

a sample prepared according to this technique can be preserved depends upon the thickness of the lacquer film. Samples prepared during the course of the present work were kept up to 2 weeks before the films began to tear.

The authors made no attempt to use the liquid counting techniques for absolute β -counting. The absorption of the β -particles by the solution, and the back-scattering from the cup, tend to make the corrections that must be applied in order to find the true disintegration rate of a sample by this method very large. However, for most practical applications of radioactive tracers in chemical analysis, it is only necessary to know the ratio of the counting rate of the "unknown" sample to that of an empirical standard, and for this purpose the liquid counting technique is excellent. It is desirable to have the amounts of inactive materials in the "unknown" and standard approximately the same, but no accurate control is necessary. Because the solution absorbs part of the β -rays, the activity of a given sample counted as a liquid is in general about half that of the same sample counted as a solid, for β -energies greater than 1 mev. The relative loss in counting rate is of course greater for lower energy particles, but this is no serious handicap when the radioactive isotope can be obtained in reasonably high specific activity. The great gain in precision that can be obtained with liquid samples more than compensates for the loss in observed counting rate.

In order to obtain the maximum precision from the liquid counting method, the Geiger tube used must count reproducibly to within the limits of error desired for the experiment, and it should be stable during the period of the investigation. The authors tested a number of commercially available Geiger tubes and found that many were completely unsuited for use in precise analytical work. Some of the tubes could not reproduce the activity of a given sample to better than 5-10%. Most of these tubes showed a marked voltage hysteresis effect; that is, the counting rate for a given sample depended upon whether the operating voltage of the tube was approached from above or below, and upon the time the tube was maintained at constant voltage. Photosensitivity was observed with some tubes; this was a disturbing effect even with completely shielded tubes, because light that entered when the shield was opened to change samples caused a rise in counting rate which persisted for several minutes after the shield was closed. High humidity caused most of the tubes tested to count spuriously. This factor was controlled by keeping a good, dust-free drying agent in the counting shield at all times, and, on extremely moist days, by blowing a slow stream of dry air through the shield.

The tubes finally selected for use in the present work were models Nos. 100C and 200C, manufactured by the Amperex Electronic Corporation, Brooklyn, New York. These are end-window tubes with thin mica windows; they were used inside lead shields of standard design, which kept the background count at about 15 cpm. The tubes showed no voltage hysteresis and no photosensitivity; the humidity effect was controlled as above.

Four of these tubes showed equally good characteristics. A uniform sample counted 38 times over a 2-month interval in a 200C tube gave a standard deviation of the mean of .1%, so that the Geiger tube was not the limiting factor in determining the precision of the experimental results. This discussion illustrates the care which should be taken in selecting a tube for use in an analytical study. It should be pointed out that other counting instruments, such as methane-flow proportional counters and scintillation counters, are becoming increasingly well known. These instruments have much better counting characteristics and reproducibility than Geiger tubes and seem to offer a solution to this aspect of the problem involved in obtaining reproducible counting results.

The authors have applied the liquid counting method described in this paper in the development of a combined photometric-radiometric method for the determination of cerium (1). The over-all precision obtained in this work was about 1.4% standard deviation. By using any of the common methods for mounting solid samples, it would have been impossible to obtain better than 5-7% precision in the final results. Up until the present, radiometric methods of analysis have been severely limited in scope because of their poor precision. The use of the liquid counting technique, in conjunction with good counting equipment, should now permit the development of precise radiometric methods of analysis for many elements which are difficult to determine by other means, and should encourage the development of many other applications of radioactive tracers.

References

1. FREEDMAN, A. J., and HUME, D. N. *Anal. Chem.*, 1950, **22**, 932.
2. KOHMAN, T. P. *Anal. Chem.*, 1949, **21**, 352.
3. MILLER, W. W., and PRICE, T. D. *Nucleonics*, 1947, **1**, (3), 4.

Effects of Ultrasonic Waves and Nitrous Acid on the Production of Colloidal Sulfur

Shichiro Akiya, Otohiko Nomoto, and Seiichi Okui

*Institute of Pharmaceutics, Faculty of Medicine,
University of Tokyo (Akiya and Okui), and
Kobayashi Institute of Physical Research,
Kokubunji, Tokyo, Japan (Nomoto)*

Production of colloidal sulfur by mixing dilute solutions of sodium thiosulfate and HCl has been investigated by La Mer and co-workers (2-5). Colloidal sulfur begins to appear about 10 min after the addition of the acid and is recognized by the Tyndall scattering of light. La Mer and Yates (6) observed that the time of production of colloidal sulfur increased about 4 times when the distilled water used in this experiment is first irradiated by ultrasonic waves. They tentatively attributed it to the removal of the nuclei required for growth to colloidal dimensions, and they demonstrated that the effect

is not due to the production of H_2O_2 or to any detectable chemical change. Weissler (9) reports that this increase in the time of production is only observable on irradiated distilled water when it contains air or N_2 , and that water previously boiled under vacuum so as to expel the air, or saturated with CO_2 , O_2 , or He, does not produce the effect. He attributes this increase to such reaction products as NH_3 , or HNO_2 , reported by previous investigators, in irradiated distilled water.

The authors (1) previously observed the production of H_2O_2 , HNO_2 , and HNO_3 (but not of NH_3) in irradiated distilled water and made quantitative measurements thereof. The main reaction product is HNO_2 , particularly by short irradiations. So they supposed that the increase in the time of production of colloidal sulfur by irradiated distilled water was due to HNO_2 produced in it, and performed the following experiments to confirm this view.

With irradiated distilled water. To 20 ml of irradiated or unirradiated distilled water at 11°C were added 1 ml of 0.24 N - $\text{Na}_2\text{S}_2\text{O}_3$ and 1 ml of 0.24 N - HCl , and the time required for the appearance of the Tyndall beam was measured. The sample of distilled water (20 ml) was previously subjected to the action of ultrasonic waves of 470 kc/sec in a test tube of 19-mm inner diameter, provided with a water jacket for cooling. The intensity of the wave was determined by measuring the radiation pressure on a circular glass vane 15 mm in diameter, immersed in the irradiated liquid sample, by means of a balance, as described in a previous paper (7, 8).

By varying the time of irradiation at constant ultrasonic intensity (0.3 g-wt on 15-mm vane = 167 erg/cm² energy density), the authors obtained the data shown in Table 1. By varying the intensity of the ultrasonic wave

TABLE 1

Time of irradiation (min)	Amount of HNO_2 produced (mg, %)	Time of production of colloidal sulfur (min)
0 (not treated)		
0	0	11.0
3	0.12	51.5
5	0.24	62.5
10	0.45	48.0
20	0.90	34.0
30	1.00	29.5

with constant time of irradiation (5 min), the data in Table 2 were obtained.

TABLE 2

Radiation pressure (g-wt)	Energy density (erg/cm ²)	Time of production of colloidal sulfur (min)
0.1	56	47.2
.2	111	60.0
.3	167	62.5
.4	222	58.5
0.5	278	52.5

Also, the production of HNO_2 (or the chemical action in general) shows maxima at certain ultrasonic intensities (177–222 erg/cm²), as previously reported (7, 9).

With HNO_2 solutions. Solutions of HNO_2 of various concentrations were used in place of the irradiated distilled water, and the time for production was determined as in the previous manner. Table 3 gives the results.

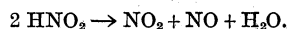
TABLE 3

Concentration of HNO_2 (mg, %)	Time of production of colloidal sulfur (min)
0	11.0
0.005	12.5
.01	13.5
.02	17.0
.04	28.0
.08	48.5
.1	53.0
.12	53.0
.25	63.0
0.50	65.5
1.0	65.5
2.0	85.5
6.5	No colloid produced

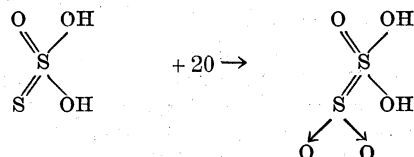
These show that the effect of irradiated distilled water on the time of production of colloidal sulfur coincides with that of HNO_2 , as long as the time of irradiation does not exceed 5 min. The decrease of the effect by longer irradiation (Table 1) is explained by the increased amount of H_2O_2 produced in the irradiated water. This substance reacts with HNO_2 and produces HNO_3 , particularly in acid solutions.

Color reaction and the detection of ions. It was observed further that $\text{Na}_2\text{S}_2\text{O}_3$ (+ HCl) and HNO_2 , when mixed, reacted and produced a yellow color, which faded gradually. The irradiated distilled water showed the same coloring when $\text{Na}_2\text{S}_2\text{O}_3$ (+ HCl) was added to it. As the yellow color fades away, SO_3'' and SO_4'' ions can be detected in the mixture of $\text{Na}_2\text{S}_2\text{O}_3$ (+ HCl) and HNO_2 solutions. When the ratio of HNO_2 : $\text{Na}_2\text{S}_2\text{O}_3$ is small, SO_3'' is predominant, whereas SO_3'' vanishes and SO_4'' increases as this ratio exceeds 1 mole: $\frac{1}{2}$ mole. The separation of sulfur was no longer observable as this ratio reached 1 mole: $\frac{1}{4}$ mole.

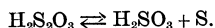
The authors reached the following conclusion from the above and other results. First, there is a production of NO_2 by the reaction:



This NO_2 produces O , which combines with $\text{H}_2\text{S}_2\text{O}_3$, producing a yellow color:



This molecule splits up at the double bond $\text{S}=\text{S}$ and takes H_2O to produce 2 molecules of H_2SO_3 , which hinders the production of sulfur in the equilibrium:



H_2SO_3 is further oxidized to H_2SO_4 by NO_2 .

La Mer and co-workers assumed this phenomenon as a phase-transition from molecularly dispersed sulfur into droplets of supercooled λ -sulfur, but the present experiments seem to indicate that the separation of sulfur itself requires time, as is indicated by the slow building up of SO_3'' and the color reaction.

References

1. AKIYA, S., and OKUI, S. *Yakugaku-zasshi (J. Pharm., in Japanese)*, **67**, 232 (1947).
2. BARNES, M. D., et al. *J. Colloid Sci.*, **2**, 349 (1947).
3. JOHNSON I., and LA MER, V. K. *J. Am. Chem. Soc.*, **69**, 1187 (1947).
4. LA MER, V. K., and BARNES, M. D. *J. Colloid Sci.*, **1**, 76, 79 (1946).
5. LA MER, V. K., and KENYON, A. S. *J. Colloid Sci.*, **2**, 257 (1947).
6. LA MER, V. K., and YATES, J. W. *Science*, **106**, 508 (1947).
7. NOMOTO, O., and OKUI, S. *J. Phys. Soc. Japan*, **3**, 47 (1948).
8. ———. *Yakugaku-zasshi*, in press.
9. WEISSLER, A. *J. Colloid Sci.*, **3**, 67 (1948).

A Simplified Recording Bubble Flow Meter¹

William G. Hammond, Chester Hyman, and Thomas E. Nelson

Department of Physiology,
University of Southern California School of Medicine,
Los Angeles

In the course of cross-transfusion experiments with rats, it became desirable to measure the rate of blood flow between the animals. The conditions of the experiment required an instrument that could fulfill the following requirements: (a) measure accurately flow rates between 0 and 15 ml/min; (b) impose the minimum resistance to flow, i.e., the minimum pressure drop; and (c) divert a minimum volume of blood from the system under investigation. In addition, simplicity of design and a method for objective recording were considered desirable.

The recent survey of flow meters by Green and others (2) critically evaluated the several methods that have been employed. Of the group, we considered the bubble flow meter as most nearly satisfying our requirements. The modification of this instrument by Selkurt (3) offers a method for recording that is fundamentally simple and accurate. The chief objections to instruments of this sort have to do with the relatively large volume of blood diverted to the meter (about 6 ml in the form described by Selkurt) and the cumbersome character of the instrument as a whole. The modifications to be described

¹This study was carried out under Contract No. W33-038 ac-19062 between the U. S. Army Air Force and the University of Southern California. The work was performed in laboratories generously provided by the Allan Hancock Foundation.

obviate these difficulties, and provide an instrument which is simple to build in any laboratory, but which nevertheless performs with remarkable accuracy.

Fig. 1 presents several drawings of the instrument.

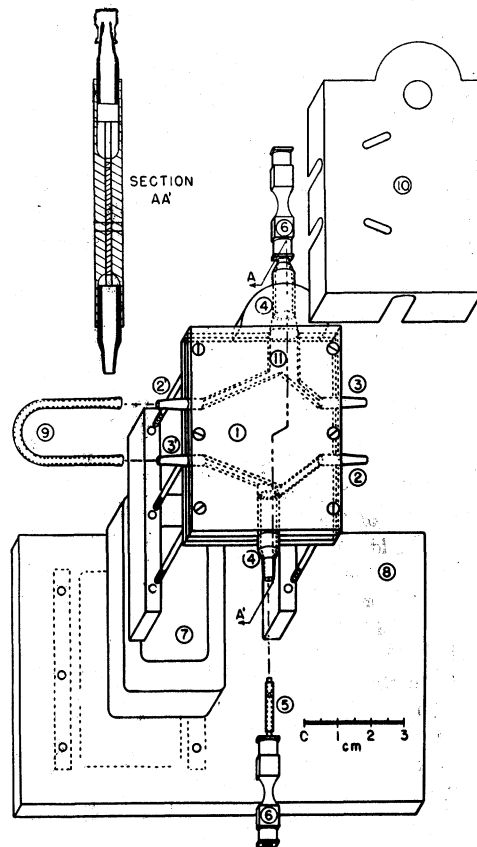


FIG. 1. Design of flow meter.

The numbers in the following description refer to the corresponding parts in the figure. The primary chamber (1) is laminated from 3 layers of lucite, the central layer being opaque and the 2 outer layers transparent. Fittings for the inflow (2) and outflow (3) tubes are turned from lucite and are cemented in place. Plastic male Luer connectors (4) are threaded into the block to provide the stability necessary for attachment of modified needles and syringes. Bubbles of desired size are injected through the lower connector via a Bunsen valve (5), with a drilled tuberculin syringe, as suggested by Bruner (1). The bubble trap (11) is emptied with any convenient-sized syringe through the upper Luer connector. Double female Luer connectors (6) are made from hypodermic needle hubs, and provide easy access to facilitate cleaning the system. The entire chamber is mounted directly in front of a General Electric, barrier-type photo emf cell (7), and the whole system mounted vertically as indicated on a suitable base (8). The two tubes (2', 3') are connected by a length of vinyl tubing (9) having an internal diameter of about 1.5 mm. The length of this tube may be varied to alter the range of the meter, while maintaining its inherent accuracy. In the model whose calibration curve