

THE EFFECT OF ULTRASONICS ON IMMISCIBLE LIQUID SYSTEMS

by

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SUMMARY

For many years there has been a growing interest in the phenomena associated with the application of high frequency sound energy to various systems. This paper is a study of ultrasonic emulsification and de-emulsification of a liquid-liquid system with possible future application to liquid-liquid extraction operation. Benzene and water were emulsified at a frequency of 250 kc and at various intensities. The emulsion properties were studied with a microscope and haemocytometer, and attempts were made to apply photometry as a method of concentration analysis. A photometer calibration curve was produced which was accurate to within  $\pm 25\%$  except at abnormal particle size distributions. This was sufficiently accurate for the purposes of this study. Irradiation of benzene-water emulsions was found to produce de-emulsification, and the rate of de-emulsification was found to increase with increasing intensity. The rate of particle formation in benzene-water emulsions was found to increase with increasing intensity of irradiation and with decreasing particle size. The rate of emulsification expressed as overall concentration was found to increase with increasing intensity of irradiation. Water was found to absorb ultrasonic energy approximately twice as readily as benzene, and a mixture of benzene and water was found to have the ability to absorb ultrasonic energy at a greater rate than either pure benzene or pure water. The equipment used was found to be approximately 4.6% efficient in the conversion of electrical energy to ultrasonic energy, and roughly 19.4% of the ultrasonic energy supplied to the oil bath and test tube was recovered as heat in the irradiated material in the test tube.

A photographic method of analysis is recommended for future study of emulsion characteristics, and a more exhaustive study of de-emulsification is also desirable. In order to correct some of the factors which cause

irreproducibility in the experimental data, the temperature of the irradiated material should be controlled. A suggestion for a more efficient crystal holder is presented in the form of a diagram.

## INTRODUCTION

The general field of ultrasonics has for many years been the subject of numerous investigations by scientists who have been primarily interested in the theoretical aspects of the phenomena produced by high frequency sound energy. In more recent years, however, there has been a growing interest on the part of engineers in the possible use of ultrasonic energy as an industrial tool. Attempts are being made to develop equipment and methods whereby this form of energy can be made applicable to chemical operations in order to enhance the quality, quantity, and rate of production of the desired product. The possible application of ultrasonic energy to liquid-liquid extraction operations was the motivating factor in undertaking the present study.

Perhaps it would be wise at this point to define the term "ultrasonic energy." Ultrasonic energy is sound energy generated at frequencies above the maximum audible frequency, which is about 20,000 cycles/sec. The word "supersonic," often misused in connection with high frequency sound, refers to the speed of an object relative to the speed of sound. Sound waves move at approximately 1,100 ft/sec in air at atmospheric pressure and normal temperatures. An object moving at a greater rate of speed than this is said to be moving at a supersonic velocity.

From an industrial point of view, perhaps one of the most important aspects of the use of ultrasonic energy is the effect of this type of energy upon immiscible liquid systems. Even in the absence of colloidal stabilizers, emulsions of great stability have been formed and broken in oil-water and mercury-water systems by the application of ultrasonic energy of high intensity. Visualize for a moment an oil-water countercurrent extraction operation which utilizes ultrasonic energy to alternately emulsify and de-emulsify the two phases. The advantage of such an operation over normal extraction operation



is apparent since through emulsification large amounts of interfacial surface are produced. Since the application of ultrasonic energy to extraction is a relatively new idea, quantitative information on emulsion characteristics, proper emulsification and de-emulsification conditions, and the overall efficiency and practicality of such an operation is badly needed and certainly must be obtained before the industrial possibilities of the idea can be fully realized. The purpose of this study is not to make a detailed quantitative investigation of the entire problem, but rather to secure information on some of the more fundamental problems faced in such an investigation and to form a sound basis for future, more exhaustive work.

Due to mounting interest in the phenomena associated with ultrasonic irradiation, some work on the fundamental aspects of the problem outlined has already been done, not to mention a large amount of experimentation not relating directly to the problem under consideration. One factor important in estimating operational efficiencies is the rate at which ultrasonic energy is absorbed and converted into waste heat in various liquid media. Alexander<sup>1</sup> states qualitatively that high frequency waves are more easily absorbed than low frequency waves and that at high frequencies energy losses due to absorption become excessive. Further information on absorption phenomena of a quantitative nature is available in the literature. Also of considerable value in ultrasonic research is the development of new equipment and methods. It is probable that it is in this phase of the work that the most rapid progress is being made. Alexander<sup>1</sup> reports a study of four different types of ultrasonic generators with the frequency ranges and the most efficient methods of application for each type. Carlin<sup>3</sup> also presents a fairly extensive discussion of ultrasonic generators complete with diagrams to aid in construction. Smith and Stumpf<sup>4</sup> investigated ultrasonic generators with emphasis on crystal per-

formance. They found that irradiation intensities vary directly as the acoustic resistance of the medium, the square of the applied voltage, and the operation frequency. The maximum voltage was found to be determined by the breakdown point of the crystal. The discovery was also made that vibration does not occur uniformly over the face of the crystal. A rather complete study of piezoelectric crystal performance and characteristics is presented by Mason.<sup>11</sup> Labaw<sup>9</sup> studied the focusing action of curved crystals, finding that a much greater intensity is obtainable close to a curved quartz crystal than from a flat crystal having the same area and thickness and drawing the same input power.

Some interesting aspects of the study of the phenomena associated with ultrasonic irradiation are the chemical and biological effects of this type of energy. Harvey<sup>8</sup> reports the ability of ultrasonics to flocculate coal particles while Mark<sup>12</sup> reports their ability to cause much deeper going changes in chemical systems. It seems that ultrasonics can affect not only intermolecular forces of the van der Waals type (1,000-10,000 cal/mol) but are even capable of disrupting strong chemical bonds (50,000-100,000 cal/mol). The viscosities of some high polymer solutions decrease upon ultrasonic irradiation but recover in time after irradiation is stopped, indicating disruption of van der Waals forces. However, at 300 kc and 10 watts per cm<sup>2</sup>, molecules having molecular weights around 100,000 can be chemically degraded so that the viscosity does not increase with time after irradiation is stopped. Mark<sup>12</sup> found that generally about 5 bonds in 1,000 were broken and that this degradation is due to friction set up between the fluid and the molecule. He also found that additional external pressure increased markedly the degrading influence of the ultrasonic field. Burger and Sollner<sup>2</sup> found that rod or plate-like particles (mica, gypsum, selenite, steatite, quartz, etc.) can be orientated with their longest axis normal to the flux of energy. Concentrated rheopectic suspensions

were solidified, and normally dilatant mixtures were found to lose this property when exposed to ultrasonic energy. (Dilatant suspensions are those in which the apparent viscosity of the suspension increases with increasing shear stress. Examples of dilatant suspensions are starch in water, mica in water, quicksand, and beach sand. Rheopectic suspensions are certain thixotropic suspensions which upon being systematically shaken or tapped will set (increase in apparent viscosity). Examples of rheopectic suspensions are gypsum in water, bentonite, and vanadium pentoxide sols.)

Relative to the present investigation, one of the more important phenomena associated with the application of ultrasonic energy to liquid systems is that of cavitation. Practically without exception the authors who have made studies of the effects of ultrasonic irradiation on immiscible liquid systems have reported cavitation as an important factor, if not the direct cause of ultrasonic emulsification. However, the only detailed study of cavitation found in the literature was made by Sollner and Bondy.<sup>16</sup> Cavitation, the formation and collapse of small cavities in liquids, can occur as soon as the hydrodynamical pressure in a liquid is reduced to the vapor pressure. It is not known as yet whether this condition can occur in an absolutely pure and gas-free liquid. Cavities have been observed to form in a streaming liquid. Water allowed to flow through a convergent-divergent tube turns opaque just after the narrowest constriction if the flow rate exceeds a certain minimum value, and the opacity continues for some distance downstream. At the same time, a loud hissing noise is heard which is caused by the collapse of these cavities as they pass into regions of higher pressure or lower temperature. From Bernoulli's equation

$$P + \frac{\rho v^2}{2g} = \text{const.}$$

where P = hydrodynamical pressure  
 $\rho$  = density  
 v = velocity

cavitation is seen to be possible, since the velocity may become high enough to reduce the hydrodynamical pressure to the vapor tension. Reynolds<sup>18</sup> developed an equation to calculate the pressure developed during the collapse of a cavity.

$$\frac{P_1^2}{2\theta} = \frac{P}{3} \left( \frac{R_0^3}{R^3} - 1 \right)$$

where P' = the pressure at infinity  
 (external atmospheric pressure)  
 $R_0$  = initial radius of the cavity  
 $\theta$  = coefficient of compressibility  
 P and R = correlated pressure and radius  
 of the cavity during collapse.

Pressures of thousands of atmospheres may be developed at the moment of the cavity's collapse, which is evidenced by the erosion effects on a ship's propeller blade (where cavitation occurs). When superheated steam is blown through a 1 mm i.d. nozzle into an oil-water interface, it condenses with the familiar rattling sound, forming a highly dispersed emulsion of the oil in water type. Emulsification ceases when the water becomes too warm to allow rapid steam condensation, which indicates that the collapse of cavities causes the emulsification. This conclusion is further substantiated by the fact that no emulsification occurs when air instead of steam is blown in at the interface. When air is added to the steam, reduced emulsification efficiency results, since air buffers the impact of the collapsing cavities. Very concentrated emulsions may be produced in this manner, using pure superheated steam and a sodium oleate solution. Sodium oleate is an emulsion stabilizer.

Kundt and Lehman<sup>17</sup> describe an interesting experiment which shows the effect of acoustic waves on liquids. A tube was filled with water which had not been de-gassed but from which even the smallest bubbles had been removed.

When the tube was exposed to ultrasonic irradiation, gas bubbles formed which continued to grow. The gas bubbles were reabsorbed if the vibrations were stopped for some time. If the water was carefully de-gassed, turbidity occurred close to the end of the tube during violent irradiation. This could only be caused by rupture of the water. The experiment, therefore, shows that acoustic waves may cause cavitation in de-gassed liquids and gas expulsion from gas-containing liquids. The following facts seem to show that cavitation may be caused by ultrasonics:

1. Liquids having a low boiling point may be made to distill at room temperature, i.e., the ultrasonic waves lower the boiling point by effectively reducing the pressure.
2. Ultrasonics evolve gas from gas-containing liquids.
3. Liquids stretched by Berthelot's method (sealed in a tube and cooled) disrupt at a higher temperature when exposed to ultrasonics.
4. Cavity formation is favored at liquid-liquid interfaces, and ultrasonics are very active at such interfaces.

Treating immiscible liquid systems with ultrasonic energy under various conditions has resulted in the following observations:

In a vacuum the irradiated liquids boiled, but did not emulsify. The cavities formed but did not collapse, which seems to indicate that the collapse of cavities is necessary in the emulsification of oil and water by ultrasonic energy. Neither would emulsification occur when the liquids were de-gassed, which seems to indicate that dissolved gas is an important factor in ultrasonic emulsification. Emulsification was found to be feeble at very low and very high external pressures and at higher temperatures. Since pressure and temperature variations were found to have such a significant effect upon cavitation, it is possible to conclude:

1. Dissolved gases favor oil-water emulsification since they form gas nuclei which favor cavity formation.

2. At higher concentrations, dissolved gases may be unfavorable to oil-water emulsification due to a buffering action on cavity collapse.
3. Normal external pressure favors oil-water emulsification since it is necessary for efficient cavity collapse.
4. Higher external pressure is unfavorable to oil-water emulsification, since it disturbs cavity formation.
5. Higher temperatures do not favor oil-water emulsification since they cause buffering of cavity collapse.

On the other hand, cavitation was found to have no effect on the formation of mercury-water emulsions ultrasonically. Emulsification was observed to take place in a vacuum and at high pressures and temperatures. It was also found that steam injected at a mercury-water interface had no emulsifying effects. A theory of mercury-water emulsification by ultrasonics has been proposed by Sollner and Bondy.<sup>16</sup> It holds that small water droplets are mechanically driven into the mercury layer where they combine. The thin mercury film around each droplet bursts upon droplet combination, forming small drops of a mercury in water emulsion in the mercury phase. These bubbles then rise to the surface where they burst, throwing a fine spray of mercury into the aqueous layer. In the absence of dissolved gases, the amount of mercury dispersed in the water is very small and soon settles out. When gases are present, concentrated and much more stable emulsions are readily obtained. This phenomenon occurs irrespective of the gas used; therefore, chemical action may be excluded as the stabilizing process. In the presence of colloidal stabilizing agents, dissolved gas is not essential in forming stable mercury-water emulsions. The protective action of gases is not yet satisfactorily explained.

Several investigators have mentioned the coagulative effect of ultrasonic energy on different types of emulsions, but again Sollner and Bondy<sup>15</sup> present the most complete discussion of the phenomenon. They term the mechanism of

coagulation by ultrasonic energy "radiation pressure." Radiation pressure is caused by the diffraction of sound energy by the individual particles. This drives them to and fro and increases the rate of spontaneous coagulation. The process is termed "orthokinetic coagulation." The particles were found to accumulate at the nodes or anti-nodes wherever stationary waves occurred. The rate of coagulation was found to depend on these zones of accumulation, since coagulation is accelerated by higher concentrations of sound energy. In water-mercury emulsions the locus of coagulation is readily separable from that of emulsification, since coagulation occurs in the interior of the aqueous layer while emulsification occurs at the bulk interface only. In water-oil systems, however, the loci of emulsification and coagulation are the same although zones of accumulation may still be observed.

Several ways have been found whereby emulsification may be suppressed so that coagulation may dominate. Emulsification requires an energy input exceeding a certain limit, and coagulation may dominate below this limit. Cavitation, and therefore emulsification, may be prevented by applying high external pressure or by raising the temperature. No study of the effect of frequency variation upon coagulation has been reported.

The rate of accumulation of particles at nodes or anti-nodes depends largely upon the particle size. It proceeds markedly and rapidly with particles having a diameter of about  $1\mu$ . Nodal accumulation is not observed with particles of truly colloidal size. In aqueous systems, the less dense particles are found to accumulate at the nodes, the more dense at the anti-nodes. In one experiment reported by Sollner and Bondy,<sup>15</sup> the lower end of a test tube 50 cm long and 1 cm wide was exposed to ultrasonic vibrations with a crystal current of 115 ma. When filled with a 4% toluene (in water) emulsion, more or less regular whitish zones appeared almost immediately in the lower and middle parts

of the tube. If the vibrations were stopped for a moment, large drops which formed from the accumulated drops rose toward the surface. During irradiation these drops were at first retained at the level of their formation, but shortly afterwards, upon growing large, they jumped from one zone to the next, thus gradually forming a coherent layer of toluene on top of the liquid. If the irradiation was continued for some minutes, the liquid in the lower and middle parts of the tube became transparent and relatively free of toluene. The top 10-15 cm never became clear. This range was smaller at lower energy inputs, but there was always an emulsion close to the interface. Substantially the same results were obtained with an organic liquid heavier than water. The phenomenon becomes more apparent in shorter, narrower columns where the effects of eddy currents are absent. At lower impressed crystal currents (40-50 ma.) the same results were obtained but the reaction occurred more slowly. At still lower energy inputs zones of accumulation and coagulation occurred in an ordinary test tube with no emulsification.

Considerable information of a qualitative nature and limited information of a quantitative nature have been furnished by investigators of emulsion formation. Alexander<sup>1</sup> reports that 50-60 grams of benzene can be emulsified per liter of water in two minutes, the concentration failing to increase upon further irradiation. Clayton,<sup>4</sup> working at 300 kc with oil-water systems, reports immediate emulsification with the emulsion proceeding from the walls of the containing vessel. With toluene-water systems he found a limiting concentration of 4.2-4.5% by volume, at which point emulsification and coagulation counterbalanced each other. It was found that this maximum concentration decreased with time of irradiation due to the suppression of emulsification by de-gassing effects and temperature rise. Daniewski<sup>6</sup> found that the rate of formation of water-kerosene emulsions with ultrasonics in the



frequency series 150, 395, 1160, 3000, and 9,000 kc increases at constant frequency as a linear function of the strength of vibration. At constant intensity, however, the rate of formation was found to decrease with increasing frequency, the maximum being at 150 kc. Marinescu<sup>10</sup> found that the particle size depends on amplitude and not frequency, and Mark<sup>12</sup> reports the degree of dispersion as mostly moderate with average particle diameters ranging from 1 to 20 $\mu$  and surface energies of the order of magnitude of 100 to 1,000 calories per mole of dispersed substance. Richards,<sup>13</sup> studying benzene and water systems at 300 kc found that the benzene layer was emulsified first. With low sound intensities and a water wetted test tube, the emulsion was found to come slowly off the walls into the benzene layer, while in a perfectly dry test tube no emulsification took place unless the intensity was sufficient to agitate the bulk interface considerably. When the vibrations of the glass container were damped out as much as possible, no emulsification took place even at the interface. Richards concluded that emulsification was principally due to transverse waves in the glass walls, the characteristics of which depend on frequency and wall thickness. Freundlich and Gillings<sup>7</sup> worked with toluene and water systems at three frequencies, and their principal findings are recorded in the following table:

<u>EFFECT SOUGHT</u>	<u>OBSERVATIONS AT.....</u>		
	<u>214 kc</u>	<u>4.8 kc</u>	<u>0.4 kc</u>
Degassing of liquids	Vigorous at low intensities	High intensity needed for complete removal	The effect proceeds slowly
Production of o/w emulsions	Produced by indirect irradiation at 1/40 maximum intensity	Can be produced at high intensity under proper conditions	No stable emulsion produced
	At both frequencies effect due to cavitation.		
Coagulation of disperse systems	Easily observed directly in liquid systems. Coagulation is a limiting factor in some dispersion systems.	Best observed in smokes	Not studied

Sollner and Bondy<sup>15</sup> found several factors which made reproducible quantitative data difficult to obtain in emulsion studies. The thickness of the walls of the containing vessel and the distance from the source of irradiation were found to be important factors. They found the particle size to depend on the mechanical vibrational energy input, but they were unable to find a direct relation between this quantity and the electrical energy supplied to the generator. The properties of the emulsions formed were found to vary with temperature, but during irradiation isothermal conditions were impossible to maintain due to the rapid rise in temperature of the irradiated material. In spite of these difficulties, however, they were able to obtain emulsions whose properties were reproducible to within  $\pm 20\%$ . Some semi-quantitative data was taken with 3 cc. of oil in 3 cc of 1N KCl to determine the effect of charge. The crystal current was 110 ma. and the concentration was estimated from opacity measurements which were found to be sufficiently accurate. The stability of the emulsion formed was moderate, the emulsion concentration being somewhat smaller after several hours. The droplets had

a tendency to settle out and the viscosity of the solution was found to play an important part in the settling-out process. The data for these runs are presented in Table I.

TABLE I

SUBSTANCE	DEGREE OF OPACITY	
	WATER PHASE	OIL PHASE
water-benzene	++++	+
water-toluene	++++	+
water-xylene	++++	+
water-cyclohexane	++++	+

Additional data were taken using 3 cc. of toluene and 3 cc. of distilled water in a glass test tube 1 mm. thick and 15 mm. i.d. The concentration of the emulsion was calculated from density using a pycnometer, and a fresh test tube was used in each run. The rate of emulsification was found to equal the rate of coagulation at emulsion concentrations of from 4.2% to 4.5%. With a crystal current of 80 ma., the maximum emulsion concentration was reached in 3 minutes and with a current of 115 ma., the maximum was reached in 30 seconds. The rate of formation was found to increase strongly with increasing energy input. The results of these runs are presented in Table II.

TABLE II

TIME...MIN.	DISPERSED PHASE...VOL. %		
	CRYSTAL CURRENT...MA.50	80	115
1/4	--	--	3.5
1/2	--	1.1	4.5
1	0.0	2.3	3.9
2	--	3.1	--
3	--	4.1	--
5	0.5	3.9	3.1
10	--	--	2.8
15	1.8	4.2	2.7
30	1.8	--	--

The degree of dispersion was determined in the following manner: A small amount of the emulsion was diluted with 5 to 10 times its volume of a

2% gelatine solution. A drop of this stabilized emulsion was dried at 50°C for 30 minutes on an object slide having a cavity. It was then photographed with a water immersion lens at 1,000 magnification; 300 drops were counted and measured. The authors state that the method is inaccurate due to a large variation in particle size, a significant error being caused by the occasional appearance of very large particles. Particle size data are presented in Table III.

TABLE III

TOLUENE-WATER

<u>CRYSTAL CURRENT-MA</u>	<u>TIME-Min.</u>	<u>WEIGHT PERCENT OF DISPERSE PHASE</u>					
		<u>0-2u</u>	<u>2-4u</u>	<u>4-6u</u>	<u>6-8u</u>	<u>8-10u</u>	<u>10-12u</u>
50	3	2.3	28	36	34	0	0
50	15	2.3	28	47	23	0	0
800	1/2	5.5	30	21	20	24	0
80	3	1.5	25	29	20	25	0
115	1/4	2.3	29	28	33	7.7	0
115	3	2.8	24	25	22	26	0

From their data Sollner and Bondy concluded that short irradiation periods and small energy inputs favor highly dispersed emulsions of low concentrations, and that long irradiation periods and high energy inputs favor large particle sizes. The addition of a stabilizing colloid tends to produce a higher degree of dispersion and more rapid dispersion. The indication is, however, that the addition of a stabilizer does not keep the emulsion from being coagulated by the ultrasonic beam.

### SCOPE OF STUDY

In order to form a sound basis for future work in ultrasonic emulsification and de-emulsification, several aspects of the general problem will undergo investigation in the present study. As will be recalled, Sollner and Bondy<sup>15</sup> determined emulsion concentration from density measurements with a pycnometer, and estimated concentration from opacity measurements, but the balance of the literature failed to reveal a more satisfactory method of determining small emulsion concentrations. As a result, part of the present study will be devoted to finding a convenient method for determining emulsion concentrations. Since photometry has been found to be highly satisfactory as a method of chemical analysis, an attempt will be made to apply it to emulsion concentration determination. If applicable to emulsions with wide variations in particle sizes, it is a method of analysis that can be used with simplicity and rapidity.

The meager quantitative data presented in the literature covering the effects of time and intensity of irradiation upon particle size and distribution prompted further investigation of the matter in this study. Information of this type merits consideration since it indicates the conditions under which various emulsion characteristics dominate. A microscopic method of analysis will be used which is more rapid and which in all probability will give much more consistent results than the method of analysis used by Sollner and Bondy, who spent considerable time preparing a very small sample of emulsion for microscopic analysis, providing an excellent opportunity for the emulsion characteristics to vary. By the method to be employed, about 3,000 droplets can be counted and classified according to size, whereas only about 300 were counted by Sollner and Bondy. The proposed procedure not only lessens the probability of error due to very large particles, but eliminates the discrepancies

which doubtless occur in the dilution and drying operation employed in the previous study.

An excellent qualitative approach to emulsion destruction has been made in the literature, but quantitative data in this field are as yet still lacking. This study will, therefore, attempt to throw some light on the efficiency of ultrasonic irradiation at various intensities as a de-emulsifier. Studies will be made of normal settling to be compared with the settling results of irradiated material to determine the effect of continued irradiation upon oil-in-water emulsions.

From a chemical engineering standpoint, efficiency of operation is always an important consideration. It is not known as yet whether an ultrasonically controlled counter-current liquid-liquid contact operation would be industrially feasible. If it can be shown that emulsions can be efficiently formed and broken by ultrasonic energy, the result will be of potential industrial value. It is hoped that the present study will indicate to a certain extent the practicality of such an operation, and perhaps suggest methods by which a truly efficient operation can be devised.

STRATHMORE PARCHMENT

100% RAS U.S.A.

### EQUIPMENT

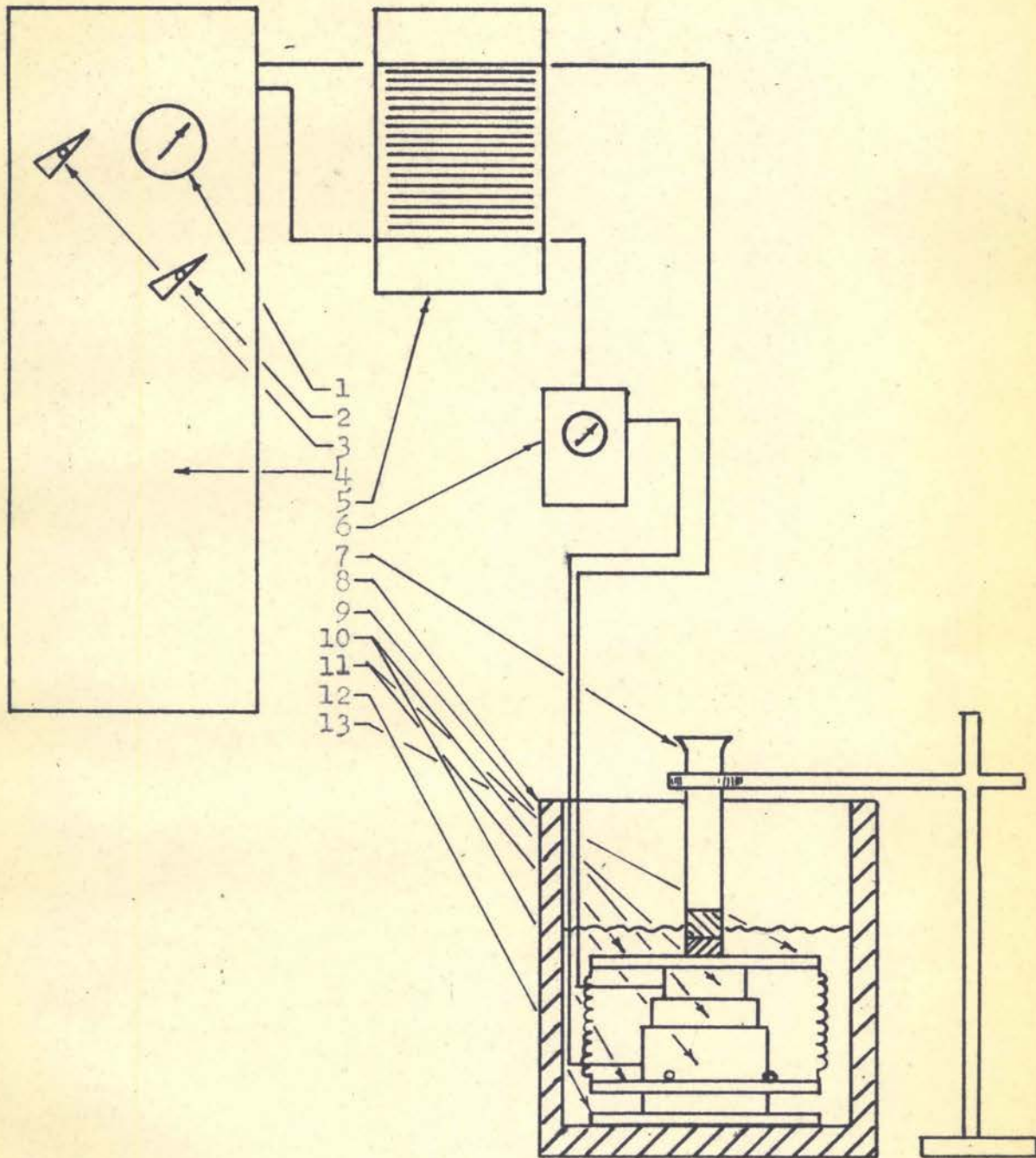
The ultrasonic generator used in this study was designed and built from war surplus equipment by the staff of the Research and Development Laboratory of Oklahoma A & M College under the supervision of Professor J. R. Norton. Generally speaking, the 3 main parts of the generator were the power supply, the oscillator, and the power amplifier. The power supply contained two No. 304 TL tubes and was capable of producing 3,000 watts in one tube and 1,000 watts in the other. A Hartley oscillator was used in the generator with a No. 811 tube, and the power amplifier contained two No. 304 TL tubes, one being employed to neutralize the other. In addition to the tubes, the primary features of the power amplifier were a tank coil and a condenser used to resonate the circuit at the oscillator frequency which was 250 kc.

The apparatus was arranged as shown schematically in Figure 1 with the operating conditions manually controlled by dials numbered 2 and 3. Dial No. 2 regulated the flow of energy from the power supply to the power amplifier, and dial No. 3 rotated the condenser which resonated the circuit. Meter No. 1 of Figure No. 1 registered the plate current as D.C. milliamperes while meter No. 6 indicated the actual current supplied to the crystal holder as AC milliamperes.

The test tube, number 8 of Figure 1, was a standard 1 inch round bottomed tube made of pyrex glass. The thickness of the test tube wall was approximately  $3/64$  inch.

The crystal and crystal holder are drawn approximately to scale in Figure 2. The crystal holder was of the resonant cavity type designed so that the resonant cavity may be adjusted to the specific crystal in use. However, it was found that the depth of the resonant cavity did not significantly affect the height of the column of oil created above the crystal during irradiation.

FIGURE 1  
DIAGRAM OF APPARATUS





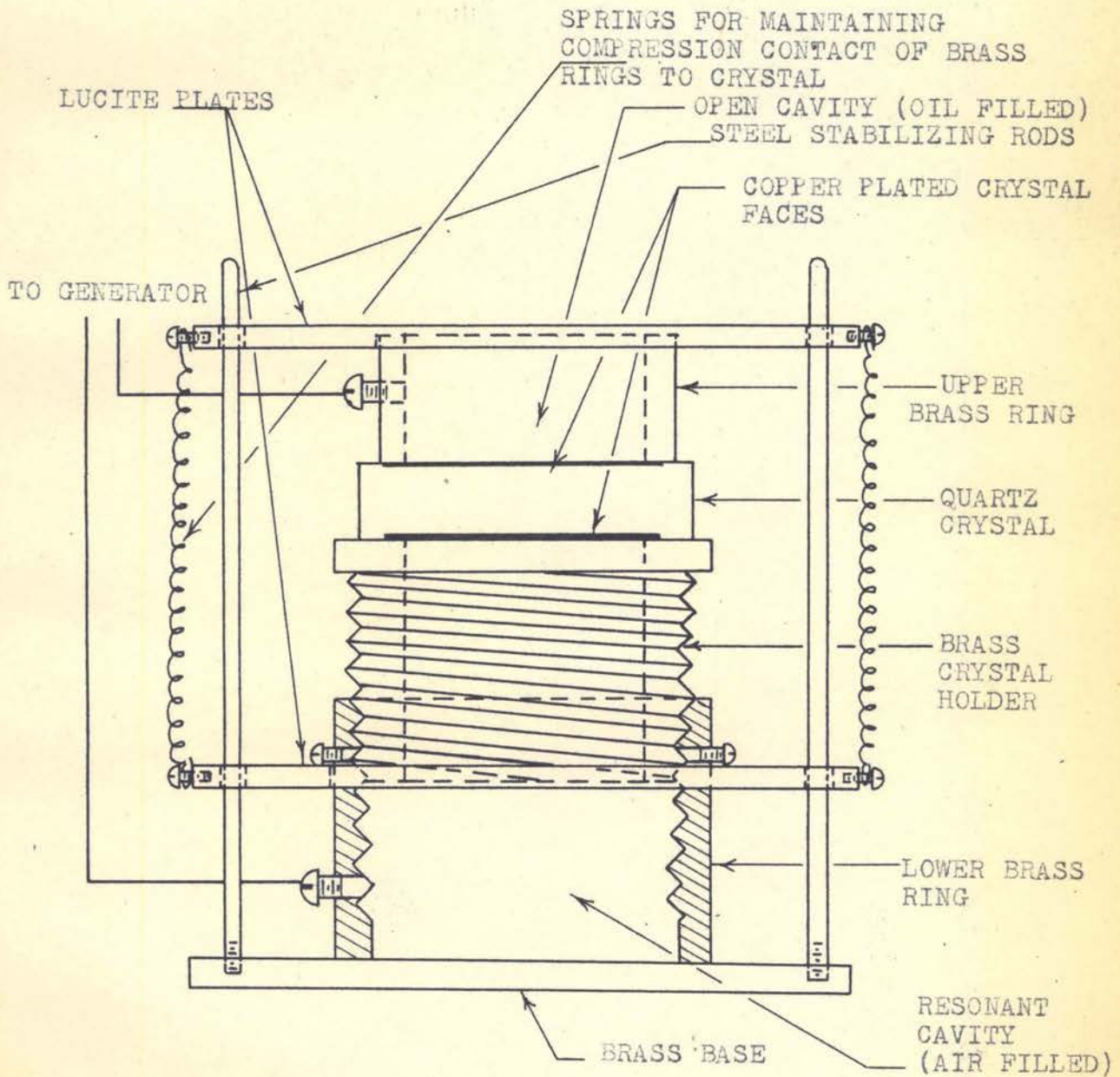
KEY TO FIGURE 1

1. PLATE CURRENT METER (DC MILLIAMPERES).
2. DIAL TO REGULATE THE ENERGY SUPPLY TO THE POWER AMPLIFIER.
3. DIAL TO RESONATE THE CIRCUIT.
4. GENERATOR CONTAINING POWER SUPPLY, POWER AMPLIFIER, AND OSCILLATOR.
5. LARGE TANK COIL.
6. CRYSTAL CURRENT METER.
7. TEST TUBE CONTAINING IRRADIATED MATERIAL.
8. CROCK CONTAINING OIL BATH.
9. QUARTZ CRYSTAL.
10. LUCITE PLATES.
11. UPPER AND LOWER BRASS RINGS.
12. BRASS BASE OF CRYSTAL HOLDER.
13. TRANSFORMER OIL BATH.

FIGURE 2

DIAGRAM OF CRYSTAL HOLDER

DRAWN APPROXIMATELY TO SCALE



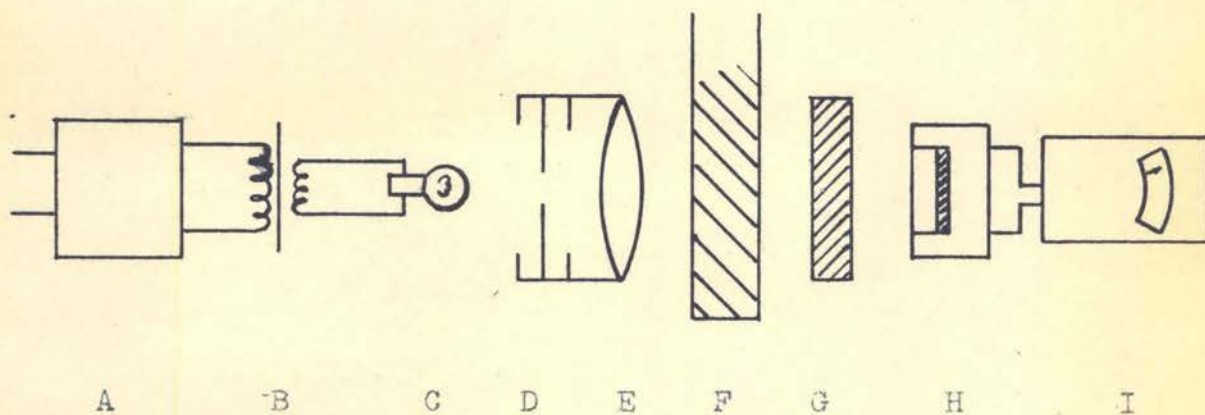
An X cut quartz crystal was used in this study. It was placed in the crystal holder as shown in Figure 2. The diameter of the crystal was 2 inches, its thickness 7/16 inch. Each side of the crystal had a thin layer of copper plated on for better contact with the crystal holder. The diameter of the copper plates was 1-5/8 inches.

The microscope used contained a small scale built into the eyepiece with which observed objects could be measured. This scale was calibrated at a magnification of 440 with a stage micrometer. It was found that at this magnification each scale division was equal to 3.3 microns.

The Cenco Sheard Sanford Photometer is shown schematically in Figure 3, where the component parts are briefly explained. It is a product of the Central Scientific Company. The principal of photometry is the Bouguer-Beer Law, which may be expressed as  $I = I_0 10^{-\epsilon cl}$  where  $I_0$  is the intensity of the incident light,  $\epsilon$  the molecular extinction coefficient, and  $I$  the intensity of light transmitted through a solution of concentration  $c$  and thickness  $l$ .<sup>5</sup> This law applies strictly only for monochromatic radiation, and also if the substance does not undergo molecular change as a result of absorbing such radiation. It has been found, however, that the above relationship still holds sufficiently well to permit chemical analysis with high sensitivity and accuracy even when a rather wide spectral band, selected by means of a light filter, (G of Figure 3) is used.

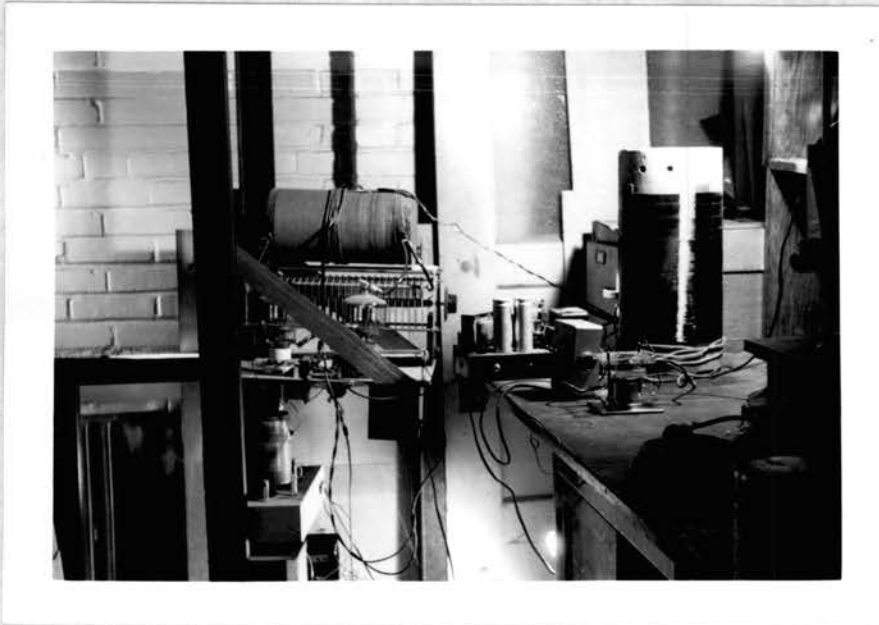
Since equipment limitations prevented the production of emulsions in large quantities, the standard absorption cells furnished with the photometer were not usable and others had to be devised. The two types of absorption cells used are pictured in Figure 5 along with the cell holders which were necessary to adapt the cells to the photometer. Cell type 1 was made by cementing to a small U-shaped piece of brass, cut from a length of brass

FIGURE 3  
SCHEMATIC DIAGRAM OF PHOTELCOMETER



- A- Constant voltage transformer
- B- Step down transformer
- C- Light source
- D- Iris Diaphragm
- E- Lens
- F- Absorption cell
- G- Light filter
- H- Photoelectric cell
- I- Micro-ammeter

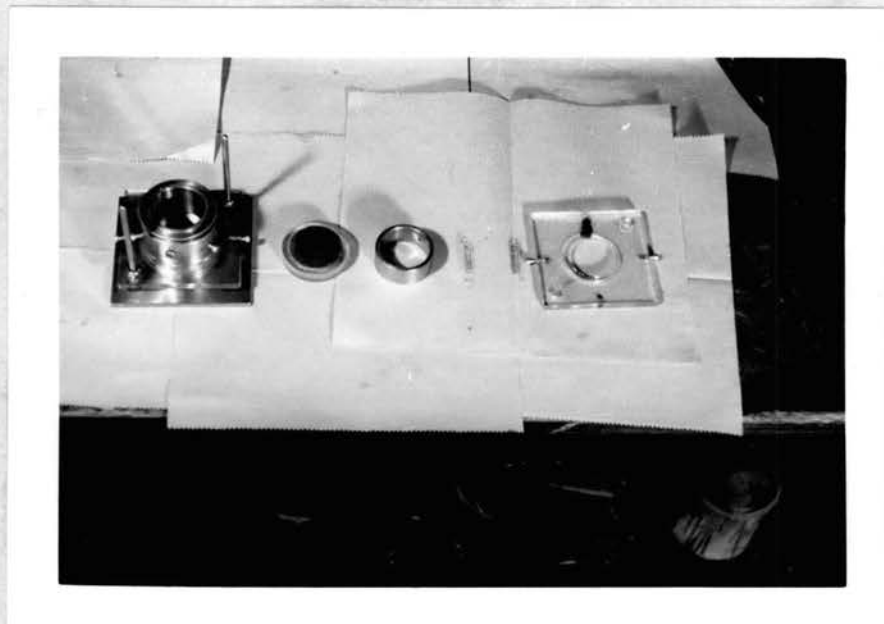
FIGURE 4



COMPLETE SETUP MINUS OIL BATH

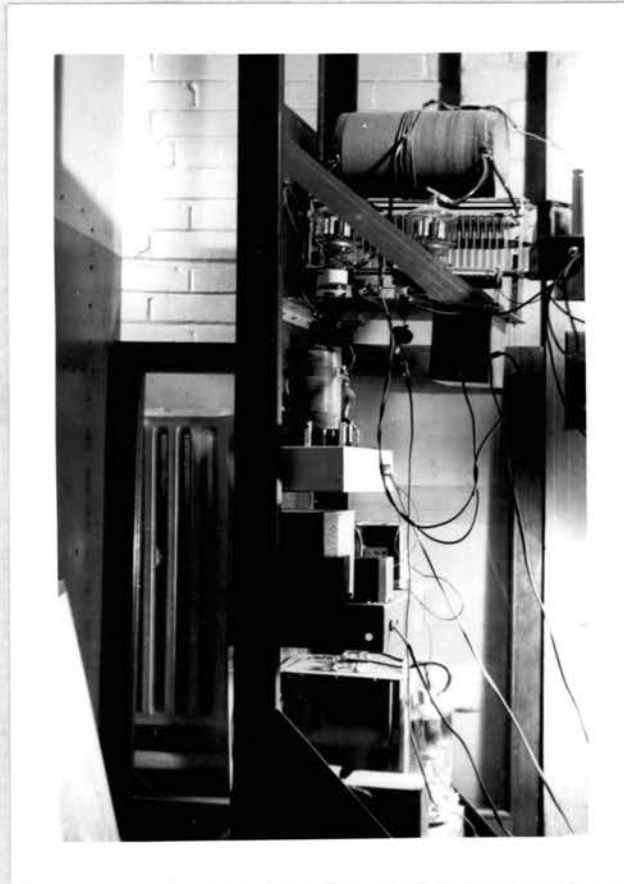
FIGURE 5

CRYSTAL HOLDERS, PHOTELOMETER, CELLS, AND CELL HOLDERS

FIGURE 6

COMPONENT PARTS OF CRYSTAL HOLDER

FIGURE 7



GENERATOR, POWER AMPLIFIER, OSCILLATOR, AND POWER SUPPLY

strip 0.15 cm. thick, two pieces of glass plate ground to shape. DeKhotinsky cement was used. The completed cell has a width of 1.3 cm., is 5.3 cm. high, and has a total thickness of 0.6 cm. When filled with emulsion, the absorbing thickness is the thickness of the brass strip or 0.15 cm. Cell type 2 is simply a small vial 1.2 cm. in diameter and 3.6 cm. high. The cell holders were made of lucite blocks, cut to fit the sliding cell holder of the photometer. The lucite blocks were cut so that the absorption cells might be inserted in them, and so that light passing through the cells encountered no lucite. The side of the lucite block which faced the photometer light source was painted black which permitted light to pass through the absorption cell only.

#### LEVY-HAUSSER COUNTING CHAMBER

Pictured in Figure 10 is the Levy-Hausser counting chamber which was used for emulsion analysis in the present study. The manufacturer is Arthur H. Thomas, Philadelphia. The important parts of the counting chamber are as follows:

- D--Matte pre-focusing surfaces
- E--Focusing lines leading to ruled surfaces
- I--Chamber charging inclines
- A--Ruled Area
- B--Cover Slip

The chamber is charged by placing a drop of the emulsion at I and allowing it to be drawn into the ruled chamber by capillary action. The ruling is the improved Neubauer Ruling which consists of nine square millimeters, each divided into 16 squares with the central square millimeter divided into 400 small squares each with an area of  $1/400$ th of a square millimeter. The chamber depth is 0.1 mm. The number of particles counted is converted to a volume basis by the following relation:



LEVY-HAUSSEK COUNTING CHAMBER

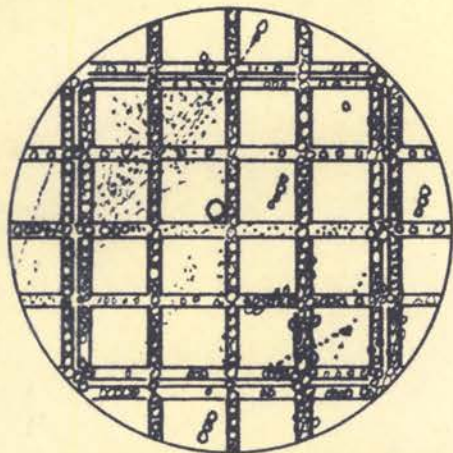


FIGURE 8

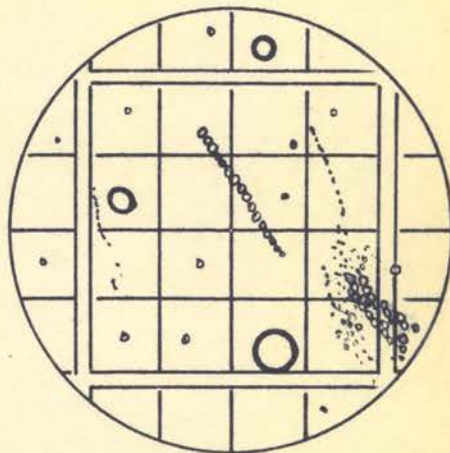


FIGURE 9

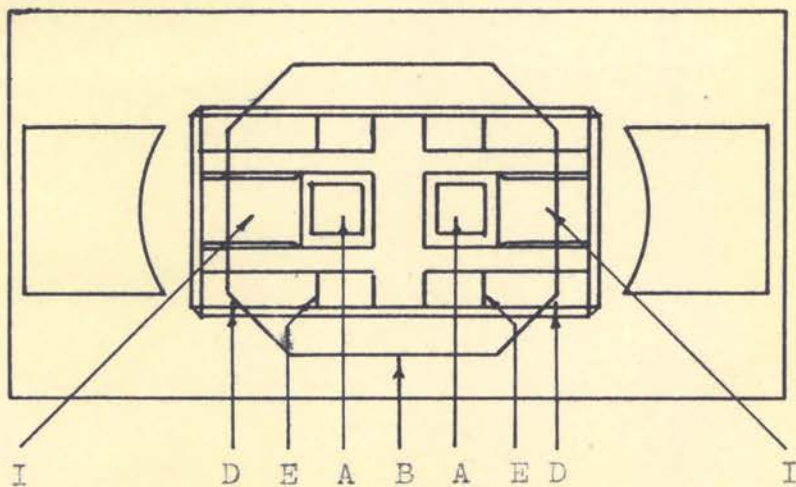


FIGURE 10

$$\frac{\text{No. of Particles} \times 4000}{\text{No. of smallest squares counted}} = \text{particles/mm}^3$$

Figures 8 and 9 are sketches of the appearance of an emulsion in the chamber through the microscope. An image such as Figure 8 is seen when the microscope is focused on the bottom of the chamber while Figure 9 shows how the top of the same section of the chamber would appear.

PROCEDURE

A series of runs was made in order to determine if a relationship exists between emulsion concentration and the quantity of light transmitted through a photometer cell filled with emulsion. Both types of photometer cells were used. The general procedure for taking data with each type was the same. Two nearly identical cells of each type were found to be necessary. Before each series of runs, the two cells of each type were both filled with tap water and checked against each other in the photometer to be sure that the zero concentration reading for both was the same. One cell was left filled with tap water in order that the zero concentration reading on the photometer could be checked from time to time. The other cell contained the emulsion to be measured. The procedure was as follows:

1. The blood counting chamber, the test tube, and the photometer cells were cleaned and dried.
2. Into the test tube were introduced, from a 10 ml graduated cylinder, 7 cc. of  $H_2O$  and 5 cc. of benzene.
3. The generator was checked, tuned in, and adjusted to the desired output intensity.
4. The test tube was placed in the oil bath and irradiated for the desired length of time.
5. The test tube was removed from the bath and allowed to stand for a specified setting time if this was desired.
6. A sample of emulsion was drawn from the water layer with a medicine dropper. Contamination of the sample by the benzene layer was avoided by bubbling air out of the end of the medicine dropper as it was lowered through the benzene into the water layer. A drop was placed in the blood counting chamber and the remainder was placed in the photometer cell.

7. The photelometer was re-checked with the cell containing tap water, following which the concentration reading was taken on the emulsion sample.

8. The blood counting chamber was then observed with a microscope at a magnification of 440. What was considered to be an adequate number of squares was observed, and the particles were counted and classified according to size.

Some of the photelometer calibration data were used for plotting particle size and distribution versus time and intensity of irradiation. Additional data to determine these factors were taken, using the same procedure but with the observation of a larger number of particles to minimize the errors involved.

The procedure for taking normal settling data was as follows:

1. The photelometer cell and test tube were cleaned and dried.
2. Into the test tube were introduced, from a 10 ml graduated cylinder, 7 cc. of  $H_2O$  and 5 cc. of benzene.
3. The test tube was irradiated at a specified intensity for a specified length of time.
4. The test tube was removed from the oil bath and a sample of emulsion drawn from the water layer for photelometer analysis.
5. The photelometer cell was cleaned and dried.
6. After the emulsion had been allowed to stand for 8 to 10 minutes, it was then gently swirled to provide uniform particle distribution, and another sample drawn for photelometer analysis.
7. Steps 5 and 6 were repeated for various settling times.

The counting and classifying procedure was as follows:

1. The microscope was focused on the lower surface of the counting chamber.
2. For the desired number of squares the particles were counted in each

size range beginning with the largest size range visible. For convenience, a hand counter was employed. When all the visible particles in a particular size were counted, the counter was reset and the next size range was counted.

3. The microscope was focused on the top of the counting chamber.
4. Step 2 was repeated.

The effect of ultrasonic irradiation upon the rate of settling was determined in the following manner:

1. The photometer cell and test tube were cleaned and dried.
2. Into the test tube were introduced, from a 10 ml graduated cylinder, 7 cc. of  $H_2O$  and 5 cc. of benzene.
3. The test tube was irradiated at a specified intensity for a specified length of time.
4. The test tube was removed from the oil bath and a sample of emulsion drawn from the water layer for photometer analysis.
5. The entire benzene layer was removed from the test tube.
6. The photometer cell was cleaned and dried.
7. After standing for 7 to 8 minutes, the emulsion was irradiated for two minutes, and a sample was immediately taken for photometer analysis.
8. Steps 6 and 7 were repeated several times.

When investigating the efficiency of the equipment used in the present study, three series of runs were made, one with 12 cc.  $H_2O$ , and a second with 12 cc. benzene, and the third with 5 cc. benzene and 7 cc.  $H_2O$ . The procedure was as follows:

1. The electric stirrer was turned on to keep the oil bath uniform in temperature, and room temperature was recorded.
  2. The generator was checked, tuned, and adjusted to the proper intensity.
- The test tube containing the liquid or liquids to be irradiated was placed in

the oil bath and allowed to come to temperature equilibrium.

3. The temperature of the oil bath and liquid in the test tube were measured and recorded.

4. The thermometers were removed, the generator was turned on, and the time and intensity of irradiation were recorded.

5. The test tube thermometer was pre-heated to the expected temperature of the sample in the test tube.

6. After irradiation, the thermometers were replaced and the temperature of the test tube was measured after 30 seconds and after 1 minute to determine the final temperature and the rate of temperature drop off.

7. The temperature of the oil bath was measured after it had become constant.

The incremental power input to the Power Amplifier under load was determined in the following manner:

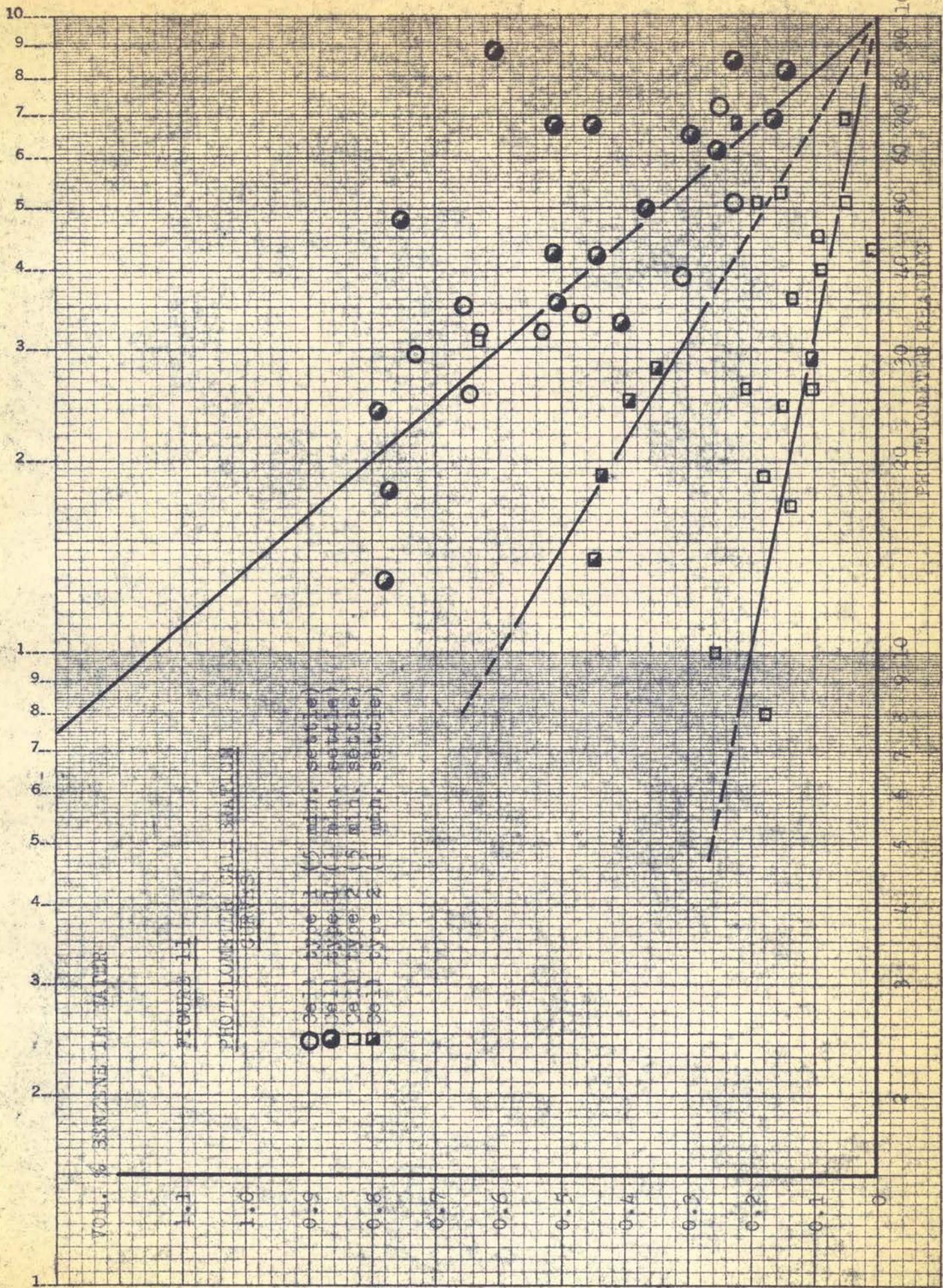
1. The crystal was disconnected and the no load plate current was recorded from the d.c. milliammeter.

2. The crystal was reconnected and the plate current was again recorded from the d.c. milliammeter.

3. Steps 1 and 2 were carried out at 3 different crystal current levels.

DISCUSSION OF RESULTS

Due to the fact that it will possibly be very useful in future studies of ultrasonic emulsification and de-emulsification, photelometry is one of the more important aspects of the present study. But for the fact that the particles which comprise the usual emulsion have such diverse particle sizes, photelometry would easily provide an accurate method of emulsion concentration determination. The results of this investigation as presented in Table IV and Figures 11 and 11-A show that in spite of the particle size distribution effects, photelometry can be applied with reasonable accuracy to the determination of emulsion concentrations. There are, however, certain limitations in its application which must be kept in mind. The curves of Figures 11 and 11-A represent experimental runs made using two types of photelometer cells, the principal difference between them being their thickness. The two lower curves are the results of determinations on the thicker of the two cells. In order to determine the effect of particle size distribution upon photelometry, two general methods of changing this property were used. One method is based upon a statement made by Sollner and Bondy<sup>15</sup> that particle size distribution will vary with the intensity of irradiation, the other method being based on physical considerations which indicate that large particles will settle out more rapidly than small ones. Emulsions were, therefore, produced at varying intensities, and some were allowed to settle a period of time after irradiation before being subjected to photelometer and microscopic analysis. As seen from Figure 11, allowing the emulsions to settle before analysis does not have a radical effect upon analysis with the thinner of the two cells or cell type 1. There is a scattering of points, but most of them fall well within an error of  $\pm 25\%$ . However, the effect of a settling period is seen to be quite pronounced when using the thicker of the two cells or



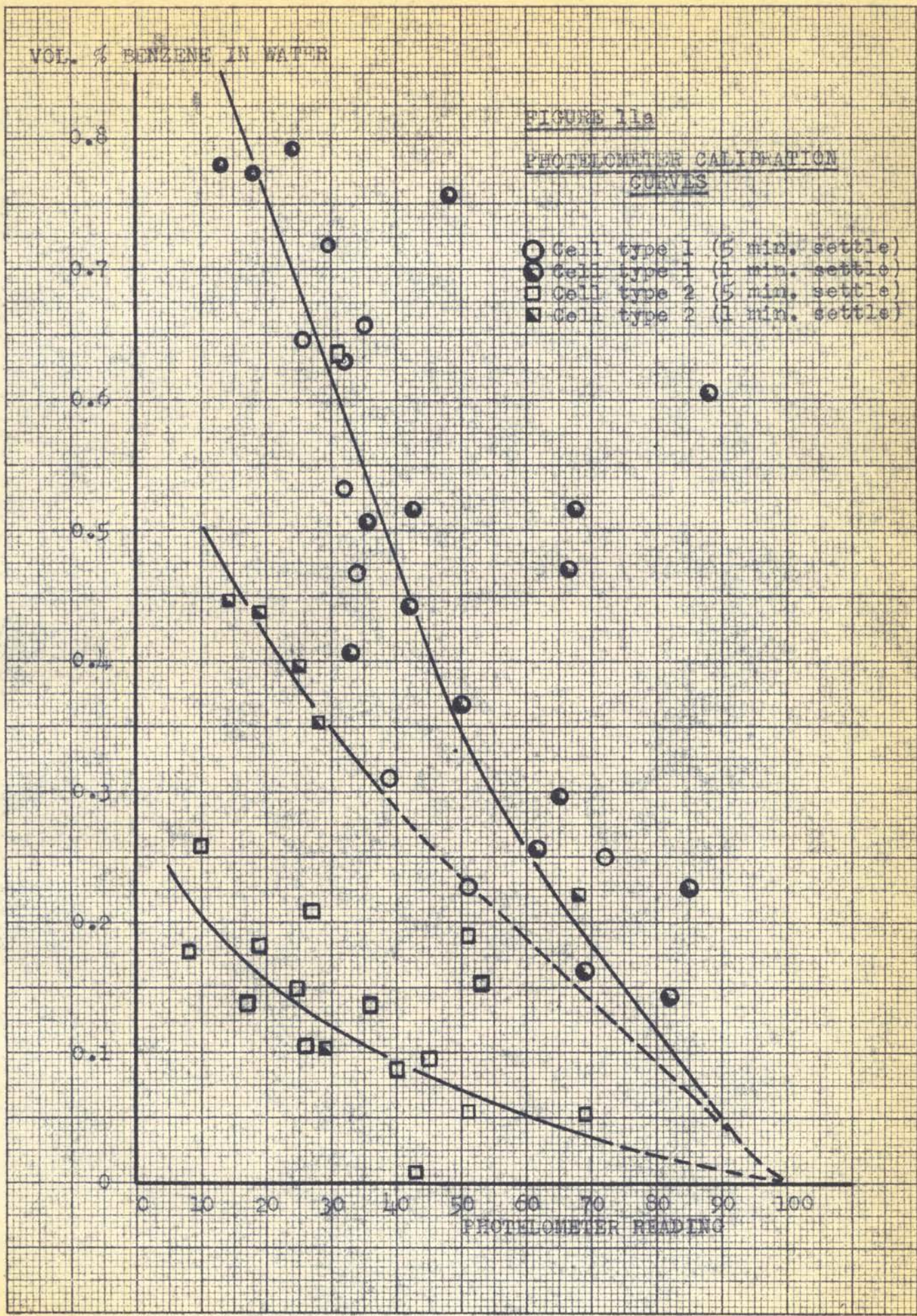


VOL. % BENZENE IN WATER

FIGURE 11a

PHOTOLUMETER CALIBRATION  
CURVES

- Cell type 1 (5 min. settle)
- Cell type 1 (1 min. settle)
- Cell type 2 (5 min. settle)
- Cell type 2 (1 min. settle)



cell type 2. Although at a constant settling time, the results are generally more consistent for cell type 2 than for cell type 1, it is seen that for the same quantity of light transmitted two emulsions may differ in concentration by as much as 100% if they are allowed to settle for different lengths of time. Though there is some indication, the data fail to show conclusively that such a large difference in concentration is due to the settling of large droplets. Part of the discrepancy may possibly be due to the precipitation of benzene during the settling process. During irradiation, the temperature of the emulsified material rises considerably, causing the solubility of benzene in water to increase. The cooling which takes place during the five-minute settling period could conceivably cause the benzene to precipitate in the form of droplets too fine to be detected in the microscopic analytical procedure, but nevertheless effective in reducing the amount of light transmitted by the emulsion. The possible occurrence of such a phenomenon may be responsible for the irregular data taken in runs 44 and 45 and listed in Table XI. In these runs, made under normal settling conditions, the number of particles in each particle size range is seen to decrease consistently with settling time, except those in the smallest size range. The number of particles in the 0-3 $\mu$  diameter range is observed to increase for nearly an hour in run 44 and to increase markedly during the first few minutes in run 45. The particles observed in this size range were all much smaller than those that normally appear in this size range and could easily have been precipitated benzene. If, then, the precipitation of benzene does occur, additional inaccuracies enter into the normal settling results of Figure 12, since the actual settling rate would be higher than that indicated by the photometer readings.

Water-in-benzene emulsions were not studied because they were found very unstable relative to benzene-in-water emulsions. Preliminary investigations

indicated that the concentrations of water-in-benzene emulsions were very sensitive to the temperature rise of the benzene during emulsification, and that agitation is very effective as a means of de-emulsification in this case. Normal settling is very rapid. Since the method of analysis used is relatively slow, the resulting low degree of accuracy did not make such a study of water-in-benzene emulsions advisable.

Several attempts were made to analyze the more concentrated emulsions by diluting them before subjecting them to microscopic and photometer analysis. Attempts were made to dilute the emulsions with plain tap water, tap water saturated with benzene, and irradiated tap water, none of which were successful. Runs AYC-12 and \*AYC-12 record a typical attempt to dilute an emulsion before analysis.

A sample of emulsion was diluted to twice its original volume with saturated tap water and the results of the microscopic and photometer analyses are presented in Table V (Run AYC-12). The results of a microscopic analysis of the undiluted emulsion are presented in Table V (Run \*AYC-12). The concentration of the diluted emulsion should be half that of the undiluted emulsion, but this is definitely not the case. The concentrations of the two samples, as calculated from the microscopic analysis of each sample, differ by a factor of 10, indicating that significant changes in emulsion characteristics occur during dilution. If the dilution does cause such radical changes in emulsion properties, doubts arise concerning the accuracy of the method of analysis used by Sollner and Bondy,<sup>15</sup> who employed a dilution operation.

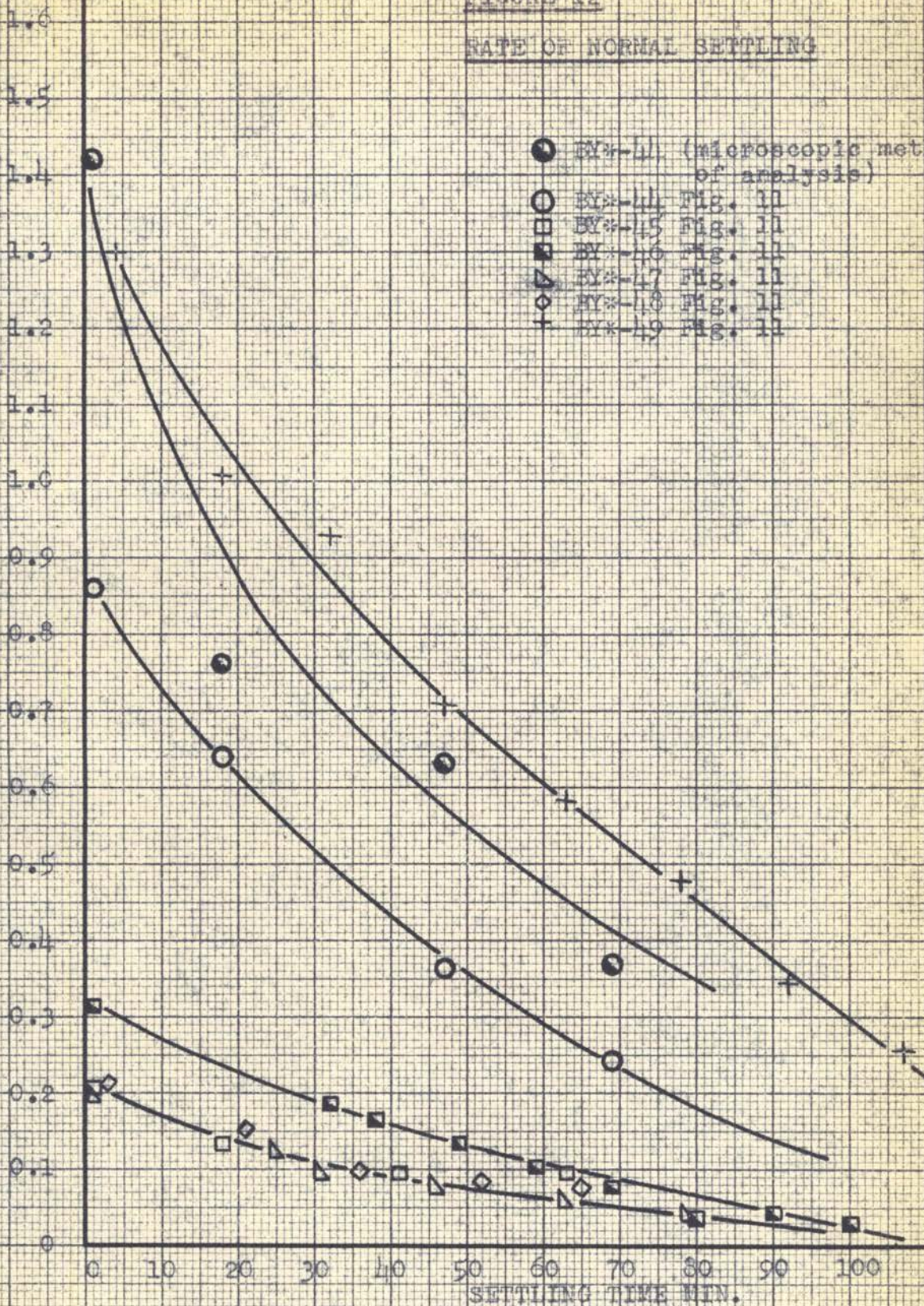
A variation in the intensity of irradiation is also seen to have an effect on concentration determinations with both cell types. Six runs (64-69) were made at high intensity to determine the effect on analysis with cell type 1 and three runs were made at low intensity (36-38) to discover any effect on

VOL. % BENZENE

FIGURE 12

RATE OF NORMAL SETTLING

- EX-11 (microscopic method of analysis)
- EX-11 Fig. 11
- EX-15 Fig. 11
- EX-16 Fig. 11
- △ EX-17 Fig. 11
- ◇ EX-18 Fig. 11
- + EX-19 Fig. 11



determinations using cell type 2. Of runs 64 through 69, only runs 64 and 65 are in disagreement with the calibration curve by more than  $\pm 25\%$ . The great discrepancy between run 64 and the calibration curve is shown by the experimental data to be caused by the presence of very large particles having diameters as large as 82.5 microns. The data do not give a plausible explanation for the large error in run 65.

Experimental runs 36, 37, and 38 gave points falling well above the 5 minute settle curve for cell type 2. The data show that the emulsions produced in these three runs contained a high percentage of large particles, indicating that particle size distribution has a pronounced effect upon concentration determinations using cell type 2. It may be concluded, then, that the use of cell type 1 gives fairly reliable results when small quantities of large particles are present. That this is not true for large amounts of large particles is substantiated by run 44, in which the benzene-water mixture was violently agitated before emulsification, causing large particles to be present in great quantities after emulsification. The comparison between the concentration determined by actual count and the concentration determined from the photometer reading and the calibration curve may be seen in Figure 12. The concentration from actual count is seen to be substantially higher than that from the calibration curve, especially at the lower settling times, indicating that large amounts of large particles cause inaccuracies in analysis with cell type 1.

As noted previously, a rather laborious microscopic procedure was used to determine emulsion concentration to be checked against the photometer. The emulsions were placed in a blood counting chamber and, at a magnification of 440, the particles were counted and classified according to size. Such an operation involves errors which can significantly affect the results. Certainly

the movement of the small particles due to convection currents would make it difficult not only to classify, but to get an accurate count, especially in emulsions of high concentration. Counting and classifying a representative number of droplets is necessarily time-consuming and during this time interval changes take place in the emulsion. Droplets of benzene were observed to shrink as much as 4 or 5 microns over a 10 minute period. This was probably due to an increase in temperature from the heat of the microscope illuminating lamp. These conditions made rapid counting and classifying essential to good results with this method of analysis. Since such rapidity of analysis on the part of the investigator is practically impossible, it is recommended that in future investigations of this type, a method of photographic analysis be used whereby the freshly prepared emulsion is permanently recorded as it appears in the blood counting chamber through the microscope, and the particles counted and classified at leisure. In this manner, not only could the particles be counted and classified according to size much more accurately but much larger quantities of particles could be quickly photographed before their condition changed. Certain errors in sampling the emulsion and taking the photometer reading add to the inaccuracy of the analysis. It was never quite certain, for example, that the drop of emulsion placed in the blood counting chamber was a representative sample, and that the particle size distribution was not altered as the drop was drawn by capillary action into the ruled section of the chamber. The uncertainty of a representative sample is due largely to the tendency of the particles to accumulate at the nodes or antinodes wherever stationary waves occur in the test tube. The sampling was done with a medicine dropper and even though the test tube was swirled gently before the sampling, the uncertainty remains. Momentary fluctuations of the line current were also observed to produce fluctuations of the light intensity of the light source

in the photometer. This occurred in spite of the fact that a constant voltage transformer was used. The danger of this condition affecting the results was minimized by standardizing the photometer with a cell filled with tap water immediately before the light transmitted by an emulsion was measured.

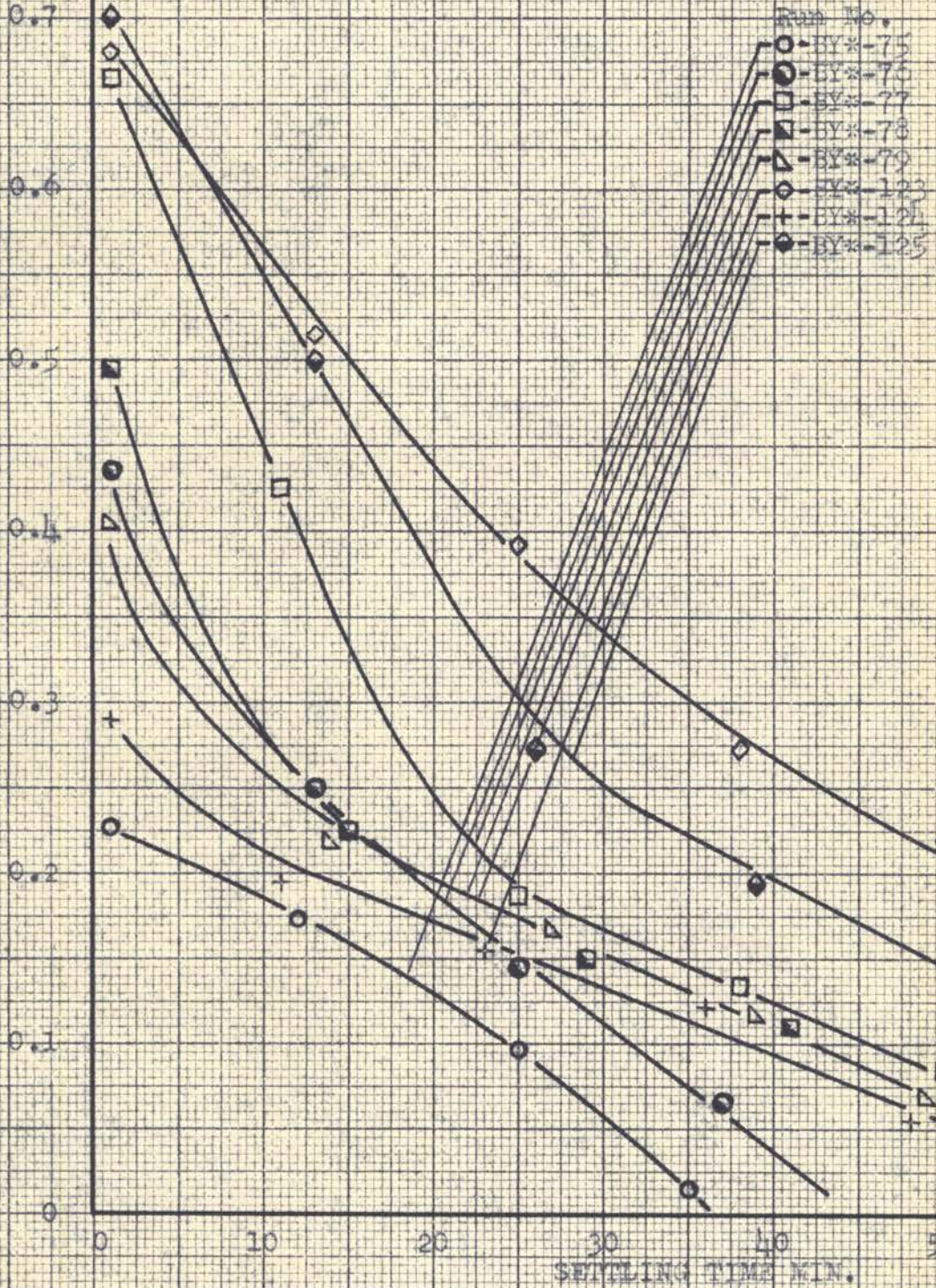
A series of runs was made to determine the rate of normal settling and the rate of de-emulsification, the results of which appear in Tables IX and X, and which are plotted in Figures 12 and 13, respectively. The rate of normal settling curves show two significant settling characteristics, initial high settling rate, and an increasing settling rate with increasing concentration. The per cent of benzene in all cases was determined from the cell type 1 calibration curve of Figure 11 and is of course subject to the errors inherent in that curve. In addition, the normal settling curves are apt to be inaccurate at very high and very low concentration due to the fact that some extrapolation of the calibration curve was necessary. Extrapolations at lower concentrations can be made with reasonable accuracy since the curves all reach zero concentration at a photometer reading of 100. At higher concentrations, however, inaccuracies in extrapolations occur since it is not known precisely over what path the curve rises to infinity. The only extrapolation at higher concentrations was made in run BY<sup>4</sup>-49 at a photometer reading of 7.5. Since the curve extends to a photometer reading of 14, the error in extrapolation probably does not exceed 10%.

The effect of irradiation upon the rate of settling is shown graphically in Figure 13 and is seen to be quite pronounced when compared to the normal settling curves of Figure 12. In comparing these two sets of curves it may be generally concluded that irradiating at a specified intensity for a period of two minutes before each concentration determination as outlined in the procedure causes the emulsion to settle roughly at double the rate it would

VOL. % BENZENE

FIGURE 13

THE EFFECT OF IRRADIATION ON THE RATE OF SETTLING





settle normally. As in the case of Figure 12, the concentrations of Figure 13 were determined from the photometer reading and the cell type 1 calibration curve of Figure 11. The effect of intensity of irradiation on the rate of settling is also shown to a certain extent in Figure 13. Runs 77, 123, and 125 show the effects of high, low, and medium intensities, respectively, with the most effective de-emulsification being obtained with the higher intensity and the less effective de-emulsification obtained at lower intensities. The rest of the data presented follow a similar pattern of more effective de-emulsification at higher intensities. This is in agreement with the literature. Although the curves of Figure 13 show conclusively that ultrasonic irradiation definitely has a de-emulsifying effect on benzene-water emulsions, it unfortunately fails to indicate exactly how this phenomenon of de-emulsification occurs. It cannot be determined from the data whether rapid settling occurs during irradiation or in the normal settling period immediately following irradiation. Sollner and Bondy<sup>15</sup> give evidence that rapid settling takes place after the irradiation period since the large particles formed by orthokinetic coagulation (that due to random contact) cannot settle out rapidly due to their tendency to collect wherever stationary waves occur. This, in all probability, is what has occurred in the runs presented in Figure 13. However, to substantiate or disprove this conclusion, it is recommended that additional runs be performed, measuring the concentration and particle size distribution of the emulsion immediately before and after irradiation. This could not be done in the present study due to the lack of a rapid counting and classifying technique.

Figures 14 through 19 show the formation of particles in various size ranges as a function of intensity and time of irradiation and Figure 20 shows overall concentration as a function of intensity and time of irradiation.

FIGURE 1A

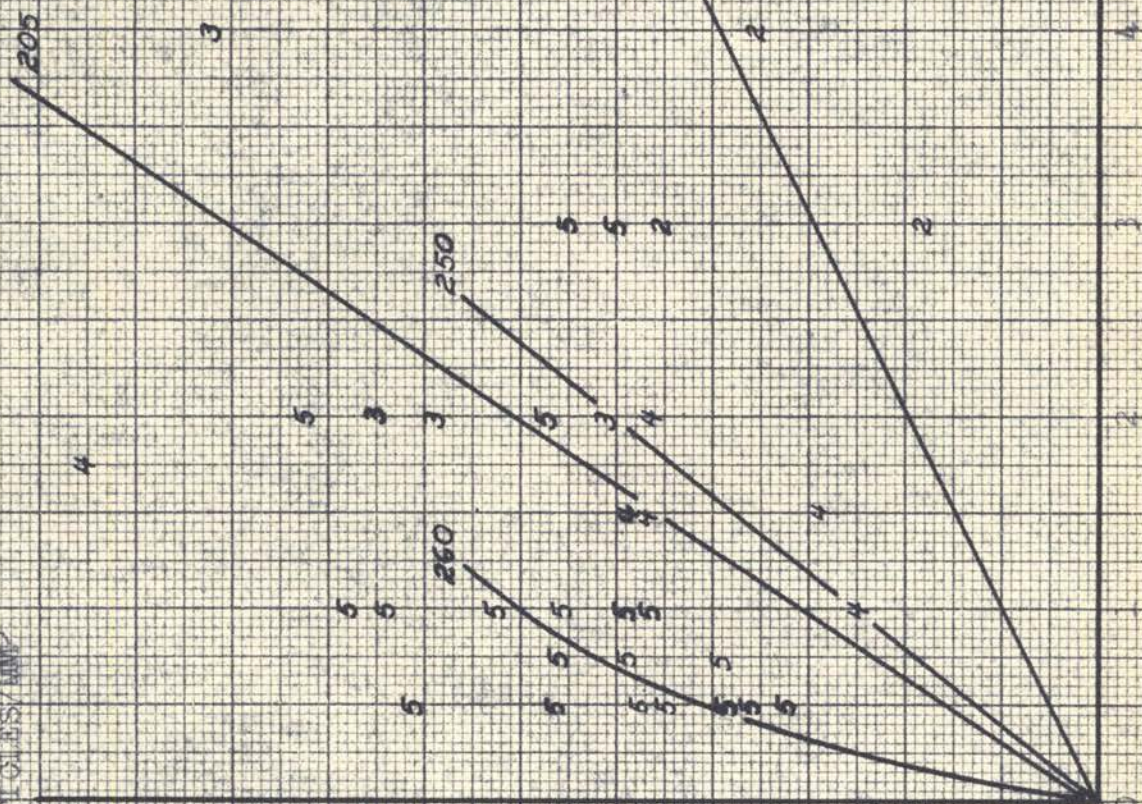
PARTICLE CONCENTRATION VS. TIME OF IRRADIATION AT CONSTANT INTENSITY

Particle diameter  
0-3 $\mu$

Intensity  
5-260mc.  
4-250mc.  
3-205mc.  
2-150mc.

PARTICLES/MM<sup>3</sup>

10x10<sup>5</sup>  
9x10<sup>5</sup>  
8x10<sup>5</sup>  
7x10<sup>5</sup>  
6x10<sup>5</sup>  
5x10<sup>5</sup>  
4x10<sup>5</sup>  
3x10<sup>5</sup>  
2x10<sup>5</sup>  
1x10<sup>5</sup>  
0



TIME OF IRRADIATION (MIN.)

8

7

6

5

4

3

2

1

0

PARTICLES/MM<sup>3</sup>

FIGURE 15

PARTICLE CONCENTRATION VS. TIME OF IRRADIATION AT CONSTANT INTENSITY

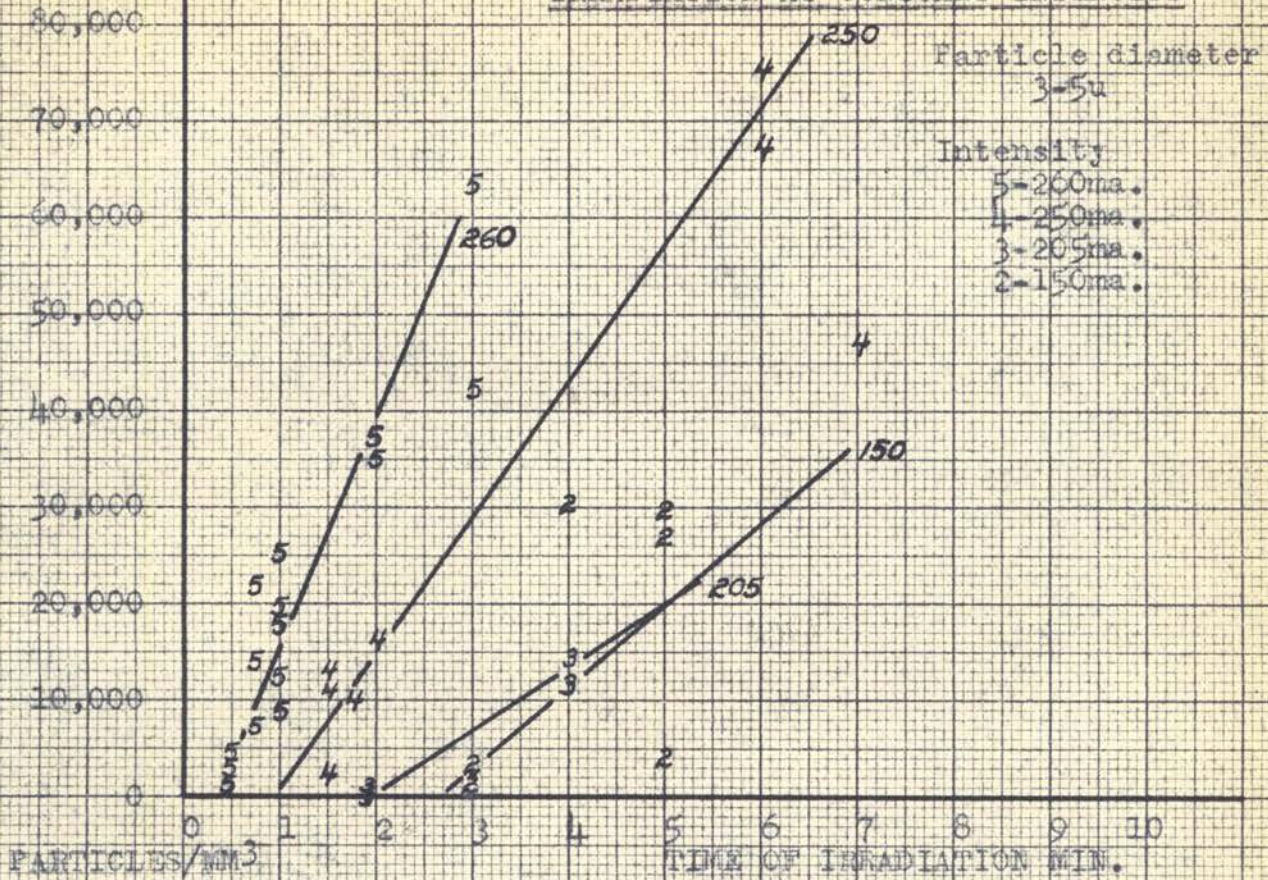
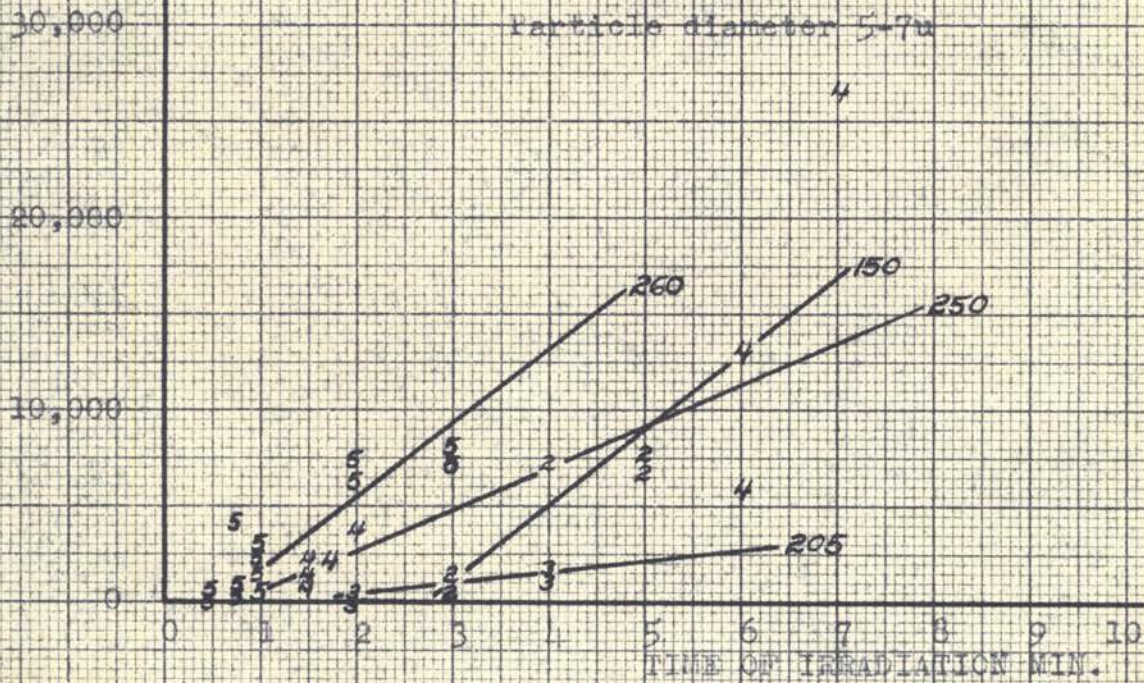
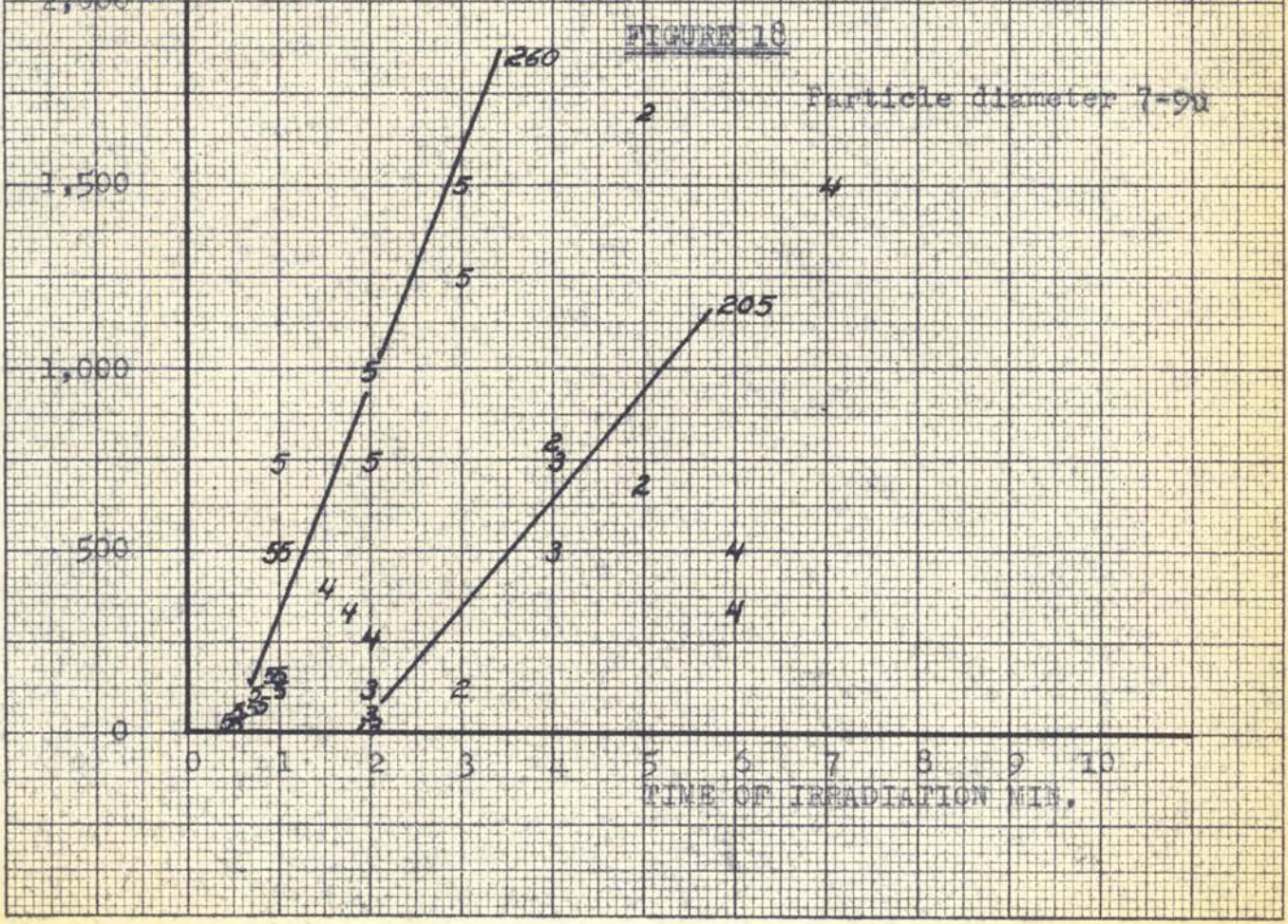
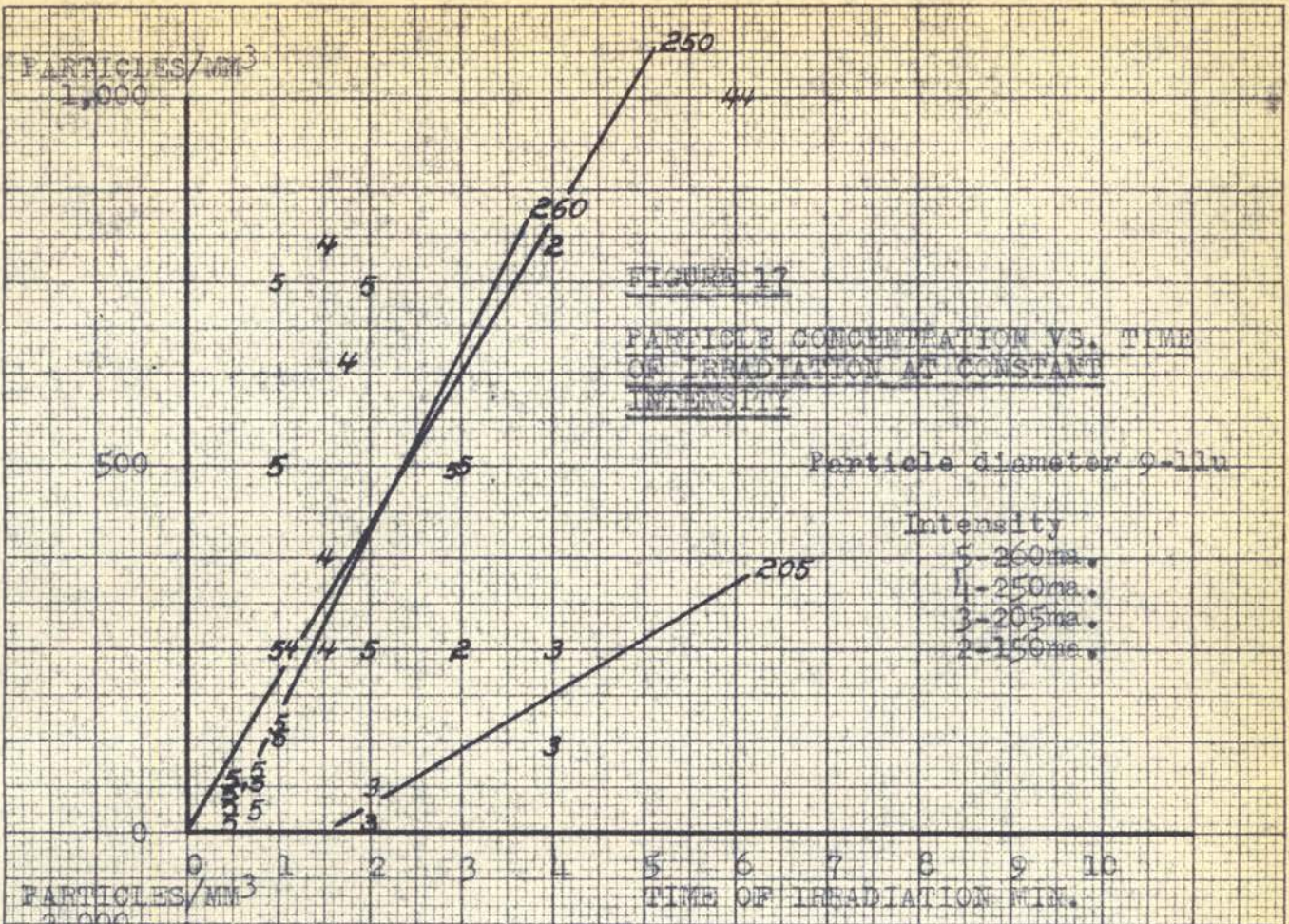


FIGURE 16

Particle diameter 5-7u





PARTICLES/MM<sup>3</sup>

1,500

1,000

500

0

VOL. % BENZENE

0.8

0.7

0.6

0.5

0.4

0.3

0.2

0.1

0

FIGURE 19

PARTICLE CONCENTRATION VS. TIME OF IRRADIATION AT CONSTANT INTENSITY

Particle diameter 11-20 $\mu$

Intensity

- 5-260ma.
- 1-250ma.
- 3-205ma.
- 2-150ma.

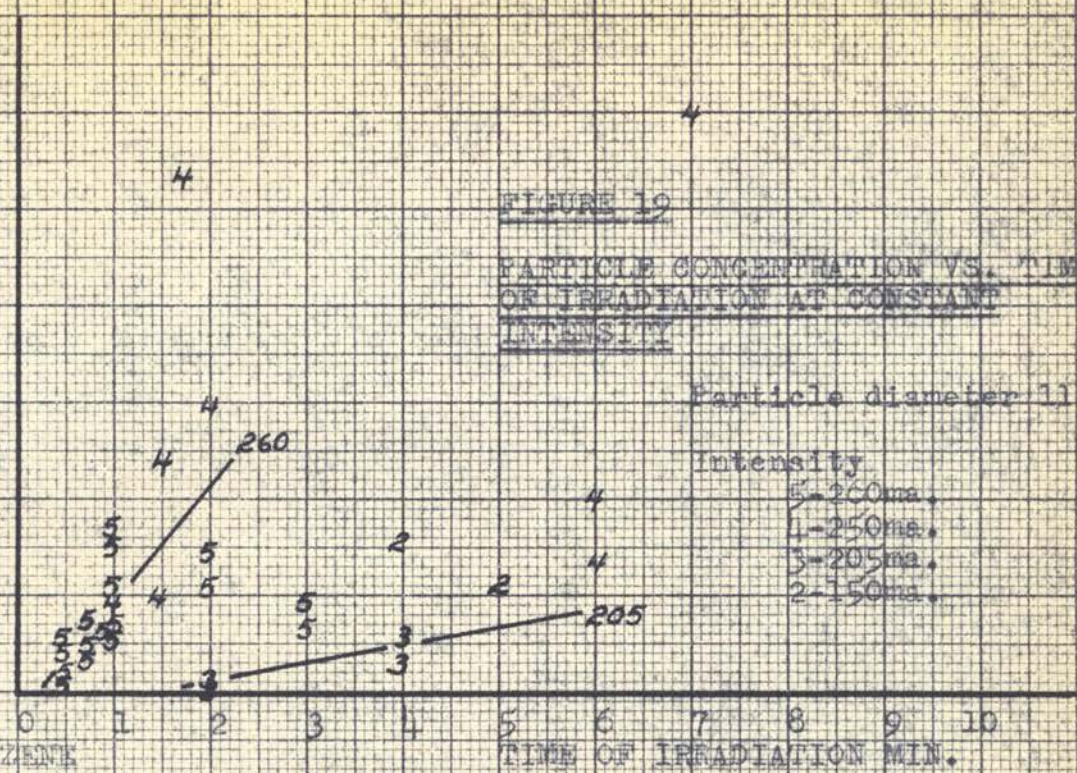
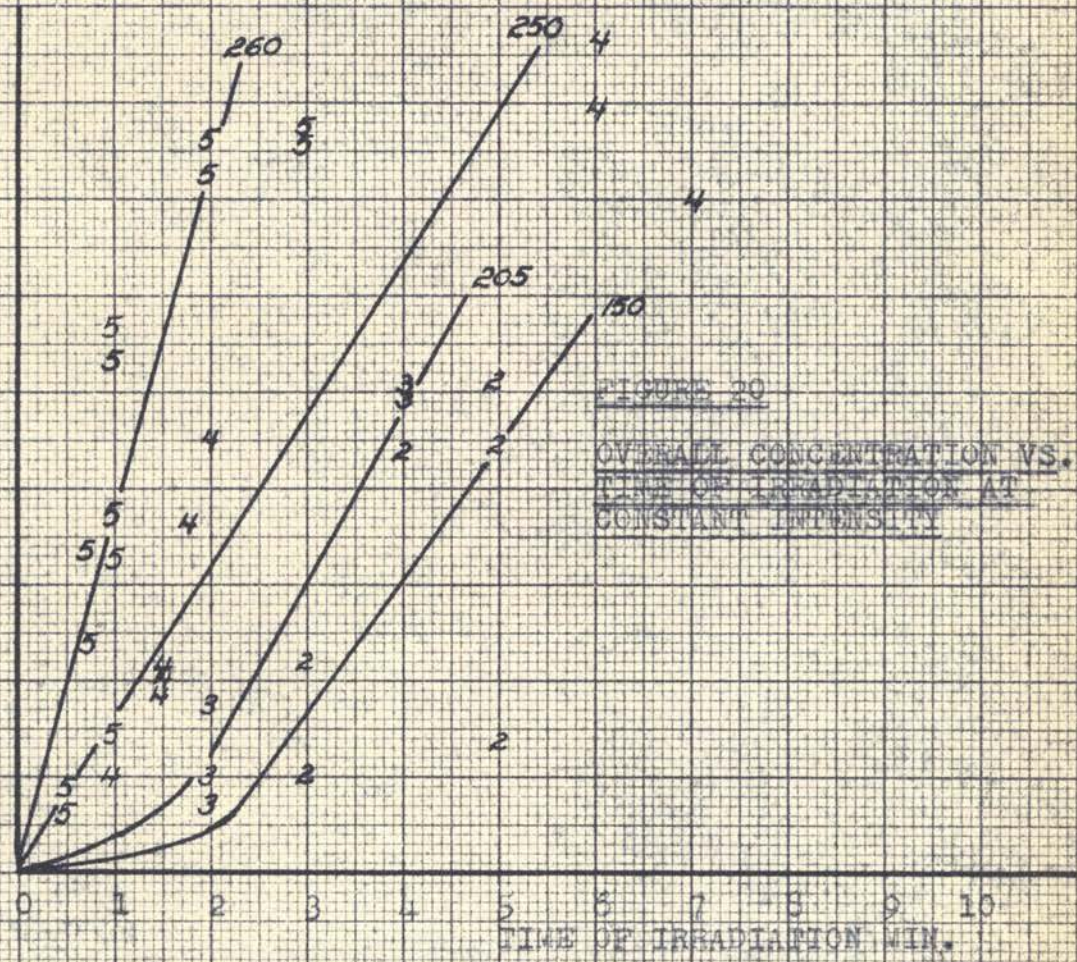


FIGURE 20

OVERALL CONCENTRATION VS. TIME OF IRRADIATION AT CONSTANT INTENSITY



MADE IN U.S.A.

Perhaps the most prominent feature of these results is that the curves for intensities of 260 ma. and 205 ma. do not seem consistent with the curves for intensities of 250 ma. and 150 ma. There are a number of reasons for this inconsistency. During the preliminary tests of the apparatus the crystal was placed in the brass and lucite crystal holder described previously. The performance of the crystal when held in this manner was poor since crystal vibrations were damped considerably by the pressure exerted by the crystal holder. But of considerably more importance was the continual arcing which occurred between the screws holding the springs in the lucite plates and the brass rings contacting the copper plate on the crystal, which could, if not controlled, conceivably cause irreparable damage to the crystal. Presumably a very satisfactory solution to the problem was obtained by removing the lucite plates and allowing the upper brass ring to be held on the crystal only by gravity. In this manner not only was the danger of arcing removed, but the damping effect of the pressure on the crystal was also eliminated. However, these changes were made at the expense of good consistent contact between the crystal and the crystal holder. The experimental runs at 250 ma. and 150 ma. were made with the apparatus in this arrangement. As more and more runs were made, the already bad contact in the crystal holder became gradually worse until small arcs between the brass rings and the crystal began to destroy the copper face of the crystal. In order to restore the apparatus to usefulness, the lucite plates were replaced. Also, substituted for the pointed screws which had caused previous arcing were blunted screws. The springs which fastened the crystal holder together were adjusted so as to provide good contact, but with not as much damping of the crystal vibrations as before. The data for 260 ma. and 205 ma. were taken under these conditions. It is unexpected that two sets of data taken under such different

operating conditions could be completely consistent with each other.

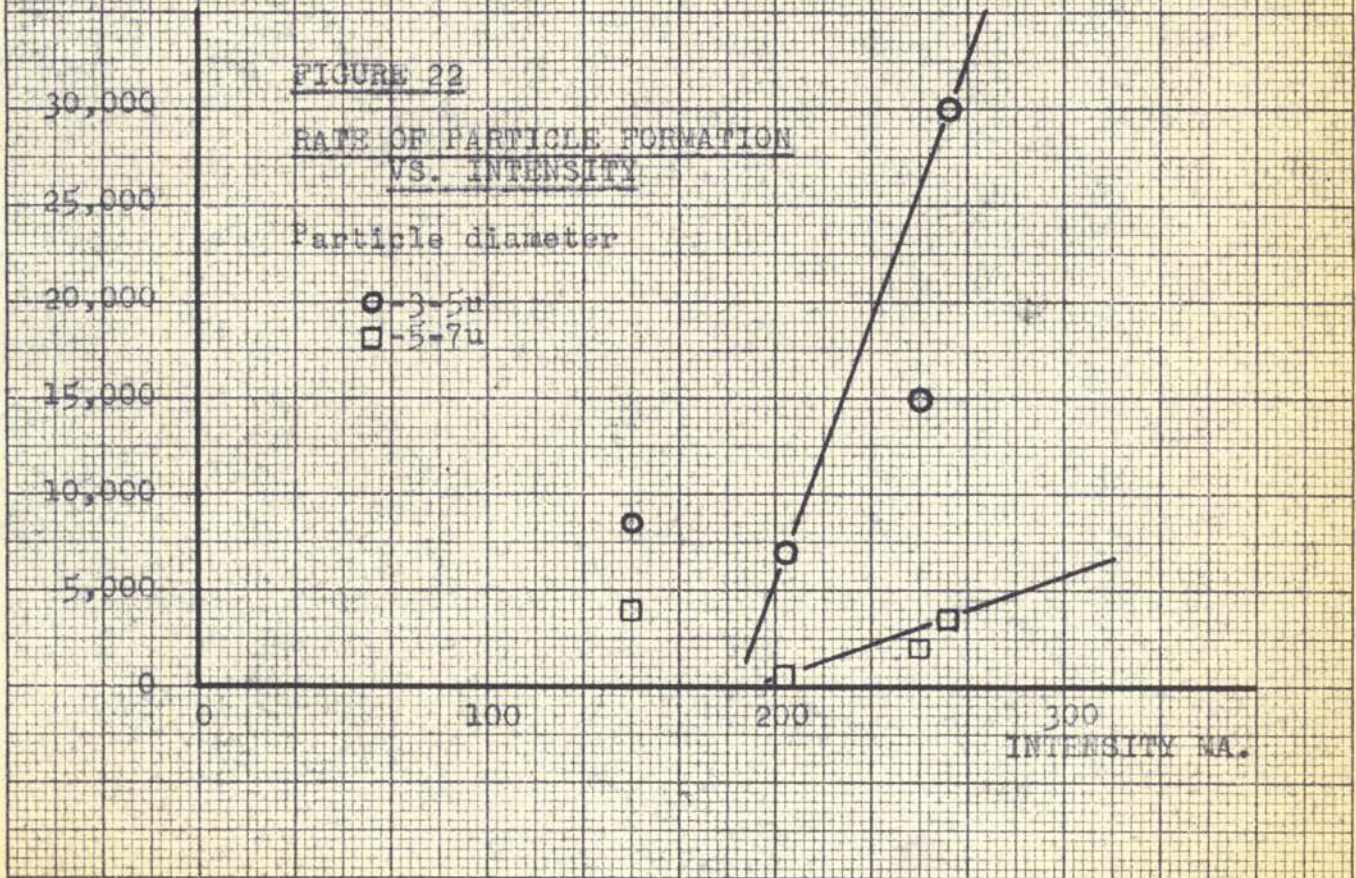
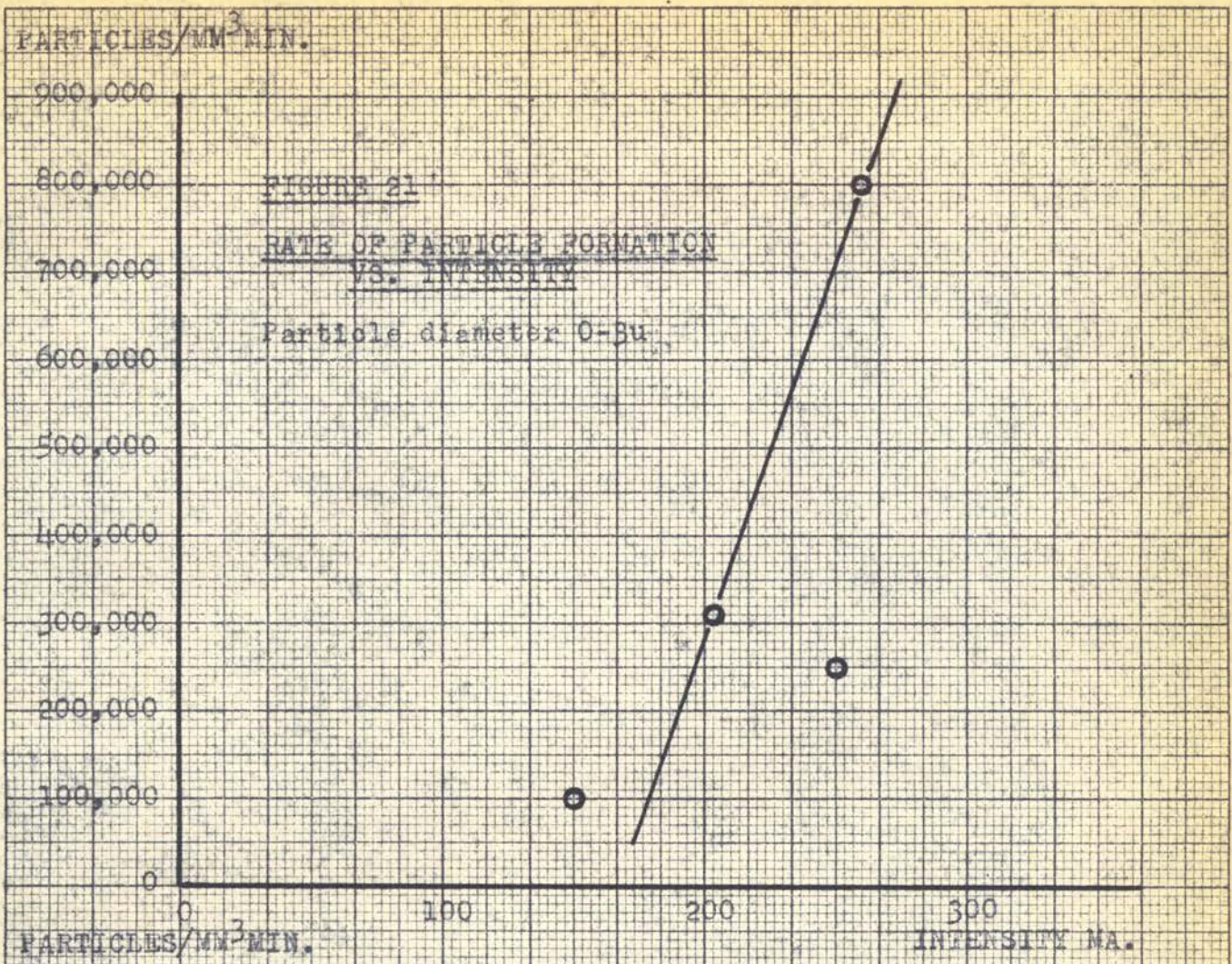
In relation to each other, the 260 ma. and the 205 ma. curves show an increasing intensity, while the 250 ma. and 205 ma. curves, although consistent with each other in this respect in some particle size ranges, became completely inconsistent in other particle size ranges. This condition of the 250 ma. and the 205 ma. curves is in all probability due to the inadequacy of the data. In some cases the data are so badly scattered as to make the construction of a representative curve very precarious. This condition seems to be the most prevalent in the larger particle size ranges. Although subject to intensity fluctuations during emulsification and the other analytical errors involved in the construction of Figure 11, the dominant reason for the scattering of the data is to be found in the counting and classifying procedure. The data show that for runs 50 through 74 a greater effort was made to count a representative number of large particles than in the previous runs where only very few particles were observed. Generally, between 16 and 32 small squares in the blood counting chamber encompass a representative number of small particles, but evidently at least 25 times this many squares must be counted before the larger particles are adequately represented.

The results of Figure 20 show conclusively that the rate of emulsion formation increases with increasing intensity of irradiation, which is in complete accord with the literature. It was observed on several occasions that the emulsion concentration seemed to reach a maximum and drop slowly with increasing time of irradiation. Certain portions of the data indicate this to be the case. However, sufficient data were not taken to justify a definite conclusion. De-gassing and heating effects as the result of continued irradiation have been shown by the literature to suppress cavitation and emulsification.<sup>16</sup> These conditions might well have prevailed in this investigation

since the test tube containing the emulsified material was very close to the quartz crystal during irradiation. It is recommended in future work that in order to eliminate any discrepancies caused by extreme temperature variations, stirring devices be placed in the oil bath to keep it at a uniform temperature and that cooling coils be placed around the test tube to prevent the suppresion of cavitation due to excessive temperature rise. Extreme care must be taken in any operation such as the latter to prevent grounding of the crystal holder. Figures 21-24 are plots of the slopes of the lines of figures 14-19 and are necessarily subject to the same analytical and procedural errors. The slope lines of figures 21-24 are drawn through the 260 and 205 ma. points since the data indicate these to be the more reliable. From these lines it may be concluded that the rate of particle formation increases with increasing intensity and with decreasing particle size.

The results of the study of the ability of various media to absorb ultrasonic irradiation is presented in Table XII and Figure 25. These results indicate that the rate of absorption increases with increasing intensity and that ability of water to absorb ultrasonic irradiation is roughly twice that of benzene. Benzene-water mixtures are capable of absorbing more ultrasonic energy than either pure water or pure benzene. This is possibly due to the reflection of the energy by the individual particles of the emulsion until it is dissipated as heat. The results of the efficiency determinations are presented in Table XII as three separate and distinct efficiencies.  $E_1$  represents the ability of the apparatus to convert electrical energy to ultrasonic energy and is expressed as the per cent of the power supplied to the power amplification section of the generator which is applied to the crystal holder. The electrical power supplied to the crystal holder was determined from the temperature rise of the irradiated material and the oil





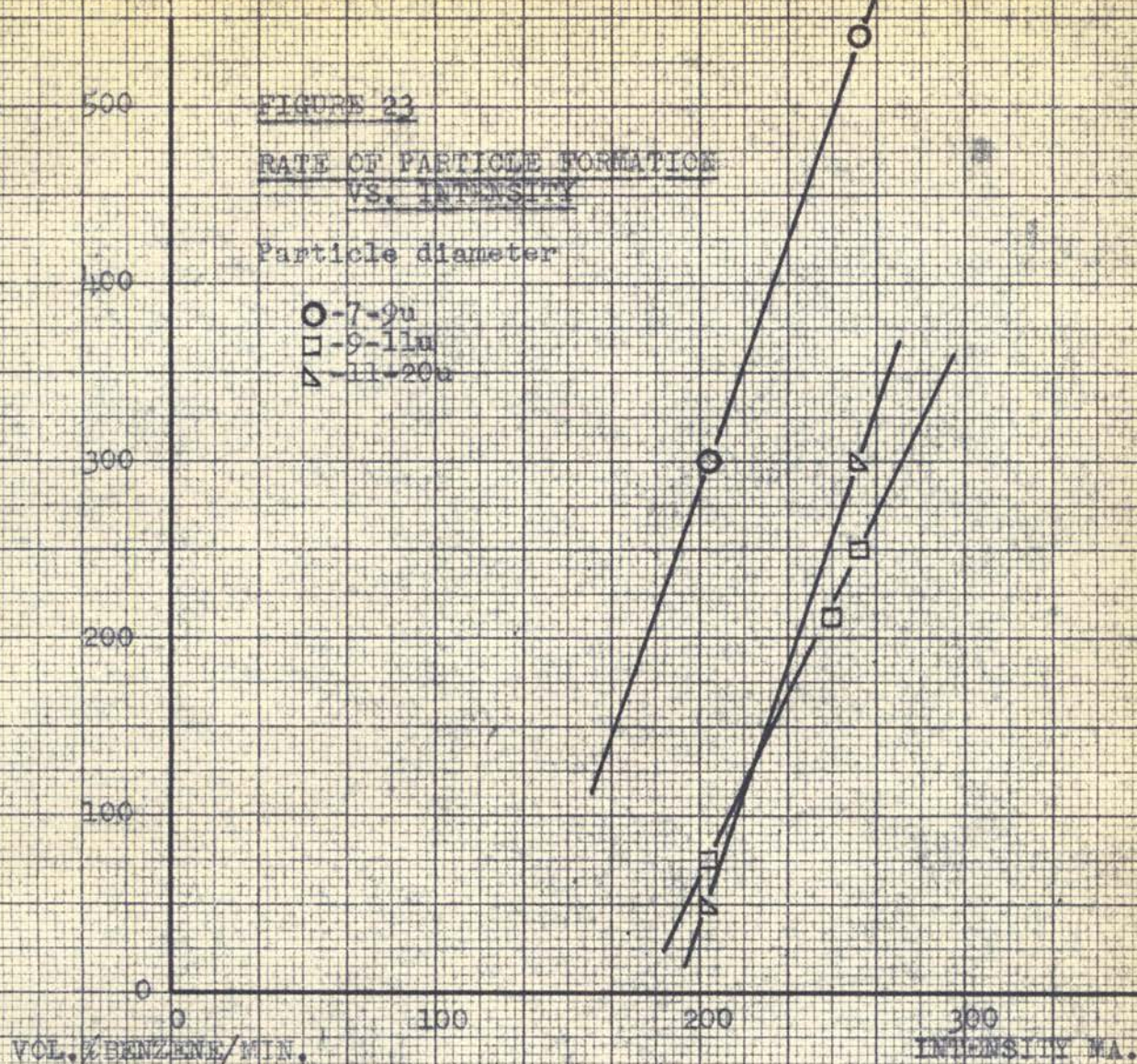
PARTICLES/MM<sup>3</sup>MIN.

FIGURE 23

RATE OF PARTICLE FORMATION  
VS. INTENSITY

Particle diameter

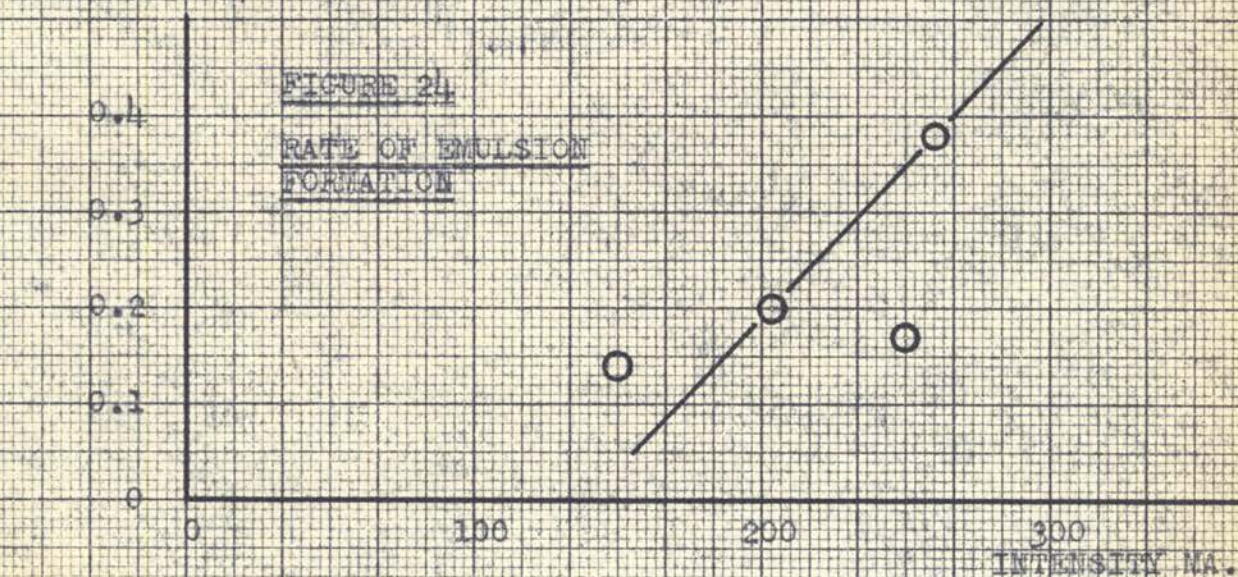
- - 7-9 $\mu$
- - 9-11 $\mu$
- △ - 11-20 $\mu$



VOL. % BENZENE/MIN.

FIGURE 24

RATE OF EMULSION  
FORMATION



CALORIES

FIGURE 25

ULTRASONIC ABSORPTION

Irradiated material

7ml H<sub>2</sub>O & 5ml benzene

○ - 225ma.

● - 175ma.

12ml H<sub>2</sub>O

□ - 225ma.

◻ - 175ma.

10ml benzene

△ - 225ma.

250

200

150

100

50

0

0

1

2

3

4

5

6

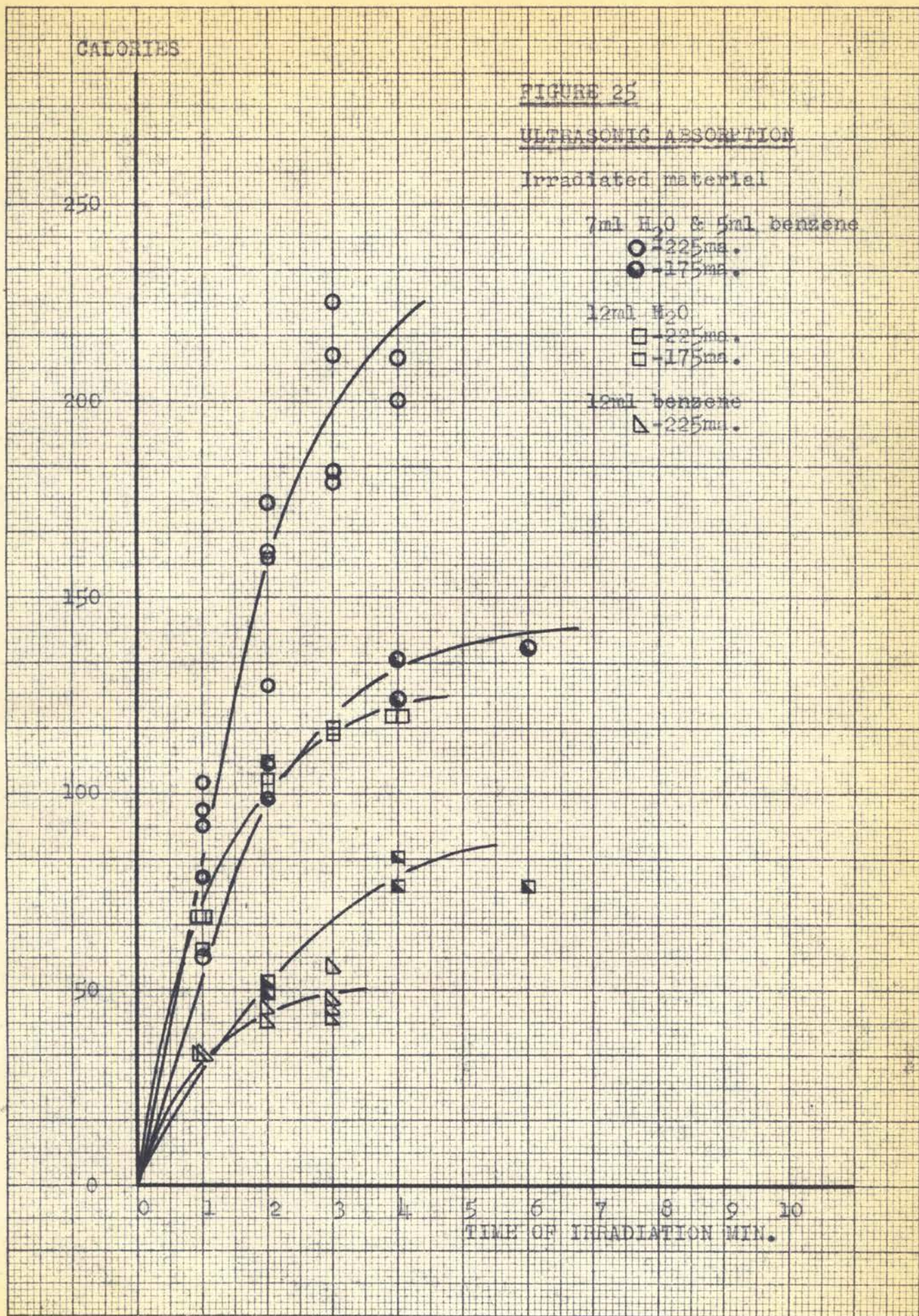
7

8

9

10

TIME OF IRRADIATION MIN.



bath surrounding the crystal holder during irradiation. These values are presented in the  $\Delta H_1 + \Delta H_2$  column of Table XII. The incremental electrical power supplied to the power amplification system of the generator under load is the product of the incremental plate current supplied to the power amplifier and the plate voltage which is 3,000 volts. The incremental plate current is the difference between the full load plate current at a given crystal current value and the no load plate current. These figures are tabulated in columns 2 and 3 of Table XIV. Column  $E_3$  of Table XII relates the energy absorbed in the oil bath and irradiated material to the total energy supplied to the power amplifier. The values of  $E_1$  and  $E_3$  in Table XII indicate that tremendous electrical power losses are sustained in the power amplifier. These losses, for the most part, are attributed to the heating of wires and tubes, and direct losses from the large tank coil to the atmosphere. Due to lack of the proper equipment, the energy losses in the power supply and oscillator were not determined, but they can be estimated from the performance data of similar equipment. In radio equipment, the highest possible efficiency of conversion of line energy to radio frequency energy in the plate circuit is approximately 20%. When another amplifier or an antenna is drawing energy from the plate circuit, the highest possible coupling efficiency between the two is approximately 75%. However, data are not available on the performance of a piezoelectric crystal when coupled to an amplifier. If the performance of a coupling between an amplifier and a crystal may be compared to the performance of a coupling between an amplifier and an antenna, the highest possible overall efficiency from the line to the crystal in this study would be approximately  $0.75 \times 0.20 \times 100$  or 15%. The data indicate that most of the losses occurred in the coupling between the amplifier and the crystal circuit. Since the efficiency of conversion of amplifier plate circuit energy to

crystal energy was 4.6%, an approximate overall energy efficiency from the line to the crystal of 1% was obtained in this study. Column E<sub>2</sub> of Table XII expresses the per cent of the electrical power supplied to the crystal holder which is recovered as heat in the irradiated material.

In the way of recommendations to improve the efficiency of operation, one of the major desirable changes is an improvement in the generator. The results of efficiency determinations indicate that there are considerable power losses in the power amplification system of the generator. The crystal holder should also be redesigned. Submitted is a drawing of an improved crystal holder which might possibly be more efficient than the one now in use.

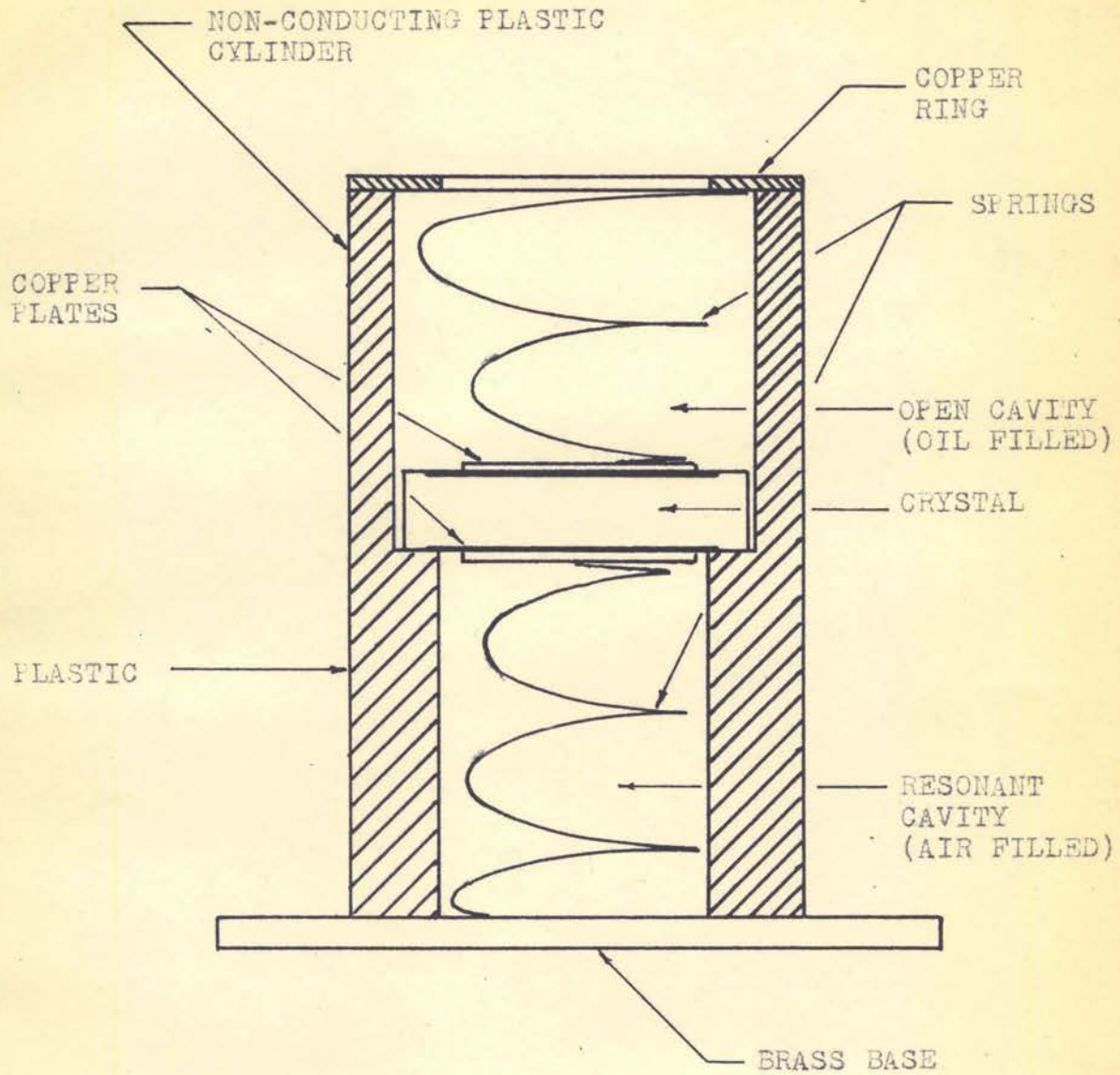
### CONCLUSIONS

1. Photometer analysis of emulsion concentration with a thin absorption cell is accurate to within  $\pm 25\%$  except when unusually large amounts of large particles are present.
2. The method of counting and classifying particles used in this study is usable but inadequate when trying to obtain truly quantitative data.
3. Irradiation of benzene-water emulsions causes de-emulsification and the rate of de-emulsification increases with increasing intensity of irradiation.
4. The rate of emulsification (total volume emulsified) increases with increasing intensity of irradiation.
5. The rate of particle formation in emulsification increases with increasing intensity and decreasing particle size.
6. An average of 4.6% of the electrical power supplied to the power amplifier is applied to the crystal holder.
7. An average of 19% of the electrical power supplied to the crystal holder is absorbed by the irradiated material.
8. The rate of absorption of ultrasonic energy in benzene and water increases with increasing intensity. The ability of water to absorb ultrasonic energy is roughly twice that of benzene. A mixture of the two materials absorbs ultrasonic energy more strongly than either one alone.

RECOMMENDATIONS

1. The development of a photographic method of counting and classifying the particles of the emulsion is recommended.
2. A more careful investigation of the rate and mechanism of de-emulsification is recommended.
3. Adequate temperature control of the irradiated material during irradiation is recommended.
4. A more efficient crystal holder is recommended.

FIGURE 26  
SUGGESTED CRYSTAL  
HOLDER





У  
ИСКУССТВО

21

APPENDIX

ПОЛНОЕ ИМЯ

СЛОВАСКОЕ ОБЪЯСНЕНИЕ

NOMENCLATURE

A - Emulsification runs.

B - De-emulsification runs.

Y - Runs made at 250 kc. (All runs in this study were made at this frequency.)

C - Runs used as calibration data.

\* - Analyzed with cell type 1.

\*\* - Agitated before irradiation.

u - Micron.

No asterisk (\*) - Analyzed with cell type 2.

$\Delta H_1$  - Energy absorbed by the test tube.

$\Delta H_2$  - Energy absorbed by the oil bath.

$E_1$  - The per cent of the incremental electrical energy in the power amplifier plate circuit which is applied to the crystal holder.

$E_2$  - The per cent of the energy supplied to the crystal holder which is absorbed by the irradiated material.

T - Temperature of the oil bath.

t - Temperature of the irradiated material.

$E_3$  - The per cent of the electrical energy in the power amplifier plate circuit which is applied to the crystal holder.

TABLE IV  
PHOTELOMETER CALIBRATION

<u>RUN NO.</u>	<u>TIME OF IRRADIATION (MIN)</u>	<u>CRYSTAL CURRENT (MA)</u>	<u>SETTLING TIME (MIN)</u>	<u>PHOTELOMETER READING</u>	<u>VOLUME PER CENT BEN-ZENE CALCULATED FROM MICROSCOPIC MEASUREMENTS</u>
AYC-1	1	280	15	43.0	0.00812
AYC-2	2	286	5	24.5	0.150
AYC-3	2	280	5	19.0	0.181
AYC-4	1	260	5	17.0	0.139
AYC-5	1	260	5	8.0	0.178
AYC-6	1	260	64	26.0	0.104
AYC-7	1	250	5	45.0	0.0967
AYC-8	2	250	5	10.0	0.259
AYC-9	0.5	245	5	40.0	0.087
AYC-10	0.5	245	35	69.0	0.0532
AYC-11	0.5	250	5	51.0	0.190
AYC-12	4	245	5	51.0	0.0564
*AYC-12	4	245	5	-	0.5041
AYC-13	4	250	5	31.0	0.636
AYC-36	4	150	5	53.0	0.154
AYC-37	6	150	5	27.0	0.209
AYC-38	7.5	150	5	36.0	0.137
AYC-30	3	150	1	29.0	0.103
AYC-31	3	150	1	68.0	0.221
AYC-32	5	150	1	14.0	0.447
AYC-33	4	150	1	19.0	0.438
AYC-39	4	150	1	28.0	0.353
AYC-40	3	150	1	25.0	0.396
AYC*-15	4	240	5	25.5	0.646
AYC*-16	4	250	5	32.0	0.532
AYC*-17	4	250	5	29.5	0.733
AYC*-18	3	250	5	32.0	0.628
AYC*-19	3	250	5	39.0	0.310
AYC*-20	2.5	250	5	34.0	0.467
AYC*-41	6	150	5	72.0	0.250
AYC*-42	10	150	5	51.0	0.227
AYC*-43	4	150	5	35.0	0.657

Note: AYC-12 is \*AYC-12 diluted to twice its original volume

TABLE IV Con't

PHOTELOMETER CALIBRATION

<u>RUN NO.</u>	<u>TIME OF IRRADIATION (MIN)</u>	<u>CRYSTAL CURRENT (MA)</u>	<u>SETTLING TIME (MIN)</u>	<u>PHOTELOMETER READING</u>	<u>VOLUME PER CENT BEN-ZENE (CALCULATED FROM MICROSCOPIC MEASUREMENTS)</u>
AYC*-21	6	250	1	13.0	0.780
AYC*-22	6	250	1	18.0	0.773
AYC*-23	7	250	1	24.0	0.792
AYC*-24	2	250	1	42.0	0.442
AYC*-25	1.5	250	1	65.0	0.297
AYC*-26	1	250	1	82.0	0.143
AYC*-27	1.5	250	1	69.0	0.163
AYC*-28	1.75	250	1	48.0	0.757
AYC*-29	1.5	250	1	66.5	0.470
AYC*-34	5	150	1	42.5	0.516
AYC*-35	5	150	1	67.5	0.516
AYC*-64	0.5	245	1	88.0	0.605
AYC*-65	0.5	240	1	85.0	0.226
AYC*-66	1	275	1	33.0	0.406
AYC*-67	1	255	1	35.5	0.506
AYC*-68	0.75	255	1	61.5	0.257
AYC*-69	0.75	255	1	50.0	0.367

STRATHMORE PARCHMENT

100% RAG U.S.A.

TABLE V

EMULSION CHARACTERISTICS

RUN NO.	TIME OF IRRAD.	CRYSTAL SETTLING		PHOTEL. READING							SQUARES COUNTED	SIZE OF SQUARES	
		CURRENT	TIME		0-3u	3-5u	5-7u	7-9u	9-11u	11-20u			
AYC-1	1 min.	280 ma.	15 min.	43.0	968	-	1	-	-	-	-	8	L
AYC-2	2	286	5	24.5	973	9	4	-	-	1 <sup>13</sup>	-	16	S
AYC-3	2	280	5	19.0	1,855	29	3	-	-	1 <sup>15</sup>	-	24	S
AYC-4	1	260	5	17.0	1,740	37	-	4	3	-	-	32	S
AYC-5	1	260	5	8.0	1,890	52	13	1	2	2 <sup>12</sup>	-	32	S
AYC-6	1	260	64	26.0	839	4	-	-	1	-	-	16	S
AYC-7	1	250	5	45.0	1,800	6	-	-	-	-	-	32	S
AYC-8	2	250	5	10.0	1,081	174	71	7	9	1 <sup>12</sup>	-	40	S
AYC-9	0.5	245	5	40.0	1,011	21	4	-	3	-	-	32	S
AYC-10	0.5	245	35	69.0	897	7	-	1	-	-	-	32	S
AYC-11	0.5	250	5	51.0	1,005	16	4	2	-	2 <sup>20</sup>	1 <sup>13</sup>	32	S
AYC-12	4	245	5	51.0	1,080	-	-	-	-	-	-	32	S
*AYC-12	4	245	5	-	1,896	221	66	25	8	2 <sup>13</sup>	2 <sup>12</sup> 1 <sup>20</sup>	32	S
AYC-13	4	250	5	31.0	375	107	106	23	4	-	-	16	S
AYC*-15	4	240	5	25.5	899	104	81	9	1	-	-	12	S
AYC*-16	4	250	5	32.0	1,420	86	39	3	2	1 <sup>12</sup>	-	12	S
AYC*-17	4	250	5	29.5	2,875	270	6	1	-	-	-	12	S
AYC*-18	3	250	5	32.0	1,123	187	40	1	1	1 <sup>14</sup>	1 <sup>13</sup>	12	S
AYC*-19	3	250	5	39.0	787	42	16	-	1	2 <sup>13</sup>	-	12	S
AYC*-20	2.5	250	5	34.0	1,187	155	22	4	4	1 <sup>20</sup>	-	16	S
AYC*-21	6	250	1	13.0	2,821	201	17	1	3	1 <sup>13</sup>	-	12	S
AYC*-22	6	250	1	18.0	1,198	151	26	1	2	1 <sup>13</sup>	-	8	S
AYC*-23	7	250	1	24.0	634	94	53	3	-	2 <sup>13</sup>	1 <sup>12</sup>	8	S
AYC*-24	2	250	1	42.0	1,843	66	14	1	-	2 <sup>13</sup>	1 <sup>19</sup>	16	S
AYC*-25	1.5	250	1	65.0	1,941	54	3	-	1	1 <sup>12</sup>	-	16	S
AYC*-26	1	250	1	82.0	909	1	2	-	1	1 <sup>13</sup>	-	16	S
AYC*-27	1.5	250	1	69.0	2,314	20	20	-	3	-	-	32	S
AYC*-28	1.75	250	1	48.0	3,145	31	6	1	2	2 <sup>13</sup>	2 <sup>16</sup>	12	S
AYC*-29	1.5	250	1	66.5	2,338	56	10	2	4	2 <sup>19</sup>	1 <sup>12</sup>	20	S

TABLE V (Cont'd)

EMULSION CHARACTERISTICS

RUN NO.	TIME OF CRYSTAL SETTLING			PHOTEL. READING	EMULSION CHARACTERISTICS						SQUARES COUNTED	SIZE OF SQUARES
	IRRAD.	CURRENT	TIME		0-3u	3-5u	5-7u	7-9u	9-11u	11-20u		
AYC-30	3 min.	150 ma.	1 min.	29.0	1,463	24	10	1	-	-	32	S
AYC-31	3	150	1	68.0	1,823	14	2	-	1	-	16	S
AYC-32	5	150	1	14.0	885	45	11	1	-	-	6	S
AYC-33	4	150	1	19.0	893	78	18	2	2	1 <sup>12</sup>	10	S
AYC*-34	5	150	1	42.0	2,048	95	24	6	-	1 <sup>16</sup>	14	S
AYC*-35	5	150	1	67.5	590	9	-	-	-	-	8	S
AYC-36	4	150	5	53.0	1,152	36	23	2	2	1 <sup>16</sup>	32	S
**AYC-37	6	150	5	27.0	1,405	53	43	9	4	1 <sup>13</sup> 1 <sup>11</sup>	36	S
AYC-38	7.5	150	5	36.0	2,518	6	2	-	-	-	32	S
**AYC-39	4	150	1	28.0	1,407	6	6	1	-	-	10	S
**AYC-40	3	150	1	25.0	2,587	1	2	1	1	-	12	S
AYC*-41	6	150	5	72.0	2,086	45	44	5	2	1 <sup>12</sup> 1 <sup>19</sup> 1 <sup>13</sup>	48	S
AYC*-42	10	150	5	51.0	1,772	68	45	5	2	1 <sup>13</sup>	32	S
**AYC*-43	4	150	5	35.0	2,447	83	51	6	5	1 <sup>13</sup> 1 <sup>16</sup>	16	S

Note: Run AYC-12 records an attempt to dilute an emulsion with tap water to twice its original volume.

\*AYC-12 records the analysis data on the undiluted emulsion.

(2<sup>13</sup>) when seen in this table indicates two particles, each thirteen microns in diameter.

Squares of size (L) have an area of 1/16 mm<sup>2</sup>.

Squares of size (S) have an area of 1/400 mm<sup>2</sup>.

TABLE VI

RUN NO. AY#-	50	51	52	53	54	55	56	57	58	59
TIME OF IRRADIATION (MIN)	1	0.5	1	1	0.5	0.5	2	2	3	3
CRYSTAL CURRENT (MA)	260	255	260	265	255	260	265	265	265	260
PHOTELOMETER READING	47.0	88.0	75.0	51.0	88.5	84.0	20.0	22.0	19.0	20.0
SETTLING TIME (MA)	1	1	1	1	1	1	1	1	1	1

NO. OF PARTICLES

PARTICLE DIAMETER (MICRONS)	<u>NO. OF 1/400 mm<sup>2</sup> SQUARES OBSERVED</u>									
	11-20u	36	5	15	16	10	15	36	26	23
NO. SQUARES	400	400	400	400	400	400	400	400	400	400
9-11u	25	2	15	14	5	6	3	1	2	2
NO. SQUARES	400	400	400	400	400	400	16	16	16	16
7-9u	3	-	16	13	5	5	4	3	5	6
NO. SQUARES	16	400	400	400	400	400	16	16	16	16
5-7u	9	-	1	7	5	9	25	29	32	29
NO. SQUARES	16	400	16	16	400	400	16	16	16	16
3-5u	102	2	37	51	17	13	142	150	170	255
NO. SQUARES	16	16	16	16	16	16	16	16	16	16
0-3u	3,116	1,799	2,500	2,231	1,549	1,447	2,286	3,285	2,000	2,200
NO. SQUARES	16	16	16	16	16	16	16	16	16	16

Remarks:

7cc of H<sub>2</sub>O and 5cc of benzene used in all runs.

In run 50, the largest particles were in the neighborhood of 30 microns in diameter.

In run 56, the smallest visible particles were about 3 microns in diameter.

TABLE VI Con't

EMULSION CHARACTERISTICS

RUN NO. AY-	60	61	62	63	AYC*-70	71	72	73	74
TIME OF IRRADIATION (MIN)	0.5	1	0.75	0.5	2	2	2	4	4
CRYSTAL CURRENT (MA)	290	275	255	250	205	205	205	205	205
PHOTELOMETER READING	44.0	15.0	20.0	43.0	87.0	71.0	82.0	37.5	38.0
SETTLING TIME (MIN)	1	1	1	1	1	1	1	1	1

NO. OF PARTICLESNO. OF 1/400 mm<sup>2</sup> SQUARES OBSERVED

PARTICLE DIAMETER (MICRONS)	NO. OF 1/400 mm <sup>2</sup> SQUARES OBSERVED								
11-20u	7	17	19	5	2	-	2	8	12
NO. SQUARES	400	400	400	400	400	400	400	400	400
9-11u	2	14	9	2	-	6	1	12	1
NO. SQUARES	400	400	400	400	400	400	400	400	16
7-9u	1	16	4	3	1	11	2	3	2
NO. SQUARES	400	400	200	400	400	400	400	16	16
5-7u	4	2	2	1	4	1	11	4	6
NO. SQUARES	16	16	16	16	400	16	400	16	16
3-5u	5	37	31	1	3	2	15	48	58
NO. SQUARES	16	16	16	16	400	16	400	16	16
0-3u	2,249	1,860	2,246	1,291	2,049	2,760	3,000	3,686	4,842
NO. SQUARES	16	16	16	16	16	16	16	16	16



TABLE VII  
EMULSION CHARACTERISTICS

RUN NO. AYC#-	<u>64</u>	<u>65</u>	<u>66</u>	<u>67</u>	<u>68</u>	<u>69</u>
TIME OF IRRADIATION (MIN)	0.5	0.5	1	1	0.75	0.75
CRYSTAL CURRENT (MA)	245	240	275	255	255	255
PHOTELOMETER READING	88.0	85.0	33.0	35.5	61.5	50.0
SETTLING TIME (MIN)	1	1	1	1	1	1

NO. OF PARTICLES

PARTICLE DIAMETER (MICRONS)	<u>NO. OF 1/400 mm<sup>2</sup> SQUARES OBSERVED</u>					
	<sup>1</sup> 82.5	<sup>1</sup> 25	<sup>1</sup> 27 <sup>1</sup> 28	<sup>2</sup> 24	<sup>2</sup> 23 <sup>1</sup> 27	<sup>1</sup> 22 <sup>1</sup> 29
20u	1	1	1	-	2	1
20u	1	1	1	-	2	1
19u	-	-	-	-	-	-
18u	-	-	-	-	-	-
17u	-	-	-	1	-	-
16u	-	-	2	-	-	-
15u	-	-	-	1	-	-
14u	-	1	1	1	-	1
13u	-	2	4	3	2	5
12u	-	1	1	4	1	1
11u	-	-	2	1	1	1
NO. SQUARES	400	400	120	280	400	400
9-11u	-	2	2	3	3	8
NO. SQUARES	400	400	16	16	400	400
7-9u	1	2	2	2	8	11
NO. SQUARES	400	400	16	16	400	400
5-7u	-	5	9	12	4	16
NO. SQUARES	16	400	16	16	16	16
3-5u	10	14	76	80	58	89
NO. SQUARES	16	16	16	16	16	16
0-3u	2,849	1,903	1,971	2,966	1,565	1,966
NO. SQUARES	16	16	16	16	16	16

TABLE VIII  
PARTICLE SIZE DISTRIBUTION VS.  
TIME AND INTENSITY OF IRRADIATION

RUN NO.	PARTICLE DIA. - MICRONS						TIME	MA.	CONC. <sup>a</sup>
	0-3u	3-5u	5-7u	7-9u	9-11u	11-20u	(MIN)		FIG. 11
AYC*-21	942,000	67,200	5,680	334	1,000	334	6	250	0.865
AYC*-22	598,000	75,400	13,800	500	1,000	500	6	250	0.792
AYC*-23	317,000	47,000	26,500	1,500	-	1,500	7	250	0.700
AYC*-24	462,000	16,500	3,500	250	-	750	2	250	0.450
AYC*-25	485,000	13,500	750	-	250	250	1.5	250	0.215
AYC*-26	250,000	250	500	-	250	250	1	250	0.103
AYC*-27	289,000	2,500	1,250	-	375	-	1.5	250	0.187
AYC*-28	1,050,000	10,350	2,000	334	668	1,335	1.75	250	0.365
AYC*-29	468,000	11,200	2,000	400	800	600	1.5	250	0.205
AYC-30	183,500	3,000	1,250	125	-	-	3	150	0.345
AYC-31	456,000	3,500	500	-	250	-	3	150	0.135
AYC-32	590,000	30,000	7,450	666	-	-	5	150	0.460
AYC-33	357,000	30,800	7,200	800	800	400	4	150	0.425
AYC*-34	710,000	27,100	6,870	1,715	-	286	5	150	0.200
AYC*-35	295,000	4,500	-	-	-	-	5	150	0.200
AYC*-50	777,000	25,500	2,250	750	250	360	1	260	0.375
AYC*-51	450,000	500	-	-	20	50	0.5	255	0.065
AYC*-52	625,000	9,250	250	160	150	150	1	260	0.150
AYC*-53	558,000	12,750	1,750	130	140	160	1	265	0.327
AYC*-54	387,500	4,250	50	50	50	100	0.5	255	0.063
AYC*-55	362,500	3,250	90	50	60	150	0.5	260	0.090
AYC*-56	573,000	35,500	6,250	1,000	750	360	2	265	0.763
AYC*-57	822,000	37,500	7,260	750	250	260	2	265	0.733
AYC*-58	500,000	42,500	8,000	1,250	500	230	3	265	0.775
AYC*-59	550,000	63,800	7,250	1,500	500	160	3	260	0.763
AYC-60	562,000	1,250	40	10	20	70	0.5	290	0.250
AYC-61	465,000	9,250	500	160	140	170	1	275	0.455
AYC-62	562,000	7,750	500	80	90	190	0.75	255	0.415
AYC-63	323,000	250	250	30	20	50	0.5	250	0.430
AYC*-64	712,000	2,500	-	10	-	20	0.5	245	0.065
AYC*-65	476,000	3,500	50	20	20	60	0.5	240	0.085
AYC*-66	492,500	19,000	2,250	500	500	433	1	275	0.568
AYC*-67	740,000	20,000	3,000	500	750	289	1	255	0.530
AYC*-68	391,000	14,500	1,000	80	30	90	0.75	255	0.237
AYC*-69	491,000	22,250	4,000	110	80	110	0.75	255	0.338
AYC*-70	512,000	30	40	10	-	20	2	205	0.073
AYC*-71	690,000	500	250	110	60	-	2	205	0.175
AYC*-72	750,000	150	110	20	10	20	2	205	0.103
AYC*-73	918,000	12,000	1,000	750	120	80	4	205	0.510
AYC*-74	1,208,000	14,500	1,500	500	250	120	4	205	0.500

a - Read from smooth curves of Fig. 11 using Photometer Reading.

TABLE IX  
RATE OF NORMAL SETTLING

<u>RUN NO.</u>	<u>TIME OF IRRAD. (MIN)</u>	<u>CRYSTAL CURRENT (MA)</u>	<u>SETTLING TIME (MIN)</u>	<u>PHOTELOMETER READING</u>	<u>VOLUME PER CENT BENZENE FROM FIG. 11<sup>a</sup></u>	<u>VOLUME PER CENT BENZENE CALC. FROM MICROSCOPIC DATA</u>
BY*-44	5	250	1	18.0	0.860	1.42
			18	28.0	0.640	0.762
			47	48.0	0.365	0.631
			69	61.0	0.242	0.370
BY*-45	8	170	1	66.0	0.208	
			18	77.0	0.135	
			41	83.0	0.097	
			63	90.0	0.095	
BY*-46	6	250	1	52.0	0.317	
			32	69.0	0.188	
			38	72.0	0.168	
			49	77.0	0.135	
			59	82.0	0.103	
			69	86.0	0.078	
			80	93.0	0.037	
			90	92.0	0.043	
			100	94.0	0.043	
			BY*-47	4	210	1
15	79.0	0.122				
31	83.0	0.095				
46	86.0	0.078				
63	89.0	0.060				
79	93.0	0.037				
BY*-48	5	205	3	65.0	0.215	
			21	74.5	0.152	
			36	82.5	0.100	
			52	85.0	0.085	
			65	86.0	0.078	
BY*-49	8	195	4	7.5	1.30	
			18	11.5	1.08	
			32	15.5	0.950	
			47	23.5	0.708	
			63	32.0	0.585	
			78	39.5	0.480	
			92	49.5	0.345	
			107	59.0	0.257	

Note: 7cc of H<sub>2</sub>O and 5cc of benzene were irradiated in all runs.

a - Read from smooth curve of Fig. 11 using Photolometer Reading.

TABLE X  
EFFECT OF IRRADIATION ON SETTLING

<u>RUN NO.</u>	<u>TIME OF IRRAD. (MIN)</u>	<u>EMULSIFICATION CRYSTAL CURRENT (MA)</u>	<u>SETTLING TIME (MIN)</u>	<u>DE-EMULSIFICATION CRYSTAL CURRENT (MA)</u>	<u>PHOTEL. READING</u>	<u>CONCEN. VOL. % FIG. 11<sup>a</sup></u>
BY*-75	2.0	270	1	-	63.0	0.227
			12	240	71.5	0.173
			25	250	83.0	0.097
			35	250	97.0	0.015
BY*-76	3.0	250	1	-	43.0	0.435
			13	250	60.0	0.250
			25	250	75.5	0.145
			37	250	88.0	0.065
BY*-77	3.0	250	1	-	26.5	0.665
			11	225	43.5	0.425
			25	225	69.0	0.187
			38	225	77.0	0.135
			50	225	85.0	0.085
BY*-78	2.5	250	1	-	38.5	0.495
			15	180	63.5	0.225
			29	180	75.0	0.148
			41	180	81.0	0.110
BY*-79	3.0	225	1	-	45.0	0.405
			14	180	64.0	0.220
			27	180	72.0	0.168
			39	180	79.5	0.119
			49	205	87.5	0.070
BY*-123	4.5	225	1	-	25.5	0.680
			13	180	37.0	0.515
			25	180	46.0	0.392
			38	180	57.0	0.273
			50	180	64.0	0.220
BY*-124	1.5	225	1	-	55.0	0.290
			11	180	68.0	0.195
			23	180	74.0	0.155
			36	180	79.0	0.122
			48	180	90.0	0.055
BY*-125	4.0	225	1	-	24.0	0.700
			13	220	38.0	0.500
			26	220	57.0	0.273
			39	220	68.0	0.195
			51	220	75.0	0.150

Note: 7cc of H<sub>2</sub>O and 5cc of benzene were irradiated for several minutes. The entire layer of benzene was then drawn off and the benzene in water emulsion allowed to settle with a two minute irradiation period prior to each concentration reading.

a - Read from smooth curve of Fig. 11 using Photometer Reading.

TABLE XI  
NORMAL SETTLING

RUN NO.	<u>44</u>	<u>44</u>	<u>44</u>	<u>44</u>	<u>45</u>	<u>45</u>	<u>45</u>	<u>45</u>
TIME OF IRRADIATION (MIN)	5				8			
CRYSTAL CURRENT (MA)	250				170			
PHOTELOMETER READING	18.0	28.0	48.0	61.0	66.0	77.0	83.0	90.0
SETTLING TIME (MIN)	1	18	47	69	1	18	41	63

NO. OF PARTICLES

NO. OF 1/400 mm<sup>2</sup> SQUARES OBSERVED

PARTICLE DIAMETER (MICRONS)	<u>44</u>	<u>44</u>	<u>44</u>	<u>44</u>	<u>45</u>	<u>45</u>	<u>45</u>	<u>45</u>
11-20u	2	1	-	1	-	-	-	-
NO. SQUARES	8	16	16	16	16	16	32	16
9-11u	2	8	1	2	-	-	-	-
NO. SQUARES	8	16	16	16	16	16	32	16
7-9u	13	11	1	1	-	-	-	-
NO. SQUARES	8	16	16	16	16	16	32	16
5-7u	112	84	36	12	2	3	8	2
NO. SQUARES	8	16	16	16	16	16	32	16
3-5u	145	126	37	28	7	3	6	-
NO. SQUARES	8	16	16	16	16	16	32	16
0-3u	545	2,029	4,586	1,958	1,459	2,069	1,994	1,494
NO. SQUARES	8	16	16	16	16	16	32	16

TABLE XII

## ABSORPTION AND EFFICIENCY RESULTS

RUN NO.	TIME OF IRRAD. (MIN)	CRYSTAL CURRENT (MA)	IRRAD. MATERIAL	$\Delta H_1$	$\Delta H_2$	$\Delta H_1 + \Delta H_2$	$E_1$	$E_2$	$E_3$
80	1	225	12cc H <sub>2</sub> O	69.6	308	378			
81	1	225	"	61.2	308	369			
82	1	225	"	69.6	308	378			
83	2	225	"	109	770	879			
84	2	225	"	104.5	692	797			
85	2	225	"	100.8	692	793			
86	3	225	"	117.5	924	1,942			
87	3	225	"	116.2	924	1,040			
88	4	225	"	120	1,153	1,273			
89	4	225	"	120	1,153	1,273			
90	2	180	"	39.2	231	280			
91	2	180	"	52.8	308	361			
92	4	180	"	84.0	692	776			
93	4	180	"	76.7	539	616			
94	6	180	"	76.7	846	923			
95	1	225	5cc benz.	58.2	308	366	6.3	15.8	4.0
96	1	225	7cc H <sub>2</sub> O	96.2	693	789	13.5	12.2	8.6
97	1	225	"	103	925	1,028	17.7	10.0	11.1
98	1	225	"	92.0	231	323	5.6	28.5	3.5
99	1	225	"	79.5	308	388	6.7	20.5	4.2
100	2	225	"	127	616	743	6.4	17.0	4.0
101	2	225	"	160	693	853	7.4	18.9	4.6
102	2	225	"	174	693	867	7.5	19.6	4.7
103	3	225	"	179	693	872	5.0	20.4	3.1
104	3	225	"	182	693	875	5.0	20.5	3.2
105	3	225	"	212	924	1,136	6.5	18.6	4.1
106	3	225	"	225	924	1,149	6.8	19.4	4.1
107	4	225	"	211	1,232	1,443	6.2	14.6	3.9
108	4	225	"	200	1,232	1,432	6.1	13.9	3.9
109	2	225	"	162	616	778	6.7	20.5	4.2
110	2	180	"	107	231	338	3.2	31.4	2.3
111	2	180	"	99.0	231	330	3.1	29.8	2.2
112	4	180	"	134	616	750	3.5	17.8	2.5
113	4	180	"	124	693	817	3.8	15.2	2.8
114	6	180	"	147	924	1,061	<u>3.3</u>	<u>12.9</u>	<u>2.5</u>
115	1	225	12cc benz.	33.8	308	342	Ave. 6.5	19.4	4.6
116	1	225	"	33.8	308	342			
117	2	225	"	46.0	616	662			
118	2	225	"	42.2	616	658			
119	3	225	"	55.8	848	904			
120	3	225	"	45.6	848	894			
121	4	225	"	48.6	1,155	1,204			
122	4	225	"	46.5	1,155	1,202			

TABLE XIII  
ABSORPTION AND EFFICIENCY DATA

RUN NO.	TIME OF IRRAD. (MIN)	CRYSTAL CURRENT	t <sub>1</sub> °C. (TEST TUBE)	t <sub>2</sub> °C.	T <sub>1</sub> °C. (OIL BATH)	T <sub>2</sub> °C.	Δ <sub>b</sub>	Δ <sub>T</sub>	MATERIAL IN TEST TUBE	OBSERVATION TIME (MIN. AFTER IRRAD.)	RATE OF (v) DROP-OFF (v/min)	ROOM TEMPERATURE
80	1	225	28.4	33.2	28.4	28.8	4.8	0.4	12ml	1	1.0	28.4
81	1	225	28.9	34.0	29.0	29.4	4.1	0.4	H <sub>2</sub> O	1	1.0	28.4
82	1	225	29.6	34.4	29.7	30.1	4.8	0.4	"	1	1.0	28.4
83	2	225	29.9	37.0	30.0	31.0	7.1	1.0	"	1	2.0	28.4
84	2	225	31.1	37.8	31.0	31.9	6.7	0.9	"	1	2.0	28.4
85	2	225	31.7	38.1	31.7	32.6	6.4	0.9	"	1	2.0	28.4
86	3	225	26.9	34.7	26.8	28.0	7.8	1.2	"	1	2.0	27.5
87	3	225	27.5	35.2	27.5	28.7	7.7	1.2	"	1	2.0	27.5
88	4	225	28.5	36.5	28.5	30.0	8.0	1.5	"	1	2.0	28.0
89	4	225	29.9	37.9	29.9	31.4	8.0	1.5	"	1	2.0	28.0
90	2	180	30.9	34.0	31.0	31.3	3.1	0.3	"	1	1.0	28.7
91	2	180	31.0	34.4	31.1	31.5	3.4	0.4	"	1	1.0	29.0
92	4	180	31.0	36.0	31.1	32.0	5.0	0.9	"	1	2.0	29.3
93	4	180	31.5	36.2	31.6	32.3	4.8	0.7	"	1	1.6	29.0
94	6	180	31.7	36.7	31.7	32.8	5.0	1.1	"	1	1.4	27.5
95	1	225	25.3	30.7	25.4	25.8	5.4	0.4	5ml	1	1.2	25.5
96	1	225	25.6	34.5	25.6	26.5	8.9	0.9	benz	1	2.0	25.5
97	1	225	25.7	35.0	25.7	26.9	9.3	1.2	7ml	1	2.6	25.7
98	1	225	27.7	35.7	27.7	28.0	8.0	0.3	H <sub>2</sub> O	1	2.4	27.0
99	1	225	28.0	35.0	28.0	28.4	7.0	0.4	"	1	2.0	27.5
100	2	225	28.4	39.2	28.4	29.2	10.8	0.8	"	1	3.6	27.5
101	2	225	29.1	42.8	29.1	30.0	13.7	0.9	"	1	4.4	27.6
102	2	225	30.0	45.2	30.0	30.9	15.2	0.9	"	1	4.4	27.9
103	3	225	25.0	39.8	25.0	25.9	14.8	0.9	"	1	5.4	22.0
104	3	225	25.9	41.9	25.9	26.8	16.0	0.9	"	1	4.6	22.5
105	3	225	23.8	43.1	23.8	25.1	19.3	1.2	"	1	5.0	21.0
106	3	225	24.8	44.2	24.8	26.0	19.4	1.2	"	1	6.0	21.7
107	4	225	26.4	44.8	26.4	28.0	18.4	1.6	"	1	5.4	22.0
108	4	225	27.3	44.7	27.3	28.9	17.4	1.6	"	1	5.2	22.0
109	2	225	28.0	41.4	28.0	28.8	13.4	0.8	"	1	4.9	22.6
110	2	180	28.0	37.3	28.0	28.3	9.3	0.3	"	1	2.8	22.9
111	2	180	27.8	36.8	27.8	28.1	9.0	0.3	"	1	2.2	23.2
112	4	180	27.7	39.2	27.7	28.5	11.5	0.8	"	1	3.6	23.0
113	4	180	28.0	38.9	28.0	28.9	10.9	0.9	"	1	3.2	23.3
114	6	180	28.5	40.0	28.5	29.7	11.5	1.2	"	1	4.0	23.7
115	1	225	22.0	26.7	22.0	22.4	4.7	0.4	12ml	1	3.0	23.0
116	1	225	22.7	27.2	22.7	23.1	4.5	0.4	benz	1	3.2	23.3
117	2	225	23.1	30.0	23.1	23.9	6.9	0.8	"	1	3.6	23.9
118	2	225	24.0	30.4	24.0	24.8	6.4	0.8	"	1	3.2	24.2
119	3	225	24.9	32.4	24.9	26.0	7.5	1.1	"	1	5.2	24.8
120	3	225	26.0	33.0	26.0	27.1	7.0	1.1	"	1	3.4	26.9
121	4	225	27.0	34.5	27.0	28.5	7.5	1.5	"	1	3.6	26.5
122	4	225	28.2	35.6	28.2	29.7	7.4	1.5	"	1	3.2	26.6

TABLE XIVDATA FOR DETERMINATION OF POWER SUPPLIED BY POWER AMPLIFIER

Plate voltage 3,000 volts

CRYSTAL CURRENT		NO LOAD PLATE CURRENT		FULL LOAD PLATE CURRENT	
(AC)	(MA)	(DC)	(MA)	(DC)	(MA)
	225		50		185
	205		50		182
	180		48		172

TABLE XVD. C. ENERGY IN THE POWER AMPLIFIER PLATE CIRCUIT

CRYSTAL CURRENT (MA)	TIME OF IRRAD. (MIN)	INCREMENTAL ENERGY (CAL)	TOTAL ENERGY (CAL)
225	1	5,840	9,250 <sup>7960</sup>
225	2	11,670	18,500
225	3	17,500	27,800 <sup>error</sup>
225	4	23,400	37,100
180	1	5,350	7,400
180	2	10,700	14,800
180	3	16,100	22,200
180	4	21,400	29,600
180	5	26,800	37,000
180	6	32,100	44,400

TABLE XVIDATA FOR CALCULATION OF E<sub>2</sub>WEIGHT OF OIL BATH

Weight of oil plus crock	= 4,073 g.
Weight of crock	= 2,326 g.
Weight of oil	= 1,747 g.

MISCELLANEOUS DATA

Cp of transformer oil at 20°C	= 0.44 cal/g°C.
Cp of benzene from 6-60°C	= 0.419 cal/g°C.
Density of benzene	= 0.872 g/cc.



SAMPLE CALCULATIONCONCENTRATION CALCULATION:

AYC*-21	0	1	2	3	4	5	
(2u)-	(2,281)	x	(4.18)	x	(333)	x (10 <sup>-9</sup> )	0.00393
(4u)-	(201)	x	(33.5)	x	"	x "	0.00224
(6u)-	(17)	x	(113)	x	"	x "	0.000639
(8u)-	(1)	x	(268)	x	"	x "	0.0000829
(10u)-	(3)	x	(523)	x	"	x "	0.000523
(13u)-	(1)	x	(1,150)	x	"	x "	0.000383
							<u>0.007734</u>
							0.773% benzene by volume

Column 0 = the average particle size of each group into which the particles were classified except above 10 microns where column 0 represents the actual particle size.

Column 1 = the number of particles observed in the size group indicated.

Column 2 = the volume of a sphere in cubic microns of diameter indicated in column 0.

Column 3 = the counting chamber factor to convert to particles per cubic millimeter.

Column 4 = the factor to convert from cubic microns to cubic millimeters.

Column 5 = the concentration expressed as cubic millimeters per cubic millimeter.

CALCULATION OF PARTICLES PER CUBIC MILLIMETER:

The number of particles per cubic millimeter is the product of the number of particles observed in a particular size group and the counting chamber factor associated with the number of chamber squares of a particular area observed.

For the smallest squares with an area of  $1/400 \text{ mm}^2$ , the factor is:

$$(4,000)/(\text{no. of squares counted})$$

For the largest squares with an area of  $1/16 \text{ mm}^2$ , the factor is:

$$(160)/(\text{no. of squares counted})$$

For run no. AYC\*-21:

Number of particles (0-3u) in diameter counted = 2,821

Number of smallest squares counted = 12

$$\text{Particles /mm}^3 = (2,821) (4,000/12) = \underline{942,000}$$

RATE OF t DROP OFF

This figure was obtained by recording the temperature of the irradiated material at 30 seconds and at 1 minute after irradiation. Twice the difference between these two readings is the rate of t drop of per minute.

For Run no. 80

$$t_{30} = 33.7^{\circ}\text{C.}$$

$$t_2 = 33.2^{\circ}\text{C.}$$

$$\Delta t = 0.5^{\circ}\text{C.}$$

Rate of t drop of 1<sup>o</sup>/Minute.

INCREMENTAL ENERGY POWER AMPLIFIER PLATE CIRCUIT

$$P = V(I_2 - I_1) t$$

Where V = plate voltage (volts)

I = full load plate current (amps) at a given crystal current

I<sup>2</sup> = no load plate current (amps)

t = time of irradiation (min)

For Run no. 100

crystal current = 225 ma.

time of irradiation = 2 min.

from Table XIV at 225 ma.

no load plate current = 50 ma.

full load plate current = 185 ma.

plate voltage = 3,000 volts

$$P = (3,000) (0.185 - 0.050) (2) = 810 \text{ watt min.}$$

$$(810) (1/1,000) (1/60) (860,445 \text{ g. cal./kwh.}) = 11,670 \text{ g. cal.}$$

The values in Table XV are simply the g. calories/min. calculated by this method times the time of irradiation at given values of the crystal current.

TOTAL ENERGY IN POWER AMPLIFIER PLATE CIRCUIT

$$P = V(I_2) t$$

For run no. 96

crystal current = 225 ma.  
time of irradiation = 1 min.

From Table XIV at 225 ma.  
full load plate current = 185 ma.  
plate voltage = 3,000 volts

$$P = (3,000) (0.185) (1) (1/1,000) (1/60) (860,445)$$

$$= \underline{9,250 \text{ cal/min.}} \quad \text{error}$$

7,960

CALCULATION OF ENERGY ABSORBED BY THE IRRADIATED MATERIAL:

$$H_1 = (C_p N) (\Delta t)$$

For run no. 100

Material in test tube = 5cc of benzene  
7cc of water

$$t_1 = 28.4^\circ\text{C}$$

$$t_2 = 39.2^\circ\text{C}$$

Rate of t drop off = 3.6°/min.

$$\Delta t = 10.8^\circ\text{C}$$

$\Delta t$  corrected for drop off = 14.4°

$C_p$  for benzene = 0.419 cal/g°C

$C_p$  for H<sub>2</sub>O = 1.0 cal/g°C

Density of benzene = 0.872 g/cc

$$H_1 = N C_p \times \Delta t = (7) (1.0) (0.419) (5) (0.872) = (14.4)$$

$$\underline{H_1 = 127 \text{ cal.}}$$

CALCULATION OF ENERGY ABSORBED BY THE OIL BATH:

For run no. 100

Material- transformer oil

$$T_1 = 28.4^\circ\text{C}$$

$$T_2 = 29.2^\circ\text{C}$$

$$\Delta T = 0.8^\circ\text{C}$$

CALCULATION OF ENERGY ABSORBED BY THE OIL BATH, cont'd.

$C_p$  for the oil = 0.44 cal/g<sup>o</sup>C  
 Weight of the oil = 1747 g.

$$H_2 = NC_p \Delta T = (1747) (0.44) (0.8) = \underline{616 \text{ cal.}}$$

The electrical energy supplied to the crystal holder is assumed to be completely converted to heat and is therefore the sum of  $\Delta H_1$  and  $\Delta H_2$ .

$$127 + 616 = \underline{743 \text{ cal.}}$$

CALCULATION OF EFFICIENCIES:

$E_1$  is the efficiency of conversion of incremental energy from the power supply to energy applied to the crystal holder, and is calculated from figures in Table XII and XV.

For run no. 107

Crystal current = 225 ma.

Time of irradiation = 4 min.

From Table XII the energy applied to the crystal holder is the sum of  $\Delta H_1$  and  $\Delta H_2$ .

$$\Delta H_1 + \Delta H_2 = 1,443 \text{ cal.}$$

From Table XV the incremental energy supplied at 225 ma. for four minutes is 23,400 cal.

$$E_1 = (\Delta H_1 + \Delta H_2) / P = (1,443 / 23,400) (100) = \underline{6.2\%}$$

$E_2$  is the per cent of the electrical energy supplied to the crystal holder which is absorbed in the irradiated material.  $E_2$  is calculated from the figures of Table XII and is expressed as:

$$(\Delta H_1) / (\Delta H_1 + \Delta H_2)$$

For run no. 107

$$E_2 = (211 / 1,443) (100) = \underline{14.6\%}$$

CALCULATION OF  $E_3$ 

$E_3$  is the efficiency of conversion of total energy in the power amplifier plate circuit to energy applied to the crystal holder and is calculated from figures in Tables XII and XV.

For run no. 107

Crystal current = 225 ma.

Time of irradiation = 4 min.

From Table XII  $\Delta H_1 + \Delta H_2 = 1,443$  cal.

From Table XV the total energy supplied at 225 ma. for four minutes = 37,100 cal.

$$E_3 = (1,443/37,100) (100) = \underline{3.9\%}$$

CALIBRATION OF AC CRYSTAL CURRENT  
METERS

Figures 28 and 29 are the calibration curves for the two crystal current meters used in the course of this study. Meter number 1 was used in runs 1 through 49 at which point it was damaged beyond repair. Meter number 2 was used in all subsequent runs. Both meters were calibrated with a Weston model 735 Industrial Circuit Tester which consists of an ammeter coupled with a resistance box to vary the current. The current was adjusted to an even scale reading on the crystal current meter with the resistance knob, and the Weston ammeter reading was then recorded.

Both meters were radio frequency meters of the thermocouple type and, therefore, independent of frequency.

AMPERES

FIGURE 27

CALIBRATION OF CRYSTAL CURRENT METERS

AC Meter No. 2  
Serial No. 6750

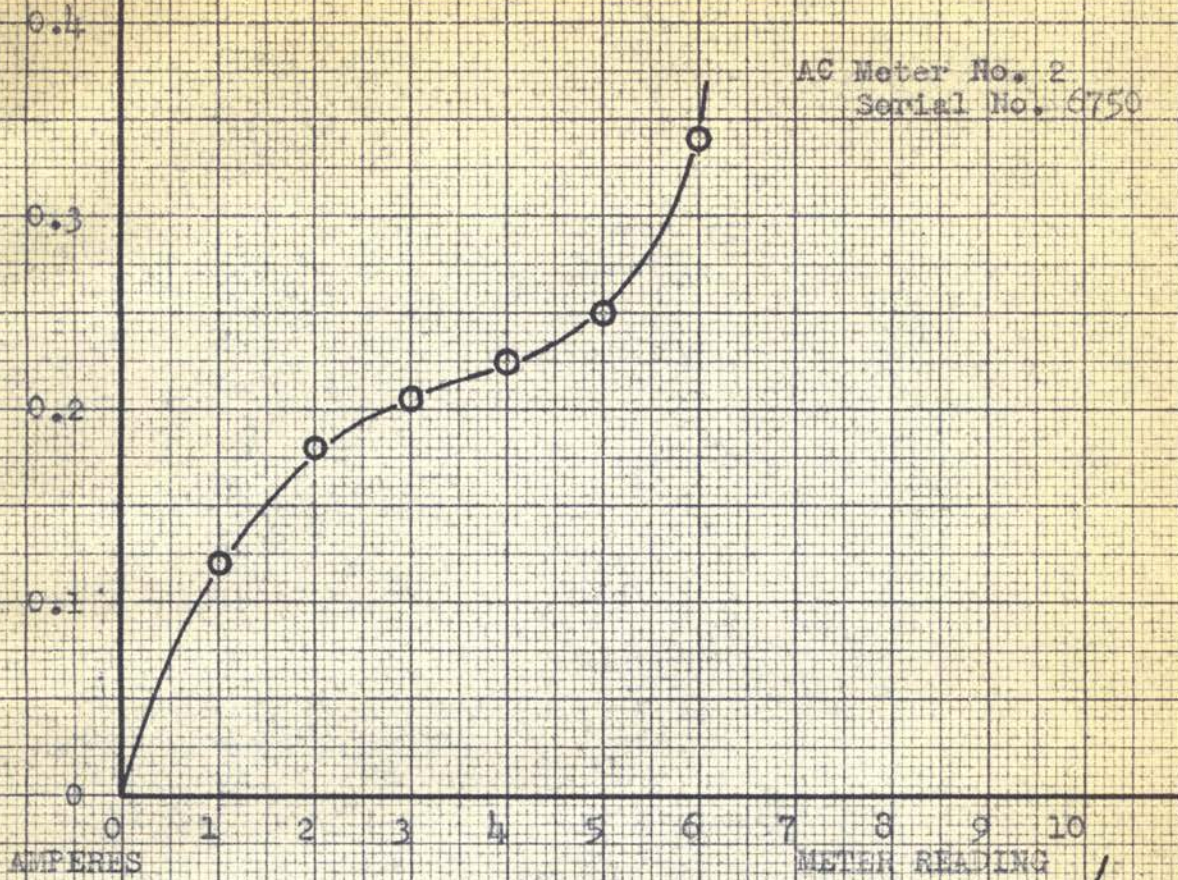
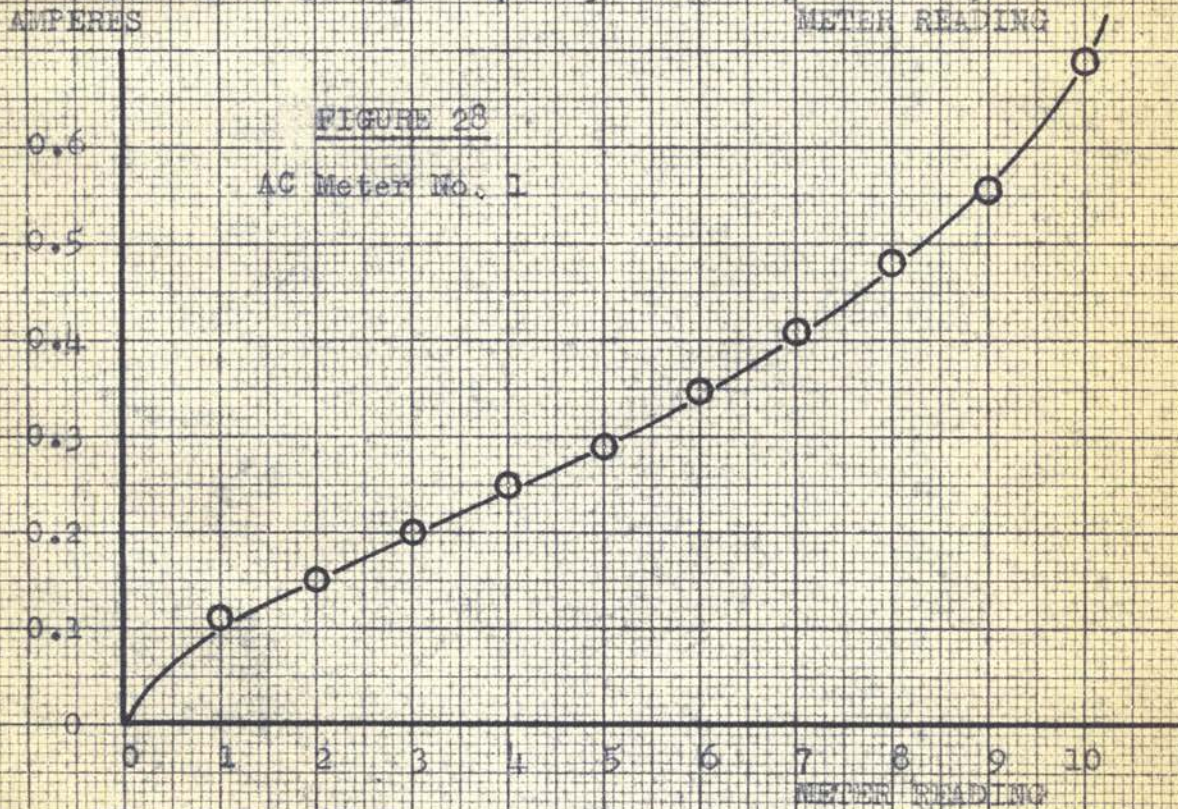


FIGURE 28

AC Meter No. 1



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