

terpreting the results of measurements that require extended periods to perform. For example, changes in relative elevation determined by repeated leveling surveys between widely separated points could reflect both intersurvey and intrasurvey deformation. Castle *et al.* (16) suggest that in some cases movements are the reason that elevation differences measured around closed circuits do not always sum to zero. Finally, the possibility that episodic aseismic deformation is common and widespread in southern California suggests that a monitoring strategy focused on episodic deformation (17) would permit an assessment of the likelihood of a specific deformation event triggering an earthquake.

ROBERT C. JACHENS
WAYNE THATCHER
CARTER W. ROBERTS
ROSS S. STEIN

U.S. Geological Survey,
Menlo Park, California 94025

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12. One line of evidence supports this conclusion: gravity changes in the Glendale area (the south terminus of the leveling routes to Tejon Pass and Palmdale) relative to Riverside were stable within 5 μ gal from 1977 to 1981. A single 16- μ gal excursion in 1979.1 was localized at the Glendale base station and absent at stations 10 to 20 km away.
13. In order to avoid the uncertainties in choosing datum levels for each of the time histories, the correlation coefficients were determined from the population of changes between adjacent pairs of nearly coincident δg and $\delta \Delta$ or δg and $\delta \epsilon$ observations.
14. It recently has come to light that some leveling data may contain errors resulting from interaction between magnetic fields and automatic compensators in leveling instruments. At this time the error is poorly understood but appears to vary with the make and model of the instrument, would be different for individual instruments, and would be subject to changes with time in any particular instrument. We have identified one point in the leveling data reported here, the 1979 elevation at Tejon Pass, that might be contaminated by a magnetically induced error. If a 1982 laboratory calibration of the instrument used in this survey is applicable to the 1979 results, then the 1979 relative elevation at Tejon Pass would be approximately 200 mm higher than that shown in Fig. 2. At present we do not know whether, in general, laboratory calibrations are strictly applicable to field survey results nor whether it is valid to apply a calibration of this particular instrument obtained in 1982 to data acquired with it in 1979 [National Geodetic Survey, *Prof. Surv.* 2-5, 38 (1982)].
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18. We thank J. C. Savage for providing us with the strain data as well as performing additional analyses for us.

25 May 1982; revised 10 September 1982

Syneresis of Vitreous by Carbon Dioxide Laser Radiation

Abstract. *In carbon dioxide laser surgery of the vitreous a process of vaporization has been advocated. In this report syneresis, a thermal liquefaction of gel, is shown to be over ten times more efficient on an energy basis than vaporization. Syneresis of vitreous is experimentally shown to be a first-order kinetic process with an activation energy of 41 ± 0.5 kilocalories per mole. A theory of laser surgery in which this figure is used agrees closely with results from laser experiments on human eye-bank vitreous. The syneresis of vitreous by carbon dioxide laser radiation could lead to a more delicate form of ocular microsurgery, and application to other biological systems may be possible.*

For applications in ophthalmology, the short penetration depth of CO₂ laser radiation ($\sim 10 \mu\text{m}$ at $10.6 \mu\text{m}$) is advantageous, since a significant local effect can be achieved in ocular tissues without damaging underlying or neighboring structures. Carbon dioxide lasers have been used for scleral dissection, in filtering procedures for glaucoma (1), and as a photocoagulation to seal fibrovascular fronds and retinal tears at the time of vitrectomy (2). It has been suggested that CO₂ laser radiation could be used in a vitrectomy to "vaporize" regions of vitreous (3-5) and thus avoid the traction on adjacent structures evident when me-

chanical instruments are used. In this report we show experimentally and theoretically that there is a more efficient way to remove vitreous. By using thermal syneresis, the same effect can be achieved with over ten times less energy expenditure per unit mass (53 cal/g compared to 576 cal/g for vaporization). This new type of surgery involves local heating of the vitreous gel (with CO₂ laser radiation) from the ambient vitreous temperature of 37°C to a temperature at which the gel is converted to a liquid (6), which can be removed by aspiration. The greatly reduced energy requirement for this process may lead to a much more

delicate form of ocular microsurgery. The chances of damage to the retina, which can be caused by a temperature elevation of only 10° to 20°C (7), are greatly reduced.

The vitreous body is a transparent semisolid gel interposed between the lens and the retina. It is the simplest connective tissue, but knowledge of its structure and function is incomplete. The water content, between 98 and 99.7 percent (8), is held in a two-part gel or semigel consisting of a fibrous protein, collagen, and a mucopolysaccharide, hyaluronic acid. Such a two-component structure has greater mechanical stability than the collagen network alone. Because of the large domain of solution occupied by the hyaluronic acid molecules (65 ml/g), such a structure can physically entrain large quantities of water (6). Collagen is composed of a triple helical arrangement of three polypeptide chains (9). In the native state these are cross-linked, forming fibrils (15 to 25 nm in diameter) randomly distributed in a loose network (less than 1 to 1.5 μm between elements) (9). A low concentration of collagen fibrils, as in the owl monkey (25 $\mu\text{g/ml}$), leads to a liquid vitreous; a greater concentration (for instance, 286 $\mu\text{g/ml}$ in humans), leads to a gel-like vitreous (10).

The collagen network and hence the vitreous can be shrunk by processes such as heat, radiation, freezing, and thawing (10). When a solution of collagen is heated, the triple helical structure is destroyed and randomly coiled molecules are produced (9). This helix-to-coil transition represents the conversion of collagen to gelatin (9). In such a thermal denaturation a shortening of the fibrils occurs which results in a volume decrease of the network of collagen fibrils and hence of the gel itself. As an example, after heating, the vitreous gel from human eye-bank eyes is found to consist of both liquid and gel portions. We measured the rate of this process by the following method. With the temperature of the vitreous sample held constant, the liquid portion was drawn off and measurements of the weight of the gel as a function of time were recorded. The data were fit by the equation, $W(t) = W_0 \exp(-kt)$, where W_0 is the initial weight of the vitreous gel, k is the specific rate constant, and t is time. Values of k were determined for a range of temperatures and are plotted in Fig. 1 against inverse temperature. The solid line fit to the experimental points is a plot of the Arrhenius equation $k(T) = A \exp(-E/RT)$, where A is the preexponential factor, E is the activation energy, R is 1.987 cal/

mole-K, and T is the absolute temperature. The value of E that gives the best fit to the experimental points is 41 ± 0.5 kcal/mole. For comparison, data on the thermal shrinkage of tuna vitreous gel from (6) give $E = 50 \pm 1$ kcal/mole (Fig. 1). The collagen contents of tuna vitreous (217 $\mu\text{g/ml}$) and human vitreous (286 $\mu\text{g/ml}$) are similar (10), but the mucopolysaccharide content of tuna vitreous (660 $\mu\text{g/ml}$) is much higher than that of human vitreous (240 $\mu\text{g/ml}$) (10). This probably results in the higher activation energy.

The experimental arrangement used to study the syneresis of vitreous by CO_2 laser radiation is shown as an inset to Fig. 2. The output from a CO_2 laser is transmitted through a probe, via a dielectric waveguide of the Marcattili-Schmeltzer type (11), into a sample of vitreous gel. The infrared waveguide is a straight, hollow quartz tube (inside diameter, 0.0165 inch) closed at the output end with an infrared transmitting window of type IIa diamond. The diamond window provides high transmission of CO_2 laser radiation and high thermal conductivity (12). Diamond was the only material that was easy to clean and totally resistant to laser damage. The infrared waveguide is sheathed in a stainless steel tube (inside diameter, 0.081 inch) which projects 0.056 inch beyond the surface of the diamond window. The annular space between the waveguide and the sheath is coupled to a vacuum source (21 mmHg) and serves as an aspiration channel for the liquefied vitreous.

Experimental results on the rate of removal of vitreous gel from human eye-bank eyes are shown in Fig. 2. Both continuous-wave (CW) and pulsed CO_2 lasers gave the same removal rate when the rate was plotted against average power. However, use of a CW laser resulted in the formation of a gas bubble at the tip of the probe through which 10.6- μm radiation would pass with little attenuation, leading to a stream of bubbles as long as 1 to 1.5 cm moving rapidly away from the tip of the probe. Clearly, this would be a potential hazard to surrounding ocular tissue. A pulsed CO_2 laser operating at 400 Hz (with a 10 percent duty cycle) did not lead to a stream of bubbles, presumably because any bubble formed had time to collapse between pulses. We therefore consider pulsed CO_2 lasers better suited to this form of vitreous surgery.

The data presented in Fig. 2 can be accounted for by a simple model in which it is assumed that the laser power is absorbed by vitreous gel in a small region at the surface of the diamond

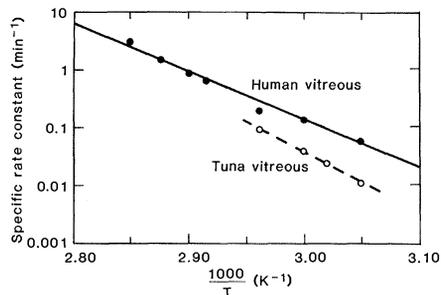


Fig. 1. Temperature dependence of the specific rate constant for the reaction that converts gel vitreous to liquid vitreous for (●) human eye-bank eyes and (○) tuna (6) together with a plot of the Arrhenius equation with activation energies of (—) 41 and (---) 50 kcal/mole.

window. The actual volume in which gel vitreous is converted to liquid (dashed region in inset to Fig. 2) is enlarged by laser-induced agitation. Such agitation is readily observed under experimental conditions and, while not fully understood, may be due to local boiling. Fresh gel at room temperature is presented to the laser beam as the liquid is aspirated, resulting in a steady-state process. Equating laser input power to the power carried away by aspiration in the heated liquid and by conduction into the diamond window gives an expression relating the rate of removal of vitreous and its temperature rise to the laser power input. The Arrhenius equation, fit to the results of the thermal syneresis rate experiment, provides a second expression for these two quantities. No account was taken of any chemical energy released or taken up by the syneresis process. Using

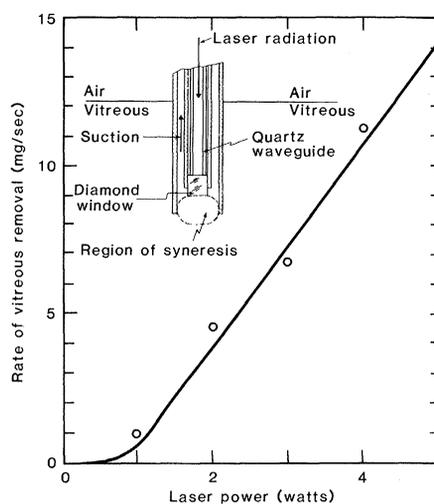


Fig. 2. Rate of removal of vitreous gel at room temperature from human eye-bank eyes as a function of CO_2 laser power (○) together with results from a simple theoretical model (—) based on a value for the heated volume determined by the best fit to the experimental points. The experimental arrangement is shown as an inset.

the heated volume as an adjustable parameter, the simultaneous solution of these two equations was fit to the experimental data (curve in Fig. 2). The calculated average temperature rise was 72.4°C , and the size of the heated volume was 14 μl . The results with the model (curve in Fig. 2) have a simple physical interpretation. The slope of the curve between 1 and 4 W is a measure of the power carried away by the hot aspirated liquid, while the intercept (~ 0.75 W) is the power lost by conduction into the diamond window.

The good fit of the theoretical expression to the experimental results, without including chemical energy, sets an upper limit on the laser energy expended in any chemical reaction of no more than 1 percent of the total input energy. We find then from Fig. 2 that water is released with an energy expenditure of less than 1.6×10^{-2} kcal/mole. Such a low value would be expected if syneresis were a steric reaction where the collagen network is just severely distorted, squeezing the water out.

In conclusion, the syneresis of vitreous by CO_2 laser radiation may eventually lead to a new type of ocular microsurgery. The thermal shrinkage of collagen has a very general application. Corneal stromal collagen shrinks to approximately one-third of its original length when heated to 60° to 70°C (13). Thermokeratoplasty, which makes use of this fact, has been employed to correct optical problems and to treat corneal hydrops (14). The striking similarity between the vitreous and the synovial fluid in the joint (15) indicates that CO_2 laser joint surgery may be possible. Other applications may exist in biological and biomedical research and practice.

T. J. BRIDGES
C. K. N. PATEL
A. R. STRNAD
O. R. WOOD, II

Bell Telephone Laboratories,
Holmdel, New Jersey 07733

E. S. BREWER
D. B. KARLIN

Cornell University Medical College,
New York 10021

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14 June 1982; revised 7 September 1982

Growth Enhancement of Plants by Femtomole Doses of Colloidally Dispersed Triacontanol

Abstract. Colloidal dispersions of crystalline 1-triacontanol in water, upon foliar application to corn (*Zea mays* L.) seedlings, resulted in growth increases at femtomole dosages (spray concentrations as low as 1 nanogram per cubic decimeter). The maximum growth increase occurred at 100 nanograms per cubic decimeter; at both higher and lower concentrations lessened growth increase was observed. The dispersions were prepared by sonication, with control of temperature and composition. Selected surfactants, which facilitate the dispersion process, are effective at 1 percent of the 1-triacontanol composition and are nontoxic.

1-Triacontanol (TRIA) increases plant growth and sometimes increases crop yields (1). Attempts to exploit this discovery to increase the yield of food crops have met with variable success (2). The mode of application of the compound appears to have been a poorly controlled parameter and may have been partly responsible for this variability. We have addressed this problem by preparing a stable colloidal dispersion of crystalline particles of TRIA in water.

The administration of TRIA to the plant, as well as its transport within the plant, requires dispersal in water, either as a solution or as a colloid. The water solubility of TRIA can be estimated, by

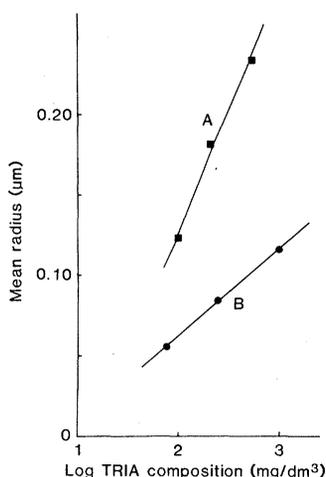


Fig. 1. Mean particle radius as a function of TRIA composition (A) without dispersant; (B) with dispersant (1 percent TAS relative to the TRIA composition). Each value of \bar{r} is the mean of two data points. The average standard deviation for \bar{r} from separate sets of similar determinations is 6.5 percent of \bar{r} (ten sets of data; $N = 4$ in each set).

extrapolation of data on lower homologs (3), to be less than $2 \times 10^{-16}M$ (9×10^{-14} g/dm³). Thus the solubility of TRIA is probably not a factor in its activity as a plant growth stimulant. Effective use requires that it be colloidal dispersed.

Methods for forming colloids fall into one of two classes. The colloidal particle is formed either by shearing apart a larger particle, or by assembling it from many smaller aggregates or from molecules. The second method has been the one most commonly followed. Specific procedures included precipitation by dilution of solutions in dimethyl sulfoxide (4) or acetone (5), dilution of a solution in a liquid nonionic surfactant (6), or dilution of TRIA solubilized in a micellar solution of mixed soap and nonionic surfactants (2).

In our study of the colloidal dimensions of dispersions, we have estimated particle size by a cumulant analysis of quasi-elastic light scattering (QELS) data (7). Dispersions prepared by dilution methods were highly and erratically polydisperse, having particle radii (r) ranging from 0.02 to 35 μm . At sufficiently high composition (10 to 100 mg/dm³), dispersions formed by dilution are visibly heterogeneous. The micellar solution (2) appears to be metastable; over a period of months the solution deposits large crystals of TRIA. Thus, from all these test preparations, the fraction of TRIA that is effectively dispersed is uncertain. Further, the particle number concentration is likewise uncertain, uncontrolled, and relatively small (8-11).

We have now prepared uniform colloidal dispersions of TRIA in water having

mean equivalent hydrodynamic particle radii (\bar{r}) of 0.05 to 0.3 μm and modest polydispersity ($\delta\bar{r} \cong 0.5\bar{r}$) by using ultrasonic dispersion of coarse suspensions (12). Such colloids are polydisperse, but the dispersity is reproducible and narrow compared to that of colloids formed by dilution. As would be expected, these colloids are stable over long periods of time. Although a small fraction of the material may generate a visible amount of flocculated material after some months, no substantial quantitative changes were evident in samples a year old.

Successful dispersion requires control of temperature, composition, sonic energy input, and it is facilitated by the presence of a dispersant. The temperature must be near or above the melting point (90°C), but below the boiling point of water. In the absence of a dispersant, the TRIA composition must be ~ 0.5 g/dm³; the lower the composition, the smaller the particles formed (Fig. 1). Use of an effective dispersant decreases the resulting particle size at a given TRIA composition, or makes it possible to increase the composition to ~ 4 g/dm³ and still form stable colloids (Fig. 1).

The dispersant presumably functions by retarding the coalescence of very small liquid TRIA droplets produced during the explosive energy flux released by cavitation (12). It must be surface

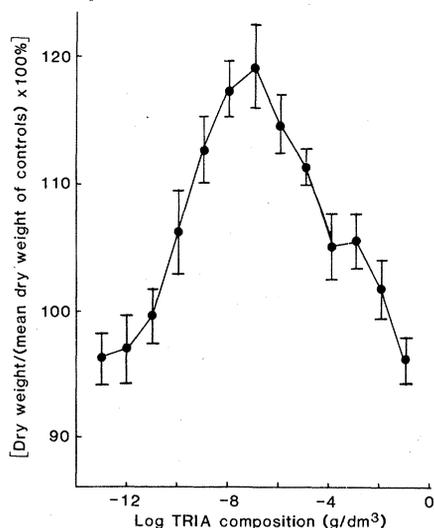


Fig. 2. Dry weight of corn shoots as a function of TRIA composition in the foliar spray, expressed as percent of controls. The controls were sprayed with TAS solution (10^{-3} g/dm³). Seven-day-old shoots were sprayed and harvested 7 days later. The error bars calculated from shoot weight data on twelve pots, correspond to ± 1 standard error (standard deviation, s/\sqrt{n}). Data from two experiments of six pots each were combined. Each pot contained four shoots, weighed together. The mean shoot weight of the 12 control pots was 0.442 g ($s = 0.032$ g, or 7.3 percent of mean).