

Ultrasonic Sensing of Concentration and Stability in Mixtures

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Introduction

An ultrasonic wave is a high frequency pressure fluctuation that travels in a material. As it travels, the wave is changed in ways which are representative of the properties of the material. There are many changes in the ultrasonic wave travel that can be used to infer material variations: wave amplitude (attenuation), energy frequency distribution and travel time are just a few. Travel time is the time required for a ultrasonic signal to travel between fixed sensors, passing through the material under test.

In this article, the travel time of the wave is used to sense changes in the concentration of a liquid mixtures. Sedimentation of solid particles in a suspension, or breaking of an emulsion will cause a change in the relative component concentration along a vertical column of the suspension or emulsion. By monitoring the travel time at many heights along the column, the stability of liquid mixtures such as suspensions, dispersions, emulsions and mixtures can be quantified.

Due to the unique properties of ultrasonic waves, this sensing is completely non-destructive and non-intrusive to the liquid under study. The waves pass through the liquid without effecting the liquid in any way (as is done for medical ultrasonic imaging). Thus samples of a dispersion can be monitored virtually continuously as they settle. This can be done on a real time basis or over long periods of time without tying up the instrument.

Most other known techniques for sensing liquid mixtures are destructive to the sample under test and require that the sample be placed (or pumped) into an internal chamber. The sample cannot be removed until the stability test is complete. Thus equipment of this type is unsuitable for testing a large number of samples which settle slowly under natural conditions. Similarly, centrifugation techniques are often unsuitable because the settling does not take place under natural conditions. Visual methods for sensing sedimentation or creaming can be done non-intrusively but they are not very quantitative. Normally only the interface location is detected and this typically does not form until significant settling or creaming has occurred. Another common technique, freezing and sectioning, is not only destructive to the sample but is time consuming and labor intensive, often requiring hours to develop a concentration profile. In contrast, the average measurement time for an ultrasonic measurement is 1 to 2 minutes.

Typical industry applications that benefit from ultrasonic sensing include:

- Settling in suspensions
- Concentration in liquids/polymers & slurries
- Dispersion stability & shelf life
- Quality control testing
- Effectiveness of emulsion breakers
- Effectiveness of solids removal
- Optimum thickener & surfactant

Applications cross a wide number of industries including food, pharmaceutical, minerals, paint, ink & dye, water treatments, argochemicals and many others.

Operating Principles

The speed of an ultrasonic wave in a material depends on the compressibility and density of the material at the frequency of the wave. Thus the wave speed depends on the speed of sound through the individual components and the volume ratios of these components, provided that the suspended particles or emulsion droplets are much smaller than the wavelength of the ultrasound. Note that the wavelength for a 1 MHz ultrasonic wave in water is about 1.5 mm. Under these conditions, the sound speed V is a simple function of the volume fraction of each component:

$$V = V_c / \sqrt{\left\{ \left[1 - \phi \left(1 - \frac{\rho_d}{\rho_c} \right) \right] * \left[1 - \phi \left(1 - \frac{\rho_c V_c^2}{\rho_d V_d^2} \right) \right] \right\}}$$

where V_d , V_c , ρ_d , ρ_c are the velocities and densities of the dispersed and continuous components respectively, and ϕ is the ratio of the dispersed component to the continuous component.

In practice, measurements of the ultrasonic travel time are used to sense changes in concentration. The travel time inversely related to the ultrasonic wave speed as :

$$\text{TOF} = L/V$$

where L is the distance traveled through the liquid mixture. A pair of ultrasonic sensors are scanned along the outside of a sample container and TOF measurements are made at multiple heights. By comparing the measured TOF to a TOF vs. concentration calibration curve, a graph of the concentration profile of a sample can be generated. The TOF method can also be used, without scanning, as a quick and non-destructive measure of component concentration in non-settling materials. It is important to note that both the sound speed and density of each

component in the above equation are dependent on temperature. To avoid the influence of temperature changes on the TOF reading, all measurements are made with the sample contained in a temperature controlled bath.

An empirical technique is used to develop the calibration relation between TOF and concentration. The relation is found by measuring the TOF for samples of known concentrations and fitting a curve to these values. Once calibration is done, TOF readings can be automatically converted to concentration and displayed directly as concentration changes.

Test Apparatus

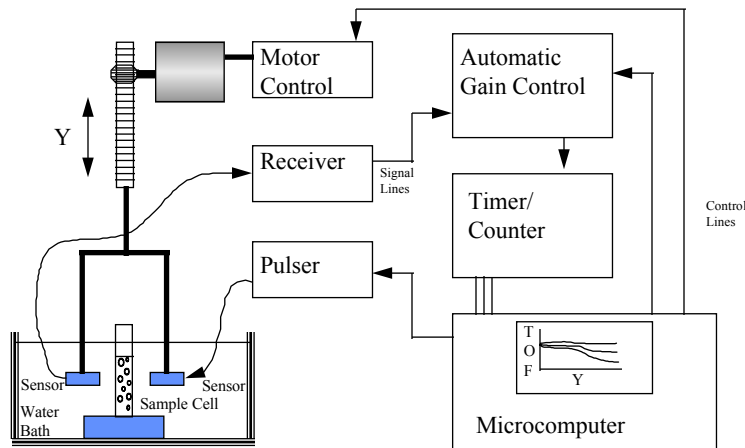


Figure 1. shows the apparatus used to measure TOF along the height of a sample container. For each timing cycle, under control of the microcomputer, the pulser generates a high voltage, short time duration (50 nanosecond) pulse to excite the piezoelectric transmitting sensor. Ultrasonic waves then pass through the water in the bath, the walls of the container and the liquid sample and are received by the receiving sensor. The ultrasonic wave is converted into a voltage signal and amplified by a fixed amount in the receiver. The automatic gain circuit limits the average received signal over several cycles to a set amplitude of one volt. This compensates for attenuation changes in the sample. Upon initiation of each cycle, the timer/counter starts counting clock ticks. When the ultrasonic wave is received at the sensor, and the amplified signal voltage exceeds a threshold value (e.g. 0.2 volts), the timer is stopped and the TOF interval is recorded. Many timing cycles occur each second, and the TOF values for thousands of readings are averaged to obtain the TOF at each height.

Almost any sample container can be used to hold the liquid mixture under test. Ultrasonic waves must pass easily through the walls of the container. Metals, glass and plastics are all excellent conductors of ultrasonic waves. Plastic containers are preferred because of the, low attenuation and lower internal reflection than glass. Plastic containers are also available with flat, parallel sides which minimize TOF errors due to variations between containers. For high-accuracy, high-repeatability concentration studies, precision stainless steel tubes are used. This eliminates any container distortion which could change the path length and effect the TOF reading.

Experimental measurements

The technique described here has been tested on a broad base of industrial products and applications. These include coal-slurry stability testing, oil-water emulsion stability and concentration, measuring creaming and sedimentation in pharmaceutical and agrochemical emulsions, crude oils, polymer lattices, fabric softeners, and powder dispersions.

Figure 2 shows the accuracy to which concentration measurements can be made using the ultrasonic method. To develop the TOF vs. concentration calibration curve, four samples of a non-settling polymer polyol were prepared at several concentrations. TOF readings were then taken in a stainless steel tube at a constant water bath temperature of 20°C. Figure 2 shows the calibration curve fitted to the four calibration data points. Once available, the calibration was used to calculate the concentration for another sample prepared at 40% concentration. The TOF for this test sample was 25.3 microseconds, which converts to a concentration of 39.93 an error of only 0.2%. The ultrasonic sensing technique takes only about 5 minutes, including the time for the sample to reach a constant temperature. The only other known technique for this polymer concentration measurement takes 6 hours of repeated centrifugation.

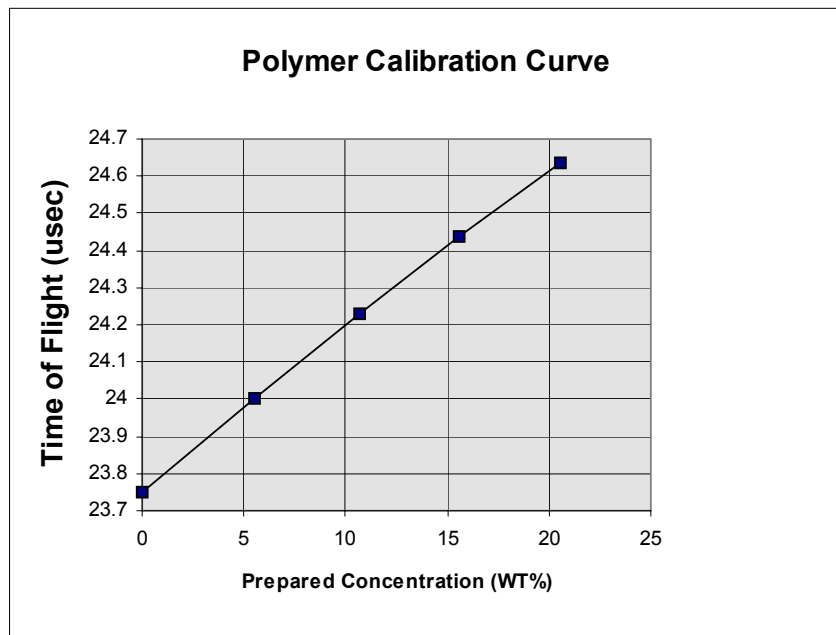


Figure 2.

As an example of measurements on an unstable suspension, TOF readings for a printer ink suspension are shown in Figure 3. Repeated measurements were taken for each sample for the days indicated, up to 24 days. For each measurement, the samples were placed in a water bath with the SCA scanner, and allowed to equilibrate to 35°C. After testing, the samples were returned to the shelf to settle further. In this plot, the height at which the reading is taken is plotted on the bottom, and the concentration is plotted on the left axis. Thus, the concentration reading for the bottom of the tube is at the far left. On the first day, the concentration was uniform at 16.5% all along the container (no settling). It appears that settling can be detected after just one day with a build up of solids at the bottom of the sample (0.5cm). A sharp interface in concentration begins to appear after 5 at a level about 0.7 cm from the bottom of the container. Neither this interface nor the lower concentration at the top could be observed by eye. The formation of the interface and its movement is governed by the particle size and viscosity of the slurry. Also, please note the progressive movement of this interface towards the bottom of the container. After 24 days, significant settling had occurred, and the concentration at the bottom reached about 40%, with the top dropping to 11%. By the 4th month, the settling was very pronounced, with the bottom concentration at 50% and the top at 3%.

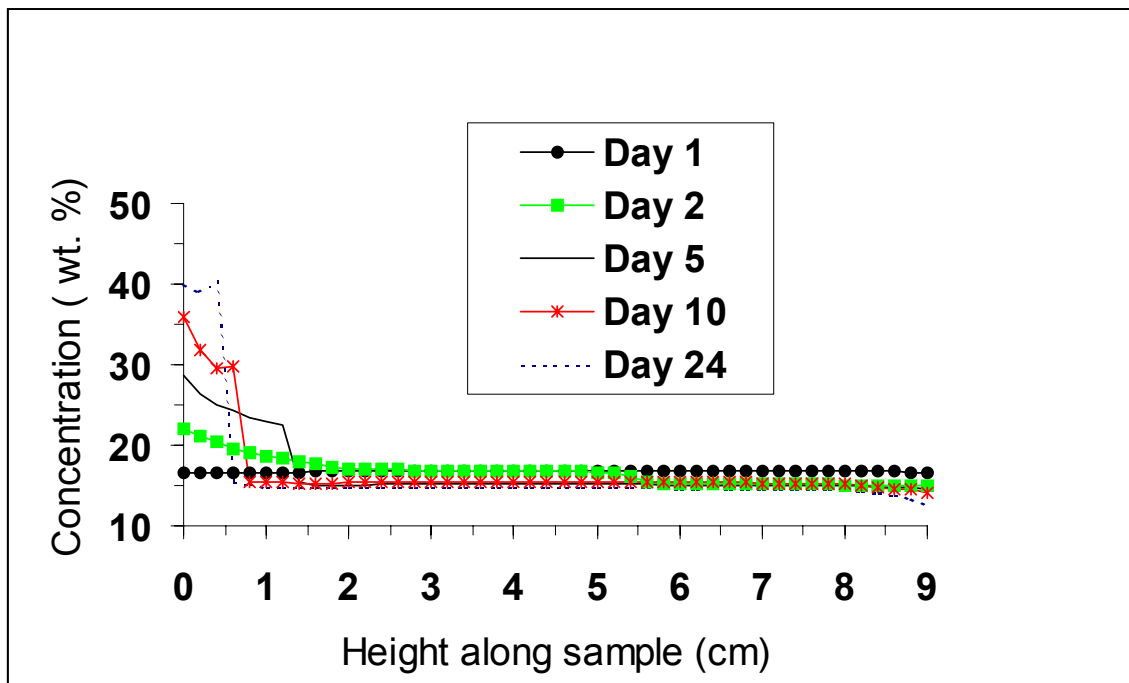


Figure 3.

Extensive measurements have confirmed the use of the ultrasonic method for sensing solids t concentration of dispersions, suspensions and slurries. As long as the particle size is less that the wavelength, it does not significantly effect the TOF measurement. Several tests have shown no effect for a change from 1 to 60 micron particle sizes. In addition, studies on silicone fluids indicate little or no effect by varying viscosity over a range of 740 cp. to 9300 centipoise.

Summary and Conclusions

Unlike other sensing methods, ultrasonics provides a rapid, non-intrusive measurement of liquid mixture properties. Due to the high precision of ultrasonic timing instrumentation, concentration profiles can be measured to within 0.1% concentration for typical liquid samples. The repeatability on successive sample measurements is excellent - some samples have been re-tested over a year period.