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Radiation-Induced Hidden Absorption Effects in Polystyrene Based Plastic Scintillator *

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Radiation damage studies were performed on polystyrene based plastic scintillators. Three multi-component systems, each containing two organic fluorescent compounds in a polystyrene matrix, were analyzed. In these systems, p-terphenyl was used as the primary dopant with either dimethyl-POPOP, 3HF, or BBQ as the secondary dopant. In addition, undoped polystyrene samples were also irradiated. Absorbance, fluorescence, and beta excitation measurements were carried out on each sample before, immediately after, and two weeks after irradiation. Radiation-induced absorption in the polymer was detected in the 300–400 nm spectral region. However, no substantial damage was noted in the dopants for scintillator samples irradiated at 10 Mrad.

Plastic scintillators have been commonly used as particle detectors in nuclear and high energy physics experiments. They are based on a polymer matrix typically doped with two fluorescent compounds referred to as the primary dopant and the secondary dopant or wavelength shifter [1]. Plastic scintillators can be fabricated into many forms such as sheets, rods, and even optical fibers rendering them suitable for many detector geometries. In addition, they exhibit a short fluorescence decay time which allows them to be used in high count rate experiments. Currently, their main drawback is their susceptibililty to radiation damage [2].

This study focuses on the radiation-induced damage to the polymer base and its effect on the scintillation light. The irradiation results will show how damage to the polymer matrix plays a major role in the scintillation light losses for the systems studied. Damage to the dopants does not appear to be the major contributing effect in these systems.

Experimental

Styrene was purified using a *tert*-butylcatechol removal column supplied by Aldrich Chemical Co. and was then vacuum distilled. Three multi-component samples were prepared, each consisting of a styrene solution doped with p-terphenyl (1.25% by weight) and a wavelength shifter (0.01% by weight). In this study, the wavelength shifters used were 1,4-bis-2-(4-methyl-5-phenyl-oxazolyl)benzene (dimethyl-POPOP or DMPOPOP), 3-hydroxyflavone (3HF), and 7H-benzimidazo[2,1–a]benz[de]isoquinoline-7-one (BBQ). Samples containing a single dopant in a styrene solution were also made. The concentration of each dopant was the same as in the multi-component samples just mentioned, i.e., 1.25% for p-terphenyl, and 0.01% for each of the wavelength shifters. In addition, solutions of undoped styrene were also prepared. The solutions were placed in Pyrex test tubes, degassed by repeated freeze-pump-thaw cycles, and then polymerized in a silicone oil bath. The polymerization cycle was 24 h. at 110 °C, 48 h. at 125 °C, 12 h. at 140 °C, and then a ramp down at 10 °C/h. to 90 °C. The polymerized samples were machined into 1 cm thick disks and then polished.

The samples that were then to be irradiated were first placed in stainless steel cans. The cans were then evacuated for a period of a week in order to remove all moisture and dissolved gases from the samples. Finally, the cans were back-filled with dry nitrogen and sealed. The samples were irradiated at the Nuclear Reactor Laboratory of the University of Michigan using a ^{60}Co source. The doped samples were irradiated to an integrated dose of 10 Mrad and the pure polystyrene samples to doses of 1, 5, 10, 50, and 100 Mrad. In all exposures, the dose rate was approximately 1 Mrad/h.

Absorbance, fluorescence, and beta excitation measurements were performed before, immediately after, and two weeks after irradiation. This last measurement was recorded after the samples were annealed in an oxygen atmosphere. Absorption/transmittance and fluorescence spectra were recorded using a Hewlett-Packard 8451A spectrophotometer. For all absorption/transmittance measurements, unirradiated pure polystyrene was used as the reference. The light yield measurements used a ^{207}Bi beta source (1 MeV electrons) for excitation. The scintillation light was viewed by a Hamamatsu R669 photomultiplier tube which was coupled directly to a Lecroy Model 3001 qVt multi-channel analyzer.

Results and Discussion

Irradiation of pure polystyrene

Pure polystyrene samples were irradiated at five dose levels. Immediately after irradiation the transmittance spectra (Figure 1) show a significant increase in absorption in the 350–600 nm range. All spectra indicate the formation of an absorption band at 525 nm whose strength increases with increasing radiation levels. After these measurements, the samples were annealed in oxygen for two weeks. The transmittance spectra recorded after the annealing process (Figure 2) prove that the samples undergo a substantial recovery, particularly for those irradiated at higher doses. However, considerable permanent absorption does remain in the polymer as a result of the radiation.

Another prominent feature is observed in the samples immediately after irradiation. When excited using 313 nm light, the samples fluoresce in the wavelength region between 500 and 600 nm (Figure 3). Before irradiation, polystyrene shows little fluorescence at wavelenghts longer than 320 nm when excited with 313 nm light. Unirradiated polymer has a fluorescence peak at approximately 320 nm. After irradiation, the normal 320 nm fluorescence appears at longer wavelengths (380 nm), probably due to the increase in conjugation of the polymer. In addition, a new fluorescence band is detected at 550 nm. This fluorescence decreases as the absorption band at 525nm disappears. Exciting this species with 500 nm light yields a fluorescence spectrum (Figure 4) that agrees with the 550 nm peak seen in Figure 3. Irradiation favors the formation of several excited species. Among these new species, one is clearly detected. It absorbs at 525 nm, fluoresces at 550 nm, and is long-lived. This excited species is observed for several weeks if the sample is kept in a nitrogen atmosphere. If the sample is placed in an oxygen atmosphere, however, the diffusion of oxygen into the sample appears to quench this fluorescent species instantly. The oxygen induced quenching of this species can be monitored under UV light. We observed that the volume within the sample that continued to exhibit green fluorescence decreases with time when the sample remained in an oxygen environment.

Pulse radiolysis measurements on polystyrene films and in cyclohexane solution [3, 4] have assigned a similar absorption to singlet excimers of polystyrene. However, this species is short-lived. Other absorptions detected in this region have been assigned to charge transfer complexes with longer decay times.

Irradiation of doped polystyrene

The three doped polystyrene samples were irradiated to a dose of 10 Mrad. Figures 5-7 give transmittance data for these three scintillator samples before irradiation, immediately after irradiation, and after a two week oxygen anneal. For reference, the fluorescence distribution for the sample is also included with its transmittance data. As in the case of the pure polymer, we also see significant annealing in these samples. In addition, the induced absorption seen at 525 nm in the undoped polymer is also present in the doped samples.

Light yield measurements were performed on these samples using beta excitation as described in Section 2. The pulse height distributions for the 3HF sample is shown in Figure 8. The reduction in light output after annealing was 19±1.5% for the DMPOPOP sample, 22±1.5% for the 3HF sample, and 19±1.5% for the BBQ sample (Figure 9). However, looking at the transmittance data in Figures 5-7, we see that transmission losses cannot account for all of the light loss in any of the three samples. Transmission loss can only account for a 3±2% loss in the DMPOPOP sample, 1±2% loss in the 3HF sample, and a 6±2% loss in the BBQ sample.

One possible explanation for the observed light loss is that the dopants are affected by the radiation. In order to study this, we used front-surface UV excitation to directly stimulate fluorescence of the various dopants. Samples of polystyrene doped only with a single compound were prepared so that we could study the primary and the various secondaries independently. Figure 10 shows the fluorescence from p-terphenyl in a sample with 1.25% p-terphenyl in polystyrene. The excitation wavelength was 313 nm. The data show the fluorescence distributions before irradiation and after irradiation (10 Mrad) and annealing of the sample. As can be seen, there is little change in the fluorescence. The integrated intensity changes by 2±2%. The p-terphenyl fluorescence area is integrated between 320–380 nm since after irradiation the polymer fluorescence is detected at 380 nm. The intensity of the excitation source was monitored by using a fluorescence standard and the curves in Figure 10 have been corrected for changes in the excitation source intensity. Figures 11-13 show the same data for samples prepared with 0.01% of the three secondaries, DMPOPOP, 3HF, and BBQ, in polystyrene. In all three figures we see a pronounced change in fluorescence intensity after the 10 Mrad irradiation and anneal. The drop in integrated fluorescence yield for DMPOPOP, 3HF, and BBQ is 42±2%, 51±2%, and 43±2% respectively. However, we also see evidence for polystyrene fluorescence. In the data for 3HF and BBQ, the 380 nm fluorescence seen in the irradiated pure polystyrene samples (Figure 3) is also clearly evident. In the DMPOPOP sample, the polystyrene fluorescence and the fluorescence from DMPOPOP overlap, so no clear second peak is seen. However, we do see increased fluorescence after irradiation in the band between 320 and 395 nm. Again, this would indicate a contribution from polystyrene fluorescence. The radiation induced absorption in polystyrene at 313 nm is competing with absorption by the secondary. Figure 14 shows absorption data for samples of unirradiated pure polystyrene (reference: air), irradiated polystyrene, and unirradiated polystyrene doped with DMPOPOP, 3HF, and BBQ. As can be seen from these data, polystyrene absorption in the region between 320 and 380 nm has increased significantly after irradiation and does compete favorably with absorption by the secondaries. This effect does not eliminate the possibility, however, that some of the drop in light yield for the three secondaries could still be due to radiation induced degradation of the dopant.

In order to explore this in more detail, additional fluorescence measurements were performed using excitation light of longer wavelength. In these cases, the wavelength of the excitation light is less strongly attenuated by the radiation induced absorption in the polystyrene. Figure 15 gives the fluorescence data for DMPOPOP doped polystyrene using $\lambda_{ex} = 380$ nm. The difference in integrated intensity is now only 10%. Figure 16 shows data for the 3HF sample with $\lambda_{ex} = 360$ nm and Figure 17 shows data for the BBQ sample with $\lambda_{ex} = 404$ nm. The loss in integrated intensity is 22% and 4% for 3HF and BBQ respectively. For the 3HF case with $\lambda_{ex} = 360$ nm and to a lesser extent for the DMPOPOP case with $\lambda_{ex} = 380$ nm, polymer absorption is still significant (Figure 14.) The 22% and 10% drops in intensity can, therefore, only be interpreted as upper bounds on the light loss due to dopant degradation. The actual losses are likely much less since we see such dramatic changes in the loss ratios when 313 nm excitation light is used versus 360 nm or 380 nm light. Polymer absorption in the wavelength region of p-terphenyl fluorescence competes with the transfer between the primary (p-terphenyl) and the secondary. One can estimate the size of this effect by comparing the fluorescence distributions (using $\lambda_{ex} = 350$ nm) before and after irradiation for a given secondary dopant. These data are shown in Figures 18-20. The loss factors are $20\pm2\%$, $26\pm2\%$, and $22\pm2\%$ for DMPOPOP, 3HF, and BBQ respectively.

Conclusions

The light loss that was measured in the three test scintillators using beta excitation (Section 3) can be explained by the following mechanism. Upon excitation by ionizing radiation, energy is transferred in a plastic scintillator in a two step process. First, polystyrene excitation is transferred to p-terphenyl via Förster transfer. This is then followed by p-terphenyl fluorescence and then by reabsorption and emission by the secondary. Polymer absorption in the wavelength region of p-terphenyl fluorescence competes with the transfer between the p-terphenyl and the secondary. The radiation-induced polymer absorption, as represented by the losses measured for the fluorescence intensity of the three secondaries under 350 nm excitation, can completely account for the light loss observed in the three test scintillators under beta excitation.

References

[1] Birks, J. B. *The Theory and Practice of Scintillation Counting*; Pergamon Press, The McMillan Co.: New York, N. Y., 1964.

[2] Marini, G. *et. al.*, *Radiation Damage to Organic Scintillation Materials*, CERN pub. 85-08, 1985.

[3] Washio, M.; Tagawa, S.; Tabata, Y. *Radiat. Phys. Chem.* **1983**, *21*, 239.

[4] Tabata, Y.; Tagawa, S.; Washio, M. In *Materials for Microlithography*; Thompson, L. F.; Wilson, C. G.; Frechet, J. M. J., Eds., ACS Symposium Series; American Chemical Society: Washington, D. C., 1984, Vol. 266; pp. 151-163.

Figure Captions

Figure 1. Transmittance data for pure polystyrene immediately after irradiation.

Figure 2. Transmittance data for irradiated pure polystyrene after the annealing process.

Figure 3. Fluorescence spectra of pure polystyrene: before (A), immediately after(B), and two weeks after 10 Mrad irradiation (C). Excitation wavelength 313 nm.

Figure 4. Fluorescence spectrum of irradiated pure polystyrene. Excitation wavelenght 500 nm.

Figure 5. Transmittance data for the p-terphenyl plus DMPOPOP sample: before (A), immediately after (B), and two weeks after 10 Mrad irradiation (C). Dotted line indicates DMPOPOP fluorescence.

Figure 6. Transmittance data for the p-terphenyl plus 3HF sample: before (A), immediately after (B), and two weeks after 10 Mrad irradiation (C). Dotted line indicates 3HF fluorescence.

Figure 7. Transmittance data for the p-terphenyl plus BBQ sample: before (A), immediately after (B), and two weeks after 10 Mrad irradiation (C). Dotted line indicates BBQ fluorescence.

Figure 8. Pulse height distribution of the p-terphenyl plus 3HF sample.

Figure 9. Relative pulse height measurements using ^{207}Bi as excitation source. (B) before 10 Mrad irradiation, (A) immediately after irradiation, (AA) after annealing process.

Figure 10. p-Terphenyl fluorescence in polystyrene: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 313 nm.

Figure 11. Fluorescence spectra of the p-terphenyl plus DMPOPOP sam-

ple: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 313 nm.

Figure 12. Fluorescence spectra of the p-terphenyl plus 3HF sample: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 313 nm.

Figure 13. Fluorescence spectra of the p-terphenyl plus BBQ sample: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 313 nm.

Figure 14. Absorption spectra of irradiated polystyrene (A) and non-irradiated samples of polystyrene (B), 3HF (C), DMPOPOP (D), and BBQ (E) in the region of p-terphenyl fluorescence (F).

Figure 15. Fluorescence spectra of the p-terphenyl plus DMPOPOP sample: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 380 nm.

Figure 16. Fluorescence spectra of the p-terphenyl plus 3HF sample: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 360 nm.

Figure 17. Fluorescence spectra of the p-terphenyl plus BBQ sample: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 404 nm.

Figure 18. Fluorescence spectra of the p-terphenyl plus DMPOPOP sample: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 350 nm.

Figure 19. Fluorescence spectra of the p-terphenyl plus 3HF sample: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 350 nm.

Figure 20. Fluorescence spectra of the p-terphenyl plus BBQ sample: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 350 nm.

FIGURE 1

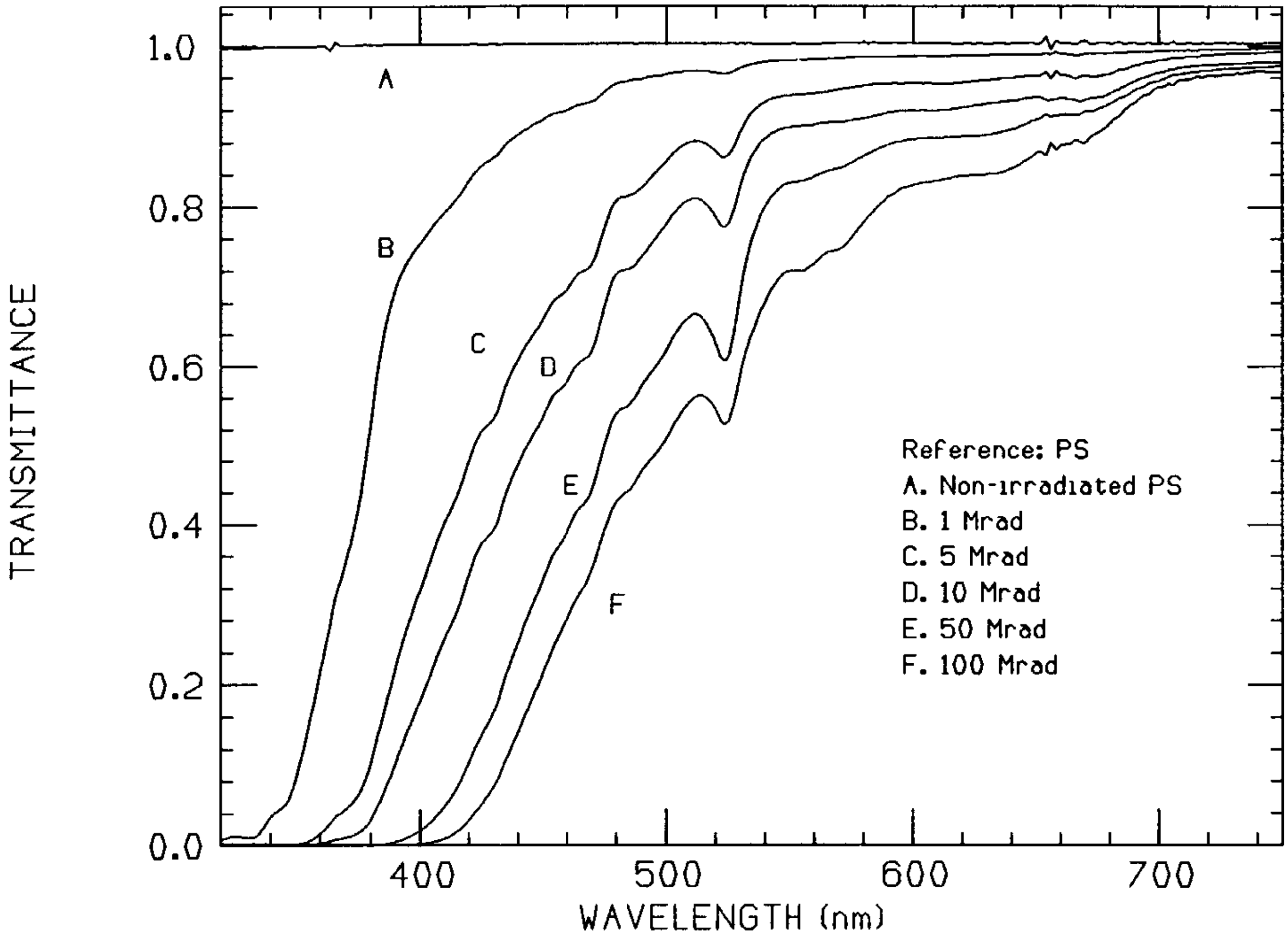
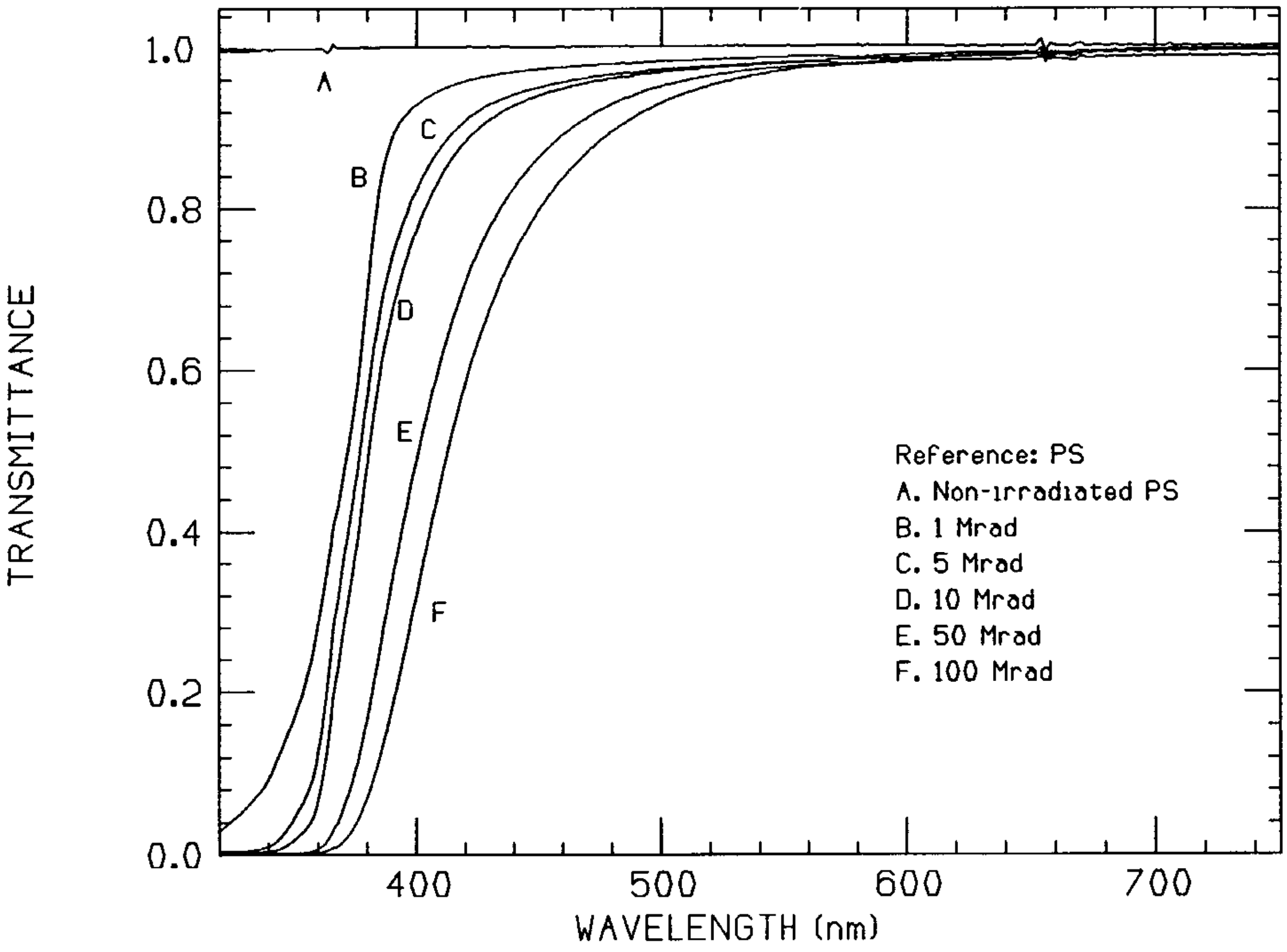

TRANSMITTANCE
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
WAVELENGTH (nm)
A
B
C
D
E
F
Reference: PS
A. Non-irradiated PS
B. 1 Mrad
C. 5 Mrad
D. 10 Mrad
E. 50 Mrad
F. 100 Mrad

FIGURE 2



TRANSMITTANCE
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
WAVELENGTH (nm)
A
B
C
D
E
F
Reference: PS
A. Non-irradiated PS
B. 1 Mrad
C. 5 Mrad
D. 10 Mrad
E. 50 Mrad
F. 100 Mrad

FIGURE 3

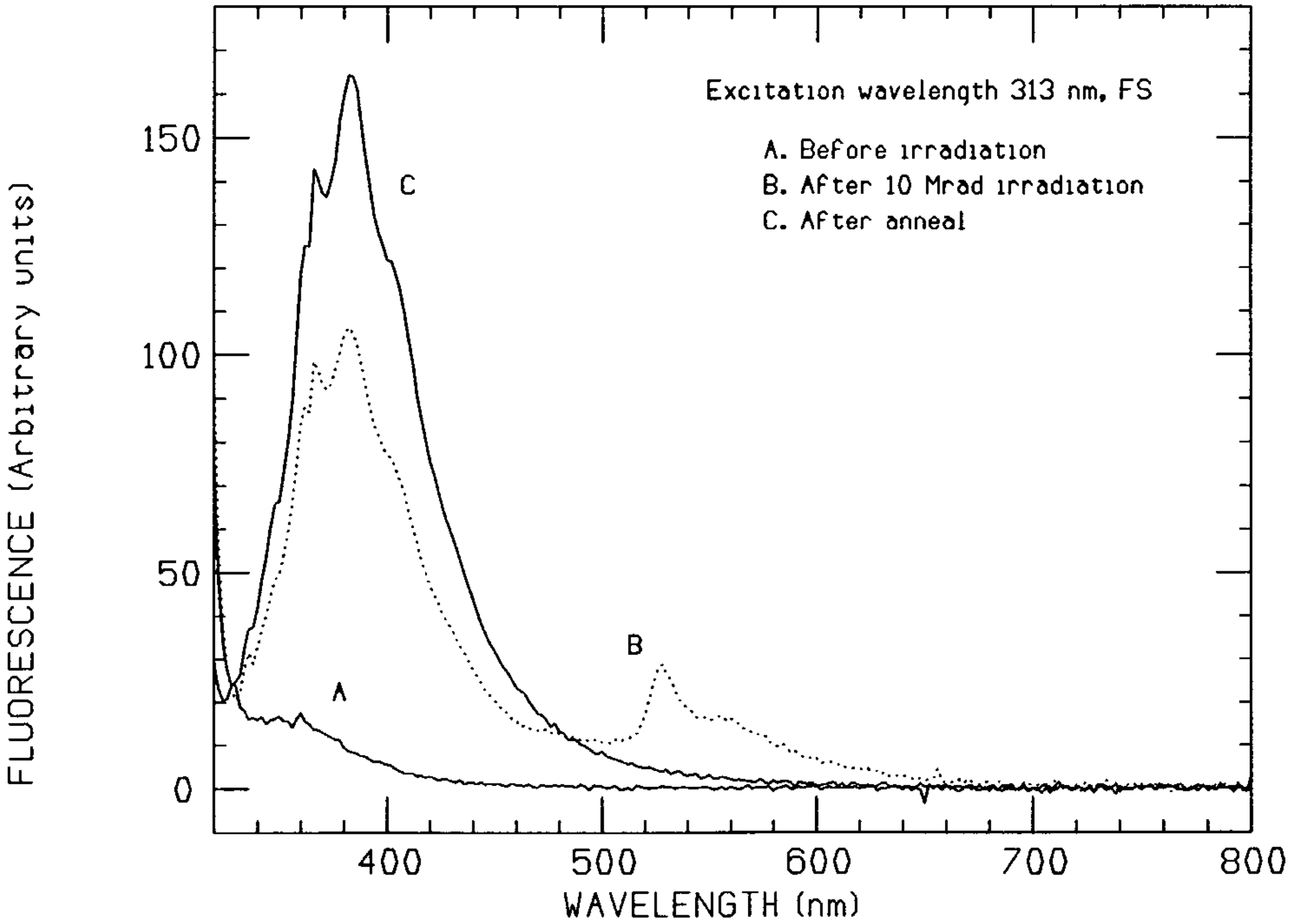

Excitation wavelength 313 nm, FS
A. Before irradiation
B. After 10 Mrad irradiation
C. After anneal
C
B
A
150
100
50
0
400
500
600
700
800
WAVELENGTH (nm)
FLUORESCENCE (Arbitrary units)

FIGURE 4

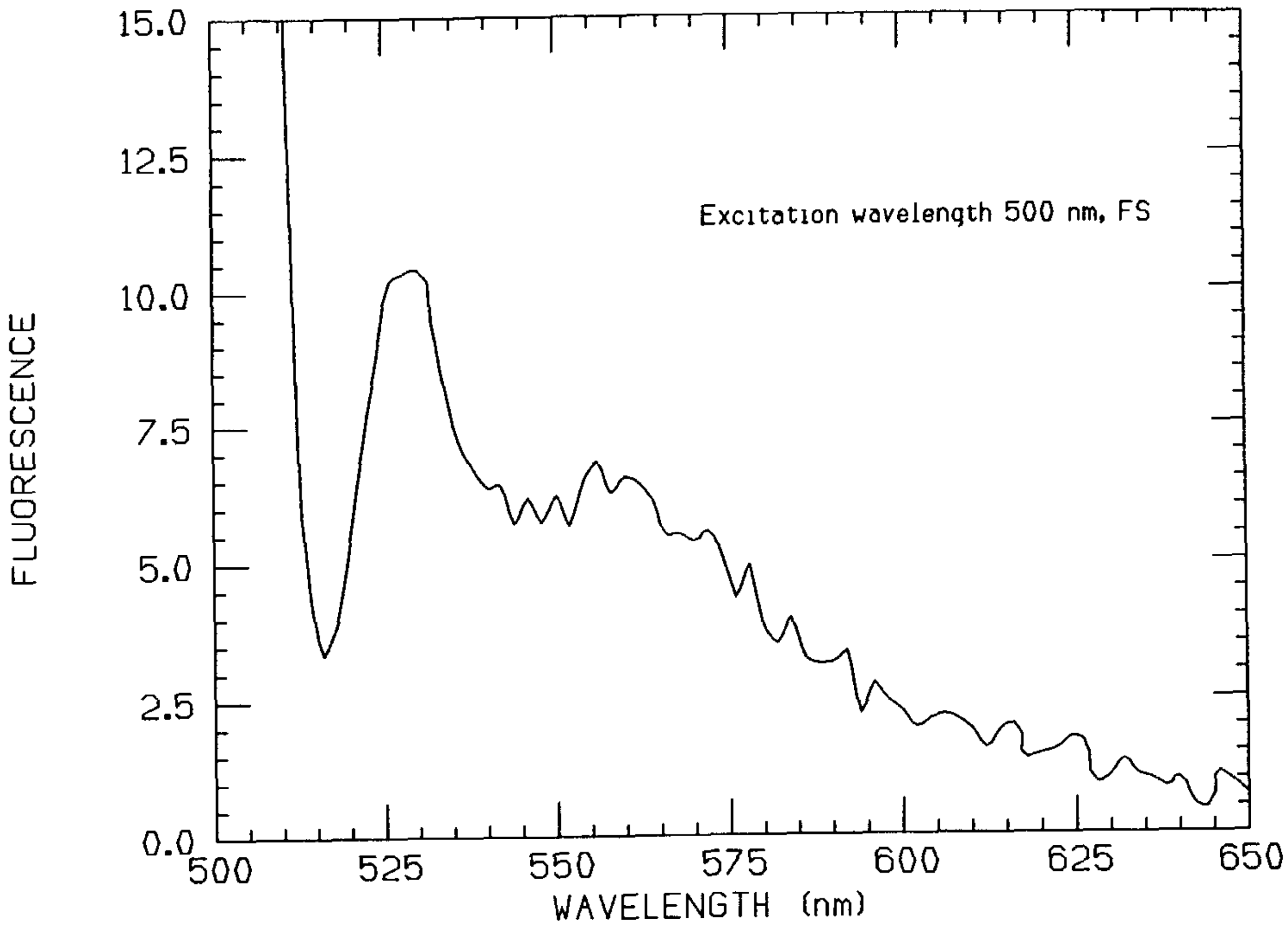
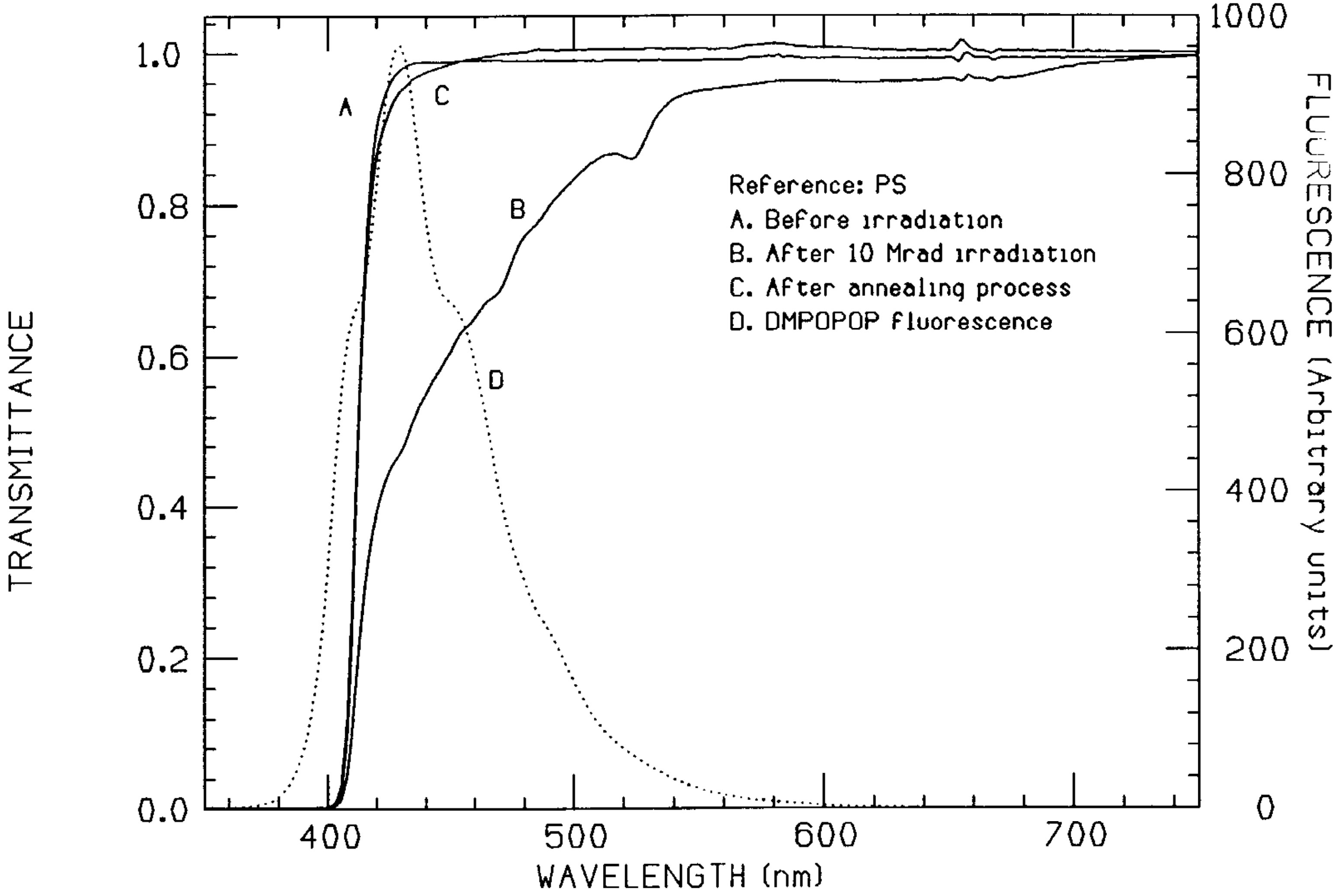
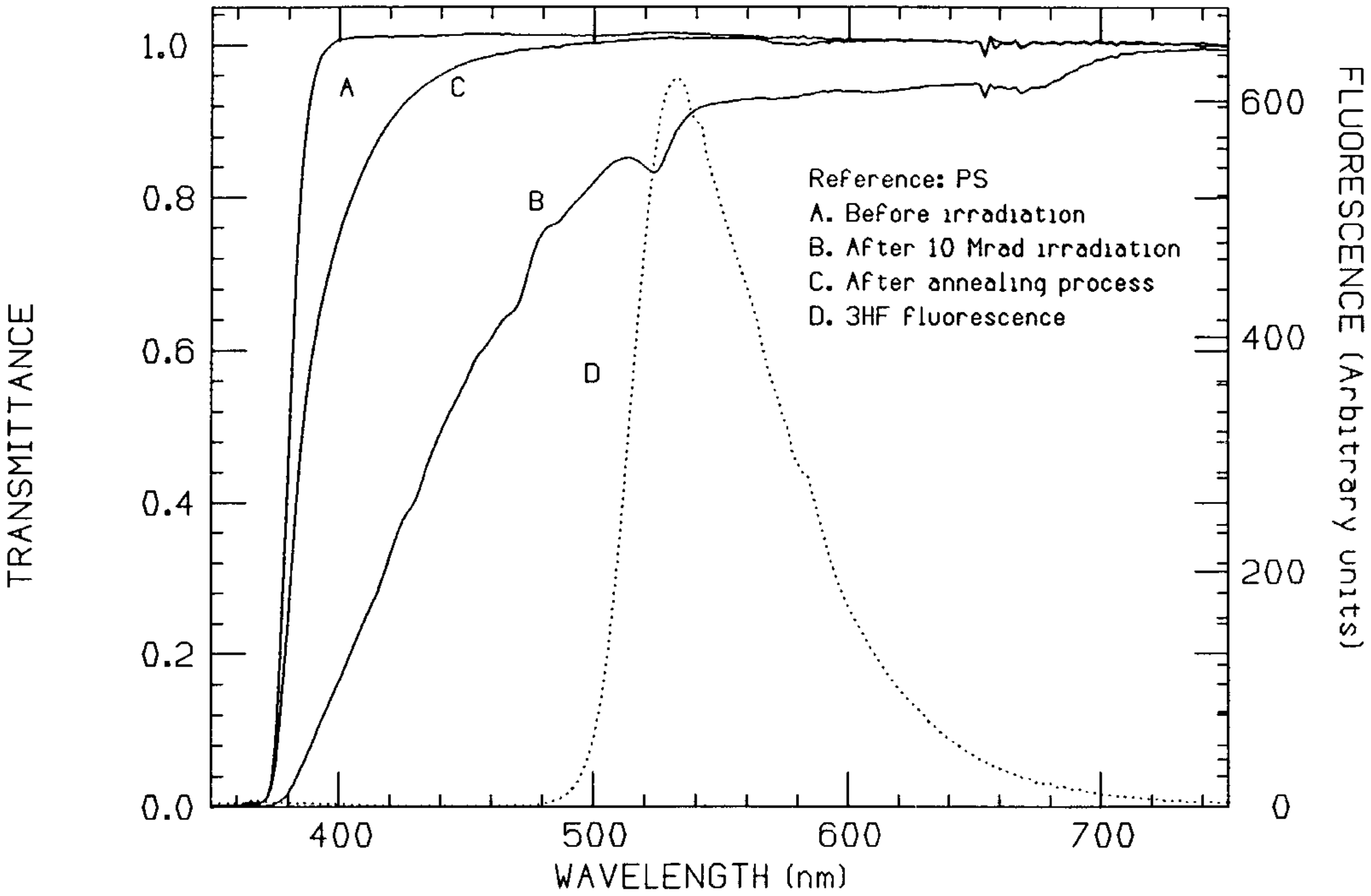

15.0
12.5
10.0
7.5
5.0
2.5
0.0
FLUORESCENCE
500
525
550
575
600
625
650
WAVELENGTH (nm)
Excitation wavelength 500 nm, FS

FIGURE 5



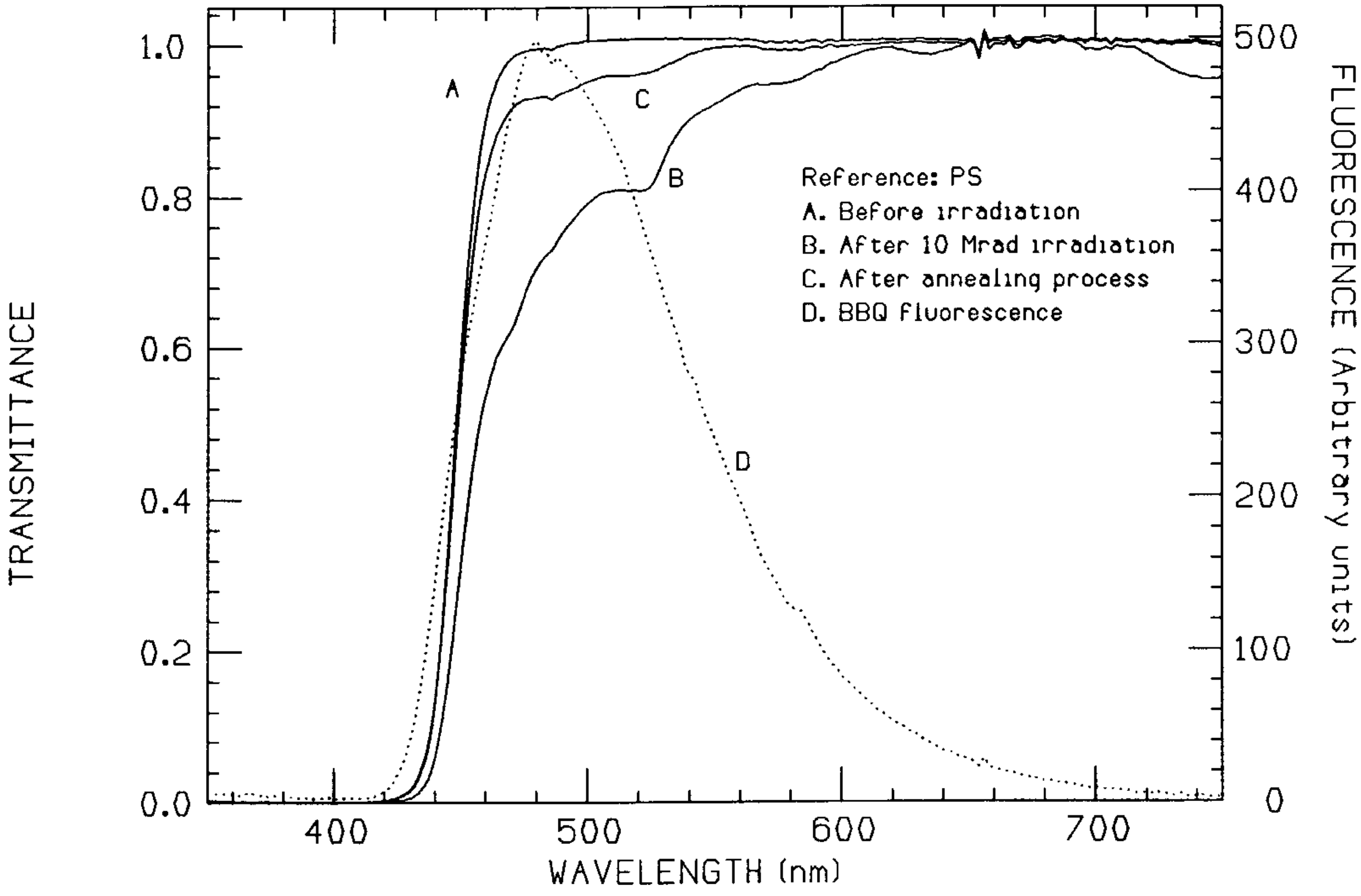
TRANSMITTANCE
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
WAVELENGTH (nm)
FLUORESCENCE (Arbitrary units)
1000
800
600
400
200
0
A
B
C
D
Reference: PS
A. Before irradiation
B. After 10 Mrad irradiation
C. After annealing process
D. DMPOPOP fluorescence

FIGURE 6



TRANSMITTANCE
1.0
0.8
0.6
0.4
0.2
0.0
FLUORESCENCE (Arbitrary units)
600
400
200
0
400
500
600
700
WAVELENGTH (nm)
A
B
C
D
Reference: PS
A. Before irradiation
B. After 10 Mrad irradiation
C. After annealing process
D. 3HF fluorescence

FIGURE 7



Reference: PS
A. Before irradiation
B. After 10 Mrad irradiation
C. After annealing process
D. BBQ fluorescence
A
B
C
D
TRANSMITTANCE
1.0
0.8
0.6
0.4
0.2
0.0
FLUORESCENCE (Arbitrary units)
500
400
300
200
100
0
400
500
600
700
WAVELENGTH (nm)

FIGURE 8

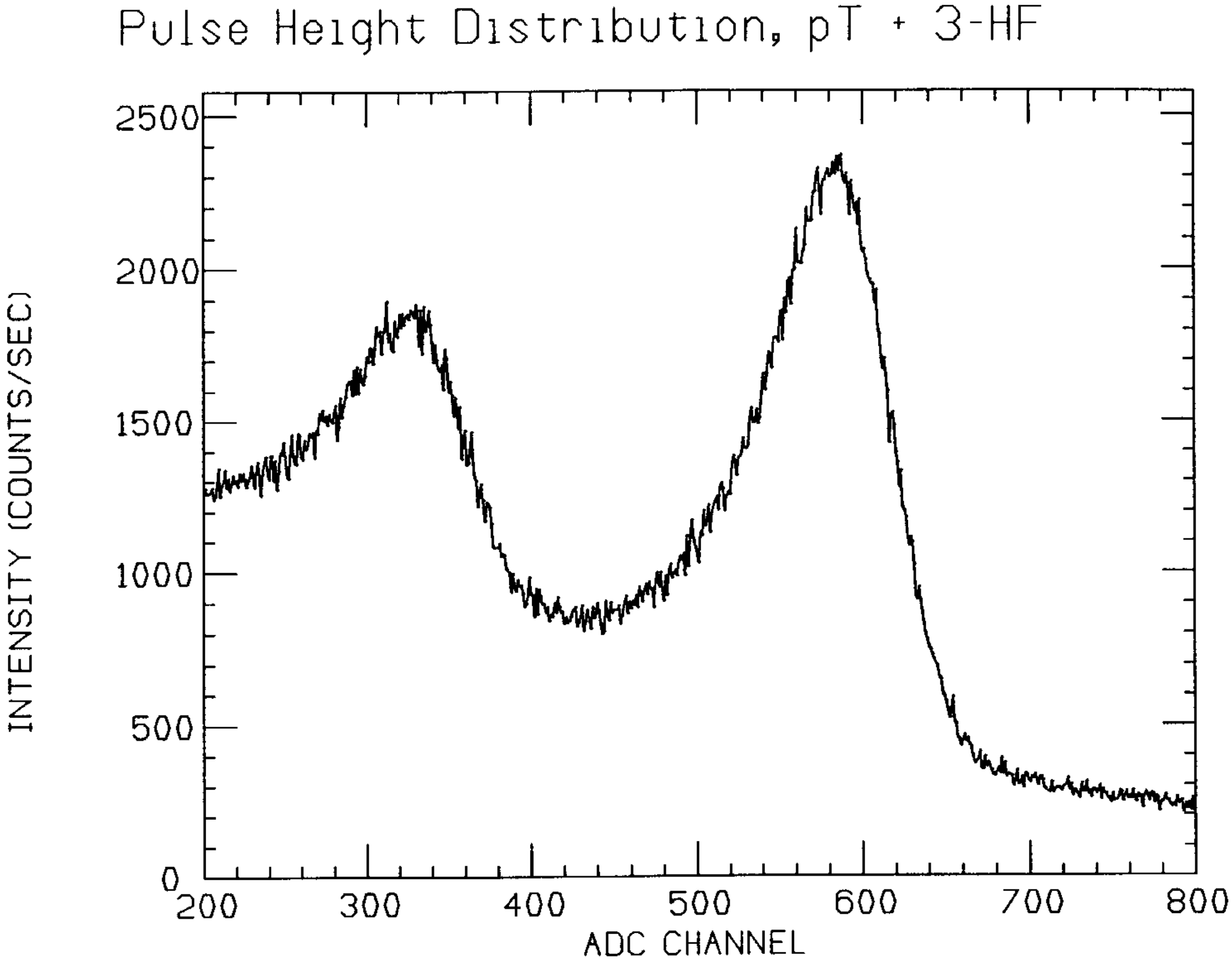

Pulse Height Distribution, pT + 3-HF
INTENSITY (COUNTS/SEC)
2500
2000
1500
1000
500
0
200
300
400
500
600
700
800
ADC CHANNEL

FIGURE 9

RELATIVE PULSE HEIGHT MEASUREMENTS

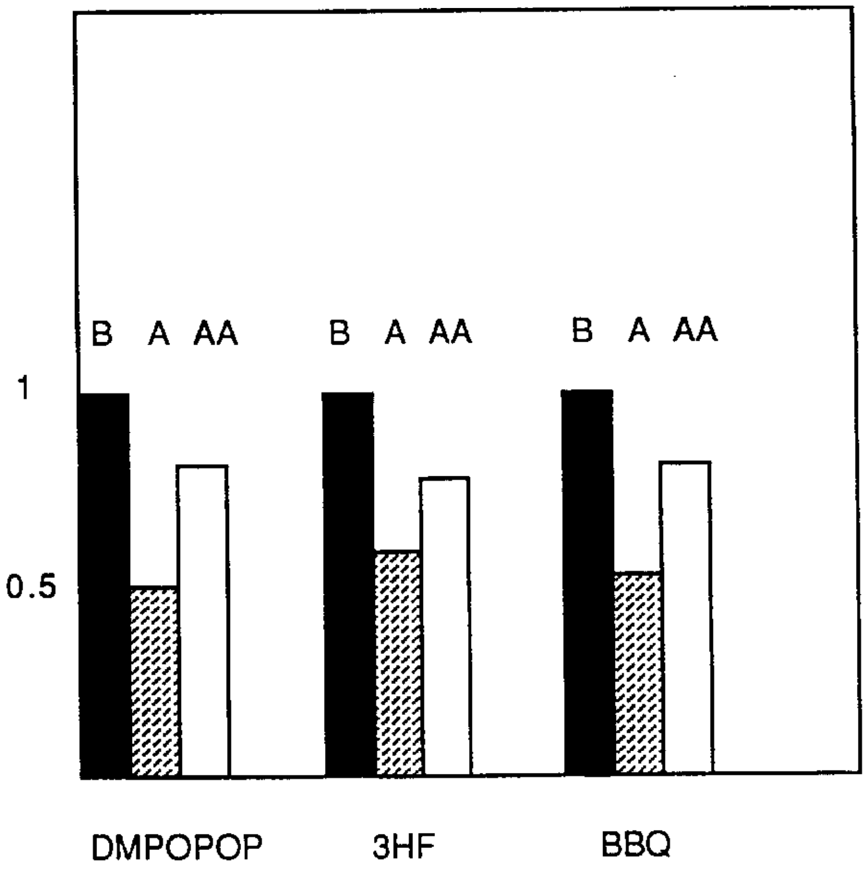


FIGURE 10

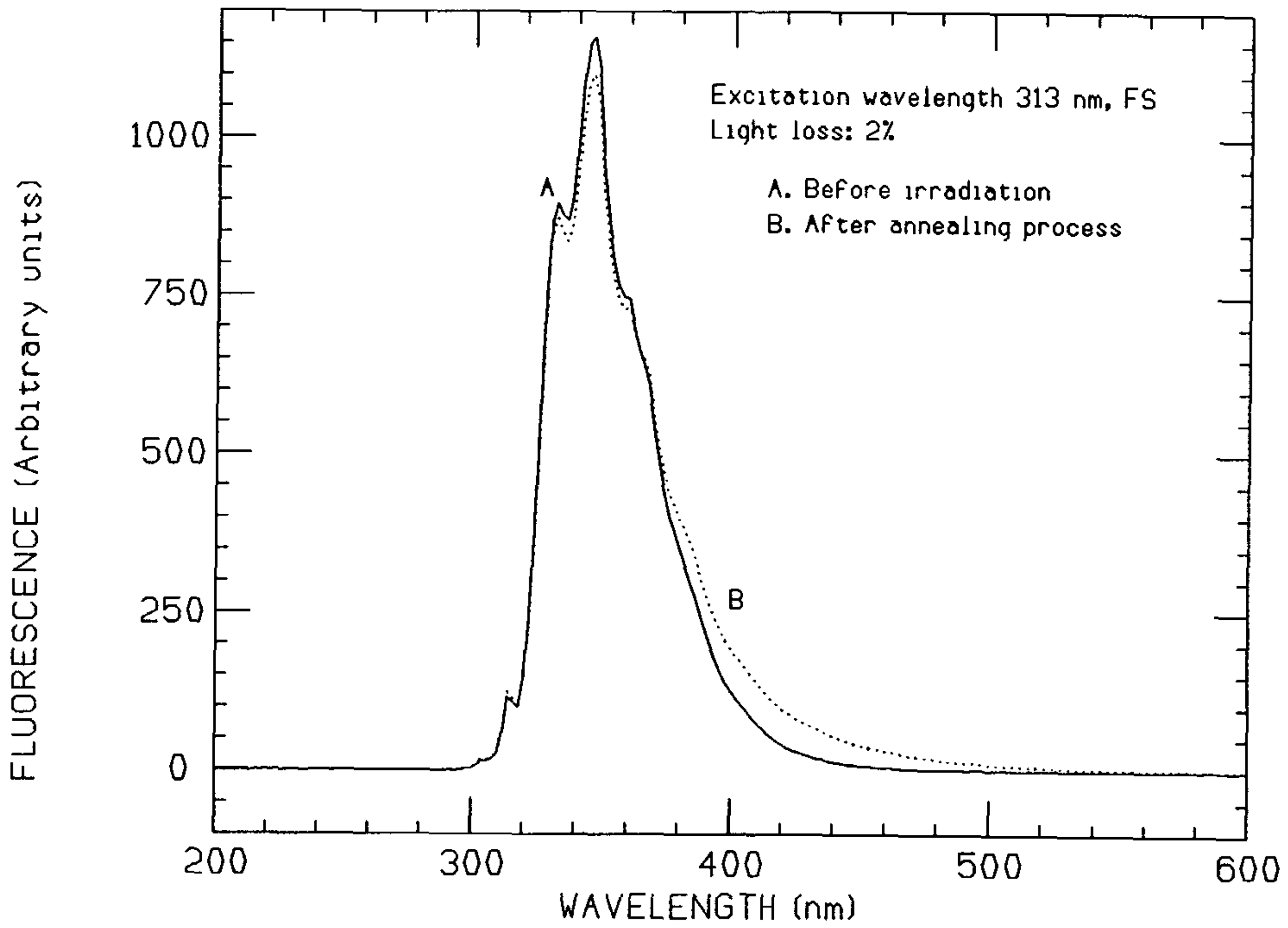

Excitation wavelength 313 nm, FS
Light loss: 2%
A. Before irradiation
B. After annealing process
A
B
1000
750
500
250
0
FLUORESCENCE (Arbitrary units)
200
300
400
500
600
WAVELENGTH (nm)

FIGURE 11

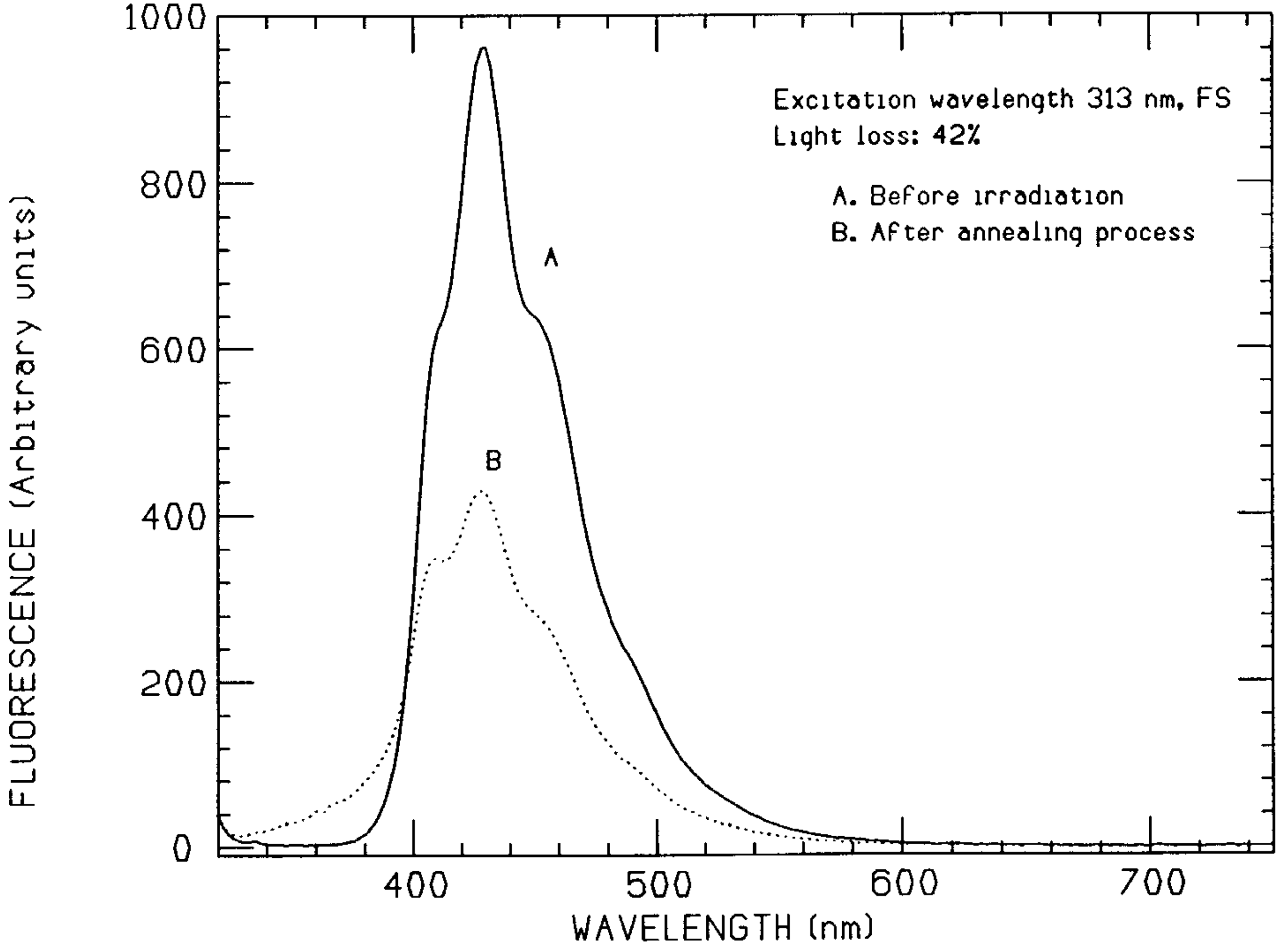

Excitation wavelength 313 nm, FS
Light loss: 42%
A. Before irradiation
B. After annealing process
A
B
1000
800
600
400
200
0
400
500
600
700
FLUORESCENCE (Arbitrary units)
WAVELENGTH (nm)

FIGURE 12

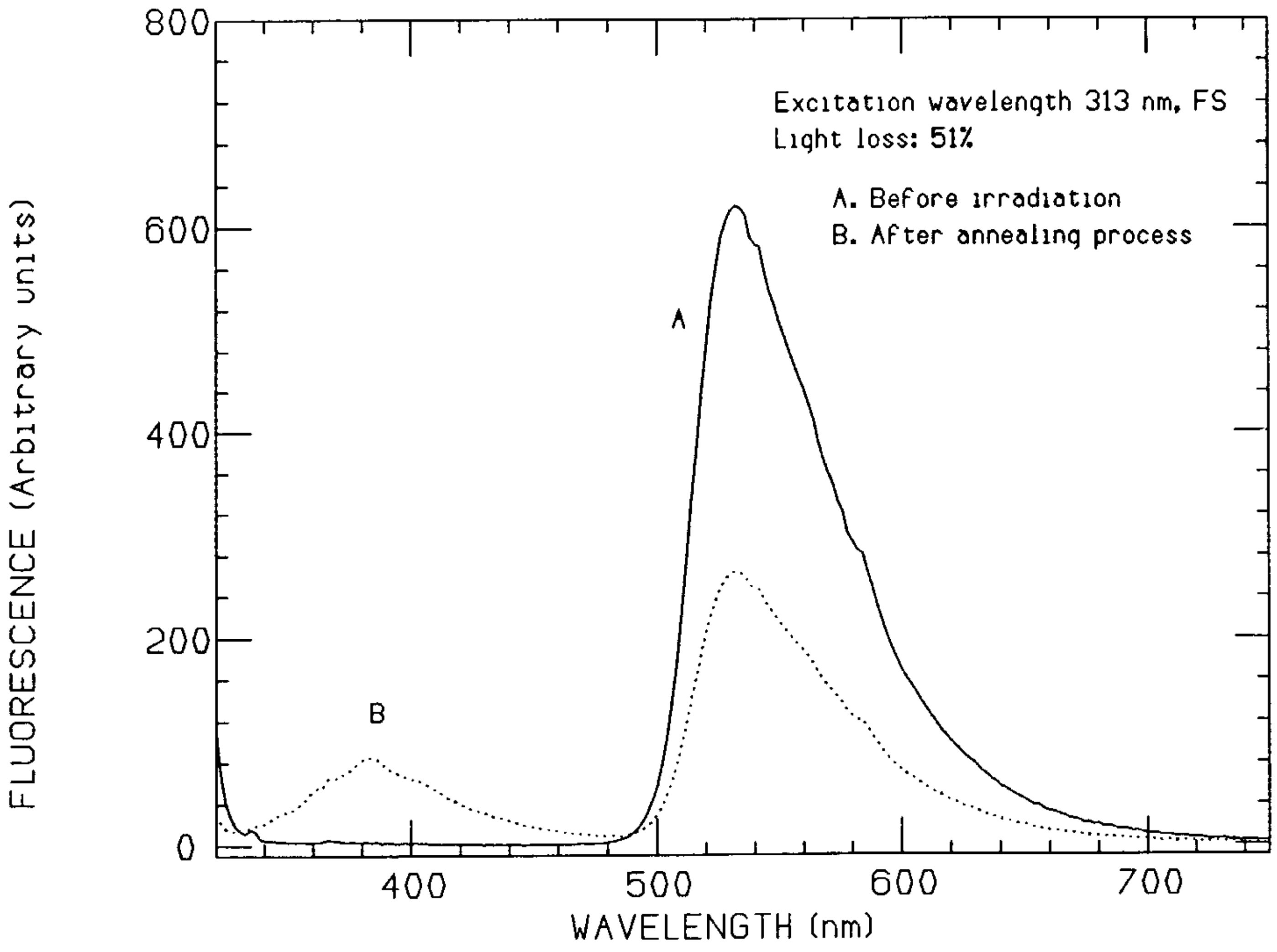

Excitation wavelength 313 nm, FS
Light loss: 51%
A. Before irradiation
B. After annealing process
A
B
800
600
400
200
0
400
500
600
700
FLUORESCENCE (Arbitrary units)
WAVELENGTH (nm)

FIGURE 13

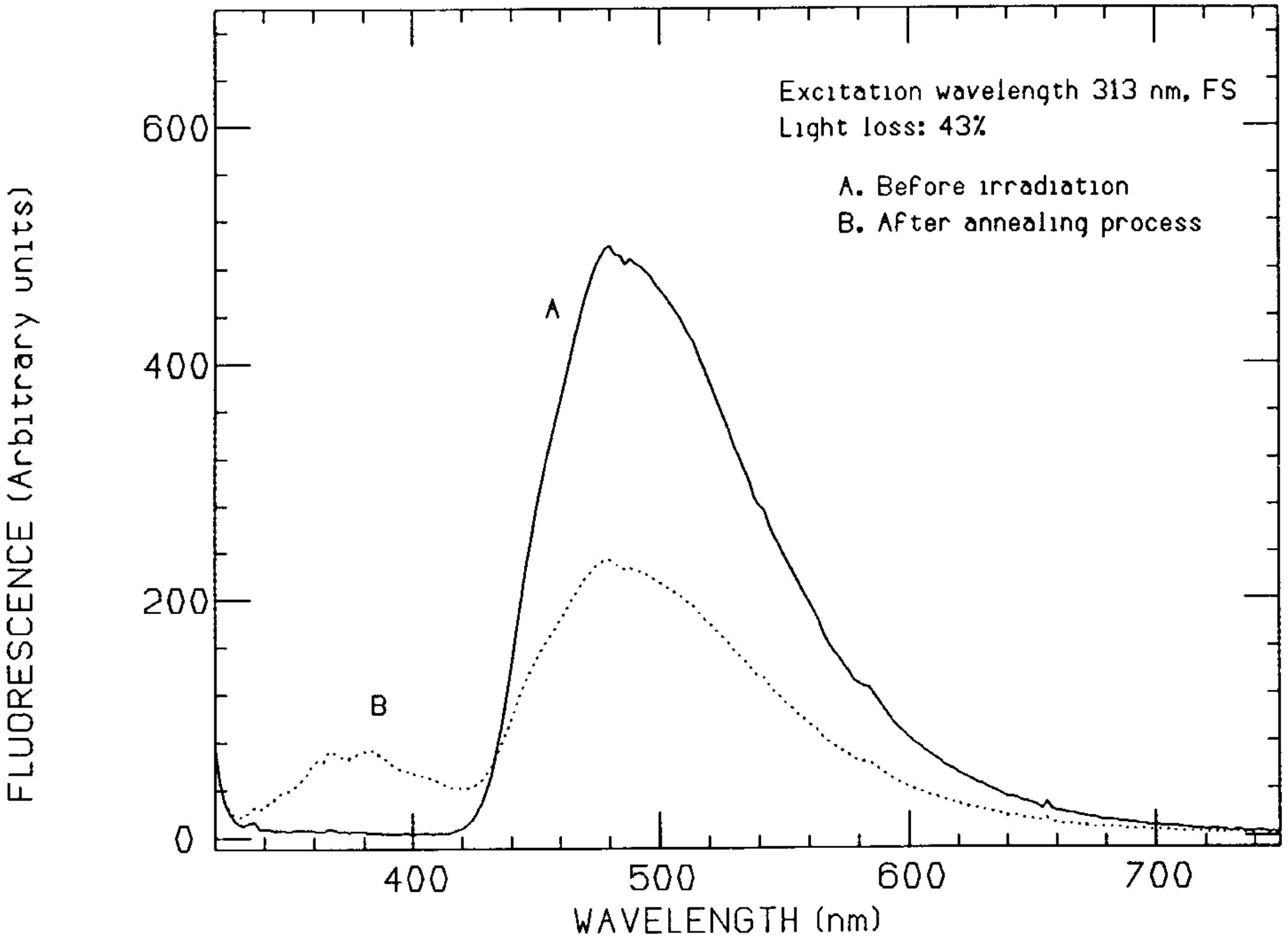

Excitation wavelength 313 nm, FS
Light loss: 43%
A. Before irradiation
B. After annealing process
A
B
FLUORESCENCE (Arbitrary units)
0
200
400
600
400
500
600
700
WAVELENGTH (nm)

FIGURE 14

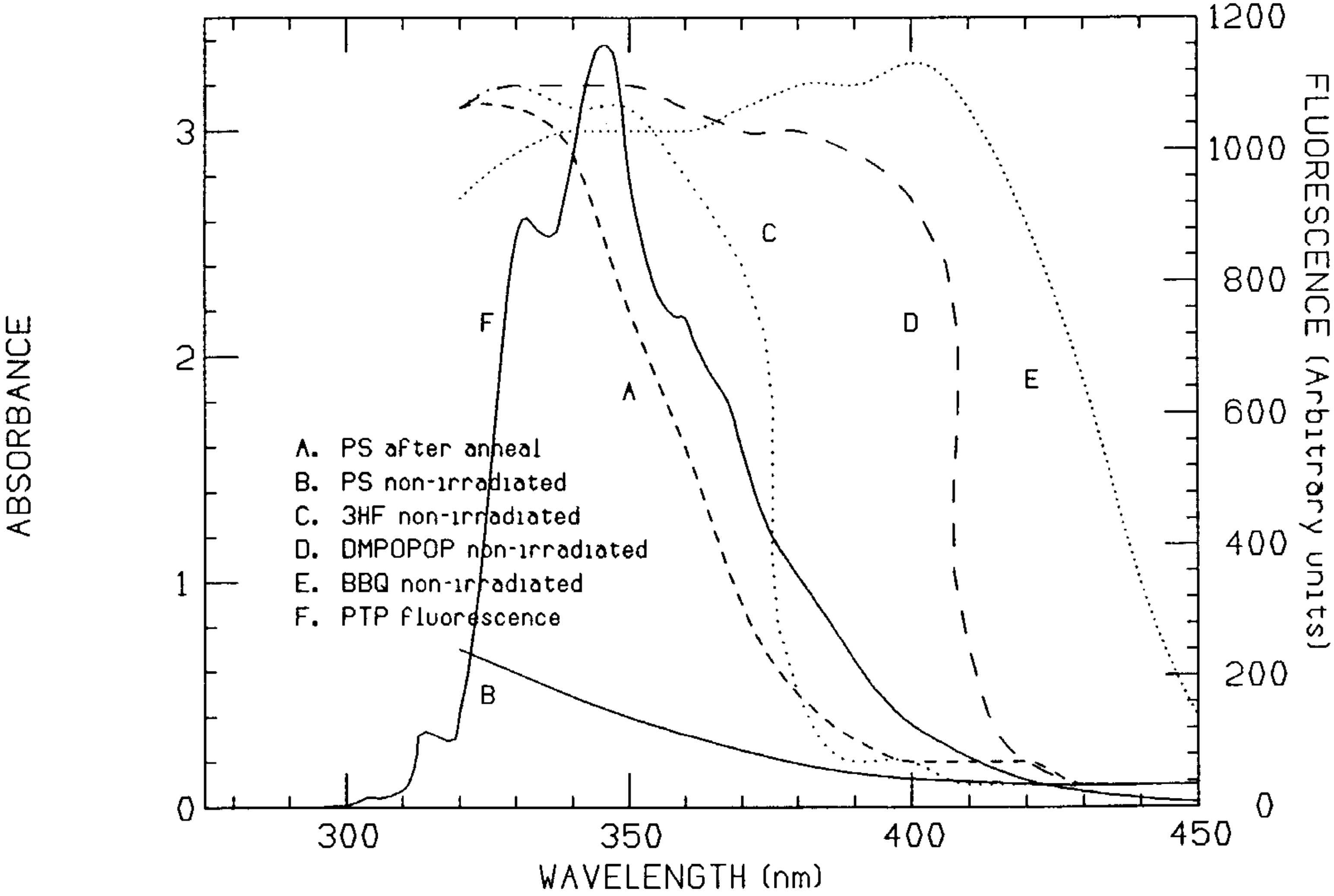

ABSORBANCE
0
1
2
3
FLUORESCENCE (Arbitrary units)
0
200
400
600
800
1000
1200
300
350
400
450
WAVELENGTH (nm)
A. PS after anneal
B. PS non-irradiated
C. 3HF non-irradiated
D. DMPOPOP non-irradiated
E. BBQ non-irradiated
F. PTP fluorescence
A
B
C
D
E
F

FIGURE 15

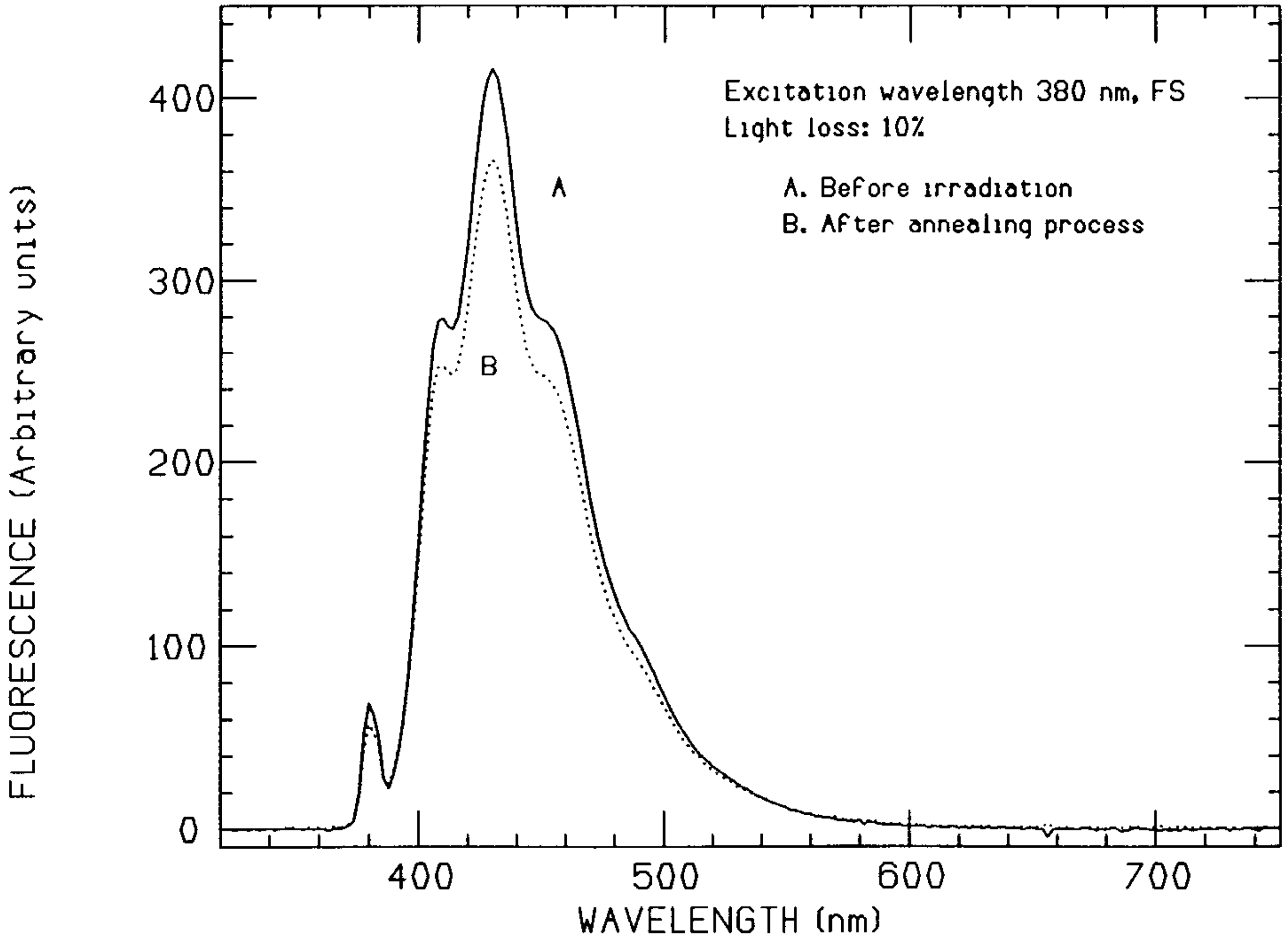
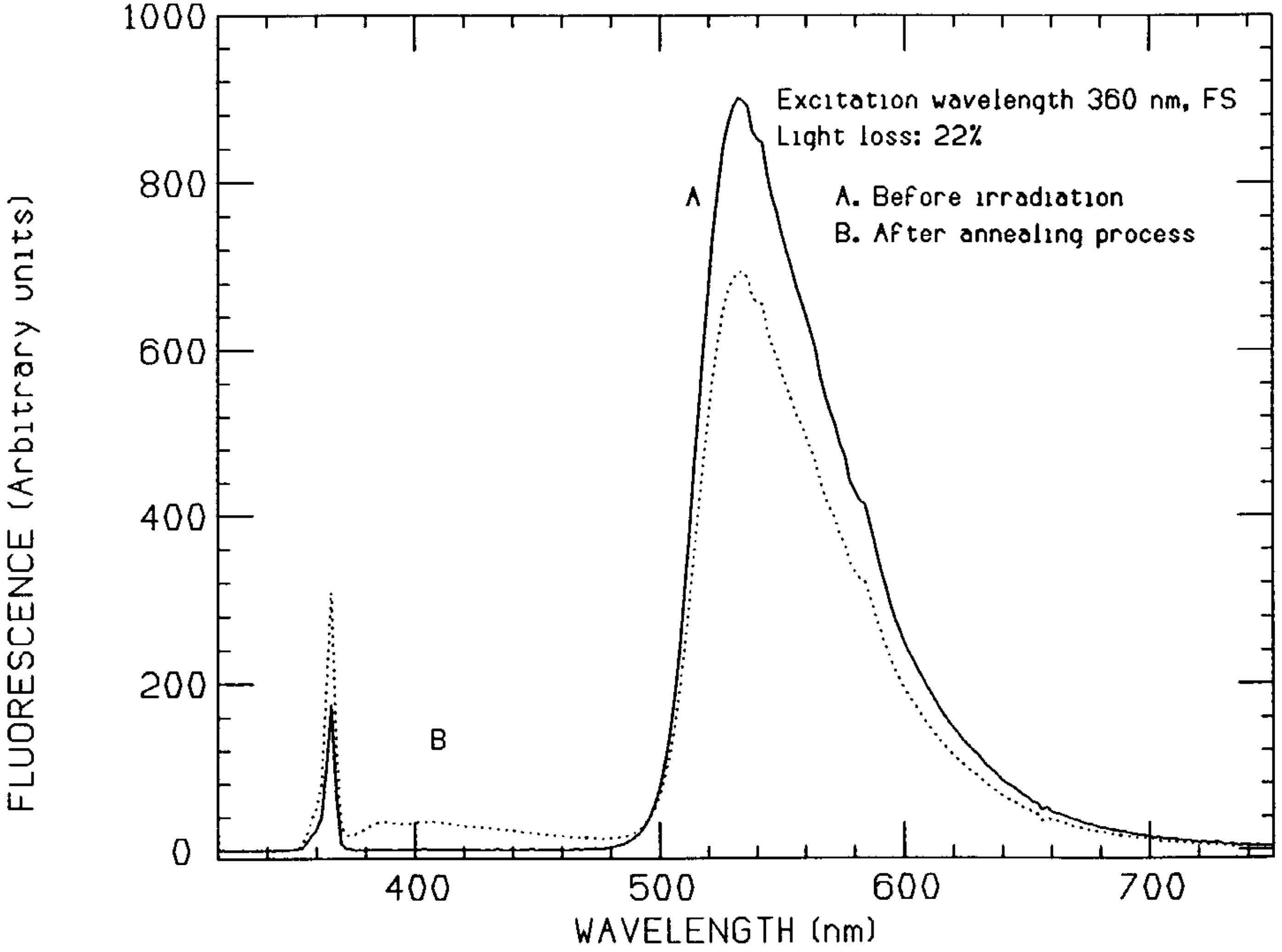

Excitation wavelength 380 nm, FS
Light loss: 10%
A. Before irradiation
B. After annealing process
A
B
FLUORESCENCE (Arbitrary units)
0
100
200
300
400
400
500
600
700
WAVELENGTH (nm)

FIGURE 16



Excitation wavelength 360 nm, FS
Light loss: 22%
A. Before irradiation
B. After annealing process
A
B
1000
800
600
400
200
0
FLUORESCENCE (Arbitrary units)
400
500
600
700
WAVELENGTH (nm)

FIGURE 17

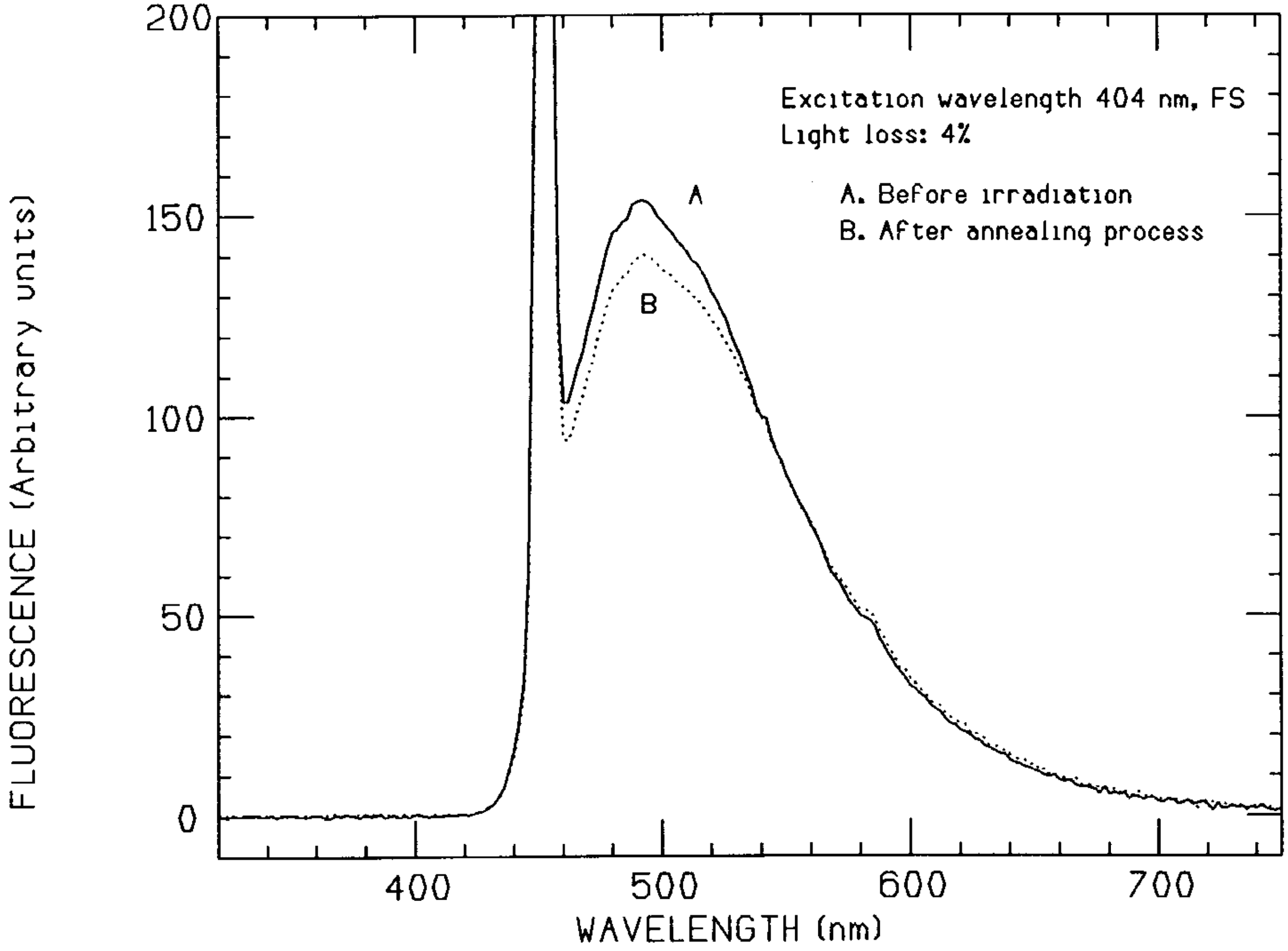

Excitation wavelength 404 nm, FS
Light loss: 4%
A. Before irradiation
B. After annealing process
A
B
FLUORESCENCE (Arbitrary units)
200
150
100
50
0
400
500
600
700
WAVELENGTH (nm)

FIGURE 18

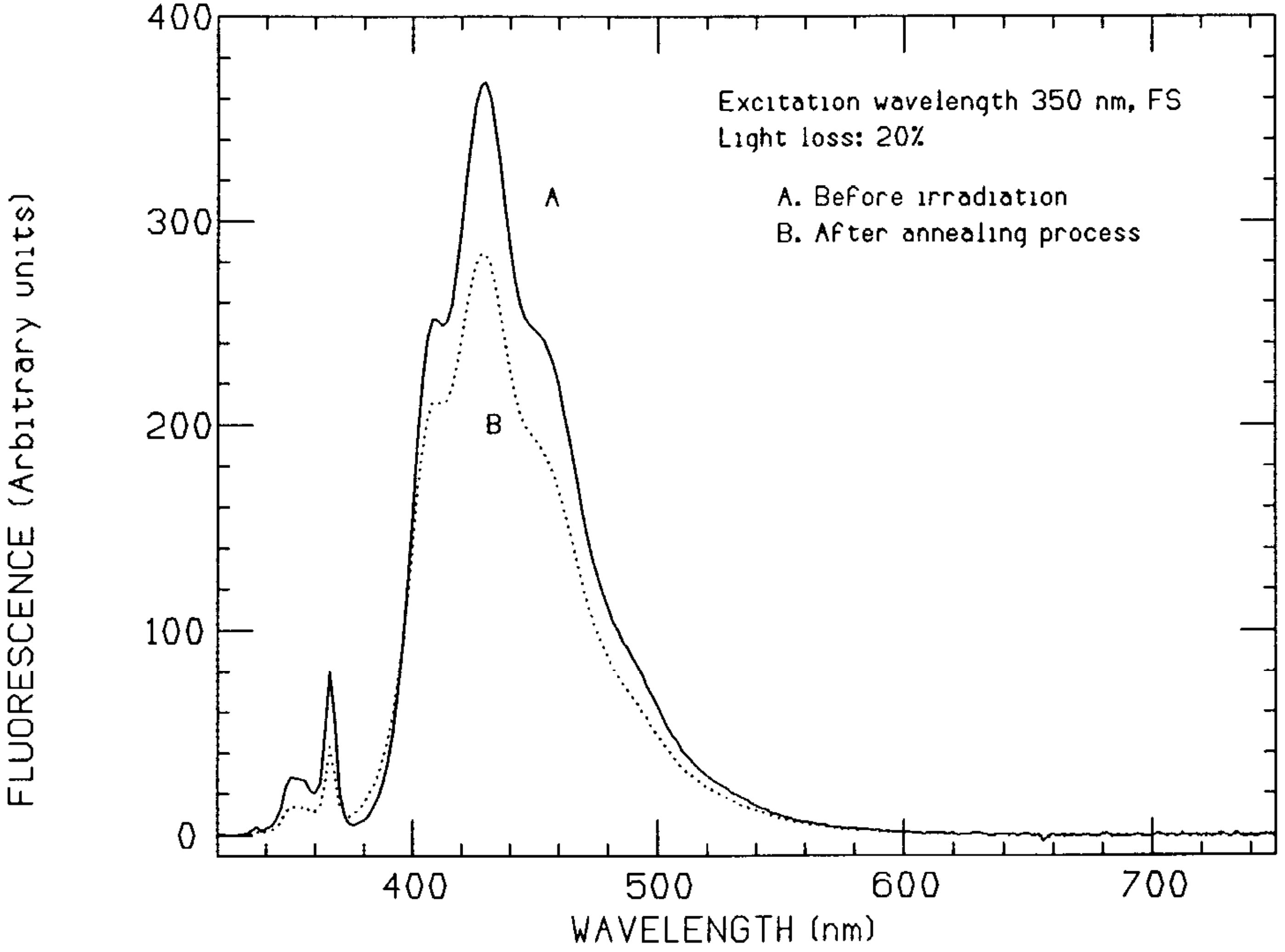

Excitation wavelength 350 nm, FS
Light loss: 20%
A. Before irradiation
B. After annealing process
A
B
FLUORESCENCE (Arbitrary units)
0
100
200
300
400
400
500
600
700
WAVELENGTH (nm)

FIGURE 19

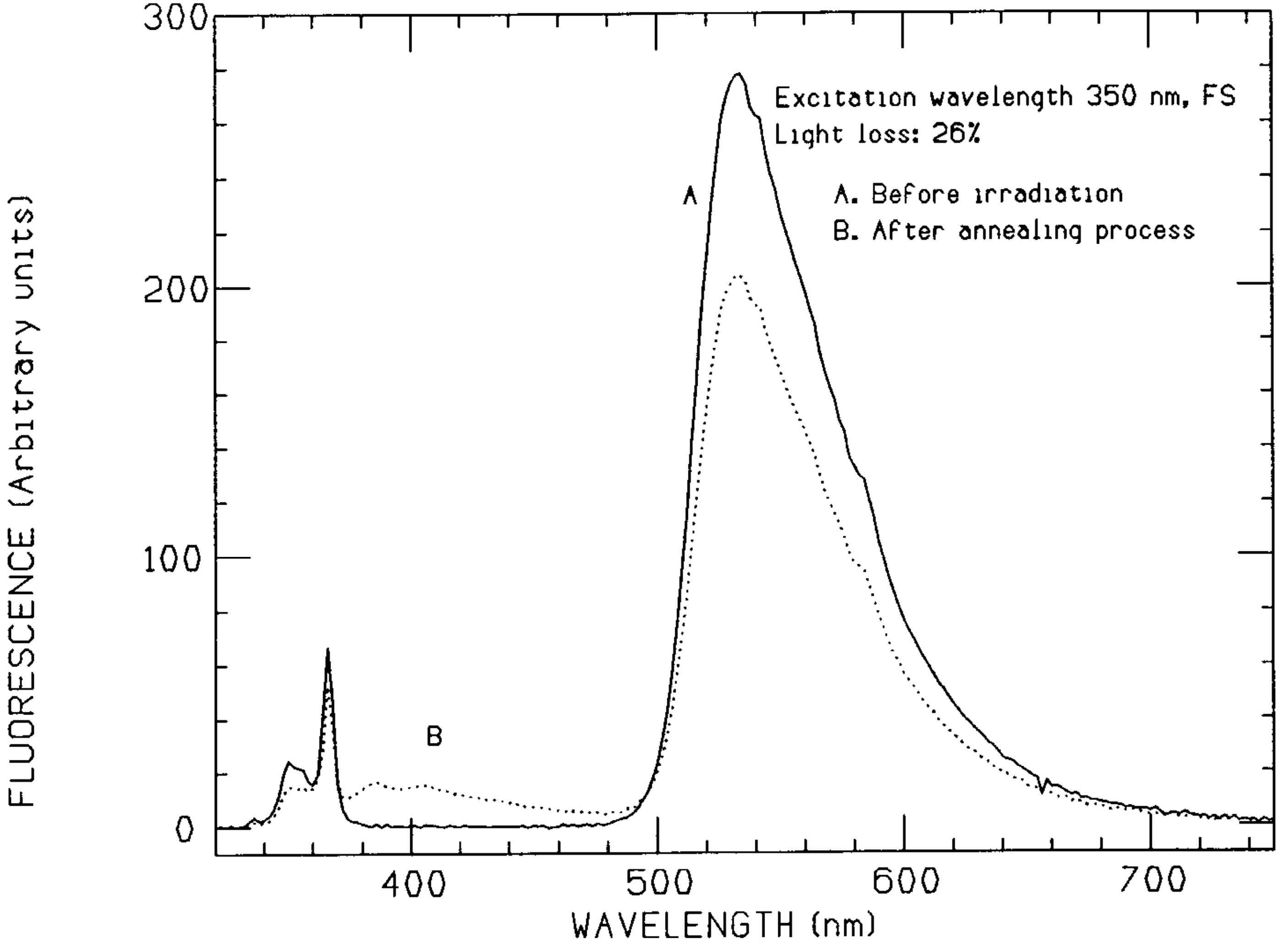
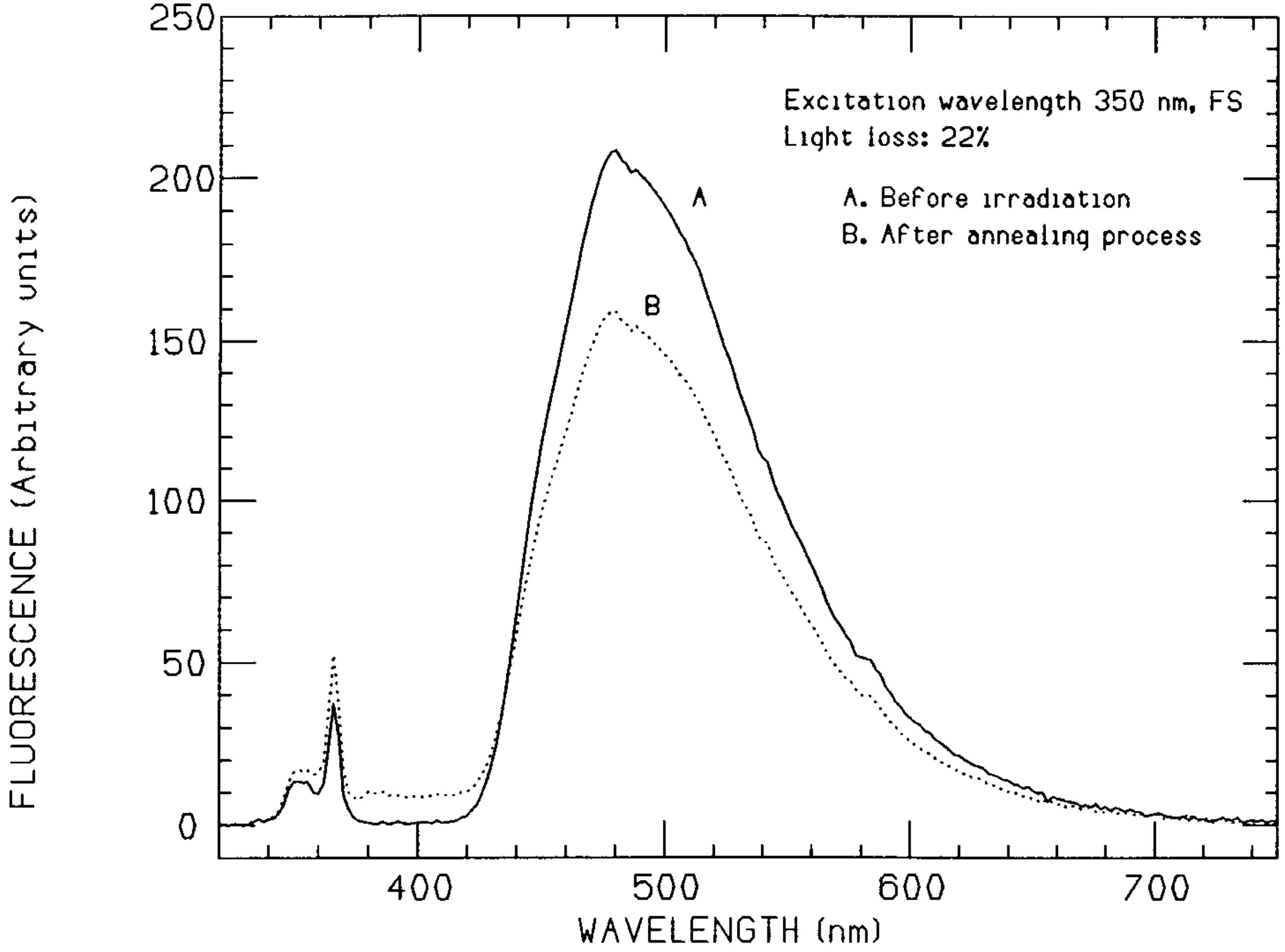

300
200
100
0
400
500
600
700
WAVELENGTH (nm)
FLUORESCENCE (Arbitrary units)
Excitation wavelength 350 nm, FS
Light loss: 26%
A. Before irradiation
B. After annealing process
A
B

FIGURE 20



Excitation wavelength 350 nm, FS
Light loss: 22%
A. Before irradiation
B. After annealing process
A
B
FLUORESCENCE (Arbitrary units)
0
50
100
150
200
250
400
500
600
700
WAVELENGTH (nm)