

Energy input from microwaves and ultrasound – examples of new approaches to green chemistry

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Saving resources by optimizing reaction conditions and new process technologies

Pressure and temperature are important parameters in reaction processes in chemical systems. However, it is a less well-known fact that other thermally initiated reactions can lead to sustainable results. The basic requirement is to capture the energy required by a reaction. Not only the energy required for the synthesis, but also that required for cooling are of interest here.

In order to minimize energy and control reactions with a view to green chemistry, attempts are being made to make the energy input in chemical systems as efficient as possible. Approaches are being taken and possibilities investigated to use until now scarcely used forms of energy, so-called non-classical energy forms, in order to optimize the duration and product yield and avoid undesired side-products. Teams working in this area are also interested in the energetic aspects of the preparation of starting substances and products and the conditioning of reaction systems (*eg* surface activation, emulsification, homogenisation, degassing, *etc*).

What do we mean by classical and non-classical energy forms? In classical processes energy is added to the system by heat transfer, electromagnetic radiation in the ultraviolet (UV), visible or infrared (IR) range or in the form of electrical energy. On the other hand, microwave radiation, ultrasound and the direct application of mechanical energy are among the non-classical forms.

In the following communication we will look at the specific properties and principles of action of microwaves and ultrasound, and the possibilities for the chemistry of the future will be presented briefly and illustrated using selected, basic experiments.

Energy application via microwaves

The hotplate versus the microwave oven

We are faced with the problems of energy application on a daily basis: if you heat milk on an electric ring there are a number of well-known pitfalls: initially the milk does not seem to heat up at all and then suddenly it froths up and burns on the bottom of the pan. An alternative is the microwave oven. The milk – for example in a glass or cup – heats quickly and starts to boil slightly, depending on the power output of the microwave, but does not burn.

Heating a solid increases the chaotic movement of the smallest particles. In solids the homogeneous temperature equalization occurs via heat convection. Energy is transferred in collisions from energy-rich (warmer) particles to energy-poorer ones. In liquids and gases convection (the free movement of particles in liquids or gases) achieves heat equalization between areas with different temperatures. In metals the temperature equalization occurs via the excitation by vibration of delocalized electrons.

When the hotplate is heated up, a considerable temperature difference results – a so-called temperature gradient – between the hotplate and the external temperature of the solid being heated (Figure 1). The internal energy of the solid increases as a result of heat transfer or convection, the temperature gradient decreases. In the case

of liquids and mobile solids (eg powders) this process is assisted by stirring or circulation.

In the microwave field the heating process often occurs more homogeneously and thus more rapidly than with the hotplate, provided energy can be applied to the solid in this way (Figure 1). Materials which have dipoles and are polarisable can be heated directly via microwave radiation. Substances which contain water – most foodstuffs – can thus be heated very well in a microwave oven. However, the penetration depth of microwaves is limited. The deeper heating effect of reaction fluids or melts is aided in large reactors by external turbulence or heat conductance or convection.

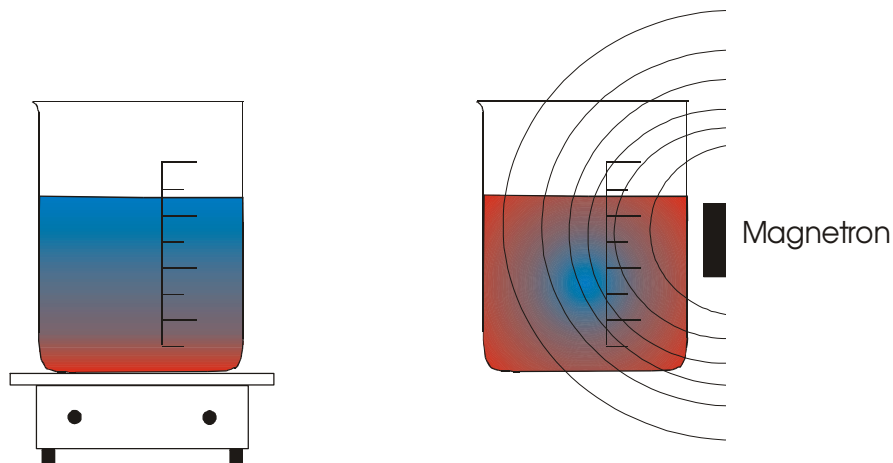


Figure 1 Temperature gradient in a liquid heated on a hotplate (left) and in a microwave oven (right). (Colour key: the temperature increases from blue to red).

Metals and metal surfaces reflect microwaves. However, some of the radiation energy is transferred to delocalized electrons (electron gas), which are excited and vibrate. If this energy cannot be sufficiently dissipated in the metal, as is for example the case in the irradiation of thin, angular or sharp metal surfaces, the metal heats up very rapidly. If the excitation is considerable, cracking occurs. A well-known example is the gold-rimmed plate in the microwave oven

What are microwaves?

Electromagnetic radiation is energy which is discharged from mobile, electric charges and spreads out as a wave. The wavelength of this radiation decreases with increasing energy. If the wavelength is in the range 1 mm to 1 m (300 MHz to 300 GHz), one refers to microwaves. Household microwave ovens produce radiation with a fixed frequency of 2.45 GHz. In the electromagnetic spectrum microwaves lie between radio waves (1 m to 10^4 m) and infrared waves (760 nm to 0.5 mm).

Microwave radiation is produced by electrical discharge (lightning), for example. Humans and animals also emit measurable quantities of microwaves in addition to thermal radiation [1]. Technically microwaves can be produced using a magnetron. This is a transmitter known as a real-time tube, in which electrons are emitted from a cylindrical hot cathode and accelerated towards the sheath-like anode which surrounds it. During their trajectory the electrons are diverted by a vertical magnetic field as a result of the Lorentz force which occurs. This causes the electrons to be deflected tangentially onto the specially constructed anode surface, so that they

cause resonance vibrations there. The microwave radiation is finally emitted from an antenna of the magnetron in a complicated oscillator [2].

Microwaves are propagated in a vacuum at the speed of light, like any other form of electromagnetic radiation however, they are reflected by metal surfaces. As a result of this property, microwaves can be screened effectively using metal sheets and even close-meshed wire nets. The metal casing and the perforated sheet at the front of household microwave ovens screen the microwaves.

The heating of different materials and substances by the alternating electromagnetic field caused by microwaves results due to the triggering of rotational vibrations of dipolar molecules, in other words the excitation of electrons, particularly the delocalized electrons of metals. The degree of excitability also depends on the substance and is known as susceptibility. The key factors which influence the heatability of materials in a microwave field are the surface texture, the surface-volume relationship and the homogeneity. Table 1 illustrates how large the spectrum of substances that can be excited by microwaves is, and how strongly they can be heated. The power output of the microwave oven used and the amount of substance investigated have to be taken into account.

Substance	Time / min	Temperature / K	Volume or mass	Microwave power output / W
Water	1	354 (b.p. 373)	50 cm ³	560
Methanol	1	338 (b.p. 338)	50 cm ³	560
Butan-1-ol	1	382 (b.p. 390)	50 cm ³	560
Hexan-1-ol	1	365 (b.p. 431)	50 cm ³	560
Hexane	1	298 (b.p. 341)	50 cm ³	560
Graphite	1	1556	25 g	1000
Copper(II) oxide	0.5	974	5 g	500
Nickel(II) oxide	6.25	1578	25 g	1000
Iron(II) diron(III) oxide	2	583	5 g	500

Table 1: The heating of different substances in a microwave field [3], beginning at room temperature (298 K)

The uncontrolled heating of body tissue by microwaves is, once again, under intense discussion, particularly since the mobile phone revolution. Health risks occurring as a direct or indirect result of the electromagnetic radiation in this frequency range are feared.

The first criterion for the evaluation of the health hazard caused by microwaves is the intensity or even radiation capacity of microwaves. Whilst microwaves with a frequency of 2.45 GHz and an intensity of less than 100 mW cm⁻² are used therapeutically for the local irradiation of body tissue, the same treatment for the entire body with the same intensity leads to a drastically increased risk of heart attack

and arteriosclerosis after only a few minutes. This occurs as a result of excessive, direct heating of deeper tissues, which, as a result of their higher water content, heat up more rapidly than the upper skin layers, which have a lower water content. However, the thermoreceptors are located here. These are responsible for adequate heat dissipation into the body interior. They are not sufficiently stimulated by microwaves and a delayed and inadequate temperature control results in the irradiated tissues [1].

In Germany, a reference value of 0.2 mW cm^{-2} for exposure to microwave radiation applies to the general population. This value is exceeded by some mobile telephones with transmission capacities of 4 W - in some cases considerably. This is the reason why some scientists and experts describe them as health hazards. The microwave ovens available for private use however, are closed radiation sources. The metal casing with the perforated metal sheet on the door of the device, which makes it partially transparent, screens the surroundings from the microwave radiation to such a degree that the radiation is less than 5 mW cm^{-2} at a distance of 5 cm [4]. The casing should not be modified by laymen (*eg* by drilling a hole), as otherwise a radiation leak may occur. However, if you would rather convince yourself of the safety of your microwave oven, it is worth purchasing a microwave leak tester. These are usually available at low cost in electrical stores.

Energy input from microwaves: not only good for the home

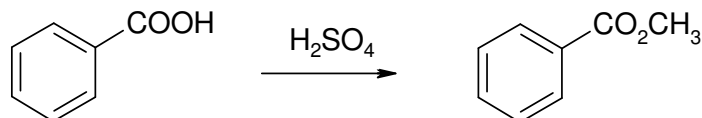
Microwave ovens are commonly used in catering kitchens and in the foodstuffs industry. A well-known example is the drying of potato chips, see [5].

In synthetic chemistry, 1986 was an important year for the use of microwave devices.

Since then countless syntheses initiated by microwaves have been carried out on a laboratory scale. The result is often a drastic reduction in the reaction time with comparable product yields, if microwaves are used instead of classical methods of energy input. Unwanted side-reactions can often be suppressed and solvents dispensed with.

Numerous reactions, such as esterifications, re-esterifications, Diels Alder reactions, hydrolyses [6] or the production of inorganic pigments, have been investigated in recent years. Two reactions illustrate nicely the advantages of this non-classical means of energy input.

In the classical method for the esterification of benzoic acid with methanol, the acid is mixed with the alcohol in a round-bottom flask. After the addition of a small amount of sulfuric acid, which acts as a catalyst, the flask is heated in an oil bath. A reflux condenser ensures that neither evaporating products nor educts are lost.



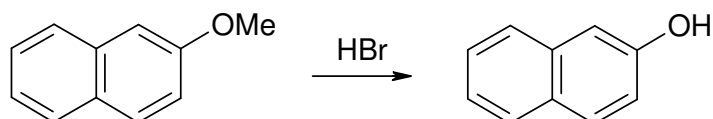
In order to heat the reaction mixture with microwaves, it is placed in a specially constructed and tightly sealed Teflon container which is permeable to microwaves.

Excess pressure builds up as a result of the heating. As the comparison in Table 2 shows, the reaction time can be reduced in this way from 80 minutes to one minute.

	Conventional	Microwave device
Solvent	methanol	methanol
Reaction temperature / K	185, reflux	393 (pressure = 333 kPa)
Yield / %	92	92
Reaction time / min	80	1

Table 2 A comparison of microwave and conventional heating for the esterification of benzoic acid with methanol

Another example here is the cleaving of ethers. The extraction of naphthol from 2-methoxynaphthalene (naphthylmethylether) has a reaction time of 72 hours when hydrogen bromide is used. In microwave ovens – in a sealed Teflon container as in the example above – the reaction time is reduced to 5 minutes as shown in Table 3.



	Conventional	Microwave device
Solvent	ethanoic acid	ethanoic acid
Reaction temperature / K	388, reflux	411 (pressure = 400 kPa)
Yield / %	81	80
Reaction time	72 hours	5 minutes

Table 3 A comparison of microwave and conventional heating for the cleavage of 2-methoxynaphthalene

In general, microwave radiation is used whenever materials and substances that are poor heat conductors but good absorbers of microwaves have to be heated rapidly but homogeneously.

Today, microwave technologies are being tested as energy- and cost-saving alternatives in most areas. Hopes are high for example in the field of green extraction of pollutants from contaminated soil, or for the improvement of the breakdown of biomass waste by fermentation as part of green biorefinery.

Introductory experiments with the microwave oven

Simple experiments with microwave ovens can be carried out with normal household models provided certain conditions (safety risks, limited test evaluation) are fulfilled.

In the following section the properties and irregularities of the microwave field produced inside these household appliances are demonstrated in some selected experiments.

Microwave heating of different fat products

The effect of the water content on the heating rate of foodstuffs in a microwave oven is illustrated by the melting behaviour of different fat products. In the following experiment, the melting times of semi-fat butter, butter and anhydrous frying fat are measured and compared.

Equipment and chemicals

Household microwave oven (800 W), 3 beakers (250 cm³), knife, 3 hour-glasses (approximately 9 cm), scales, semi-fat butter, butter, frying fat

Procedure

50 g pieces of each of the fat products are weighed in a beaker and covered with an hour-glass. The samples are heated one after the other at maximum power in a microwave oven. In all cases the beaker should be situated in the middle of the rotating glass plate in the microwave oven. The time it takes for the sample to melt completely is measured.

Observations and evaluation

Average values are shown in Table 4.

	Water content / %	Melting time / sec
Semi-fat butter	60	20
Butter	15 %	40
Frying fat	0 %	70

Table 4 Melting times for different types of fat

The fat molecules, which have a low polarity, are only slightly excited by the microwave radiation. The heating effect is based largely on the water content of the fat products. The higher the water content is, the faster the sample heats up.

Heating a two-phase system in a microwave oven and on a hotplate

Compared with conventional heating on a hotplate, a more homogeneous and thus more rapid heating of food is achieved in a microwave oven. The following experiment shows this:

If you layer a saturated copper(II) sulfate solution with water and heat it once on a hotplate and once in the microwave oven, you can observe the different convection behaviour of this two phase system very well.

Equipment and chemicals

Household microwave oven (800 W), 2 beakers (150 cm³, tall form), piston burette (25 cm³), hotplate, 2 glass rods, copper(II) sulfate solution (approx. 1.2 mol dm⁻³), distilled or deionised water

Procedure

80 cm³ of water are carefully layered with 20 cm³ of copper(II) sulfate solution in two beakers with a piston burette. One sample is heated on the hotplate, the other in the microwave, both until they reach boiling point. A glass rod is placed in each solution to prevent boiling delay. The time until boiling is measured and the changes in the phase mixture are observed.

Observations and evaluation

By carefully layering the copper(II) sulfate solution with water, a two-phase system is obtained with deep-blue copper sulfate as the lower phase. When the sample is

heated on the hotplate, just before it begins to boil rising concentration currents due to heat convection can be observed. The phase separation however, remains largely stable until the sample begins to boil. The phases are then mixed by rising gas bubbles. In contrast, the phase separation in the sample heated in the microwave remains some time after the sample has begun to boil. The only observation to be made is a few gas bubbles rising to the surface. The sample in the beaker boils after a short time, but in a smoother fashion than the other sample, which is due to more homogeneous heating of the liquid.

Detection of the inhomogeneity of a microwave field in a household microwave oven

Uniform heating in a microwave oven depends, on the one hand on the polarity and structure of the food, and on the other on the geometry and homogeneity of the microwave field. Inside the microwave oven, reflection of the microwaves on the inner walls causes interference, which in turn produces an inhomogeneous electromagnetic field. The microwave fields of household microwave ovens show areas of complete field loss as well as so-called hot spots, areas with a higher radiation intensity. Technically this problem is partially solved by incorporating a rotating glass plate in the microwave oven. The substance to be heated is heated more homogeneously as a result.

Equipment and chemicals

Household microwave oven (800 W), 2 Styropor[®] plates, paper towels, thermal fax paper

Procedure

Experiment A

A Styropor[®] plate is cut to fit the diameter of the rotating plate in a microwave oven and covered with a paper towel, which is then moistened with water. The fax paper is then placed flat on the paper towel. The plate is then placed on the rotating plate inside the microwave oven. The oven door is then closed and the microwave oven turned on to maximum power until a blackening of the fax paper occurs.

Experiment B

A second Styropor[®] plate is cut to fit the inner area of the microwave oven. The same procedure as in Experiment A is followed, except that the plate is placed on the bottom of the microwave oven, in place of the rotating plate.

Observations and evaluation

After approximately 5 seconds, the fax paper rapidly begins to turn black in both experiments. In the first experiment, one can clearly see a broad, black ring from the fax paper around the rotation axis of the glass plate. In the second experiment a reproducible pattern of black dots and bands characteristic of the microwave oven used results.

In the hotspot zones of the inhomogeneous microwave field, the moist paper towel heats up much faster and water evaporates earlier here than in the other areas of the paper towel. The hot steam causes the blackening of the thermal paper.

Compact discs in the microwave oven

When using a household microwave oven, not only the dipole excitation but also the electron excitation is of significance because the latter can cause dangerous spark discharges (see above). Excitation by microwaves can be demonstrated most impressively by thin metal layers on a Compact Disc (CD) [6].

Equipment and chemicals

Household microwave oven (800 W), CD

Procedure

The CD is placed in the middle of the rotating glass plate with the non-printed side facing upwards. The microwave oven is turned on at maximum power, but for no longer than 5 seconds, because otherwise pyrolysis of the plastic polycarbonate occurs.

Observations and evaluation

Shortly after the microwave oven is turned on, the CD glows intensely at irregular intervals. The hissing typical of electrical spark discharges can be heard. The thin aluminium coating between the carrier disk and the lacquer layer of the CD is electronically stimulated to such a degree that it starts to glow. This does not occur at regular intervals, however. The deflagration of the metal coating begins in numerous places *via* spontaneous ignition sparks. These spread out in a matter of seconds forming spark gaps over the entire area of the CD. This deflagration leaves characteristic burn marks on the plastic carrier material, which form a filigree, fractal-like pattern.

The production of high temperatures using activated carbon and graphite as susceptors

In industry as well as in the laboratory, it is no problem to produce relatively high temperatures. For example, electric arc furnaces, fan burners or electric arcs can be used. The use of microwave radiation can bring advantages here, especially when the rapid and cost-effective heating of small amounts of substances is concerned. The following experimental protocol and experiments show this very impressively. Only the substances are selectively heated, the inside of the microwave oven is heated only moderately.

If granulated activated carbon is irradiated in a microwave oven, the carbon glows after only a very short time. After a minute, according to [3], a temperature of around 1500 K is reached (at 1000 W). The very good properties of activated carbon (or even graphite) as a susceptor – a substance that absorbs microwave radiation intensely, can be explained by the partly delocalized electron system and the high electrical internal resistance resulting from the pronounced pore structure, but above all they are due to the temperature dependence and the dielectricity of this substance.

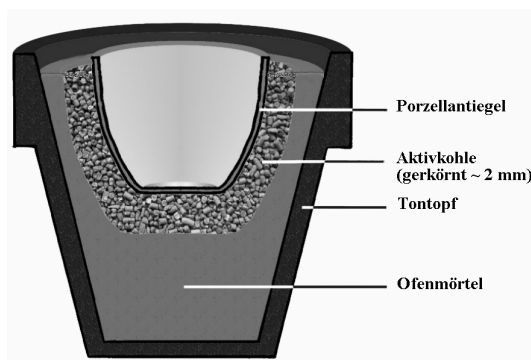
This known effect – which can be seen to a lesser degree with some carbides and metal oxides [3] – can be used to produce high temperatures for different physical and chemical processes.

The basic principle is to place a crucible in activated carbon in a temperature-resistant container (crucible materials consisting of quartz or porcelain are heated scarcely or not at all by microwave radiation due to their transparency) (Figure 2). In these crucibles experiments such as glass production and the smelting of metal powders and alloys can be carried out.

Fire-proof container in a microwave oven

In order to produce a fire-proof container a small earthenware pot and mortar are required. Thus the process can be carried out at low cost. Although the carbon and the crucible quickly begin to glow after the microwaves have been switched on, the heating of the inner side and the front plate of the microwave oven through heat reflection is not critical after an operating time of 10 minutes. However, because the earthenware pot gets very hot, it should not be placed directly on the rotating glass plate. Pieces of breeze block (or similar) are suitable as a fire-proof underlayer. They can be cut to the dimensions of 6 cm x 6 cm x 3 cm using appropriate tools. The construction is placed in a microwave oven without rotating plate in an area of high radiation intensity.

An earthenware flowerpot (100 cm³) is filled with mortar (from the DIY store) and a metal or porcelain crucible (40 cm³) is pressed down deeply into this. Beforehand, the outer surface of the crucible is covered with Clingfilm so that it can be removed easily once the cement has dried and hardened. The cement mould produced is then filled with granulated activated carbon and the actual porcelain smelting pot (20 cm³) is placed on top. The free space between the crucible and the mould is also filled with granulated activated carbon (see Figure 2). This element is the actual reaction apparatus, with which crucible temperatures up to approximately 1500 K can be produced in the microwave oven.



Labels. Porzellantiegel = Porcelain crucible; Aktivkohle = activated carbon (granulated 2 mm); Tontopf = earthenware pot; Ofenmörtel = mortar

Figure 2: High-temperature crucible with activated carbon

Glass production

The production of glass by simple means is time-consuming. There are formulations which can be melted with a Bunsen burner, but these contain lead compounds [8]. With the procedure described here it is possible to produce lead-free glass as well. The whole procedure takes only ten minutes.

Production of lead-free borosilicate glass

Equipment and chemicals

Fire-proof container with crucible (see above), piece of breeze block (or similar), household microwave oven (800 W), crucible tongs, spatula, mortar and pestle, boric acid, quartz sand, calcium carbonate, sodium carbonate, lithium carbonate.

Procedure

10.6 g of boric acid, 1 g of quartz sand, 1.7 g of calcium carbonate, 1.8 g of sodium carbonate and 2.5 g of lithium carbonate are mixed carefully in a mortar, *cf* [9]. Avoid dust.

The crucible is half-filled with the mixture, the element is placed on the breeze block in the microwave oven and the oven door is closed. The microwave oven is operated at maximum power until the mixture in the crucible begins to glow and smoke. Finally, the element is removed rapidly from the microwave oven using the crucible tongs and placed on a heatproof mat. The crucible is removed from the mould using the crucible tongs and the melt is poured onto a heatproof mat (alternatively, a tiled bench top is suitable), making sure that as few glass beads as possible are produced.

Observations and evaluation

The crucible glows uniformly after approximately two minutes heating in the microwave. The glass mixture swells over the edge of the crucible initially, but then collapses and turns into a thin melt. This then starts to smoke after about four minutes and becomes largely homogeneous and free of bubbles.

The cold glass beads can be removed easily from the tiled benchtop, but large beads fracture very easily as a result of tension in the glass due to the rapid cooling. Coloured glass can be produced using this method by adding traces of cobalt(II) oxide (deep blue), copper(II) sulfate (blue), chromium(III) oxide (green) or iron(III) oxide (yellow).

Production of alloys and metal melts

Metallurgical processes often require high temperatures. This also applies to the production of alloys such as brass and bronze. Their extraction is also interesting from a historical point of view.

Isolation of bell bronze

Equipment and chemicals

Fire-proof element with crucible (see above), piece of breeze block (or similar), household microwave oven (800 W), crucible tongs, spatula, hammer, anvil, copper (fine powder), tin (fine powder)

Procedure

8 g of copper are mixed homogeneously with 2 g of tin in a crucible. The element is irradiated for 5 minutes at 600 W in a microwave oven. Once the crucible has cooled, the molten metal is removed and hammered into shape on the anvil.

Observations and evaluation

The crucible glows after it has been heated for about a minute in a microwave oven. The product is a melt with slag attached. After hammering, a bronze-coloured piece of metal is produced.

Isolation of Thenard's Blue (*cf* [7])

The French chemist Thenard was commercially very successful with his isolation of cobalt spinel, CoAl_2O_4 , by annealing cobalt carbonate with aluminium(III) oxide using potassium chloride as the fluxing agent. *Thenard's Blue*, a deep blue pigment, is a very popular colour for ceramics, due to its chemical resistance [1]. This

transformation is more rapid and has a higher yield when the procedure described is carried out in a microwave oven, compared with annealing in a crucible over a Bunsen burner flame.

Equipment and chemicals

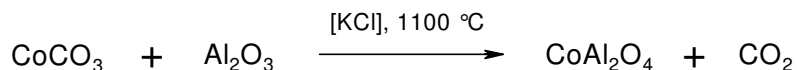
Fire-proof container with crucible (see above), piece of breeze block (or similar), household microwave oven (800 W), crucible tongs, mortar and pestle, beaker (100 cm³), hotplate, filter funnel with paper filter, cobalt carbonate (harmful), aluminium(III) oxide, potassium chloride, hydrochloric acid 25 % (irritant), distilled or deionised water

Procedure

1.7 g of cobalt carbonate, 2 g of aluminium(III) oxide and 5.5 g of potassium chloride are mixed carefully in a mortar. The mixture is annealed in a crucible with fire-proof element for five minutes at 400 W in a microwave oven. After cooling, the product is removed from the crucible and crushed in a mortar. The powder is boiled for five minutes with approx. 20 cm³ of hydrochloric acid in a beaker. After cooling, the mixture is diluted carefully with approx. 50 cm³ of water and the solid is filtered off. The filter cake is dried.

Observations and evaluation

The reaction mixture is dark gray. After annealing and pulverizing, a deep-blue powder results, whose colour becomes more intense after treatment with hydrochloric acid and drying. The annealing causes the metal oxides to combine to form a mixed oxide with spinel structure. The reaction can be described in the following way.



Energy input by ultrasound

Ultrasound is the term used for sound waves in the frequency range 16 kHz to 10 MHz, in other words the frequency range just above the human threshold of audibility.

At the turn of the century, Galton developed a flow whistle, in which air passes a so-called ultrasonic edge, causing it to vibrate and emit ultrasound [8]. Today, electricity is used as the energy source to produce ultrasound. To put it simply: a transducer is excited causing vibrations. These are transferred to a fluid and emitted, because in gaseous media ultrasound has a very limited range.

The applications of ultrasound today are so numerous that only a few selected examples will be mentioned here. The following areas are well-known:

- Ultrasound fields with high frequency (> 2 - 5 MHz) and low intensity are used in diagnostic medicine. Here one makes use of differences in the reflection capabilities of body tissues and the Doppler effect. In this way individual organs can be examined and an image produced. It is also possible to see the blood flow in blood vessels and thus recognize changes such as constrictions. This method, which is not harmful or stressful to the patient, has been constantly improved in the last twenty years and has replaced other methods of examination such as X-ray.

- Ultrasound methods have been used for decades for testing materials, for example for testing weld seams or for locating hidden cracks in construction parts.
- Ultrasound with low frequency (< 1 MHz) but high performance intensity brings about physical and chemical processes. Examples are the formation of emulsions and the displacement of dirt from surfaces, both for cleaning and activation. For example, ultrasonic baths are used for cleaning purposes. Sensitive surfaces, such as the lenses of glasses, can be cleaned without damaging them in this way. This process also has advantages for deposits that are not easily accessible, but have to be removed. For these reasons, ultrasound baths are used by both opticians and many natural science laboratories. Other applications can be mentioned here: the smashing of kidney stones, the initiation or acceleration of radical reactions, the degradation of organic contaminants in polluted water and the excitation of sonoluminescence [9].

How does low frequency ultrasound work?

Ultrasound energy enters systems by cavitation, depending on the sonic frequency, or to a larger extent by dissipation. The terms cavitation and dissipation will be explained below.

In the cavitation process small bubbles are formed in liquids at mechanically weak points, usually at phase boundaries, as a result of intense sonication. These bubbles increase in size due to resonance in areas of underpressure. [10]. Small gas bubbles present in the liquid initiate the process. Above a certain size the bubbles become unstable and collapse non-symmetrically (Figure 3). Tiny zones of excess heat are formed, where a temperature of 5000 K and a pressure of 50 MPa can occur temporarily. In aqueous systems the tearing of the bubbles can lead to the formation of hydrogen and hydroxyl radicals in the gas zone. These can react further to produce hydrogen peroxide or oxygen directly, or they can dissolve in the water layer surrounding the bubble and then react. The latter process can occur without any difficulty, because a layer of supercritical water is formed temporarily as a result of the pressure and temperature conditions around the bubble. This has hydrophobic properties, in contrast to water under normal conditions, as do the radicals [11].



Figure 3 Collapsing cavitation bubble (from [10]).

The effects described are not confined to water. In non-aqueous systems, acoustic irradiation can also cause the formation of radicals.

Dissipation means the dispersion and scattering of particles, the degradation of surface layers and the heating of media by the transfer of vibrations in a high-frequency field of alternating pressure. The input of dissipative energy by ultrasound will become established in the future.

The use of ultrasound

Like microwave radiation, ultrasound has increasing significance as a non-classical form of energy in physical and chemical process engineering, where the aim is again the effective exploitation of energy and raw materials. Ultrasound can accelerate reactions in mono- and multi-phase systems that have at least one liquid phase. The reactions occur at low temperatures (*cf* the estimated parameters in cavitation implosion) and in some cases proceed selectively.

The development of ultrasound applications is not by any means completed, on the contrary, we are in the middle of a phase of exciting new developments. One example illustrates this: in future we will save water and surfactants by doing our washing with ultrasound. Even if washing machines that use ultrasound are not yet in production, industry has attached a lot of significance to this project of the future. Design prizes have already been awarded for new machines. However, the further development and optimization of ultrasound reactors is particularly important for future developments.

The following areas of application have aroused considerable interest:

- Surface cleaning: layers of dirt are eroded and displaced by ultrasound, so that they are then suspended in the liquid and can be washed away. Examples: ultrasonic cleaning baths for sensitive and poorly accessible objects, sonotrodes for dental clearance.
- Emulsification without the addition of emulsifying agents: The phase to be dispersed is distributed very finely in the dispersion agent by high-frequency ultrasound. Example: the homogenization of milk.
- Degassing liquids: the acoustic field causes tiny gas bubbles to agglomerate and finally outgas from the liquid.
- Sterilization: The cell membrane or cell wall of micro-organisms is destroyed by the alternating pressure field caused by ultrasound. As a result the cells perish.
- Extraction: Phase transitions are accelerated and the distribution equilibrium of the extract between the extracted substance and the extraction agent is reached more rapidly.

The examples named describe applications where the physical effects of ultrasound are in the foreground. So-called sonochemical applications are also based on physical effects, but they have a direct or indirect effect on chemical reactions. These are illustrated by the following examples:

- Surface activation of catalysts and metal surfaces: many chemical reactions take place between a liquid and a gas or a solid on their surfaces. If the latter is covered with dirt, or in the case of metal surfaces, with an oxide layer, the reaction cannot take place at all, or only at a reduced rate, because the particles in the liquid or gas phase cannot reach the surface of the solid reaction partner. Ultrasound removes these interfering deposits, so that the entire surface is available for the reaction. The reaction proceeds more rapidly.

- With the saponification of esters the reaction proceeds on the boundary between the aqueous acid or base phase and not in the water-soluble ester phase. Ultrasound accelerates the particle transition at the phase boundary and thus the reaction, compared with the classical reaction procedure with heating and stirring. Esterification can be carried out sonochemically at room temperature.
- Oxidations in aqueous media are usually based on ultrasound-induced cavitation processes, as a result of which oxidizing agents can be formed in the solvent – albeit in minimal amounts. An example is the oxidation of iodide ions (see below).

Simple experiments with ultrasound

Commercially available ultrasonic cleaning baths, which have a fixed frequency of between 20 and 40 kHz (35 kHz here) and a power output of < 150 W, are suitable for the experiments described here. The cleaning bath is placed on a suitable lifting platform (labjack) for all experiments and filled with distilled water according to the operating instructions. The piece of metal or reaction vessel is suspended in the water and fixed to a retort stand using a suspension clamp. Erlenmeyer flasks are the best reaction vessels available, because sonic transmission is hindered only very slightly by the flat bottom of the flask.

The lifting platform can be used to adjust the suspension depth so that the ultrasonic resonance in the reaction medium can be optimized. This has proved to be the case if the surface of the liquid in the reaction vessel is just below the water surface of the bath.

The ultrasonic bath slowly heats up during operation [11]. The best test results are achieved when the temperature of the water in the bath is kept low by adding crushed ice.

Do not place your hands in the water bath whilst the device is switched on as peeling of the periosteum can occur.

Physical effects of ultrasound

The cleaning of equipment in ultrasonic baths is well-known. In the first experiment it will be shown that dirty surfaces cannot be cleaned by the action of ultrasound in a water bath alone. The solution is very simple: If a surfactant is added to the water, even very persistent dirt on the surface can be removed.

Cleaning effect of an ultrasonic bath

Equipment and chemicals

Ultrasonic bath, two clay shards from a flowerpot, fat, coal dust (activated carbon), washing-up liquid

Procedure

First, the clay shards are rubbed uniformly and thinly with a mixture of coal dust and fat. One of the shards is then treated for ten minutes in the ultrasonic bath filled with distilled water. The shard is then placed to one side for later comparison. Some washing-up liquid is then added to the water in the bath and the second shard sonicated for ten minutes. Finally, the degree of cleaning of the two shards is compared.

Observations and evaluation

The shard that was sonicated in water containing washing-up liquid was cleanest.

This observation seems at first to downplay the effect of ultrasound. Two questions arise: What effect does the addition of surfactant have and what is the advantage of cleaning this way?

Dirt often consists of hydrophobic deposits (eg fat). Ultrasound erodes and fragments the dirt particles on the surface of a dirty object, but not those particles present in the solution. These are adsorbed to the surface. Cleaning is achieved only when surfactant is added, enabling the dirt particles to be suspended in the water. This cleaning procedure is advantageous because the surfaces of materials are not affected by mechanical action and poorly accessible areas can be reached. Sonication also has an anti-microbial effect.

However, this cleaning method is not universally applicable. Ultrasound can erode paint layers from surfaces, for example. Sensitive materials are attacked and eroded by the microjets caused by the collapse of cavitation bubbles. The following experiment is generally suitable for testing the function of ultrasonic baths.

Destruction of aluminium foil by ultrasound [from 11]

Equipment and chemicals

Ultrasonic bath, household aluminium foil (thickness 13 μm), pair of tweezers

Procedure

A smooth piece of aluminium foil is held vertically with a pair of tweezers in the high resonance region of the ultrasonic bath and sonicated for approximately one minute.

Observations and evaluation

The piece of foil showed considerable material erosion. Holes and frayed edges are clearly visible.

Reactions induced by ultrasound

In the previous experiments, only physical phenomena were observed and the chemical reactions which occur were ignored. If we restrict ourselves to aqueous systems, then the essential reaction steps have already been named: splitting of water molecules into free hydroxyl radicals and hydrogen atoms, which, amongst other things recombine to form hydrogen peroxide. The OH radicals in particular are responsible for the transformation of water pollutants, as a result of their high oxidation potential. The target products in aquasonolysis are either biologically degradable intermediate products or water, or mineral acids as mineralization products.

Oxidation of iodide ions to elemental iodine

Equipment and chemicals

Ultrasonic bath, 2 Erlenmeyer flasks (100 cm^3), retort, lifting platform (labjack), potassium iodide solution (approximately 1 mol dm^{-3}), starch solution

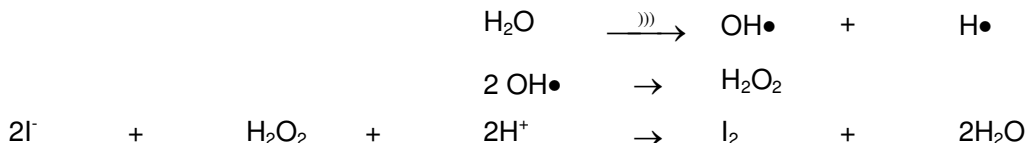
Procedure

Two Erlenmeyer flasks are both filled with approximately 30 cm³ of potassium iodide solution and 5 cm³ of starch solution. One of the flasks is suspended in the ultrasonic bath and sonicated for approximately 15 minutes.

Observations and evaluation

After sonication for several minutes, the previously colourless mixture turns yellow-brown. A solid is formed at the bottom of the flask which changes colour from violet to black during the sonication. The control shows no change.

Hydrogen peroxide is formed as a result of sonication, and oxidizes iodide to iodine:



The iodine reacts with starch to form the well-known iodine-starch complex, which is precipitated as a solid by ultrasound.

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