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Using ultrasound for environmental sample preparation: what's the buzz?

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The application of ultrasound in sample preparation has been shown to facilitate and accelerate each stage, reducing overall sample preparation time. In addition, ultrasound assisted techniques reduce energy and solvent consumption, reducing the overall cost of analysis. The ultrasound process aligns with numerous Green Chemistry principles, which is an advantage for environmental chemists.

Ultrasound is used in a variety of applications, including sonograms in healthcare and SONAR (sound navigation and ranging) systems in naval ships. When applied to chemical applications, it is known as 'sonochemistry' or, more generally, as 'sonication' (*1*). It has been applied to sample preparation at many stages, including extraction, precipitation, and derivatisation. Ultrasound assisted techniques are becoming more utilised by analytical chemists due to the versatility, flexibility, and ease of use of the techniques, combined with the advantages of reduced energy consumption and cost (*2*).

Cavitation

Ultrasonic waves alternate between expansion and compression cycles, generating bubbles in the liquid medium. The formation, growth and implosion of these bubbles is known as cavitation (**Figure 1**). The process results in extreme changes in local temperatures and pressures which help to facilitate chemical reactions (*1*), driving the extraction and derivatisation processes. The cavitation process depends highly on the intensity and frequency of the ultrasound (*3*), the time and temperature of the reaction, and the properties (viscosity, volatility *etc.*) of the solvent (*1*).

Direct vs indirect sonication

In most studies, a sonication probe (direct sonication) or sonication bath (indirect sonication) are used to implement the ultrasound to the sample. Although direct sonication is more intense, there is increased possibility of cross contamination (*4*), as the probe is submerged in the sample. Indirect sonication, using a bath, allows for the ultrasound to be applied to multiple samples at once; however, a lack of uniformity in ultrasound transmission is a potential limitation (*5*)

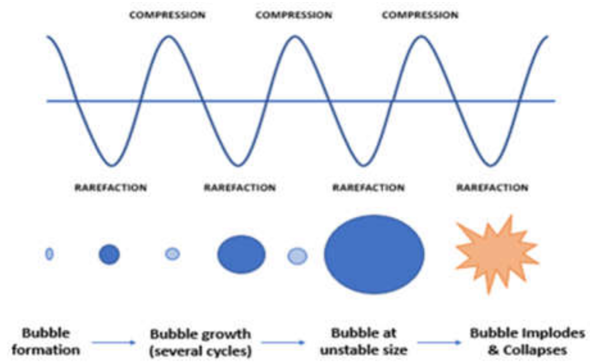

Figure 1. Schematic of cavitation process in ultrasonication. Adapted from (6).

The novel method of a sonotrode (*7*) (**Figure 2**) offers similarities to both the ultrasonic bath and the sonication probe by applying intense indirect sonication – the ultrasonic waves cross the walls of the sample vial – without possibility of sample loss or contamination. The sonotrode is suitable for use with smaller solvent volumes (µl-ml), making it ideal for both extraction and derivatisation, with the added benefit of reduced solvent waste. The sonotrode offers control over operating parameters, including amplitude, ultrasound application (continuous or pulsed), and time, and thus optimisation of the extraction or derivatisation methods.

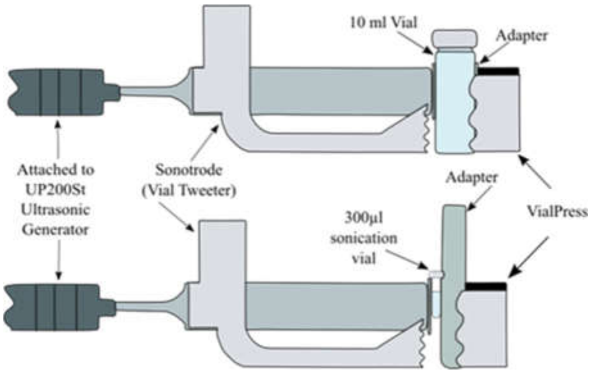

Figure 2. Schematic of sonotrode set-up for a) extraction, 10 ml glass crimp seal vial with fine plastic adapter b) derivatisation set-up, 300 µl glass crimp seal vial with large plastic adapter. Adapted from (7).

Ultrasound assisted extraction

Solid environmental samples including soil, sediment, sludge, and biosolid pellets, often require lengthy extraction and sample preparation steps prior to analysis. Ultrasonic assisted extraction (UAE) is an alternative to traditional extraction methods such as solid liquid extraction (SLE) and newer techniques, *e.g.* microwave assisted extraction (MAE) for analyte removal from solid matrices (*2*). The technique has seen a rise in application over the last 10 years, especially pharmaceutical and personal care product (PPCP) analysis in sewage sludge (*3*). Extractions with UAE can be completed in minutes, with reduced solvent consumption and energy use, higher reproducibility, and reduced costs compared to older techniques like Soxhlet (*2*).

Ultrasound assisted derivatisation

Ultrasonic assisted derivatisation (UAD) is a fairly new technique which is applied to accelerate silylation derivatisation (*8*) when gas chromatography (GC) is used as the analysis technique. Conventional derivatisation generally requires heating to around 60°C for upwards of 30 mins (*9*), whereas UAD has been undertaken in as little as 1 min (*5*). Ultrasound application provides intense mixing of the sample, which will influence the number of collisions (*10*) between the analyte compound and derivatisation reagent, facilitating the reaction. Reaction times have been reduced by ~90%, with increased yields and similar LODs to conventional heating methods (*11*).

Green Chemistry

There are 12 principles of Green Chemistry (*12*), as shown in **Table 1**, based on the fundamental concept of making chemistry 'benign by design' (*13*). Sonochemistry and 'Green Chemistry' share objectives of energy efficiency and waste reduction (*1*). This is because of the intent that sonication facilitates the reaction, be it extraction or derivatisation, which will reduce the sample preparation time vastly. The energy savings attributed to the reduced sample preparation time and the reduction in heating align with principle 6 – design for energy efficiency. Sonication also is shown to reduce solvent use, in comparison to more traditional techniques, and thus a reduction in waste is achieved (*2*).

Combining UAE and UAD with GC methods could also further reduce the solvent consumption in comparison to liquid chromatography (LC) methods. GC is not as susceptible to matrix effects, does not require analysis in positive and negative ion mode, and has a gaseous mobile phase – all contributing to reduced solvent consumption.

Table 1. *Anastas and Warner's 12 principles of Green Chemistry* (12)

Twelve Principles of Green Chemistry	
1.	Prevention
2.	Atom economy
3.	Less hazardous chemical synthesis
4.	Designing safer chemicals
5.	Safer solvents and auxiliaries
6.	Design for energy efficiency
7.	Use of renewable feedstocks
8.	Reduce derivatives
9.	Catalysis
10.	Design for degradation
11.	Real-time analysis for pollution prevention
12.	Inherently safer chemistry for accident prevention

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