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RADIOPHOTOLUMINESCENCE SPECTRA OF SILVER-ACTIVATED DOSIMETER GLASSES

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ABSTRACT

The radiophotoluminescence (RPL) spectra of silver-activated phosphate glasses of different compositions under 365 mμ excitation have been measured in the 400 to 750 mμ range. The apparatus, specially designed for this type of measurement, uses a red-sensitive photomultiplier tube and permits comparison of the relative RPL intensity with the known output of a NBS-calibrated lamp for each wavelength interval.

Shape and maximum of the RPL spectrum depend on the type of photomultiplier tube, if no corrections for the photomultiplier spectral response are made. After corrections, a steep RPL increase above ca. 500 mμ, spectral radiant intensity maxima between 615 (French C.E.C. glass) and 640 mμ (DT-60 glass) depending on the glass composition, and a slow increase in the red have been observed. For a constant glass base composition, the Ag concentration of from 0.5% to 5% did not affect the spectrum. Also the dose level and the degree of the RPL build-up after exposure had only minor influence on the spectrum. During thermal annealing, a RPL increase in the blue has been observed. After a megarad exposure, a permanent RPL which could not be annealed has been found. Some further experiments are suggested.

SUMMARY

The absolute radiophotoluminescence spectra of several commercial and experimental Ag-activated dosimeter glasses have been measured with a specially designed apparatus. Depending mainly on the glass base composition, maxima between 615 and 640 mμ and a slow decrease in the red have been found. The effect of build-up, silver concentration and dose of the RPL spectral shape is small. The influence of very high doses and thermal annealing also has been measured.

I. INTRODUCTION

Radiophotoluminescence (RPL) spectra of silver-activated sodium chloride and a metaphosphate glass containing different amounts of $AgPO_3$ (2-16%) were first measured by Schulman, et al.,[1] in the 420 to 640 mμ range. Maximum response was obtained at 630 mμ. In a later publication,[2] a RPL spectrum was given for the Navy DT-60 dosimeter glass containing 8% $AgPO_3$ (4.3% Ag). A poorly resolved minor peak was observed around 480 mμ with a main peak at 640 mμ. Recently, Yokota and Nakajima[3] published a RPL spectrum for their low Z, low predose glass which peaked at 610 mμ (50% of the maximum RPL at 545 and 685 mμ). This spectrum had been measured in a spectrofluorometer with automatic correction for the detector response characteristics designed by Uehara, et al.[4] Other authors (see, for instance, 5 and 6) measured "relative" RPL spectra (uncorrected for the luminescence detector response) and found maxima around 560-590 mμ, depending on the red sensitivity of the photomultiplier tube. The value of this type of measurements is rather limited.

A knowledge of the RPL spectra is of both practical and theoretical interest. It allows a combination of optical filter and RPL detector to be chosen that will give optimal sensitivity together with high background (predose) discrimination. There is also a correlation between luminescence and the coordination of the activating ion in the glass. For instance, it has been concluded from the fluorescence spectra that the Mn^{2+} ion has octahedral symmetry in phosphate and borate glasses (maximum ca. 600 mμ in the relative spectrum) but is tetrahedrally coordinated in silicate glasses (maximum ca. 520 mμ).[7]

II. THE SPECTROFLUOROMETER

The fluorometer used in the measurements (Figs. 1 and 2) was developed for checking the constancy (i.e., in color and intensity) of

the fluorescence standards which are part of the U.S. Navy's phosphate glass casualty-dosimeter system.[8] In order to serve as an "absolute" device in a useful sense, this fluorometer makes use of a standard light source which is reproducible within known limits in its intensity and spectral energy distribution. Barbrow[9] has shown that a tungsten-filament lamp calibrated for luminous intensity and color temperature can be used as an approximate standard of spectral radiant intensity (S.R.I.). Lamps so calibrated can be obtained from the National Bureau of Standards, and readily yield values of S.R.I. at a selected plane in microwatts per cm^2 per 10-millimicrons spectral interval, over a wavelength range of special interest for dosimeter-glass fluorescence measurements--namely, from 400 to approximately 750 millimicrons.

Briefly, the fluorometer is designed to compare (i.e., in radiant intensity for each specified wavelength interval) the fluorescence spectrum of a sample of photoluminescent glass to the emission spectrum of the standard lamp. In order to make such a comparison useful, certain conditions have been met:

(a) The photoluminescent-glass sample is excited by a known flux of UV light, which has been chopped at 13 cycles-per-second to provide an a-c signal from the photomultiplier (which sees the dispersed fluorescence) into a tuned, phase-sensitive amplifier. The UV light, from a 250-watt Hg-arc lamp, is essentially the 365-mμ mercury line passed by a 5-mm Corning No. 5860 glass filter. UV output is monitored by a vacuum photocell and recorded by a second pen on the same recorder chart as the fluorescence spectrum.

(b) Owing to the temperature dependence of its fluorescence, the glass sample is held at the convenient temperature of 25 ± 1°C while its spectrum is being recorded. This is achieved by thermally insulating the sample from the UV lamp and filter, using a radiant-heat-absorbing water cell, and cooling the sample-holder by temperature-controlled water.

(c) The radiant intensity of the standard lamp, which provides the reference spectrum, is reduced by neutral density filters (or by a glass attenuating sphere) to a value comparable to that of the weak fluorescence of the glass. An opal-glass diffusion screen (SC) is added, being in effect a neutral filter, and also providing a light source geometrically similar to the fluorescing glass.

The photomultiplier scans the photoluminescent-glass spectrum coming from the monochromator, which is provided with an automatic wavelength drive. After amplification, the photomultiplier signal is sent through a 4-step, low-pass filter for noise control, and is

recorded on a strip-chart recorder. The attenuated spectrum of the standard lamp is then superimposed on the same chart.

The essential steps in obtaining the spectral-energy output of the dosimeter glass are:

(a) Determining the S.R.I. of the standard lamp at the plane of exit of the lamp beam from the attenuator (i.e., from the opal-glass diffuser). This requires reducing the non-attenuated lamp value,[9] for each required wavelength interval, by applying the spectral transmittance factor of the "neutral" attenuator for that wavelength interval.

(b) Comparing the recorder-chart ordinates of the glass-fluorescence spectrum to the corresponding ordinates of the attenuated lamp spectrum. Owing to the geometrical design of the fluorometer, it is only necessary to move the diagonal plane mirror (M-1) from one to the other of its pre-set positions in order to substitute the known standard-lamp output for the unknown output of the fluorescent-glass sample, as seen by the monochromator entrance slit. Thus, the spectral radiant intensity of the glass is obtainable by a simple comparison of ordinates.

If the primary concern, as in the present case, is to determine the shape of fluorescence spectra, the relative spectral transmittance of the attenuator is sufficient for obtaining spectra normalized to peak value = 100.

The major known sources of error are the following:

(a) Standard-lamp spectral data: Reference 9 gives the following: "The uncertainty of the spectral data computed by this procedure is probably no greater than 3% but may be as much as 5%. This estimate of total uncertainty is based upon the following estimates of contributing uncertainties:" ..." 2% from uncertainty in the determination of color temperature, and 1% from photometric uncertainty."

(b) The spectral transmittance of the "neutral" attenuator has been obtained by a spectrophotometric measurement, and may add an error of 2 or 3%.

(c) The overall linearity of the electronic circuits should probably not be counted on to better than 2%.

(d) It was necessary to use 1.0-mm slits to obtain the desired combination of signal/noise and scanning speed. However, since

fluorescence spectra are typically broad bands of wavelengths, a slit-width of this size is tolerable. The manufacturer of the monochromator (a Perkin-Elmer Model 98 single-pass Littrow instrument of effective aperture f/4.5 using the manufacturer's "standard" fused quartz prism) gives the resolution at the above slit-width as follows: At 400 mμ, 10.5 mμ; at 500 mμ, 20 mμ; at 600 mμ, 34 mμ; at 700 mμ, 52 mμ.

As a result of these sources of uncertainty, a cumulative error as great as 10% could occur in the absolute values (i.e., in microwatts per cm^2 per 10 mμ). However, for the present purpose, namely the measurement of changes in spectral distribution and intensity, by far the larger part of the uncertainty in (a), (b) and (d) is common to all spectra recorded and should disappear from the final results, which should then be reliable to within 5%.

III. RESULTS

In order to demonstrate the effect of the photomultiplier tube response characteristics on the relative spectra and for the selection of a proper detector, uncorrected spectra have been measured using different types of photomultiplier tubes. Three commercial dosimeter glasses and one experimental one used in the experiment have the following composition:

TABLE I

Composition of Some Dosimeter Glasses

Glass type, author	Composition (% wt)					
	Ag	Al	Li	P	O	Others
DT-60 (Schulman, et al.)[2]	4.3	4.7	-	28.4	44.1	10.8 Ba 7.7 K
Toshiba (Yokota, et al.)[3]	4.2	4.6	3.6	33.3	53.5	0.8 B
C.E.C. (Francois, et al.)[10]	2.4	3.5	2.5	33.8	52.5	0.5 Be 4.7 Na
Experimental glass (Becker)[11]	0.6	0.5	7.3	34.7	55.9	1.0 B

Glass blocks 8 x 8 x 4.7 mm in size have been exposed to identical doses of Co^{60} radiation under electron equilibrium. After stabilization by a 20 min 150°C heat treatment[5,12] for obtaining maximum RPL, the relative spectra in Fig. 3 have been obtained with a IP 21 photomultiplier tube (S-4 photocathode) and the spectra in Fig. 4 with a IP 22 (S-8 photocathode). Because the second tube was less sensitive, the glasses had to be irradiated with 1000 R instead of 200 R. As expected, the different blue-to-red-sensitivity ratios of the two photomultiplier tube types causes RPL peaks at different wavelengths (560-570 mμ and 600-610 mμ, respectively), different slopes of the intensity decrease in the red, and different ratios between the RPL intensity in the blue and the red. The different peak heights are in good agreement with the results of sensitivity comparisons, which have shown about twice the sensitivity for the Yokota than for the Schulman type glass.[12,13] The IP 22 tube was selected for further experiments because this tube permitted measurements with reasonable accuracy up to ca. 750 mμ.

By correction for the photomultiplier tube sensitivity, "absolute" spectra (spectral radiant intensity as a function of wavelength) have been obtained. For better comparison, the spectra are normalized at their peak intensity = 100 (Fig. 5). It can be seen that there are considerable differences between the glasses in the intensity in the blue, the peak wavelength and the slope in the red, in particular, between the Schulman glass and the three other glasses. In some of our experimental glasses[5] containing the same amount of Ag (ca. 4%), but different phosphate glass bases, similar differences have been found (Fig. 6). The wavelength of maximum intensity, however, is about 620 mμ in all these glasses. In still another experiment, the glass base was kept constant and the Ag concentration varied (Fig. 7). For concentrations between 0.5 and 5% Ag_2O, no differences in the RPL spectra have been found. The 0.1% Ag_2O glass spectrum also may be more similar to the others than it appears from Fig. 7, because the low absolute RPL intensity of this glass did not permit very accurate measurements in the lower wavelength regions.

In another experiment, the possible effect of the gamma dose level on the RPL spectrum has been studied. The upper dose limit was given by the possible discoloration of the glass, the lower dose limit by the sensitivity of the instrument. Poor accuracy because of nearness to the lower limit of measurability in the 50 R glass may in part be responsible for the increase in the relative intensity below 500 mμ in the results presented in Fig. 8. Above 520 mμ, no difference in the RPL spectrum can be seen between glasses which had been exposed to 50, 500 and 5000 R. Glasses with a low Ag content such as an experimental glass with 0.6% Ag exhibit a considerable build-up after exposure. The RPL immediately after a short time exposure may be only a few percent of the

final RPL after stabilization.[12] If the RPL spectra of such a glass after exposure and after stabilization are compared, only a small difference in the spectral shape can be seen in spite of the very different absolute intensities (Fig. 9).

During thermal annealing, however, a relative increase of the low-wavelength part of the RPL spectrum can be seen if compared with the spectrum of the same glass after keeping it for 100 days at room temperature after exposure to 1000 R gamma radiation in order to obtain the maximum RPL intensity (Fig. 10). There may be thermally-more-stable luminescence centers with a peak intensity below 400 mμ. Because of the proximity of the 365 mμ excitation line, no measurements in this region could be made. The blue RPL disappears during the final stages of thermal annealing.

It has been demonstrated in previous experiments[5] that after extremely high gamma exposure a permanent increase in predose which cannot be annealed will result. Indeed, after 10^6 R and 2 hours annealing of the discolored glass at 400°C, the luminescence of the glass shows a peak probably below 400 mμ and extending into the red (Fig. 11). Obviously, this effect cannot be omitted by a red filter.

IV. RECOMMENDATIONS

It would be desirable to extend these experiments, in particular, to measure the spectral distribution below 400 and above 750 mμ; to measure the spectra as a function of the excitation wavelength and to increase the sensitivity in order to make measurements of the "predose" spectra of the modern low predose glassses and, may be, to find methods for a better discrimination of predose and luminescent surface contamination against the radiation induced effect.

The use of a UV laser for excitation, which has recently been suggested by Kastner, et al.,[14] may help solve problems of intense and sufficiently monochromatic excitation. The spectrum may also be determined during the ca. 3 μsec decay time of the RPL after the end of a pulsed excitation, which has been found to be by ca. a factor of ten longer than the predose decay time.

In reader design, it would be desirable to use RPL light detectors having a sensitivity extending to at least 700-800 mμ for the better utilization of the RPL output in the red and for better discrimination against disturbing "spurious" luminescence and scattered excitation light.

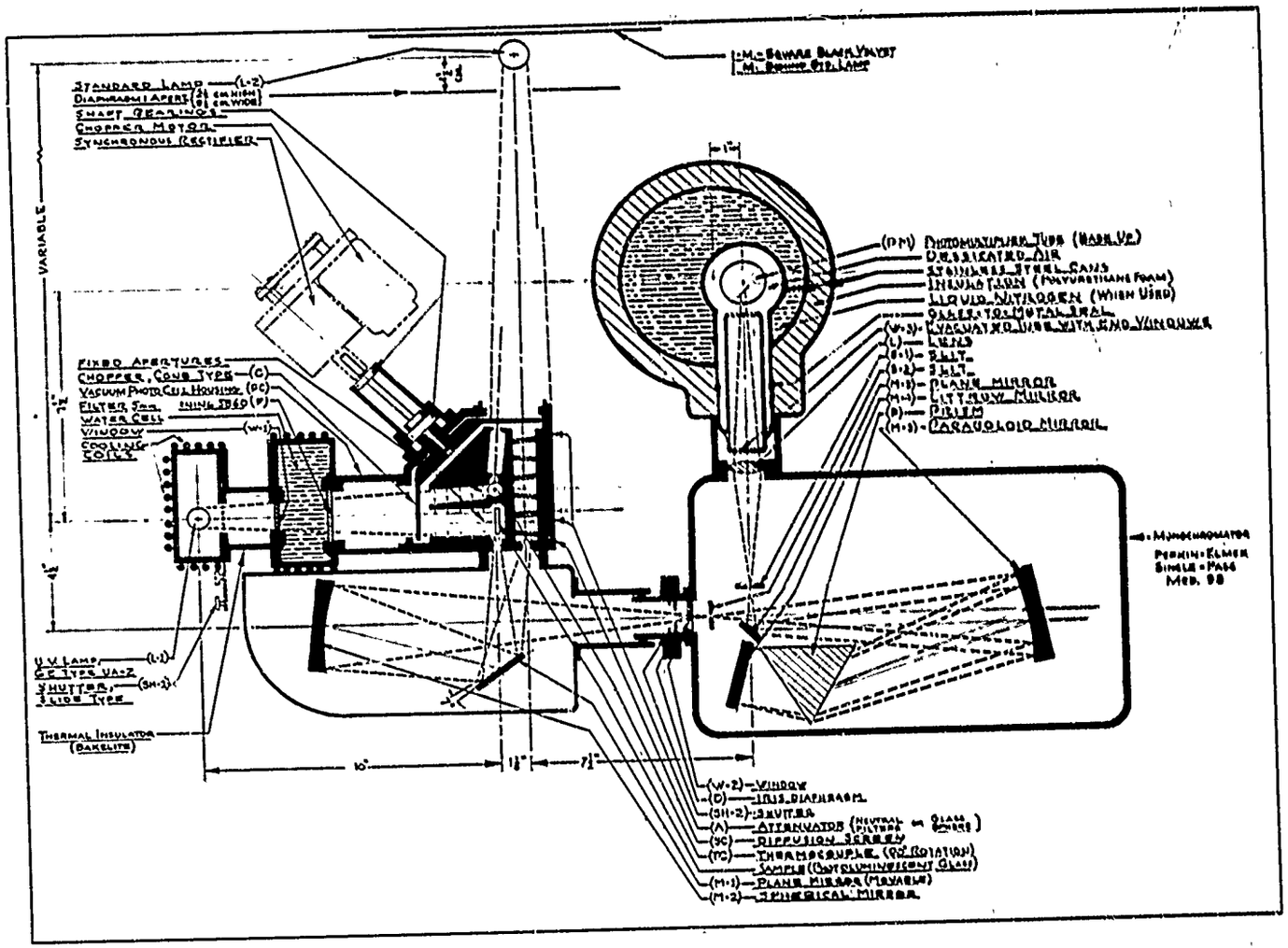

Fig. 1 Optical arrangement of fluorometer.

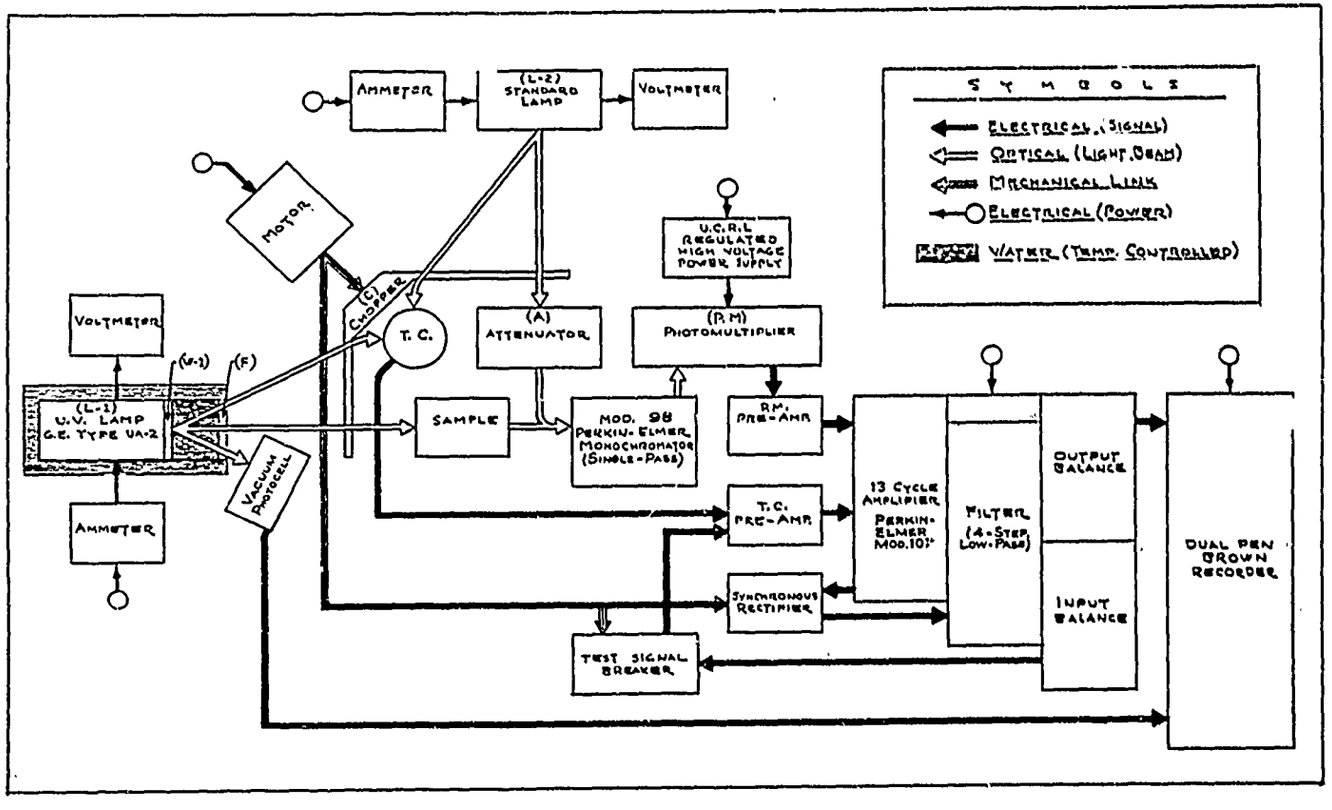

Fig. 2 Signal block diagram of fluorometer.

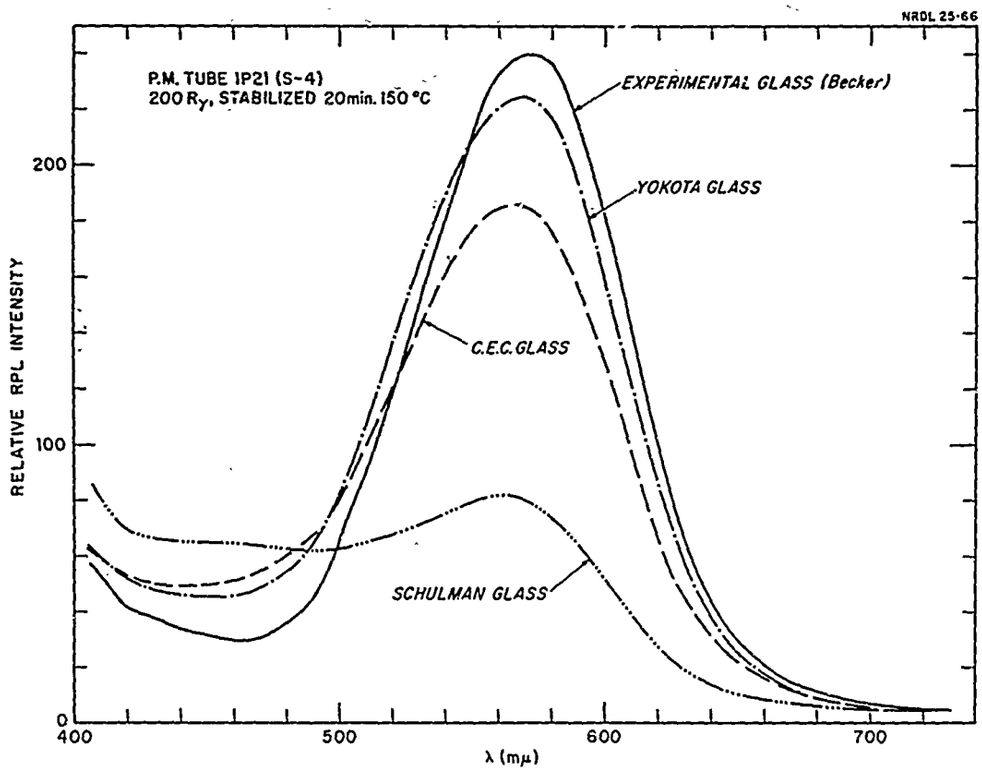

Fig. 3 Relative radiophotoluminescence (RPL) intensity of different dosimeter glasses as a function of wavelength, uncorrected for photomultiplier tube IP 21 response.

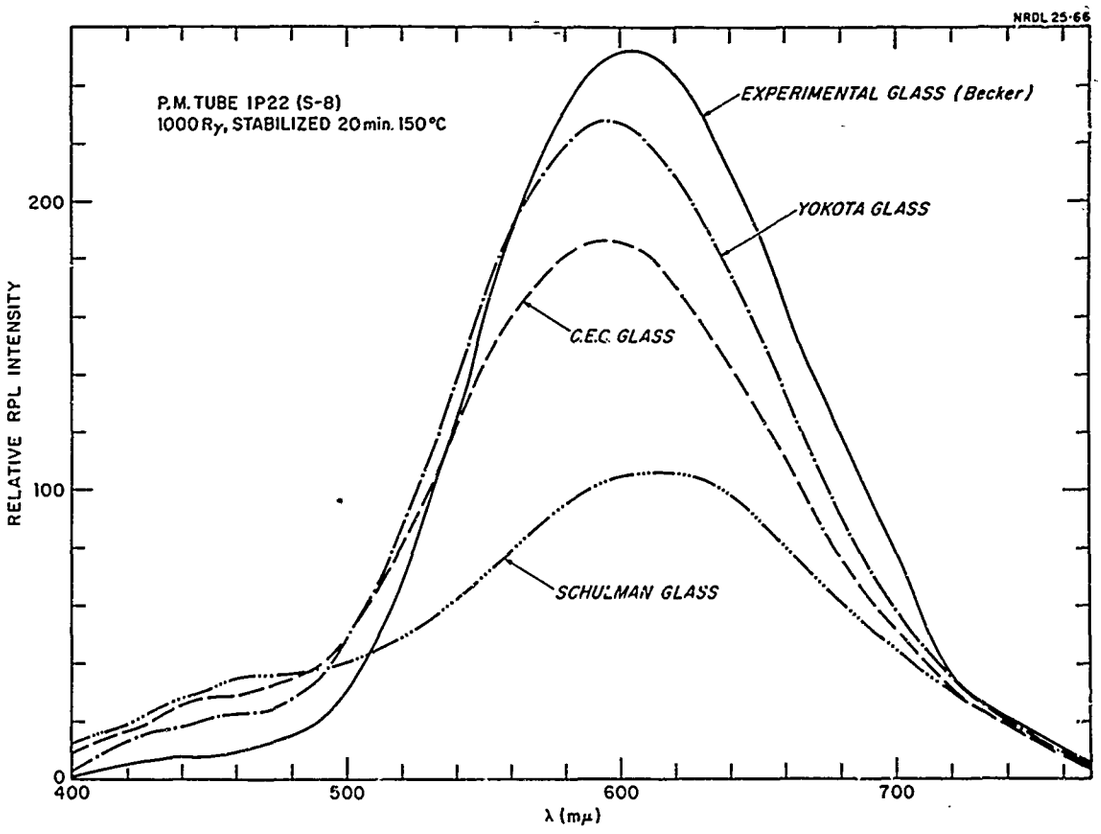

Fig. 4 Relative radiophotoluminescence (RPL) intensity of different dosimeter glasses as a function of wavelength, uncorrected for photomultiplier tube IP 22 response.

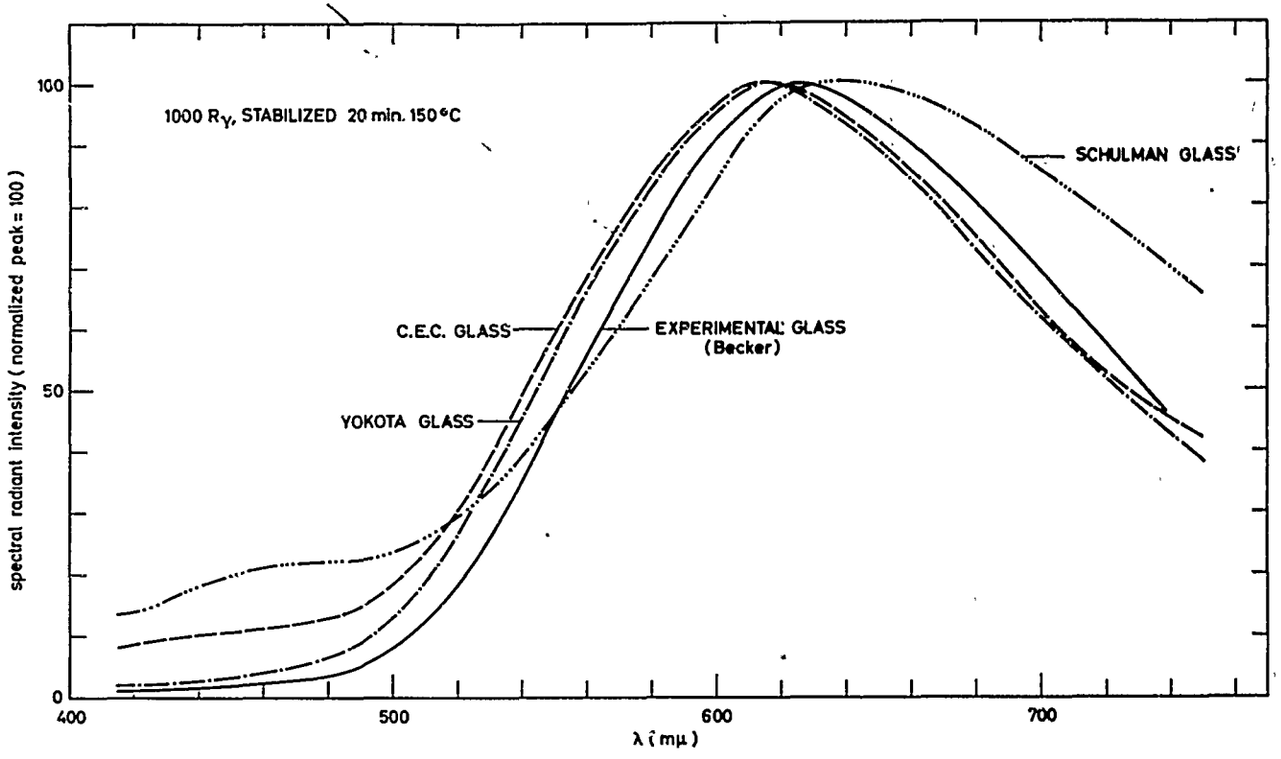

Fig. 5 Spectral radiant RPL intensity of dosimeter glasses as a function of wavelength, normalized for peak intensity = 100.

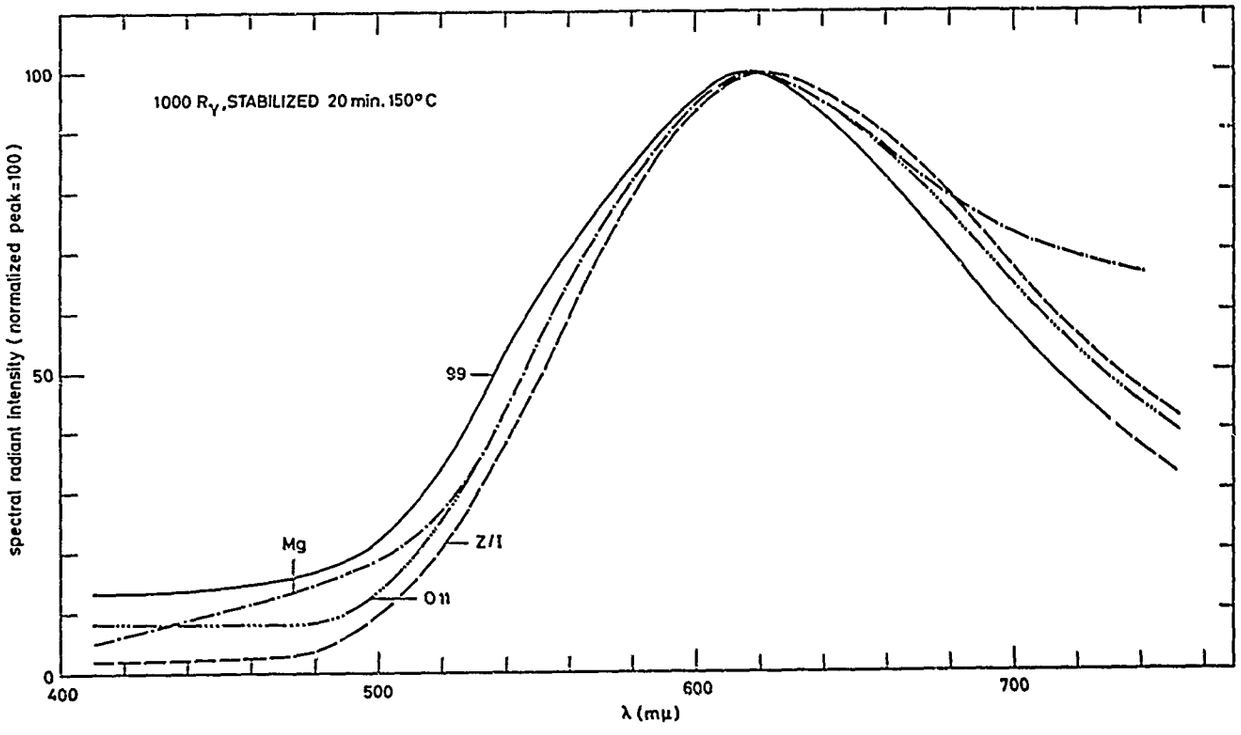

Fig. 6 RPL spectra of several experimental glasses[5] (same Ag concentration, different phosphate glass base), normalized for peak intensity = 100.

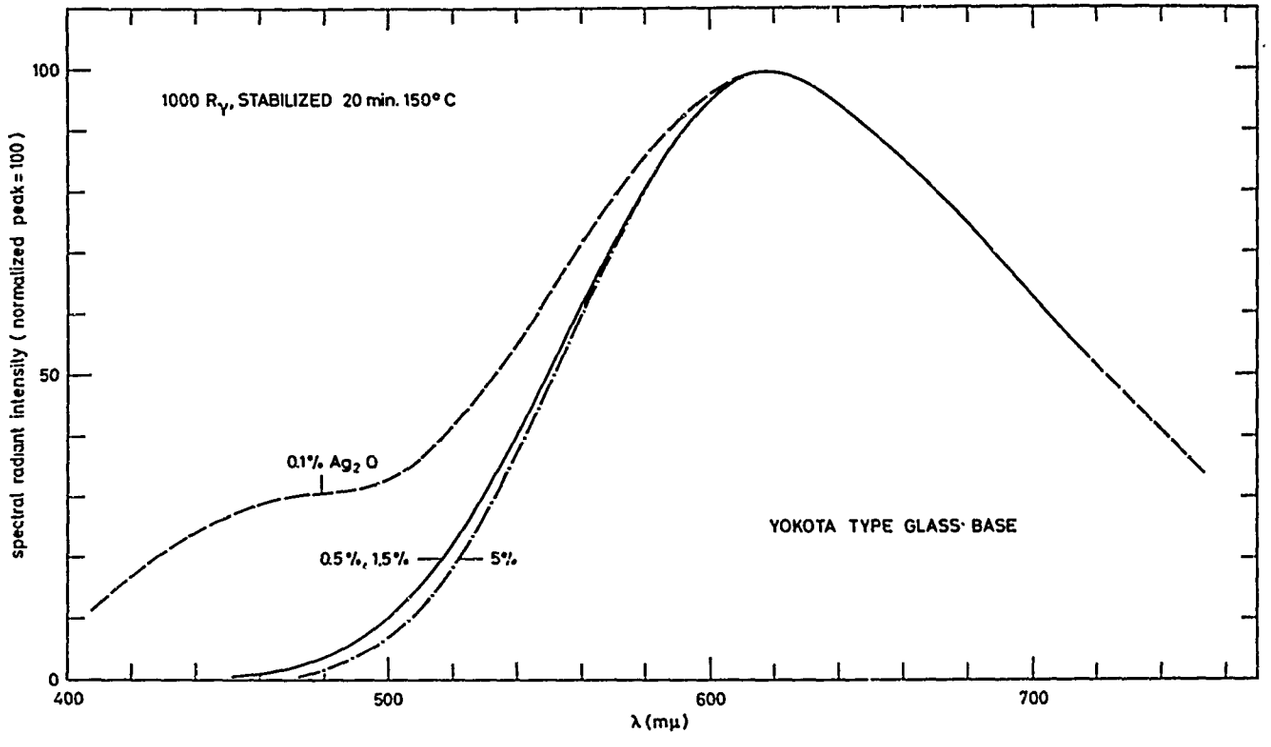

Fig. 7 RPL spectra of several experimental glasses (different Ag concentration constant glass base), normalized for peak intensity = 100.

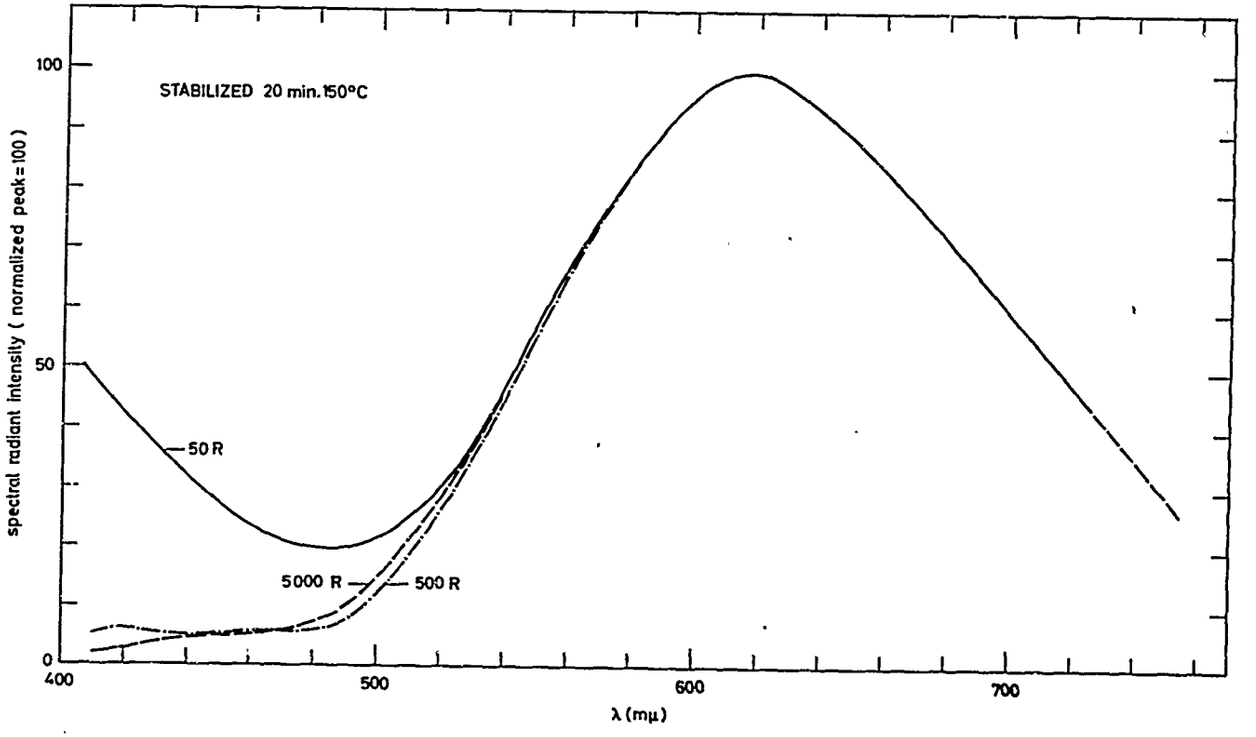

Fig. 8 RPL spectra of Yokota type dosimeter glass at different gamma dose levels, normalized for peak intensity = 100.

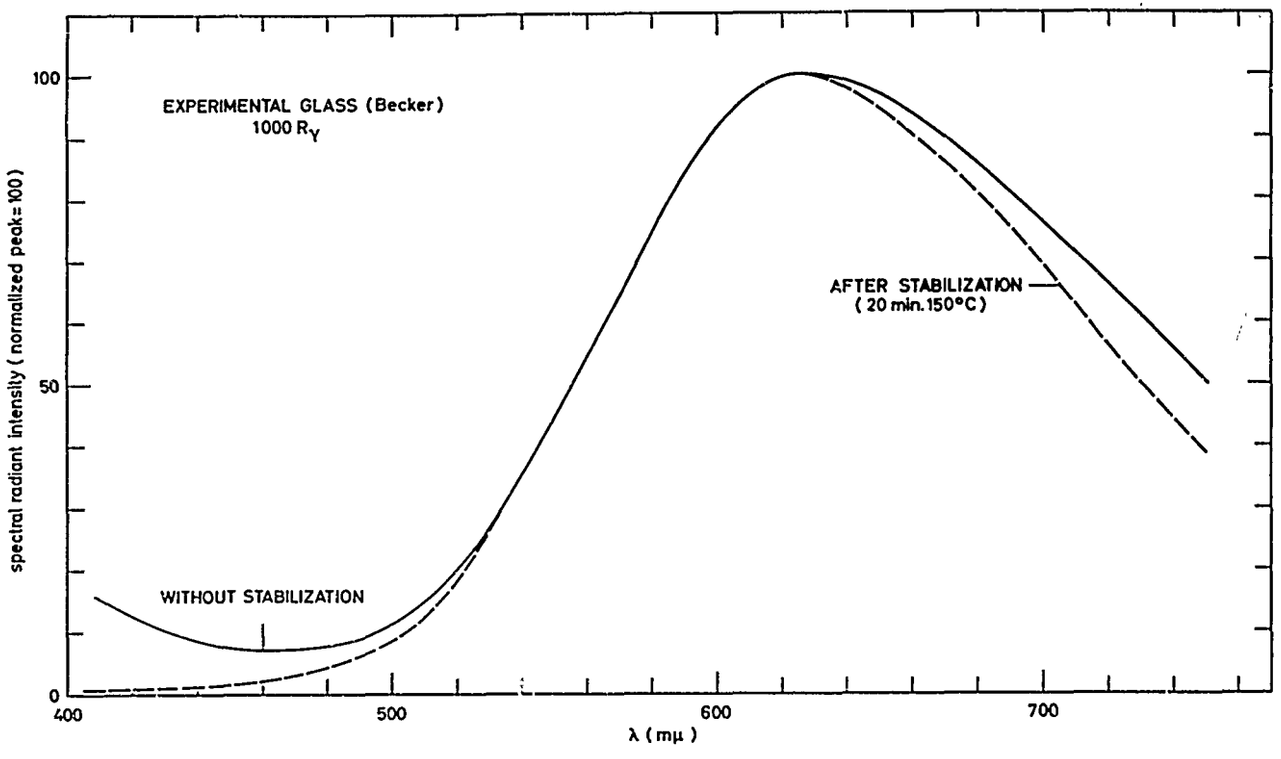

Fig. 9 RPL spectra of an experimental glass before and after stabilization by a 20 min 150°C heat treatment, normalized for peak intensity = 100.

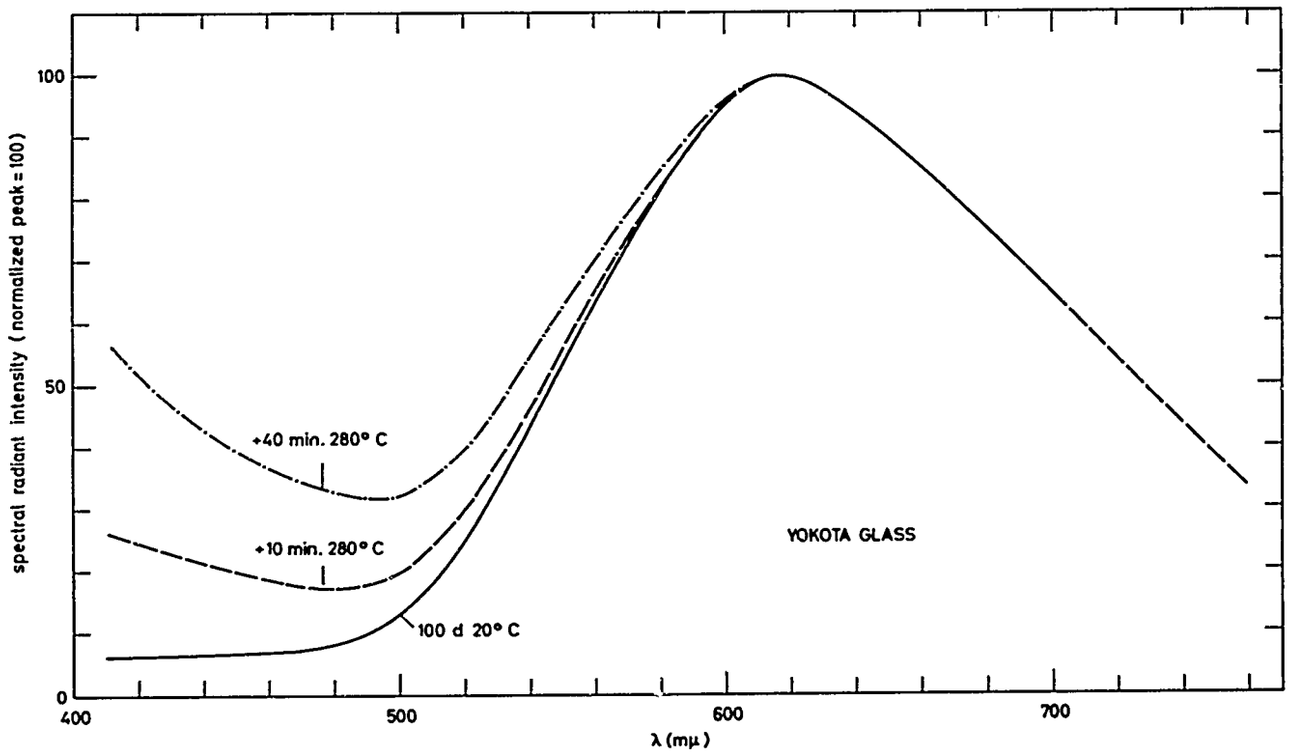

Fig. 10 Changes in the RPL spectrum of a dosimeter glass during thermal annealing, normalized for peak intensity = 100.

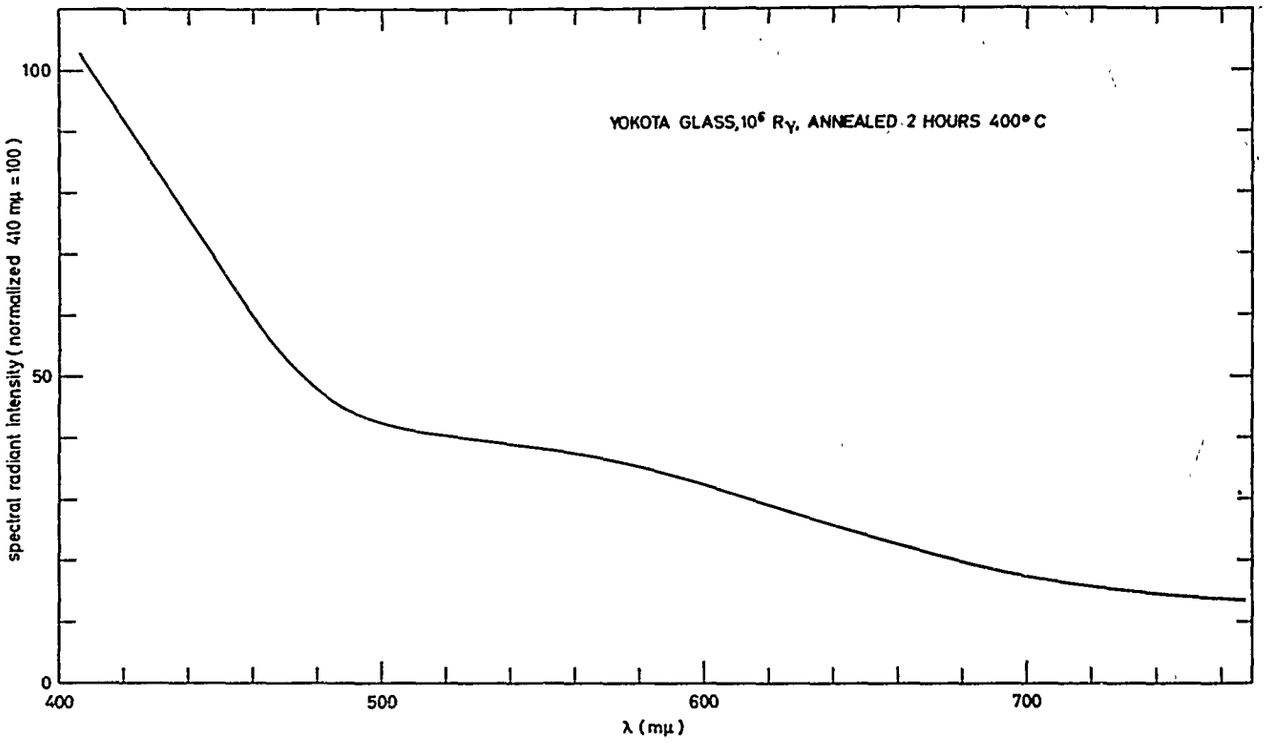

Fig. 11 Residual luminescence spectrum of a dosimeter glass after exposure to 10^6 R gamma radiation and thermal annealing (2 hours 400°C).

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