

Dynamic Surface Tension and Dilational Stress Measurements Using the Drop Shape Method

By Roger P. Woodward, Ph.D.

First Ten Angstroms, 465 Dinwiddie Street, Portsmouth, VA 23704
Tel: 1.757.393.1584 Fax: 1.757.393.3708 email: sales@firsttenangstroms.com

Dynamic surface tension refers to measurements in which the interface is purposefully not at equilibrium. The principal uses are the study of surfactants and interfacial rheology. FTÅ offers instrumentation providing the following methods:

- **Pulsating Bubble.** A bubble is formed in a small vessel containing the test fluid. The size of the bubble is modulated by changing the pressure in the chamber with a pump. Normally the bubble is small enough that it can be considered spherical. The size of the bubble can be inferred from the change in fluid volume caused by the pump. Direct measurement of bubble volume is also possible from the video image when the fluid is transparent. If the bubble is truly spherical, then surface tension can be computed from the pressure using the Young-Laplace equation because the two radii in it are equal and known. High modulation rates are practical because the bubble size is quite small (bubble radius <1mm). Modulation is made even easier by venting the bubble to the atmosphere and applying the varying pressure to the bulk fluid side: a large bore can connect the pump piston to the chamber so fluid viscosity is not a limiting factor. The bore to the bubble tip must be small in order to have a small (viz., spherical) drop and this will limit rapid fluid flow, but will not limit gas flow.
- **Pulsating Drop.** A pendant drop is formed and its size modulated by a pump. When drop shape analysis is used to determine surface tension, the drop must be large enough for gravity to clearly distort the spherical shape. Alternatively, if the drop is kept small so it is spherical, a pressure sensor can be used analogous to the pulsating bubble method.

There are two pairs of choices: bubble or drop and large or small. There is also a third, less obvious, choice, which is how to determine drop size. We can rely on the pump or we can independently measure the drop/bubble shape by image analysis.

This paper will concentrate on techniques and results using drop shape for both surface tension determination and size determination. Therefore we are limiting ourselves to the (large) pendant drop in this discussion.

Method. A companion paper, *Surface Tension Measurements Using the Drop Shape Method*, by this author, discusses basic techniques for surface tension drop shape analysis. Magnification was calibrated by measuring the diameter of a 4mm sapphire ball with the image analysis system. The diameter of the ball was independently determined by a micrometer reading to $1\mu\text{m}$. We will now discuss the additional specific issues for dynamic, as opposed to equilibrium, measurements.

- **Drop Size.** Both the drop and bubble methods have a limited range of bubble sizes which satisfy the relevant assumptions on curvature radii. These must be determined empirically for any combination of tip size and surface tension and the modulation adjusted accordingly. When weak or slow acting surfactants are present, the surface tension will change significantly during the test, so an acceptable drop volume at the beginning may not be at the end. There is some trail-and-error required to build up experience.
- **Drop Formation.** This is a more subtle issue. Basically there is always an interface present between the liquid and vapor phases *within the dispense tip*. Therefore surfactants will

be adsorbing at this interface even while an experiment is not being run, and this provides a small “enriched” volume that changes the concentration somewhat within the overall drop volume. While the absolute volume of enriched fluid may be small compared to the final drop volume, its effect may be noticeable. The enriched volume can be remixed, and the issue resolved, before the drop is formed as long as the remixing does not introduce such turbulence that the drop itself is disturbed. The following protocol is appropriate for a pendant drop syringe pump system:

1. Prime the pump so fluid is just visible at the tip. You do not want any significant volume showing. This will be the “enriched” interface.
 2. To start the run, the pump should rapidly aspirate enough volume to draw the fluid level to the top of the needle: e.g., 20 μ l for a small bore needle.
 3. The same volume is now rapidly dispensed back down the needle to restore fluid to the original primed level. It has now been mixed, particularly if the fluid originally in the needle was forced back into the larger diameter of the needle hub or syringe.
 4. The desired drop is dispensed.
- **Modulation Waveform.** There are three basic tests, each having a different time function for the drop volume: a linear ramp which expands the drop until it falls off the tip, a sinusoidal (sine wave) time function, and a square wave. The sinusoidal function is particularly easy to analyze mathematically because the Fourier transform is an obvious fit, but the ramp and square waves also reveal interesting behavior. In specifying the waveform, remember that, for viscoelastic work, which presumes sinusoidal modulation, the strain rate is the relative change in surface area per unit time. Therefore the same effect can be achieved with a smaller modulation going faster as with a larger modulation going slower. Thus, for some purposes, there is a tradeoff between

frequency and amplitude. This has implications for the resolution of the measurement. If noise is the limiting factor, use greater modulation at a lower frequency. If cross-talk (see below) is the issue, use less modulation at higher frequency.

- **Pump Program.** Once the modulation has been decided, the pump must be programmed. Consideration must be made for the pressure drop across the dispense needle; this pressure increases rapidly as the bore diameter decreases ($1/r^4$). As a rule of thumb, the pressure drop across a 25mm \times 0.5mm ID bore will be significant at 5 μ l/s flow. Larger diameter needles significantly reduce the pressure. The pump program can be programmed to loop and to gradually make the volume larger or smaller, combining a ramp and a sinusoid.

Baseline Measurements. The following set of measurements on pure water illustrate the basic resolution possible with the drop shape system. We expect water to show no response to modulation, so whatever response there is can be considered random noise or “cross-talk” from the modulation. Unless this cross-talk is constant in amplitude, it can not be subtracted out and therefore constitutes a limit on detectability for the system.

Linearity of Water Response. We first establish the basic linearity of the measurement, i.e., is that the surface tension measurement is independent of drop size. Figure 1 shows the drop volume and surface tension of a drop grown at constant rate, starting at $t=0$. At extremely small volumes the drop is spherical and can not be successfully measured (the software detects this). This drop was dispensed on a 22GA SS needle (nominal OD=0.71mm) at the rate of 1 μ l/s. The mean, μ , of the surface tension data is 73.00mN/m and the standard deviation, σ , is 0.207mN/m. The coefficient of variance, COV, is 0.284%.

Images were captured every 0.1s and the data was filtered to a response time of 0.2s. Figure 2 shows the initial drop analyzed and Figure 3 the last, to illustrate the range of shapes and volumes.

While the average value of the surface tension is basically constant, there will always be *some* slope to the surface tension response. This may occur from lighting and optical effects, or it can simply be the result of electronic noise in the image capture. The response can be deterministic and repeatable from an instrumentation bias, or it can be random from noise. If it is noise, the slope will vary in amplitude and sign from run to run.

In the particular measurement shown in Figure 1, the slope is 0.025mN/m per μl and the deviation from the average is $\pm 0.113\text{mN/m}$. This is a representative for drop shape measurements. The important point is to establish the general magnitude of the cross-talk. The noise level in Figure 1 is typical for a dynamic measurement where the volume is being modulated. While equilibrium measurements use time domain filtering to smooth the data, filtering is limited for dynamic measurements.

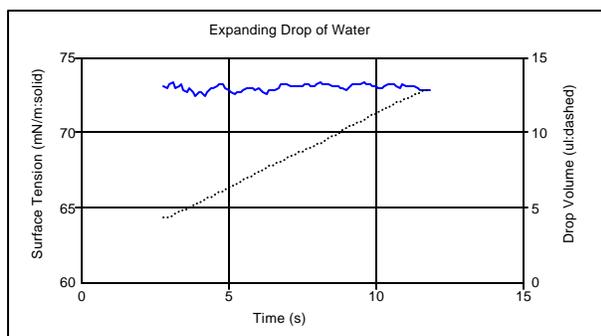


Figure 1. Surface tension/volume for water.

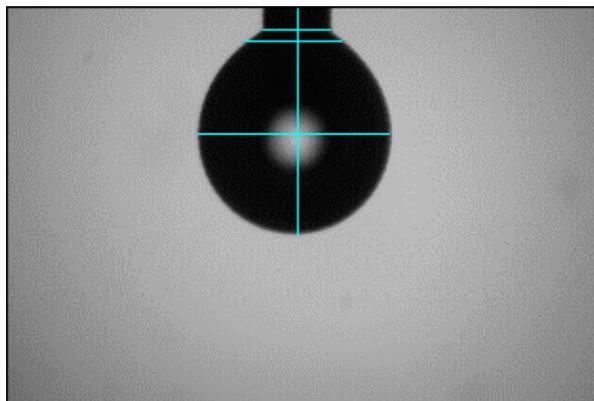


Figure 2. First image in run.

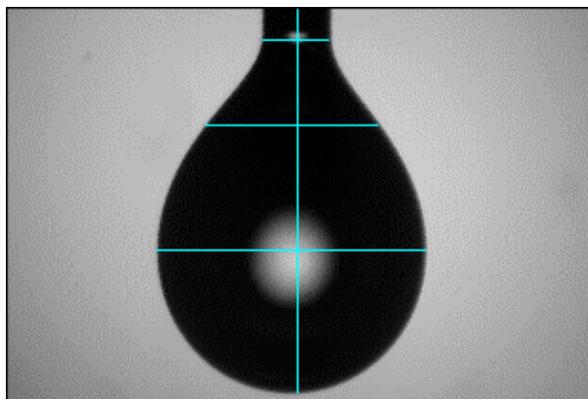


Figure 3. Last image in run.

Sine Wave Modulated Volume on Water.

Figure 4 shows the surface tension and drop volume for sinusoidal pump modulation. The mean is 73.00mN/m, $\sigma=0.252\text{mN/m}$, and $\text{COV}=0.346\%$. The noise is only slightly worse than in the preceding ramp experiment.

As the strain rate is increased (e.g., by pumping the same volume at a faster rate), the noise level will rise to a typical level of 1%, at which point viscosity and turbulence are clearly limiting. This limit is pump, fluid, and tip diameter dependent, so it must be determined individually. However, a good indicator is when the measured modulation volume does not agree with the programmed volume. For the case illustrated, the sinusoid period is 9s. The observed volume modulation is in agreement with the pump program. As the strain rate was increased (using shorter periods), the limit for this combination occurred at 3s. A larger needle would lower this limit somewhat.

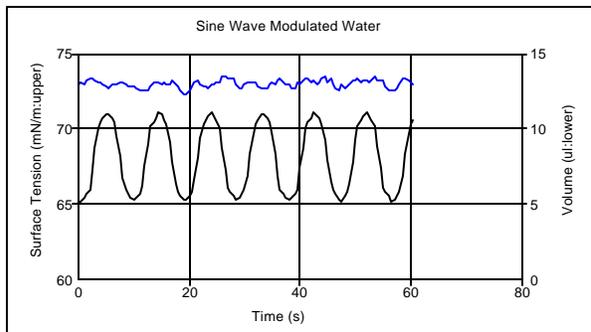


Figure 4. Surface tension/volume for water.

Fourier methods (FFT's) may be used to analyze the surface tension and surface area waveforms. The motivation for this is that the frequency component corresponding to the modulation can be easily picked out from the spectrum and other frequencies rejected; this is called frequency domain filtering. Figure 5 shows the amplitudes of the surface tension and surface area Fourier peaks as time functions. By the way, the amplitude is the amplitude A of the corresponding sine wave (i.e., $A\sin(\omega t)$); what is commonly observed on the time domain plots such as Figure 4 is the peak-to-peak value which is twice that of the Fourier amplitude of the sine wave. Finally, note the spectra are for the surface area rather than the drop volume. The amplitudes extracted from Fourier spectra are called *differential tension* and *differential area* to emphasize their calculation.

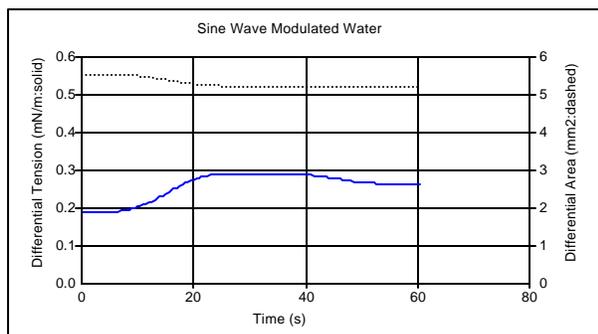


Figure 5. Differential tension and area for time domain waveform in Figure 4.

The time response of differential tension and area is obtained by subdividing the overall time in Figure 4 and computing the Fourier transform within each subdivision. The responses from each transform are then stitched back together to make a continuous time function. Figure 4 has a total of 6 cycles; each subdivision in Figure 5 used 2 cycles, so 3 subdivisions resulted. The duration of each subdivision is a tradeoff between smoothness (more cycles result in less variance) and time resolution (fewer cycles result in quicker response). One cycle is the minimum while 4 to 8 cycles are preferred. Ideally the differential tension would be zero, showing no cross-talk or noise. The observed value, which is typical for this level of modulation, averages 0.25mN/m. Actual Fourier spectra for this example are shown in Figure 6. The surface area spectrum is dashed in the plot; it shows a distinct peak at the

modulation frequency ($1/9s=0.111\text{Hz}$). The tension spectrum is the solid line. It has a peak at the modulation frequency, but larger peaks at the 2nd and 4th harmonics of the modulation frequency, plus other peaks not harmonically related to the modulation. The harmonically related peaks contribute to cross-talk as the system is not perfectly linear. The slope discussed previously causes a small, but observable, signal in the tension data. This is the source of the non-zero differential tension in Figure 5. In summary, the resolution of this system is a few tenths of a mN/m and is set by both non-linearity and noise.

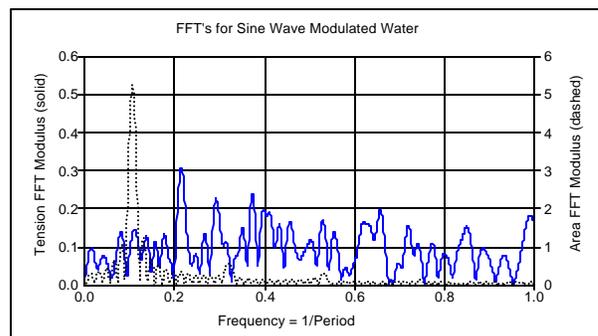


Figure 6. Fourier spectra of surface tension and drop area for sine wave modulation.

Viscoelastic data can be obtained from dynamic surface tension when the time domain waveform for surface area is also known (see Macosko in the References section). The *modulus* is the change in tension per unit change in surface area. The elastic modulus is in-phase with the modulation and the loss modulus is 90 degrees out of phase. These are known as dilational stress measurements. Figure 7 shows these as time functions; ideally both would be zero, but cross-talk is roughly $\frac{1}{2}$ mN/m in these moduli.

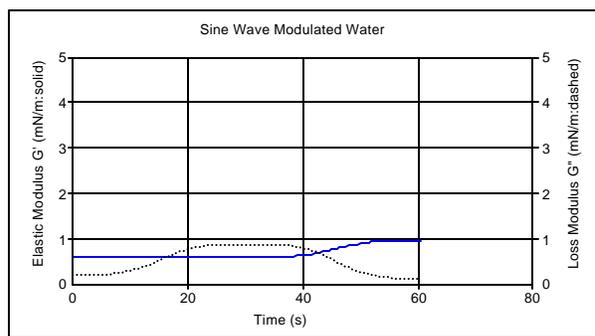


Figure 7. Elastic and loss moduli for water.

SDS Example. A 0.0025% solution of sodium dodecyl sulphate (SDS) was tested as a surfactant example. Figure 8 shows a long term equilibrium surface tension test with no modulation. The drop was formed quickly at $t=0$. Figure 9 shows the first 90 seconds in detail. The surface tension rises briefly to that of water before the surfactant takes effect.

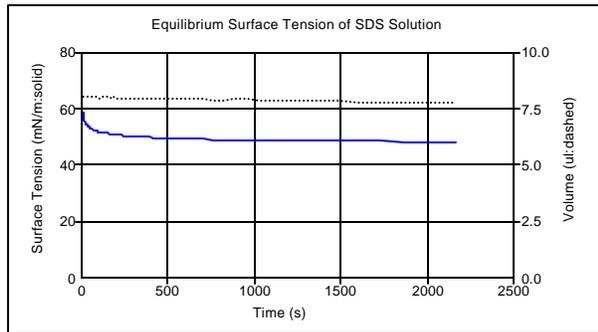


Figure 8. Equilibrium surface tension.

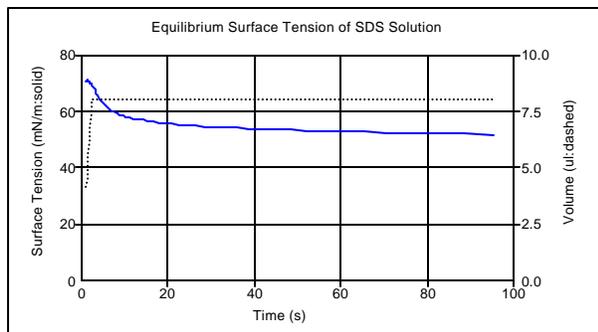


Figure 9. Initial drop formation.

Figure 10 shows the sine wave modulated surface tension and drop volume. This response has been corroborated on a pressure-based pulsating bubble instrument whose data is shown in Figure 11. The minor variations in response are attributed to age differences between the two samples.

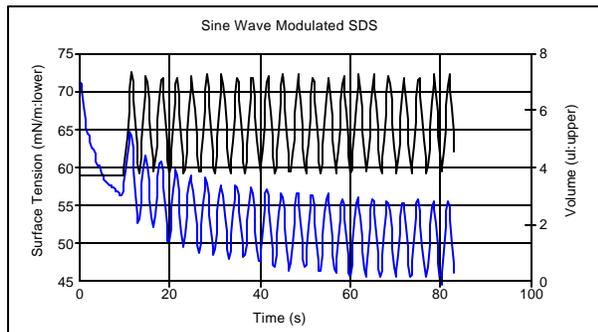


Figure 10. Surface tension/volume for SDS.

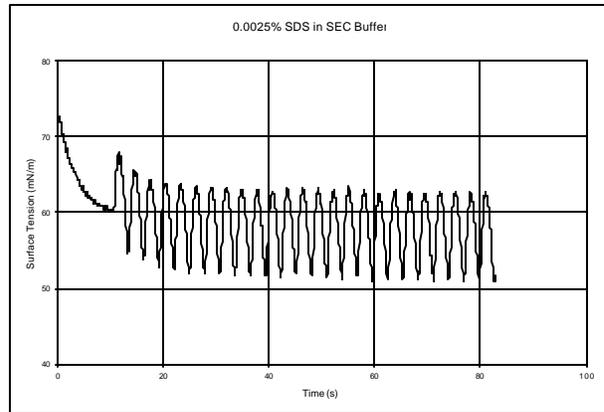


Figure 11. Pulsating bubble data for SDS.

Figures 12, 13, and 14 show differential surface tension, Fourier spectra, and elastic and loss moduli for the SDS sample. Fourier data was averaged over two cycles of modulation, so the response is not full until 20s as modulation began at 10s in Figure 10. The variance in the tension data is roughly $\pm 1/4$ mN/m. This can be reduced by taking the Fourier transforms over longer periods (e.g., 6-8 cycles). The average differential tension amplitude is 5.25mN/m, which corresponds to 10.5mN/m peak-to-peak in Figure 10. The ratio of max to min surface area is $\times 1.66$.

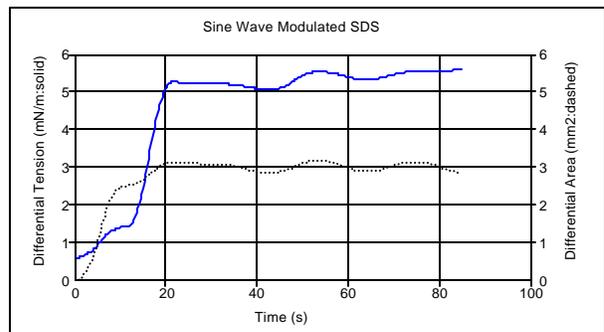


Figure 12. Differential tension and area for SDS.

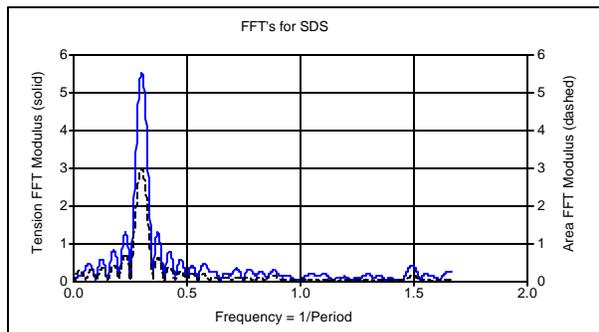


Figure 13. Fourier spectra for SDS.

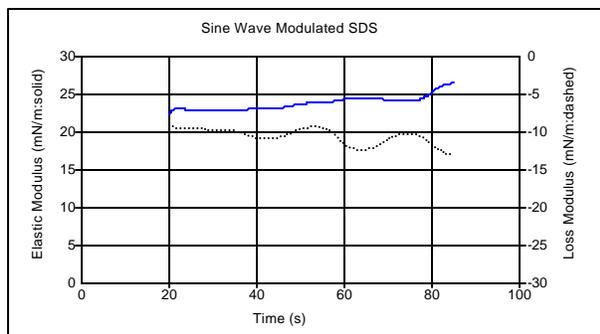


Figure 14. Elastic and loss moduli for SDS.

That the loss modulus is negative is a consequence of the phase angle between the area and surface tension being negative ($\approx -25^\circ$). A similar phase shift, -28° , is observed in Figure 11 data. Normally the angle is positive and the loss modulus is positive; however, the strain rate in this run is high and this causes non-linear effects (and recall the interpretations of viscoelasticity are based on assumptions of linearity). This causes the tension “sine wave” to have flattened peaks on its positive excursion compared to those on its negative excursion. This effect can be seen in a higher than normal peak at the second harmonic in the tension FFT. Notice the moduli magnitudes are much greater than in Figure 7, so instrument cross-talk is not an issue.

The same SDS sample was modulated by a square wave. Figure 15 shows the time response. Notice how there are two time constants present: the long term (100’s of seconds) concentration of the surfactant in the interfacial region and the short term (a few seconds) reorganization of that concentration as it is modulated by the change in surface area.

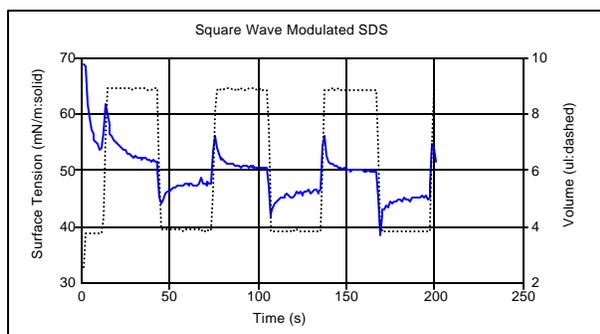


Figure 15. Surface tension/volume for SDS.

Oil Contaminated Water Example. This example illustrates a very low concentration solution and a low modulation measurement. The sample was water which had been in contact with a residue of cutting oil. Figure 16 shows the time response and Figure 17 the elastic and loss moduli. The loss modulus stays essentially zero but the elastic modulus increases greatly after 1000s when the surface becomes organized.

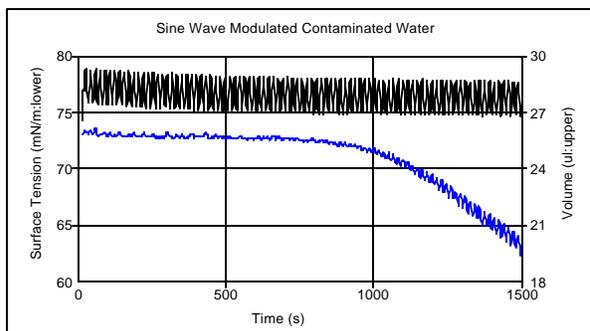


Figure 16. Surface tension/volume for sample.

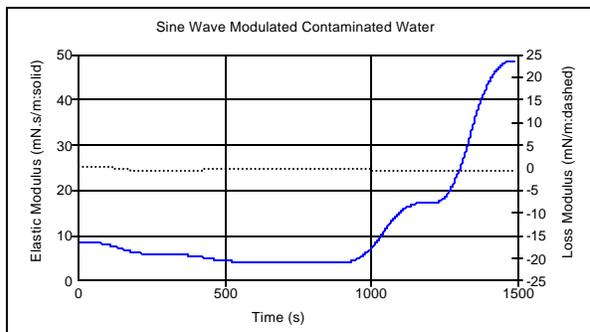


Figure 17. Elastic and loss moduli for sample.

References.

- *Fundamentals of Adhesion*, L. Lee, ISBN 0-306-43470-9
- *Rheology, Principles, Measurements, and Applications*, C. Macosko, ISBN 0-471-18575-2
- *Physical Chemistry of Surfaces*, A. Adamson, ISBN 0-471-61019-4
- *Wettability*, J. Berg, ISBN 0-8247-9046-4