HIGH-RESOLUTION ULTRASONIC SPECTROSCOPY FOR ANALYSIS OF INDUSTRIAL EMULSIONS AND SUSPENSIONS

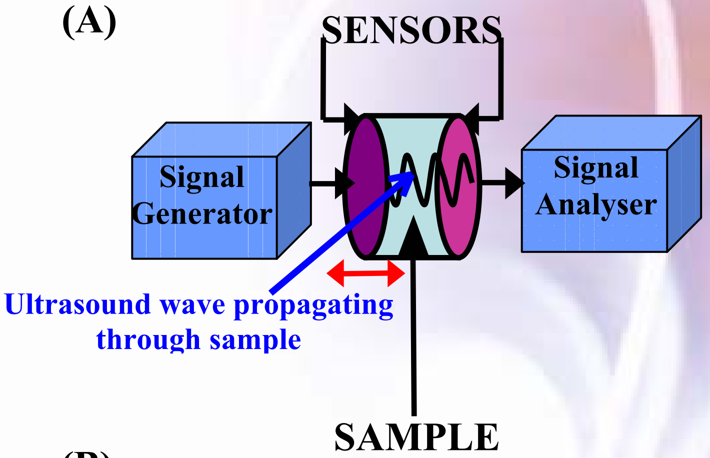
Ultrasonic Scientific

No optical transparency required

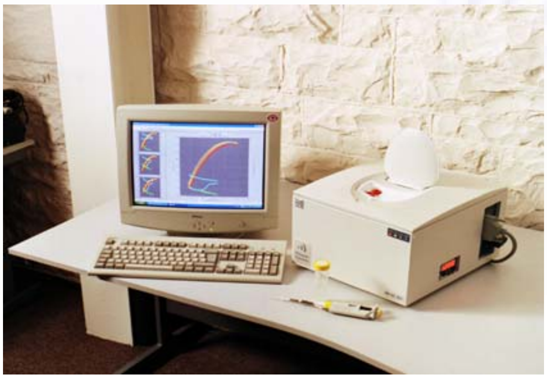
High-Resolution Ultrasonic Spectroscopy is a novel technique for non-destructive material analysis based on precision measurements of parameters of high-frequency sound waves, propagating through analysed samples. These waves propagate through most materials including opaque samples and allow direct probing of intermolecular forces. Award winning HR-US ultrasonic spectrometers from Ultrasonic Scientific provide an unprecedented range of new analytical capabilities for research, product development, quality and process control in biotech, pharmaceutical, food, chemical and petrochemical, polymer and other industries. Applications of this technique include analysis of chemical reactions, conformational transitions in polymers and biopolymers, aggregation and gelation phenomena, particle sizing, phase transitions, stability of emulsions and suspensions, formation of micelles and CMC measurements, ligand binding, composition analysis and many others.

Fig. 1 ***(A)*** ***Principles of operation***
(B) ***Dual award-winning HR-US 102 spectrometer***

(A)



(B)



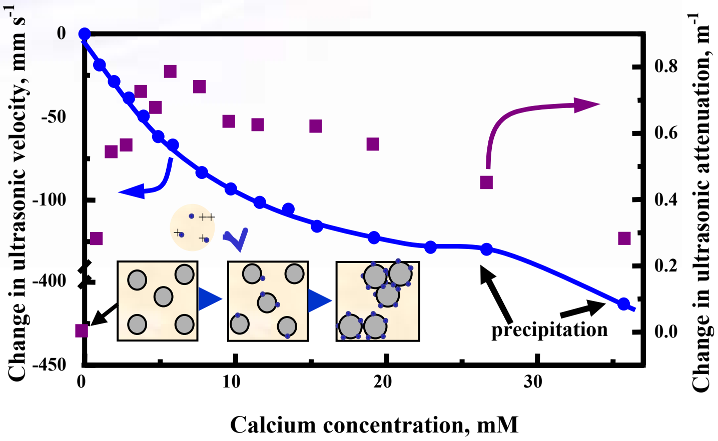
This publication describes the application of HR-US series of high-resolution ultrasonic spectrometers for characterisation of emulsions and suspensions. HR-US high-resolution ultrasonic spectrometers measure two parameters, ultrasonic attenuation and velocity. The parameters are physically independent, allowing to probe the different levels of organization of the samples to be characterized. Attenuation is mainly determined by the scattering of ultrasonic waves in non-homogenous samples (emulsions, dispersions) and fast chemical relaxation (in homogenous mixtures). The density and the elasticity of the medium determine ultrasonic velocity. A major advantage of the ultrasonic technique is the ability to make measurements directly, in the original samples, without having to make dilutions. The preparation of serial dilutions is commonly required when using optical techniques to reach the optical transparency and avoid multiple scattering effects.

The following examples illustrate the application of the HR-US 102 spectrometer for the analysis of adsorption of ligands on the surface of particles and heat-stability of emulsions and suspensions.

Binding of ligands to surface of colloid particles.

Figure 2 shows the change in ultrasonic velocity and attenuation measured in a polystyrene particle suspension during the course of its titration with a concentrated solution of calcium cations. Data for 11 MHz is shown only. The absorption of ligands (metal ions) on the surface of particles is an important phenomenon with regards to colloidal stability of suspensions. The added cations accumulate on the surface of the polystyrene particles. This binding is accompanied by the dehydration of the external layer of the particles, and results in a decrease in ultrasonic velocity. When the concentration of cations on the particle surface increases, it results in the electrostatic neutralisation of particle charge followed by aggregation and precipitation indicated by an additional decrease in ultrasonic attenuation and velocity at high concentrations of calcium.

Fig. 2 Ultrasonic monitoring of binding of calcium ions with polystyrene particles (0.5%)



Thermal stability of emulsions and dispersions

In the second example, ultrasonic measurements were used for the comparative analysis of the thermal stability of two different coating emulsions and the effects of thermal cycling (between 0.5 and 50ºC) on the emulsions was investigated. Reversible changes of ultrasonic parameters were observed in one of the emulsions (sample 1) during several consequent cycles of heating and cooling. The regular profile indicates that this emulsion remains stable after thermal treatment. In contrast, a sharp drop in ultrasonic velocity and attenuation in the second sample was observed at the first heating circle around 40ºC that did not recover during the next ramps. This indicates the irreversible changes in the emulsion. The decrease in ultrasonic parameters can be explained by the temperature-induced coagulation of the oil particles. The aggregation of the original particles into larger particles, following the phase separation between oil and water phases, results in the diminishing of the scattering contributions to ultrasonic parameters. This should be accompanied by a decrease in ultrasonic velocity and attenuation as seen in Figure 3. One remarkable observation in Figure 3 is that the slope of temperature dependence of the velocity in the second emulsion changes sign at a temperature around 35-38ºC. The velocity increases with temperature (between 0 and 38ºC) correspond to those in water. After breakpoint, the temperature slope corresponds to one in oil phase, showing phase separation of the emulsion.

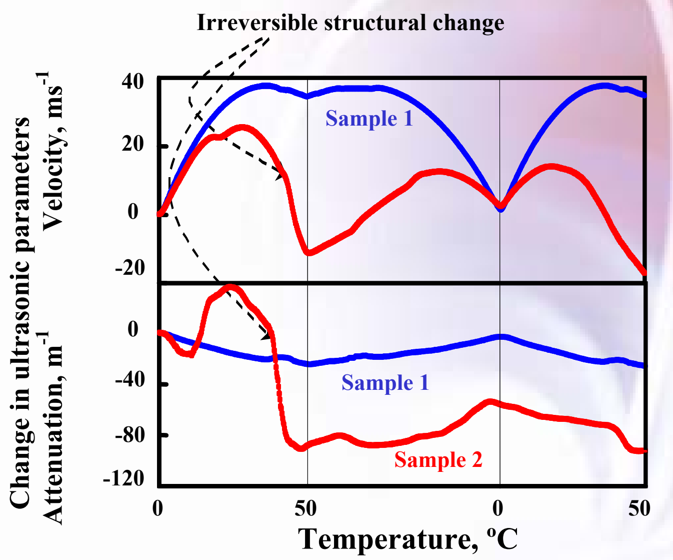


Fig. 3 Characterisation of thermal stability of coating emulsions

Heat stability of milk based drinks.

Adding calcium ions to low fat milk reduces the stability of the milk's casein micelles, causing it to coagulate on heating or when it is added to hot beverages. Additives can be used to stabilise the system, and HR-US 101 has been used to establish the best stabiliser to use. When the milk coagulates, ultrasonic attenuation increases as aggregation increases absorption and scattering, and ultrasonic velocity decreases as the aggregates have a compressible core, which slows the waves down. Temperature ramp regime of HR-US ultrasonic spectrometers allows fast and accurate (0.1 degree) determination of coagulation point and thus asses the stabilising effect of different compounds. The effect of three different compounds on coagulation of milk fortified with 25mM of calcium is shown in Figure 4. Potassium citrate was shown to be the most effective, followed by sodium carbonate, and sodium acetate was the least effective.

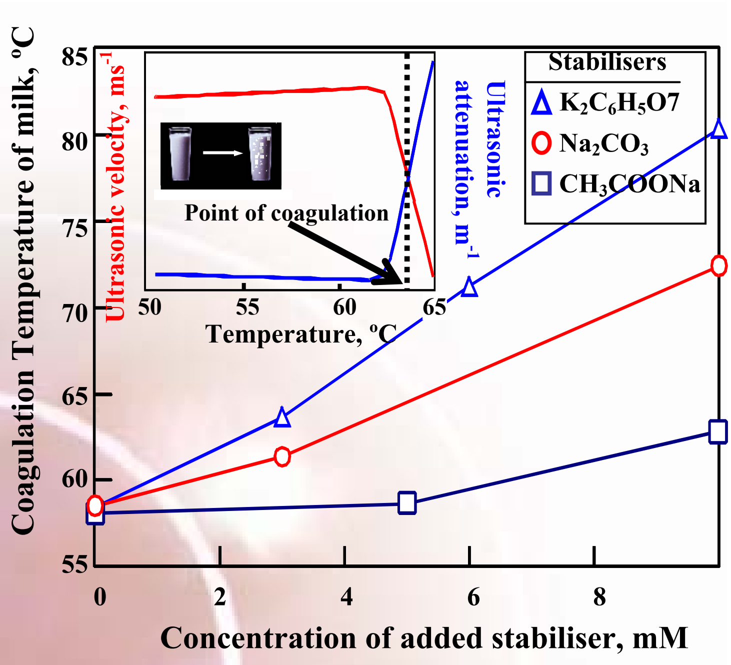


Fig. 4 Ultrasonic analysis of coagulation in calcium-fortified (25 mM calcium chloride) milk. Insert: Temperature profile of ultrasonic velocity and attenuation at 7 MHz. Main: Dependence of coagulation temperature on the concentration of stabilisers added

Conclusion

These results demonstrate the power of HR-US high-resolution measurements for the characterisation of emulsions and dispersions. The measurements can be performed in small samples (typically 1 ml, lower and higher volume of sample compartments available), are done under well-controlled temperature conditions (down to 0.01ºC).

For more information on our products and their application visit our web site:
www.ultrasonic-scientific.com

Contact us on info@ultrasonic-scientific.com
Call: +353 1 2180600 Fax: +353 1 2180601

Ultrasonic Scientific Ltd,
Richview Office Park,
Clonskeagh,
Dublin 14,
Ireland.