Measurement of the Quantum Efficiency of TMAE and TEA from Threshold to 120 nm*

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Several existing and planned high energy physics experiments incorporate detectors which use either TMAE (tetrakis-dimethyl-aminoethylene) or TEA (triethylamine) as their photosensitive agent. Understanding the operation of these devices requires knowledge of the absolute photoionization quantum efficiencies and absorption lengths of TMAE and TEA. In an experiment performed at the National Synchrotron Light source at Brookhaven National Laboratory, we have measured these parameters from 120 nm to 280 nm. The quantum efficiencies were normalized to the known photoionization yields of benzene and cis-2-butene. The results of these measurements and details of the experiment are presented in this paper.

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Many modern high energy physics experiments incorporate detectors which use photosensitive gases. Cerenkov ring-imaging detector[1] used at the Omega spectrometer[2] and those being designed for SLD[3] and Delphi[4] must detect photons over large areas. A photosensitive gas in a time projection chamber provides these detectors with large area coverage at a reasonable cost. Another experiment[5] plans to use the fast ultraviolet scintillation light of barium fluoride crystals and the low ionization threshold of TMAE (tetrakis-dimethylaminoethylene) together in a low pressure multiwire proportional chamber as a highly efficient photon veto detector.

We have measured the absolute quantum efficiency and the absorption length of TMAE and TEA (triethylamine), two of the vapors most commonly used in photoionization detectors. Our measurements were performed using the U9A line on the vacuum ultraviolet ring at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The apparatus for our experiment is illustrated in Fig. 1. A system of mirrors located upstream of the equipment illustrated in Fig. 1 directed light from the synchrotron ring down our line. The mirrors and vacuum windows in the beamline limited the useful light intensity to wavelengths greater than 120 nm. Light of a particular wavelength was selected by a 50 cm Seya-Namioka monochromator operated in first order. An elliptical mirror at the exit of the monochromator focussed the light into a small ionization chamber (M3) filled with the vapor under test. The ionization chamber

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consisted of two parallel plates, each 8.6 cm long and 1.5 cm
wide, spaced 1 cm apart. They were mounted inside a stainless
steel cylinder with front and back lithium-fluoride windows. The
total path length of gas between the windows was 9 cm. A small
voltage was applied across the two plates to collect the charges
freed by photoionization. Because we operated the chamber at
very low pressure (usually less than 1 torr), parallel plate gas
amplification could occur even at low voltages. We made current
measurements at various voltages from 15 to 50 volts to assure
ourselves that no such amplification occurred. The light
transmitted through the chamber fell upon a glass wedge coated
with sodium salic.late. The salicylate shifted the ultraviolet
light to wave lengths detectable by a RCA 1P28 photomultiplier.
The current in the photomultiplier (M1) which viewed the sali-
cylate wedge was used as a measure of the transmitted light
intensity. The incident light intensity was monitored by a
second photomultiplier (M2) which viewed a small screen coated in
a similar manner placed in front of the chamber. By observing
the salicylate fluorescence, we removed the wavelength dependence
of the photomultiplier response from the measurements. Bandpass
filters placed in front of the photomultipliers M1 and M2 reduced
the backgrounds from scattered light.

Absorption measurements were made by scanning the monochro-
mator from 120 nm to 280 nm, and recording the current observed
in the two photomultipliers M1 and M2 for the vapor-filled and,
later, for the evacuated chamber. If we define

R=Current(M1)/Current(M2)

(where Current(M_i) is the average current from the photomulti-
plier with the light on minus the average current with the light
off), then the transmittance of the vapor is given by

T_{vapor} = R(Chamber with vapor)/R(Chamber evacuated).

At very short wavelengths, a significant fraction of the trans-
mitted light was scattered, non-monochromatic light in the beam.
We corrected the transmittance ratio to compensate for this
effect. The correction* was significant only below 135 nm.
Plots of μ, the inverse absorption length in the equation
$I = I_o\,e^{-\mu l}$, for TMAE and TEA are given in Figs. 2 and 3. Both
of these plots have been extrapolated to 1 torr pressure. Data
were taken at .062, .142, and .311 torr for TMAE and at 4.87,
1.05, and .19 torr for TEA. After correcting for the scattered
light, we found the inverse absorption length to be proportional
to pressure. The absorption curves for TEA are consistent with
published data.[6] The absorption curves for TMAE, while consis-
tent with recent measurements done for the Omega RICH counter[2]
and the SLD CRIDs[7], are inconsistent with the original measure-
ments made by Nakato, et al.[8] We see a quite flat absorption
spectrum without the large peak around 190 nm that was observed

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* We obtained the scattered light correction from the
high pressure TEA run (which should have absorbed all the light
below 220 nm). We assumed that this correction was proportional
to beam intensity; this assumption is consistent with our data.
The scattered light correction is important only in the transmis-
sion measurements. The quantum efficiency is calculated from the
gas absorption which is approximately 100% at these short wave
lengths.

in Ref. 8. This could be due to the higher purity of our sample.

While the absorption cross section can be determined at each wavelength independent of the chromatic behavior of our two monitors M1 and M2, the absolute quantum efficiency of the gas cannot. If we assume that the salicylate response does not vary with wavelength[9] and that the responses of the wedge and the screen are similar,* then we can determine a relative quantum efficiency by forming the following ratio:

$$QE_{rel} = M3/ (M2 * (1. - T_{vapor}) * T_{FW})$$

where

QE_{rel} is proportional to the quantum efficiency of the vapor as a function of wavelength,

M3 and M2 are the currents in the ionization chamber and the screen photomultiplier respectively,

T_{vapor} is the transmission of vapor as measure by the M1/M2 ratio given above, and

T_{FW} is the transmission of the front window of the ionization chamber.**

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* One source of systematic uncertainty in this experiment arises from our assumption about the flatness of the salicylate response. According to ref. 9, the fluorescence response of salicylate varies slowly with wavelength by about +/- 10%. A second source of systematic error is the relative tracking of M1 and M2. With the ionization chamber removed from the system, we find that the ratio of M1/M2 varies within the limits of +/- 15%. We therefore assign an overall systematic uncertainty of 20% to our measurements.

** T_{FW} was measured by comparing a cell empty run with a special run taken with the front window removed from the chamber.

The absolute quantum efficiency can be determined by calibrating with known standards. We used cis-2-butene for which the quantum efficiency is known at 123.6 nm[10] and benzene which is known at 132.6 nm[11]. The agreement between these two normalization points is 2%.

The absolute quantum efficiency for TMAE is shown in Fig. 4. The shape of this quantum efficiency curve agrees with the relative quantum efficiency measured by Ekelin.[12] We also agree with the curve measured by Ref. 8, except we see no evidence for their "autoionization" shoulder at 190 nm. This discrepancy in quantum efficiency is in the same region where we disagree with the absorption measurement of Ref. 8. Michau, et al. have recently measured the quantum efficiency of TMAE at 210 nm to be 8% +/- 2%.[13] This is in good agreement with our value of 7.7% in the same region. We observe consistent quantum efficiencies for our three different pressures. The measurement presented in Fig. 4 was taken at .142 torr; however, the two other pressures appear identical.

The TEA photoionization quantum efficiency curve is given in Fig. 5. The shape of this curve is similar to that measured by Ekelin; however, the quantum efficiency is only one half of that measured by D. Salomon, et al.[14] at 147 nm. Increasing our normalization by a factor of two would mean that both our benzene and our cis-2-butene measurements were incorrect, and furthermore that the quantum efficiency of TMAE below 150 nm would be greater than 100%. In addition, detectors which use TEA usually find

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fewer photoelectrons than they expect.[15] They usually attribute this loss to unfound (and unknown) impurities in their gas systems. Our measurements indicate that the TEA quantum efficiency is lower than previously reported.

An interesting feature of Fig. 5 is the small amount of current present between 167 nm (the TEA vapor ionization threshold) and 200 nm. This shoulder which was not present at all in the 4.87 torr run, corresponds to a 2.5% quantum efficiency in the 1.05 torr run (the one plotted in Fig. 5), and a 3.7% quantum efficiency in the .19 torr run.* D. Anderson has suggested that this quantum efficiency above threshold, which has been previously observed,[16] is due to the photoelectric effect on a liquid film on the windows of the chamber.[17] The absorption measurements indicate that the thickness of any film on the chamber windows is proportional to the pressure of the vapor in the chamber. Why the 4.87 torr measurements show no above-threshold efficiency is hard to reconcile with this explanation.

In summary, we have measured the absorption length and absolute quantum efficiencies of TEA and TMAE by direct measurement of the light transmission through and the photoionization current of the vapor. The quantum efficiency has been normalized using two reference standards at two different wavelengths and

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*   Incidentally, the runs were taken in that order, with the 4.87 torr run separated from the other two by about one hour (one beam fill of the ultraviolet ring). The runs themselves take about 20 minutes. During the fill time, the chamber was held at 1.05 Torr.

then extrapolated over then entire wavelength region of our measurement. We find our results for TMAE to be in agreement with other recent measurements and our results for TEA to be lower than previously reported but consistent with the lower quantum yields observed in detectors.

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     Lett. 118B, 230 (1982). This paper suggests that TMAE would
     behave similarly; we see no such behavior.

Figure 1.

Apparatus used to measure quantum efficiencies and inverse
absorption lengths of TEA and TMAE. M1 and M2 are
photomultipliers observing sodium salicylate monitors.
M3 is vapor ionization chamber. Entire beam line is
evacuated except for ionization chamber.

Figure 2.

Inverse absorption length of TMAE versus wavelength. This
plot has been extrapolated to a pressure of 1 torr in
the chamber.

Figure 3.

Inverse absorption length of TEA versus wavelength. This
plot has been extrapolated to a pressure of 1 torr in
the chamber.

Figure 4.

Photoionization quantum efficiency of TMAE versus wave-
length. Plotted are the results of the measurement
made at .142 torr. The other two pressures are in
agreement with this measurement.

Figure 5.

Photoionization quantum efficiency of TEA versus wavelength.
Plotted are the results of the measurement made at 1.05
torr. The other two pressures are in agreement with
this measurement except above 170 nm (see discussion in
text).

Fig. 1

Monochromator

Ionization Chamber

M3

M1

M2

Trans-
mission
Monitor

Beam Intensity Monitor

NSLS
U9A
Beam
Port
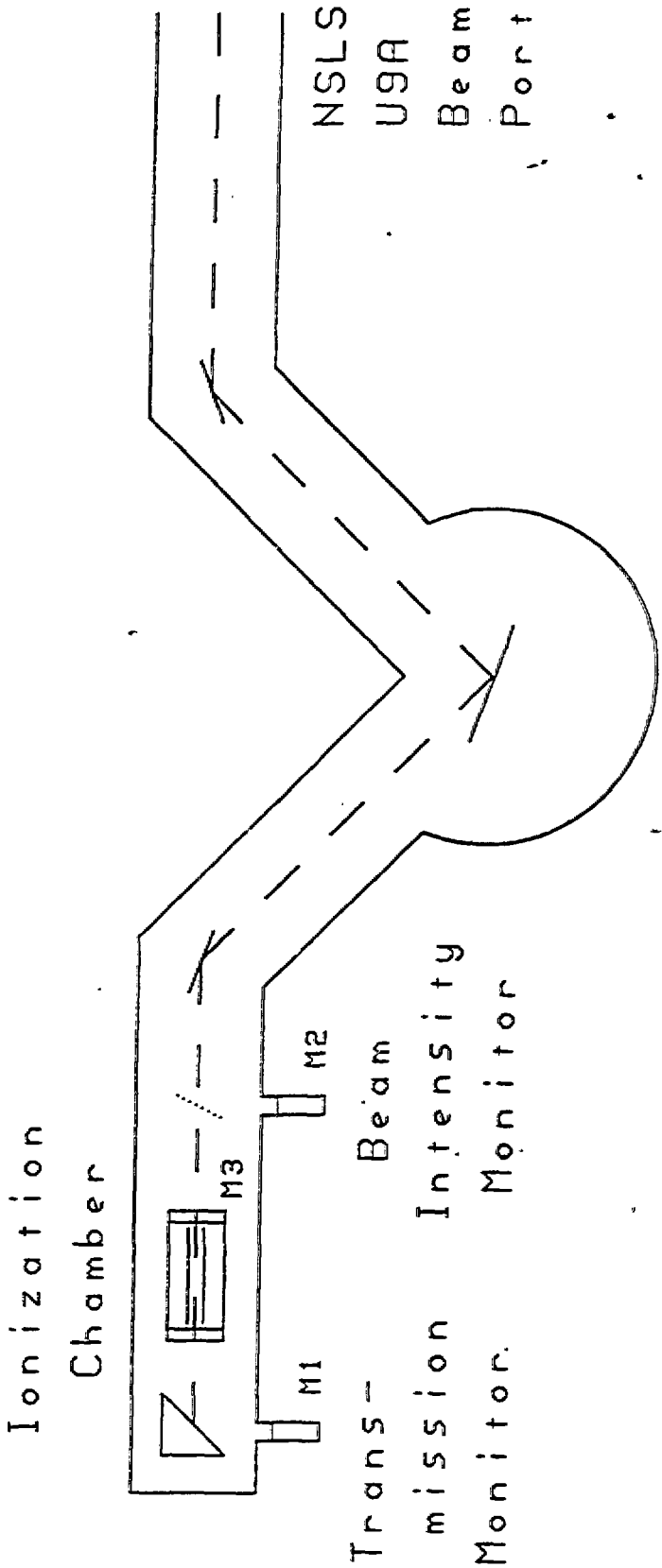
FIGURE 2 – TMAE INVERSE ABSORPTION LENGTH – 1 TORR
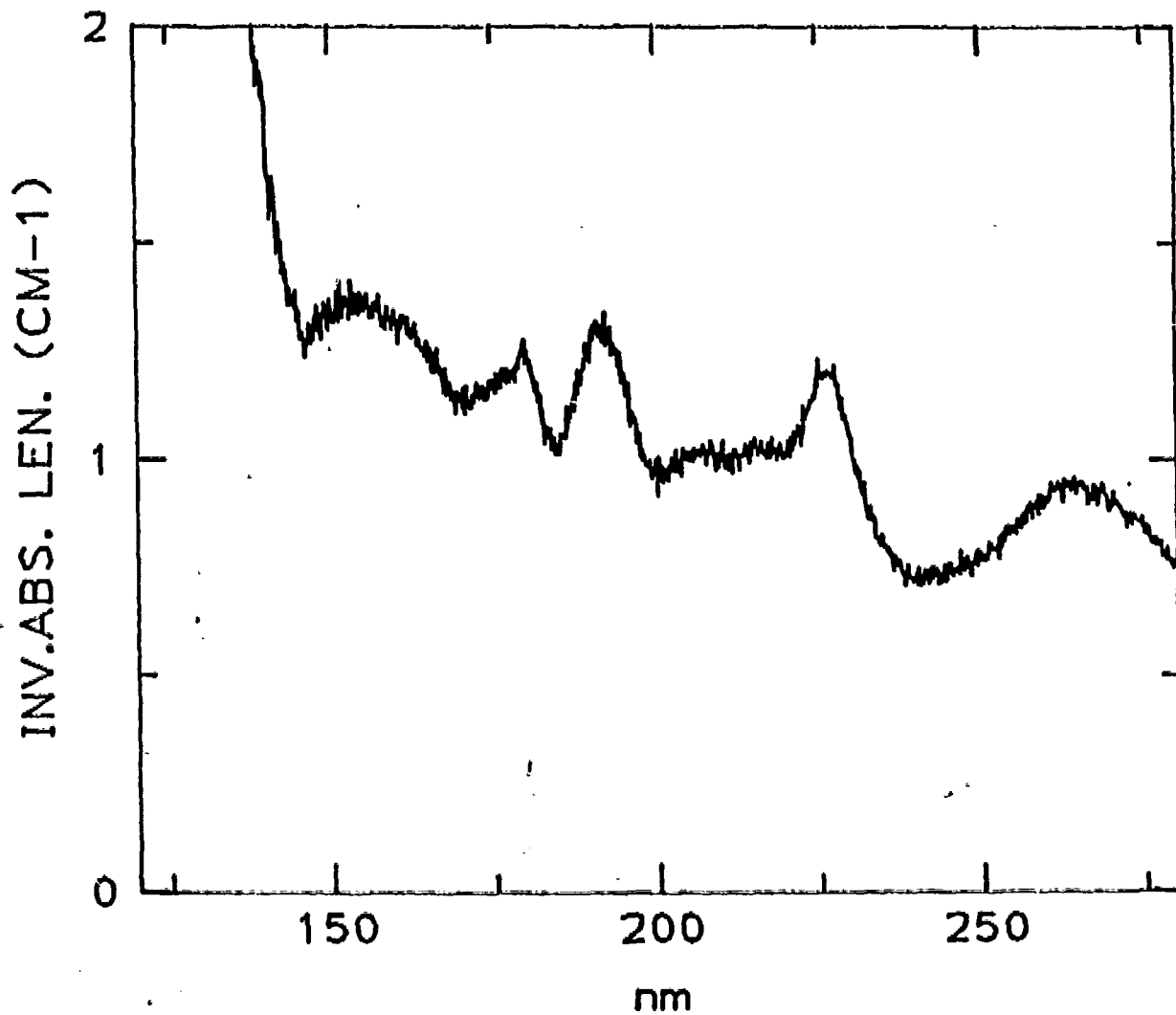
FIGURE 3 – TEA INVERSE ABSORPTION LENGTH
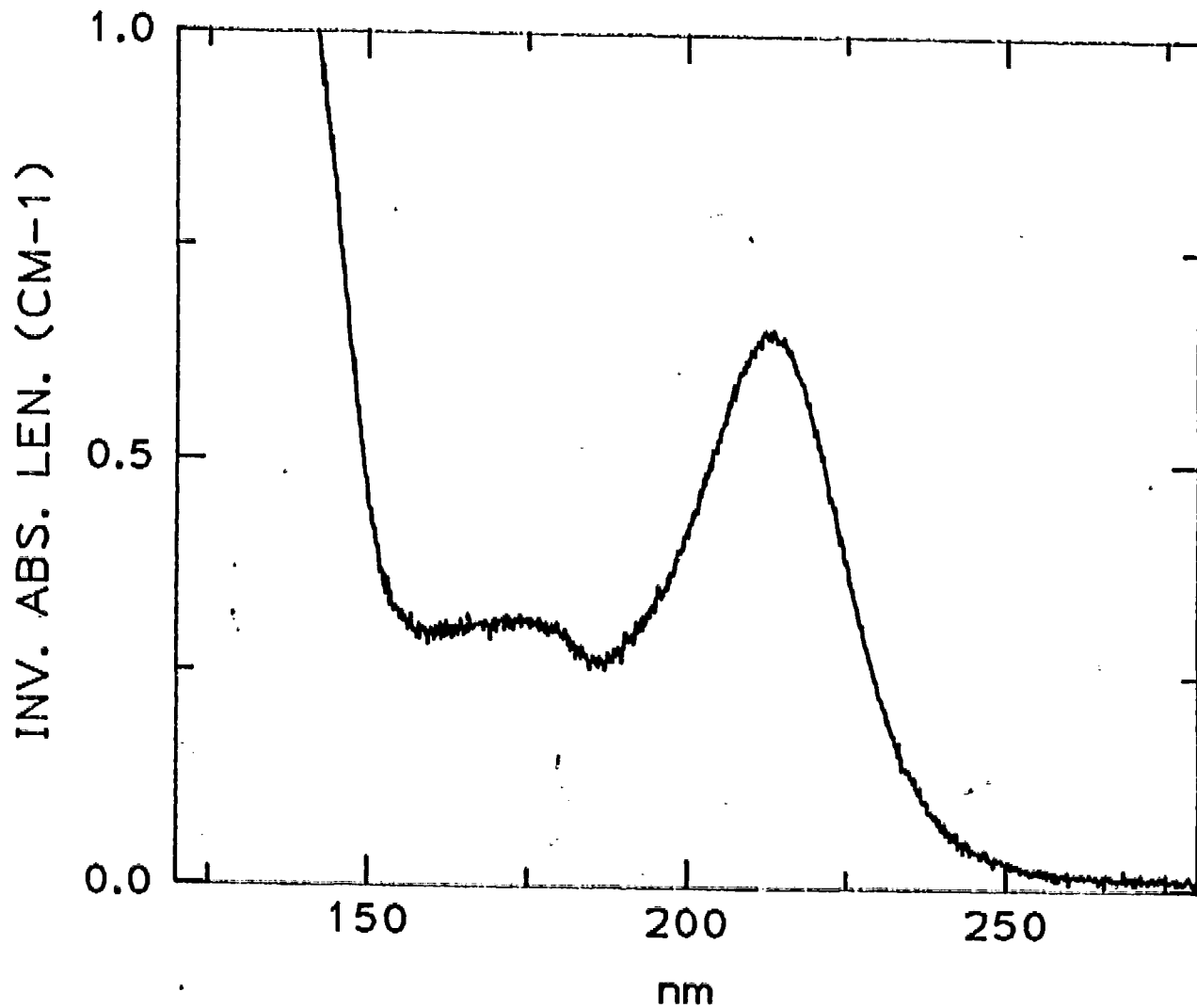
FIGURE 4 TMAE QUANTUM EFFICIENCY

FIGURE 5   TEA QUANTUM EFFICIENCY
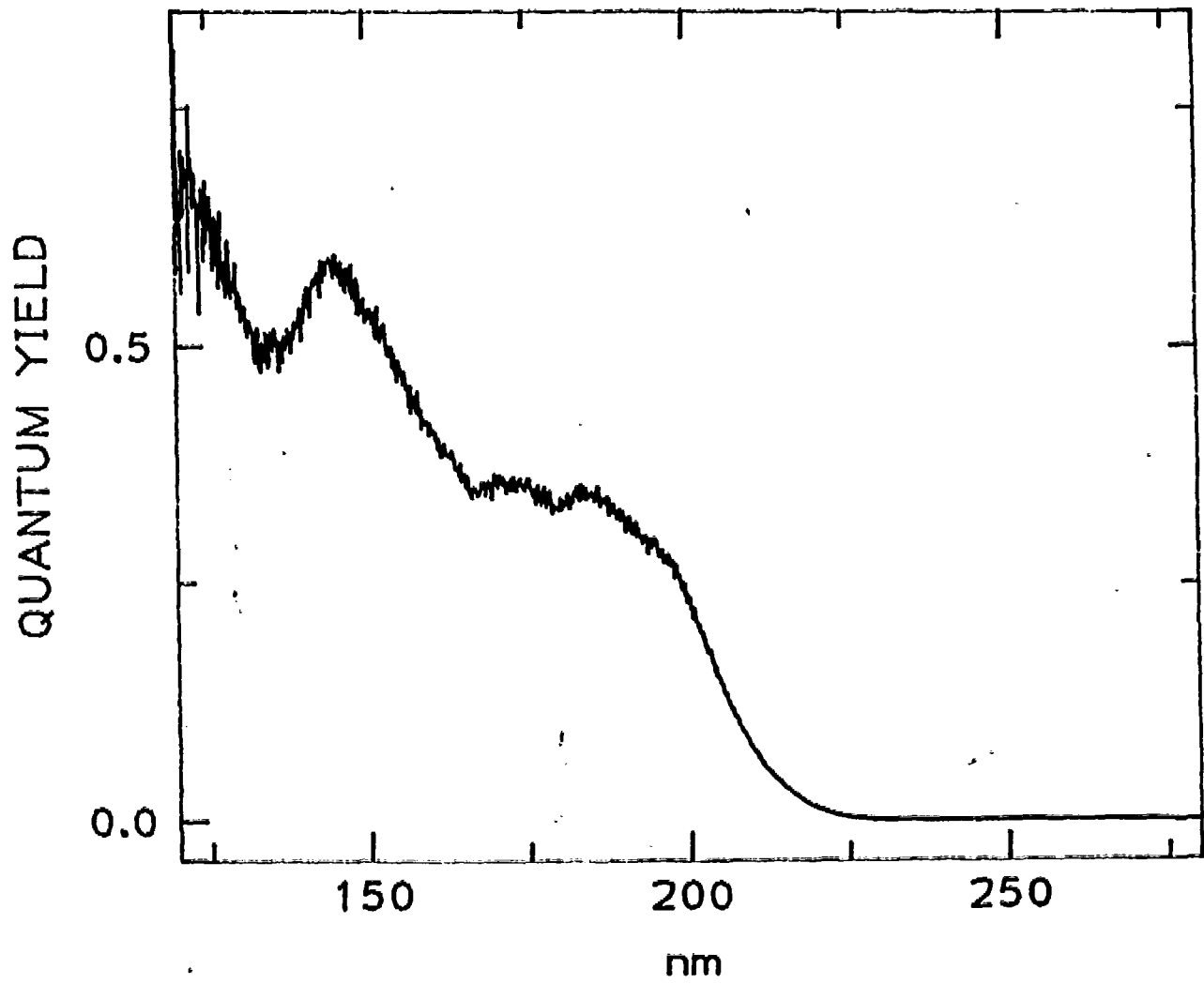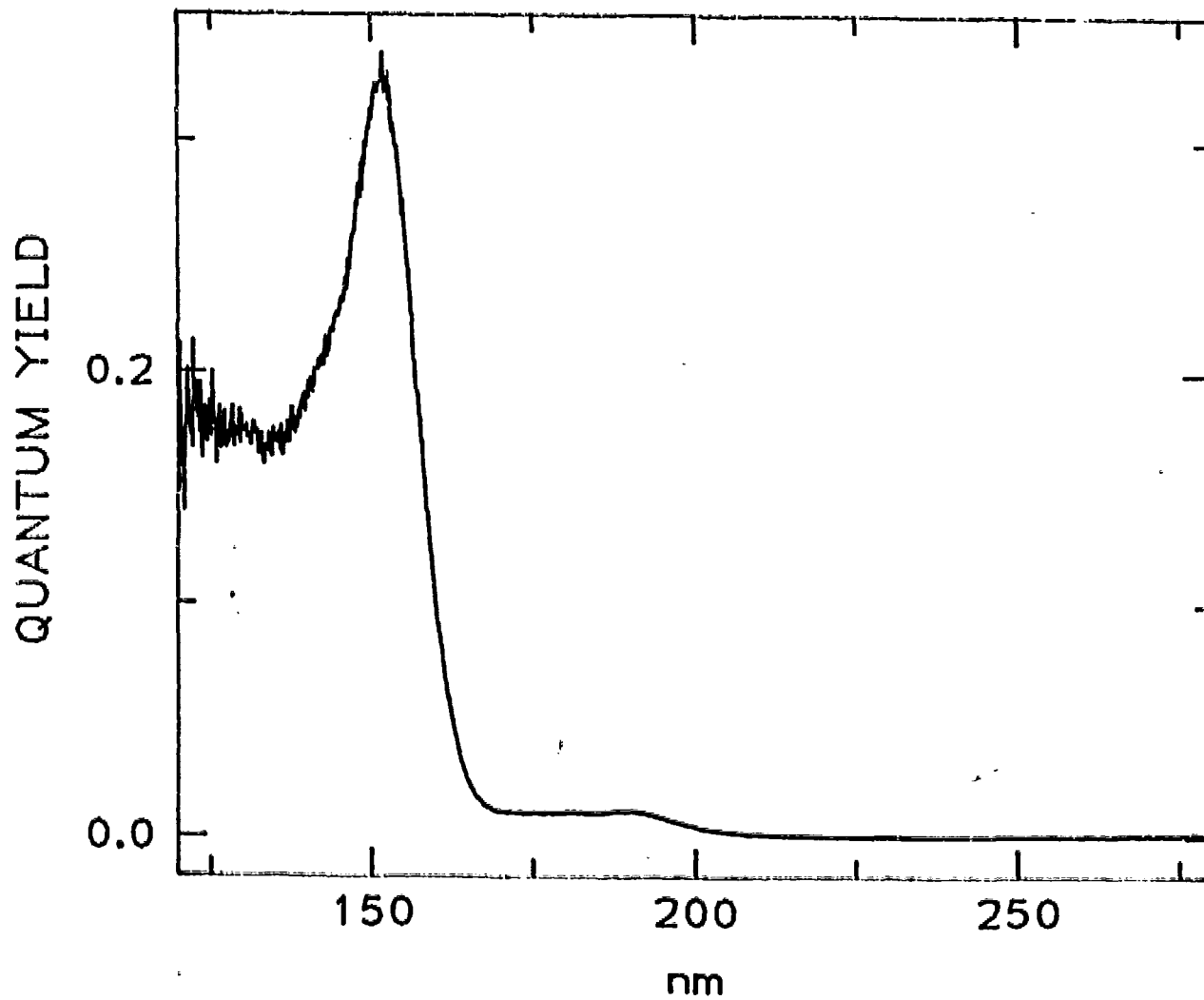
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