

## Application of Luminescence Spectroscopy to the Analysis of Fuels

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Luminescence spectroscopy is based on the absorption and re-emission of light by a molecule, ion or atom. It is of great analytical utility because the emitted light is characteristic of the electronic structure of the emitting species. The phenomenon of luminescence is not a newly discovered one. The first monograph on luminescence was written by Liceti<sup>1</sup> in 1640. In 1845 Herschel<sup>2</sup> reported on the luminescence characteristics of quinine sulfate. Stokes<sup>3</sup> in 1852 observed that in all cases the light emitted from a molecule was at longer wavelengths than that which it absorbed. His observation was termed the "Stokes shift" and has since become well understood. In 1895 Weidman and Schmidt<sup>4</sup> and in 1907 Stark and Mayer<sup>5</sup> reported the first systematic study on luminescence of aromatic molecules.

Lommel<sup>6</sup> in 1877 first reported on the quantum efficiencies of certain molecules, and in 1907 Nichols and Merritt<sup>7</sup> discussed their observations of the interesting "mirror image" relationship between absorption and emission spectra. From the preceding observation it is apparent that the luminescence properties of molecules have been known for a long time. The successful exploitation of luminescence had to wait, however, until other areas of technology were sufficiently advanced to permit the observation and measurement in a controlled and quantitative manner.

That fluorescence and phosphorescence techniques are being accepted rapidly in all areas of analytical chemistry is emphasized by referring to the 1964 and 1966 Analytical Chemistry Annual Reviews<sup>8,9</sup> covering the four-year period from December 1961 to December 1965, in which 1,049 references to a large variety of analytical applications of fluorescence and phosphorescence are contained.

Before proceeding into the discussion of specific applications of fluorescence and phosphorescence, the relationship of these phenomenon to each other and the absorption process should be shown (Fig. 1).

In both fluorescence and phosphorescence spectroscopy one may determine two different kinds of spectra (Fig. 2). The difference between these two spectra is that the emission spectrum is obtained by spectrally recording the light emitted from a sample while being excited by some selected wavelength of light. An excitation spectrum on the other hand is obtained by measuring the intensity of emitted radiation from a sample at a specific wavelength as the excitation light is varied continuously.

For example, Figure 3, the absorption spectrum of a 1 ppm anthracene solution, and Figure 4, the excitation and emission spectra of the same sample, show great structural similarity. The emission bands are all at longer wavelength than the absorption band, but the excitation bands fall at exactly the same wavelength as the absorption bands. A significant point is that the excitation spectrum of a molecule gives the same information as its absorption spectrum.

roscopy in fuels analysis is the method for qualitatively and quantitatively determining anthracene and naphthalene at low concentrations in a benzene-type matrix. The three aromatic types represent the majority of aromatic molecules in fuels.

### Experimental

All standard samples were prepared using reagent grade anthracene and naphthalene after recrystallization from a saturated hydrocarbon. The matrix was made from a 50/50 volume/volume mixture of toluene and o-xylene, spectroquality from Matheson, Coleman and Bell.

The spectra were run on a Hitachi-Perkin-Elmer MPF-2A Fluorescence Spectrophotometer. High quality, low-fluorescence, silica sample cells were used for obtaining the data.

### Discussion of Results

A sample containing 10 ppm naphthalene and 10 ppm anthracene in the matrix was prepared and the qualitative emission spectra of the sample determined at several excitation wavelengths. Figure 5 shows the emission spectra obtained from the sample excited at 270m $\mu$  and at 280m $\mu$ . The principal emission, Spectrum A, is observed in the region between 360 and 440m $\mu$ , with a low intensity emission band in the 300 to 340m $\mu$  range. The emission between 380 and 440m $\mu$  arises from the anthracene whereas that in the 300 to 340m $\mu$  region arises from the naphthalene. Spectrum B in this figure was taken from the sample without removing it from the instrument. The only change was the excitation wavelength from 270 to 280m $\mu$ . Some rather dramatic changes in the spectrum are evident. The overall intensity of both band systems has been increased greatly and the ratio of the naphthalene to anthracene emission has completely reversed. It is apparent from this spectrum that one could easily determine the concentration of each of these components independently of the other in this aromatic matrix. One cannot do such an analysis by absorption spectroscopy.

The spectrum shown in Figure 6 was from the sample excited at 290m $\mu$ . In this case the naphthalene intensity continued to increase sharply, whereas the anthracene decreased. The spectra shown in Figure 7 show the anthracene intensity increasing and the naphthalene intensity fading. The Spectrum A was produced by exciting the sample at 300m $\mu$  whereas Spectrum B was produced by the 310m $\mu$  excitation.

The series of spectra shown in Figure 8 were run while exciting with 320, 330 and 340m $\mu$  excitation respectively and in these spectra all evidence of naphthalene presence was lost. The significance of the behaviour noted in Figures 6, 7 and 8 is that one can take a mixture of aromatic hydrocarbons and produce different spectra dependent on the wavelength of excitation. By choosing the appropriate excitation wavelengths, one can emphasize the presence of one component relative to the others and in many cases completely eliminate the appearance of any component other than the one of specific interest.

Our next point of concern was ability to selectively excite the three aromatic types, benzene, naphthalene and anthracene, individually. For this experiment the sample containing 10 ppm naphthalene and 10 ppm anthracene in the o-xylene-toluene matrix was diluted 1:100 with isooctane giving concentrations of 0.1 ppm naphthalene, 0.1 ppm anthracene and 1% o-xylene-toluene. The series of three spectra shown in Figures 9, 10 and 11 were obtained by exciting this solution with 290, 290 and 350m $\mu$  radiation respectively. Figure 9 shows the emission

spectrum of the benzene-type aromatics. Figure 10 is that of naphthalene and Figure 11 is that of anthracene. One not only can qualitatively identify these three aromatic types, but can determine their approximate concentration by simply altering the excitation wavelength and measuring the emission from each aromatic type independently of the others.

While the data shown in the preceding discussion indicate the qualitative applicability of luminescence spectroscopy to the basic types of aromatic molecules found in petroleum and coal based fuels, it does not provide an insight into the usefulness of the technique for quantitative analysis. Hercules<sup>10</sup> has shown that luminescence intensity and concentration are related as follows:

$$(S_f)_\lambda = f(\theta) g(\lambda) I_0 \phi_f abc \left[ 1 - \frac{abc}{2!} + \frac{a^2bc^2}{3!} - \dots - \frac{a^2bc^n}{(n+1)!} \right]$$

Where  $abc$  are the molar absorptivity, cell path and concentration respectively;  $f(\theta)$  is the solid angle of interception of radiation by the detector;  $g(\lambda)$  is the quantum conversion factor for the detector which is a function of wavelength;  $I_0$  is the intensity of the exciting radiation and  $\phi_f$  is the quantum efficiency of the molecule. There are two concentration regions where this arrangement may be greatly simplified. The one of greatest interest to the analytical chemist is the one in which the concentration of fluorescent materials is small. In such case  $abc < 0.05$ . This allows us to write Equation 1 as

$$(S_f)_\lambda = f(\theta) g(\lambda) I_0 \phi_f abc$$

From this equation it may be seen that the relationship between fluorescence intensity and concentration will be linear through a point of maximum concentration,  $C_{max} = \frac{0.05}{(a)_\lambda b}$ , where  $(a)_\lambda$  is the molar absorptivity

of the compound at the wavelength of excitation. It should be emphasized that this concentration is not the maximum at which useful data may be obtained. Beyond this level the curve relating fluorescence intensity to concentration is not linear. A calibration curve relating concentration to fluorescence intensity can be used to extend the range of useful analysis over at least another order of magnitude.

The other extreme condition where equation one may be simplified is that of very high concentration of absorbing and emitting molecules such that the absorption of incident radiation is almost complete. In that case, equation one may be reduced to

$$(S_f)_\lambda = f(\theta) g(\lambda) \phi_f$$

showing that the detector signal is independent of fluorescer concentration. This condition is important in determining quantum efficiencies for quantum counters and scintillation counters. Analysis under these conditions is most effectively done by using front surface illumination and viewing of the sample. With this geometry, penetration effects and self-absorption problems are minimized. This geometry is generally required when the fluorescence or phosphorescence spectrum of a solid, opaque or highly turbid sample is analysed. Using the front surface viewing geometry even raw crude oil samples may be excited and their luminescence observed.

As indicated by the terms in Equation (1) there is an intermediate concentration range for each absorber and fluorescer at which the intensity concentration relationship will become nonlinear. One generally observes that the fluorescence intensity approaches a limiting value as the concentration is increased. The principal precaution,

Therefore, in using luminescence techniques for quantitative analysis is to realize that there is a range above which the concentration intensity curve will become nonlinear, and if it is required to work in the nonlinear region, a sufficient number of standard points be taken to accurately describe the intensity concentration curve.

Curves showing the intensity concentration relationship for naphthalene and anthracene in Figures 12 and 13. The naphthalene standards were prepared in o-xylene-toluene matrix. Each contained 10 ppm anthracene. The anthracene standards were prepared in the same matrix and each contained 10 ppm of naphthalene. The curves are practically linear in the lower concentration range, but begin to deviate from linearity at the higher end of the range.

In order for a measurement technique to be useful for quantitative analysis, stability of the measurement system must be such that good repeatability is possible. Unfortunately, the feeling exists that fluorescence measurement is imprecise. Admittedly, this has been true in many cases but it was an equipment rather than a technique limitation. Figure 14 shows an example of excellent repeatability; three spectra of a 10 ppb anthracene sample are superimposed and one would be hard pressed to show better repeatability by any other analytical technique at end of the range.

Summary For a measurement technique to be useful for quantitative analysis, stability of the measurement system must be such that good repeatability is possible. Luminescence spectroscopy has broad application in the analysis of fuels and related products. All aromatic types can be subjected to analysis by fluorescence or phosphorescence and it is possible by using the incremental excitation technique to obtain spectra of each aromatic type completely independent of the others present and, therefore, more effectively analyze for components of mixtures by any other analytical technique.

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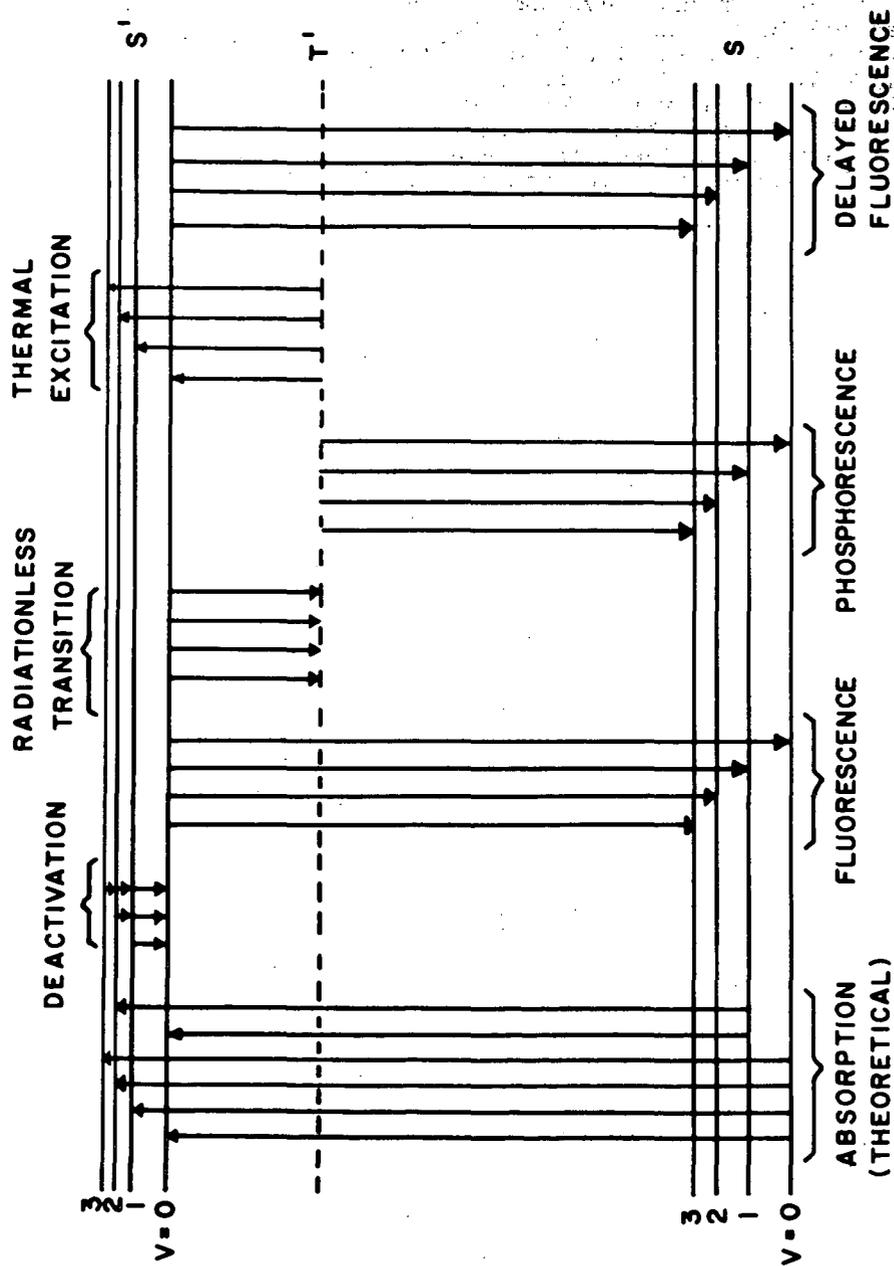


FIGURE 1

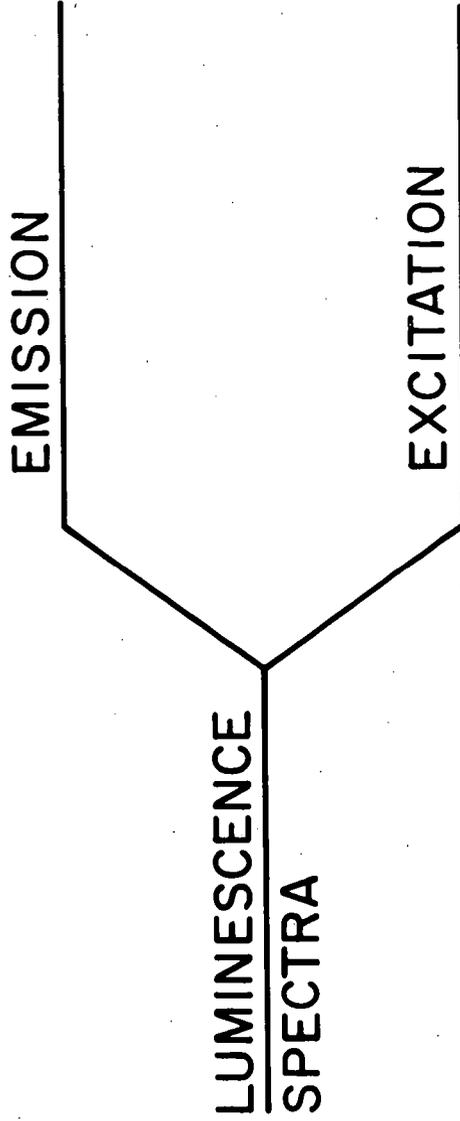


FIGURE 2

SAMPLE ANTHRACENE  
 ORIGIN EtOH  
 CONC. 0.1 ppm

CELL PATH 1.0 CM  
 REFERENCE EtOH  
 OPERATOR SGP  
 REMARKS

SPLIT WIDTH 2544  
 RESOLUTION 350  
 SCAN SPEED

CURVE NO. 57517  
 ORD. EXP. 3  
 PEN RESPONSE 2-20-67  
 DATE

UV  
 100001

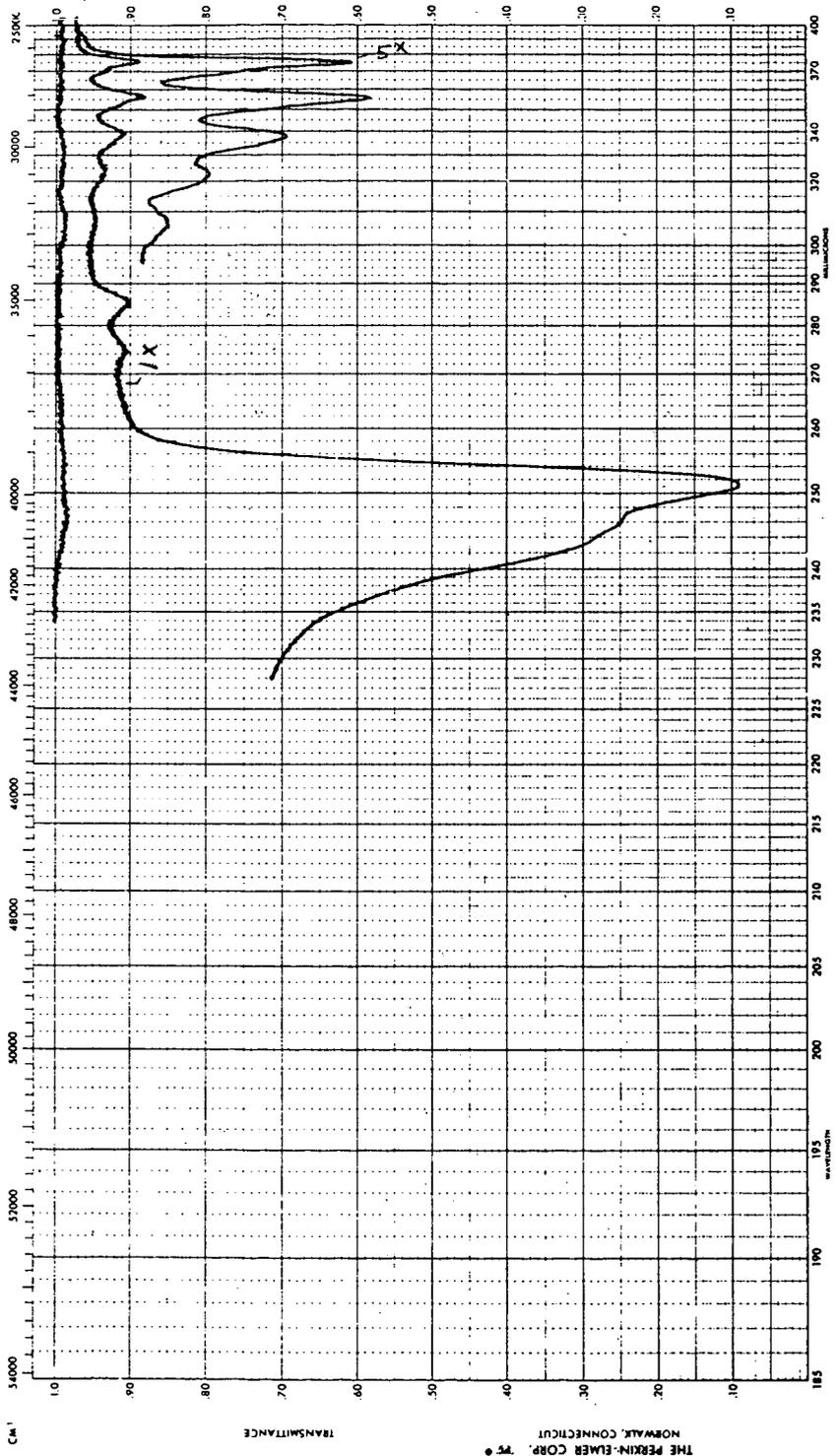


FIGURE 3

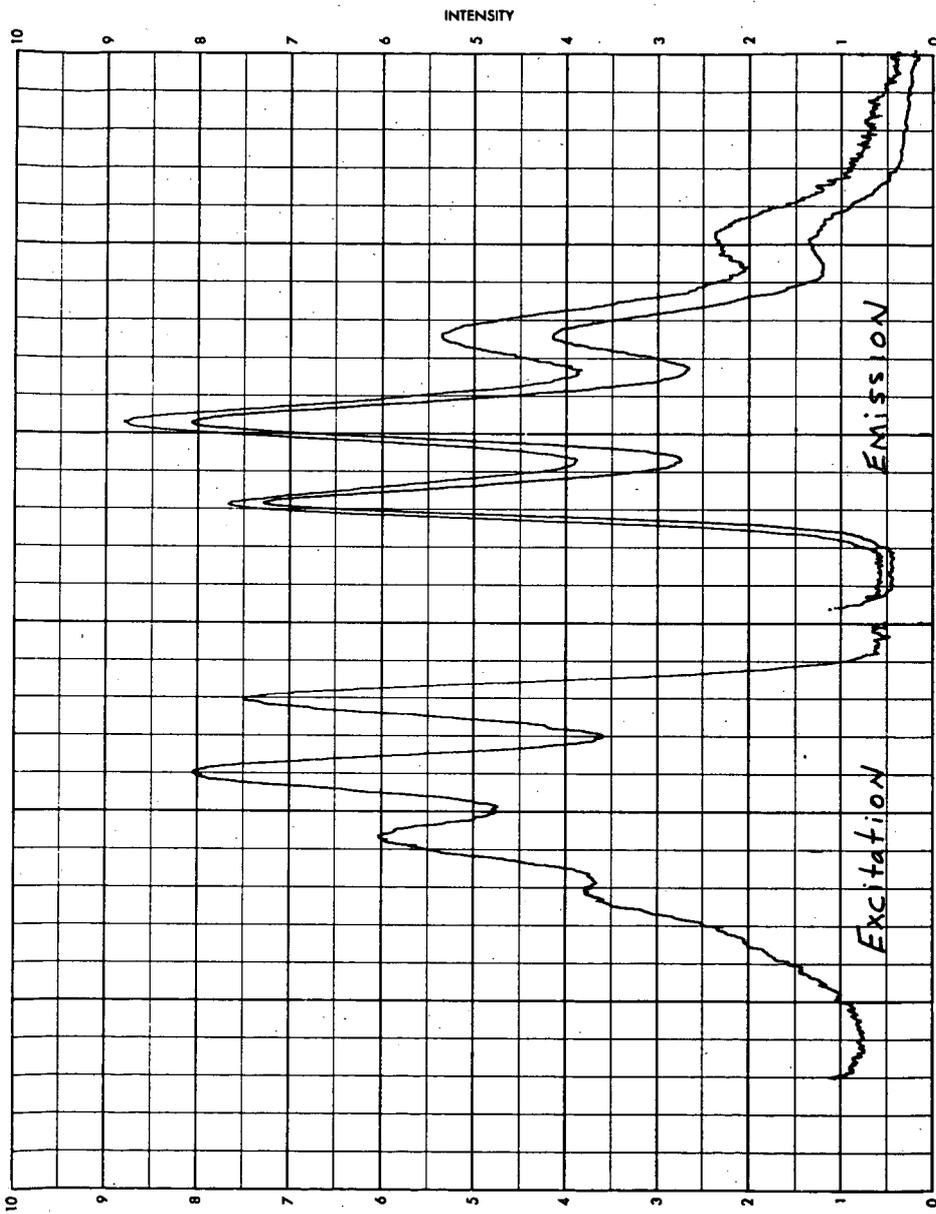
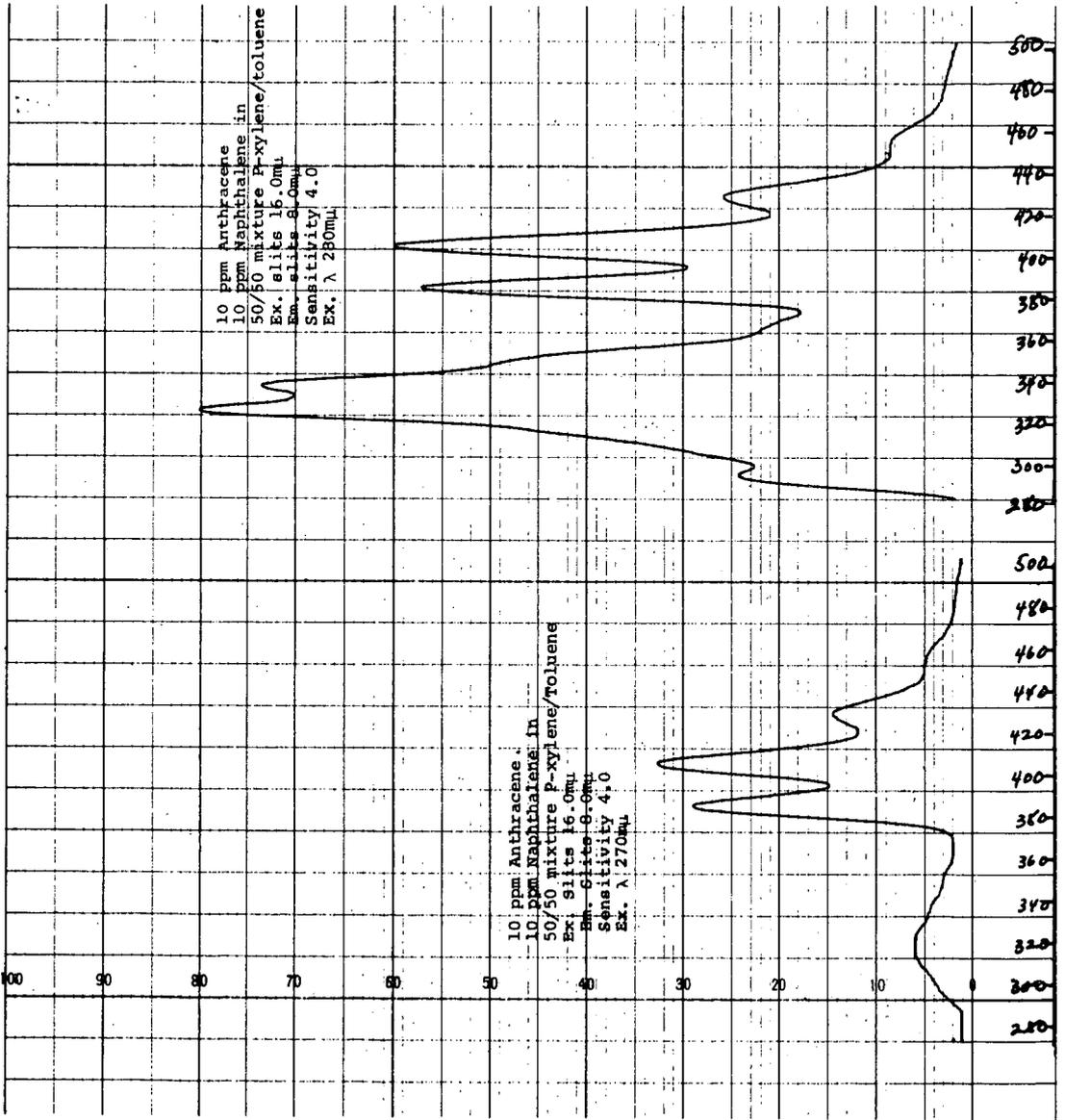


FIGURE 4



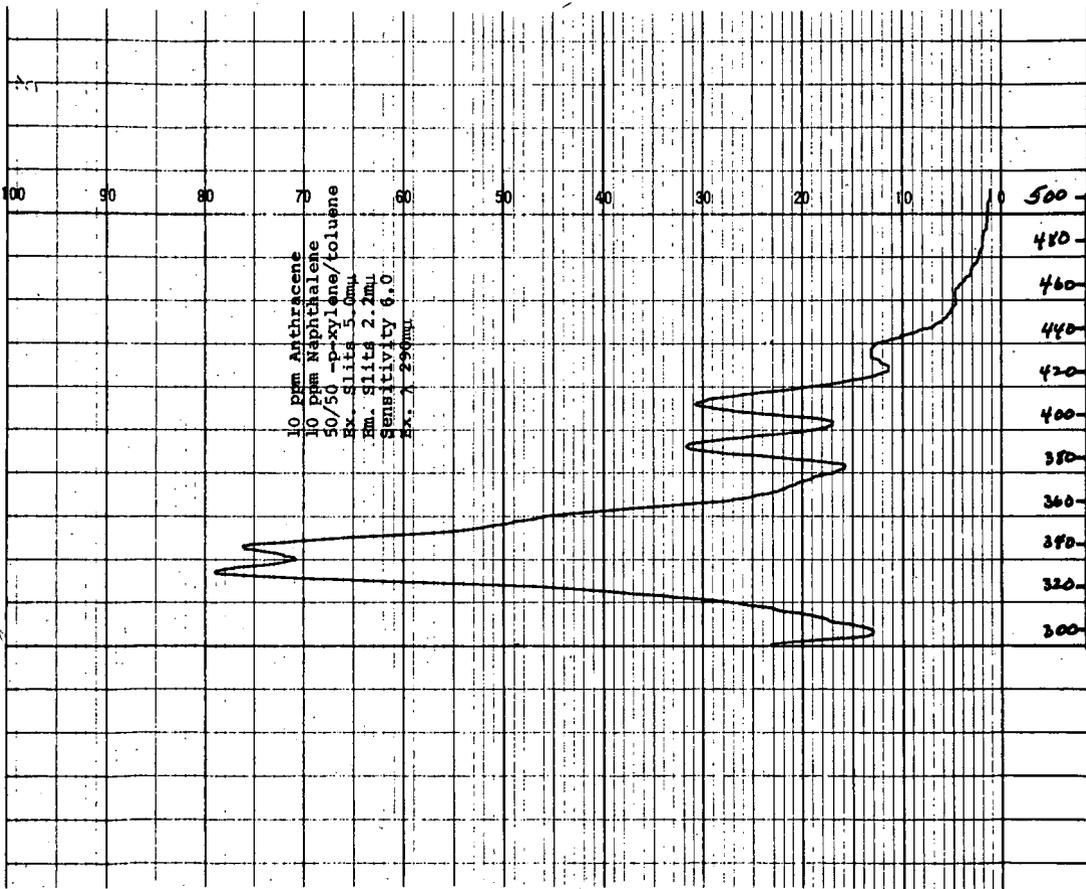


FIGURE 6

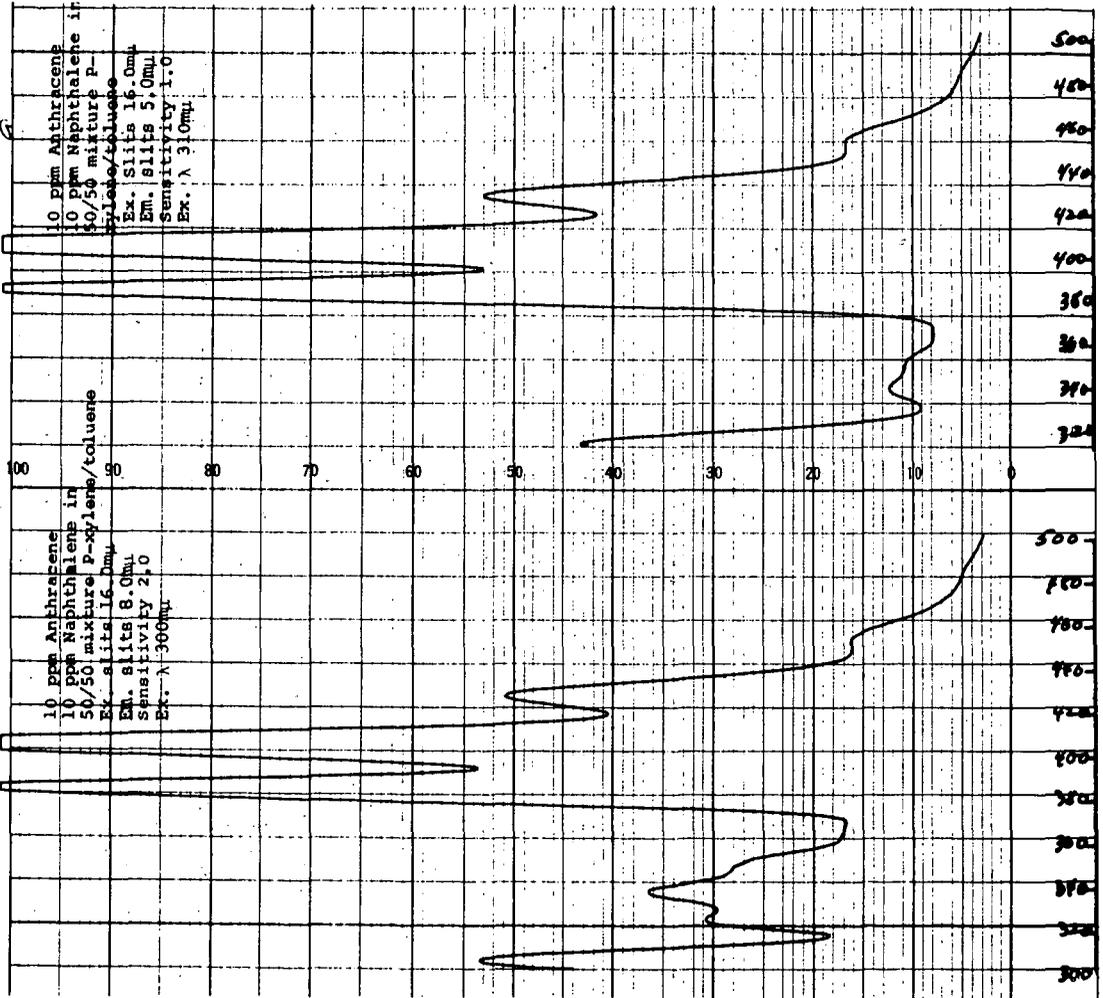


FIGURE 7

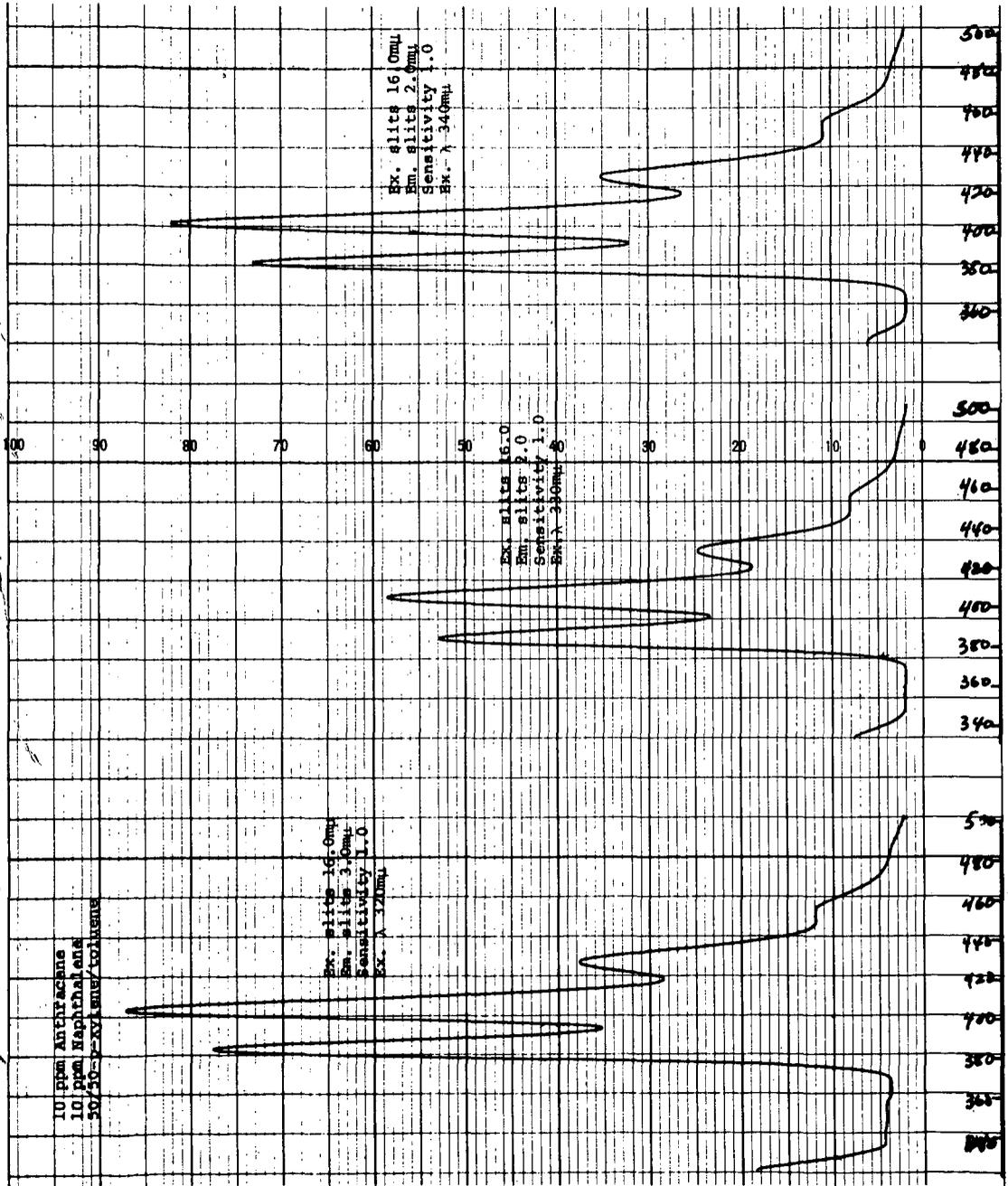
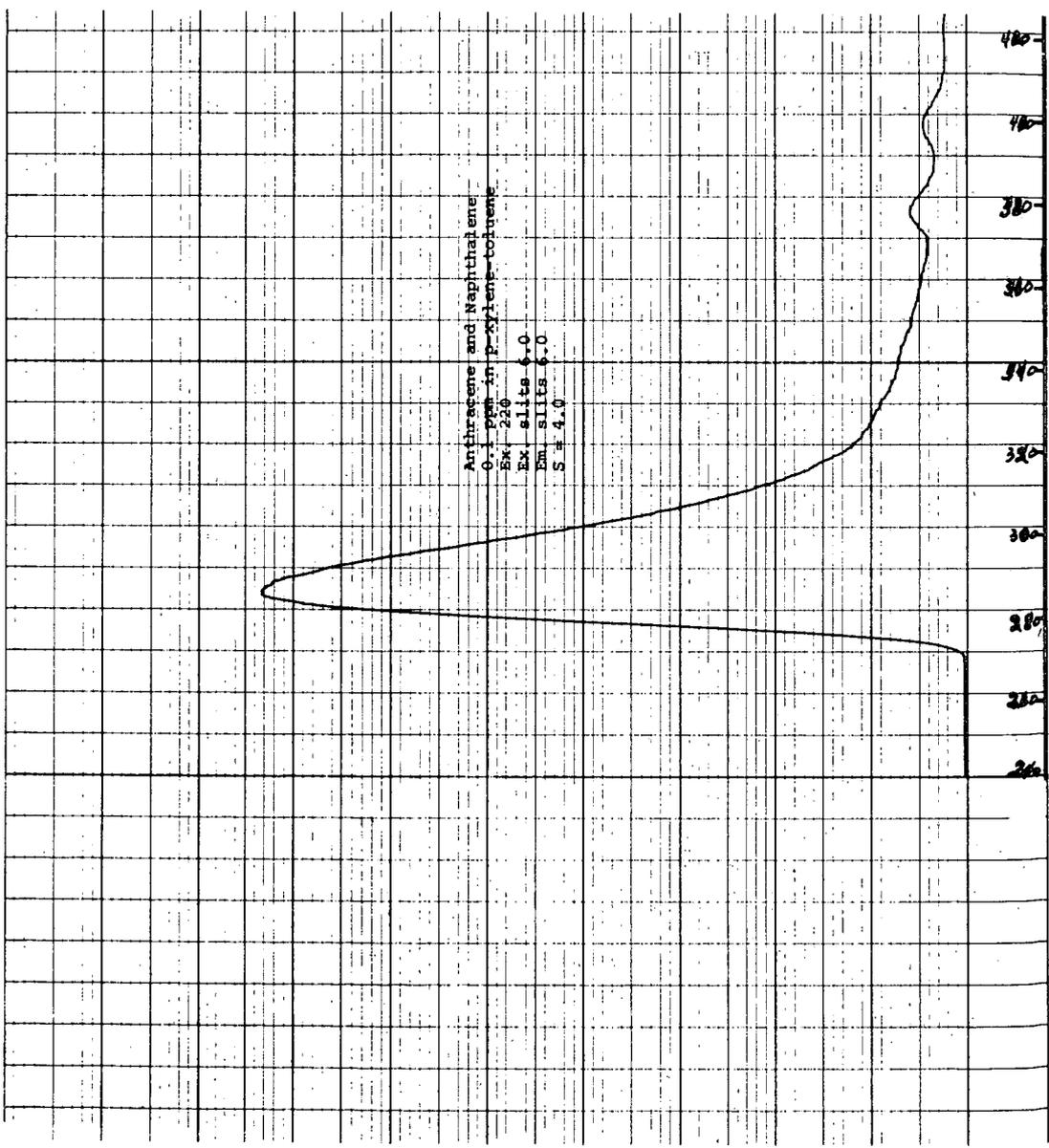


FIGURE 8



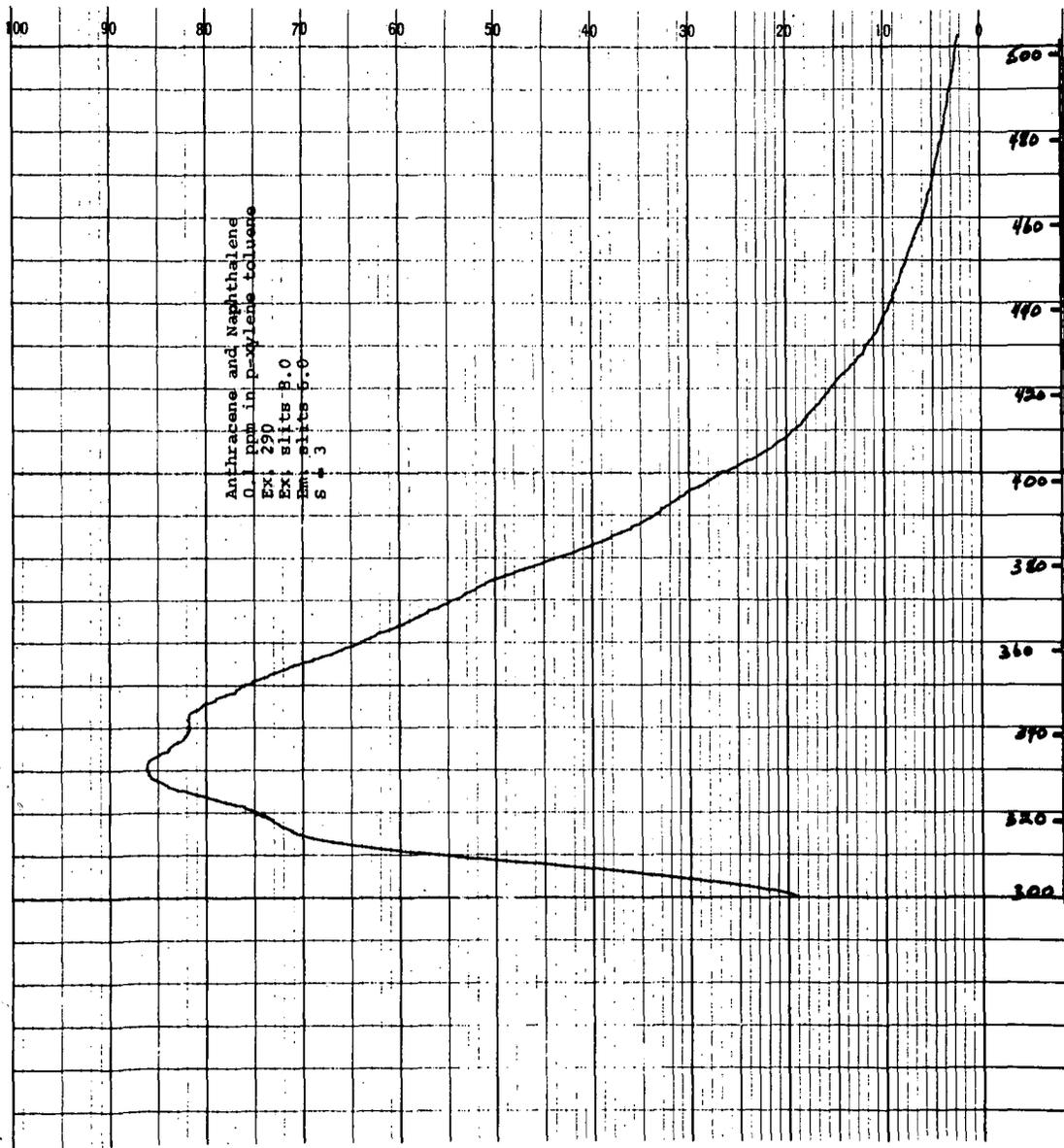


FIGURE 1C

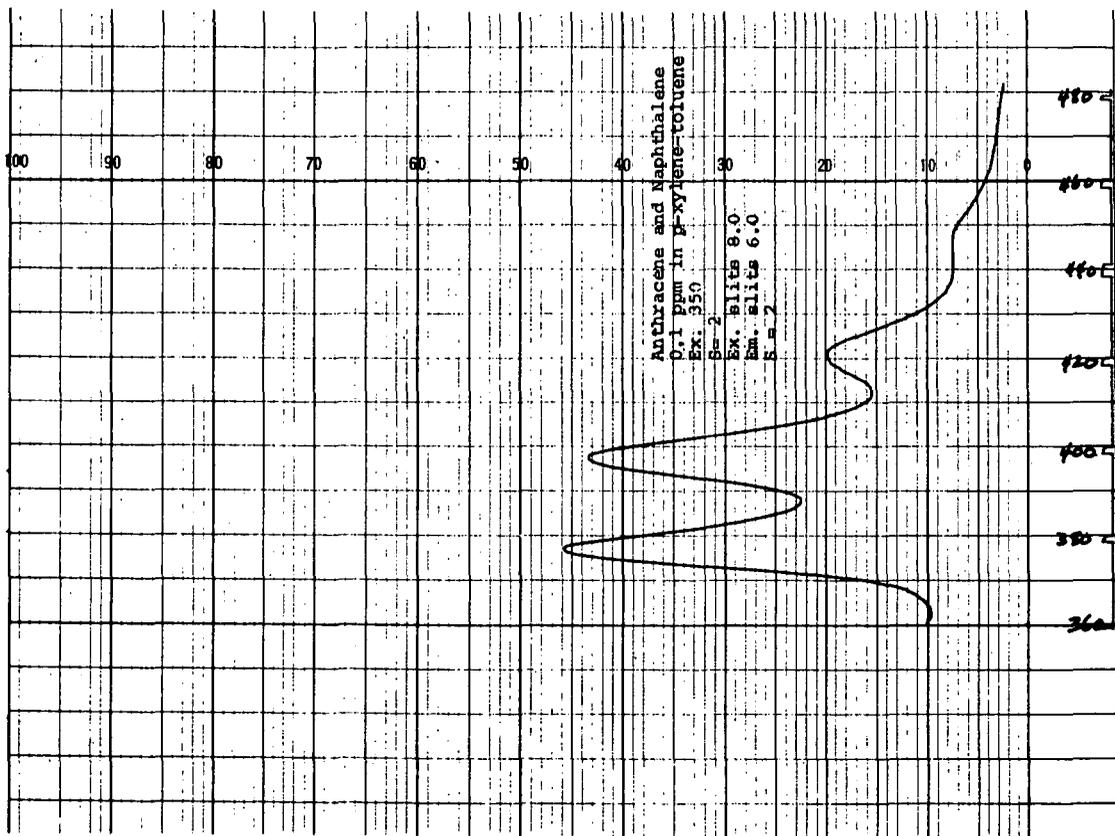


FIGURE 11

# NAPHTHALENE IN MATRIX

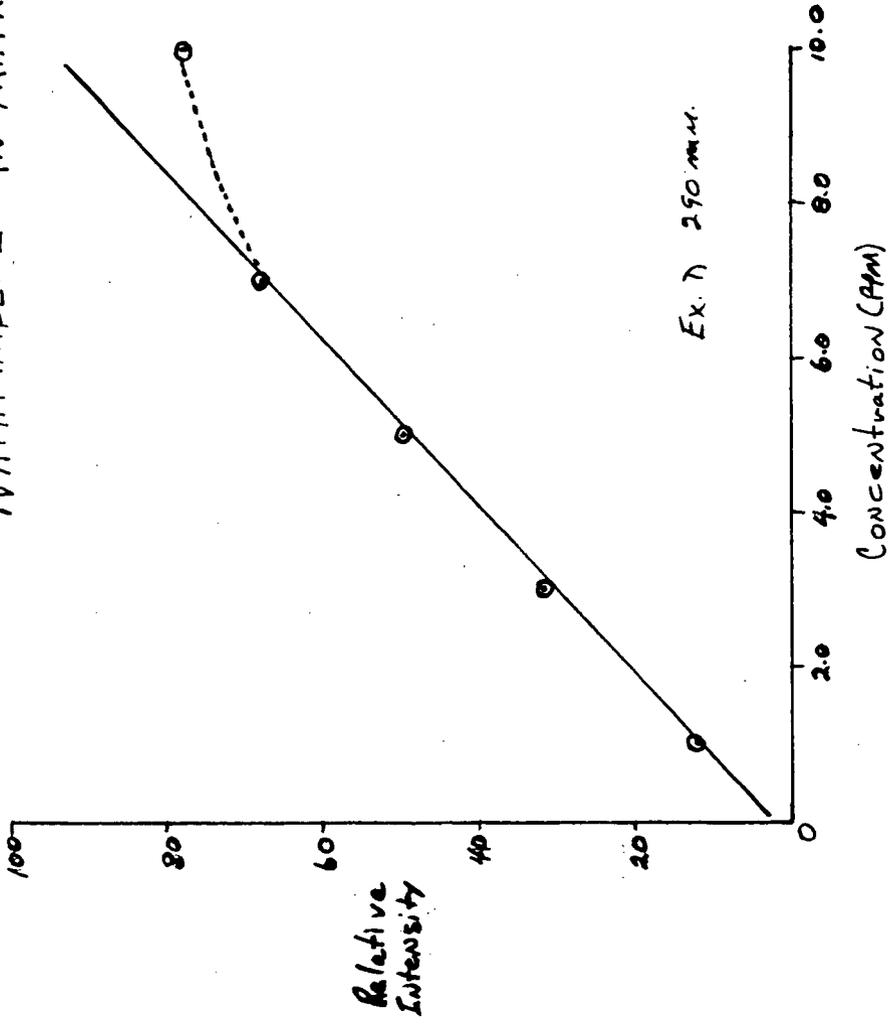


FIGURE 12

ANTHRACENE IN MATRIX

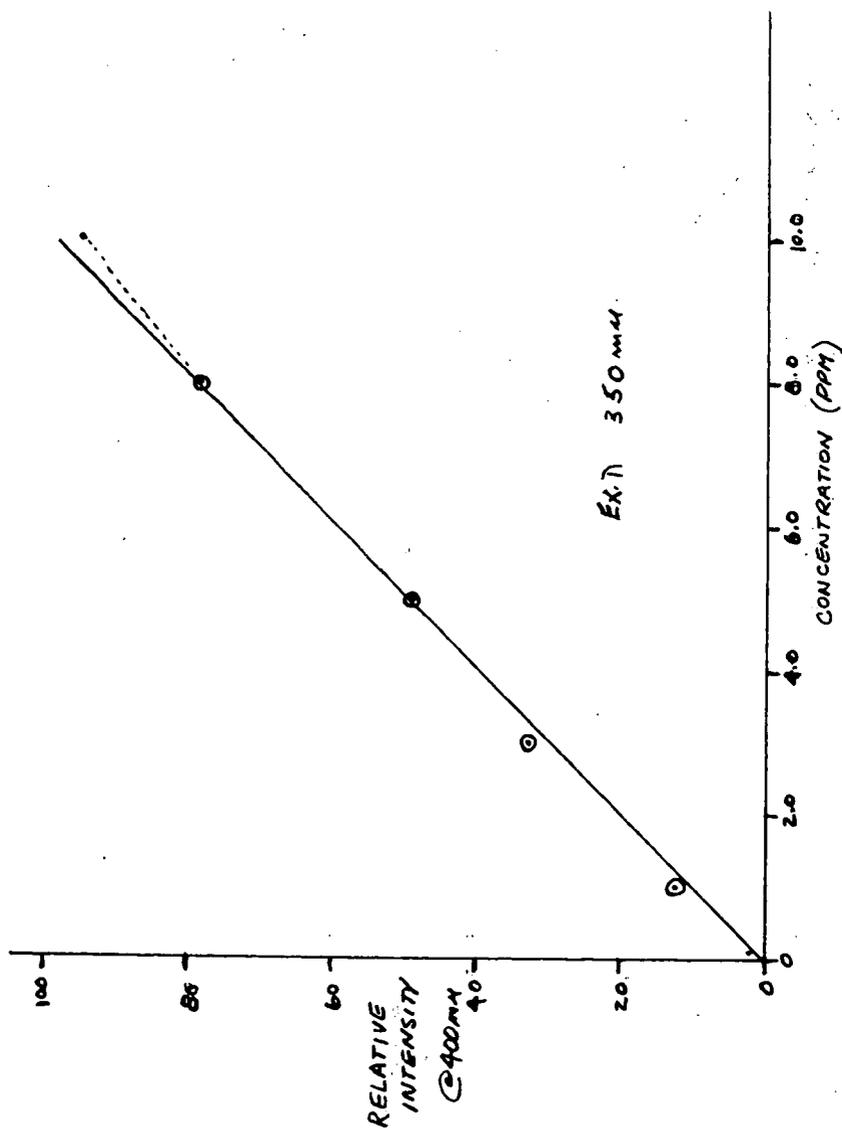


FIGURE 13

