Fluorescence Spectrometry in the Characterization of High-Boiling Petroleum Distillates

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Use of fluorescence spectrometry as a qualitative analytical technique in the characterization of high-boiling petroleum distillates is reported. Examples of fluorescence emission and fluorescence excitation spectra obtained from compound types in 400–500 °C distillates are shown. Among the compound types identified were carbazoles, 11*H*-benzo[*a*]carbazoles, 7*H*-benzo[*c*]carbazoles, perylenes, coronenes, benzo[*ghi*]perylenes, and chrysenes. Fluorescence and excitation peak maxima of 35 aromatic model compounds are reported. The separation scheme which produced samples suitable for fluorescence analysis involved the use of ion exchange chromatography, gel permeation chromatography, and thin-layer chromatography.

ALTHOUGH MANY WORKERS have attempted to use fluorescence spectrometry 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 spectrometry 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 spectrometric 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 spectrometry. The separation scheme was designed to isolate concentrates of compound types, not individual compounds.

This paper demonstrates that fluorescence spectrometry 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 Wasson, Tex., 400–500 °C distillate were examined. Carbazoles, 11*H*-benzo[*a*]carbazoles, 1,2,7,8-dibenzphenanthrenes (picenes), 7*H*-benzo[*c*]carbazoles, chrysenes, benzo[*a*]pyrenes, and perylenes were identified in the acid concentrates by fluorescence spectrometry. Examination of other 400–500 °C concentrates resulted in the identification of coronenes, benzo[*ghi*]perylenes, 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 grams 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 SPECTROMETRY. Infrared analyses were performed using a Perkin-Elmer Model 421 infrared spectrometer. Methylene chloride was used as the solvent for all infrared analyses.

FLUORESCENCE SPECTROMETRY. 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.

Reagents. 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 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 research grade which had been passed over silica gel. Fluorescence analysis of this material did not detect aromatic hydrocarbons or other fluorescing impurities.

Procedure. 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

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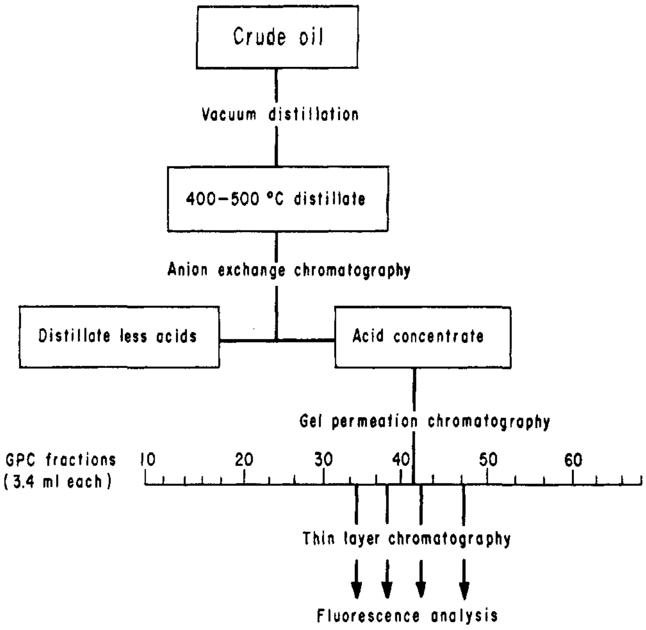

Figure 1. Separation scheme

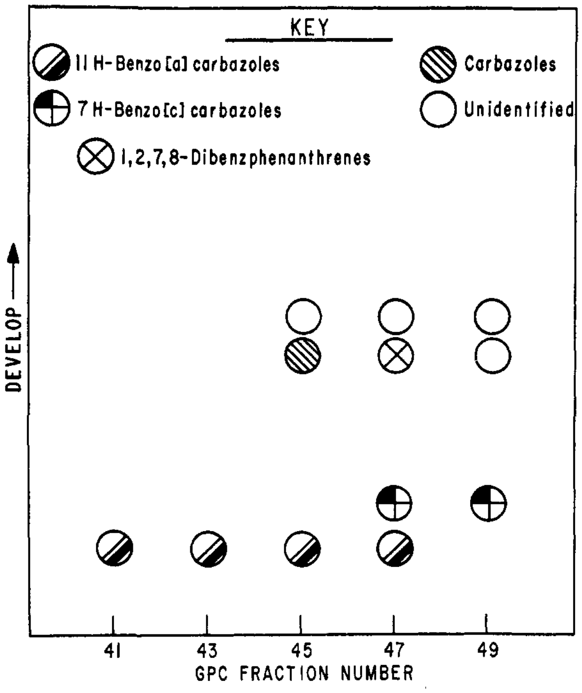

Figure 2. Thin-layer chromatogram of Wilmington acid GPC fractions

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 eximer 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 compounds.

Separation Procedure. A diagram of the separation procedure is shown in Figure 1. Samples of a Wilmington, Calif., crude oil and a Wasson, Texas, 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 spectrometry 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 fluorescence impurities were not being extracted from the silica gel. In addition, a solvent blank was analyzed by fluorescence spectrometry 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 spectrometry 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 I. The most intense peak in each spectrum is in italic type, 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 Spectrometry 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

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Table I. Fluorescence Excitation and Fluorescence Emission Spectra of Model Compounds[a]

Compound	Fluorescence excitation spectra, wavelength, nm	Fluorescence emission spectra, wavelength, nm
Fluorene	*268* 275(s) 293 303	*303* 310
Naphthalene	269 *278* 288	*324* 338 350
9-Methylcarbazole (*N*-Methylcarbazole)	249 *293* 322	*334* 349 365(s) 378(s)
Carbazole	249 *293* 320	*335* 351 364(s)
2-Methylcarbazole	250 *297* 319	*335* 350 365(s) 385(s)
3-Methylcarbazole	252 *296* 325	*342* 358 372(s) 378(s)
11*H*-Benzo[*b*]fluorene (2,3-Benzofluorene)	270 288 306 *319* 326 342	*342* 351 359 369
11*H*-Benzo[a]fluorene (1,2-Benzofluorene)	255 *265* 296 306 318	*347* 365 382(s)
Triphenylene	*262* 277 288	*354* 364 373 381(s) 391(s)
11*H*-Benzo[a]carbazole (1,2-Benzocarbazole)	255 *279* 306	*354* 372 392 413
7*H*-Benzo[c]carbazole (3,4-Benzocarbazole)	*263* 286 324	*362* 369 381 402
Chrysene	261 *271* 297 308 322	*363* 375 383 404 427
Phenanthrene	261 278 285 *296*	348 357 *365* 385
7*H*-Dibenzo[*c*,*g*]carbazole (3,4,5,6-Dibenzocarbazole)	278 303 350 *363*	*367* 386 405
Dibenz[*a*,*c*]anthracene (1,2,3,4-Dibenzanthracene)	269(s) 279 *289*	*377* 388 398 409(s)
Picene (1,2,7,8-Dibenzphenanthrene)	*287* 304 328	*377* 398 421 449
Anthracene	*260* 312 325 341 358 377	*380* 401 424 451
13*H*-Dibenzo[*a*,*i*]carbazole (1,2,7,8-Dibenzocarbazole)	*290* 321 334 348	*380* 401 425
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
Benzo[*b*]chrysene (2,3,7,8-Dibenzphenanthrene)	255 *289* 305	*394* 418 444 470(s)
Dibenzo[*g*,*p*]chrysene (1,2,7,8-Dibenzochrysene)	280 292 *303* 340 353	*395* 409
Dibenz[*a*,*h*]anthracene (1,2,5,6-Dibenzanthracene)	*301* 324 335 351	*396* 407 418 446 473
Naphtho[1,2,3,4-*def*]chrysene (1,2,4,5-Dibenzopyrene)	276 293 *305* 330 342 358 376	*397* 408 420 446
Benz[*c*]acephenanthrylene (3,4-Benzofluoroanthene)	255 299 *310*	*403* 413 429 459 489(s)
Benzo[*a*]pyrene (1,2-Benzopyrene)	256 269 286 *300* 333 349 365 385	*405* 410 429 457
Dibenzo[*c*,*g*]phenanthrene (3,4,5,6-Dibenzophenanthrene)	239 272 *312* 332	*405* 424 446(s)
Benzo[*ghi*]perylene (1,12-Benzoperylene)	291 *302* 331 348 364 385	399 408 *420* 446
Dibenzo[*def*,*mno*]chrysene (Anthanthrene)	260 296 *308* 384 401 407 422 430	*432* 459 494
Benzo[*rst*]pentaphene (3,4,9,10-Dibenzopyrene)	247 274 285 *297* 316 332 355 373 395	*434* 450 462 480 494
Perylene	*255* 370 388 410 438	*440* 466 500 540(s)
Coronene	292 *303* 324 340	411 422 428 435 *446* 455 475 485 508
Dibenzo[*b*,*def*]chrysene (3,4,8,9-Dibenzopyrene)	272 300 *312* 399 422 448	*451* 480 518
Fluoranthene	241 256 266 280 *290* 311 326 344 360	409(s) 418(s) 436 *463*
Ovalene	314 328 *342* 399 422 448	450 462 475 482 490 *503* 509 514 539

[a] The most intense peak in each spectrum is in italic type. Shoulders are indicated by (s).

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.

11*H*-Benzo[*a*]carbazoles were identified in GPC fractions 35 through 43. Figure 3 shows the fluorescence emission and fluorescence excitation spectra of 11*H*-benzo[*a*]carbazoles found in the Wilmington 400–500 °C acid concentrate together with the corresponding spectra of the model compound 11*H*-benzo[*a*]carbazole. Visual examination of the thin-layer chromatographic plate indicated that 11*H*-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 11*H*-benzo[*a*]carbazoles and 7*H*-benzo[*a*]carbazoles in cracked gas oils using ultraviolet spectrometry. In the work described here, a quantitative estimation of the benzcarbazoles in the acid concentrate is precluded by the use of thin-layer

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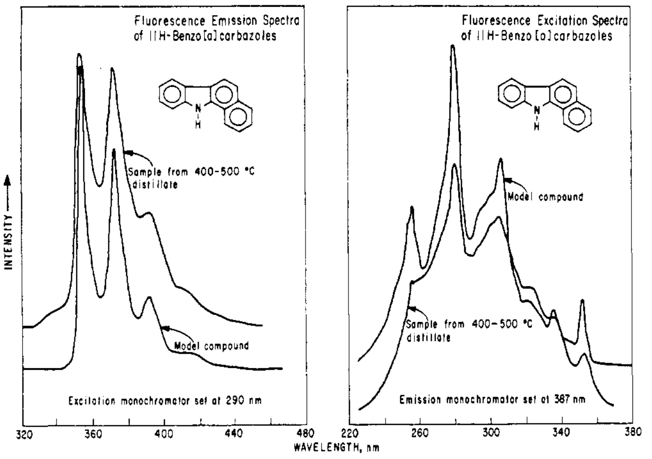

Figure 3. Fluorescence emission and excitation spectra of 11*H*-benzo[*a*]carbazoles

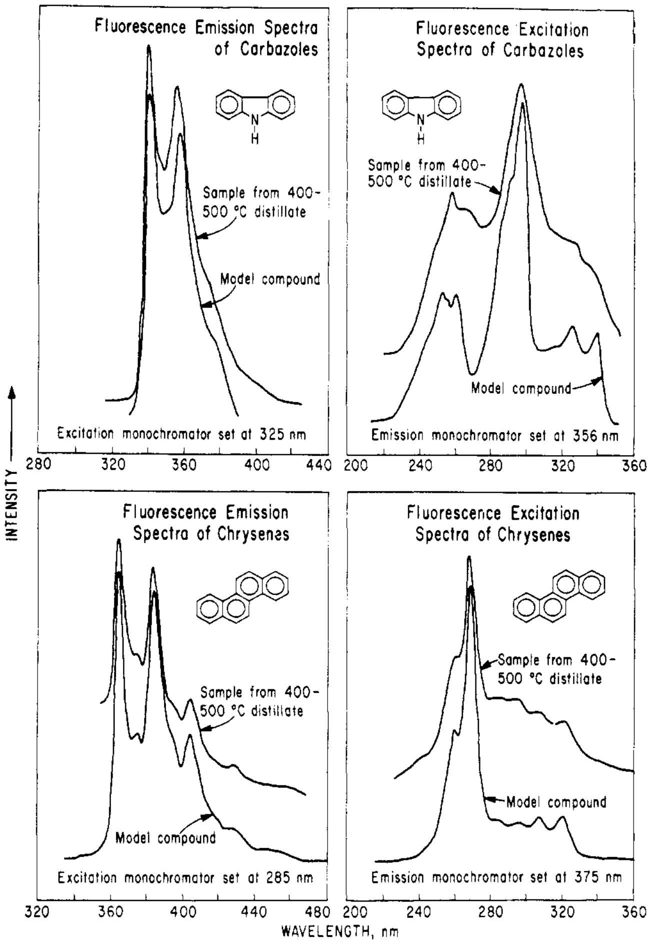

Figure 4. Fluorescence emission and excitation spectra of carbazoles and chrysenes

chromatography as well as by problems inherent in the fluorescence method.

The appearance of the 11*H*-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 Wasson 400–500 °C acid concentrate containing 11*H*-benzo[*a*]carbazoles indicated that a homologous series was indeed present.

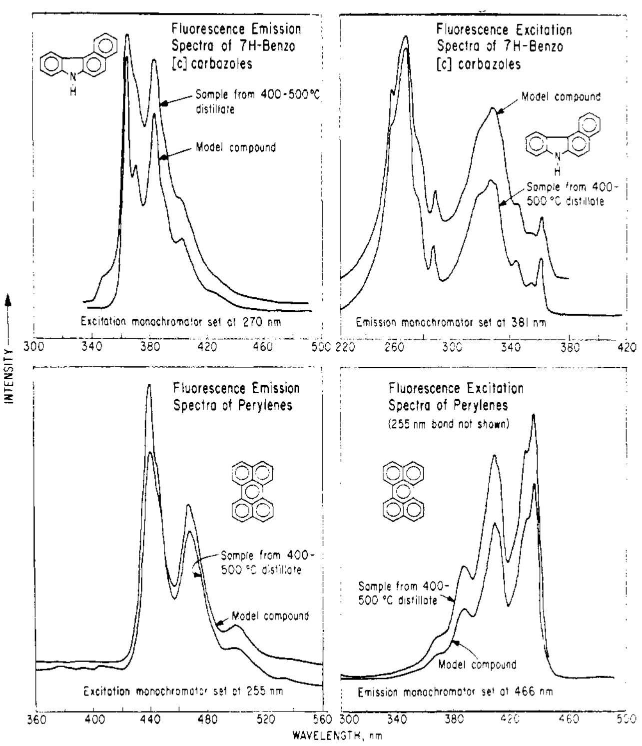

Figure 5. Fluorescence emission and excitation spectra of 7H-benzo[*c*]carbazoles and perylenes

Although a complex mixture of alkyl-substituted 11*H*-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 is 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′: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 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 spectrometry.

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 spectrometry 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 11*H*-benzo[*a*]carbazoles.

7*H*-Benzo[*a*]carbazoles, benzo[*a*]pyrenes, and perylenes were observed in Wilmington acid concentrate GPC frac-

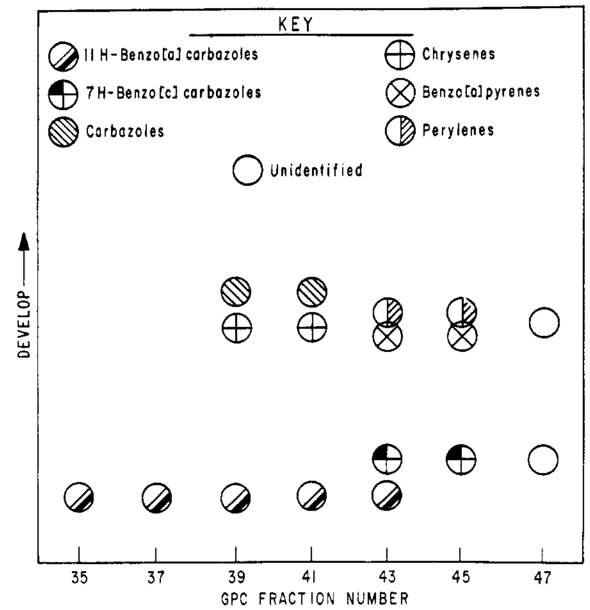

Figure 6. Thin-layer chromatogram of Wasson acid GPC fractions

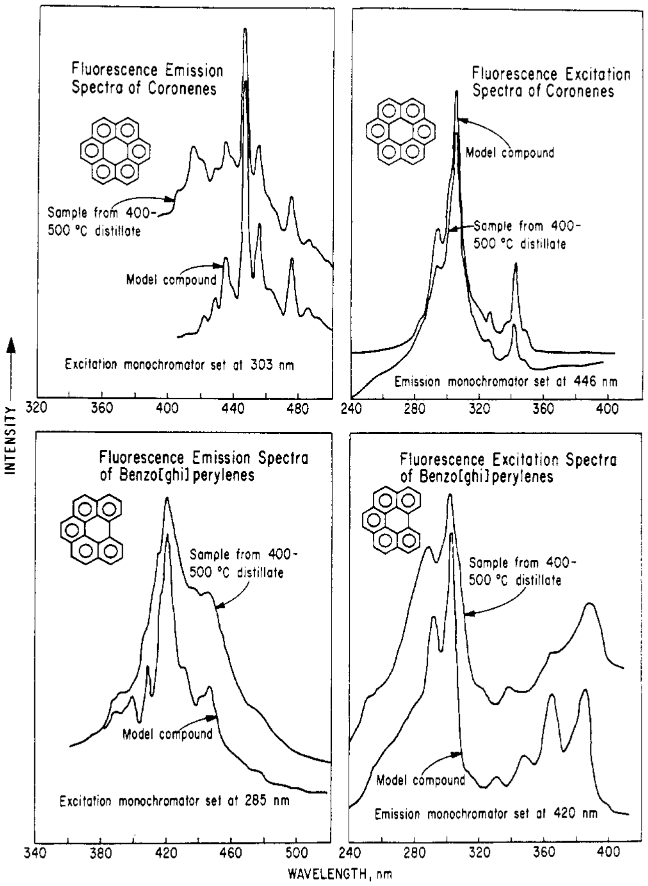

Figure 7. Fluorescence emission and excitation spectra of coronenes and benzo[*ghi*]perylenes

tions 43 through 45. The emission and excitation spectra of 7*H*-benzo[*c*]carbazoles and perylenes obtained from GPC fractions 43–45 together with the corresponding model compound spectra are shown in Figure 5. 7*H*-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 spectrometry 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 Spectrometry to the Characterization of a Wasson 400–500 °C Acid Concentrate. A survey of the fluorescing aromatic compound types in a Wasson 400–500 °C acid concentrate indicated that compound types similar to those found in the Wilmington oil were present in the Wasson oil. 11*H*-Benzo[*a*]carbazoles, carbazoles, and 7*H*-benzo[*c*]carbazoles were identified in various TLC fractions 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 Wasson acid concentrate; however, 1,2,7,8-dibenzphenanthrenes (picenes) were identified in the Wasson acid concentrate.

Application of Fluorescence Spectrometry In 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 spectrometry is a powerful analytical technique for characterizing high-boiling petroleum fractions, when used under proper experimental conditions. Data useful for identification of compound types can be obtained only 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 to avoid problems such as concentration quenching and eximer formation.

For qualitative applications, such as the identification of compound types in high-boiling distillates, the fluorescence technique has proved useful for the following reasons. First, 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. Second, the

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(18) W. L. Orr and J. R. Grady, *Geochim. Cosmochim. Acta*, **31**, 1201 (1967).

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. Third, because of the high sensitivity of the instrumentation, very small samples, micrograms or nanograms, may be used.

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Determination of Rare-Earth, Yttrium, and Scandium Abundances in Rocks and Minerals by an Ion Exchange–X-Ray Fluorescence Procedure

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The method involves the dissolution of a geologic sample in an appropriate acid medium, separation of the rare earths, yttrium, scandium, and barium by a strong acid cation exchange procedure, removal of the barium as a barium sulfate precipitate, and collection of the remaining ions on ion exchange paper. The concentrations of the individual elements are determined by X-ray fluorescence. Single element standards are used to establish corrections for the various interferences in the complex rare-earth X-ray spectrum. The method yields a precision of ±10 to ±20% for all elements down to concentrations of 1 to 2 μg/gram. Detection limits normally range from 0.5 to several μg/gram. Comparison with literature values for the U.S.G.S. standard rocks indicates relatively good agreement (10–30%) at the ppm level.

DURING THE PAST ten to fifteen years, trace elements have come to play an important role in the delineation of geologic processes. These elements, which are present in very small amounts (usually 0.1 to several hundred parts per million), are considered to be more responsive to changes in the geologic environment than are the major elements which compose the bulk of the rock system. Among the most useful, and the most popular, of these trace elements are the rare earths, yttrium, and scandium.

The widespread use of trace element data has been occasioned mainly by the development of precise and extremely sensitive methods of analysis. Rare-earth abundances, in geologic materials, are usually obtained by neutron activation (*1–3*) or isotope dilution (*4*, *5*) procedures. Spark source mass spectrography (*6*, *7*) is also currently used. Few X-ray fluorescence procedures have been developed for the determination of trace amounts of the rare-earth elements in geologic materials. Rose and Cuttitta (*8*) have described a method for the determination of semimicrogram concentrations of the rare-earth elements but the technique has not been extended to the microgram level. Russian investigators have long used X-ray fluorescence procedures but descriptions of their methods (*9*) are few and the procedures apparently require a significant amount of preconcentration.

Although neutron activation and isotope dilution procedures yield excellent precision and high sensitivity, they are both tedious and time consuming, and the general applicability of the methods is somewhat limited by the availability of equipment. The procedure described below permits the determination, with sufficient precision, of rare-earth, yttrium, and scandium abundances in most rocks and minerals. The method is roughly five times as fast as neutron activation or isotope dilution procedures and does not require any special equipment beyond a good X-ray fluorescence spectrometer.

EXPERIMENTAL

Apparatus. The X-ray fluorescence spectrometer used in this study was a General Electric XRD-6VS. The operating conditions are listed in Table I. A vacuum path was used for all determinations. A Baird Atomic beta counter was used to determine the activity of the ^{154}Eu tracer. Both Vycor and Pyrex ion exchange columns were used. The inside diameter of these columns was 2.1 cm and they were filled with resin to a height of 15 cm. Vycor glassware, platinum dishes, and Polypropylene and Teflon beakers were used throughout the procedure.

Reagents and Standards. Vapor distilled hydrochloric, sulfuric, and nitric acids were used throughout the chemical procedure. The hydrofluoric acid was commercial ACS reagent grade.

Dowex 50W-X8, 200–400 mesh cation exchange resin was used in the ion exchange portion of the method. Reeve Angel SA-2 ion exchange paper was used as the ion collector and support for the X-ray portion of the procedure. The ion exchange resin used in this paper is Amberlite IR-120.

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