

The University of Manitoba

THE DECAY TIMES OF ORGANIC SCINTILLATORS

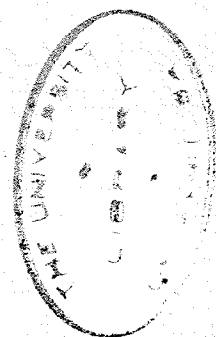
Being a Thesis submitted to the Committee
on Postgraduate Studies in partial
fulfilment of the requirements for
the Degree of Master of Science

by

William Robert Wall

Winnipeg, Manitoba

August, 1956.



A B S T R A C T

The decay times of some organic scintillators have been studied. The decay times were obtained through measurements of the amplitude of photomultiplier pulses as a function of multiplier load resistance. The finite rise time of the pulse amplifier used in conjunction with the multiplier was corrected for through the use of the amplifier indicial response and Duhamel's superposition theorem.

The data collected indicated that within experimental errors organic solution decay times were not influenced by changes in solvent or by changes in solute concentration. There was noted a marked change in decay time for changes in solute. These results were predicted by the present theories of scintillation processes.

There was noted a linear variation of quencher concentration with the reciprocal of the decay time for a liquid solution. This indicated that the quenching process was a collisional one and not static.

The decay times of several new scintillators were determined. These included metal-loaded liquids and several gels.

A C K N O W L E D G E M E N T S

To Dr. W. Turchinetz, Assistant Professor of the Physics Department, University of Manitoba, I am indebted for encouragement to undertake the study and for his early instructions concerning research procedure. Throughout the whole period of the study I found his friendly guidance and his discerning criticism invaluable.

I wish to express my sincere appreciation to the National Research Council whose bursary and summer supplements have made this research possible.

I wish to thank also the many individuals whose sympathetic and friendly co-operation has aided me in the completion of this study. Among these, I would like to mention:

Dr. R.W. Pringle, 53 Orchard Road, Edinburgh.

Dr. K.I. Roulston, Department of Physics,
University of Manitoba.

Professor R.J. Johnston, Department of Electrical
Engineering, University of Manitoba.

W.R. Wall,
August, 1956.

T A B L E O F C O N T E N T S

	Page
ABSTRACT	i
ACKNOWLEDGMENTS	ii
LIST OF FIGURES	v
CHAPTER 1: HISTORICAL	
1.1 Introduction	1
1.2 Pulsed Crystal Method	2
1.3 Pulsed Multiplier Method	3
1.4 Modulated Multiplier Method	4
1.5 Pulse Amplitude Method	4
CHAPTER 2: EXPERIMENTAL - PART ONE	
2.1 Introduction	6
2.2 The Hy-Tramp	6
2.3 High Gain Photomultiplier	9
2.4 Signal Delay	11
2.5 Photography	14
CHAPTER 3: THEORETICAL CONSIDERATIONS	
3.1 The Theory of the Multiplier Output Circuit	16
3.2 The Pulse Amplitude Method	18
3.3 Consideration of Approximations	20
3.4 The Amplifier Correction Curve	21
CHAPTER 4: EXPERIMENTAL - PART TWO	
4.1 The Amplifier Correction Curve	26
4.2 The Load Resistor Correction Curve	34
4.3 Decay Time of Anthracene	37
4.4 Unknown Decay Time Measurement	40

CHAPTER 5: RESULTS	47
CHAPTER 6: DISCUSSION OF RESULTS	
6.1 Experimental Errors	50
6.2 Other Experimental Decay Times	51
6.3 Plastic Solutions	52
6.4 Liquid Solutions	53
6.5 Scintillating Gels	54
6.6 The Kinetics of Quenching Processes	55
6.7 Experimental Quenching	57
APPENDIX 1: MULTIPLE DECAY SCHEME	60
APPENDIX 2: FINITE RISE TIME DECAY SCHEME	62
APPENDIX 3: LAPLACE TRANSFORM THEOREM	64
APPENDIX 4:	
Table 1	65
Table 2	66
Table 3	67
BIBLIOGRAPHY	73

LIST OF FIGURES

	page
1. Hy-Tramp Schematic	8
2. Photomultiplier Assembly	10
3. K1295 Multiplier Schematic	12
4. 6342 Multiplier Schematic	13
5. Graphical Computation for Amplifier Correction Curve	25
6. The Step Function Generator	27
7. The Indicial Response	28
8. Curves of Table 3	30
9. Calculated Response Functions	31
10. Amplifier Correction Curve	33
11. Stray Capacity Measurement Circuit	35
12. Stray Capacity Decay Pulses	35
13. Stray Capacity Decay Plot	36
14. Load Resistor Correction Curve	38
15. Schematic for Anthracene Decay Measurement	39
16. Anthracene Pulses	39
17. Semi-log Plot of Anthracene Pulses	41
18. Schematic for Decay Time Measurements	42
19. Typical Data for Stilbene Measurement	44
20. Variation of (Decay Time) ⁻¹ With Quencher Concentration	58

CHAPTER 1

HISTORICAL

1.1 INTRODUCTION

The accurate measurement of scintillation decay times is a rather important task. Such measurements not only yield the frequency limitation of the scintillation counter but also furnish data useful in the illumination of the scintillation mechanism itself. Hence there are found numerous contributions in the recent literature (1, 2, 3) in this experimental field.

Because the decay times of the fluorescence from organic scintillators are in the milli-microsecond (mus.) region they are very difficult to measure. It is only quite recently that reliable techniques have become available for such measurements.

Most organic scintillators have rise times which are, for all practical purposes, zero and decay times of the order of one or two mus. Because of multiplier transit time spread the pulse is stretched slightly so that rise time of the output electrical* pulse is about one mus. This voltage pulse, in a normal multiplier, has an amplitude in the millivolt region. The standard method of measuring such pulses is through the use of an oscilloscope. If the pulse can be displayed faithfully, and photographed, then a simple measurement yields the time taken for the pulse to decay to $1/e$ of its peak height.

* 'Electrical' refers to current or voltage and not to charge.

The difficulties that arise with this procedure are three in number.

First of all, sufficient linear gain must be obtained in order to make appreciable deflections on the scope. This can be obtained, with slower pulses, through the use of conventional amplifiers. But, due to the short decay times of pulses from organic scintillators, amplifier bandwidths well in excess of 500 MC/S are required to pass the high frequency components of the pulse. Since this is difficult to achieve, the usual procedure has been to use extra high gain photomultipliers.

Secondly, a linear oscilloscope sweep speed must be obtained in the low mps. range. Since all sweep circuits are non-linear for the initial portion of sweep, it is required that the sweep be well under way by the time the decay pulse appears at the Y-plates. This necessitates a delay somewhere in the multiplier circuit.

Thirdly, the trace intensity must be such that individual pulses are bright enough to be photographed. This requires the ultimate in high speed available light photography.

1.2 PULSED CRYSTAL METHOD

Of the various methods that have been employed, one of the first and the most straightforward was that used by Swank and Buck (4). This method was called the pulsed crystal

method of measurement because the scintillator was excited by a ^{pulsed} 7.5 k.e.v. X-ray tube*. The point here was that by using the 7.5 k.e.v. X-ray one gets nearly total absorption and hence a monoenergetic photon source in the scintillator. Thus output multiplier voltage pulses were all the same size and so could be superimposed on the oscilloscope recording camera to give an intense image. The trigger for the scope was obtained from the pulse generator which triggered the X-ray tube. A delay was inserted between the pulse generator and the X-ray tube. This delay was of sufficient length to insure that the decay pulses reached the Y-plates well after the sweep had started. The gain problem was solved by using a high gain multiplier.

1.3 PULSED MULTIPLIER METHOD

Singer, Neher and Ruehle (3) employed what was termed the pulsed photomultiplier method. It was found that, by applying the dynode voltage in the form of a short extra high tension (EHT.) pulse, the frequency response of the multiplier tube could be extended and the peak multiplier output current increased with no distortion. The pulse applied to the multiplier was 10,000 volts in magnitude and 0.1 microseconds long. This procedure enabled current gains as high as 10^9 to be achieved. The sweep trigger was obtained from the EHT. pulser. Then, a delay was inserted between the pulser and multiplier. The photography was accomplished through the recording of single traces on a special travelling wave oscilloscope tube using an

* These X-rays are the characteristic X-rays of the target.

f/1.2 lens and Kodak Linagraph pan film.

1.4 MODULATED MULTIPLIER METHOD

A third and very radical procedure was due to Birks and Little (5) and was called the modulation method. The light from an air discharge tube was modulated by a 7.5 MC/S signal. This light excited the scintillator. The photomultiplier itself was modulated at 15 MC/S. Observations were made on the phase and modulation of both the incident light and of the output multiplier current. The fluorescence decay time was then computed either from the phase lag between input light and multiplier emission or from the relative modulation of the two. This method completely bypasses the three difficulties of section 1.1.

1.5 PULSE AMPLITUDE METHOD

The last main method, due to Kallmann, Furst and Bittman (6) was called the pulse amplitude method because the basic measurements were on the amplitude of the photomultiplier pulse as a function of multiplier load resistor. A standard scintillation counter apparatus was constructed with the normal slow amplifiers and differential pulse height analyzer. The scintillator to be measured was mounted and irradiated with γ rays. The end point of the resultant spectrum was determined. The value of this end point was plotted as a function of multiplier load resistor. It was possible to extract from such a plot the decay time of the scintillator. Because of

the slowness of the electronics following the multiplier the method gave poorer results for the shorter decay times. But this method did bypass the problems of delay and photography.

CHAPTER 2

EXPERIMENTAL - PART ONE2.1 INTRODUCTION

The procedure employed in the present work was largely governed by the equipment available. A Tektronix Type 517 oscilloscope and several high-gain multiplier tubes were available. The scope could produce a 5 millimicrosecond per centimeter sweep which was ample for the display of organic decay pulses. However, the scope Y-amplifiers had insufficient bandwidth in that their rise time was about 7 μ s. Hence these amplifiers could not be used as they would have distorted fast pulses with decay times in that region of time. Therefore, if the direct measurement approach was to be adopted, the three problems of gain, delay and photography had to be surmounted.

2.2 THE HY-TRAMP

The deflection sensitivity of the scope Y-plates was about 40 volts per centimeter. With normal multiplier voltages (1400 on an R.C.A. No. 6342) output pulses as high as 0.1 volts could be easily obtained. To get appreciable deflections on the scope a gain of from 200 - 400 was required beyond the multiplier.

To obtain such a gain a new type of secondary emission tube called a Hy-Tramp, was tested. The performance figures of the tube indicated gains of the order of 400 with a rise time of about 1 μ s.

The Hy-Tramp is a combination tetrode and seven dynode secondary emission amplifier. The input signal was applied to the control grid of the tetrode (Figure 1) whence it travelled and was multiplied in amplitude down the dynode chain. This tube was essentially an auxiliary photomultiplier.

The Hy-Tramp was connected as suggested by the manufacturers' data* with one exception. It was suggested that the dynodes be battery driven but it was decided to use a single power supply and a string of dynode dropping resistors. To stabilize the dynode voltages under pulse conditions the dropping resistors were shunted by condensers.

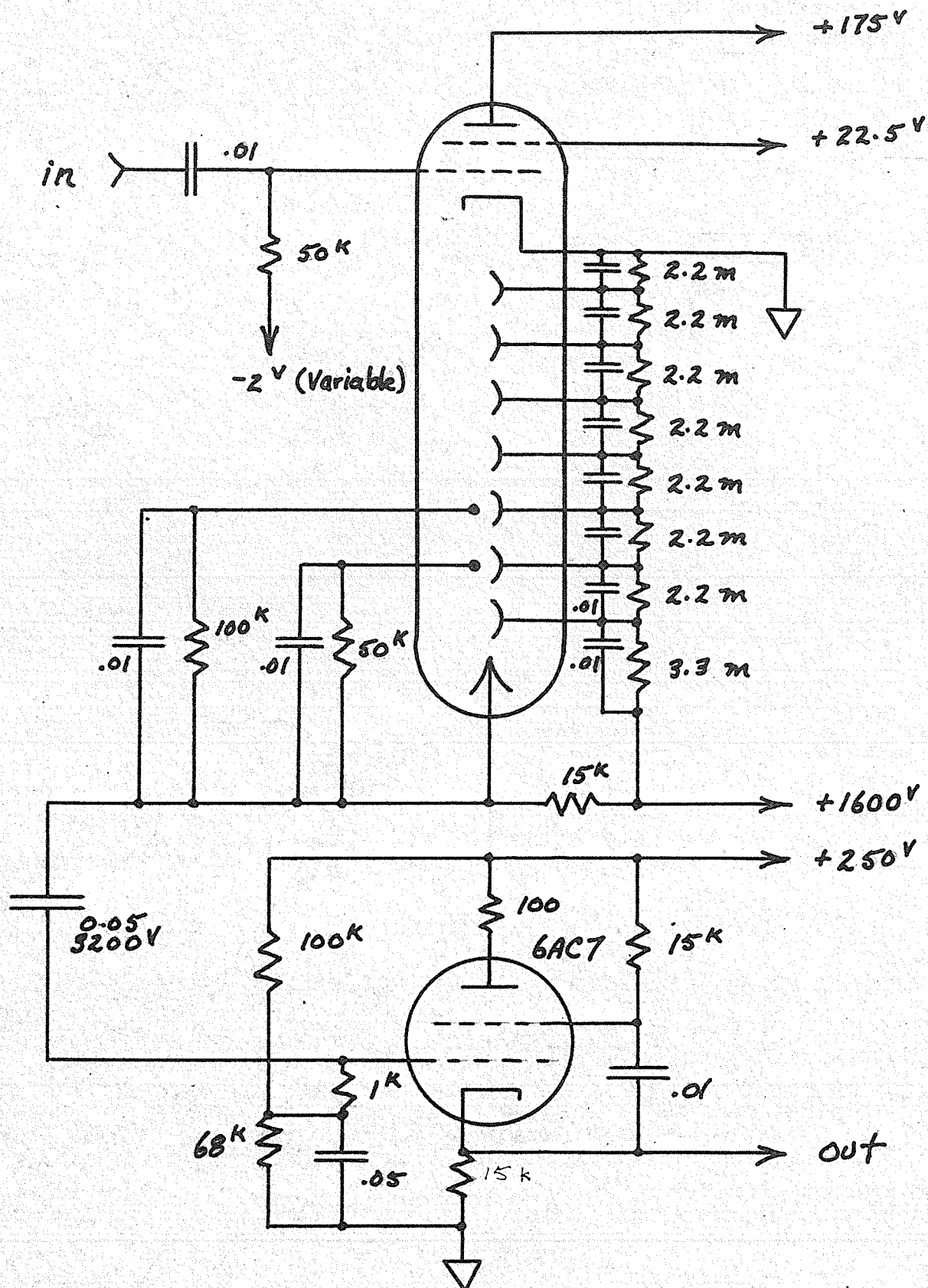
When the tube was tested it was found to have a gain of 400 with a 15000 ohm load resistor. This gain measurement was quite uncertain due to a very high noise level in the tube of about 0.1 volts as referred to the input. Signal pulses in excess of 0.2 volts blocked the Hy-Tramp.

It was thought that perhaps this noise level was due to stray light effects or perhaps due to pick-up. A light-tight metal container was constructed for the tube and all the power lines were filtered. However, the noise level did not drop below 0.1 volts as referred to the input. Altering the values of the dynode and tetrode voltages did not have any appreciable effect. It was concluded that the noise originated in the tetrode for if the tetrode were cut off through biasing the grid quite negative the noise ceased.

* Manufacturer is National Union.

FIGURE No. 1

Basic Hy-Tramp Schematic as suggested by
the manufacturer



The photomultiplier signal was in the 0.1 volt range. Hence, if the Hy-Tramp were used as an auxiliary amplifier, the signal would have been submerged by the noise. This would have been impossible to work with and so the Hy-Tramp was abandoned.

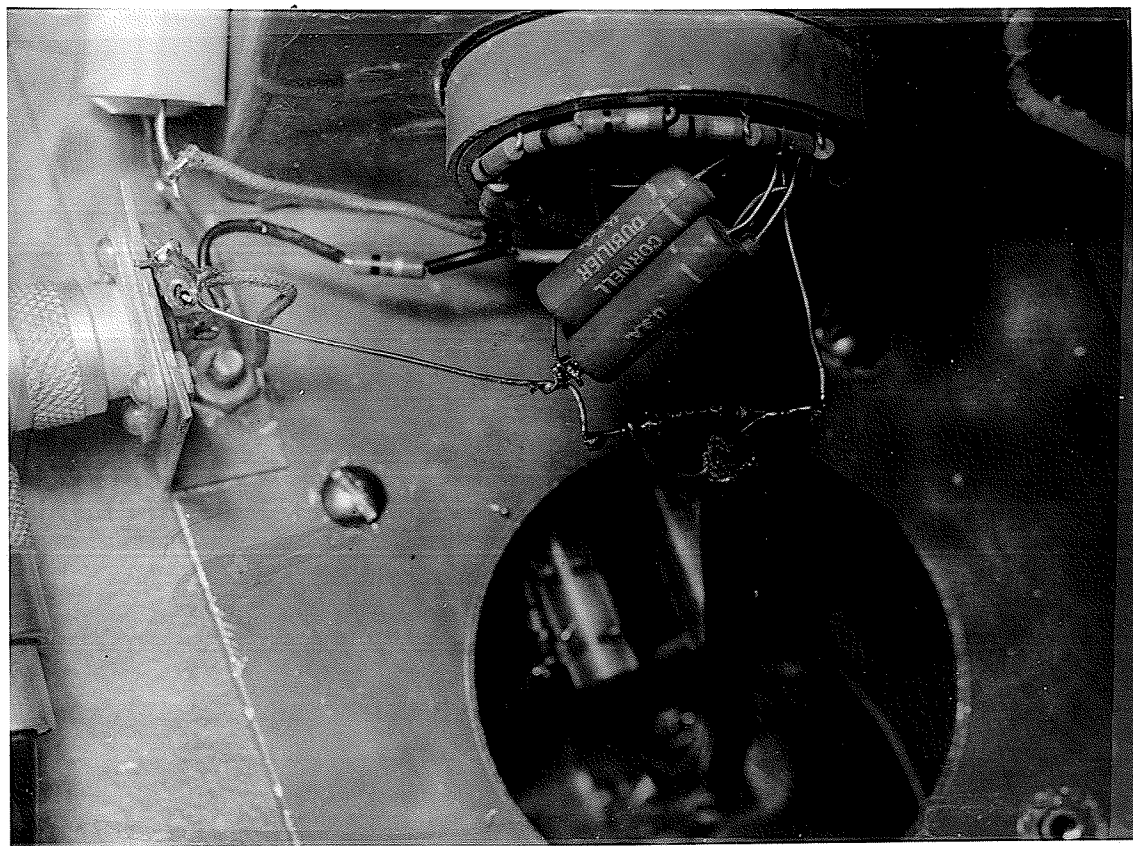
2.3 HIGH GAIN PHOTOMULTIPLIERS

It was then decided that the multiplier would have to drive the Y-plates directly. Because the decay pulses were so fast, stray reactances had to be minimized in the wiring of the multiplier and in the leads to the Y-plates. The scope was especially constructed to make such a task relatively easy. There was a panel on the side of the scope which could be removed, revealing the Y-plate terminals. The multiplier was mounted directly onto the side of the scope, over the panel hole. With this arrangement the signal leads were only about 3 inches (Figure 2). Careful wiring of the multiplier bases ensured a minimum of stray capacity.

For the multiplier output current to faithfully follow the decay of the scintillator, the load resistor must be extremely low (see equation 3, chapter 3). A tentative value of 200 ohms was chosen for this resistor. To drive the Y-plates appreciably the multiplier was required to have sufficient gain to develop about 20 volts across this resistor. None of the multiplier tubes available were able to approach this figure without exceeding their specified anode supply voltages. Hence the problem was to find a type of tube which would stand overvoltages.

FIGURE NO. 2

Photograph showing photomultiplier mounted on the side of the scope with the short signal leads from the multiplier to the Y-plates.



The first of such tubes tested was a Dumont type K1295 (Figure 3). This was a 12 stage experimental multiplier. The Dumont specifications indicated a gain of 2.6×10^6 at 106 volts per dynode. The photomultiplier overloaded at an anode supply voltage of 1900V. With this voltage there was insufficient gain.

The second tube tested was an R.C.A. type 6342, 10 stage multiplier (Figure 4). According to specifications this tube was especially designed to minimize transit time spread. Upon testing the tube it was found that even with an anode supply as high as 3 kilovolts no appreciable signs of overloading were present. At this voltage pulses of about 10 volts appeared on the load resistor. This was sufficient for observation.

2.4 SIGNAL DELAY

The problem of triggering the scope was then considered. Taking into account the delay in the trigger circuit built into the scope, it was calculated that a signal delay of about 60 μ sec. would have had to have been inserted between the multiplier and the Y-plates. There was no method whereby a pulse could be delayed without serious distortion for periods in excess of 20 or 30 times its own length. Hence the triggering of the scope on each pulse was an impossibility. Therefore the scope was left to trigger on its own built-in pulse generator. Thus the scintillation pulses appeared randomly on the face

FIGURE No. 3

Dumont K1295 Photomultiplier Schematic

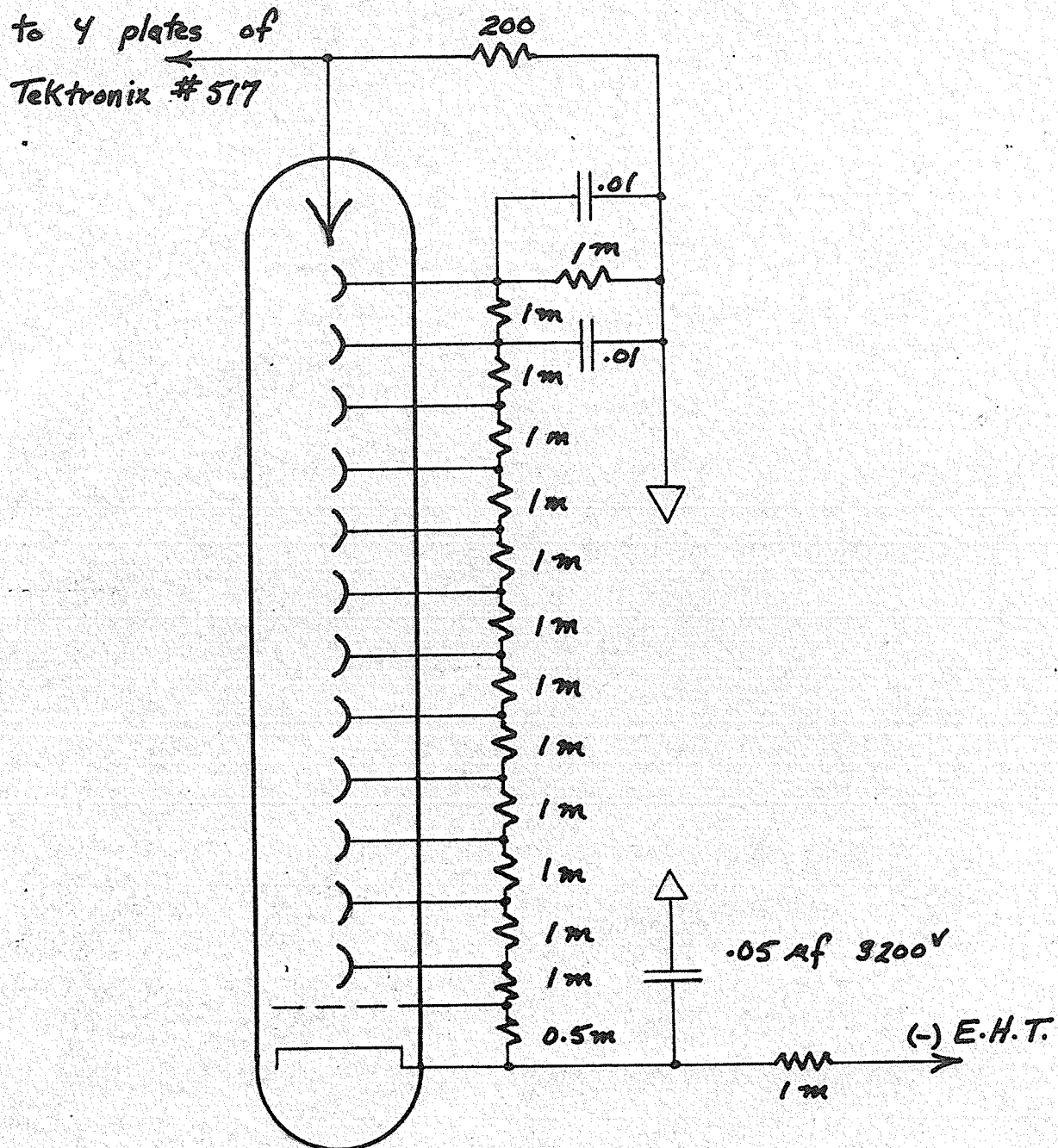
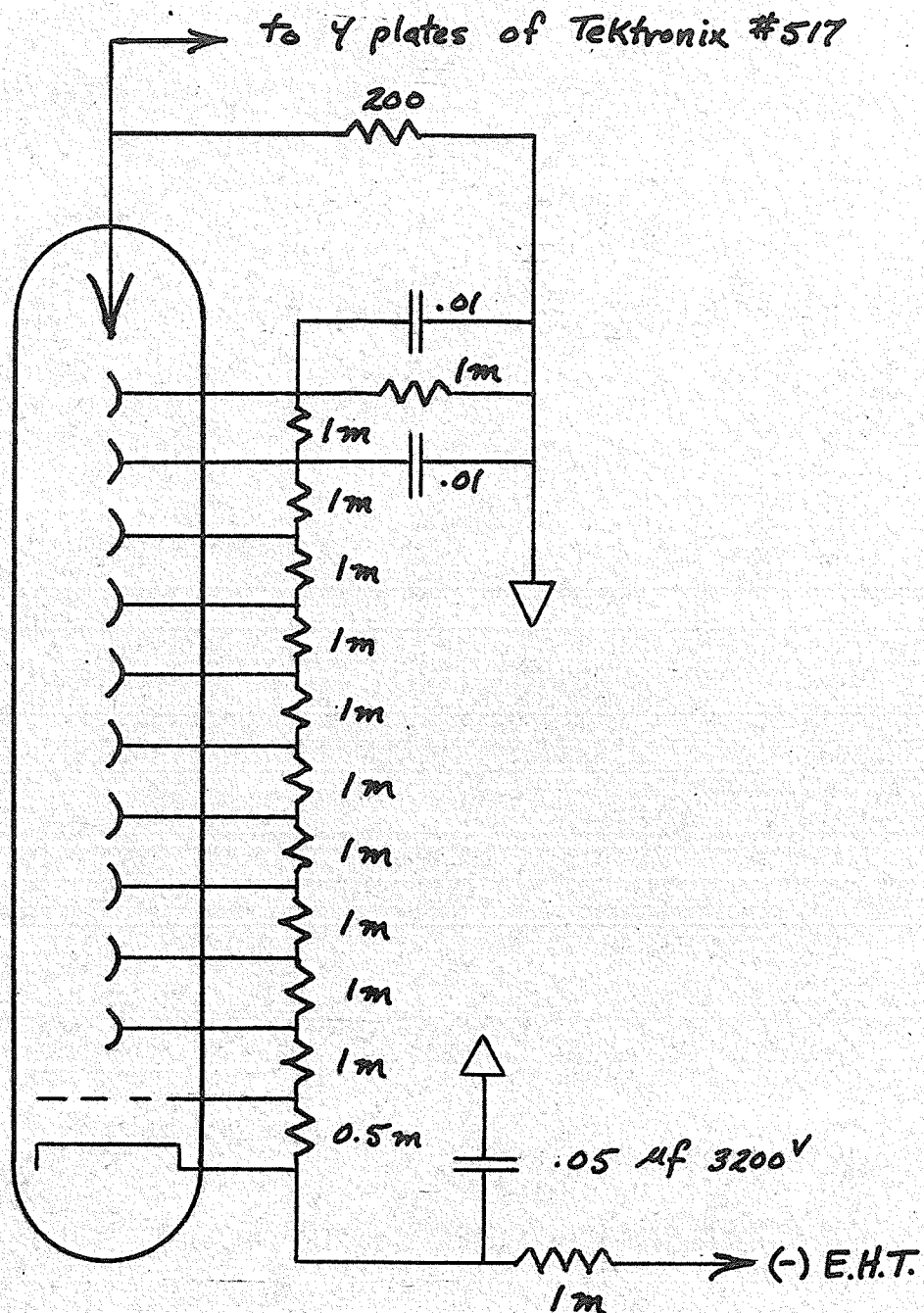


FIGURE No. 4

R.C.A. 6342 Photomultiplier Schematic



of the scope. It was hoped that these could be photographed.

2.5 PHOTOGRAPHY

To accomplish the photography the fastest commercial lens available at that time was purchased. This was an Angenieux lens which had a focal length of one inch and a maximum aperture of $f/0.95$. This lens fitted a Bolex 16 m.m. camera which was available in the Physics department. The most sensitive commercial film was obtained from Kodak which had an A.S.A. rating of 600 and was called Linagraph Pan.

Because of the small pulse size on the scope screen, and of the small photographic negative size, it was required that the camera's field only cover an area of about 4 square centimeters. The lens itself would only focus down to a distance of 18 inches, at which distance the field was too large. An extension sleeve was constructed to fit between the lens and the body of the camera. This enabled focussing down to two inches with a camera field of 6 square centimeters.

It was found that the trace intensity of a single pulse was insufficient to cause a record on the film. Several developers, DK60, D72, Promicrol and Microphen were tried, all yielding negative results. The latter two developers increase the effective film speed by factors of from 2 to 6 as a function of the developing time. The D-72 developer was a straight paper developer which when applied to films yields extreme contrast together with an unknown increase in film

speed. Presensitizing the film was tried. This was accomplished by exposing the film to a mercury vapor atmosphere for 48 hours. This causes an increase in A.S.A. rating of about two times. With the mercury sensitized film and the D-72 developer a mere ghost of a trace was discernable. However, this was too uncertain to measure.

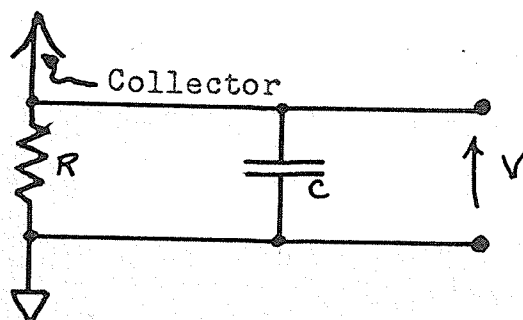
The reason for the failure of the photography lay in the fact that the scope trace intensity was too low. The standard method of beam intensification by beam blanking and unblanking was already operative in the scope itself. This intensity had a relatively low upper limit due to a very bad halo effect in the tube. If the intensity was increased beyond this upper limit the halo obscured the pulses. Private communication with the Tektronix Company revealed that halo was a fault of this type of scope and that it could only be minimized. Another cathode ray tube was obtained which had been checked by Tektronix for minimum halo. This tube, although an improvement over the previous one, still did not allow sufficient beam intensity for photographs.

This development ended hopes of performing the measurements in a direct manner. It was then thought that the pulse amplitude method of section 1.5, would yield good results with suitable modifications to correct for slow electronics.

CHAPTER 3

THEORETICAL CONSIDERATIONS3.1 THE THEORY OF THE MULTIPLIER OUTPUT CIRCUIT

The basis of the pulse amplitude method lies in the variation in response of the output circuit of the multiplier as a function of load resistor. The output circuit consists essentially of a load resistor, R , shunted by some stray capacitance, C .



Following the analysis of Swank (7) we assume, as a first approximation that the multiplier delivers a current pulse which has zero rise time and a single exponential decay. The zero rise time assumption is valid if photomultiplier transit time spread is neglected. The cases of finite rise time and multiple decay times are treated later. The multiplier current pulse assumed is of the form:

$$I(t) = \frac{A}{\sigma} e^{-t/\sigma} \quad (1)$$

where σ is the scintillator decay constant. A is the maximum charge collected on the anode.

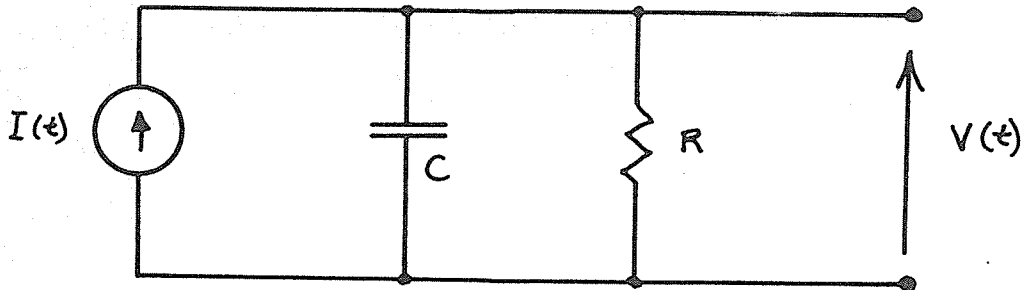
The form of equation (1) arises from the differentiation of charge pulse collected at the anode. This charge pulse has

the form $Q(t) = A e^{-t/\sigma}$

$$\text{then } \frac{d}{dt} [Q(t)] = \frac{A}{\sigma} e^{-t/\sigma} = I(t)$$

The decay time here is taken to be the time taken for the pulse to fall to $1/e$ of its initial amplitude.

The equivalent circuit of the output is then:



Using Kirchhoff's current law we have that:

$$I(t) = \frac{V(t)}{R} + C \frac{dV(t)}{dt} \quad (2)$$

Taking Laplace transforms of both sides of (2) we get:

$$I(s) = \frac{V(s)}{R} + C s V(s) + C V(0+) \quad (2a)$$

where:

$$I(s) = \mathcal{L}\{I(t)\}$$

$$V(s) = \mathcal{L}\{V(t)\}$$

$$V(0+) = 0$$

Therefore:

$$V(s) = \frac{I(s)}{\frac{1}{R} + Cs} \quad (2b)$$

We had

$$I(t) = \frac{A}{\delta} e^{-t/\delta}$$

Then

$$I(s) = \frac{A}{\delta} \int_0^{\infty} e^{-st} e^{-t/\delta} dt$$

$$= \frac{A}{\delta} \left\{ \frac{1}{s + 1/\delta} \right\}$$

Substituting for $I(s)$ in (2b) we obtain

$$V(s) = \frac{\frac{A}{\delta}}{(s + 1/\delta)(s + 1/RC)}$$

Taking inverse Laplace transforms we get:

$$V(t) = \frac{A}{C} \frac{RC}{RC - \delta} \left\{ e^{-t/RC} - e^{-t/\delta} \right\} \quad (3)$$

From the above expression it is seen that, for the voltage output pulse to decay as the scintillator decays, the inequality, $RC \ll \sigma$, must be satisfied. Taking a common value for σ of 4 nps. and a value for C of about 8 picofarads (p.f.) yields a load resistor of about 5 ohms. Some experimenters, notably Swank and Buck (4) have used load resistors of 200 ohms. For this case RC is approximately equal to σ and the output voltage does not follow the scintillator decay faithfully.

The maximum amplitude of the voltage pulse can be obtained by setting

$$\frac{d}{dt} \{ V(t) \} = 0$$

solving for the time at which the maximum occurs and substituting this time into the form of $V(t)$ to obtain the maximum voltage.

$$V_m = \frac{A}{C} \gamma^{\frac{1}{1-\gamma}} \quad (4)$$

where

$$\gamma = \frac{RC}{\sigma}$$

3.2 THE PULSE AMPLITUDE METHOD

Consider the effect on V_m if two different load resistors R_1 and R_2 are chosen such that:

$$R_1 C \gg \sigma \quad \text{i.e. } \gamma \gg 1 \quad \text{and} \quad V_{m1} = \frac{A}{C} \quad (5)$$

$$R_2 C \ll \sigma \quad \text{i.e. } \gamma \ll 1 \quad \text{and} \quad V_{m2} = \frac{A R_2}{\sigma} \quad (6)$$

Taking the ratio of the pulse amplitudes gives the result

$$\sigma = \frac{V_{m1}}{V_{m2}} \cdot R_2 C \quad (7)$$

From this last equation it is seen that a measure of σ can be obtained if the output circuit elements, R_2 and C , are known and if the pulse amplitude ratio, as defined above, is measured.

Because the pulses for V_{m2} have very fast decay times, the only apparatus which is adequate for measurements on the amplitude of such voltage pulses is the scope. If the scope is to be used, the expression for σ in equation (7) must be modified. The reason is that V_{m1} is about 40 times V_{m2} . Since the scope gain is constant an attenuator must be used to observe V_{m1} . This attenuation factor is frequency dependent and this dependence is unknown. Because of this the pulse amplitude ratio is unknown. However, the unknown attenuator^{difficulty} can be circumvented if a comparison procedure is employed.

Suppose one had a standard scintillator with a known decay time. The standard would have various parameters as follows:

$$\sigma_s, V_{m1}^s, V_{m2}^s, A_1^s, A_2^s$$

where two different A's are introduced to account for the attenuator. Similarly the unknown scintillator would have σ , V_{m1} , V_{m2} , A_1 and A_2 .

Taking pulse amplitude ratios yields:

$$\frac{V_{m1}}{V_{m2}} = \frac{A_1}{A_2} \frac{\sigma}{R_2 C}$$

$$\frac{V_{m1}^s}{V_{m2}^s} = \frac{A_1^s}{A_2^s} \frac{\sigma_s}{R_2 C}$$

Since the frequency components of V_{m1} and V_{m1}^s are equal, due to the decay being that of the multiplier output circuit, it can be assumed that:

$$\frac{A_1^s}{A_2^s} = \frac{A_1}{A_2}$$

now $\frac{A_1^s}{A_2^s} = \frac{V_{m1}^s}{V_{m2}^s} \cdot \frac{CR_2}{\sigma_s}$

hence $\frac{V_{m1}}{V_{m2}} = \frac{V_{m1}^s}{V_{m2}^s} \cdot \frac{\sigma}{\sigma_s}$

or $\sigma = \sigma_s \cdot \frac{V_{m1}}{V_{m2}} \cdot \frac{V_{m2}^s}{V_{m1}^s} \quad (8)$

Using equation (8) the unknown decay time can be obtained.

3.3 CONSIDERATION OF APPROXIMATIONS

There are several uncertainties about this procedure which must be discussed.

First of all, suppose that the decay pulse is not a pure exponential. It could very possibly happen that the decay be the sum of two or more exponentials. The mathematics of such a situation is worked out in Appendix 1. It turns out that the decay time measured is a weighted mean decay time. This is quite satisfactory for our purposes because the primary use of the decay measurements in this work is to furnish the frequency limitation of a scintillator. For this purpose an effective or weighted mean decay time is desirable.

Secondly it is known that, due to multiplier transit time spread, the multiplier current pulse does not have a zero

rise time, but has a rise time which is finite. To roughly investigate the effect of such an occurrence a pulse with a linear finite rise time is assumed in Appendix 2. With such an assumption the effect on the decay time is negligible.

The last uncertainty is that due to the 7 millimicro-second rise time of the scope amplifiers. When a low load resistor is used to measure V_{m2} , the amplifiers will distort this fast pulse so that the observed pulse will be smaller than V_{m2} . The size of this observed pulse will decrease as the decay time decreases.

This effect can be corrected for mathematically by the application of Duhamel's Theorem if the response of the amplifier to a unit step function of voltage is known.

3.4 THE AMPLIFIER CORRECTION CURVE

In the following discussion of Duhamel's Theorem there is required one theorem in Laplace transforms which is not too commonly used. This theorem deals with complex multiplication and is stated in Appendix 3.

For any system which has an input and an output we can write an equation as follows:

(Response Function) = (Systems Function) x (Driving Function) or symbolically:

$$r(t) = g(t) \times d(t)$$

If the Laplace transform of the above is taken we get:

$$R(s) = G(s) \times D(s)$$

where

$$\begin{aligned} R(s) &= \mathcal{L}\{r(t)\} \\ G(s) &= \mathcal{L}\{g(t)\} \\ D(s) &= \mathcal{L}\{d(t)\} \end{aligned}$$

The system being dealt with here is an amplifier. For this case $r(t)$ and $d(t)$ are voltages. The systems function $g(t)$ is a transfer function and is frequency dependent due to the finite rise time of the amplifier. If the amplifier were perfect $g(t)$ would be a constant -- the gain of the amplifier.

We define the indicial response of the amplifier to be the functional form of $r(t)$ when the driving function is a unit step function, $u(t)$. Symbolically we have

$$\begin{aligned} r(t) &= A(t) \quad \text{when} \quad d(t) = u(t) \\ \text{i.e.} \quad A(t) &= g(t) u(t) \end{aligned}$$

taking the Laplace transform of this yields

$$\mathcal{L}\{A(t)\} = \mathcal{L}\{g(t)\} \cdot \mathcal{L}\{u(t)\}$$

$$\text{or} \quad A(s) = G(s) \cdot \frac{1}{s}$$

$$\text{because} \quad \mathcal{L}\{u(t)\} = 1/s$$

$$\text{hence} \quad G(s) = s A(s) \quad \text{in general.}$$

$$\text{we had} \quad R(s) = G(s) D(s)$$

substituting for $G(s)$ yields

$$R(s) = s A(s) D(s)$$

(9)

Equation (9) is valid for all driving and response functions.

We now wish to transform equation (9) back into the time domain. Recall that the Laplace transform of a derivative

has the form: $\mathcal{L}\left\{\frac{df(t)}{dt}\right\} = sF(s) - f(0+)$

where $\mathcal{L}\{f(t)\} = F(s)$

The term $f(0+)$ is the value of $f(t)$ as t approaches zero from positive time values.

Thus equation (9) can be rewritten thus:

$$\mathcal{L}\{r(t)\} = \mathcal{L}\left\{\frac{dA(t)}{dt}\right\} \times \mathcal{L}\{d(t)\} + A(0+) \mathcal{L}\{d(t)\}.$$

or we may write it:

$$\mathcal{L}\{r(t)\} = \mathcal{L}\left\{\frac{dd(t)}{dt}\right\} \mathcal{L}\{A(t)\} + d(0+) \mathcal{L}\{A(t)\}$$

These two equivalent forms arise depending on which term the s is linked to in equation (9).

Then, if the theorem of Appendix 3 is invoked there results:

$$r(t) = A(0+)d(t) + \int_0^t d(\tau) \frac{d}{d\tau} [A(t-\tau)] d\tau \quad (10)$$

or

$$r(t) = d(0+)A(t) + \int_0^t A(t-\tau) \frac{d}{d\tau} [d(\tau)] d\tau \quad (11)$$

These are the two formulas representing Duhamel's Theorem. They give the response function due to any driving function, the only unknown being the indicial response.

The problem we are to solve is the effect of the amplifier on a pulse of amplitude, say B , and decay time, say α . This will be the driving function. If the indicial response, $A(t)$, is known it is possible to compute the resultant response function.

Since the form of $A(t)$ is known only graphically because it will be obtained through a scope picture, it would be difficult to obtain accurately its differential with respect to time. Hence equation (11) will be used.

Assume as a first approximation that the driving function has zero rise time, an initial height of unity and a decay time of α . In other words:

$$d(t) = e^{-\alpha t}$$

then

$$d(0+) = +1$$

and

$$\frac{d}{dt} \{ d(t) \} = -\alpha e^{-\alpha t}$$

We then have

$$r(t) = A(t) - \alpha \int_0^t A(t-\tau) e^{-\alpha \tau} d\tau \quad (12)$$

We have to evaluate graphically the shape of the curve

$$y = \int_0^t A(t-\tau) e^{-\alpha \tau} d\tau \quad (13)$$

When the last equation is solved for a particular value of t , this value can be substituted into equation (12) to yield the value of the response function for this time value. By using several time values the response function can be sketched in.

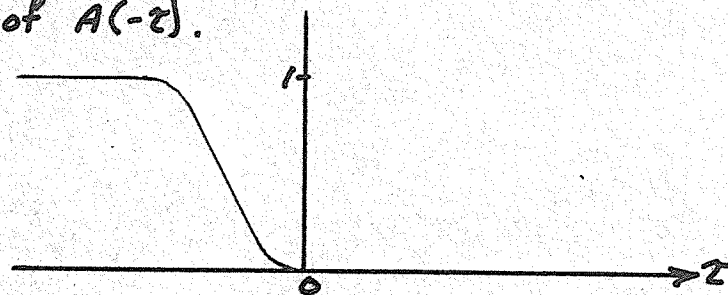
The actual procedure is best explained through the medium of the graphs. Hence see Figure 5.

This, then, establishes the method.

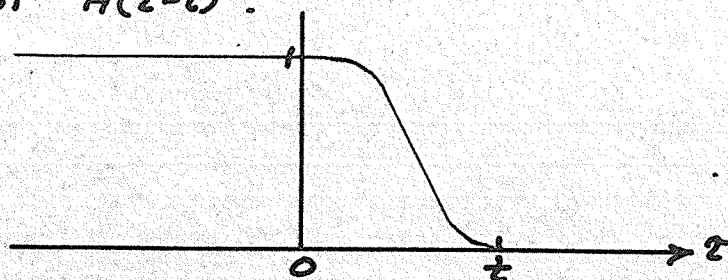
FIGURE No. 5

Graphical computation of the value of $\int_0^t A(t-\tau)e^{-\alpha\tau}d\tau$.

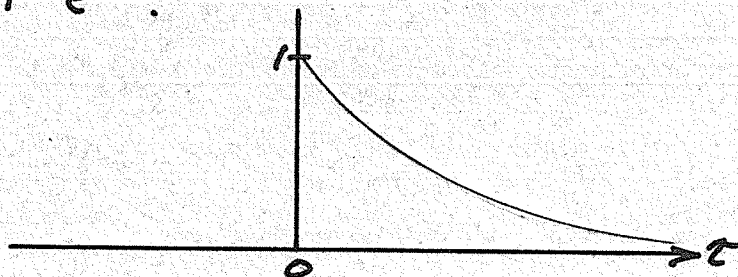
(a) Graph of $A(-\tau)$.



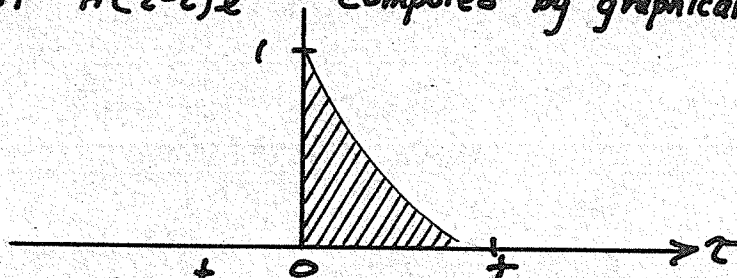
(b) Graph of $A(t-\tau)$.



(c) Graph of $e^{-\alpha\tau}$.



(d) Graph of $A(t-\tau)e^{-\alpha\tau}$ computed by graphical multiplication of (b) + (c).



The value of $\int_0^t A(t-\tau)e^{-\alpha\tau}d\tau$ is then obtained by measuring with a planimeter the shaded area.

CHAPTER 4

EXPERIMENTAL PART TWO4.1 THE AMPLIFIER CORRECTION CURVE

A simple step function generator was constructed using a single pole single throw mercury switch as in Figure 6. The switch was mounted on a 'see-saw' board. By tipping the latter the switch was thrown quickly. The pulses from this generator were fed into the Y-plates of the scope, bypassing the amplifiers to ascertain whether the step function so generated was in fact a step. With the scope running on its internal trigger generator, occasionally a sweep would show the rise of the function generator. This rise was vertical within the limits of visual observation. The pulses from this generator were then fed into the oscilloscope Y-amplifiers through the cathode follower. The trace which resulted on the screen was photographed. One photographic exposure was the superposition of twenty or thirty pulses. This procedure was possible because the output pulses were all of the same magnitude due to the nature of the mercury switch contact. Three exposures were made, enlarged, plotted and averaged to yield the response function of Figure 7. The greatest deviation of any one photograph from the mean of the response function was never greater than 2%* at any point.

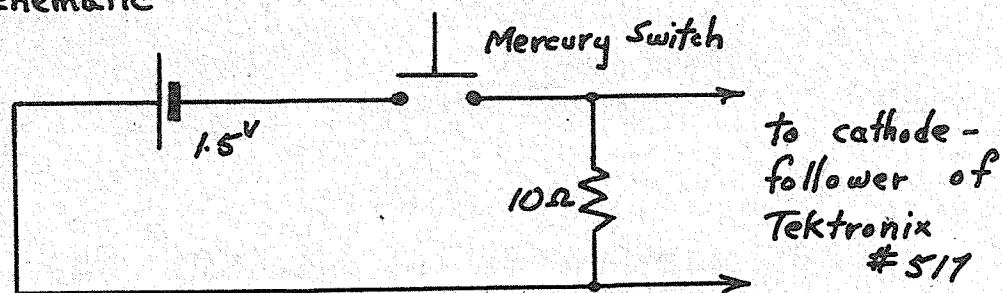
A driving function of the form e^{-at} was chosen to correspond to the shape of the pulses delivered by the photo-multiplier. The response for this sort of input was determined

*of full scale.

FIGURE No. 6

The Step Function Generator.

(a) Schematic



(b) Photograph.

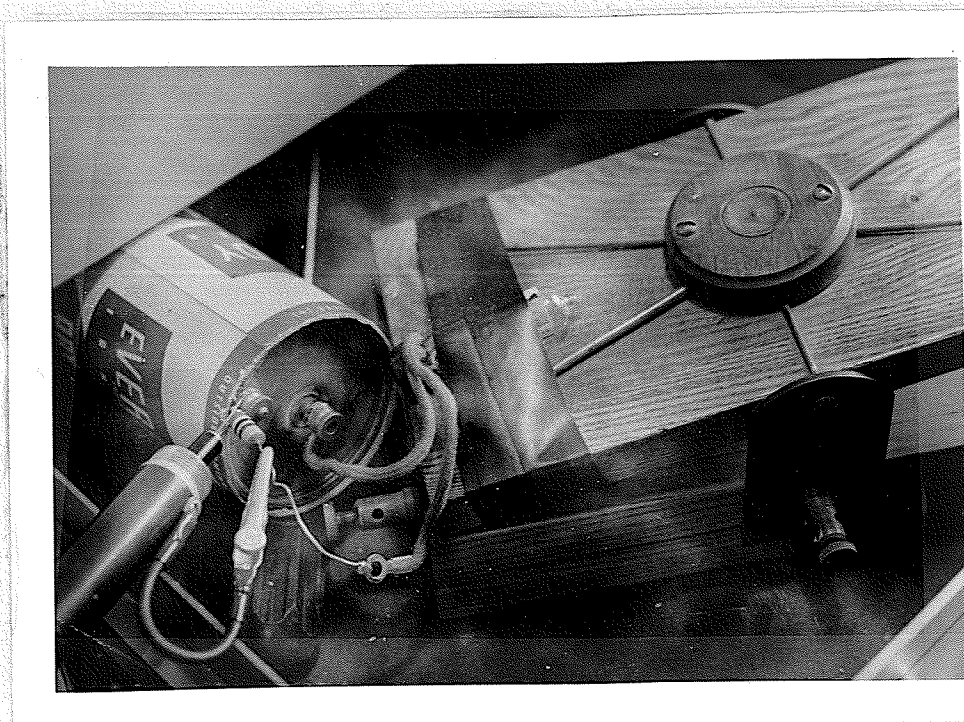
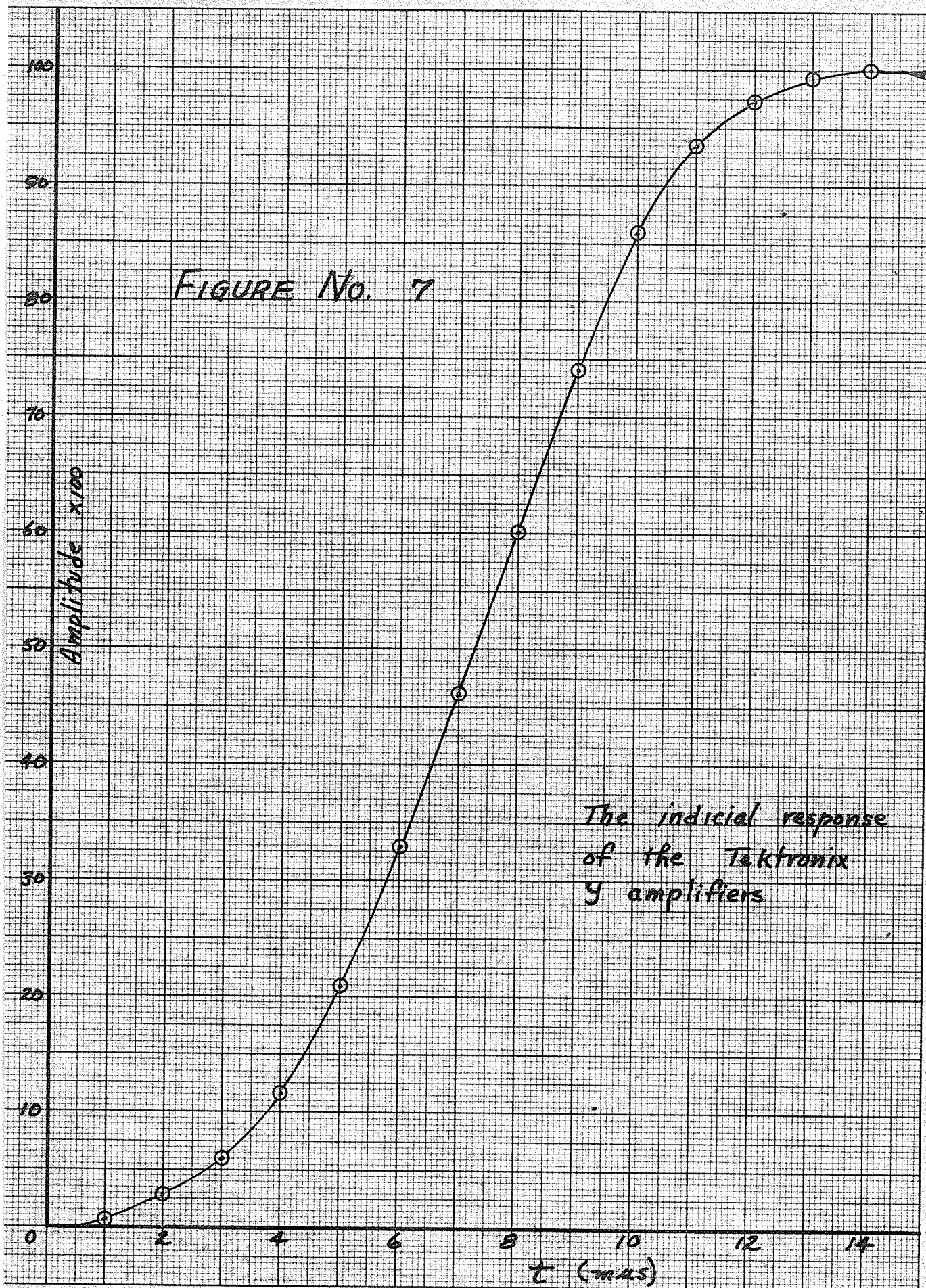


FIGURE No. 7



for three values of α i.e. $\alpha = 0.1 \times 10^9 \text{ secs}^{-1}$, $\alpha = 0.2 \times 10^9 \text{ secs}^{-1}$ and $\alpha = 0.4 \times 10^9 \text{ secs}^{-1}$. These values of α cover the range of decay times normally encountered with organic scintillators.

From the experimental indicial response of Figure 7, Table I, (Appendix 4) was drawn up giving the values of the function $A(\tau)$. Tables number II and number III (Appendix 4) show the calculations involved in obtaining the function $A(t - \tau)e^{-\alpha\tau}$ for $\alpha = 0.2 \times 10^9 \text{ secs}^{-1}$. Tables III were used to draw the curves of Figure 8. The areas under these curves were measured with a planimeter to give the value of t

$$y' = \int_0^t A(t - \tau) e^{-\alpha\tau} d\tau$$

Then

$$y = \alpha \int_0^t A(t - \tau) e^{-\alpha\tau} d\tau \quad \text{was computed}$$

Finally the response function $r(t)$ was computed from

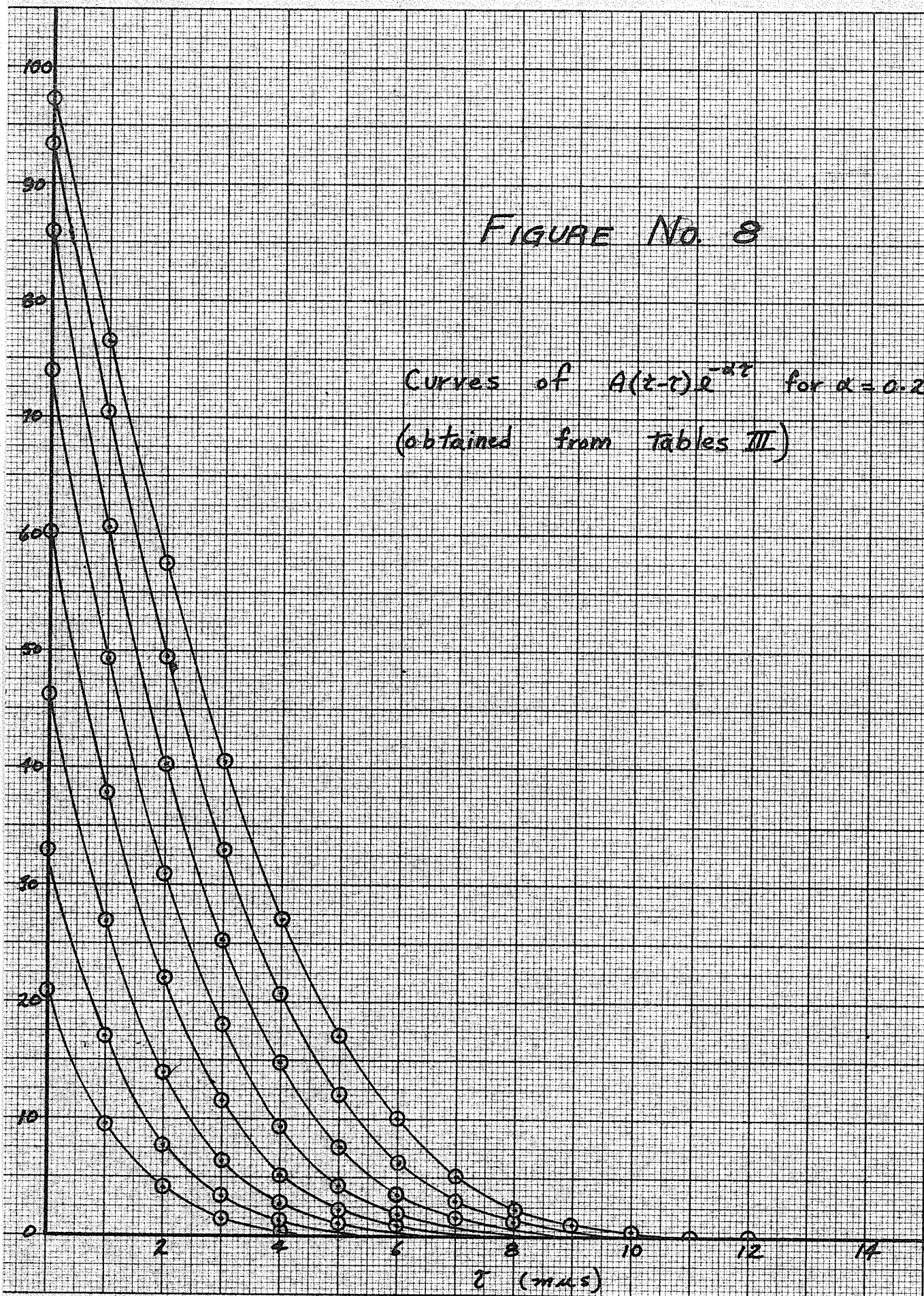
$$r(t) = u(t) - y(t)$$

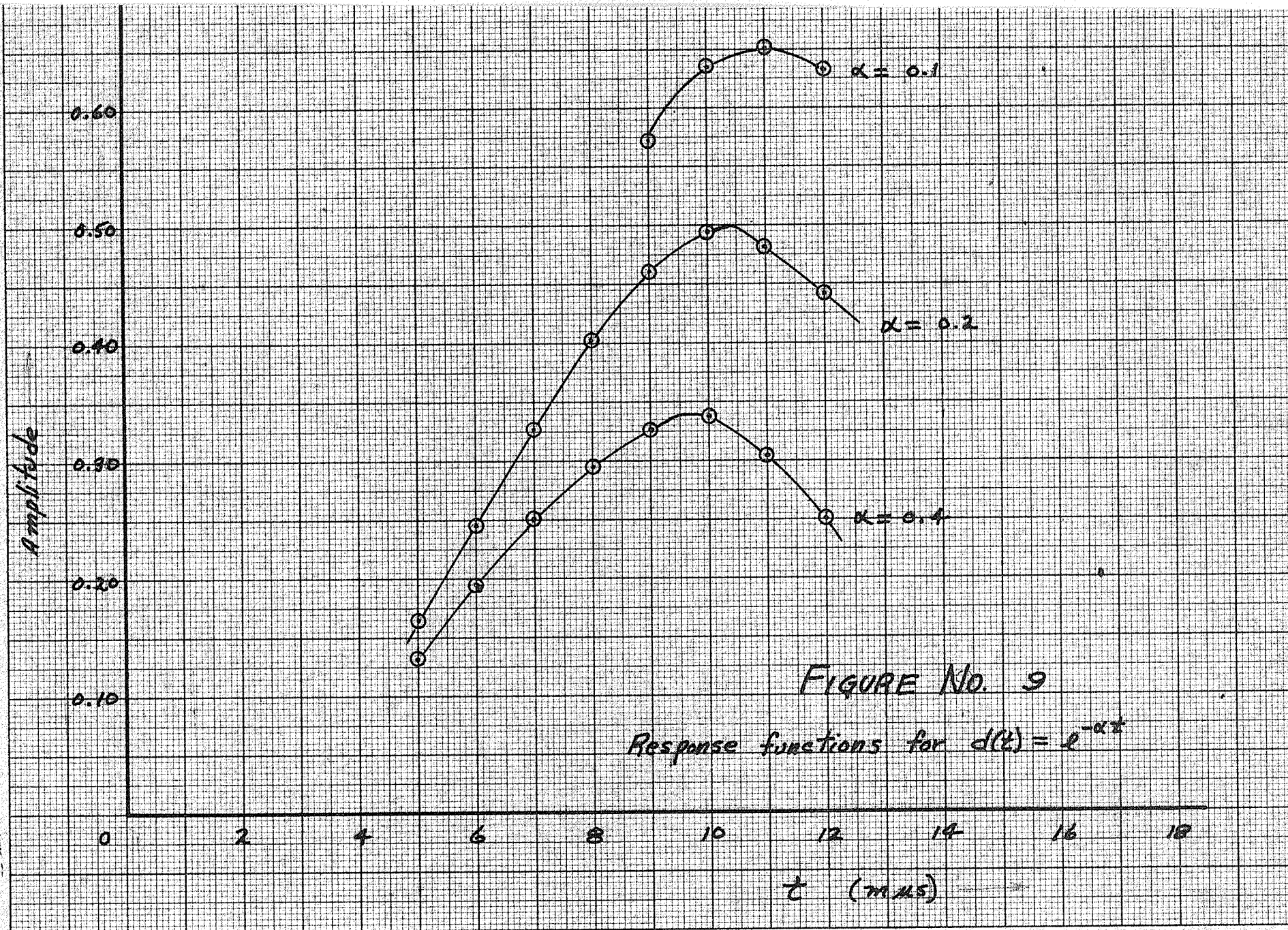
This whole procedure was repeated for the other two values of α and the graph was plotted of the three responses to the three different driving functions (Figure 9).

By measuring the maximum height reached by each of the response functions a graph can be plotted showing the amount the amplifier reduces the amplitude of a pulse of the form $e^{-\alpha t}$ as a function of α . This then yields a correction curve for the value of V_{m2} of equation (8). If the decay time of the standard used in equation (8) is long enough so that the amplifier rise time is much less than the decay time, V_{m2}^S will require no correction. In such a case a direct correction curve

FIGURE No. 8

Curves of $A(t-\tau)e^{-\alpha\tau}$ for $\alpha=0.2$
 (obtained from tables III)





of observed decay time vs true decay time can be easily constructed from the maximum heights of the response functions of Figure 9. This follows from equation (8) for if V_{m2} be reduced by, say 40%, due to the distortion of the amplifiers then the observed decay time will be 40% longer than the true decay time.

The graph of Figure 10 showing the correction to the observed decay time was drawn using the response function maxima of Figure 9.

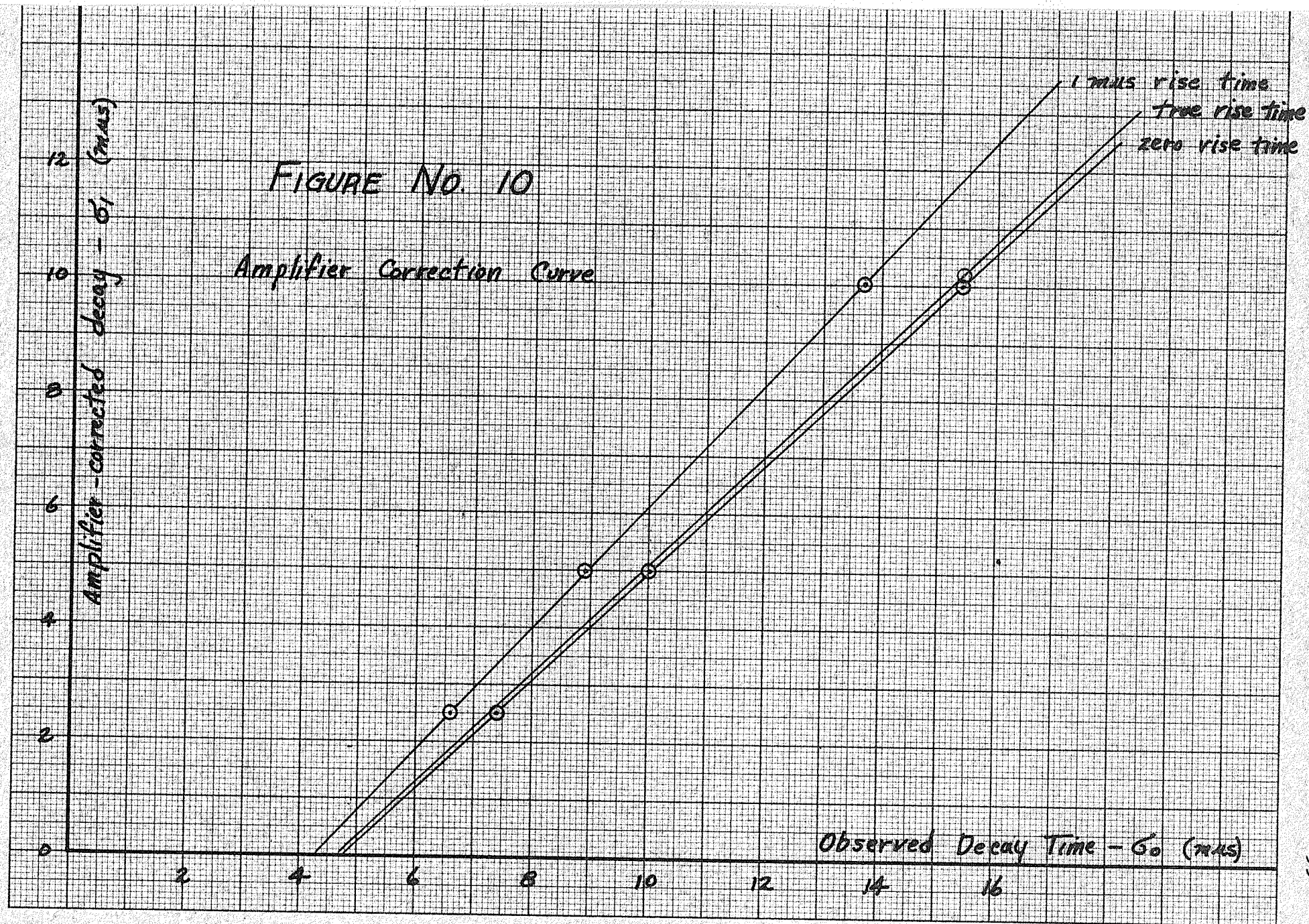
The above correction curve is valid only for driving functions of the form $e^{-\alpha t}$; in other words for zero rise time pulses. In practice the multiplier delivers a pulse which has a rise time of about one or two μms . To investigate the consequences of a driving function having a finite rise time, the above analysis was repeated using a function of the form:

$$\begin{aligned} d(t) &= t & 0 \leq t \leq 1 \\ &= e^{-\alpha(t-1)} & 1 \leq t \leq \infty \end{aligned}$$

where t is measured in μms .

This represents an exponential decay pulse which rises linearly to its maximum value in one μms . The actual shape of the rise of the multiplier pulse is almost certainly not linear, but a linear rise approximation will give a good measure of the effect of a finite rise time.

Using the new driving function a new correction curve was obtained and plotted on Figure 10. The choice of one millimicrosecond for the rise time of the driving function was completely arbitrary because the rise time of the actual pulse delivered by



the multiplier to the amplifier was unknown. To evaluate the rise time of the multiplier pulse and thus establish the true amplifier correction curve, a scintillator whose decay time was known was measured. The assumption was made that the effect of the true rise time was the same as a linear rise time. A point was plotted on Figure 10 whose co-ordinates were the known and observed decay times of the scintillator. The position of this point relative to the zero rise time line and the 1 μ s. rise time line was taken as a measure of rise time of the multiplier pulse. The true decay time line was drawn through this point by the use of ratios, the 1 μ s. and zero rise time lines being used as reference lines.

4.2 LOAD RESISTOR CORRECTION CURVE

In the measurement of an unknown decay time the inequality of formula (6) must be satisfied, viz.:

$$R_2 C \ll \sigma$$

To find the upper limit of R_2 which satisfies the above, C must be determined. In order to obtain the magnitude of the stray anode capacity, C , the circuit of Figure 11 was employed.* Photographs were taken of the decay pulses observed on the scope (Figure 12). The decay was plotted on semi-logarithmic paper (Figure 13), and the time constant was computed. The load resistor was measured on a G.R. resistance bridge and the value of the stray capacity was computed and found to be 13.8 ± 0.2 pf.

For decay times in the two or three μ s. region, R_2 must then be about two ohms to satisfy inequality (6). Photo-

* Note $RC \gg \sigma$

FIGURE No. 11

Circuit for the measurement of the stray capacity of the output of the R.C.A. 6342 multiplier.

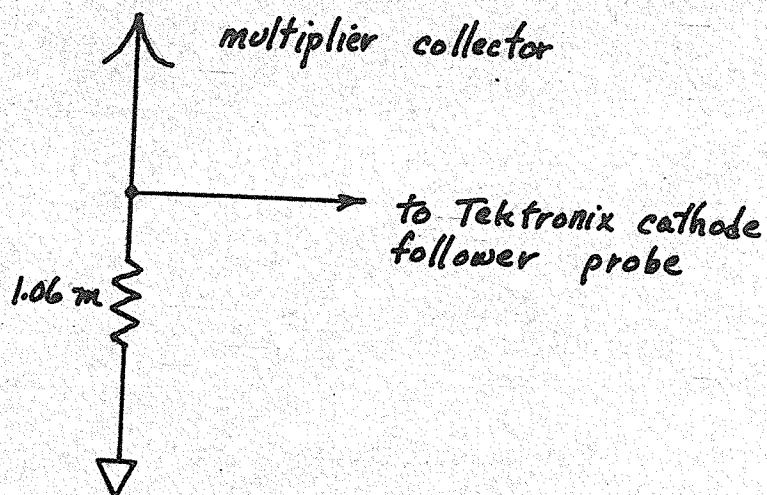


FIGURE No. 12

Typical decay pulses obtained from the above circuit.

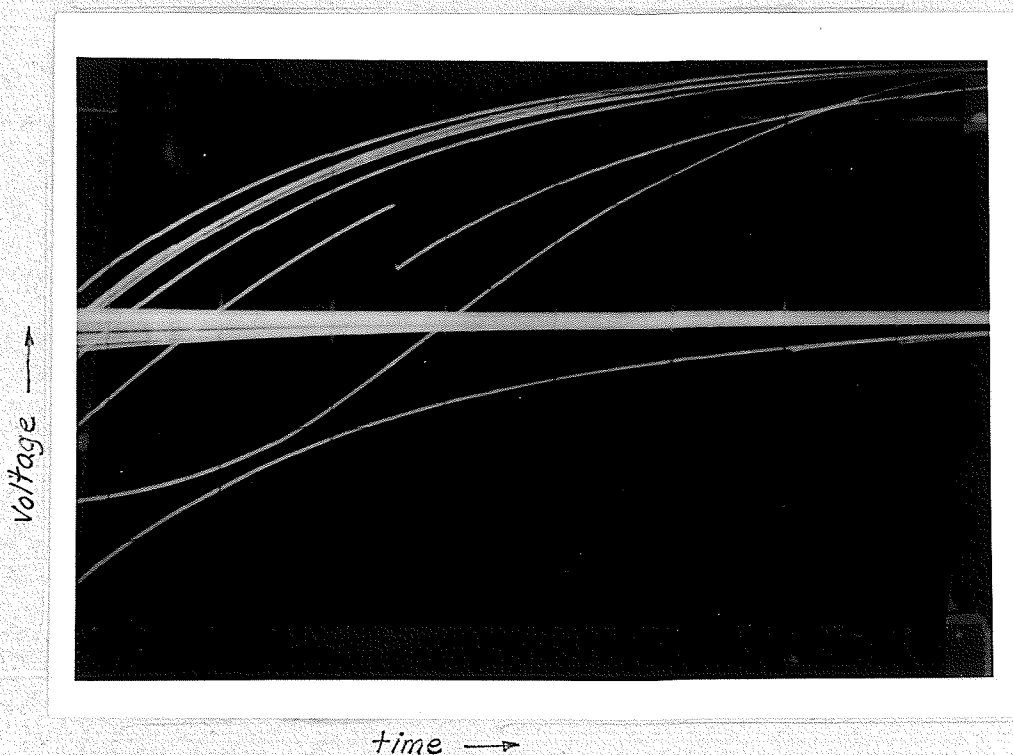
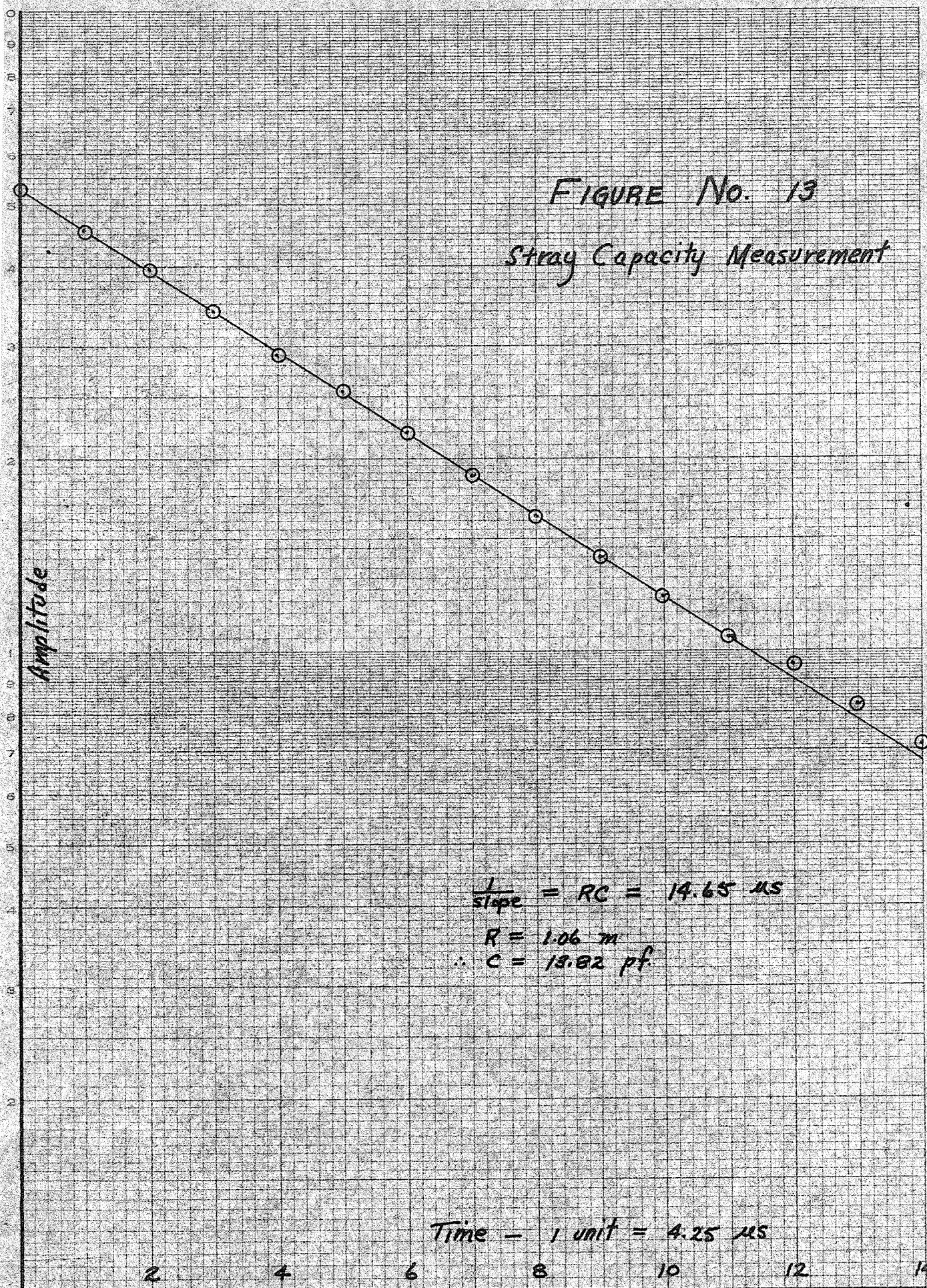


FIGURE No. 13
Stray Capacity Measurement



multipliers running with normal dynode voltages deliver inconveniently small pulses when loaded by only two ohms. Hence the multiplier must either be supplied with a higher load resistor or its gain must be increased through the use of higher dynode potentials, if pulses of the order of 0.1 volts are to be produced. Increasing the gain by using higher potentials is not too satisfactory due to possible non-linearities in the tube. A load resistor of 53 ohms was found to be the minimum value of R_2 compatible with gain requirements. This size of load resistor does not satisfy inequality (6). Inequality (6) was, however, assumed and a correction curve, Figure 14, was drawn up using equation (4) as follows:

$$V_m = \frac{A}{C} \gamma^{\frac{1}{1-\gamma}} \quad (4)$$

Assuming $R_2 C \ll \sigma$ then:

$$V_{m2} = \frac{A}{C} \gamma$$

If $R_2 C < \sigma$ as in the case of $R_2 = 53$ ohms then:

$$V'_{m2} = \frac{A}{C} \gamma^{\frac{1}{1-\gamma}}$$

The error then lies in the assumption that

$$\gamma = \gamma^{\frac{1}{1-\gamma}}$$

which error can be computed.

If, for a given σ this error amounts to, say $A\%$, then the observed decay time σ_1 will be $A\%$ longer than σ . Using this procedure the load resistor correction curve was drawn up.

4.3 DECAY TIME OF ANTHRACENE

The standard scintillator used to obtain the ratio $\frac{V_{2m}^s}{V_1^s}$ of equation (8) was anthracene. To measure the decay time of the anthracene sample available for the experiment the circuit of Figure 15 was used. Using a scope sweep of 20 $\mu s./cm.$ it was

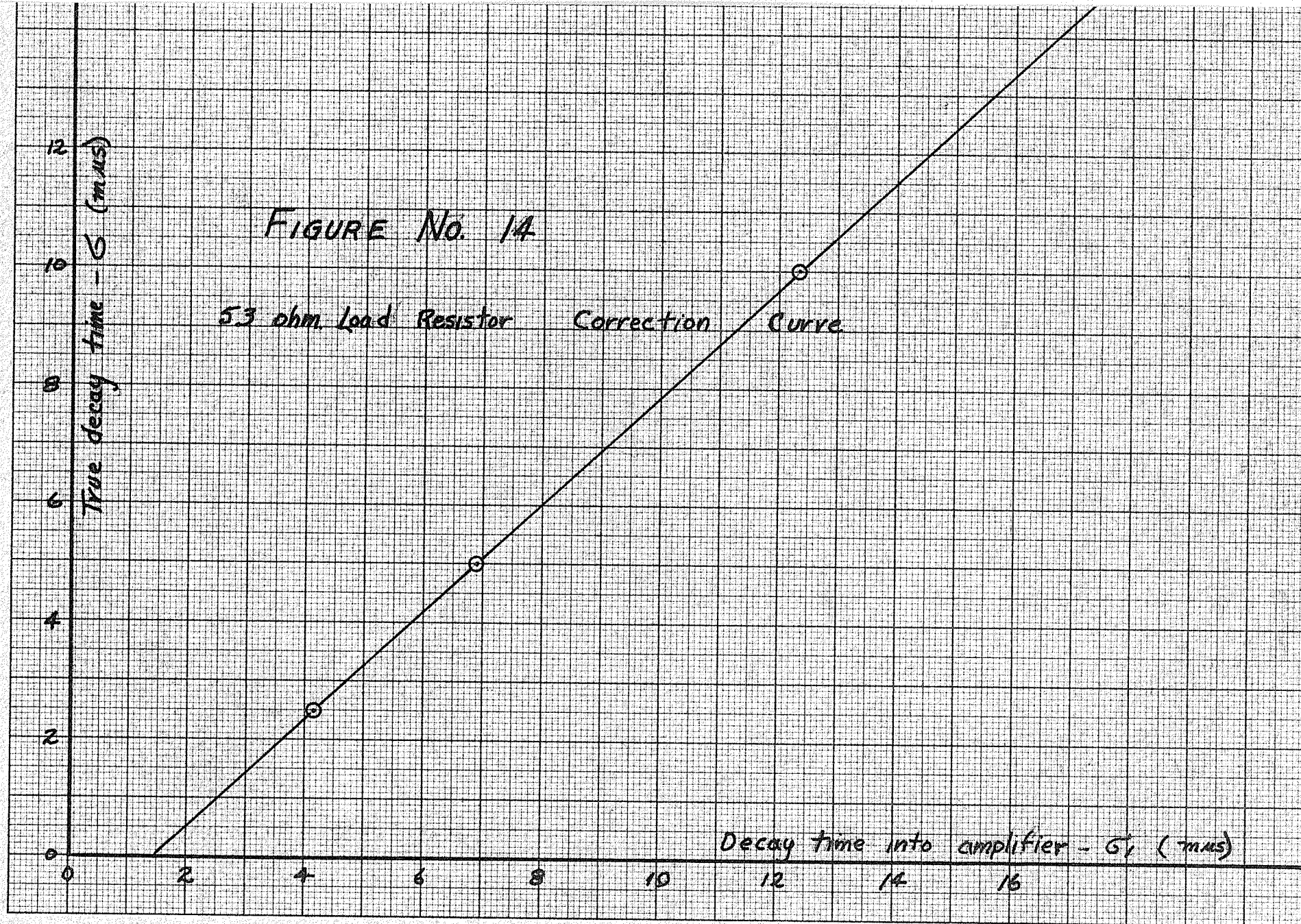


FIGURE No. 15

Circuit for the measurement of
single anthracene pulses.

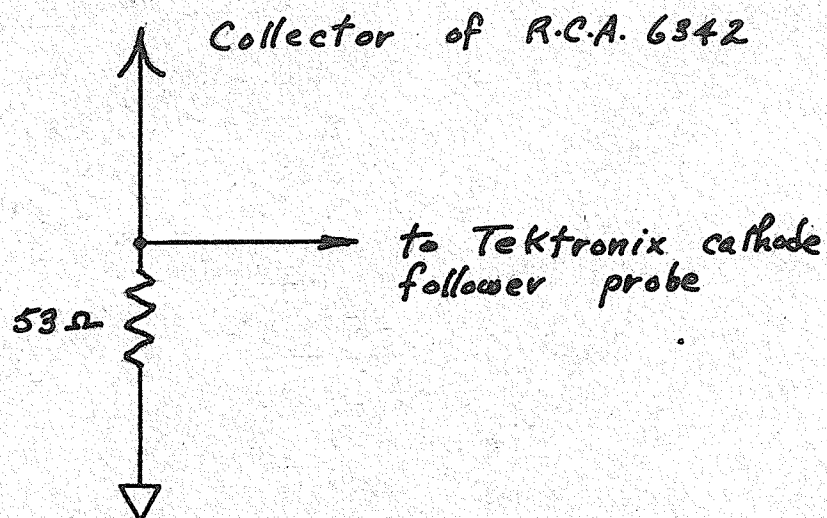
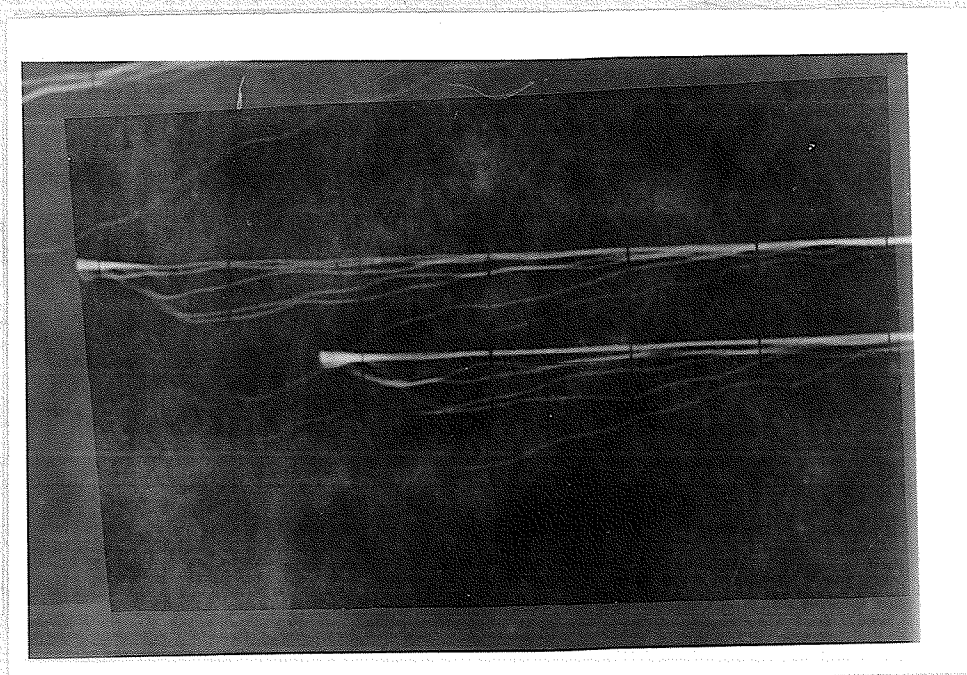


FIGURE No. 16

Typical photograph of single
anthracene pulses.



possible to obtain photographs of single anthracene pulses (Figure 16). Since the anthracene decay time was about three times the rise time of the scope amplifiers, the amplifiers did not distort the decay appreciably. The photography was accomplished through the use of a press camera with an $f/4.7$ lens in conjunction with Ilford H.P.3. film which has an A.S.A. rating of 200. This film was developed for 10 minutes in Kodak Dektol developer (press concentration). Twenty anthracene pulses were measured and plotted on semi-logarithmic paper. (For examples see Figure 17.) The decay time of a pulse was taken to be the inverse of the slope of the best straight line through the points. The decay time of anthracene was taken to be 31.5 ± 1 μ ps., the average of the twenty pulses.

4.4 UNKNOWN DECAY TIME MEASUREMENT

The circuit of Figure 18 was set up to perform the decay time measurements. The basic procedure was to mount the scintillator on the photomultiplier using a silicone grease optical bond between the multiplier photocathode and the scintillator. No light reflectors were used as the light reflector only serves to increase the number of photons incident on the photocathode and does not change the distribution of photons. A Co^{60} source was fixed beside the multiplier to supply the excitation gamma rays. The photomultiplier was run with a dynode potential of 1500 volts. The Compton spectrum of the scintillator was then displayed on the scope. This spectrum was photographed using a press camera as in section 4.3.

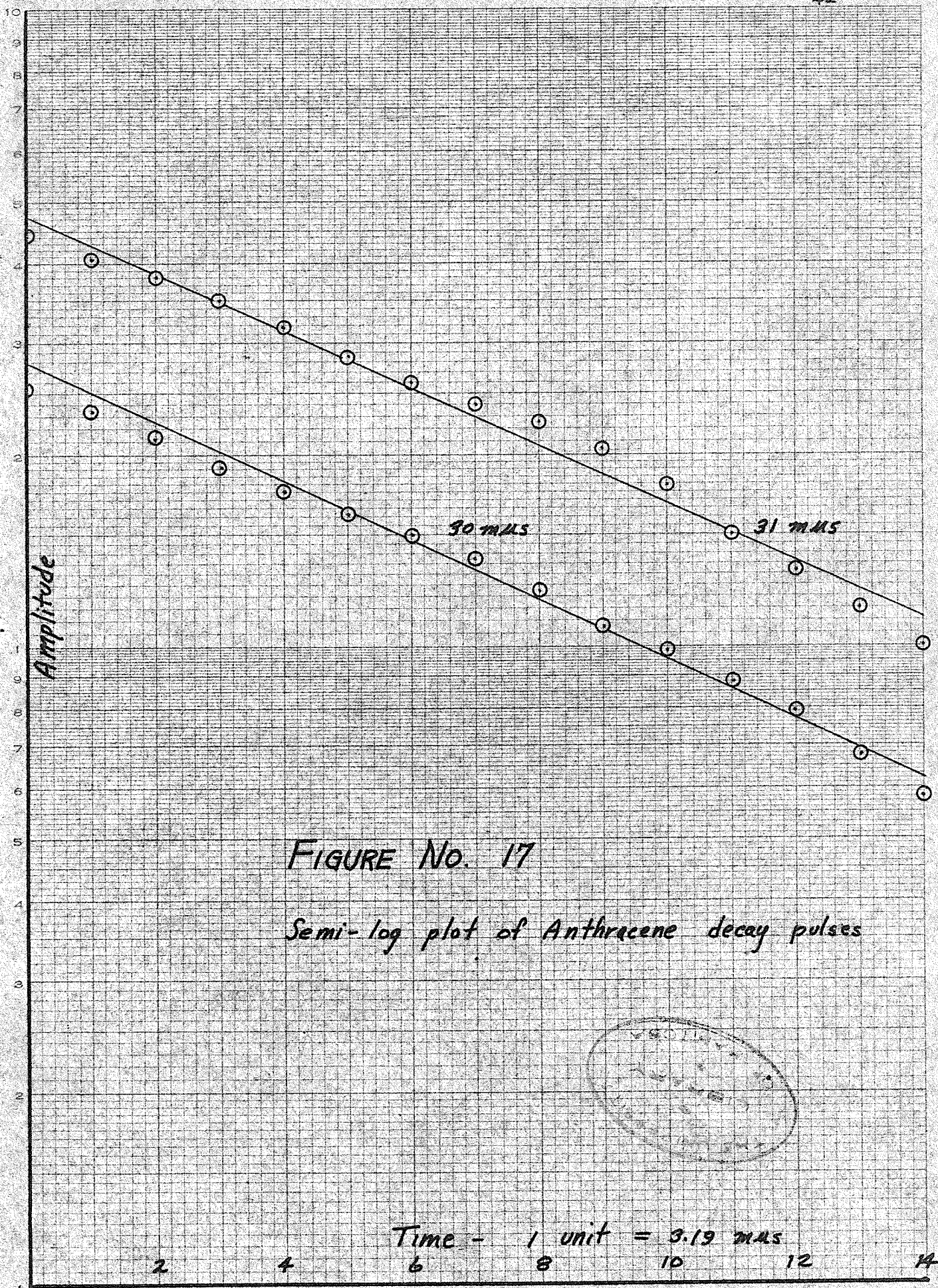
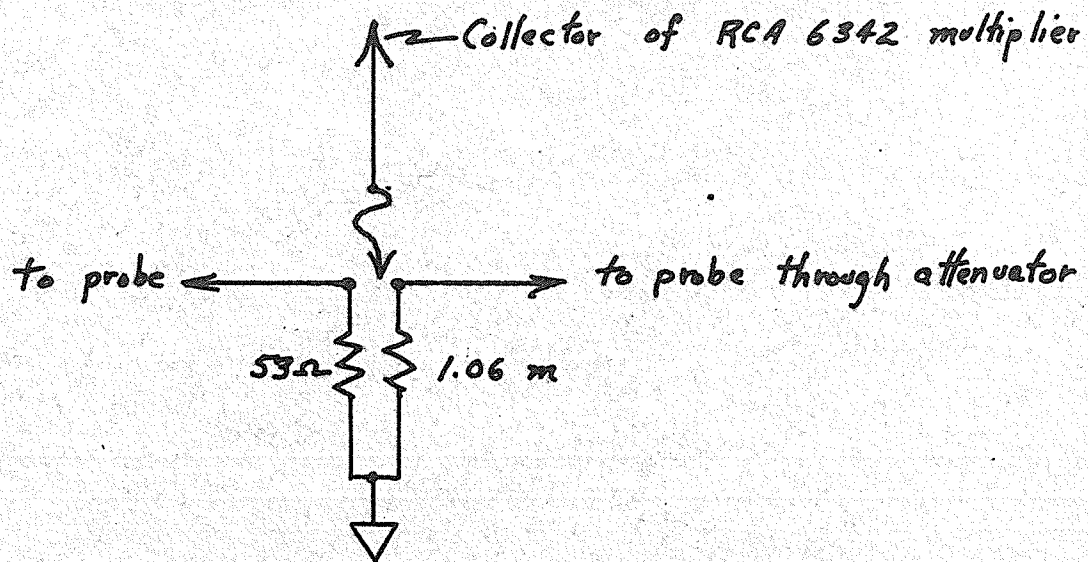


FIGURE NO. 18

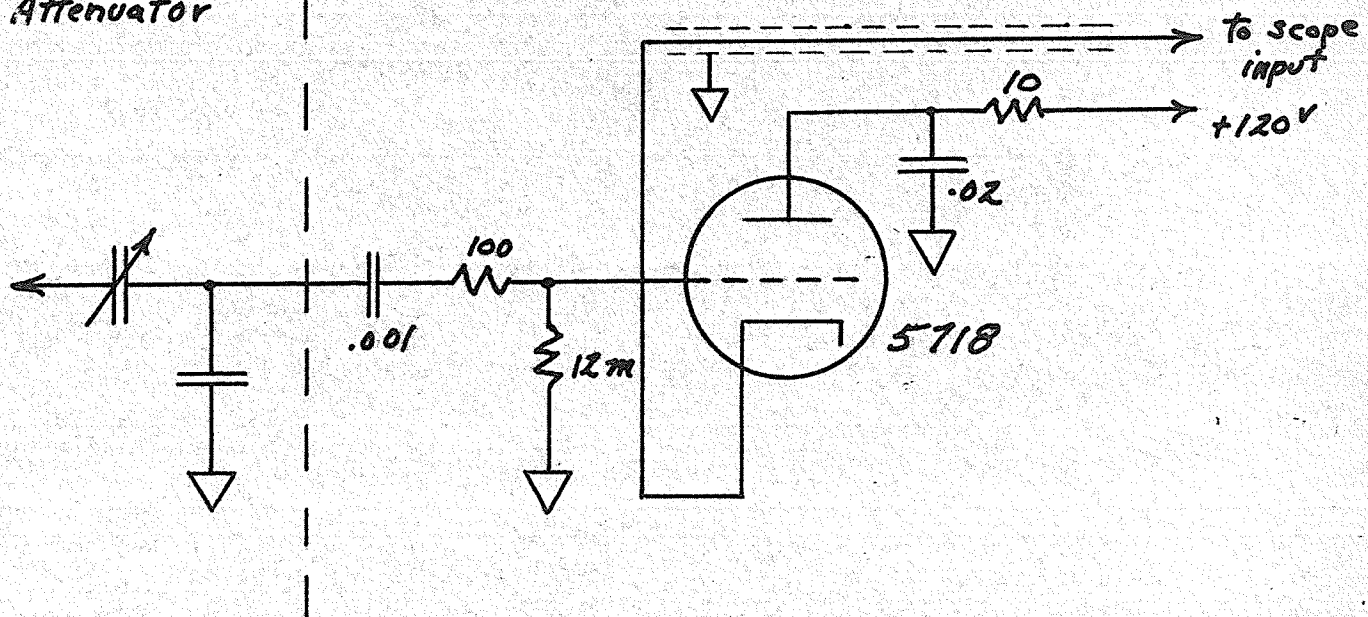
Schematic for decay time measurements.

Dynode connections for 6342 multiplier as in Figure 4.



Capacitive
Attenuator

Tektronix 517 Probe



With load resistor $R_1 = 1.06$ megohms, the multiplier output was fed into the scope cathode-follower through a capacitance attenuator. The peak of the Compton spectrum then observed corresponded to V_{m1} . With load resistor $R_2 = 53$ ohms, the scope cathode follower was connected directly to the multiplier output. V_{m2} was then taken to be the peak of this new spectrum. Hence for each scintillator two photographs were taken. The same sweep speed (10 mps./cm.) was used for both load resistors. Therefore the high load resistor spectrum was a series of parallel horizontal lines displaced vertically. This was in sharp contrast to the low load resistor spectrum which comprised the normally encountered pulse spectrum. (see Figure 19). The exposure times were two minutes for the R_1 spectrum and ten minutes for the R_2 spectrum. The difference in exposure time arose from the two spectrum intensities being different. The film development time was ten minutes in Kodak Dektol developer. Because the spectrum base line was blurred due to the time exposures, the base line was aligned with a horizontal grid line on the scope. This enabled accurate determination of the base line. The measurement of the spectrum amplitude was performed by projecting the film through a photographic enlarger onto a sheet of graph paper.

Anthracene, the standard scintillator, was photographed and the ratio $\frac{V_{m2}}{V_{m1}}$ was measured and found to be unity. This measurement was repeated three times initially and subsequently remeasured once each day unknown scintillators were tested. These later measurements were of the form of a daily calibration.

FIGURE NO. 19

Typical measurement photograph for Stilbene showing the two Compton spectra.



It was found that the anthracene ratio remained unity within 3% throughout the duration of the experiment.

To determine the position of the correction line of Figure 10, a liquid scintillator was prepared, the decay time of which was known. This solution was composed of phenylcyclohexane with 3 g/l p-terphenyl and 0.01 g/l diphenylhexatriene (PCH). The solution was bubbled for 20 minutes with nitrogen to remove any dissolved oxygen. This procedure was necessary for oxygen acts as a quencher (8). A similar solution was measured by Swank and Buck (4) and their quoted decay time was 8.0 ± 0.08 μ s. It was not known whether Swank's solution was bubbled with nitrogen. However, the solution must have been relatively oxygen free for the presence of oxygen would have caused Swank's decay time to be much lower (see effect of oxygen quenching, section 6.7). Bittman, Furst and Kallmann (6) also measured this solution (again unbubbled) and found a decay time of 6.3 ± 2 μ s. Because Swank's value was more accurately determined, the true decay time of this solution was assumed to be 8.0 ± 0.08 μ s*. Due to the 53 ohm load resistor this decay time of 8 μ s. was stretched to 10.2 μ s. This correction was obtained from Figure 14. Hence, on the amplifier correction curve of Figure 10, the value of 10.2 μ s. should correspond to the measured value of the decay time. The decay time of the liquid was measured and plotted on Figure 10 opposite the value of 10.2. By using ratios the true correction line was drawn and the rise time of the multiplier pulse was estimated.

*If Sand B's value is in error this error will be transmitted to all the unknown decay times measured.

A series of organic scintillators were measured. These included plastics, liquids and gels. The steps in the measurement procedure were as follows:

- 1) The two Compton spectra were photographed.
- 2) The peaks of the spectra were measured and the ratio $\frac{V_{m1}}{V_{m2}}$ obtained.
- 3) Equation (8) was used to obtain the observed decay time i.e.

$$\sigma_0 = \sigma_s \cdot \frac{V_{m1}}{V_{m2}} \cdot \frac{V_{m2}^s}{V_{m1}^s}$$

or
$$\sigma_0 = 31.5 \frac{V_{m1}}{V_{m2}} \cdot 1 \text{ } \mu\text{sec.}$$

- 4) The amplifier correction curve of Figure 10 was applied to σ_0 to yield σ_1 .
- 5) The load resistor correction curve of Figure 14 was applied to σ_1 to yield the true decay time, σ .

CHAPTER 5

R E S U L T S

Sample	Contents	σ_0 (mus.)	σ_1 (mus.)	σ (mus.)
Anthracene				31.5 \pm 1
Stilbene		10.0 \pm .5	5.1	3.3 \pm .5
Plastics				
40-B	V.T. + 2g/100 ml terph. + .05 g/100 ml POPOP	9.3 \pm .5	4.4	2.7 \pm .5
53-H	V.T. + 2 g/100 ml terph. + .4 g/100 ml POPOP	9.3 \pm .5	4.4	2.7 \pm .5
52-G	V.T. + 2 g/100 ml terph. + .5 g/100 ml POPOP	9.5 \pm .5	4.6	2.9 \pm .5
54-B	V.T. + 2 g/100 ml terph. + .05 g/100 ml POPOP + .01 g/100 ml T.P.B.	11.0 \pm .5	6.05	4.2 \pm .5
42-D	V.T. + 2 g/100 ml T.P.B.	10.0 \pm .5	5.1	3.3 \pm .5
41-A	V.T. + 1 g/100 ml POPOP + 1 g/100 ml T.P.B.	10.9 \pm .5	5.95	4.1 \pm .5
24-A	2 cc V.T. + 18 cc Styrene + 2 g/100 ml terph. + .15 g/100 ml T.P.B.	11.3 \pm .6	6.3	4.4 \pm .6
24-C	10 cc V.T. + 10 cc Styrene + 2 g/100 ml terph. + .15 g/100 ml T.P.B.	11.7 \pm .6	6.7	4.8 \pm .6
51-B	V.T. + 2g/100 ml terph. + .15 g/100 ml T.P.B. + 11.4% Pb Cap.	9.0 \pm .5	4.15	2.5 \pm .5

Sample	Contents	σ_0 (mus.)	σ_1 (mus.)	σ (mus.)
Gels				
8-A	L-5 + 2 g/l terph. + 5.5%			
	Al Stear.	8.7 \pm .4	3.9	2.3 \pm .4
	L-5 + 3.1% Al-2 Et - Hex.	9.8 \pm .5	4.9	3.2 \pm .5
9-D	L-5 + 7.2% Al-2 Et - Hex.	9.4 \pm .5	4.55	2.9 \pm .5
Liquids				
L-2	Xyl. + 4 g/l terph. + 0.1 g/l POPOP	10.3 \pm .5	5.4	3.6 \pm .5
L-5	Xyl. + 4 g/l terph. + 0.1 g/l POPOP	10.0 \pm .5	5.1	3.3 \pm .5
L-10	Xyl. + 3 g/l PBD + 70 g/l Napht.	10.6 \pm .5	5.7	3.9 \pm .5
L-15	Xyl. + 9 g/l PBD + 70 g/l Napht.	10.0 \pm .5	5.1	3.3 \pm .5
L-1	Xyl. + .4 g/l terph. + .1 g/l D.P.H.	14.6 \pm .7	9.4	7.3 \pm .7
PCH	Phenylcyclohexane + 3 g/l terph. + 0.1 g/l D.P.H.	15.4 \pm .8	10.2	8.0 \pm .8
PCH-2	PCH + 0.2 (M) Bromo.	14.8 \pm .7	9.65	7.5 \pm .7
PCH-4	PCH + 0.4 (M) Bromo.	13.3 \pm .7	8.2	6.2 \pm .7
PCH-6	PCH + 0.6 (M) Bromo.	12.3 \pm .6	7.3	5.4 \pm .6
PCH-8	PCH + 0.8 (M) Bromo.	11.3 \pm .5	6.3	4.5 \pm .5
PCH-0	PCH quenched with O ₂	10.3 \pm .5	5.4	3.6 \pm .5
Gd	L-15 + 6.33% Gd-2 Et-Hex. by weight or 1.64% Gd	9.3 \pm .5	4.4	2.7 \pm .5
PVC-3	toluene + 4 g/l terph. + 2 g/l PVC	9.3 \pm .5	4.4	2.7 \pm .5
B-16-x	L-15+16.4% Pb Cap. or 6.6% Pb by weight	7.3 \pm .4	2.6	1.1 \pm .4

Glossary of Chemical Abbreviations:

<u>Symbol</u>	<u>Chemical</u>
V.T.	Vinyl toluene
terph.	p-terphenyl
POPOP	1,4-di- 2-(5-phenyloxazolyl) -benzene
T.P.B.	tetraphenyl butadiene
Pb Cap.	Lead Caprilate
Xyl.	Xylene
Al Stear.	Aluminum Stearate
Al-2 Et-Hex.	Aluminum-2 Ethyl-Hexanoate
PBD	phenylbiphenylyloxazole
Napht.	Naphthalene
D.P.H.	Diphenylhexatriene
Gd-2 Et-Hex.	Gadolinium-2 Ethyl-Hexanoate
PVC	Polyvinylcarbazole
Bromo.	Bromobenzene
(M)	Molar concentration

CHAPTER 6

DISCUSSION OF RESULTS6.1 EXPERIMENTAL ERRORS

The primary observational errors were in the measurement of the heights of the Compton spectra. In all the scintillators this error was about 3% for V_{m1} and 2% for V_{m2} giving a total of 5% for the ratio $\frac{V_{m1}}{V_{m2}}$. In the conversion of the above ratio to a true decay time for the scintillator further errors were introduced which were systematic in nature.

The first of these systematic errors was the error in the measurement of the anthracene decay time. Individual anthracene pulses had decay times ranging from 26 μ s. to 38 μ s.* The majority, however, had decays between 31 and 32 μ s. The average deviation from the mean decay time of 31.5 μ s. was 1 μ s.

The second systematic error was in the use of the Compton peak ratio $\frac{V_{m2}^S}{V_{m1}^S}$ for the anthracene standard. This ratio should have been constant since it is dependent on the attenuation factor of the capacitive attenuator. Due to observational errors its mean value is known with an accuracy of 3%.

Unknown error arose in the use of the amplifier correction curve. This curve was derived mainly from the indicial response of the amplifier. This response was known with an accuracy of about 2%. In order to find the effect of this 2% error in the indicial response on the correction curve, it would be necessary

These measurements were performed very carefully and rechecked.
(continued on page 50a).

(continuation of footnote)

The spread is genuine within experimental errors. It was thought that this spread was due to the decay time varying with the excitation energy of the radiation incident upon the anthracene crystal. Decay times were measured on pulses resulting from incident radiations ranging from 0.5 to 4 m.e.v. These measurements showed no apparent relationship between the excitation energy and the scintillator decay time. Since the number of measured decay times which differ greatly from the mean is small it is thought that this spread is a statistical one.

to repeat the computations of section 4.1 for the two extreme values of the indicial response. It was felt that this error was not too serious and that it did not warrant such tedious calculations.

Error in the load resistor correction curve (Figure 14) was due to errors in the measured values of $R_2 \neq C$ (see 4.2). Error in the product, $R_2 C$, and therefore in γ was about one per cent. Thus the error in V_m (equation 4) and also in the correction curve is less than one per cent.

It was assumed that the oscilloscope sweep speeds had negligible error ~~***~~ and that the Y deflection was linear. To have verified these assumptions experimentally would have required special test equipment which was not available.

The quoted errors of the results in Chapter 5 exclude all the systematic errors. Hence, for the unknown scintillators the true decay time quoted may have a further error of as much as six per cent. However, this systematic error was the same for all samples and thus if two unknown decay times were compared the systematic errors cancelled out. Since the experiment was designed to primarily compare decay times of various scintillators the primary error on the ratio of $\frac{V_{m1}}{V_{m2}}$ was the only relevant one.

6.2 OTHER EXPERIMENTAL DECAY TIMES

Table V, showing some of the decay time data that had been obtained by other experimenters, was compiled from the literature. Column one was taken from some of the samples of Chapter 5. From

* Note: The amplifier correction curve indirectly corrects for electron transit time spread in the multiplier.

* * Visual observation showed sweep speed to be correct to at least 20%.

this table it is seen that there was general agreement between decay times obtained in this experiment and those obtained by others.

TABLE 5

OTHER EXPERIMENTAL DECAY TIMES

Substance	Present Value	S+B(4) + 1%	S(1)	B,F+K(6)	LBE (9)	Misc. (10)
Anthracene	31.5 \pm 1	29.9 33.2 38.4 35.3	30.0 \pm .7	22.8 \pm 5	30	31 \pm 2
Stilbene	3.3 \pm .5	\leq 3.0	8.1 \pm .2	6.9 \pm 1.7	8	7.2 \pm .6
PCH	8.0 \pm .7	8.0		6.8 \pm 2		
Liquid Solutions	2 - 4					2 - 4
Plastic Solutions	2 - 5					2 - 5

6.3 PLASTIC SOLUTIONS

The plastic solutions measured had decay times which ranged from 2 to 5 μ s. It was noted from the decay times of the samples 40-B, 53-H and 52-G that the concentration of solutes for a given solvent had no effect on decay times within experimental errors. Also, from the decay times of 24-A, 24-C, 54-B and 41-A, it was found that a change of solvent for a given solute had no effect on the decay time within experimental error.

6.4 LIQUID SOLUTIONS

The liquid solutions measured showed similar results to those obtained from the plastics in that the concentration of solute and change of solvent affected the decay time negligibly. The effect of solute concentration for a given solvent was seen in samples L-10 and L-15 while the effect of solvent change for given solutes was evident from samples L-1 and PCH. The effect of a change in secondary solute was graphically illustrated by the difference in decay time between samples L-2 and L-1. Here the change of secondary solute from POPOP to D.P.H. resulted in a doubling of the decay time.

The above effects have been predicted by the general theory of the scintillation process (11, 12, 13). This process is as follows:

1. Excitation of the scintillator solvent molecules by the incident radiation.
2. Almost instantaneous transfer of the excitation energy from solvent molecule until the energy is either quenched non-radiatively or:
3. The excitation energy is transferred to a primary solute molecule.
4. The excited primary solute molecule is de-excited either non-radiatively or by photon emission.
5. Re-absorption of the primary solute radiation by the secondary solute.
6. De-excitation of the secondary solute, either

non-radiatively or by photon emission. The wavelength of the secondary solute photon is longer than that of the primary solute. Hence the secondary solute is often termed a wavelength shifter.

From the above process it is seen that the scintillation decay time is a property of the solute molecules. Hence a change in solvent should not affect the decay time. Similarly small changes in the concentration of solutes will affect only the scintillation efficiency and not the decay time. If larger concentrations of solute are added a phenomenon termed concentration quenching occurs (12). For concentrations of this magnitude the decay time ~~should~~ be affected by concentration changes.

6.5 SCINTILLATING GELS

A new type of organic scintillator, the scintillating gel had been developed at the University of Manitoba (14). The gel was developed as a means of obtaining a 4π counter. The sample whose radiation was to be measured was suspended throughout the gel to form an intimate mixture of source and scintillator.

Previous to this date, there had been no figures on the decay times of these gels. It was hoped that the effect of viscosity (15) of a gel on decay time could be checked. However, the gels available all had short decay times and no effect was observable.

6.6 THE KINETICS OF QUENCHING PROCESSES

There are two types of processes by which fluorescence may be quenched. The first of these is the "collisional" type which begins after the potentially fluorescent molecule has been excited. The second is the "static" type which begins before the fluorescent molecule has been excited. In the collisional process the excited fluorescent molecule interacts with a quencher molecule which results in a thermal degradation of the excitation energy. In the static process some of the fluorescent molecules form a complex molecule with the quencher molecule. This complex is not capable of fluorescence. Hence in the static case the number of molecules that can fluoresce is reduced.

For both processes one can write a Stern-Volmer type equation (15):

$$\frac{F_0}{F} - 1 = K[Q] \quad (14)$$

where F_0 is the fluorescent intensity of the solution before addition of the quencher

F is the fluorescent intensity after the quencher addition

K is a quenching constant

$[Q]$ is the concentration of quencher.

Also Perrin (16) has shown that

$$\frac{F_0}{F} = \frac{N_0 \sigma_0}{N \sigma} \quad (15)$$

where N_0 and N are the numbers of excited molecules that may be de-activated in the absence and presence of quencher respectively.

σ_0 and σ are the decay times before and after the addition of quencher respectively.

For the case of ideal collisional quenching $N = N_0$ and there results

$$\frac{F_0}{F} = \frac{\sigma_0}{\sigma} \quad (15a)$$

Substituting for $\frac{F_0}{F}$ in (14) one obtains

$$\frac{\sigma_0}{\sigma} - 1 = K[Q] \quad (16)$$

This last equation predicts that for collisional quenching the concentration of quencher will vary linearly with the inverse of the decay time.

In the case of complex formation the complex molecules are unable to emit. Then $N/N_0 = \alpha$, the degree of dissociation of the complex. If β denotes the mean free life of the fluorescent molecules then we can write that (reference 17)

$$\sigma = \frac{1}{\frac{1}{\beta} + \frac{1}{\sigma_0}} \quad (17)$$

If the mean free life of the complex is denoted by Σ and the concentration of fluorescent molecules is termed $[M]$ we may write for the steady state:

number of complexes formed/unit time = number of

complexes broken down/unit time

$$\text{or } \frac{1}{\beta} \cdot \alpha[M] = \frac{1}{\Sigma} \cdot (1-\alpha)([M]) \quad (18)$$

from (17)

$$\frac{1}{\beta} = \frac{1}{\sigma} - \frac{1}{\sigma_0}$$

substituting for $1/\beta$ in 18 we get

$$\left(\frac{1}{\sigma} - \frac{1}{\sigma_0}\right)\alpha = \frac{1}{\Sigma}(1-\alpha)$$

or

$$\frac{1}{\alpha} = 1 + \frac{\Sigma}{\sigma_0} \left(\frac{\sigma_0}{\sigma} - 1\right) \quad (19)$$

from 15 we get
$$\frac{F_0}{F} = \frac{N_0}{N} \cdot \frac{G_0}{G} = \frac{1}{\alpha} \frac{G_0}{G} \quad (15b)$$

Substituting for $1/\alpha$ in (15b) we get:

$$\frac{F_0}{F} = \frac{G_0}{G} \left(1 + \frac{E}{G_0} \left[\frac{G_0}{G} - 1 \right] \right) \quad (20)$$

Substituting for $\frac{F_0}{F}$ in (14) we have

$$\frac{G_0}{G} \left(1 + \frac{E}{G_0} \left[\frac{G_0}{G} - 1 \right] \right) - 1 = K[Q] \quad (21)$$

which is of the form

$$[Q] = A \left(\frac{1}{G} \right)^2 + B \left(\frac{1}{G} \right) + C$$

This represents a parabola opening out in the positive $[Q]$ direction.

6.7 EXPERIMENTAL QUENCHING

Due to the low atomic number of organic scintillators their scintillation spectra show no photopeak. In an attempt to raise the atomic number liquid and plastic solutions have been loaded with metals such as lead and gadolinium.

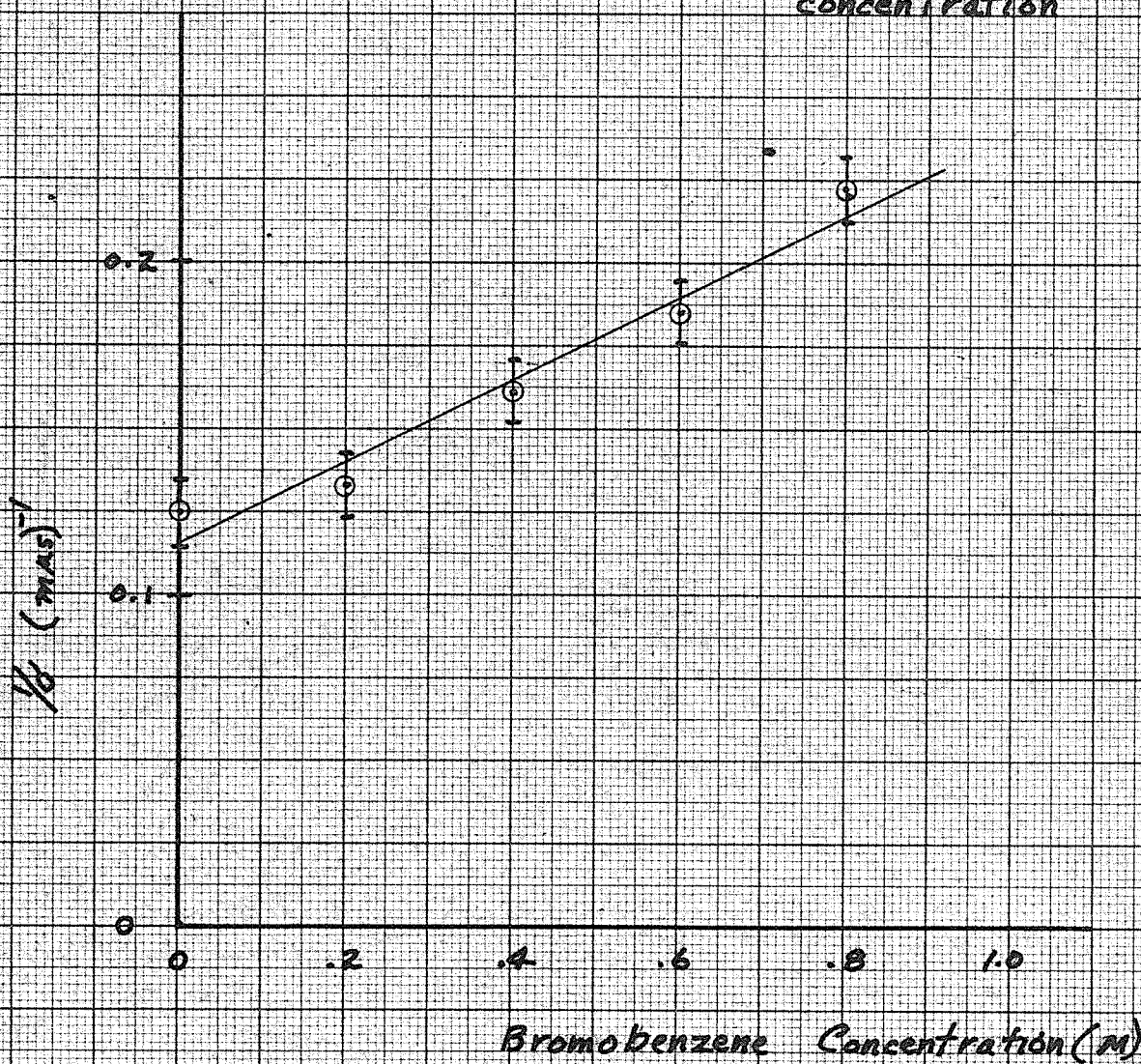
The decay times of two such liquids were measured namely samples Gd and B-16-x. The scintillations from these samples were partly quenched by the metal additions, the latter, lead loaded one, very heavily. The lead sample showed a marked decrease in decay time.

A similar effect was noted when the liquid PCH was bubbled with oxygen to saturation. The decay time of the oxygen free sample was reduced by 55% upon saturation with oxygen.

To further investigate the effect of quenchers the samples PCH-2, PCH-4, PCH-6 and PCH-8 were measured. Figure 20

FIGURE NO. 20

Variation of (decay
time)⁻¹ with quencher
concentration



was plotted showing the relation of the concentration of bromobenzene and the reciprocal of the decay time.

From the shape of the curve of Figure 19 it was obvious that a parabola of the sort described above could not fit the points. A straight line, however, was possible. Using the method of least squares a straight line was fitted to the points of Figure 19. It was found that all the experimental points lay on the least squares line within experimental errors. Therefore within the experimental limits the quenching by bromobenzene was of the collisional type. The quenching curve as obtained by the method of least squares is:

$$\frac{1}{\tau} = 0.123[Q] + 0.116$$

where τ is in μ ps.

$[Q]$ is in (M)

APPENDIX 1

M U L T I P L E D E C A Y S C H E M E

Suppose the scintillator has two decay components.

The current function then assumed must be of the form:

$$I(t) = \frac{A_1}{\alpha} e^{-t/\alpha} + \frac{A_2}{\beta} e^{-t/\beta}$$

There the A_1 and A_2 are maximums of the decays α and β respectively.

Proceeding in a similar manner as before (section 3.1)

we get

$$V(s) = \frac{\frac{A_1}{C\alpha}}{(s + 1/\alpha)(s + 1/RC)} + \frac{\frac{A_2}{C\beta}}{(s + 1/\beta)(s + 1/RC)}$$

and we get

$$V(t) = \frac{A_1 R}{RC - \alpha} \{ e^{-t/RC} - e^{-t/\alpha} \} + \frac{A_2 R}{RC - \beta} (e^{-t/RC} - e^{-t/\beta})$$

Case (a) if $R_1 C \gg \alpha$ and $R_1 C \gg \beta$

$$V_1(t) = \left(\frac{A_1}{C} + \frac{A_2}{C} \right) e^{-t/RC}$$

and

$$V_{m1} = \frac{A_1 + A_2}{C}$$

Case (b) if $R_2 C \ll \alpha$ and $R_2 C \ll \beta$

$$V_2(t) = \frac{A_1' R_2}{\alpha} e^{-t/\alpha} + \frac{A_2' R_2}{\beta} e^{-t/\beta}$$

$$V_{m2} = \frac{A_1' R_2}{\alpha} + \frac{A_2' R_2}{\beta}$$

where the primed A's are introduced to account for the gain change of the attenuator.

Then the ratio

$$\frac{V_{1m}}{V_{2m}} = \frac{A_1 + A_2}{CR_2 \left(\frac{A_1'}{\alpha} + \frac{A_2'}{\beta} \right)}$$

If a standard is obtained it will have parameters: $A_S, A_S^1, \sigma_S,$

$V_{ms1}, V_{ms2}.$

$$\frac{V_{ms2}}{V_{ms1}} = \frac{A_S'}{A_S} \cdot \frac{R_2 C}{\sigma_S}$$

We make the assumption that

$$k = \frac{A_3}{A_3'} = \frac{A_1}{A_1'} = \frac{A_2}{A_2'}$$

Now consider the quantity γ_i defined by:

$$\gamma_i = \frac{V_{ms2}}{V_{ms1}} \cdot \frac{V_{m1}}{V_{m2}} = \frac{(A_1 + A_2) \alpha \beta}{k \sigma_s (A_1' \beta + A_2' \alpha)}$$

let $A_2' = BA_1'$ then $A_2^1 = BA_1^1$

$$\text{then } \gamma_i = \frac{(1+B) \alpha \beta}{\sigma_s (\beta + B \alpha)}$$

then the unknown decay time $\sigma = \gamma_i \sigma_s$

$$\sigma = \frac{(1+B) \alpha \beta}{\beta + B \alpha}$$

This expression is a sort of weighted average decay time.

APPENDIX 2

FINITE RISE TIME DECAY SCHEME

The current pulse actually delivered by the photomultiplier has a finite rise time. The shape of this leading edge will probably resemble some sort of Gaussian distribution. Mathematically this is rather unwieldy to manipulate so a simplifying assumption will be made which will indicate any serious errors in neglecting the rise time. It will be assumed that the pulse has a linear rise.

We would have:

$$I(t) = \alpha t \quad 0 \leq t \leq a$$

$$= \frac{A}{\sigma} e^{-\frac{t-a}{\sigma}} \quad a \leq t \leq \infty$$

then

$$\begin{aligned} \mathcal{L}\{I(t)\} &= \int_0^{\infty} e^{-st} I(t) dt \\ &= \int_0^a e^{-st} \alpha t dt + \int_a^{\infty} \frac{A}{\sigma} e^{-st} e^{-\frac{t-a}{\sigma}} dt \\ &= \frac{\alpha}{s^2} (-st-1) \Big|_0^a + e^{-as} \frac{A}{\sigma} \int_0^{\infty} e^{-s(t-a)} e^{-\frac{t-a}{\sigma}} d(t-a) \end{aligned}$$

$$I(s) = \frac{\alpha e^{-as}}{s^2} (-as-1) + \frac{\alpha}{s^2} + \frac{A/\sigma e^{-as}}{s + 1/\sigma}$$

$$V(s) = \frac{I(s)}{c(s + 1/Rc)}$$

$$\therefore V(s) = \frac{1/c \left\{ \frac{\alpha}{s^2} - \frac{\alpha e^{-as}(1+as)}{s^2} + \frac{A/\sigma e^{-as}}{s + 1/\sigma} \right\}}{s + 1/Rc}$$

$$= \frac{\frac{\alpha}{c}}{s^2(s + 1/Rc)} - \frac{\frac{\alpha}{c} e^{-as}}{s^2(s + 1/Rc)} - \frac{\frac{\alpha}{c} a e^{-as}}{s(s + 1/Rc)} + \frac{\frac{A}{c\sigma} e^{-as}}{(s + 1/\sigma)(s + 1/Rc)}$$

Taking inverse Laplace transforms:

$$V(t) = u(t-a) \frac{AR}{RC-\delta} \left\{ e^{-t/RC} - e^{-t/\delta} \right\} - R^2 \alpha C [1 - e^{-t/RC}] \\ + R^2 \alpha C [1 - e^{-t/RC}] u(t-a) + \alpha R t [u(t) - u(t-a)] \\ + R \alpha a e^{-t/RC} u(t-a)$$

Case 1: $R_1 C \gg \sigma \quad R_1 C \gg a$

$$\text{then } V_1(t) \doteq \frac{A_1}{C} e^{-t/RC} u(t-a)$$

Case 2: $R_2 C \ll \sigma \quad R_2 C \ll a$

$$\text{then } V_2(t) \doteq \frac{A_2 R_2}{\delta} e^{-t/\delta} u(t-a) \\ + \alpha R_2 t [u(t) - u(t-a)]$$

$$\therefore V_{m1} \doteq A_1/C \quad V_{m2} = \frac{A_2 R_2}{\delta}$$

These were the same values we had assuming zero rise time.

APPENDIX 3

LAPLACE TRANSFORM THEOREMCOMPLEX MULTIPLICATION

If two functions $f_1(t)$ and $f_2(t)$ are Laplace transformable and if

$$F_1(s) = \mathcal{L}\{f_1(t)\} \quad \text{and} \quad F_2(s) = \mathcal{L}\{f_2(t)\}$$

then

$$\mathcal{L}^{-1}\{F_1(s)F_2(s)\} = \int_0^t f_1(t-\alpha)f_2(\alpha) d\alpha.$$

or

$$\mathcal{L}^{-1}\{F_1(s)F_2(s)\} = \int_0^t f_1(\alpha)f_2(t-\alpha) d\alpha.$$

APPENDIX 4

TABLE ITHE INDICIAL RESPONSE $A(+\tau)$

τ (mus.)	100 $A(\tau)$
0	0
1	0.6
2	2.8
3	6.0
4	11.55
5	20.8
6	32.8
7	46.2
8	60.2
9	74.0
10	85.9
11	93.4
12	97.3
13	99.3
14	100.0

TABLE IIVALUES OF $e^{-\alpha\tau}$ for $\alpha = 0.2 \times 10^9 \text{ sec.}^{-1}$

τ (m μ s.)	$100 e^{-\alpha\tau}$
0	100.0
1	81.9
2	67.0
3	54.9
4	44.9
5	36.8
6	30.1
7	24.7
8	20.2
9	16.53
10	13.53
11	11.08
12	9.07
13	7.43
14	6.08
15	4.98
16	4.08
17	3.33
18	2.73

TABLE III (a)

VALUES OF $A(t - \tau) \times e^{-\alpha\tau}$ for $t = 5 \text{ } \mu\text{s}$.

τ	$100A(t - \tau)$	$100 e^{-\alpha\tau}$	$100A(t - \tau)e^{-\alpha\tau}$
5	0.0	36.8	0
4	0.6	44.9	0.3
3	2.8	54.9	1.538
2	6.0	67.0	4.02
1	11.55	81.9	9.46
0	20.8	100.0	20.8

(b)

VALUES OF $A(t - \tau)e^{-\alpha\tau}$ for $t = 6 \text{ } \mu\text{s}$.

τ	$100A(t - \tau)$	$100 e^{-\alpha\tau}$	$100A(t - \tau)e^{-\alpha\tau}$
6	0	30.1	0
5	.6	36.8	.2
4	2.8	44.9	1.26
3	6.0	54.9	3.29
2	11.55	67.0	7.73
1	20.8	81.9	17.03
0	32.8	100.0	32.8

TABLE III (c)

VALUES OF $A(t - \tau)e^{-\alpha\tau}$ for $t = 7$ μ s.

τ	$100A(t - \tau)$	$100e^{-\alpha\tau}$	$100A(t - \tau)e^{-\alpha\tau}$
7	0	24.7	0
6	.6	30.1	0.2
5	2.8	36.8	1.03
4	6.0	44.9	2.69
3	11.55	54.9	6.34
2	20.8	67.0	13.93
1	32.8	81.9	26.9
0	46.2	100.0	46.2

(d)

VALUES OF $A(t - \tau)e^{-\alpha\tau}$ for $t = 8$ μ s.

τ	$100A(t - \tau)$	$100e^{-\alpha\tau}$	$100A(t - \tau)e^{-\alpha\tau}$
8	0	20.2	0
7	0.6	24.7	0.1
6	2.8	30.1	0.84
5	6.0	36.8	2.15
4	11.55	44.9	5.19
3	20.8	54.9	11.42
2	32.8	67.0	21.95
1	46.2	81.9	37.8
0	60.2	100.0	60.2

TABLE III (e)

VALUES OF $A(t - \tau)e^{-\alpha\tau}$ for $t = 9$ μ ps.

τ	$100A(t - \tau)$	$100e^{-\alpha\tau}$	$100A(t - \tau)e^{-\alpha\tau}$
9	0	16.53	0
8	0.6	20.2	0.1
7	2.8	24.7	0.7
6	6.0	30.1	1.8
5	11.55	36.8	4.25
4	20.8	44.9	9.34
3	32.8	54.9	18.0
2	46.2	67.0	30.9
1	60.2	81.9	49.3
0	74.0	100.0	74.0

(f)

VALUES OF $A(t - \tau)e^{-\alpha\tau}$ for $t = 10$ μ ps.

τ	$100A(t - \tau)$	$100e^{-\alpha\tau}$	$100A(t - \tau)e^{-\alpha\tau}$
10	0	13.53	0
9	0.6	16.53	0
8	2.8	20.2	0.6
7	6.0	24.7	1.5
6	11.55	30.1	3.5
5	20.8	36.8	7.66
4	32.8	44.9	14.74
3	46.2	54.9	25.3
2	60.2	67.0	40.3
1	74.0	81.9	60.6
0	85.9	100.0	85.9

TABLE III (g)

VALUES OF $A(t - \tau)e^{-\alpha\tau}$ for $t = 11 \text{ m}\mu\text{s}$.

τ	$100A(t - \tau)$	$100e^{-\alpha\tau}$	$100A(t - \tau)e^{-\alpha\tau}$
11	0	11.08	0
10	0.06	13.53	0
9	2.8	16.53	0.5
8	6.0	20.2	1.2
7	11.55	24.7	2.85
6	20.8	30.1	6.26
5	32.8	36.8	12.07
4	46.2	44.9	20.7
3	60.2	54.9	33.0
2	74.0	67.0	49.6
1	85.9	81.9	70.3
0	93.4	100.0	93.4

(h)

VALUES OF $A(t - \tau)e^{-\alpha\tau}$ for $t = 12 \text{ m}\mu\text{s}$.

τ	$100A(t - \tau)$	$100e^{-\alpha\tau}$	$100A(t - \tau)e^{-\alpha\tau}$
12	0.0	9.07	0
11	0.06	11.08	0
10	2.8	13.53	0.4
9	6.0	16.53	1.0
8	11.55	20.2	2.3
7	20.8	24.7	5.1

TABLE III (h) (continued)

τ	$100A (t - \tau)$	$100e^{-\alpha\tau}$	$100A (t - \tau)e^{-\alpha\tau}$
6	32.8	30.1	9.9
5	46.2	36.8	17.0
4	60.2	44.9	27.0
3	74.0	54.9	40.6
2	85.9	67.0	57.5
1	93.4	81.9	76.5
0	97.3	100.0	97.3

(i)

VALUES OF $A (t - \tau)e^{-\alpha\tau}$ for $t = 13 \text{ } \mu\text{s.}$

τ	$100A (t - \tau)$	$100e^{-\alpha\tau}$	$100A (t - \tau)e^{-\alpha\tau}$
13	0.0	7.43	0
12	0.6	9.07	0
11	2.8	11.08	0.3
10	6.0	13.53	0.7
9	11.55	16.53	1.8
8	20.8	20.2	4.2
7	32.8	24.7	8.1
6	46.2	30.1	13.9
5	60.2	36.8	22.2
4	74.0	44.9	33.3
3	85.9	54.9	47.2
2	93.4	67.0	62.5
1	97.3	81.9	78.7
0	99.3	100.0	99.3

TABLE III (j)

VALUES OF $A(t - \tau)e^{-\alpha\tau}$ for $t = 14$ μ s.

τ	$100A(t - \tau)$	$100e^{-\alpha\tau}$	$100A(t - \tau)e^{-\alpha\tau}$
14	0	6.08	0
13	0.6	7.43	0
12	2.8	9.07	0.25
11	6.0	11.08	0.7
10	11.55	13.53	1.3
9	20.8	16.53	3.4
8	32.8	20.2	6.6
7	46.2	24.7	11.4
6	60.2	30.1	18.1
5	74.0	36.8	27.2
4	85.9	44.9	38.6
3	93.4	54.9	51.3
2	97.3	67.0	65.2
1	99.3	81.9	81.3
0	100.0	100.0	100.0

B I B L I O G R A P H Y

1. Sangster, R.C. and Irvine, J.W. J. Chem. Phys. 24 670 (April 1956)
2. Kallmann, H. and Spruch, G. Phys. Rev. 103 (August 1956)
3. Singer, S. Heher, L.K. and Ruehle, R.A. R. S. I. 27 No. 1 40 (1956)
4. Swank, R.K. and Buck, W.L. R. S. I. 26 No. 1 15 (1955)
5. Birks, J.B. and Little, W.A. Proc. Phys. Soc. A, 66 921 (1953)
6. Bittman, L, Furst, M. and Kallmann, H. Phys. Rev. 87 83 (1952)
7. Swank, R.K. Ann. Rev. Nucl. Sc. 4 (1954)
8. Funt. B.L. and Neparko, E. J. Phys. Chem. 60 267 (1956)
9. Liebson, Bishop and Elliot, Phys. Rev. 80 907 (1950)
10. Data due to miscellaneous authors. The average value and its standard deviation are tabulated. See reference (1).
11. Curran. "'Luminescence and the Scintillation Counter'", Butterworth's Scientific Publications (1953)
12. Garlick, G. "'Luminescent Materials'", Clarendon Press (1949)
13. Birks, J.B. "'Scintillation Counters'", Pergamon Press (1953)
14. Funt, B.L. Nucleonics 14 83 (August 1956)
15. Bowen, E.J. and Wokes, J. "'Fluorescence of Solutions'", Longmans, Green and Company (1953)
16. Perrin, F. Annales de Phys. 12 169 (1929)
17. Weber, G. Trans. Faraday Soc. 44 185 (1938)