ent G at points near the surface of the bubble is

$$G = 2\pi f \xi_0^2 / a\delta \quad (1)$$

Here δ is the boundary layer thickness defined below, a is the bubble radius (130 μm), and f is the frequency.

The boundary layer thickness can be calculated from the expression

$$\delta = (\eta/\pi\rho f)^{\frac{1}{2}} \quad (2)$$

where η and ρ are, respectively, the shear viscosity and the fluid density. If $\eta = 0.31$ poise, $\rho = 1.0$ g/cm^3, and $f = 2 \times 10^4$ hz, then $\delta = 22.0$ μm. The viscous stress is given by ηG. For the critical threshold of hemolysis, G is 1.4×10^4 sec^{-1} and the viscous stress S_c is 4500 dyne/cm^2. Taking into account experimental errors, one would expect that the standard deviation for S_c would be about 5 percent. However the velocity gradient is nonuniform for the acoustic streaming situation. As a result the maximum uncertainty in S_c is greater, very likely of the order of 1500 dyne/cm^2.

A comparison of values of critical stress for hemolysis obtained by the ultrasonic technique can be made with those obtained with hydrodynamic methods. Samples of blood treated with heparin have been sheared in a closed concentric cylinder viscometer with the bottom of the bob machined to a conical shape. Using such a device, Nevaril *et al.* (*9*) found a threshold stress for hemolysis of 3000 dyne/cm^2. In other experiments Blackshear *et al.* (*10*) have injected jets of saline into suspensions of red cells. The critical velocity gradients observed are of the order of 10^6 sec^{-1}, from which a lethal stress for normal erythrocytes of 40,000 dyne/cm^2 was calculated. Thus, my results fall within the range of values obtained by others.

Williams *et al.* (*5*) describe results for hemolysis caused by acoustic streaming near a vibrating wire. Similarity of results by both ultrasonic techniques demonstrated that details of the ultrasonic interaction with biological materials occurring in a stable bubble field can be elucidated using the vibrating wire apparatus. The comparable results also support the hypothesis that viscous stresses associated with acoustic microstreaming are the important mechanisms involved, since no bubble activity is present near the vibrating wire.

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References and Notes

1. W. L. Nyborg and J. A. Rooney, *J. Acoust. Soc. Amer.* **45**, 384 (1969).
2. S. A. Elder, *ibid.* **31**, 54 (1959).
3. C. Chuongvan, thesis, University of Vermont (1965); G. W. Willard, *J. Acoust. Soc. Amer.* **26**, 933A (1954); W. L. Nyborg and A. Rodgers, *Biotechnol. Bioeng.* **11**, 235 (1967); W. L. Nyborg and D. E. Hughes, *J. Acoust. Soc. Amer.* **42**, 891 (1967).
4. F. E. Fox and K. F. Herzfeld, *J. Acoust. Soc. Amer.* **26**, 984 (1954).
5. A. R. Williams, D. E. Hughes, W. L. Nyborg, *Science*, this issue.
6. A. R. Williams and W. L. Nyborg, *Ultrasonics* **8**, 36 (1970).
7. A. Weissler, *J. Acoust. Soc. Amer.* **25**, 651 (1953).
8. W. L. Nyborg, in *Physical Acoustics*, W. P. Mason, Ed. (Academic Press, New York, 1965), vol. 2, part B, pp. 265–331.
9. C. G. Nevaril, E. C. Lynch, C. P. Alfrey, Jr., J. D. Hellums, *J. Lab. Clin. Med.* **71**, 784 (1968).
10. P. L. Blackshear, Jr., F. D. Dorman, J. H. Steinback, E. J. Mayback, A. Singh, R. E. Collingham, *Trans. Amer. Soc. Artif. Intern. Organs* **12**, 113 (1966).
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Hemolysis Near a Transversely Oscillating Wire

Abstract. *Erythrocyte suspensions were subjected to hydrodynamic forces generated by a partially submerged tungsten wire set into transverse oscillation at 20 kilohertz. Free hemoglobin appears in solution when the oscillation amplitude exceeds a critical threshold value. The hemolysis probably results from stresses exerted on cell by a microstreaming field established near the wire.*

Rooney has shown that hemoglobin is released from both human and canine erythrocytes when they encounter small scale acoustic streaming in which velocity gradients are sufficiently high (*1*). In his experiments these gradients were produced near an oscillating gas bubble of about 250 μm diameter under conditions where undesirable concomitants of cavitation (such as the production of shock waves and high temperature "pulses") were avoided. Specifically, it was found that erythrocytes in physiological saline containing 13 percent dextran 500 require a minimum velocity gradient (G) of 14,300 sec^{-1} for hemolysis. For this dextran-saline solution, the shear viscosity coefficient (measured by capillary viscometry) is about 0.31 poise, so that the critical shear stress (ηG) becomes about 4500 dyne/cm^2.

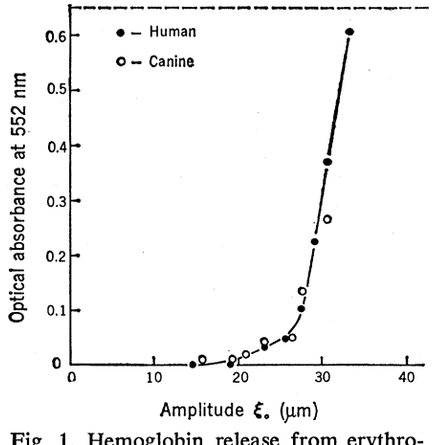

Fig. 1. Hemoglobin release from erythrocytes in suspension, brought about by a partially immersed tungsten wire set into transverse vibration for 5 minutes at a frequency of 20 khz. Osmotic hemolysis in distilled water yields an absorbance value of 0.65, as shown by dashed line.

In view of these results, we were led to consider other arrangements with which one might obtain similar results. An acoustic streaming situation which has probably received more theoretical attention than any other is that which occurs near a transversely vibrating cylinder [see, for example, Schlichting (*2*); Holtzmark, Johnson, Sikkeland, and Skavlem (*3*); Raney, Corelli, and Westervelt (*4*); and a review by Nyborg (*5*)]. Near a transversely oscillating cylinder eddying motions are established (in planes perpendicular to the axis, for an infinite rigid cylinder), with relatively high velocity gradients in a boundary layer very near the cylindrical surface, in the absence of any form of bubble activity. If only the simple approximate expression given by Schlichting is considered, the magnitude G of the maximum velocity gradient at the boundary is

$$G = 2\pi f \xi_0^2 / a\delta \quad (1)$$

Here f is the frequency in hertz, a is the radius of the cylinder, and ξ_0 is the displacement amplitude of the cylindrical surface; the parameter δ is equal to $(\eta/\pi f\rho)^{\frac{1}{2}}$, where ρ and η are, respectively, the density and the shear viscosity coefficient for the liquid. This velocity gradient applies to fluid motion along the boundary, the gradient being directed perpendicular to it. Thus if the velocity parallel to the surface is $u(z)$ at any distance z from the boundary, then G in Eq. 1 refers to the derivative $\partial u/\partial z$ at $z = 0$. The expression for G in Eq. 1 has precisely the same form as that used by Rooney (*1*) for microstreaming near a vibrating bubble. This

is essentially a coincidence; the streaming patterns for the two situations are, in general, quite different.

Proceeding from this expression, we find that a practical arrangement for use with cell suspensions should be possible at ultrasonic frequencies in the vicinity of 20 khz, if cylinders of diameter the same order as that of the bubble discussed earlier, namely, about 250 μm, are used. Thus for cylinders of radius a equal to 0.0125 cm driven at a frequency of 2×10^4 hz in a liquid of viscosity 0.31 poise one obtains

$$G = 4.5 \times 10^9 \xi_0^2$$

and

$$\eta G = 1.4 \times 10^9 \xi_0^2 \qquad (2)$$

where ξ_0 is the (oscillatory) displacement amplitude in centimeters. From Eqs. 2 we see that a displacement amplitude ξ_0 of 20 μm would yield a value of 5600 dyne cm^{-2} for ηG, somewhat greater than the threshold value reported by Rooney. A calculation of the acoustic pressure amplitude near the cylinder at this amplitude yields a value of about 0.4 atm, well under the values which one expects to be required for sonically generated cavitation.

We know of no practical means for setting a reasonable length of unsupported 0.25-mm diameter cylinder into vibration transversely at 20 khz, in such a way that the cylinder vibrates as a rigid object. However, it is a relatively easy matter to set up ultrasonic transverse waves in a wire of this diameter, with amplitudes equal to or greater than those required. This has been done by attaching one point of the wire in question to a piezoelectrically or magnetostrictively driven rod. Two kinds of arrangements have been used successfully. In one of these a free end of the wire projects into the solution of interest; in the other the wire is maintained under tension while a portion is immersed in the solution. We describe here only results obtained with the "free wire", in which the vibration wavelength λ depends on the Young's modulus Y of the material. For tungsten Y is 36×10^{11} dyne cm^{-2}, and the density ρ is 19 g cm^{-3}; for a wire of 0.0125 cm radius, λ is 0.9 cm. The vibration pattern is generally similar to that of Morse (*6*) and specifically to that of the transversely driven tube of Williams and Nyborg (*7*). To achieve maximum displacement amplitude, the length of the wire was adjusted to be an odd multiple of $\lambda/4$. Preliminary results presented below were obtained with a resonant length (2.05 cm) of 0.025-cm diameter General Electric type 218 CS tungsten wire (*8*), clamped at one end to the tip of a stainless steel velocity transformer, and driven at 20 khz by a barium titanate ceramic.

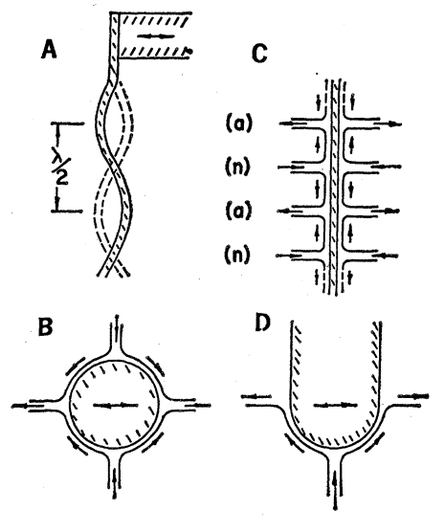

Fig. 2. Schematic of vibrating wire device and circulatory patterns. (A) Attachment of wire to driver. (B) Streaming as it occurs near a transversely oscillating rigid cylinder in plane perpendicular to axis. Arrows near boundary show U_L. (C) Streaming associated with flexural vibrations of wire in the plane of vibration; displacement nodes are at *n*, and antinodes are at *a*. (D) Streaming associated with the tip in plane of vibration.

The sonication vessel was that described by Rooney (*1*). The free end of the tungsten wire was ground to an approximately hemispherical shape with radius of curvature about equal to that of the wire shank. A traveling microscope fitted with a $\times 20$ objective and $\times 10$ eyepiece was positioned with the wire in its focal plane; by its use, displacement amplitudes were directly measured during the actual sonic process. Except at the ends, maxima of displacement amplitude occur at points separated by a distance $\lambda/2$, each having the magnitude A. The greatest amplitude ξ_{om} occurs at the free end where ξ_0 has the value $(2)^{1/2} A$. After sonication, the microspectrophotometer cells were centrifuged, and the optical density of the supernatant was measured as described (*1*).

In Fig. 1, abscissae give the maximum displacement amplitude at the free end. Human or canine erythrocytes were suspended in a solution of physiological saline containing 13 percent dextran 500 (giving a solution viscosity of 0.31 poise). Hemolysis occurred when the displacement amplitude exceeded a threshold value of about 20×10^{-4} cm According to Eqs. 2 this corresponds to an acoustic streaming velocity gradient at the boundary of 18×10^3 sec^{-1} and a shear stress S_c of 5600 dyne cm^{-2}. This value for the critical shear stress required to hemolyze human or canine erythrocytes is in good agreement with the values obtained with the bubble-associated microstreaming (*1*). It is possible that the agreement is in part fortuitous; the details of the disruption process are not yet fully understood. Uncertainty in S_c also arises from the fact that velocity gradients are not uniform in acoustic streaming situations.

The hemolysis-amplitude curves obtained with the stable vibrating bubble and with the transversely oscillating wire are similar. Both curves show a well-defined threshold amplitude, above which the rate of hemolysis rises very steeply. A difference in the curves appears at high amplitudes. The plateau noted by Rooney does not appear here, evidently because the wire produces more mixing than the bubble does.

Examinations were made with optical and electron microscopes of both control and sonicated erythrocytes to determine whether hemoglobin release was due to complete cell rupture. In the course of our study we observed some novel ultrasonic interactions with erythrocytes, such as hemoglobin-filled microspheres having a diameter of the order of a micrometer.

Equation 1 is obtained from theory for acoustic streaming near an infinite cylinder which oscillates as a rigid body. The nature of the predicted streaming is suggested by Fig. 2B. Arrows along the surface show the direction of a so-called "limiting velocity" U_L, explained in (*5*, p. 303). Return flow occurs in the outer region.

Observations of the actual streaming reveal features resulting from the fact that the cylindrical wire is neither rigid nor infinite. Thus a relatively slow large-scale circulation occurs, which is associated with the flexural vibrations of the wire (Fig. 2C). This motion transports liquid from displacement node *n* to antinode *a* in a region very near the cylindrical surface, with return occurring in the main body of the liquid. The nature of the flow is suggested in Fig. 2C; again arrows near the surface show the direction of the limiting flow U_L. A more rapid eddying occurred near the free end or tip of the wire; its nature is sensitive to the geometry of the tip. The tip was usually rounded to an approximately hemispherical shape. The tip-associated flow (Fig. 2D) is then closely related to that near a cylinder (Fig. 2B).

Full mathematical treatment of these motions has not been given except for the rigid cylinder. However, the main features of the motion can be explained qualitatively in terms of an approximate result given by Schlichting (*2*) and Nyborg (*5*, p. 303). This result, based on a "thin boundary layer" approximation, is expressed in terms of a "limiting" velocity U_L already mentioned, which is characteristic of the streaming velocity near the cylinder just outside the boundary layer. This velocity U_L is parallel to the boundary; we take U_L to be along the x direction, with a choice of meanings for x. Thus for rigid-cylinder streaming (Fig. 2B), x measures arc length along a circle around the wire, perpendicular to the axis. For streaming associated with the flexing vibrations (Fig. 2C), x measures arc length along the wire, parallel to the axis. For tip-associated streaming (Fig. 2D), x measures arc length along a great circle formed by intersecting the hemispherical tip with a plane passing through the wire axis.

Let u_0 be the amplitude of oscillatory irrotational motion (that is, oscillatory motion as it would be in the absence of viscosity) along the x direction. The Schlichting result is then

$$U_L = -(3/8\,\omega)\partial(u_0^2)/\partial x \qquad (3)$$

This expression may be applied qualitatively to any of the situations in Fig. 2.

It can readily be verified that the direction of U_L given by Eq. 3 is in agreement with the direction indicated by arrows near the wire surface in Fig. 2, B and D.

According to Eq. 3 the magnitude of U_L depends on the magnitude of $\partial(u_0^2)/\partial x$ or $2u_0\partial u_0/\partial x$. For purposes of rough comparisons suppose that A is a typical magnitude for u_0 and that in a given situation u_0 decreases from A to zero in a distance l. Then U_L is roughly proportional to A^2/l, and for given A the characteristic streaming velocity U_L varies inversely with l.

For both the situations of (Fig. 2, B and D), the length l may be taken as $\pi a/2$, one-fourth the wire circumference; for the situation of Fig. 2C we choose l as $\lambda/4$. Hence we expect U_L to be of the same order of magnitude for Fig. 2, B and D, while for Fig. 2C the magnitude of U_L will be less by about a factor of $2\pi a/\lambda$. For our typical situation ($a = 0.0125$ cm; $\lambda = 0.9$ cm), this factor is about (1/70). Since the maximum viscous stress near the wire is proportional to U_L, we see that effects of such stresses arise primarily from "cylinder streaming" (Fig. 2B) and tip-associated streaming (Fig. 2D), and not appreciably from the relatively large-scale streaming of Fig. 2C. The last-mentioned is nevertheless significant; it plays the role of transporting suspension from the outer fluid to the high-stress region near the wire; it probably explains the absence of a plateau in Fig. 1 analogous to that noted by Rooney (*1*).

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References and Notes

1. J. A. Rooney, *Science*, this issue.
2. H. Schlichting, *Boundary Layer Theory* (McGraw-Hill, New York, 1955), p. 194.
3. J. Holtzmark, I. Johnson, T. Sikkeland, S. Skavlem, *J. Acoust. Soc. Amer.* **26**, 26 (1954).
4. W. P. Raney, J. C. Corelli, P. J. Westervelt, *ibid.*, p. 1006.
5. W. L. Nyborg, in *Physical Acoustics*, W. P. Mason, Ed. (Academic Press, New York, 1965), vol. 28, chap. 11.
6. P. M. Morse and K. U. Ingard, *Theoretical Acoustics* (McGraw-Hill, New York, 1968), pp. 175 ff.
7. A. R. Williams and W. L. Nyborg, *Ultrasonics* **8**, 36 (1970).
8. The wire was donated by the General Electric Company through R. M. Cogan, Providence, R.I.
9. W.L.N. was Visiting Scientist at the microbiology department, University College, Cardiff, when most of the present work was being done. Supported in part by the Medical Research Council and in part by NIH grant GM-08209.

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Palladium: Preparation and Catalytic Properties of Particles of Uniform Size

Abstract. *A method has been developed for the preparation of uniform palladium particles of diameter from 55 to 450 angstroms. Uniform particles of gold layered on palladium were also synthesized. Hydrothermal treatment of aluminum hydroxide sol was used to prepare rods of alumina with uniform cross section from 100 to 500 angstroms and of varying lengths. The palladium was adsorbed as individual particles on alumina rods, both present in aqueous suspension. Then the suspension was dried to give a catalyst containing metal particles of uniform size dispersed in open pores produced by the intermeshing of the alumina rods. This procedure guaranteed the absence of diffusion control in the rate of reactions observed experimentally. All stages of the preparation were monitored with the electron microscope. The kinetics of the ethylene-hydrogen reaction were examined by means of a pulse technique. The number of active sites determined by carbon monoxide titration of the surface was equal to the number of surface atoms as determined by the calculation of the quantities of compounds involved in the synthesis and electron microscope examination. Furthermore, the activity per site depended on the method of preparation, being four times smaller when sodium formate was used as a reducing agent instead of sodium citrate. This may be due to the fact that the shape of particles makes certain crystallographic planes more favorable. Decrease in the size of particles to 56 angstroms produced no effect on catalytic activity beyond that due to the increase in the number of surface atoms. The activity of commercial 5 percent palladium on alumina diluted 100-fold with alumina gave 80.4 percent conversion with propylene and 82.7 percent conversion with ethylene. Thus there was little difference in the behavior of the two olefins.*

The relation between particle size and catalytic activity is of basic importance in heterogeneous catalysis. It is of great theoretical importance to determine whether the catalytic activity increases continuously as one increases the surface, whether there is a preferred size for maximum activity, or whether the catalytic activity disappears at a size at which the metallic properties of the particles also disappear. Furthermore, comparison of variation of chemical composition, catalyst support, and nuclear irradiation can be carried out more systematically if the particle size is kept constant. It is also of practical importance to be able to synthesize catalysts of maximum catalytic activity and to understand and to control each step of the catalyst preparation so as to ensure reproducible catalytic activity.

It was felt that the knowledge of systems and synthesis of colloidal gold (*1*) could be used as a guide in the preparation of palladium catalysts of desired uniform particle size and shape. In addition, the microtesting technique (*2*) would afford one an elegant means of characterizing the catalysts so prepared. We report here the hydrogenation of ethylene on palladium cata-