at different sites, see Fig. 1) resulting from reactive species (mostly radicals or radical ions) generated during the collapse.

Sonolysis in aqueous systems

It has long been known (since 1929)\textsuperscript{120} that H$_2$O$_2$ is a product of water sonolysis:\textsuperscript{121}

\[
2\text{H}_2\text{O} \overset{\text{H}_2\text{O}}{\rightarrow} 2\text{OH}^- + 2\text{H}^+ + \text{H}_2\text{O}_2 + \text{H}_2
\]

Studies and spin-trapping experiments of Riesz et al.\textsuperscript{122} gave evidence for HO$^-$ and H$^\cdot$ as intermediates. From recent results\textsuperscript{123} of such studies, temperatures of 2000–4000 K were estimated for the cavitation collapse hot-spot [from spin trapping with N-(tert-butyl)-α-phenylnitrene of H and D atoms formed in argon-saturated 1:1 H$_2$O-D$_2$O mixtures], confirming the temperatures firstly reported by Suslick et al.\textsuperscript{124} Henglein et al.\textsuperscript{125} demonstrated the trapping of HO$^-$ and H$^\cdot$ by D$_2$ to form HDO and HD, respectively. However, approximately 80% of the OH and H atoms recombine (under argon and in the absence of scavengers). The average peroxide formation rate is about 10–50 μmol l$^{-1}$ min$^{-1}$ using a probe system at 20 kHz and applying about 50 W cm$^{-2}$.\textsuperscript{121}

Irradiation of water in the presence of non-inert gases such as O$_2$, N$_2$, H$_2$, CH$_4$ or mixtures of H$_2$–CO and N$_2$–CO gives a variety of products.\textsuperscript{121}

The radicals produced by the sonolysis of water or the generated H$_2$O$_2$ can also be trapped by organic compounds dissolved or dispersed in water. Several oxidation, hydroxyl- and/or decomposition products have been detected (Table 5). However, the reaction mixtures are rather complex owing to several secondary reactions, especially in the presence of gases. For details, refer to the literature (ref. 121 and references therein).

In recent years the sonolysis of organic pollutants in water has become a developing field of research in environmental technology. Amongst the investigated compounds are chlorinated compounds,\textsuperscript{126–129} chlorofluorocarbons (CFCs),\textsuperscript{120–132} phenols\textsuperscript{133–136} and pesticides.\textsuperscript{129,127} The utilisation of ultrasound to convert environmentally hazardous substances into more benign substrates, or better still to mineralise organics into carbon dioxide, has been described recently in some reviews.\textsuperscript{138–140} Some examples are given in the following paragraphs.

\begin{table}[h]
\centering
\begin{tabular}{|l|l|}
\hline
substrate & main sonolysis products	\\
\hline
halogen compounds: & CCl$_4$, C$_2$Cl$_4$, CO$_2$, HCl, HOCl	\\
RCI & Cl$_2$, HCl, HOCl, CO$_2$, RH, ROH	\\
chlorofluorocarbons & CO, CO$_2$, HCl, HF	\\
oxygen compounds: & ROH, RCHO, RC(OH)$_2$, RCOOH	\\
ROH & CH$_4$, RH, CO, RCOOH	\\
RCOOH & CH$_4$, CO	\\
RCOOH' & CH$_4$, CO, RCOOH, R'OH	\\
sulfur compounds: & CS$_2$, Bu$_2$S	\\
cysteine & S, H$_2$S, Bu$_2$SO, polymeric species	\\
amino compounds: & cysteine	\\
amines & H$_2$, CH$_4$, RCHO, ROH, NH$_3$	\\
amino acids & H$_2$, CO, HCHO, NH$_3$, RNH$_2$	\\
\hline
\end{tabular}
\caption{Products of the aqueous sonolysis of organic compounds\textsuperscript{4}}
\end{table}

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Nagata et al. studied the decomposition of 10 ppm aqueous solutions of chlorinated hydrocarbons (1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethylene) using 200 kHz ultrasound (6 W cm⁻²). After 10 min irradiation, the concentration was reduced to about 2 ppm. The decomposition rates under argon were CHCl₃ → Cl₂ + CO₂ + 3HCl + H₂

CHCl₂ + 2H₂O → H₂O⁻⁺ + 2CO₂ + 3HCl + H₂

The sonolysis of CFC 113 CHCl₂ → CHCl₂⁻⁺ + 2CO₂ + 3HCl + H₂

The decomposition depends on the type of gas as well as the gas/liquid volume ratio, e.g., the concentration of CFC 113 is reduced from 100 ppm to about 55 ppm in a 105 ml vessel having a gas/liquid volume ratio of 45/60 and to about 15 ppm with a 70/4 ml vessel and a ratio of 10/460 (time 60 min). The experiments showed that the decomposition is due to high-temperature pyrolysis inside the bubbles and is not caused by OH radicals or by combustion with O₂ or air.

The sonolysis of phenol gives dihydroxybenzenes and quinones as primary reaction products which are further degraded into low molecular mass carboxylic acids indicating that the sonolysis occurs to lower alkanes and alkenes. It has been shown that the degradation process is similar to high-temperature pyrolysis and involves radical species following the principles of the Rice mechanism.

On irradiation of diesel fuels, the sonolytic reactions are, on the one hand, similar to the degradation of alkanes including cracking of C₁₀₅-C₂₀ components and radical-induced polymerisations, and on the other hand, comparable to processes occurring during long-term storage of fuels involving sediment formation and breaking down of longer alkane chains. Sediment analyses showed similar data to storage under ambient temperature and no sonication, in terms of molecular mass distribution (1000-10000), nitrogen content and UV and IR spectra. Using ultrasound sediment production seems to result from the same processes, but the degradation is accelerated. Thus, 6 h high-intensity sonication produced an amount of sediment which is comparable to a storage at ambient temperature for 16 months.

Ultrasound has been applied recently as a first processing step in reducing the heterotaxom content in upgrading of coal synekerate. A synkerate from direct liquefaction of sub-bituminous coal was first deasphalted by ultrasonic disaggregation in n-hexane removing 39% of N, 43% of S and 47% of O.

Another interesting application is the sonoisomerisation of alkenes mediated by either halogen radicals or metal carbonyls.

Carbon—halogen bonds are cleaved easily by ultrasound to give halogenoradicals. Thus, if alkenes are sonicated in the presence of halogenated hydrocarbons the halogenoradical can add reversibly to the double bond. The sonoisomerisation of maleic/fumaric acid and ester system, trans-dichloroethylene in the presence of CHBr₃ and bromoaalkanes, respectively, as well as cis- and trans-vinyl sulfones mediated by CBrCl₃.

A wide range of metal carbonyls (M = Cr, Mo, W, Fe, Ru, Co) catalyse the isomerisation of pent-2-ene to isomers of pent-l-ene to cis- and trans-pent-2-ene. Sonication enhances the reaction rate by a factor of about 10 compared to thermal isomerisation. The use of metal carbonyls is sonochemically as effective as in photochemical isomerisations, except for Ru₉(CO)₁₂ which is more active under sonication.

**Biological materials**

The effects of ultrasound on biological systems depend on the intensity and frequency applied. Thus, the following applications are known non-destructive sonication of biosystems where the cell membrane remains intact, and cell rupture (disintegration) to release the contents due to cavitation.

**Sonolysis in non-aqueous systems**

A wide range of organic liquids have been sonicated. Suslick et al. found that the sonolysis of higher n-alkanes leads...
Non-destructive sonication of biological materials

There are several papers on the influence of ultrasound on enzymes, microorganisms and living tissues (e.g. ref. 153,161–164). Just three recent papers will be discussed in more detail.

An interesting application deals with the increase in the permeability of human skin, resulting in the possibility of transdermal drug delivery. 165 By irradiating the skin with 1 MHz ultrasound, the transport of hydrophobic drugs could be enhanced. This is explained by the disorganisation of the membrane bilayers and the resulting formation of transportation channels due to ultrasonically induced air pockets in the keratoocytes. Insulin, γ-interferon and erythropoietin diffuse at therapeutically useful rates through the skin on exposure to 20 kHz ultrasound. The skin change is reversible as the skin reverted to its impermeable state after switching off the ultrasound. In vitro experiments showed that the blood glucose level of normal and diabetic rats can be reduced by transdermal insulin delivery to the same extent as by insulin injection. It should be noted that ultrasound has already been used to alter polymer-membrane permeability to stimulate the release of polymer-coated encapsulated drugs 166,167 and to enhance the dialysis separation of electrolytes through a cellophane membrane. 168

The influence of sonication conditions on enzymes can be exemplified by a porcine pancreas lipase catalysed hydrolysis which has been published recently 153 (Table 6). Performing the reaction in an ultrasonic bath (40 kHz, 375 W electrical power input), resulted in a seven-fold increase in the reaction rate and the stereoselectivity remained unaffected compared to a non-sonicated control experiment. The rate enhancement was explained by the authors to be due to the locally high pressure and/or the increase in catalytic surface. Under ultrasonic probe conditions (20 kHz, 600 W electrical power input) and at a higher energy density, the rate and stereoselectivities decreased, probably due to higher local temperatures causing denaturation.

Bioleaching of metals has become of increasing importance. Recently, ultrasound-assisted microbial nickel leaching using Aspergillus niger has been reported. 164 Ultrasound enhanced the leaching rate of Ni, which reached 95% after 30 min sonication, while only 25% is obtained by conventional in situ bioleaching (incubation time 14 d). Increasing the ultrasound intensity leads to a maximum, and further intensity increases decrease the leaching rate. Longer sonication decreases the leaching rate slightly to 81% after 60 min. Using different frequencies, leaching rates of 95% (20 and 43 kHz) and 86% (720 kHz) are obtained. Furthermore, indications of substantial selectivity for nickel over iron were reported (under optimum conditions 95% Ni and 0.16% Fe).

Industrial and laboratory applications

There are several industrial applications of ultrasound. However, ultrasonic plastic welding and sonocleaning are by far the most important uses. Other well established areas are ultrasonic soldering, spraying, metal welding, machining and sonocleaning in the field of metallurgy and materials sciences, cell disruption in biological sciences as well as dental scaling and ultrasonic nebulizers in medical therapy (for overviews see e.g. ref. 72,162,169–172).

Applications to solids and melts

Introduced commercially in 1963, plastic welding 172,174 is now a well established industrial process which is suitable for almost all thermoplastics with low thermal conductivity and melting temperatures (100–200 °C). Using a sonotrode, a standing wave is generated with its maximum amplitude at the contact surface of the two components to be welded. Process parameters are the sonotrode shape, the contact pressure, amplitude/power and irradiation time. The ability of ultrasound to propagate through elastic media allows welds at some distance from the ultrasonic horn (far-field processing). It requires rigid materials which are able to transmit vibrations with low attenuation, e.g. polystyrene, polyoxymethylene or styrene-acrylonitrile polymers. Thermoplastics with higher mechanical damping need a smaller distance (<6 mm) to the ultrasonic tool (near-field processing). The welding of polymer films and sheets is a typical application. Thus, PTFE sheets were joined using a 50 kHz flexural-mode transducer system. 175

In ultrasonic welding, the heat is generated inside the material using internal friction. Thus, the energy is limited to the welding zone resulting in fast welding (welds are typically performed in 0.2–1.5 s) and low part distortion. Other advantages are lower welding temperatures resulting in less material degradation and higher yields, highly reproducible weld-seam quality, high energy efficiency, no adhesives or solvents or other additives, as well as automatic processing in mass production. Special applications are the embedding of metal inserts in thermoplastics and ultrasonic bonding of synthetic fibres (especially polypropylene). The latter has the major advantage of substantially lower energy consumption compared to thermal body welding. Plastic welding requires, of course, high power intensities which are in the kW (about 1000 W cm⁻²) range at 20 kHz.

Ultrasonic welding cannot, of course, replace conventional metal welding. However, it is suitable for special applications. 121,176 In contrast to plastic welding where ultrasound is usually applied vertically, metal welding uses lateral oscillating horns, inducing frictional heating between the surfaces. Surface oxides (like on aluminium) and other contaminants are broken up, absorbed by the weld and finally the exposed metal surfaces fuse together under pressure. Ultrasonic metal welding is a form of low-temperature diffusion welding. Therefore, brittle problems resulting from recrystallisation and the formation of intermetallic compounds are avoided. Ultrasonic metal welding is used for delicate joining of metals such as electrical grade aluminium and copper, musical instruments or tiny pieces. Thus, it is applied in the semiconductor manufacturing industry for producing miniature semiconductor leads and chips as well as microbonding.

The localised use of ultrasound at some distance from the horn and the relatively cold conditions allow the machining of hard and brittle materials such as ceramics, glasses, gemstones and ferrites. Ultrasonic impact grinding or rotary abrasive machining are common applications. The cleaning effect of ultrasonic cavitation on surfaces is also the main principle in fluxless soldering. Ultrasonic erodes the oxide layer of molten solder and exposes clean metal to solder. This is especially applied to aluminium which is attacked by common alkaline

Table 6 Comparison of probe and bath systems on a sonochemical enzymatic reaction 153

<table>
<thead>
<tr>
<th>Conditions</th>
<th>%ee</th>
<th>Enantiomeric Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stirring</td>
<td>84</td>
<td>A 96</td>
</tr>
<tr>
<td>(i) probe 155 W</td>
<td>34</td>
<td>B 94</td>
</tr>
<tr>
<td>(i) probe 360 W</td>
<td>22</td>
<td>33</td>
</tr>
<tr>
<td>(i) probe 600 W</td>
<td>no reaction occurred</td>
<td></td>
</tr>
<tr>
<td>(i) bath 375 W</td>
<td>95</td>
<td>146</td>
</tr>
</tbody>
</table>

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or acid fluxes. The termination of aluminum cables and the soldering of mirror frames or heat exchangers are typical applications. Other uses are the soldering of hard metals, e.g., nickel.

Applications to liquids or solutions

Ultrasonic cleaning\(^2\) \(^{177}\) was the first industrial application of ultrasound and has been applied since the early 1950s. Commercial ultrasonic cleaners work in a frequency range of 20–60 kHz and with a power of 25–2500 W. They consist of stainless-steel tanks of 2–2001 capacity and are usually equipped with temperature-controlled heaters. However, there are also huge tanks of several hundreds or even thousands of litres which are equipped with numerous transducers. The overall power of such systems reaches several kW.

Typical objects include glassware, jewellery, lenses, spectacles, medical instruments, semiconductors, circuit boards, engine blocks, and other machining parts. Practically all materials which are sound-reflecting (glass, ceramics, metals, plastics) can be used, whereas materials such as rubber or textiles are cleaned less efficiently. Thus, the ultrasonic cleaning of precision mass standards in ethanol has been reported recently to be the most efficient method for cleaning polished stainless-steel surfaces.\(^{178}\) Sonocleaning in the 0.8–1.0 MHz range (called megasonic cleaning) has been applied successfully to the removal of particles from silicon wafers.\(^{179}\)

In ultrasonic cleaning, the conventional brush is ‘replaced’ by cavitation bubbles doing the job. Cavitation effects (microstreaming, high temperature/pressure jets and shock waves) act at or near the surface ‘brush off’ the contaminants, dirt or oxide layers which are either dissolved or (if insoluble) dispersed in the solution.

In combination with the ultrasonic effects, there are also external heating, detergents and the use of special solvents or water of a given pH value as bath liquid. The advantages of sonocleaning are less cleaning solvents needed (sometimes water can be used), use of parts with complex and non-regular shapes as well as materials having blind holes, crevices or inner surfaces, easy scale-up for large parts up to several metres, and application under clean-room conditions to computer equipment.

Besides ultrasonic cleaning, the dispersion of solids or liquids in suspensions and emulsions, respectively, and of liquids in air (atomisation) are the most common applications of ultrasound to liquids.

The preparation of dye pigments, insecticides and magnetic oxides are examples of industrial uses in solid/liquid systems. Some attention has also been paid to coal dispergation.\(^{180}\)

Ultrasonics are applied in the food industry to generate fine emulsions. Ultrasonic homogenisation is, for example, used in the production of tomato sauce, mayonnaise or yoghurt. Stable emulsions of immiscible liquids can be obtained ultrasonically.\(^{181}\) The production of tomato sauce, mayonnaise or yoghurt. Stable emulsions of immiscible liquids can be obtained ultrasonically.\(^{181}\) Furthermore, the removal of elemental sulfur from environmental samples by means of different reagents,\(^{189}\) the extraction of pentachlorophenol in soil, wood or water samples,\(^{190}\) and the solubilization of margarine in hexane for tocopherols analysis.\(^{191}\)

The fine dispersion of liquids in air or other gases is a common technique in medical nebulizers for inhalation therapy, and in sample injection in mass and atomic emission spectrometry. The spray pyrolysis of solid particle suspensions has already been mentioned.

Application of ultrasound in the 1–5 MHz range to inductively coupled plasma–atomic emission spectrometry (ICP–AES) can enhance the detection limits by a factor of 10.\(^{192}\) The efficiency of nebulisation is so high that the solvent loading of the aerosol needs to be reduced by thermal desolvation to prevent cooling of the plasma.\(^{192}\)

Ultrasonically assisted electrospray spectrometry (ESI–MS) has been applied successfully in LC–MS coupled analyses of proteins.\(^{193}\) Conventional ESI–MS has some severe limitations as the interface after liquid chromatography LC mobile phases which have high flow rates (>5 µl min\(^{-1}\)), conductivities or surface tensions are normally not applicable, e.g. the required mobile phase gradient MeOH–H\(_2\)O in nucleoside separations does not meet this criteria. By the application of an ultrasonic nebulizer, LC–MS determinations of proteins over a wide range of methanol–water mobile phase conditions (0–100%) with different flow rates could be performed easily. For a review on applications of ultrasonics in analytical chemistry, see ref 194, 195.

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