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Author(s):

Dipen N. Sinha - MST-11
Kendall N. Springer - MST-11
Wei Han - MST-11
David C. Lizon - MST-11
Shulim Kogan - MST-11

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**Los Alamos**
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# Applications of Swept-Frequency Acoustic Interferometer for Nonintrusive Detection and Identification of Chemical Warfare Compounds

**Dipen N. Sinha**, Kendall Springer, Wei Han, David Lizon, and Shulim Kogan,
*Electronic Materials and Devices Group*, MS D429
Los Alamos National Laboratory
New Mexico, NM 87545

## ABSTRACT

Swept-Frequency Acoustic Interferometry (SFAI) is a nonintrusive liquid characterization technique developed specifically for detecting and identifying chemical warfare (CW) compounds inside sealed munitions. The SFAI technique can rapidly (less than 20 seconds) and accurately determine sound speed and sound attenuation of a liquid inside a container over a wide frequency range (1 kHz-15 MHz). From the frequency-dependent sound attenuation measurement, liquid density is determined. These three physical properties are used to uniquely identify the CW compounds. In addition, various chemical relaxation processes in liquids and particle size distribution in emulsions can also be determined from the frequency-dependent attenuation measurement. The SFAI instrument is battery-operated and highly portable (< 6 lb.). The instrument has many potential applications in industry ranging from sensitive detection (ppm level) of contamination to process control. The theory of the technique will be described and examples of several chemical industry applications will be presented.

## INTRODUCTION

To meet the requirements of the Chemical Weapons Convention, the treaty that calls for eventual destruction of all chemical weapons [1], it is essential to have techniques that can be used to monitor compliance and destruction of existing stockpiles in a verifiable way. In particular, the requirements are for nondestructive and noninvasive techniques that are fast and reliable. The Swept-Frequency Acoustic Interferometry (SFAI) technique, among several others, is being developed by the US Defense Special Weapons Agency to meet such requirements.

The SFAI technique is a novel adaptation of the ultrasonic interferometry technique developed several decades ago [2,3] for determining sound velocity and absorption in liquids and gases. In the original technique, and also in more recent modifications of the technique [4,5], the transducers (sensors) needed to be in direct contact with the fluid being tested. This requirement effectively restricted the use of this technique to highly specialized laboratory characterization of fluids. In contrast, the SFAI technique extends the capabilities of the ultrasonic interferometry technique significantly and allows the determination of velocity and attenuation of sound in a fluid (liquid, gas, mixtures, emulsions, etc.,) inside sealed containers (e.g., pipes, tanks, chemical reactors, etc.,) over a wide frequency range, completely noninvasively. In addition, if the container material properties (density and sound velocity) are known, the liquid density can also be determined using the SFAI technique. Our measurements show that it is possible to uniquely identify various chemical warfare compounds and their most significant precursors based on these physical parameters (sound velocity, attenuation, frequency dependence of sound attenuation, and density).

To explain how fluid physical properties are determined using the SFAI technique, we discuss measurements on two types of containers, commercial rectangular optical glass cells and cylindrical steel. The measurements provide an ultrasonic resonance (interference) spectrum characteristic of the fluid and the container wall, over a frequency range 1-15 MHz. For reliable determination of sound attenuation and liquid density, two analytical approaches are derived from a theoretical model that is based on normal acoustic wave propagation through multiple-layered media [6]. One method is based on frequency-dependent relative strengths of minima and maxima (peaks) of the measured spectra, and the other is based on the resonance half-power bandwidth. Good agreement of extracted physical parameters with literature values demonstrates the potential of this noninvasive technique.

## THEORY

A SFAI measurement can be described in terms of planar ultrasonic wave transmission and reflection through a multiple-layered system consisting of the test fluid sandwiched between symmetric layers of transducer crystal, wear plate, coupling gel, and cell (container) wall. This multi-layer model formulation is an extension of the well-known theory of planar wave propagation through one layer[7] (a liquid layer embedded between two solid layers of infinite dimension) and the details are presented elsewhere[6]. In the multi-layered case, the sound transmission is observed experimentally as a spectrum of a series of regularly spaced peaks (see Fig. 1) that depend on the physical properties (acoustic impedance, longitudinal sound speed, and sound attenuation) and geometry (thickness) of each layer. The spectrum in Fig. 1 is a superimposition of two spectra: one originating from the container wall and the other from the liquid inside the container. The bottom frame of the figure presents the theoretical predictions from the multi-layered model that agrees very well with experimental data shown above. It should be pointed out that for use on munitions, the SFAI technique employs a novel transducer implementation where all measurements are made from one side of the container using a dual-element transducer system.

To derive the physical properties of the liquid from the observed spectrum, the full theory that includes all layers can be used. However, for rapid extraction of such properties, it is more convenient to select appropriate measurement frequency range to avoid resonance contributions from the walls (e.g., between 1 to 2 MHz, and 3 to 4.5 MHz in Fig.1). Essentially, this reduces the problem to a basic one-layer model making the analysis significantly straightforward. The intensity transmission coefficient $T_I$ for the simplified case[5] of a fluid layer of path-length $L$, attenuation coefficient $\alpha_L$ ($\alpha_L L << 1$),

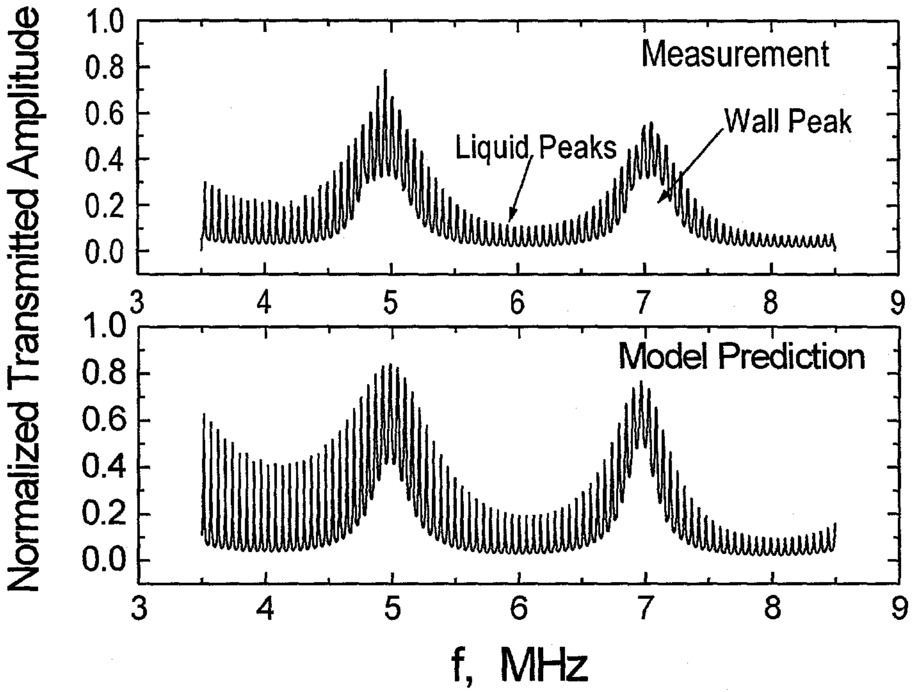


**Figure 1**. Principle of the swept-frequency interferometry technique. As the frequency applied to one transducer is swept from low to a high the detected signal from the second transducer shows the characteristic interference pattern that develops in the liquid in the resonator cavity.

and sound speed $c_L$ between two identical wall boundaries reduces to

$$T_I = \frac{1}{(1+\frac{1}{2}\sigma\,\alpha_L\,L)^2 + \frac{\sigma^2-4}{4} Sin^2 \frac{\omega}{c_L} L}. \qquad (1)$$

Here, $\sigma = z_W/z_L + z_L/z_W$, $\omega$ ($\omega$=2$\pi$f) is the angular frequency, $z_W$ and $z_L$ are acoustic impedance of wall and liquid, respectively. For most liquids inside a metal container, $\sigma \approx z_W/z_L$.

$T_I$ in Eq. (1) is a periodic function of $\omega L/c_L$ and reaches a maximum (peak) whenever the condition $2\pi f_n L/c_L = n\pi$ is satisfied, where $f_n$ is the n-th peak frequency. From this condition, the sound speed $c_L$ ( $c_L = 2$ L $\Delta f$) can be determined if the frequency difference between any two consecutive resonance peaks $\Delta f = f_{n+1} - f_n$ is measured.

However, we see from both experiments and model predictions[5] that $\Delta f$ oscillates within 1% of the mean value over the measurement frequency range due to effects of container wall resonance modulation, a characteristic behavior of the noninvasive measurement. Therefore, $c_L$ is obtained using the averaged frequency difference $<\Delta f>$

$$c_L = 2\,L < \Delta f > . \tag{2}$$

Next, we discuss how sound attenuation and liquid density are determined. The ratio of the transmission coefficient minima $T_{I,min}$ and maxima $T_{I,max}$ can be expressed in terms of $\sigma$ and $\alpha_L$ as

$$\left[\frac{1}{\left(T_{I,\min}/T_{I,\max}\right)} - 1\right]^{-0.5} = \frac{2}{\sigma} + L\,\alpha(f^2)\,. \tag{3}$$

Equation (3) shows that both $\alpha_L$ and $\sigma$ can be determined from a linear fit of the data of the transmission ratio factor TRF=$[(T_{I,min}/T_{I,max})^{-1} - 1]^{-0.5}$ vs. $f^2$. The intercept at zero frequency is related to the acoustic impedance ratio $\sigma$. If the impedance of the wall material is known, the liquid density can be determined because the liquid sound speed is determined independently as discussed above (see Eq. 2).

Another approach to determining sound attenuation coefficient is to use the half-power bandwidth of observed resonance peaks. From Eq. (1), one can derive an inverse solution for half-power bandwidth $\delta f$ in terms of acoustic properties in the fluid[5] as

$$\delta f = \frac{2\,c_L}{\pi\,\sigma\,L} + \frac{c_L\,\alpha_L(f^2)}{\pi}\,. \tag{4}$$

Similar to Eq. (3), the second term is the contribution from liquid sound absorption and is identical to the solution obtained in a previous resonator theory[8-10] for transducers in direct contact with the test liquid. The first term, the width extrapolated to zero frequency $\delta f_0$, is independent of frequency and depends on $\sigma$, $c_L$, and $L$. This term results from the reflection loss at the wall-liquid interface due to acoustic impedance mismatch and can be used to determine liquid density if the acoustic impedance of the wall is known.

Incidentally, the sound speed of the container wall can be determined independently from the interference spectrum by observing the spacing between the wall peaks. Thus, a single sweep measurement can be used to derive multiple physical properties of a liquid that include sound speed, sound absorption, frequency dependence of sound absorption, and liquid density. A combination of several of these properties can be used to uniquely identify all the chemical warfare compounds and their most significant precursors.

## INSTRUMENTATION

The SFAI system consists of an electronics unit that consists of a 486DX4-100 MHZ embedded PC-104 bus computer and a customized electronics Digital Synthesizer and Analyzer (Neel Electronics model DSA520) board. The DSA board contains all electronics for sine-wave sweep signal generation, signal detection and processing. The sweep frequency range available is 1 kHz - 15 MHz. The sweep rate can be varied from 1 - 800 frequency steps per second. With a resolution of 0.1 Hz over the entire frequency range, the system provides a frequency response directly in real-time. Typical excitation voltage levels used are 1-10 V pk-pk.

The transducer system consists of two side by side rectangular 5 MHz center-frequency broadband piezoelectric transducers. One transducer is used as the transmitter and the other as a receiver. The transducers are mounted on a flexible structure that can adapt its shape to the curvature of the container. Powerful Nd-B-Fe magnets are placed on the sides of the transducers, which allows attachment of the transducer to the surface of various types of CW munitions. Instead of coupling gel, a thin rubber sheet is used on the top surface of the transducers. A combination of the magnetic attachment and the rubber sheet provides good coupling between the transducers and the container surface. A miniature amplifier on the back of the transducer amplifies the received signal before being analyzed by the DSA board. An integrated chip temperature sensor is also mounted next to the transducers that determines the temperature of the item being tested.

The signal analysis involves a heterodyne mixing technique followed by signal rectification, envelope detection, and 14-bit digitization. The digitized amplitude spectrum is then analyzed in the PC to determine sound speed, sound attenuation, and density of the sample liquid by the methods described above. The combined measurement and analysis time is typically less than 20 seconds.

The instrument is portable, battery operated and weighs less than 6 lb. The operator simply places the transducer on the item to be tested and presses a button and all measurements and analysis are done automatically. The computer memory contains a database of the physical properties of all the common CW compounds including their temperature variations. The analysis thus takes into account item temperature variation. The system has been successfully tested on a large variety of CW munitions at the Tooele Army Depot in Utah.

## RESULTS AND DISCUSSION

We show results of SFAI measurements in optically polished rectangular glass cells (Starna Cells, Inc., CA) of liquid path length 1.0 cm and wall thickness 0.125 cm for various chemicals including CW compounds. Sound speed can be quite accurately determined from Eq. (2). Figure 2 shows the sound speed measurements for glycerin, ethylene glycol, water, toluene, benzene, and isopropanol in a glass cell over a frequency rage of 1-15 MHz. For the above liquids, the maximum standard deviation relative to the mean values of sound speeds is 0.59%. The scatter (actually an oscillation) in the sound speed data is not due to measurement error but primarily due to the wall resonance modulation effect as discussed earlier. This oscillation is also seen in predictions from our theoretical model.

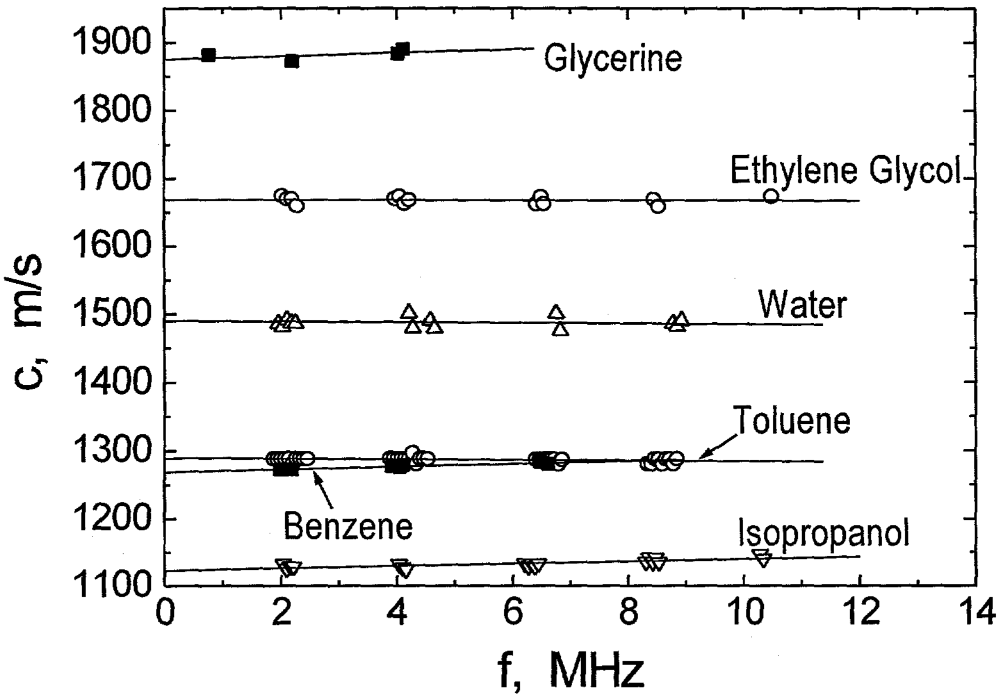


**Figure 2.** Sound speed determination for six chemicals using Eq. 2.

Figure 3 compares the sound attenuation measurement for ethylene glycol in two very different containers, a small glass cell (as in Figure 2) and cylindrical stainless steel shell with inner diameter 5.27 cm and wall thickness 0.225 cm. The resonance peak width is plotted as a function of the square of the frequency. The data are consistent with Eq. (4). Because the acoustic impedances are very different for glass and steel, the intercepts are different. The slopes of the two lines are the same indicating same sound attenuation values. This demonstrates that accurate sound attenuation measurements can be made using the SFAI technique regardless of the container geometry and container wall material properties.

Figure 4 presents the results of the noninvasive SFAI characterizations of the most common CW compounds. The data presented are for measurements made in Starna glass cells using CW agents that are better than 90% pure and at an ambient temperature of 23°C. The density for each liquid was determined using Eq. (4). This forms the basis for

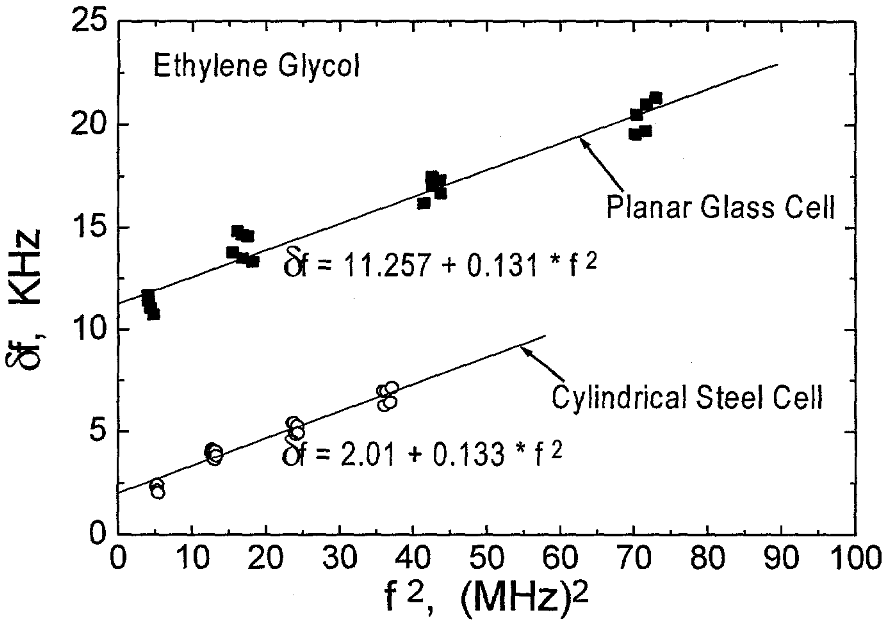


**Figure 3**. SFAI measurements on planar glass cell and cylindrical steel shell filled with ethylene glycol.

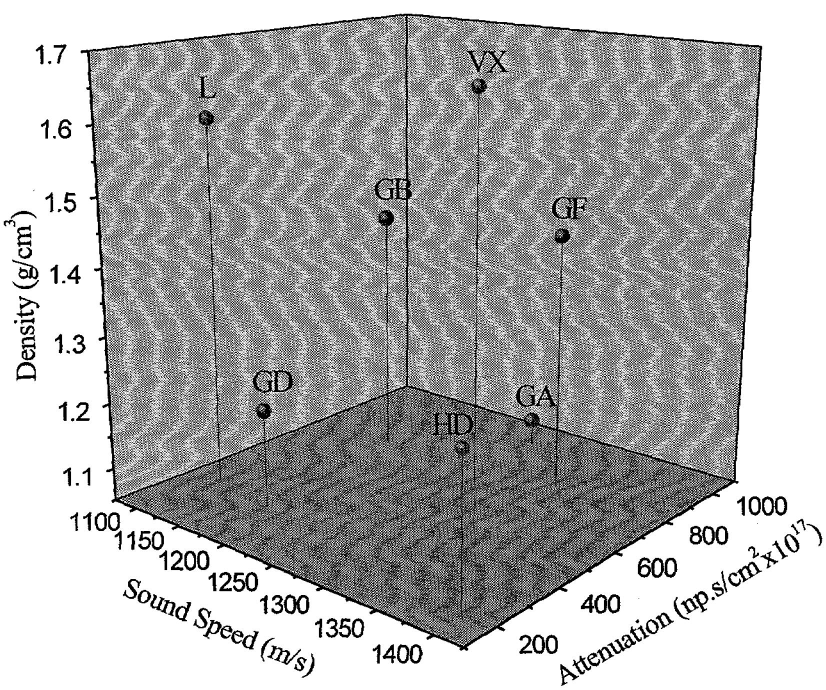


**Figure 4.** Sound speed, sound attenuation, and density determination for seven CW agents using the SFAI technique

the SFAI technique in noninvasive CW agent identification. Note that in a 3-D representation of the measured data, each liquid is clearly separated from the others and this separation is many times larger than the accuracy of the measurement. For measurements using the Starna cells, the accuracy of sound speed measurement is approximately 0.5 % and that of sound attenuation is better than 3%. Density determination is somewhat less accurate and is typically 5%. Even for munition grade CW agents (less than 60% pure), all the chemicals measured are still clearly separable. Purity has a stronger effect on sound attenuation than sound speed. All measurements were made over a temperature range between 4°C and 35°C. using a specially built temperature controlled system. The data presented in Fig. 4 demonstrates why CW compounds can be noninvasively and uniquely identified using the SFAI technique. The laboratory characterizations of the CW compounds have been verified using measurements on a large number of CW munitions at the Tooele Army Depot in Utah.

The SFAI technique can be easily adapted for studying liquid mixtures. For liquid mixtures, both sound speed and attenuation are related to mixture composition. Both mixture composition and solution concentration can be monitored with great resolution (<0.01 %) using SFAI. In the case of emulsions, the frequency-dependent sound attenuation information from this technique can be used to determine particle size distribution. The same frequency-dependednt approach can be used to study relaxation processes in chemicals and solutions.

A particular adaptation of the SFAI technique uses continuous monitoring of a single resonance peak within an appropriate frequency range. Any change in the peak frequency or width indicates changes in the physical characteristics (e.g., composition or concentration change, temperature change, etc.,) of the liquid being studied. We have been able to noninvasively monitor changes as small as 5 ppm. This is particularly suitable for sensitive monitoring of contamination levels in liquids and this may be useful in process control and as environmental sensors for water quality monitoring.

Among other application examples, we have successfully used the SFAI technique for noninvasive characterization of various types of suspensions (e.g., $TiO_2$) useful in paint, paper and pulp industries. We have also shown how this technique can be used to characterize petroleum products and also determine spoiled milk in sealed milk containers (e.g., paper cartons, plastic bottles, and Tetra Pak pouches).

In summary, the SFAI technique is highly adaptable and versatile. It has excellent resolution in detecting minute changes in liquid characteristics. Although developed for chemical weapons verification, the technique has applications in many areas of industry.

## CONCLUSION

The swept frequency acoustic interferometry technique is a versatile technique capable of noninvasively determining sound speed, sound attenuation coefficient, and density of liquids. The accuracy of the technique is not dependent on container geometry or materials properties. The theoretical model for one-dimensional wave propagation through multi-layered media provides good agreement with experiment. The instrumentation is highly portable and is fully automated. The technique has been very successful in identifying the most common chemical warfare compounds. It can be a very useful analytical tool and has a wide range of potential applications in industry. The technique can be easily adapted for continuous monitoring of liquid concentrations or compositions in process control. Besides pure liquids, the technique can be used for studying mixtures, emulsions, and suspensions.

## ACKNOWLEDGMENT

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