

FLUORESCENCE SPECTROSCOPY IN THE CHARACTERIZATION OF HIGH-BOILING PETROLEUM DISTILLATES

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INTRODUCTION

Although many workers have attempted to use fluorescence spectroscopy in the characterization of crude oils (1-5), the technique has found limited application in the characterization of crude oil fractions. This is a result of several factors. First, separation schemes have not been developed for obtaining simplified petroleum fractions that are suitable for fluorescence analysis. Second, commercial instrumentation that enables many spectra to be recorded in a small amount of time has not been available. Third, the lack of success in characterization of total crude oils has probably dampened the enthusiasm of some workers as to the potential of the fluorescence technique. Drushel and Sommers (6) successfully employed a combination of GLC and fluorescence and phosphorescence spectroscopy to identify pyridines, quinolines, indoles, and carbazoles in a light catalytic cycle oil. Their work showed that fluorescence and phosphorescence, when used under proper experimental conditions, can supplement other spectroscopic methods in the characterization of petroleum distillates. The separation scheme used here, like that of Drushel and Sommers, separates distillates into fractions that are simple enough to be analyzed by fluorescence spectroscopy. The separation scheme was designed to isolate concentrates of compound types, not individual compounds.

This paper demonstrates that fluorescence spectroscopy is an analytical technique which can be useful in the characterization of high-boiling distillates. Acid concentrates isolated from a Wilmington, Calif., 400-500°C distillate and a Wesson, Tex., 400-500°C distillate were examined. Carbazoles, 11H-benzo[a]carbazoles, 1,2,7,8-dibenzphenanthrenes (picenes), 7H-benzo[c]carbazoles, chrysenes, benzo[a]pyrenes, and perylenes were identified in the acid contents by fluorescence spectroscopy. Examination of other 400-500°C concentrates resulted in the identification of coronenes, benzo[ghi]perylens, and benz[a]anthracenes.

EXPERIMENTAL

Apparatus

Anion Exchange Chromatography. - The preparation of ion exchange resins used for obtaining acid concentrates from high-boiling petroleum distillates has been described (7).

Gel Permeation Chromatography. - The details of the gel permeation chromatographic separation of a Wilmington, Calif., 400-500°C acid concentrate have been published (8). A water-jacketed glass column, 1.3 cm i.d. by 150 cm, packed with 80 g of cross-linked styrene gel was used with methylene chloride as solvent.

Thin-Layer Chromatography. - Thin-layer chromatographic plates 20 cm by 20 cm were prepared using a slurry of silica gel G and water. The layers were approximately 250 microns thick. The plates were conditioned at 100°C for several hours and were developed using cyclohexane 85%, diethyl ether 12%, and glacial acetic acid 3%. Visualization was effected by means of long (350 nm) and short (254 nm) wavelength ultraviolet light.

Infrared Spectroscopy. - Infrared analyses were performed using a Perkin-Elmer Model 521* infrared spectrometer. Methylene chloride was used as the solvent for all infrared analyses.

*Reference to specific brand names or models of equipment is made for information only and does not imply endorsement by the Bureau of Mines.

Fluorescence Spectroscopy. - A Perkin-Elmer MPF-2A spectrofluorimeter was used for recording all fluorescence emission and excitation spectra. Continuously variable slits enabled spectra to be rapidly obtained. Fluorescence-free cells having a 1 cm path were used in this work.

Materials

Model Compounds. - The model compounds were obtained commercially. Approximately half of the compounds were found by fluorescence analysis to be contaminated with impurities that fluoresced. The desired model compounds were separated from the impurities using thin-layer chromatography on silica gel G or aluminum oxide G.

Solvents. - The methylene chloride used for the gel permeation chromatographic separation and subsequent infrared analysis was Baker and Adamson Co. reagent grade which had been flash distilled. Fluorescence analysis of this material did not detect aromatic hydrocarbons or other fluorescing impurities.

The cyclohexane used for thin-layer chromatography and fluorescence analyses was Phillips Petroleum Co. research grade which had been passed over silica gel. Fluorescence analysis of this material did not detect aromatic hydrocarbons or other fluorescing impurities.

Fluorescence Emission and Fluorescence Excitation Spectra of Model Compounds

Cyclohexane was used as the solvent for obtaining all spectra. Fluorescence emission and fluorescence excitation spectra of model compounds were recorded at room temperature in very dilute solutions (10^{-3} to 10^{-5} molar). Typical spectra were recorded at one concentration, the sample diluted tenfold, and the spectra again recorded. This process was repeated until the relative intensities of the bands within each spectrum remained constant. In only a few cases did the band intensities change when the spectra were recorded in extremely dilute solutions. Using this procedure, spectra distorted by concentration phenomena, such as excimer formation, were avoided.

Each sample was irradiated at several different wavelengths to reduce the possibility that impurities were contributing to the emission spectrum of the model compound. Similarly, excitation spectra were recorded with the emission monochromator set at different wavelengths to reduce the possibility that impurities were contributing to the excitation spectra of the model compound.

Separation Procedure

A diagram of the separation procedure is shown in Figure 1. Samples of a Wilmington, Calif., crude oil and a Wason, Tex., crude oil were vacuum distilled (7), and the nominal 400-500°C distillates were collected. The distillates were passed over an anion exchange resin, and the materials which were retained on the resin were defined as the acid concentrates (7). The acid concentrates (100-200 mg) were separated by gel permeation chromatography (8). The gel permeation chromatographic fractions were analyzed by infrared spectroscopy to determine the separation obtained by the GPC treatment. The GPC fractions that contained predominantly phenols and nitrogen compounds, fractions 35 through 47, were further separated by thin-layer chromatography. The individual TLC fractions were removed from the plate, and the samples were extracted from the silica gel with cyclohexane. Traces of silica gel were filtered from the cyclohexane solution. The fluorescence emission and fluorescence excitation spectra were then recorded. Blank extraction runs were periodically made on the silica gel (using TLC plates which had been developed) to demonstrate that fluorescent impurities were not being extracted from the silica gel. In addition, a solvent blank was analyzed by fluorescence spectroscopy before the emission spectrum of each TLC fraction was recorded to show that traces of fluorescing compounds were not present in the solvent or in the sample cell.

RESULTS AND DISCUSSION

Fluorescence Emission and Fluorescence Excitation Spectra of Model Compounds

Identification by fluorescence spectroscopy of aromatic ring systems present in complex mixtures such as petroleum distillates requires a comparison of the oil sample spectra with those of model ring systems. Fluorescence emission spectra and tables of spectra of many heterocyclic and polyaromatic compounds have appeared in the literature (9-15); but these spectra were recorded in a variety of solvents, at different temperatures, making them difficult to use in our study. These problems have been overcome by obtaining samples of heterocyclic and polyaromatic compounds and recording the emission and excitation spectra using a uniform solvent, temperature, and recording procedure. Peak maxima of both fluorescence emission and fluorescence excitation spectra of heterocyclic and polyaromatic compounds which may be used to identify aromatic ring systems are presented in Table 1. The most intense peak in each spectrum is underlined, and the compounds are listed according to the wavelength of the most intense fluorescent band. These spectra have not been corrected for variances of spectral source and phototube response with wavelength.

Application of Fluorescence Spectroscopy to the Characterization of a Wilmington 400-500°C Acid Concentrate

Figure 2 shows the TLC chromatogram of the Wilmington gel permeation chromatographic fractions. Examination of Figure 2 shows that the silica gel G thin-layer treatment did not completely separate some aromatic ring systems. Because of this incomplete separation, ultraviolet analyses were of limited value in the characterization of these fractions. Fluorescence analysis, however, was useful in characterizing these fractions because emission spectra and excitation spectra of each component ring system could be instrumentally isolated and recorded. Each sample was irradiated at several different wavelengths to obtain an optimum emission spectrum. Similarly, excitation spectra were obtained by recording the excitation spectra with the emission monochromator set at several different wavelengths.

1H-Benzo[a]carbazoles were identified in GPC fractions 35 through 43. Figure 3 shows the fluorescence emission and fluorescence excitation spectra of 1H-benzo[a]carbazoles found in the Wilmington 400-500°C acid concentrate together with the corresponding spectra of the model compound 1H-benzo[a]carbazole. Visual examination of the thin-layer chromatographic plate indicated that 1H-benzo[a]carbazoles represented a large percentage of the material found in these fractions. Snyder and Buell (16) have previously identified and made quantitative estimates of 1H-benzo[a]carbazoles and 7H-benzo[a]carbazoles in cracked gas oils using ultraviolet spectroscopy. In the work described here a quantitative estimation of the benzcarbazoles in the acid concentrate is precluded by the use of thin-layer chromatography as well as by problems inherent in the fluorescence method.

The appearance of the 1H-benzo[a]carbazole aromatic ring system in a rather large number of GPC fractions is presumably due to the presence of a homologous series. Mass spectral analysis of a GPC fraction from a Wason 400-500°C acid concentrate containing 1H-benzo[a]carbazoles indicated that a homologous series was indeed present.

Although a complex mixture of alkyl-substituted 1H-benzo[a]carbazoles appears to be present in a single TLC fraction, the fine structure of the fluorescent emission spectrum of the mixture is the same as that of the parent model compound, within the detection limits of the spectrometer. This behavior was expected, based on the work of Monkman and Porro (12) concerning the effects of methyl substitution on the fluorescence of benz[a]anthracenes and of Schoental and Scott (11) concerning the effects of methyl substitution on the fluorescence of naphtho(2':1':2)-fluorene. The effects of methyl substitution on these systems were not large. Our data suggest that alkyl substitution or multiple alkyl substitution does not significantly alter the vibrational

Table 1. - Fluorescence excitation and fluorescence emission spectra of model compounds*

| Compound | Fluorescence excitation spectra | | Fluorescence emission spectra | |
|------------------------------|---------------------------------|---------------|-------------------------------|------------|
| | Wavelength, nm | | Wavelength, nm | |
| Fluorene | <u>268</u> | <u>275(s)</u> | <u>293</u> | <u>303</u> |
| Naphthalene | <u>269</u> | <u>278</u> | <u>288</u> | <u>324</u> |
| 9-Methylcarbazole | <u>249</u> | <u>293</u> | <u>322</u> | <u>334</u> |
| (N-Methylcarbazole) | | | | <u>349</u> |
| Carbazole | <u>249</u> | <u>293</u> | <u>320</u> | <u>335</u> |
| 2-Methylcarbazole | <u>250</u> | <u>297</u> | <u>319</u> | <u>335</u> |
| 3-Methylcarbazole | <u>252</u> | <u>296</u> | <u>325</u> | <u>350</u> |
| 11H-Benzo[b]fluorene | <u>270</u> | <u>288</u> | <u>306</u> | <u>342</u> |
| (2,3-Benzofluorene) | | | <u>319</u> | <u>351</u> |
| 11H-Benzo[a]fluorene | <u>255</u> | <u>265</u> | <u>296</u> | <u>347</u> |
| (1,2-Benzofluorene) | | | <u>306</u> | <u>365</u> |
| Triphenylene | <u>262</u> | <u>277</u> | <u>288</u> | <u>354</u> |
| 11H-Benzo[a]carbazole | <u>255</u> | <u>279</u> | <u>306</u> | <u>364</u> |
| (1,2-Benzocarbazole) | | | | <u>373</u> |
| 7H-Benzo[c]carbazole | <u>263</u> | <u>286</u> | <u>324</u> | <u>381</u> |
| (3,4-Benzocarbazole) | | | | <u>381</u> |
| Chrysene | <u>261</u> | <u>271</u> | <u>297</u> | <u>363</u> |
| | | | <u>308</u> | <u>375</u> |
| Phenanthrene | <u>261</u> | <u>278</u> | <u>285</u> | <u>348</u> |
| | | | <u>296</u> | <u>357</u> |
| 7H-Dibenzo[c,g]carbazole | <u>278</u> | <u>303</u> | <u>350</u> | <u>367</u> |
| (3,4,5,6-Dibenzocarbazole) | | | | <u>386</u> |
| Dibenz[a,c]anthracene | <u>269(s)</u> | <u>279</u> | <u>289</u> | <u>377</u> |
| (1,2,3,4-Dibenzanthracene) | | | | <u>388</u> |
| Picene | <u>287</u> | <u>304</u> | <u>328</u> | <u>377</u> |
| (1,2,7,8-Dibenzphenanthrene) | | | | <u>398</u> |

Table 1. - cont'd

| Compound | Fluorescence excitation spectra | | Fluorescence emission spectra | |
|---|---------------------------------|--|-------------------------------|--|
| | Wavelength, nm | | Wavelength, nm | |
| Anthracene | 260 312 325 341 358 377 | | 380 401 424 451 | |
| Pyrene | 308 322 337 | | 374 379 384 389 395 | |
| Benz[a]anthracene (1,2-Benzanthracene) | 255 271 280 290 317 329 344 360 | | 387 408 435 462 | |
| 1,3H-Dibenz[<i>a</i> , <i>i</i>]carbazole (1,2,7,8-Dibenzocarbazole) | 297 324 338 355 373 394 | | 394 405 417 428 443 | |
| Benz[<i>b</i>]chrysene (2,3,7,8-Dibenzphenanthrene) | 255 289 305 | | 394 418 444 470(s) | |
| Benz[<i>k</i>]fluoranthene (1,2,7,8-Dibenz[<i>g</i> , <i>p</i>]chrysene) | 280 292 303 340 353 | | 395 409 | |
| Benz[<i>ghi</i>]perylene (1,2,3,8-Dibenzochrysene) | 301 324 335 351 | | 396 407 418 446 473 | |
| Benz[<i>ghi</i>]perylene (1,2,5,6-Dibenzanthracene) | 292 297 319 334 373 394 | | 396 407 418 445 | |
| Dibenzo[<i>def,p</i>]chrysene (1,2,3,4-Dibenzopyrene) | 276 293 305 330 342 358 376 | | 397 408 420 446 | |
| Naphtho[1,2,3,4- <i>def</i>]chrysene (1,2,4,5-Dibenzopyrene) | 255 299 310 | | 403 413 429 459 489(s) | |
| Benz[<i>e</i>]acephenanthrylene (3,4-Benzofluoranthene) | 256 269 286 300 333 349 365 385 | | 405 410 429 457 | |
| Benzo[<i>a</i>]pyrene (1,2-Benzopyrene) | 239 272 312 332 | | 405 424 446(s) | |
| Dibenzo[<i>c,g</i>]phenanthrene (3,4,5,6-Dibenzophenanthrene) | 291 302 331 348 364 385 | | 399 408 420 446 | |
| Benzo[<i>ghi</i>]perylene (1,12-Benzopyerylene) | | | | |

Table 1. - cont'd

| Compound | Fluorescence excitation spectra | | Fluorescence emission spectra | |
|--|--|--|--|----------------|
| | Wavelength, nm | | Wavelength, nm | |
| Dibenzo[def,mno]chrysene (Anthanthrene) | 260 | <u>296</u> 308 384 401 407 422 430 | <u>432</u> | <u>459</u> 494 |
| Benzo[nt]pentaphene (3,4,9,10-Dibenzopyrene) | 247 | 274 285 <u>297</u> 316 332 355 373 395 | <u>434</u> 450 | 462 480 494 |
| Perylene | <u>255</u> 370 388 410 438 | | <u>440</u> 466 500 540(s) | |
| Coronene | <u>292</u> 303 324 340 | | 411 <u>422</u> 428 435 446 455 475 485 508 | |
| Dibenzo[<u>b</u> ,def]chrysene (3,4,8,9-Dibenzopyrene) | 272 300 <u>312</u> 399 422 448 | | <u>451</u> 480 518 | |
| Fluoranthene | 241 256 266 280 <u>290</u> 311 326 344 360 | | 409(s) 418(s) <u>436</u> 463 | |
| Ovalene | 314 <u>328</u> 342 399 422 448 | | 450 462 475 482 490 <u>503</u> 509 514 539 | |

*The most intense peak in each spectrum is underlined. Shoulders are indicated by (s).

energy levels of the ground and excited states. Spectra of substituted ring systems in the oil are superimposable on those of the unsubstituted model compounds. This negligible effect of alkyl substitution is important because it allows mixtures of compounds having the same aromatic nucleus—compound types—to be identified by fluorescence spectroscopy.

Substitution effects would be predicted to be smaller for large polyaromatic molecules than for small molecules. Thus, as higher boiling distillates are studied, the fluorescence fine structure of the aromatic systems should not be affected by substitution, enhancing the use of fluorescence spectroscopy in the characterization of these materials.

Chrysenes and carbazoles were observed in the Wilmington acid concentrate GPC fractions 39 through 41. The emission and excitation spectra of a TLC spot from GPC fraction 41 together with corresponding model compound spectra are shown in Figure 4. These two compound types appear to represent a relatively small percentage of the material being examined. The distribution of these ring systems in only a few GPC fractions suggests that these compound types are not as extensively substituted as the 11H-benzo[a]carbazoles.

7H-Benzo[a]carbazoles, benzo[a]pyrenes, and perylenes were observed in Wilmington acid concentrate GPC fractions 43 through 45. The emission and excitation spectra of 7H-benzo[c]-carbazoles and perylenes obtained from GPC fractions 43-45 together with the corresponding model compound spectra are shown in Figure 5. 7H-Benzo[c]carbazoles and perylenes appeared to be more predominant in these GPC fractions than benzo[a]pyrenes, yet neither of these ring systems represented a large percentage of the total material being investigated. Perylene has been identified by ultraviolet absorption spectroscopy in high-boiling distillates by Carruthers and Cook (17) and also in marine sediments off southern California by Orr and Grady (18). Again, the GPC distribution of these compound types suggests that the polyaromatic ring systems are not extensively substituted.

The presence of aromatic ring systems such as chrysene and benzo[a]pyrene in the acid concentrates has not been explained. Fluorescence analysis permitted the identification of the aromatic ring systems present in the acid concentrates but yielded no information concerning substitution with OH or NH functional groups or whether small amounts of hydrocarbons have been retained in the acid concentrates by entrainment or by some bonding mechanism, such as hydrogen bonding.

Application of Fluorescence Spectroscopy to the Characterization of a Wason 400-500° Acid Concentrate

A survey of the fluorescing aromatic compound types in a Wason 400-500°C acid concentrate indicated that compound types similar to those found in the Wilmington oil were present in the Wason oil. 11H-Benzo[a]carbazoles, carbazoles, and 7H-benzo[c]carbazoles were identified in various TLC fractions as shown in Figure 6. These compound types were eluted from the GPC column in GPC fractions similar to those of the corresponding compound types of the Wilmington 400-500°C acid concentrate. Chrysenes, perylenes, and benzo[a]pyrenes were not found in the Wason acid concentrate; however, 1,2,7,8-dibenzphenanthrenes (picenes) were identified in the Wason acid concentrate.

Application of Fluorescence Spectroscopy to the Characterization of Other 400-500°C Concentrates

Figure 7 shows the fluorescence emission and fluorescence excitation spectra of ring systems which have been identified in other 400-500°C concentrates. The emission and excitation spectra of compound types isolated from these concentrates are shown here to demonstrate the general applicability of the fluorescence method for the characterization of high-boiling distillates.

CONCLUSIONS

Fluorescence spectroscopy is a powerful analytical technique for characterizing high-boiling petroleum fractions, when used under proper experimental conditions. Data which are useful for identification of compound types can only be obtained from relatively simple fractions, not from complex mixtures. Ion exchange chromatography and gel permeation chromatography together with thin-layer chromatography appear to be satisfactory methods for obtaining oil samples which are suitable for fluorescence analysis. In addition, spectra should be recorded using very dilute solutions in order to avoid problems such as concentration quenching and excimer formation.

For qualitative applications, such as the identification of compound types in high-boiling distillates, the fluorescence technique has proven useful for the following reasons: (1) Emission and excitation spectra of an individual ring system may often be instrumentally resolved even though the sample contains a mixture of aromatic ring systems. (2) The two spectra which are obtained aid in the identification of the sample. An emission spectrum alone may not permit the unambiguous identification of a ring system. When this occurs, the excitation spectrum may be used to identify the sample. (3) Due to the high sensitivity of the instrumentation, very small samples, micrograms or nanograms, may be used.

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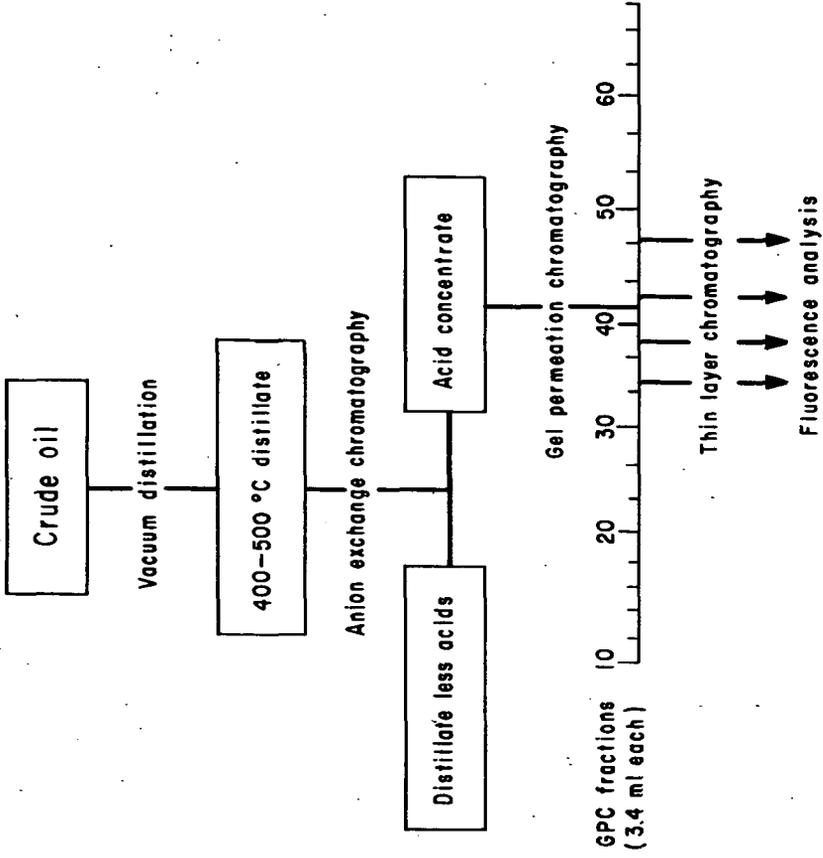


FIGURE 1.-Separation Scheme.

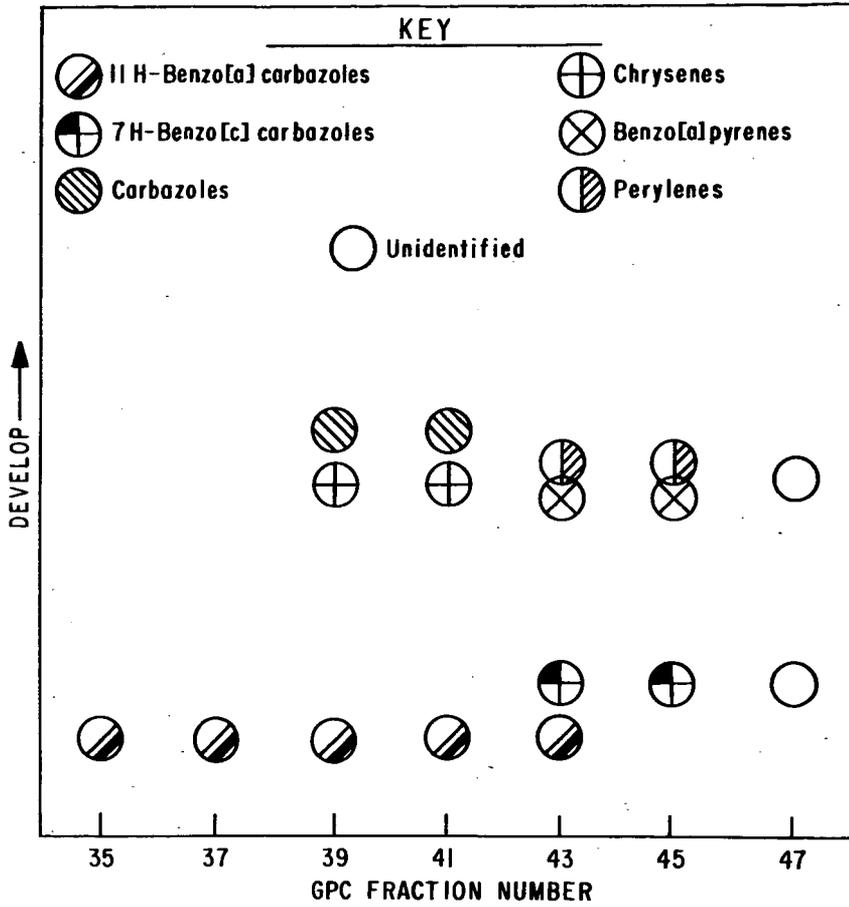


FIGURE 2.-Thin-Layer Chromatogram of Wilmington Acid GPC Fractions.

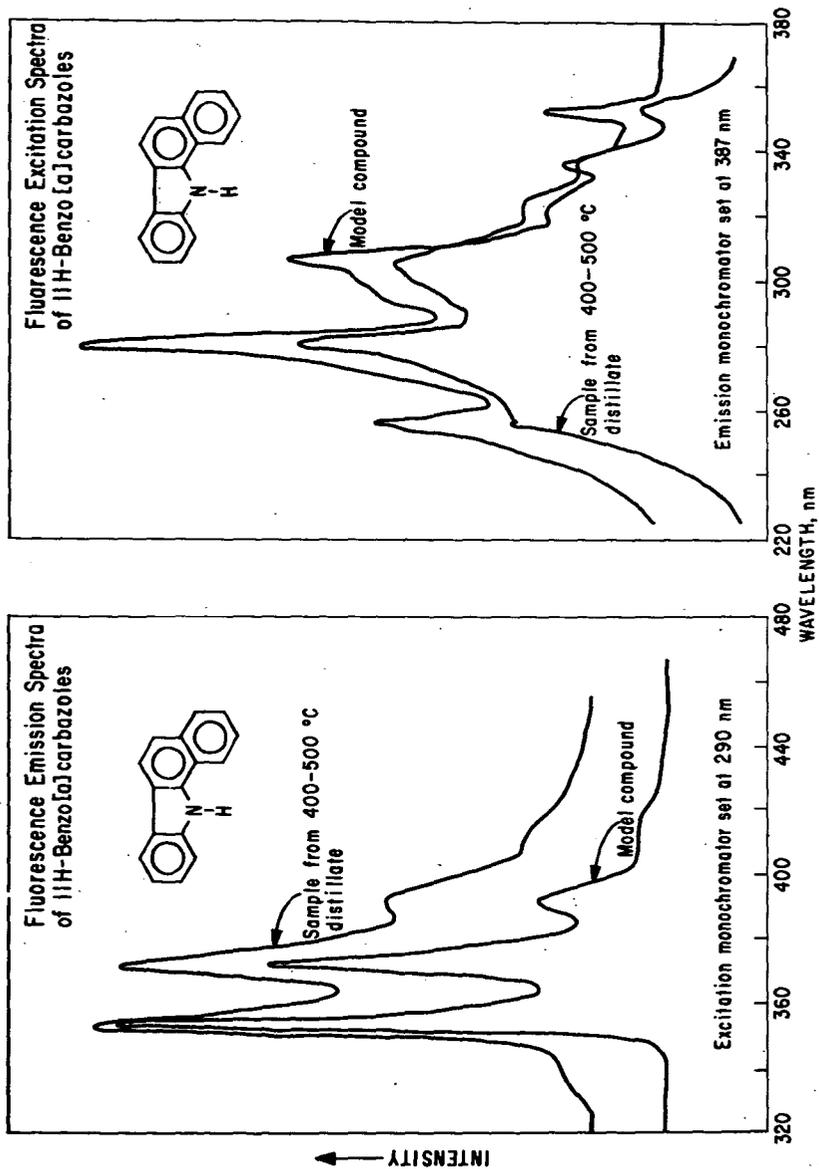


FIGURE 3.- Fluorescence Emission and Excitation Spectra.

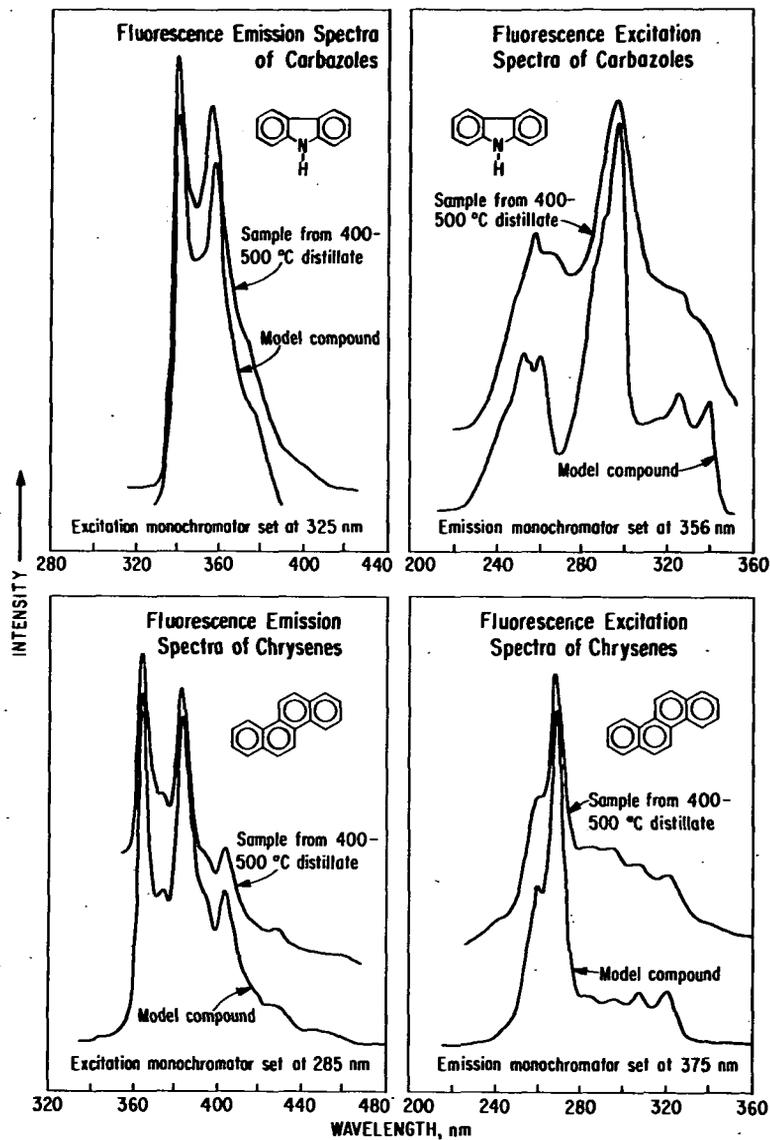


FIGURE 4-Fluorescence Emission and Excitation Spectra.

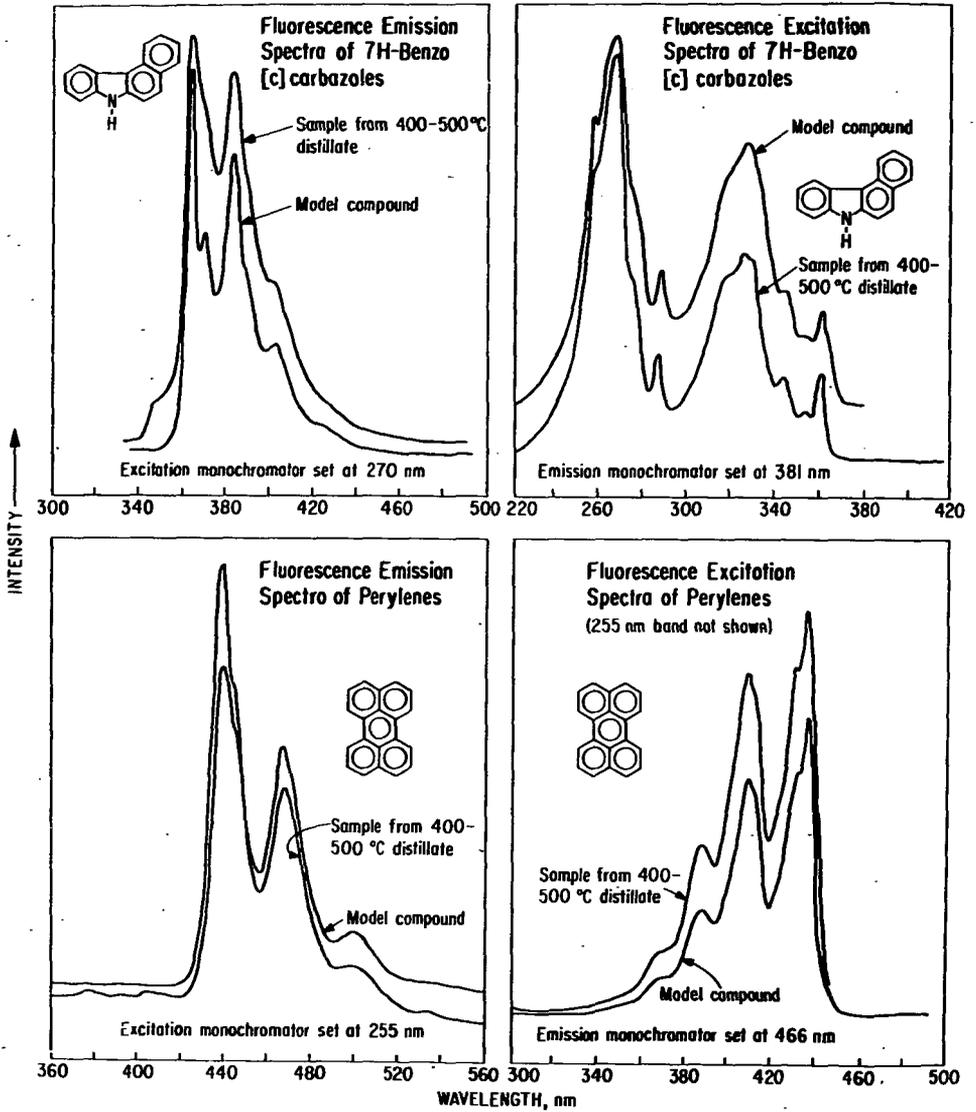


FIGURE 5-Fluorescence Emission and Excitation Spectra.

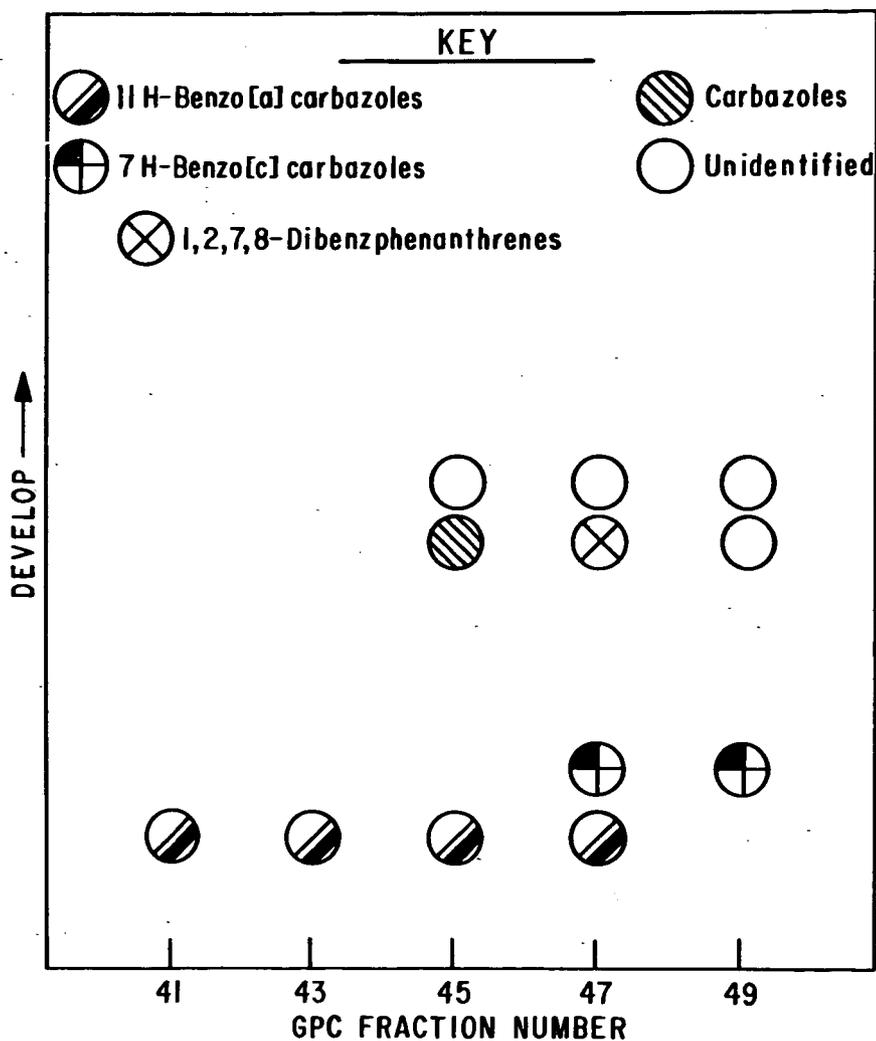


FIGURE 6.-Thin-Layer Chromatogram of Wasson Acid GPC FRACTIONS.

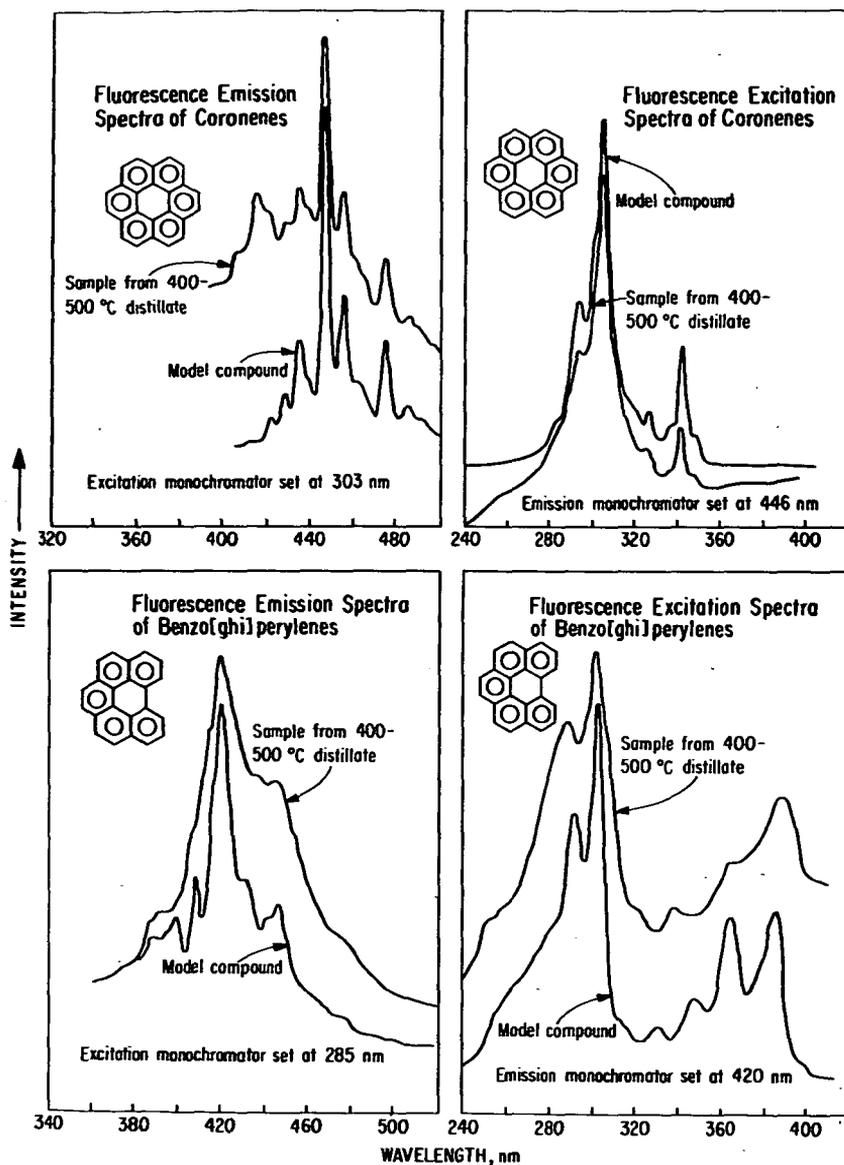


FIGURE 7-Fluorescence Emission and Excitation Spectra.

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DIVISION OF FUEL CHEMISTRY

PROJECTED PROGRAMS

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|---|---------------------------------|
| <u>Environmental Pollution Control - Part I. Removal of Oxides of Sulfur and Nitrogen from Combustion Product Gases</u> | New York, N. Y. August, 1972 |
| Robert M. Jameson | |
| <u>Environmental Pollution Control - Part II. Removal of Sulfur from the Fuel</u> | New York, N. Y. August, 1972 |
| Robert M. Jameson | |
| <u>Storch Symposium</u> | New York, N. Y. August, 1972 |
| <u>General Papers</u> | New York, N. Y. August, 1972 |
| Wendell H. Wiser | |
| <u>Symposium on the Power Industry of the Future - Fossil and Fission Fuels</u> | New York, N. Y. August, 1972 |
| Joint with IEC Division - Develop by IEC | |
| <u>Novel Combined Power Cycles</u> | Dallas, Texas April, 1973 |
| S. Fred Robson | |
| <u>Fuel from Waste Products</u> | Dallas, Texas April, 1973 |
| H. R. Appell | |
| <u>Carbon Monoxide Production and New Uses</u> | Dallas, Texas April, 1973 |
| J. S. Mackay | |
| <u>Synthetic Fuel Gas Purification</u> | Dallas, Texas April, 1973 |
| H. S. Vierk | |
| <u>Coal Gasification</u> | Dallas, Texas April, 1973 |
| L. G. Massey | |
| <u>General Papers</u> | Dallas, Texas April, 1973 |
| F. Schora | |