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ABSTRACT

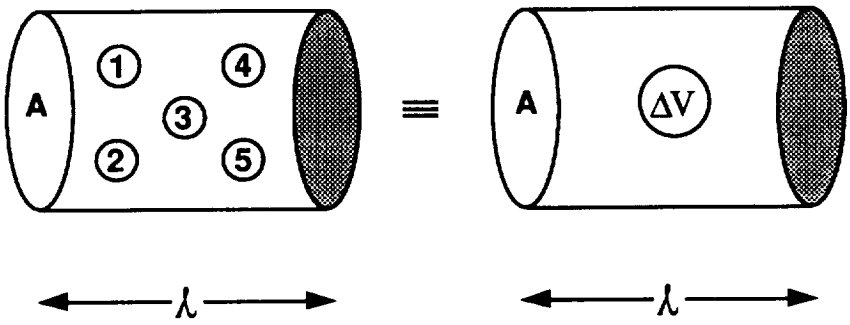
The quality of contact lens samples depends strongly on their free volume fractions. It is expected that the free volume fractions of the test samples will also impact their linear attenuation coefficients for soft x-rays. Samples with larger free volume fractions should have lower linear attenuation coefficients. Linear attenuation coefficients for Cd^{109}/Ag^{109} x-rays have been measured in five contact lens samples. It has been shown that the differences in the linear attenuation coefficients of discs from any given sample are entirely due to the differences in their respective free volume fractions. It is therefore concluded that an x-ray attenuation measurement system can serve as a quality monitor for contact lens polymers.

INTRODUCTION

Contact lenses are being used widely by a large segment of the American population. Primary qualities of good contact lens polymers are their softness, wettability, and high permeability for gases. It had previously been demonstrated (ref. 1) that all these properties are intimately related to the free volume fractions of the test samples. Free volume fractions (f) of the test samples can be measured by Positron Lifetime Spectroscopy (PLS). However, PLS requires complex, fast electronics and a rather high level of technical sophistication of the test operators. It is now proposed that a more direct and simpler technique can provide an equally good measure of contact lens sample quality. It is based on the hypothesis that the contact lens samples with larger free volume fractions (f) should have lower linear attenuation coefficients (μ) for soft x-rays. This hypothesis has been tested on a number of contact lens samples for Cd^{109}/Ag^{109} x-rays. The results and their interpretations are summarized in the following sections.

THEORETICAL BASIS

All polymers have microvoids resulting from mismatch between adjacent linear chains of molecules. These individual microvoids add up to a certain total free volume per unit volume of the polymer specimen.

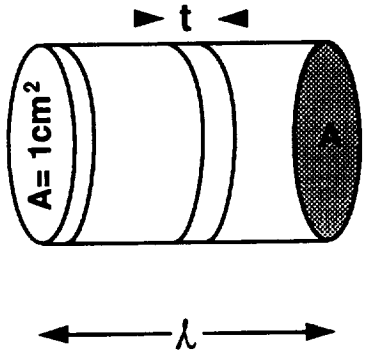


$$\frac{\Delta V}{V} = \frac{\Delta V}{A\ell} = f \qquad (1)$$

where A = x-ray beam cross section.

For an x-ray beam of cross section A of 1 cm^2, one obtains:

$$\left.\begin{aligned} \Delta V &= A\ell f \quad cm^3 \\ &= \ell f \\ &= t \end{aligned}\right\} \qquad (2)$$



where t = Thickness of the equivalent free volume section in the polymer

= (Length of polymer specimen) x (Free volume fraction in the polymer specimen)

When x-rays pass through the test polymer specimen, their attenuation is governed by the following equation:

$$I(\ell) = I_o e^{-\mu_p(\ell - t) - \mu_v t} \qquad (3)$$

where μ_p = Linear attenuation coefficient in the polymer specimen without any microvoids.

μ_v = Linear attenuation coefficient in the medium occupying the microvoid.

If the test specimen is desiccated,

$$\mu_v = \mu_{air}$$

The equation (3) can then be simplified as follows:

$$I(\ell) = I_o e^{-\mu_p(\ell - t) - \mu_{air} t}$$

$$= I_o e^{-\bar{\mu}\ell} \qquad (4)$$

where $\bar{\mu} = \mu_p(1-f)$, since $\mu_{air} << \mu_p$

Clearly, the magnitude of t in equation (4) governs the value of $\bar{\mu}$.

Suppose the respective values of free volume fractions in two specimens of a selected test sample are f_1 and f_2. Then, the generalized equations governing counting rates through them are:

$$I_1 = I_o e^{-\mu_p(\ell - t_1) - \mu_v t_1} \tag{5}$$

$$I_2 = I_o e^{-\mu_p(\ell - t_2) - \mu_v t_2} \tag{6}$$

$$\frac{I_1}{I_2} = e^{-\mu_p(t_2 - t_1) + \mu_v(t_2 - t_1)}$$

$$= e^{(\mu_v - \mu_p)(t_2 - t_1)} \tag{7}$$

In the desiccated state of the specimens, equation (7) is simplified as follows:

$$\frac{I_1}{I_2} = e^{-\mu_p(t_2 - t_1)}$$

$$= e^{-\mu_p \ell (f_2 - f_1)} \tag{8}$$

Clearly, I_1/I_2 is a strong function of the difference in the free volume fractions in the two test specimens.

EXPERIMENTAL TECHNIQUE AND RESULTS

The test samples were copolymers of silicone methacrylate and methyl methacrylate monomers cross-linked by a difunctional monomer. Their properties are summarized in Table I. The first two samples had increasing amounts of silicone methacrylate monomer but no fluorine. The last three samples had both increasing amounts of silicone methacrylate as well as fluorinated acrylate monomers. These samples were provided by Paragon Optical, Inc. They were grown in the form of 0.5" diameter by 4.9" long vertical rods and were subsequently cut into 0.1" thick discs, thus giving 49 discs per sample. Positron lifetime measurements were made in every 6th disc starting from the bottom up to the mid-level in order to detect any possible gravity-induced nonuniformity in the disc morphologies. The positron lifetime measurement technique has been described previously (ref. 2). Figure 1 shows the schematic diagram of a fast-fast positron lifetime measurement system. Figure 2 shows a typical positron lifetime spectrum in a contact lens polymer sample. The longest component lifetime

(τ_3) in each sample disc was used to calculate average microvoid size using the following equation (ref. 3):

$$\frac{1}{2\tau_3} = \left(1 - \frac{R}{R_o} + \frac{1}{2\pi} \text{Sin } 2\pi \frac{R}{R_o}\right) \tag{9}$$

where τ_3 = Lifetime in nanoseconds
R = Microvoid radius in nanometers
R_o = $R + \Delta R$
= $(R + 0.1656)$ nanometers

The free volume fraction (f) in each disc was calculated using the following equation (ref. 4):

$$f = C I_3 V_f \tag{10}$$

where C = Structural constant for the sample
I_3 = Intensity of the longest life component in the positron lifetime spectrum
V_f = $4/3\ \pi R^3$
= Microvoid Volume

The structural constant C is expected to be different for different polymer systems. It is, however, expected to be the same for all contact lens samples used in the present study since they have similar morphologies. It has been calculated by equating saturation moisture content with average free volume fraction in sample # 1 (Paraperm-02). The free volume fractions in different discs of each sample are summarized in Table II. For each sample, discs with minimum and maximum free volume fractions were selected. Linear attenuation coefficients (μ) for Cd^{109}/Ag^{109} x-rays in narrow beam geometry were measured in these two discs. Figure 3 shows schematic diagram of the experimental system used for making attenuation measurements (ref. 5). The experimental values of μ in the desiccated discs for the five selected samples are summarized in Table III. Also listed in the table are the values of $\Delta\mu$(Exptal) = μ_{max}(Exptal) - μ_{min}(Exptal).

Knowing the f(min) and f(max) values for a given sample, the μ_{max} value can be calculated from the measured value of μ_{min} as follows:

$$\frac{\bar{\mu}(\text{DISC with } f_{min})}{\bar{\mu}(\text{DISC with } f_{max})} = \frac{\mu_p(\ell - t_{min})}{\mu_p(\ell - t_{max})}$$

$$= \frac{\mu_p \ell(1 - f_{min})}{\mu_p \ell(1 - f_{max})}$$

$$= \left(\frac{1 - f_{min}}{1 - f_{max}}\right) \tag{11}$$

It is apparent that $\bar{\mu}$ (DISC with f_{min}) will give the highest value of the linear attenuation coefficient (i.e., μ_{max}) in a given sample. Similarly, $\bar{\mu}$ (DISC with f_{max}) corresponds to μ_{min} in that sample. Thus, one obtains

$$\frac{\mu_{max}}{\mu_{min}} = \frac{(1 - f_{min})}{(1 - f_{max})} \tag{12}$$

From the μ_{max}(Calculated), $\Delta\mu$(Calculated) can be determined by simply subtracting μ_{min}(Calculated) [$\equiv \mu_{min}$ (Exptal)] from it. The $\Delta\mu$(Exptal) and $\Delta\mu$(Calculated) values for the various samples are summarized in Table IV. It is apparent from the data that the two sets of values are in reasonably good agreement.

A closer scrutiny of the data summarized in Table IV shows that even though $\Delta\mu$(Experimental) and $\Delta\mu$(Calculated) are in reasonable agreement, the errors on them are rather large, thereby severely limiting the usefulness of the proposed technique only to those cases where the free volume variation is quite large (i.e., $\geq$ 25%). In the samples tested in the present study, this variation was usually $\leq$ 15%, except for sample #2 (Paraperm-EW) where it exceeded 30% of f_{min} value. For sample #2, the $\Delta\mu$ (Experimental) and $\Delta\mu$ (Calculated) values are much larger than the errors on them, clearly demonstrating the usefulness of the proposed technique. A large variation of f might be expected in contact lens samples grown in the weightless environment of the space.

RECOMMENDED PROCEDURE FOR MONITORING CONTACT LENS QUALITY

As indicated in the Introduction, polymers with high free volume fractions make the best material for contact lens manufacture. Since free volume fraction is directly related to average microvoid size, it is recommended that initial conditions be optimized to produce polymers that have the largest microvoids. Such polymers will also produce the longest positron lifetimes in them. Linear attenuation coefficients for Cd^{109}/Ag^{109} x-rays should then be measured in these optimized polymer samples. Routine attenuation measurements with Cd109/Ag109 x-rays with subsequent batches will then provide a ready quality check on the base contact lens sample materials. A Cd^{109}/Ag^{109} x-ray attenuation monitoring system is simple to operate/interpret for quality control in contact lens polymer manufacturing process.

CONCLUDING REMARKS

It had previously been demonstrated that free volume in contact lens polymers is directly related to their suitability for eye wear. It has now been shown that the linear attenuation coefficient for soft x-rays in contact lens polymers is also impacted by their free volume fractions. Thus, after first optimizing the contact lens rod growth procedure, their quality in subsequent production batches can be conveniently monitored by measuring their linear attenuation coefficients for soft x-rays.

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TABLE I

PHYSICAL PROPERTIES OF CONTACT LENS SAMPLES (REF. 1)

No.	Sample	Density (gm/cc)	Saturation Moisture Content (V/O)	Average Free(*) Volume Fraction f (%)
1	Paraperm-02	1.12 ± 0.001	1.71	1.71
2	Paraperm-EW	1.07	1.48 (ALL ± 5%)	2.01 (ALL ± 5%)
3	Fluoroperm-30	1.14	1.26	2.07
4	Fluoroperm-60	1.15	0.98	2.34
5	Fluoroperm-92	1.10	0.95	2.53

(*)Sample # 1 (Paraperm-02) was used as the reference material for calculating the free volume fractions (f) in the test samples since they all have similar morphologies.

TABLE II

FREE VOLUME FRACTIONS (*) IN SELECTED DISCS OF THE FIVE CONTACT LENS SAMPLES CALCULATED FROM POSITRON ANNIHILATION MEASUREMENTS IN THEM (REF. 1)

Disc #	Paraperm 02	Paraperm EW	Fluoroperm 30	Fluoroperm 60	Fluoroperm 92
(Bottom)					
1	0.0171	0.0201	0.0209	0.0232	0.0254
7	0.0167	0.0201	0.0217	0.0224	0.0259
13	0.0165	0.0200	0.0223	0.0218	0.0263
19	0.0162	0.0197	0.0228	0.0215	0.0265
25	0.0159	0.0191	0.0231	0.0215	0.0265
31	0.0157	0.0184	0.0232	0.0218	0.0263
37	0.0155	0.0175	0.0232	0.0223	0.0260
43	0.0153	0.0165	0.0230	0.0231	0.0255
49	0.0151	0.0151	0.0225	0.0244	0.0247
(Top)					

(*) All values have an experimental error of ± 5%. It should be noted that, contrary to expectations, gravitational forces do not appear to affect the free volume fractions in the test discs. For example, in the cases of the first two samples, the bottom discs (which presumably experience the highest gravitational loads) exhibit the highest free volume fractions.

TABLE III
SUMMARY OF LINEAR ATTENUATION COEFFICIENTS(*) FOR CD^{109}/AG^{109} X-RAYS IN CONTACT LENS SAMPLES

No.	Sample	μ_{max}(Exptal) (cm^{-1})	μ_{min}(Exptal) (cm^{-1})	$\Delta\mu$ (Exptal) (cm^{-1})
1	Paraperm-02	0.818 ± 0.004	0.803 ± 0.004	0.015 ± 0.006
2	Paraperm-EW	0.956 ± 0.005	0.916 ± 0.005	0.040 ± 0.007
3	Paraperm-30	0.886 ± 0.004	0.872 ± 0.004	0.014 ± 0.006
4	Paraperm-60	0.936 ± 0.005	0.916 ± 0.005	0.020 ± 0.007
5	Paraperm-92	0.987 ± 0.005	0.974 ± 0.005	0.013 ± 0.007

(*)μ_{max} = Linear attenuation coefficient in the disc with minimum f value.

μ_{min} = Linear attenuation coefficient in the disc with maximum f value.

TABLE IV
COMPARISON BETWEEN THE EXPERIMENTAL AND CALCULATED VALUES OF $\Delta\mu$

No.	Sample	$\Delta\mu$ (Exptal) (cm^{-1})	$\Delta\mu$ (Calculated) (cm^{-1})
1	Paraperm-02	0.015 ± 0.006	0.015 ± 0.006
2	Paraperm-EW	0.040 ± 0.007	0.042 ± 0.007
3	Fluoroperm-30	0.014 ± 0.006	0.017 ± 0.006
4	Fluoroperm-60	0.020 ± 0.007	0.021 ± 0.007
5	Fluoroperm-92	0.013 ± 0.007	0.013 ± 0.007

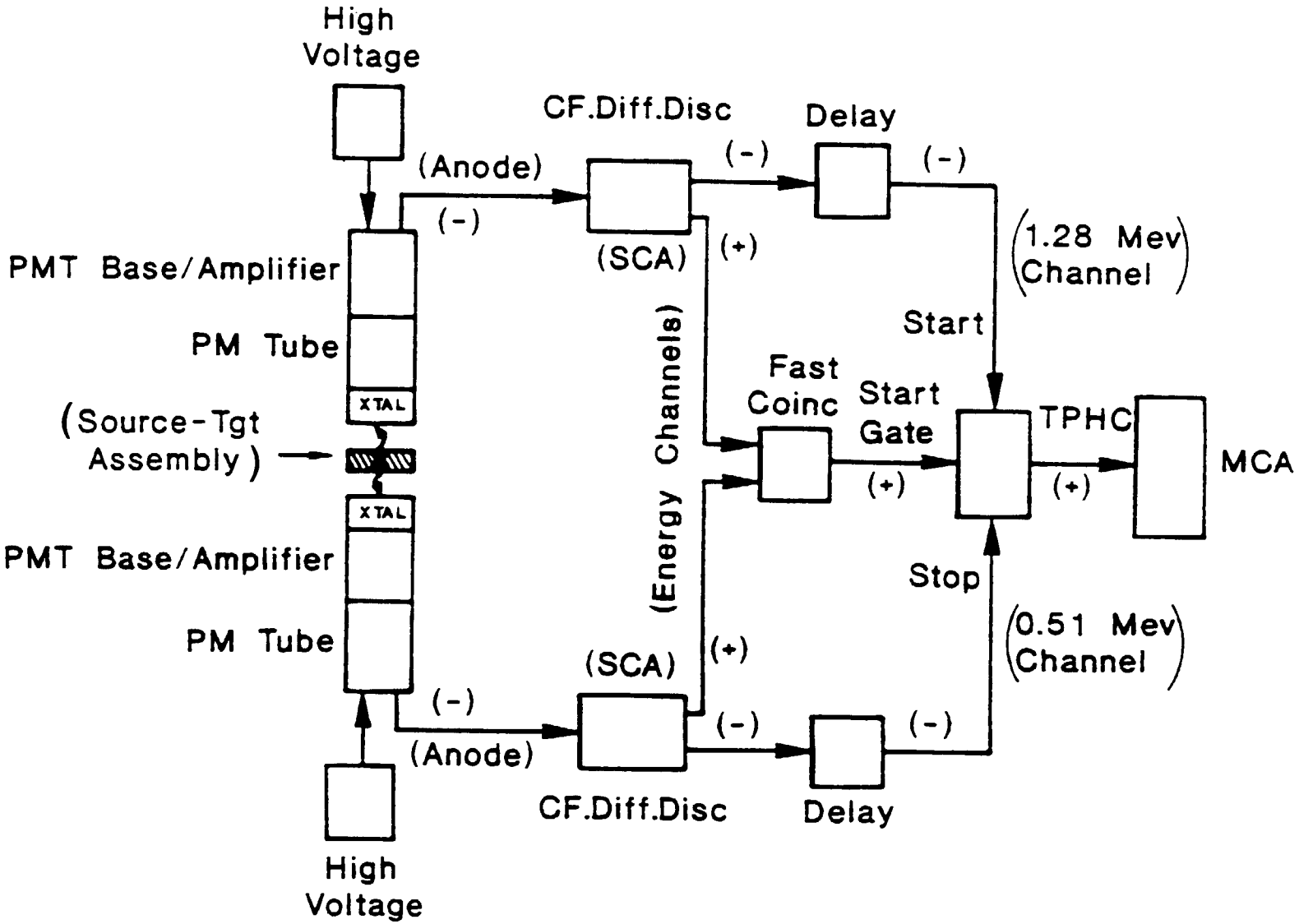

Figure-1. Schematic Diagram of A Fast-Fast Positron Lifetime Measurement System.

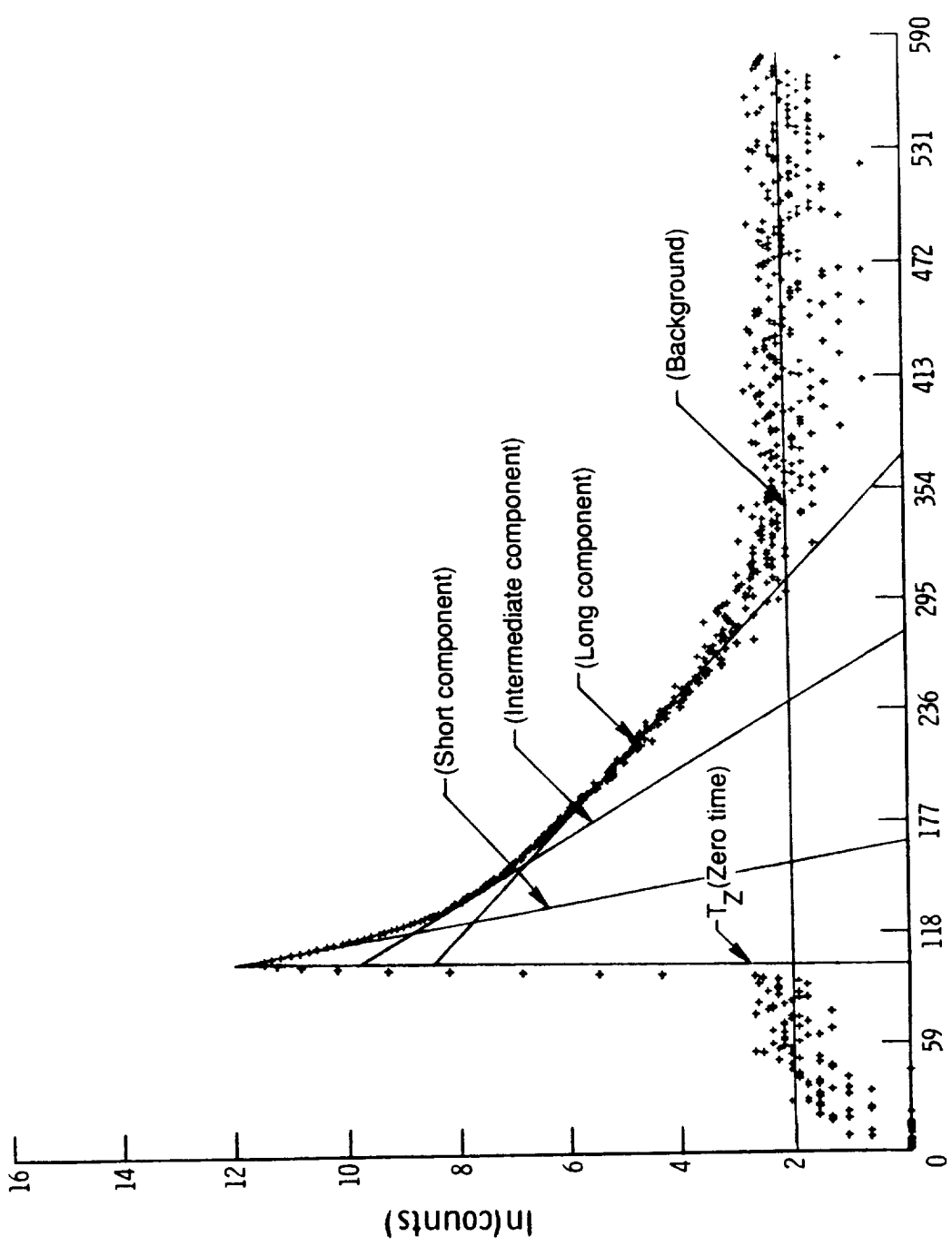

Figure-2. Typical Lifetime Spectrum in A Contact Lens Sample.

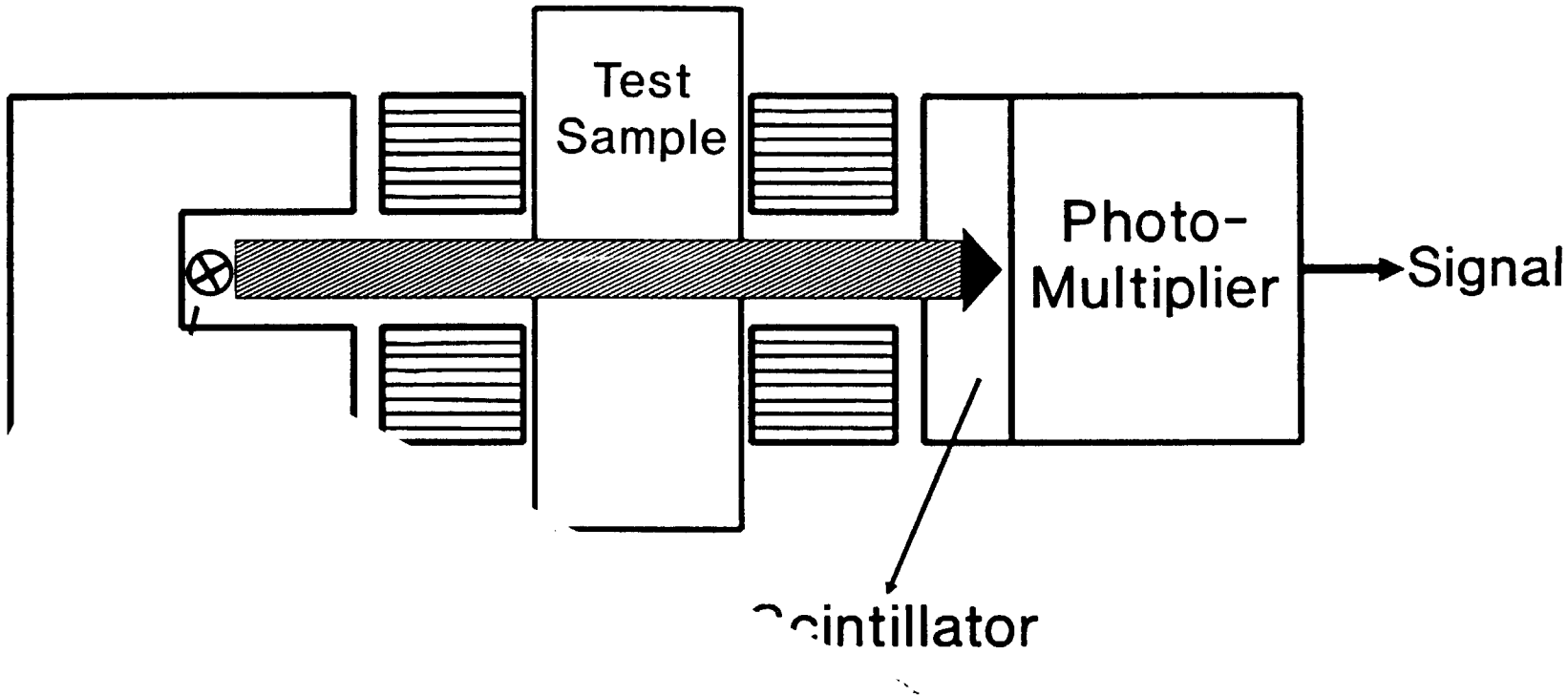

Figure-3. Schematic Diagram of the Experimental Set-Up for Measuring Linear Attenuation Coefficients in Contact Lens Samples.

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