

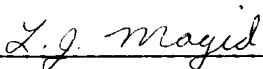
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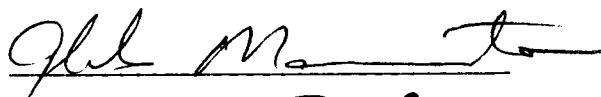
I am submitting herewith a dissertation written by Mildred Elizabeth Bateman Perry entitled "A Direct Characterization of the Polycyclic Aromatic Hydrocarbon Content of Solid Solvent-Refined Coal by Matrix Isolation Fluorescence Spectroscopy." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

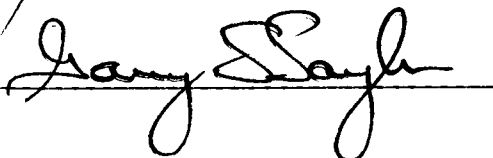


Earl L. Wehry, Major Professor

We have read this dissertation
and recommend its acceptance:







Accepted for the Council:



Vice Chancellor
Graduate Studies and Research

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A DIRECT CHARACTERIZATION OF THE POLYCYCLIC AROMATIC HYDROCARBON
CONTENT OF SOLID SOLVENT-REFINED COAL BY MATRIX
ISOLATION FLUORESCENCE SPECTROSCOPY

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Mildred Elizabeth Bateman Perry

March 1983

3066001

DEDICATION

This work is humbly dedicated to Mr. John Bond and to Mrs. Mary Keller Cox. It was Mr. Bond, my freshman chemistry instructor, who introduced me to the romance of chemistry and encouraged me to pursue the area. Mary Cox, my very good friend, taught me self-fulfilling prophecies.

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Finally, the author is grateful to her parents and family who loved her anyway.

ABSTRACT

A solid, untreated solvent-refined coal sample yields matrix isolation fluorescence spectra suitable for the identification and determination of polycyclic aromatic hydrocarbons. Several PAHs can be identified in xenon-lamp excited spectra. The capability for selective excitation of fluorescence and background suppression using the time resolution of a dye-laser spectrometer permit the unambiguous identification of PAHs including benzo[a]pyrene. Quantitative "standard addition" plots for benzo[a]pyrene, perylene, benz[a]anthracene, and pyrene in SRC I are precise and appear to be reliable. Because of the absence of a suitable solid standard reference material, the accuracy of quantitative results cannot be ascertained.

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CHAPTER I

INTRODUCTION

Public awareness of the need for developing native energy resources has been a result of recent petroleum shortages. The Committee on Nuclear and Alternative Energy Systems concludes that coal and nuclear energy are the only potential major sources for electricity generation in this century.¹ The anticipation of a long useful life of power stations demands that uncertainties about environmental effects should be resolved in a conservative fashion before widescale implementation of a fuel processing technology becomes a reality. Chemists are faced with dual challenges with respect to a future fuel processing technology: the need to characterize highly complex samples in various stages of conversion, and to aid in developing conversion processes which are economically feasible and yield a product which is environmentally acceptable.

A. THE PETROLEUM CRUNCH: A SEARCH FOR ALTERNATE FUELS

The United States, a major importer of petroleum, has abundant reserves of fossil fuels, primarily oil shale and coal, which can be utilized as an energy alternative to petroleum. Estimates place abundance of these reserves to be sufficient for all our energy needs for the next 175 years.² In its raw form, coal is a "dirty" fuel and inconvenient for use in many applications; its combustion creates environmental and ecological problems associated with emissions of air

pollutants (primarily particles) and contaminants (notably, sulfur compounds),³ and local heating of water supplies used as coolants.

Fuel processing technology (the changing of fossil fuels to more convenient forms) appears to be an attractive alternative to a continuing dependence on imported petroleum. The primary coal-conversion processes planned for development in the U.S. are coal gasification, coal liquefaction, and solvent-refined coal (SRC).⁴ Figure 1 illustrates how an eventual industry producing 15 million barrels of fuel per day might conceivably be distributed geographically.² Although the bulk of this new synfuels production is projected to occur in the United States, as shown in Figure 2, Canada, Venezuela, Brazil, and Australia may also meet a large share of their energy needs with various synfuels.² In many respects, conversion products are more environmentally acceptable than coal;^{4,5,6} however, there is increasing evidence of the formation of potentially hazardous compounds from existing conversion processes.⁴

Some coal-conversion products are believed to contain as much as 40 weight percent of polycyclic aromatic hydrocarbons (PAHs), many of which are known carcinogens or precursors to carcinogens. The development of a large-scale fuel processing technology necessitates investigation of the toxicological and environmental impact of that technology (in particular, carcinogenic PAHs need to be investigated) to alleviate potential hazards which may be imposed upon society.

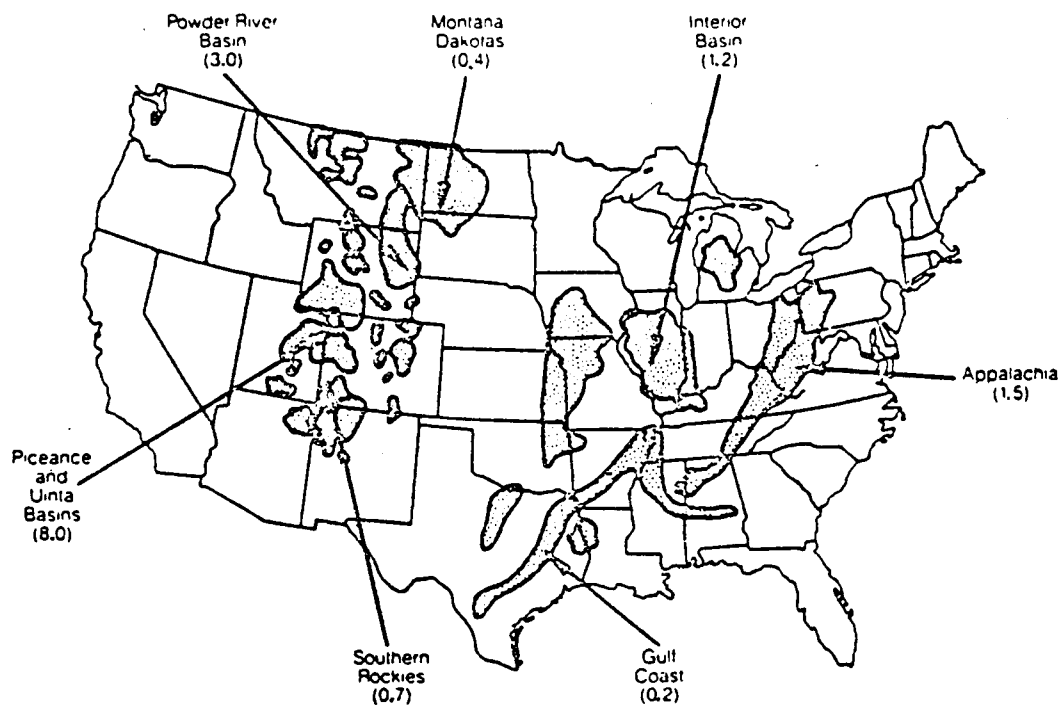


Figure 1. Assumed Distribution of Synthetics Industry².

(Million Barrels / Day Oil Equivalent)

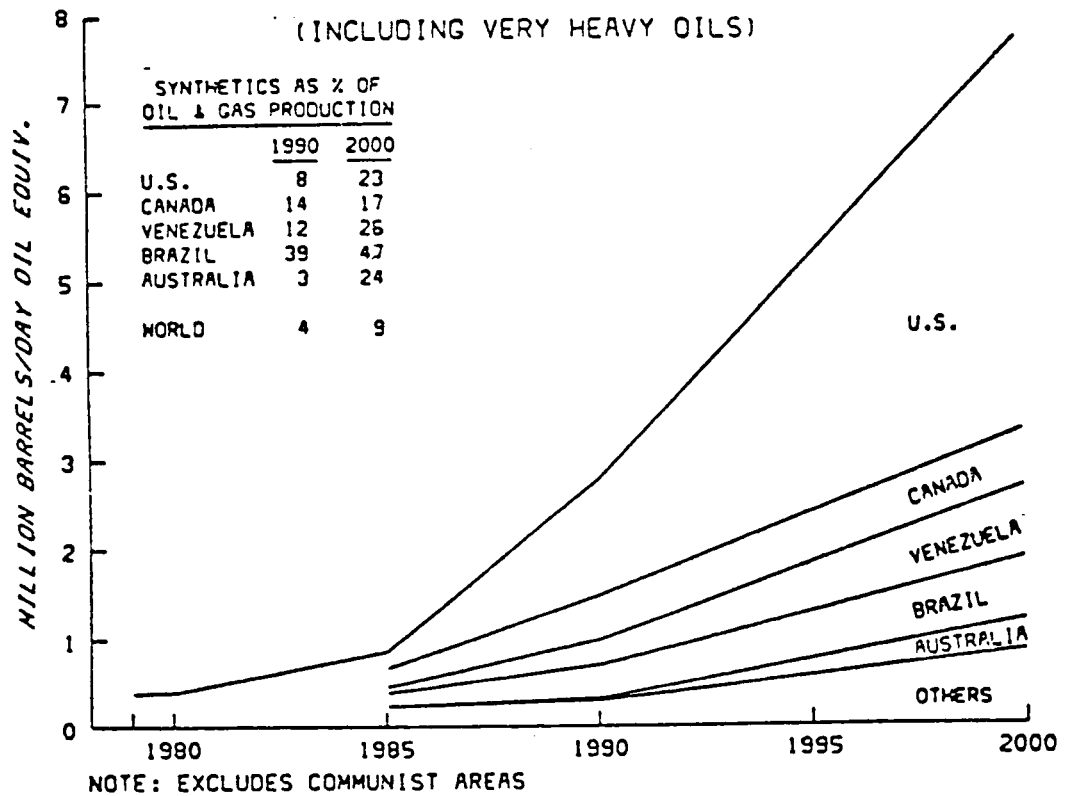


Figure 2. Synthetic Fuels Outlook².

B. THE PAH PROBLEM

The carcinogenic potential of PAHs has been reviewed.⁷ Benzo[a]pyrene (BaP) was the first chemical agent to be separated from coal tar and tested for its carcinogenic activity.⁴ Since the carcinogenic activity of BaP has been confirmed in laboratory animals and humans, environmental samples are often analyzed for BaP as an indicator of possible carcinogenic hazard.⁸ Many other PAHs have also been shown to be carcinogenic, some more active than BaP (i.e. 3-methylcholanthrene), demonstrating the oversimplification of this approach.

Analysis of environmental samples for PAHs presents special problems. The PAHs are incorporated in complex environmental matrices in a variety of ways. Samples usually contain additional classes of organic compounds, aliphatic and olefinic hydrocarbons, organometallics, etc., which place major demands upon analytical methodology. Even when the aromatic fraction has been separated from the sample, the presence of a wide variety of related compounds (nitrogen, oxygen, and sulfur derivatives of PAHs and their structural and substitutional isomers, as well as parent PAHs) defines a highly complex system for analysis. The analytical method must be highly selective if isomers are to be resolved; high sensitivity is required for detection of an individual PAH in a relatively high concentration of total PAH content.⁹ Most schemes for analysis of these "real" environmental samples require elaborate separations which are correspondingly time-consuming and subject to losses of sample constituents and/or introduction of contaminants from the pretreatment procedure.

C. ANALYTICAL METHODS

Analytical methods which have been applied to PAHs have been reviewed.^{3,10,11} Literature reference to identification and quantitation of PAHs in "real" samples acquire a variety of meanings. In many cases, the actual sample for which data are reported is a fraction or derivative of an environmental sample (air, water, or mineral) which has been subjected to a variety of pretreatment procedures. Such a sample may be more amenable to analysis, but it may bear little resemblance to the original composition of the derived fraction in the "real" sample. Losses of sample constituents and/or introduction of contaminants may occur at any step in an analytical scheme.

The introduction of errors in the analysis of trace organics has been reviewed.^{12,13} Often a radioactive tracer is added to the sample to correct for losses of analyte in the procedure, but the assumption that the tracer will behave in the same manner as its analogue in the sample matrix is not always valid. Since the environment of the analogue in the sample matrix may differ from that of the tracer, one cannot assume that the recoveries are identical. Losses of analyte may occur in solvent evaporation steps, solvent-solvent partitioning, and during the transfer of a sample from one container to another. Contaminants may be introduced to samples, even from solvents which are of the highest available purity. Methods which permit the direct analysis of PAHs in an untreated sample therefore are highly desirable.

Most analytical schemes for trace organics in complex samples begin with a simple procedure for separating the organic material from the sample matrix. Some methods commonly used include liquid-liquid

partitioning,^{8,14} sonification,^{15,16} vacuum sublimation,^{17,18} thin-layer chromatography,^{19,20} dry-column chromatography,²¹ and Soxhlet extraction,^{22,23} all of which may be followed by sequential washing of the organic fraction with acid and base to separate the basic, acidic, and neutral fractions. Finally, the sample may be subjected to analysis by various chromatographic, mass spectrometric, or optical techniques. Often, various tandem methodologies are employed for analysis of PAHs.

1. Chromatographic and Mass Spectrometric Methods

Recent advances in silane chemistry have resulted in improved resolution, shorter analysis times, and a broader range of solvents which can be used for column chromatography. Consequently, chromatography has become an almost indispensable tool for the analysis of complex environmental samples. Indeed, it is applied routinely in the analysis of samples for PAHs, and often is considered a necessary pretreatment procedure for sample characterization by other methods. Eiceman, et al.^{23,24} report about 100 organic compounds (including PAHs) identified in fly ash which was Soxhlet extracted in benzene, separated by gas chromatography (GC), and characterized by mass spectrometry (MS). Schultz, et al.²⁵ have identified PAHs in solvent-refined coal using GC/MS. Hertz, et al.²⁶ report the use of GC, MS, and high performance liquid chromatography (HPLC) to identify 9 PAHs, including BaP, in shale oil. An intensive analysis of SRC II heavy distillate using LC, GC, and MS is reported by Later, et al.²⁷

Until recently, mass spectrometry was primarily useful for structure elucidation, identification of pure compounds, or assignment of

structure to new compounds. Tandem modes of operation (MS/MS) are now numerous and have increased the utility of mass spectrometry to a "fingerprinting" capability for identification of individual compounds in complex mixtures. MS/MS has been used for the identification of PAHs in diesel engine soot.²⁸ Zackett, et al.²⁹ report the use of MS/MS for the identification of PAHs in untreated solvent-refined coal liquid (SRC II).

The primary disadvantages of these MS/MS methods are the cost of two or more mass spectrometers and the extensive library required for "fingerprinting" individual compounds as constituents of complex mixtures. Only cautious assignments can be accomplished in highly complex samples with no sample pretreatment. Mass spectrometry is highly effective as an auxiliary tool with chromatography.

2. Optical Methods at Room Temperature

PAHs usually absorb strongly in the UV and/or visible spectral regions and are often highly fluorescent. Thus, analytical methods based on UV-visible absorption or fluorescence in liquid solution media have been widely applied to the detection of PAHs.¹¹ Fluorescence can be a sensitive mode of detection for PAHs separated by HPLC.^{30,31,32} Optical methods, however, suffer major limitations for complex samples at room temperature. UV-visible absorption and emission bands for PAHs in liquid solution are broad and thus, for different compounds, may severely overlap, making the interpretation of spectra from complex samples a very difficult problem. Some techniques have been developed to partially overcome problems of spectral overlap.

Synchronously scanned luminescence helps to alleviate a broad background and some overlapping bands can be resolved.³³ The signal trace, a "synchronous spectrum," results from simultaneously varying both the excitation and emission wavelengths while maintaining the wavelength interval ($\Delta\lambda$) between them constant. "The only requirement necessary to observe a narrow peak in the synchronous mode is that either the excitation or emission spectra exhibit resolved structure in a given spectral range."¹¹ Vo-Dinh, et al.³⁴ report the use of synchronous luminescence for identification of PAHs. Derivative spectroscopy (the first or higher derivative of the signal is used for data extraction) has been used successfully for analysis of PAHs.^{35,36}

Recent work with heavy metal salts,³⁷ solid-surface luminescence methods,³⁸ and micelles³⁹ has made analysis of PAHs by room temperature phosphorescence a possibility. By using selected heavy-atom salts, specific compounds in a mixture can be caused to selectively phosphoresce,³⁷ or exhibit enhanced phosphorescence. Vo-Dinh, et al.⁴⁰ have used heavy-atom enhancement to characterize a synthoil sample for several PAHs. The method requires a minimum of sample pretreatment and is relatively inexpensive. An additional degree of selectivity has been obtained by applying the synchronous technique in combination with room-temperature phosphorescence.^{41,42}

For analysis of highly complex samples, these techniques are not necessarily sufficiently effective. Optical methods which have been applied as a primary tool for analysis of PAHs at room temperature are summarized in Table I.

TABLE I
ROOM-TEMPERATURE OPTICAL METHODS FOR PAH DETERMINATIONS

METHOD	SAMPLE TYPE	REMARKS	REFERENCE
Synchronous luminescence	pure PAHs	fingerprinting for simple mixtures	34,43,44
Phosphorescence	Mixture of 7 PAHs	Selective excitation with heavy-atom salts	37
Resonance enhanced 2-photon photo-ionization	GC separated PAHs	resolution of isomers, low (10 pg) detection limit	45
Magnetic circular dichroism	pure PAHs	substitutional isomers of methyl pyrene resolved	46
FT-IR	detector for LC	selective for heteroatom species	47
solid-surface luminescence	dry-column and t.l.c. fraction of shale oil	BaP identified	48
solid-surface luminescence	model mixtures	PAHs identified	49
Fluorescence rank annihilation	model mixtures	qualitative for PAHs	50

3. Optical Methods at Low Temperature

At cryogenic temperatures, spectral bands of most PAHs are narrow and distinctive. The severe spectral overlap observed for mixtures of PAHs at room temperature is much less extensive. If a sample is frozen in certain n-alkanes, either from solution or under matrix isolation (MI) conditions, both absorption and emission bands of some PAHs are reduced to very narrow "quasilines" (the Shpol'skii effect); energy transfer is minimized, and conditions are nearly optimum for observation of highly-resolved electronic spectral bands through the use of fluorescence or phosphorescence spectroscopy.⁵¹

Spectra of PAHs in frozen solutions are virtually identical with spectra obtained under MI conditions, if the frozen solution solvent is used as the MI matrix material, and if the MI sample is annealed. Virtually any material which has an appreciable vapor pressure at room temperature can be utilized as the matrix in an MI experiment; therefore, MI is not subject to solubility limitations encountered in frozen solution experiments.

Even under cryogenic conditions, real unfractionated samples tend to yield spectra with severely overlapping bands and a broad background when continuum excitation sources are used. Continuously tunable dye-laser spectrometers have helped to alleviate this problem. Reports of PAH analyses at low temperatures using optical methods are summarized in Table II.

The tunable dye laser offers several advantages as an excitation source in fluorescence experiments. The narrow-bandpass and high peak energy for a pulsed dye laser permit the analyst to exploit narrow

TABLE II
LOW-TEMPERATURE LUMINESCENCE METHODS

METHOD	SAMPLE TYPE	REMARKS	REFERENCE
Phosphorescence	PAHs	behavior in various matrices	52
X-ray excited optical luminescence	Fraction of coal combustion and conversion by-products	isomers resolved, PAHs identified including 3-methylcholanthrene	53
Fluorescence (Shpol'skii)	fractions of: auto exhausts, air particles, emissions from alumina reduction plant	PAHs identified	54
Fluorescence (Shpol'skii) LESS	Direct analysis of SRC II, coal liquids, and shale oil	Selective excitation of Pyrene, 4-Me-Pyrene, BaP, BkF; BaP quantified	55
Fluorescence (Shpol'skii)	HPLC fractions of pyrolyzed petroleum product	11 PAHs identified, 27 others by GC	56
Fluorescence (Shpol'skii) LESS	Complex synthetic mixture of PAHs	site-selection: of alkyl derivatives of BaA, BaP, BkF, and B[ghi]Per	57
Fluorescence line narrowing	direct analysis of SRC II	PAHs identified, isomers resolved	58
Fluorescence (MI)	LC fraction of coal liquid	BaA, chrysene, and pyrene identified, Shpol'skii effect reported for MIF, resolution of 4-ring isomers	59
Fluorescence (MI)	pure PAHs	Effect of annealing temperature on Shpol'skii effect	51
Fluorescence (MI)	Methyl chrysenes	isomers resolved	60
Fluorescence (MI)	LC fraction of shale oil	BaP identified	61

TABLE II (CONTINUED)

<u>METHOD</u>	<u>SAMPLE TYPE</u>	<u>REMARKS</u>	<u>REFERENCE</u>
Fluorescence (MI)	LC fraction from coking plant waste water sediment	6 PAHs identified including BaP	62
Fluorescence (MI)	Synthetic mixture of PAHs	time resolution for BaP in excess BkF	63
Fluorescence (MI)	pure PAHs	behavior in various matrices including Shpol'skii solvents	64
Fluorescence (MI) laser excited	polar compounds	hydroxy naphthalenes site-selection in argon or fluorocarbon matrix	65
Fluorescence (MI) laser-excited	pure PAHs	polarization of emission	66
Fluorescence (MI) laser-excited	pure PAHs	resolved methyl and methoxyl derivatives of BaP	67

absorption features inherent in low temperature samples (selective excitation), and to explore resolution in the time domain (time resolution) based on differences in rates of fluorescence decay for PAHs which may not be resolved in the spectral domain.

At short wavelengths of excitation, where the molar absorptivities of most PAHs are relatively large, a larger population of molecules may be excited to fluoresce. As the energy of the excitation wavelength decreases, approaching the energy of the 0-0 transition ($S_1^* \rightarrow S_0$) of a compound of interest, the population of molecules which are capable of absorption of that excitation wavelength decreases, and spectral narrowing may occur,⁶⁸ approaching, in the limit, the bandwidth of the excitation source. The laser technique based on this phenomenon has been called "fluorescence line narrowing," "site selection," or "energy selection" spectroscopy.

The combined capabilities of site selection and time resolution can be highly effective. Using site selection, the analyst can cause slight wavelength shifts (in the range of several Å) to occur in the emission peak, toward a spectral region in which interference may be less severe. Time resolution permits further discrimination against background scattering and short-lived fluorescence.

Certain disadvantages accompany the use of a dye-laser spectrometer. The cost ($\approx \$40,000$ – $\$100,000$) of relatively high-power dye lasers is prohibitive for many laboratories. The use of frequency-doubling crystals, to extend the laser capability into regions of interest in the UV, results in a considerable decrease in power (typically 7–10% conversion efficiency) of the excitation source and a concurrent and

proportional decrease in the fluorescence signal. In this region, site selection and time resolution, which sample fluorescence from a reduced population, become less attractive as analytical tools. However, where the lasing fundamental can be utilized, site selection and time resolution can be powerful tools for the analysis of complex samples. Other disadvantages of dye lasers include the necessity to discriminate against dye fluorescence, if a truly narrow-band excitation source is to result, and the difficulty in maintaining optimum performance of laser sources.

Fluorescence spectroscopy has been shown to be a highly sensitive and selective tool for analysis of PAHs. Frozen solution (Shpol'skii) fluorescence has been used for the direct analysis of a coal-liquid (SRC II).⁵⁵ Detection limits for MI samples are low (pg for highly fluorescent species) and analytical calibration curves are linear over a broad concentration range (3 or more orders of magnitude). Matrix isolation fluorescence spectroscopy should be a powerful tool for the direct analysis of PAH content of environmental samples.

D. MATRIX ISOLATION FLUORESCENCE SPECTROSCOPY (MIF)

The procedure for the MIF experiment has been discussed previously.^{3,9,62} The use of site selection⁹ and time resolution⁶³ with MIF has been addressed. The selective sampling capability of the method has not been adequately explored.

The MIF procedure requires a sample to be vacuum sublimed, using a Knudsen oven, onto a cryogenically cooled surface before spectral analysis. The parameters which are often varied in vacuum sublimation

techniques include temperature of the sample, temperature of the cold finger, and pressure. In the MI experiment, the temperature of the cold finger and the pressure are kept virtually constant, while the temperature of the sample (Knudsen oven) is varied. The capability for selective sublimation exists using MIF, and this simple fractionation capability, inherent to MI procedures, can be utilized for the direct analysis of environmental samples in complex matrices.

A broad range of solvents available as matrices permits additional selectivity of various parameters in the MI experiment. Fluorescence and phosphorescence quantum efficiencies vary with choice of solvent.^{66,69} Photodecomposition of sample constituents, a problem in some matrices, is less severe in others. Polar compounds, which usually exhibit broad spectral features, even with dye-laser excitation at cryogenic temperatures, have been shown to yield narrow spectral features using site selection in argon or halogenated alkane matrices.⁶⁵ The "fingerprinting" capability of Shpol'skii solvents can be used.

This work describes the direct identification and determination of PAHs in a solid solvent-refined coal (SRC I) sample and in a shale oil standard reference material (NBS SRM 1580) by matrix isolation fluorescence spectroscopy. Continuum source (xenon lamp) excitation is used when possible for a general survey of PAH content, and narrow-band (dye-laser) excitation is used for selective excitation of PAHs. Wherever possible, site selection and time resolution have been used to enhance spectral quality.

CHAPTER II

EXPERIMENTAL METHODS AND MATERIALS

A. PREPARATION OF MATRIX-ISOLATED SAMPLE DEPOSITS

AT CRYOGENIC TEMPERATURE

1. Equipment and Materials

The equipment used to perform the low-temperature matrix-isolation experiment in this laboratory has been described.^{3,9} An abbreviated diagram of the apparatus used to make the sample deposit is shown in Figure 3.

The vacuum line was constructed of 1/2" and 3/8" copper tubing and a glass trap. The trap, when cooled with liquid nitrogen, prevented vacuum pump oil vapor from entering the cryostat shroud or deposition area.

The matrix line was fabricated from stainless steel tubing, a glass flowmeter (Fischer and Porter Co., Warminster, Pennsylvania, Cat. No. 448-001) and a glass matrix reservoir ($\approx$ 2-5 ml capacity) made in the U.T. Chemistry Department glassblowing shop. A "Cajon" ultra-torr union (Cat. No. B-4-UT-6) between the organic matrix reservoir and the matrix valve facilitated exchange of matrix solvents. Specific matrix reservoirs were dedicated to specific matrix solvents. Matrix solvents used in this investigation included distilled-in-glass (UV grade) n-heptane (Burdick and Jackson; Muskegon, Michigan), 99 + mol % n-octane (MCB Manufacturing Chemists, Inc.; Cincinnati, Ohio), and 99.8% (GC) n-octane (Tridom Chemical, Inc.; Hauppauge, N.Y.); these solvents were

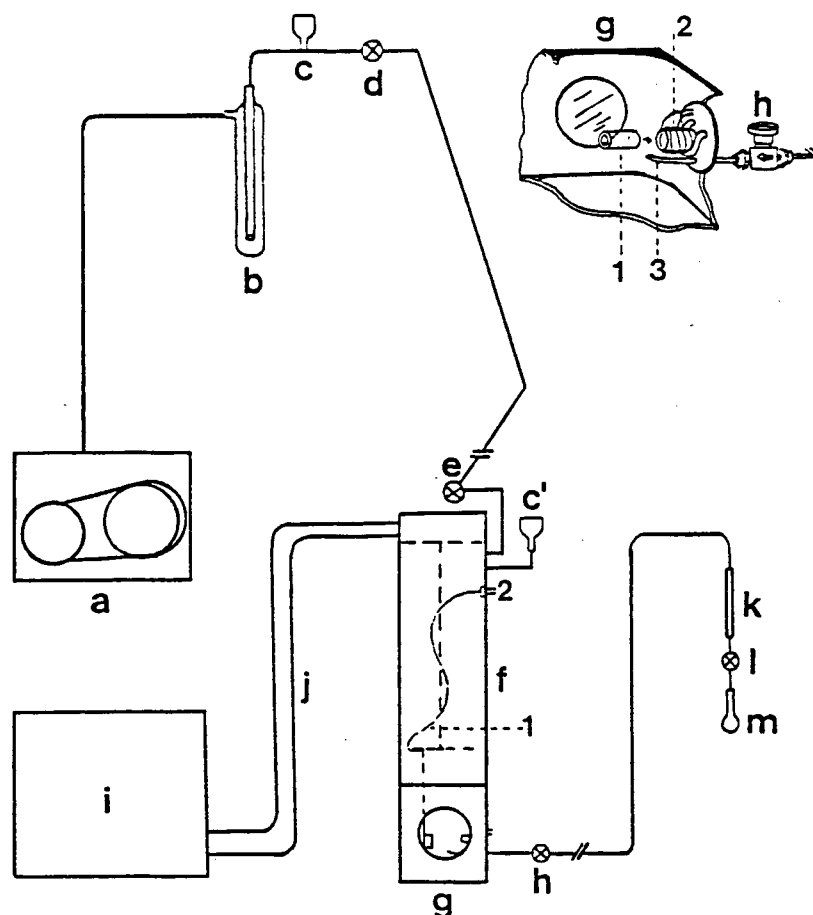


Figure 3. Apparatus for Preparing Low Temperature Matrix-Isolation Deposits.

Vacuum Line

a. Vacuum pump, b. cold trap, c. pressure gauge, d. valve

Cryostat and Sampling Head

e. rough-and-vent valve, f. shroud (1. thermocouple, 2. electrical connection), c'. pressure gauge, g. Sampling head (1. Sample cell, 2. Knudsen oven, 3. matrix line), h. valve, i. compressor, j. helium transfer lines

Organic Matrix Line

k. flowmeter, l. valve, m. organic matrix reservoir

used as received. Matrix solvents were subjected to two freeze/thaw cycles, before each deposit, to remove dissolved gases.

A Spectrim Model 21 Cryodyne helium refrigerator (CTI Cryogenics; Waltham, Mass.) was used to achieve cryogenic temperatures. A detailed description of the cryostat³ and of the associated temperature control equipment (Air Products; Allentown, Penn.)⁹ has been given. Gore⁹ concluded that background fluorescence observed from previous samples (memory effects) were not as severe when using the Model 21 Cryostat rather than the Model 20 Cryostat. The memory effects could be minimized with the Model 21 because the shroud was open to the sampling area and was relatively easy to clean, whereas the Model 20 was closed and could not be cleaned without disassembling the shroud. From among several solvent combinations studied, an approximately 1:1:1 solution of dichloromethane:isopropanol:n-hexane appeared to be most effective in removing residual SRC I from the shroud.

A cryogenic sample surface was fabricated from oxygen-free high-conductivity copper with a gold-plated, 1 cm^2 , deposition surface. This copper piece was attached to the cold finger with a machine screw and an indium (foil or gasket) interface to insure good thermal contact.

The sampling head has been described previously by Stroupe.³ The sample cell was modified (Figure 4) to accommodate solid samples by enlarging the orifice and eliminating the ground glass plug.

To prevent cross-contamination, the equipment was largely dedicated to this investigation. All SRC I experiments, all reproducibility studies, and SRC I studies using spikes of pure compounds were performed

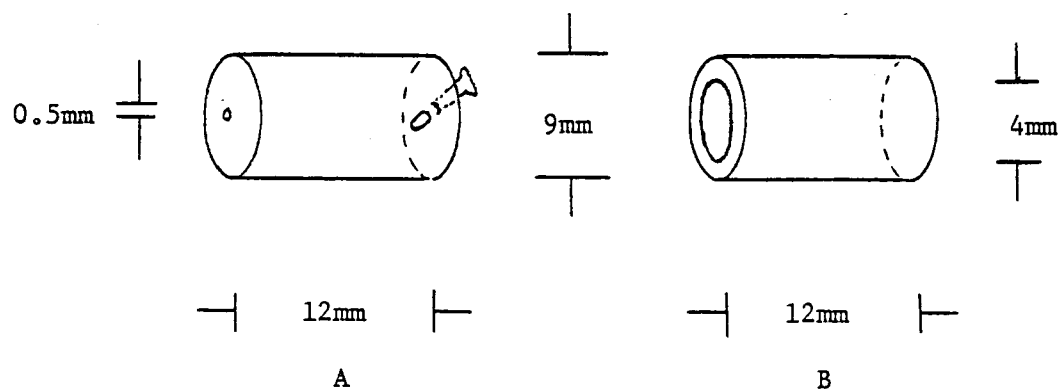


Figure 4. Comparison of Sample Cells.

A. Cell for PAH solutions.

B. Cell for solid samples.

using the SRC I sampling head and sample cell B (Figure 4). A separate, essentially identical, sampling head and sample cell A (Figure 4) were used to obtain library reference spectra as needed. Sources of PAHs used are summarized in Table III. When available, reference library spectra already available in our laboratory were accepted as authoritative.

2. Sample Considerations — Solvent-Refined Coal Solid

A solid solvent-refined coal sample (SRC I) was obtained from Peter W. Jones (Electric Power Research Institute; Palo Alto, California). Results of elemental analyses (Galbraith Laboratories; Knoxville, Tenn.) reveal that this sample is 85.89 percent carbon, 6.02 percent hydrogen, 2.07 percent nitrogen, and 0.90 percent sulfur. The remaining fraction (5.12 %) of SRC I undoubtedly also contains oxygen as well as other elements for which analyses were not performed. The SRC I in question was prepared in a Southern Company Services, Inc. pilot plant in Wilsonville, Alabama, operated by Catalytic, Inc.; the feedstock was an Illinois No. 6 coal. The date of preparation of the sample is not known. Previous investigations involving this sample include work performed by Hembree⁷ and Maple⁷⁰ in this laboratory. The solid sample remaining was in the form of two chunks, weighing 9.855g and 1.780g, respectively, and several smaller pieces. It had been stored in a brown envelope in the dark for approximately two years. At the beginning of this investigation, the sample was placed in three small brown envelopes in a desiccator (the exterior of which was painted black) under nitrogen. Small portions of the sample were pulverized, as needed, inside a glove bag using a mortar and pestle, under nitrogen. These powdered portions were stored under nitrogen, in 2-ml glass vials, in the

TABLE III

POLYCYCLIC AROMATIC COMPOUNDS USED IN THIS INVESTIGATION

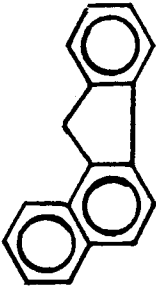
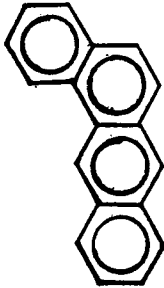
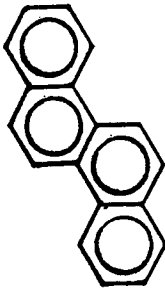
Compound	Structure	Abbreviation	Source
Benzo[a]fluorene		BaF	K & K
Benzo[b]fluorene		BbF	K & K
Benz[a]anthracene		BaA	Pauric (zone refined)
Chrysene		C	Pauric

TABLE III (CONTINUED)

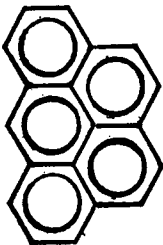
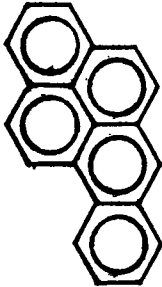
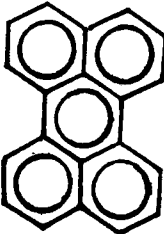
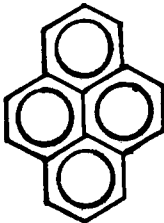
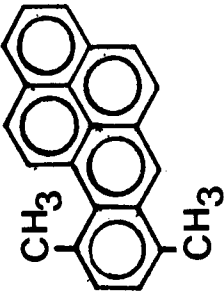
Compound	Structure	Abbreviation	Source
Benzo[e]pyrene		BeP	ENV. CANADA
Benzo[a]pyrene		BaP	Pauric (zone refined)
Perylene		Per	Aldrich
Pyrene		Py	Pauric (zone refined)

TABLE III (CONTINUED)

Compound	Structure	Abbreviation	Source
7,10-Dimethylbenzo[a]pyrene		7,10-DMBaP	Aldrich

desiccator. For work requiring SRC I, a 2-ml glass vial was removed from the desiccator (as needed), wrapped in aluminum foil, and stored under nitrogen in a "Ziploc" (Dow) storage bag; nitrogen was replenished over the sample after opening the bag and vial. Selox nitrogen, which was first passed through glass wool to trap organic vapor, and then through "Drierite" to trap water, was used to obtain the dry nitrogen atmosphere maintained over the sample.

For deposits of the solid SRC I sample, 200 μg -700 μg portions were weighed by difference on weighing paper (Fisher 09-898-12B) using a Cahn Model 7000 (10-1000 mg range) Electrobalance (Cahn Instruments; Cerritos, Calif.). The electrobalance was left turned on and was allowed to equilibrate on the 10 mg scale for at least 5 minutes prior to weighing the sample. A square of weighing paper ($\approx 30\text{mg}$) was fluted and tared; a sample was then placed on the pan and weighed. The sample was removed from the balance, and the sample was funneled through the fluted portion of the weighing paper into the sample cell. The weighing paper was reweighed and the sample weight was calculated by difference. The sample cell was rolled on a clean surface to evenly distribute the SRC I on the inside of the cell surface. For qualitative studies, it was often helpful to spike the SRC I sample with a pure PAH to verify identification of a suspected compound. Likewise, spikes of PAH solutions were used to obtain linear plots in quantitative investigations. Studies with the SRC I sample including a spike were prepared by first injecting the spike solution, evaporating the solvent, and then introducing the sample into the sample cell. The cell was wrapped with aluminum or copper foil to insure good thermal contact with the Knudsen oven.

3. Sample Considerations — NBS Shale Oil, Standard Reference Material #1580 (SRM 1580)

SRM 1580 (National Bureau of Standards, Washington, D.C.) was developed primarily for evaluating the accuracy of analytical methodology for the quantitation of trace organics in an oil matrix. Solids and water had been removed, but SRM 1580 had undergone no further sample pretreatment. The sample material (a viscous black liquid) was received as 5 1-ml aliquots sealed in amber glass ampoules.

A sample container was made (Figure 5) which would give easy access to the sample, allow the sample to be frozen and the air above the sample to be evacuated between deposits, and which would protect the sample from degradation during storage. As needed, a 1-ml ampoule of SRM 1580 was broken and the SRM 1580 was immediately transferred to the sample container with a 100 μ l syringe (Hamilton Inc.; Reno, Nev.).

For each MIF deposit of SRM 1580, the material was removed from the SRM 1580 sample container with a 10 μ l syringe. The stopcock was then closed, and the remaining sample was then frozen in an acetone/dry-ice bath or over liquid nitrogen vapor. After the sample was frozen, the stopcock was opened and the container was evacuated to approximately 5 millitorr pressure. The stopcock was then closed, the container was removed from the vacuum line and wrapped in aluminum foil. To facilitate validation of MIF results from SRC I by using MIF results from SRM 1580, the same equipment (cryostat, sampling head, and similar sample cells) was used in the analysis of both samples.

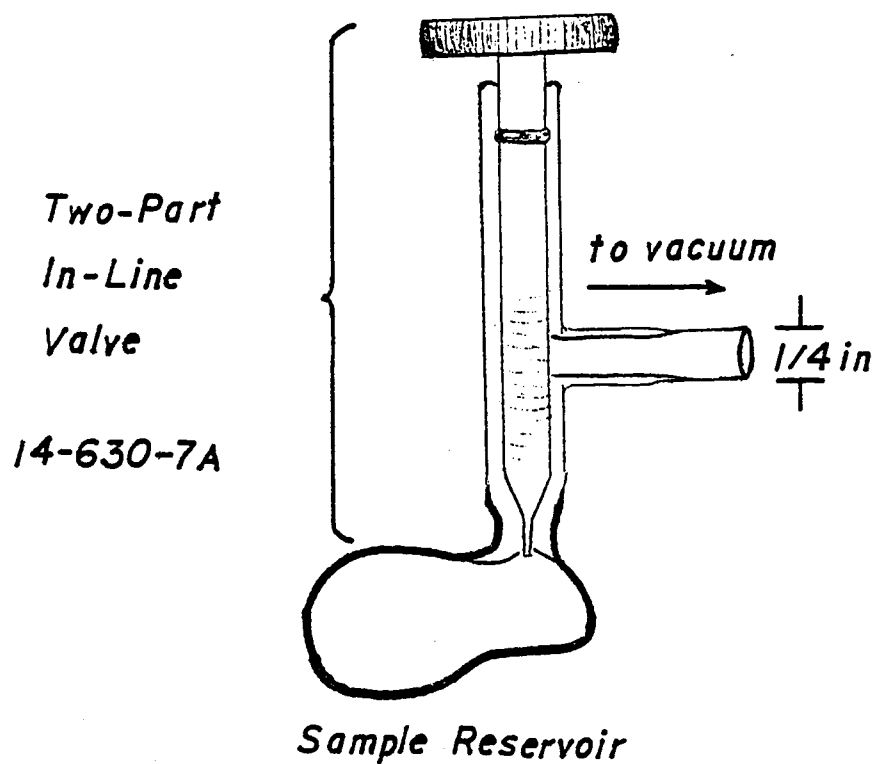


Figure 5. SRM 1580 Sample Container (Fisher, Atlanta; modified by Glassblowing Shop, Dept. of Chemistry, U.T.).

4. Preparation of a Deposit

For qualitative work, the sampling head and windows were cleaned with shelf-grade solvents, acetone followed by hexane. The sample cell and sampling surface were cleaned with distilled-in-glass acetone and hexane; hot solvents were used for cleaning the sample cell.

The deposition process was initiated by placing the prepared sample cell in the Knudsen oven, attaching the sampling head to the cryostat shroud, and opening the rough-and-vent valve (Figure 3, p 18) to evacuate the chamber. Connections were made to the organic matrix line and the matrix reservoir was evacuated through two freeze/thaw cycles performed on the matrix solvent; then, matrix valve 1 (Figure 3) was closed. When the pressure in the shroud measured 50 millitorr or less, the cryostat compressor was switched on. The rough-and-vent valve was closed before one of two conditions was met: either the pressure in the shroud (measured at pressure gauge c'; Figure 3) was equal to the pressure in the vacuum line (pressure gauge c, Figure 3), or the temperature at the cold finger was equal to 77K ($\approx$ the temperature of the cold trap on the vacuum line), whichever came first.

When the temperature of the cold finger reached its lowest value (usually $\approx$ 15K), matrix valve 1 (Figure 3) was opened and matrix alone was deposited for 5 minutes. The temperature of the Knudsen oven was increased during the sample deposition by using a variac to control an increasing voltage across a nichrome wire coiled around the oven. Finally, matrix alone was deposited again for 5 minutes (the initial and final deposition of matrix alone insures that all analyte molecules are exposed to the same matrix environment) for a total deposition time

of approximately 60 minutes. Samples deposited in n-heptane and n-octane were annealed for 5 minutes at 150 K and 155 K, respectively, and the temperature was again lowered to ≈ 15 K before viewing spectra.

Sample deposition times, including cleaning procedures and sample warm up to room temperature, were approximately 4 hours. For quantitative work, sample preparation time was long relative to data acquisition time (30-60 minutes); for qualitative work, the reverse was true (data acquisition spanned several days, several deposits, and several changes of the dye in the dye laser).

B. FLUORESCENCE STUDIES

1. Xenon Lamp Excitation of Fluorescence — Steady-State Spectrometry

The steady-state fluorescence spectrometer (Figure 6) employed in this work has been described.^{3,9,71} A 2.5 Kw high pressure xenon arc lamp (Hanovia; Newark, N.J.) served as the excitation source for this investigation. The spectra were obtained by using a Spex 1702 3/4-meter monochromator (1200 grooves/mm grating blazed at 300 nm), an RCA 8850 photomultiplier tube and photon counting. Typically, the bandpass of the excitation monochromator was approximately 7 nm; the bandpass of the emission monochromator was approximately 0.20 nm.

2. Dye-Laser Excitation of Fluorescence

A Molelectron DL 14P dye-laser pumped by a Molelectron UV 24 nitrogen laser served as a narrow-band excitation source. The dye-laser fluorescence spectrometer (Figure 7) has been described by Maple⁶⁵ and Gore.⁹ At a 10 Hz pulse repetition rate, the output pulse was approximately 7 ns in duration with a bandwidth (FWHM) of about

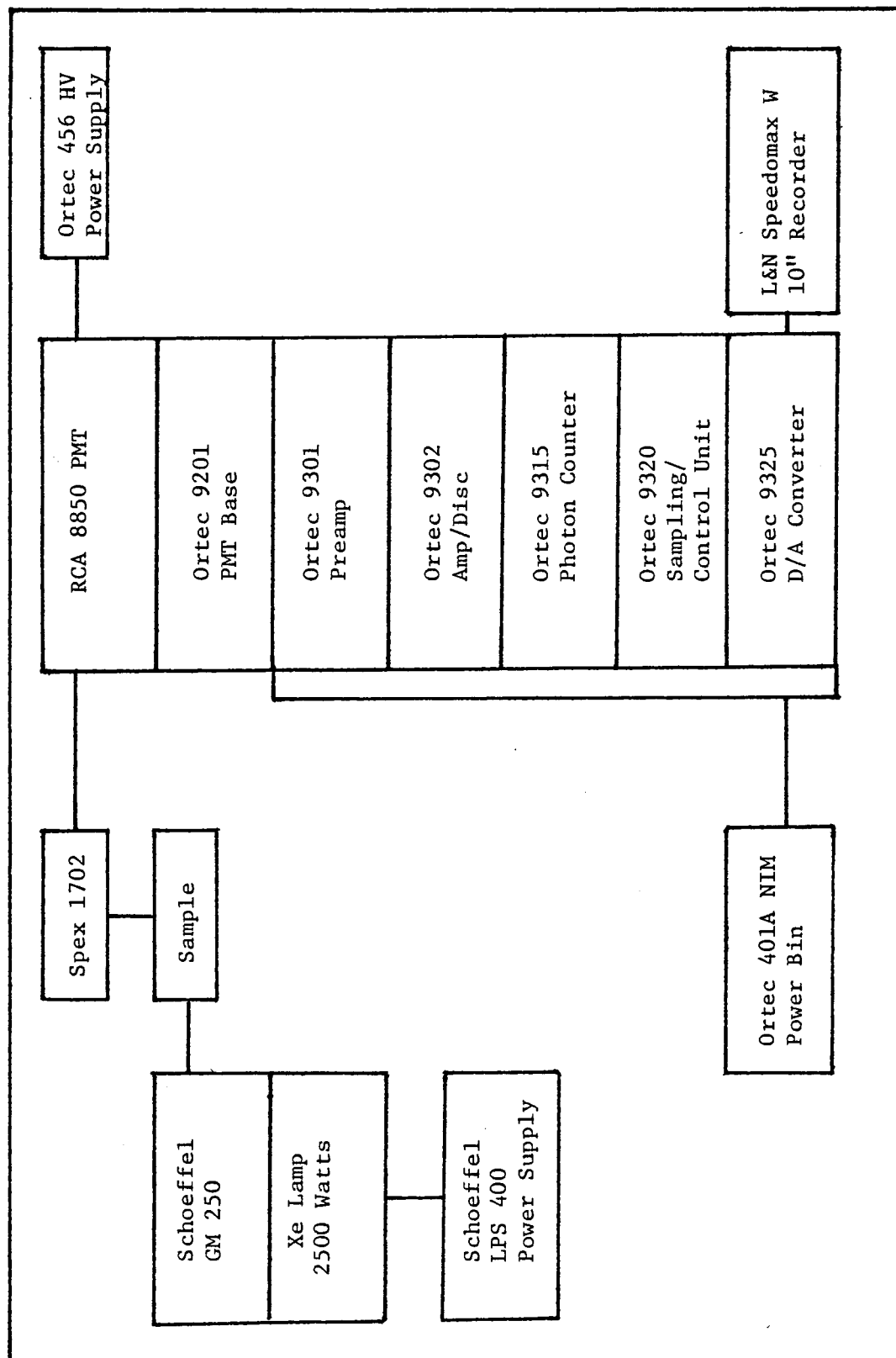


Figure 6. Schematic Diagram of the Steady-State Fluorometer.

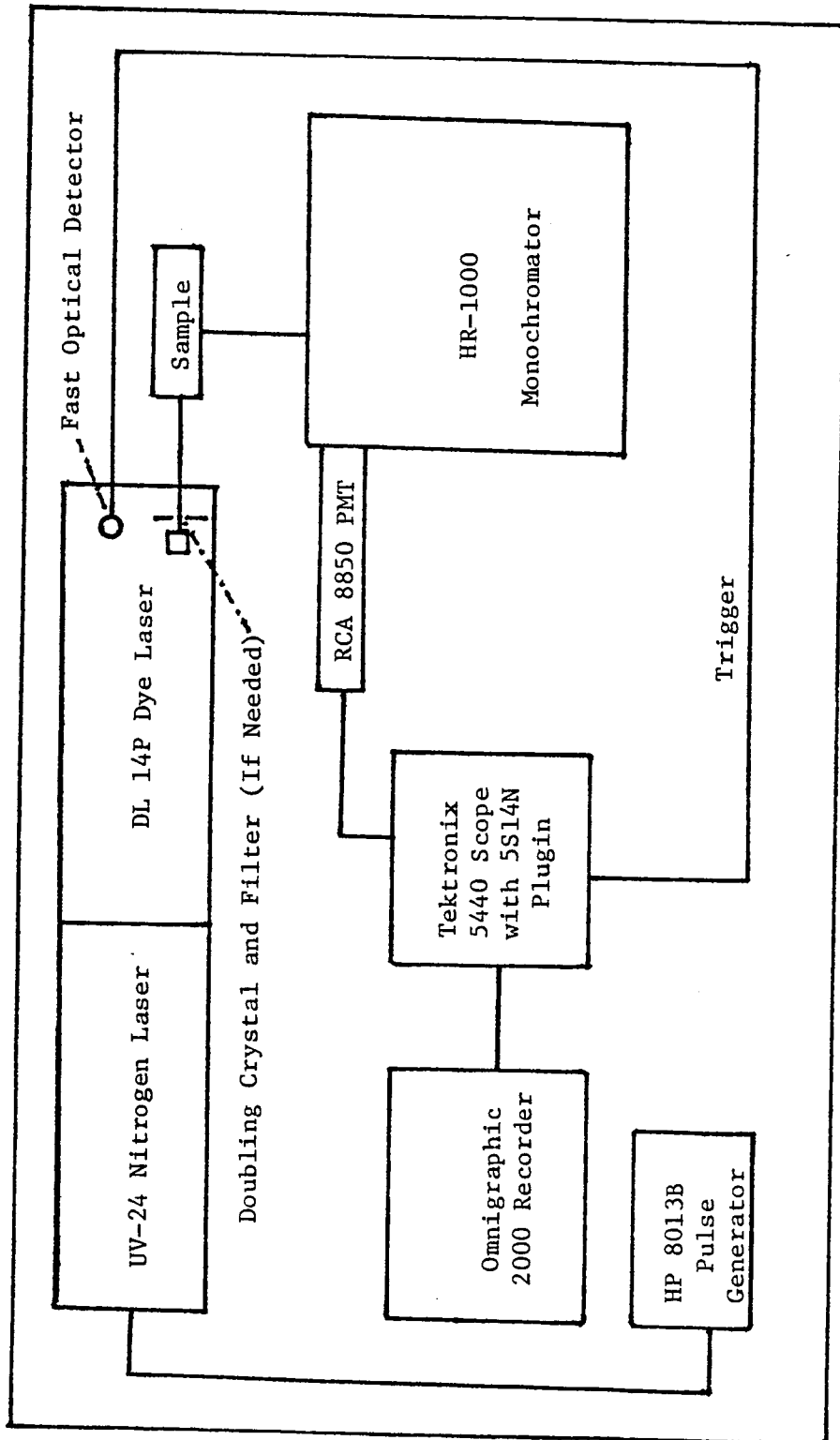


Figure 7. Schematic Diagram of the Dye Laser Spectrometer.

0.02 nm. Angle tuned KDP crystals were used for frequency doubling. Table IV (p 33) is a listing of laser dyes used.

Minor modifications in previous modes of operation of the laser spectrometer resulted in an increase in the fluorescence signal measured. In past studies, the incident exciting laser beam had been used at a glancing angle (relative to the sample surface). Use of a more acute (up to 30°) angle of incidence resulted in an increased signal, often twice as great as that produced by glancing incidence, with an accompanying increase in background, but which permitted the use of narrower emission monochromator slits and/or a lower photomultiplier tube voltage. Use of a quartz (55 mm focal length), instead of a glass, lens to collect fluorescence resulted in an increased signal. Most important, cleaning the optics of the UV 24 nitrogen laser and re-alignment of both lasers, and purchasing new dye cuvettes, gave the greatest improvements in fluorescence signals.

3. Quantitation of PAHs

All quantitative analyses were performed using the dye-laser spectrometer described previously. Experiments were designed to evaluate signal sampling procedures, to assess the precision of the method, and to determine the accuracy of the method. For each sample, experiments were performed to optimize the deposition procedure, including the amount of sample used, amount of matrix used, and the time required for the deposit. For each analyte, the optimum excitation wavelength, optimum time delay, and an appropriate internal standard had to be chosen. Parameters used in preparing quantitative plots are summarized in Table V.

TABLE IV
LIST OF LASER DYES

Abbreviation	Complete Name	Solvent	Concentration (M)	Wavelength Range (nm)
PBD	2-(4-biphenyl)-5-phenyl- 1,3,4-oxadiazole	Toluene/Ethanol 50/50	5×10^{-3}	360-386
BBQ	4,4''-bis-butylactyoxo- quarterphenyl	Toluene/Ethanol 50/50	2.5×10^{-3}	373-399
PBBO	2-(4'-biphenyl)-6-phenyl- benzoxazole	Toluene/Ethanol 70/30	5×10^{-4}	391-411
C 495	Coumarin 495	Ethanol	10^{-2}	515-583
R6G	Rhodamine 6G	Ethanol	5×10^{-3}	568-605
RB	Rhodamine B	Ethanol	5×10^{-3}	594-643

TABLE V
PARAMETERS USED FOR QUANTITATIVE PLOTS

Sample	Analyte	Int. Std.	$\lambda_{exc.}$ (nm)	Time Delay Analyte	Time Delay Int. Std.	Measurement
SRM 1580	BaP	Per, 375ng	389.3	40ns	Ons	I_F BaP/ I_F Per
SRM 1580	Py	BaP, 75ng	274.5	80ns	80ns	I_F Py/ I_F BaP
SRC I	BaP	Per, 90ng	389.3	40ns	Ons	I_F BaP/ I_F Per
SRC I	Per	BaP, 40ng	389.5	Ons	60ns	I_F Per/ I_F BaP
SRC I	BaA	BaP, 40ng	291.8	60ns	60ns	I_F BaA/ I_F BaP
SRC I	BbF	Py, 0ng	275.0	20ns	80ns	I_F BbF/ I_F Py

a. Preparing the sample deposit. Special precautions were taken in the preparation of the MIF deposits used for quantitation of PAHs. The SRC I was sieved to particles $\leq 46 \mu\text{m}$. Matrix gases and cleaning solvents were high purity. The sampling head and cryostat shroud were cleaned with distilled-in-glass (UV grade) n-hexane (Burdick and Jackson; Muskegon, Michigan); 99.8% (GC) n-octane (Tridom Chemical, Inc.; Hauppauge, N.Y.) was used as the matrix gas. Sample cells were cleaned by flaming with a Bunsen burner, followed by boiling first with either distilled-in-glass benzene (Burdick and Jackson; Muskegon, Michigan) or A.C.S. Certified toluene (Fisher Scientific; Fairlawn, N.J.), followed with two washes in hot distilled-in-glass n-hexane. Deposition conditions were duplicated as precisely as possible from sample to sample.

Four deposits of sample (including an internal standard) were used to obtain a quantitative plot. The first deposit contained no analyte spike; the remaining three deposits were spiked with varying weights of analyte.

b. Processing the signal. Since MIF spectral features are very narrow (especially in Shpol'skii matrices), the spectral peak height was assumed to be a good measure for fluorescence intensity. Background corrections were made by approximating the slope of the background preceding the peak (on the short wavelength side) and drawing a straight line along the slope midway between the negative and positive deviations of the background trace. An ordinary ruler (graduated in millimeters) was used to measure the vertical distance from the top of the spectral feature to the intersection of that line

with the slope of the background. The ratio of the analyte peak height to that of an internal standard was obtained in this manner.

c. The quantitative plot. Each point in quantitative plots represented the mean of the ratio (I_P , analyte/ I_P , internal standard) of five pairs collected sequentially for a single MIF deposit. Taking the mean of 5 ratios minimized the scatter in the data, and collecting the peaks in pairs minimized error which might result from photodecomposition of the internal standard and/or the analyte. Four points defined the quantitative plot from which the concentration of the analyte in the sample could be calculated by using a linear regression analysis. A confidence interval for the calculated value was determined at the 95% confidence level by using a procedure described by Larsen, et al.⁷² for standard addition. The accuracy of the method was evaluated by performing a replicate analysis of BaP in an NBS shale oil Standard Reference Material (SRM 1580).

CHAPTER III

RESULTS AND DISCUSSION

Evaluation of the analytical utility of matrix isolation fluorescence spectrometry for the direct analysis of real samples for PAH content required consideration of several aspects of the experiment, namely: choice of sample(s) used, limitations of the MIF procedure, and limitations involved in signal acquisition and processing.

A. REAL SAMPLES

The motivation for using SRC I as the primary sample in this work included the following considerations. First, SRC I was believed to contain PAHs at concentrations within the known range of detection for MIF. Second, it was considered to be relatively unlikely that the solid sample would have undergone appreciable degradation upon storage (in contrast, many coal-derived liquid samples are demonstrably unstable). Third, the sample was of sufficient complexity to assess the realistic potential of MIF for direct analysis of PAHs in real samples. Since, to our knowledge, the SRC I had not been previously characterized and since there were no comparable solid standard reference materials available, an NBS shale oil Standard Reference Material (SRM 1580) was chosen to evaluate the accuracy of the method for PAH analysis. The differences in procedures for the two samples arose of necessity from the fact that SRC I was solid (measured by weight) and SRM 1580 was liquid (measured by volume).

B. LIMITATIONS OF THE MIF PROCEDURE

MI spectra have been obtained for pure PAHs when the mole ratio of matrix gas to PAH was 10^2 to 10^5 .³ Deposits of real samples contain not only PAHs but also all other sample constituents which have an appreciable vapor pressure within the range of oven temperatures used in making the deposit. A typical sample size for spectral characterization of an individual PAH normally would be 50 ng to 1 μ g; approximately 30 minutes was normally required to make the deposit. For more complex samples, longer deposition times were required. Therefore, the sample size was limited by two requirements of the MIF experiment: the sample had to be large enough that individual PAHs of interest were present within the range of detection, but not so large that PAHs were not isolated in the matrix material. To some extent, the sample could be diluted in the deposit by using longer deposition times (1-2 hrs.) and/or a higher than usual flow rate for the matrix gas. The flow rate that could be used was limited by the cooling capacity of the cryostat. In addition, thick deposits tended to be highly scattering, creating additional problems in data acquisition. A reasonable compromise was reached by increasing the flow rate of the matrix gas by $\approx 25\%$ for real samples (typically ≈ 0.5 millimole/hour of matrix gas was used for deposits of pure PAHs³), and by using long deposition times (1-2 hrs.).

The choice of matrix gas to be used was an important consideration. Trial-and-error would have been very time consuming, so only the more commonly used matrix materials were considered. Nitrogen has been a commonly used matrix gas for MIF, but spectral features of most

PAHs were fairly broad ($50\text{--}100\text{ cm}^{-1}$) in this matrix. Features in lamp-excited spectra of SRC I likewise were broad (Figure 8) when nitrogen matrices were used. Dye-laser excited spectra from deposits of SRC I in nitrogen contained unexplained "glyches". Nitrogen was therefore rejected as a matrix.

Argon, another commonly used matrix material, also was considered but rejected for the following reasons. First, the fluorescence efficiency of many PAHs is relatively low in argon. Second, although line-narrowing has been demonstrated for PAHs in argon,⁹ it was observed under site-selection conditions and, although useful for resolving a compound in the presence of an interferent, gave no increase in the intensity of the fluorescence signal, but rather a decrease in the signal when compared with spectra obtained under selective excitation conditions. As noted by Gore,⁹ molar absorptivities for PAHs are very small in the excitation regions required for site selection. Indeed, the conditions required for sensitive detection of PAHs by "site selection" in argon have not yet been fully delineated, even for pure PAHs. Features of lamp-excited SRC I spectra (Figure 9) were broad. Finally, dye-laser excited SRC I spectra contained bothersome "glyches". Argon was therefore rejected as a matrix.

Shpol'skii matrices were considered to be the best choices because of the very narrow but intense "quasilines" produced for PAHs in annealed MI deposits. Since several of the PAHs of interest (BaP, BaA, and BbF) yield multiplets in n-heptane, and singlets in n-octane, these two Shpol'skii solvents were considered to be the best matrix

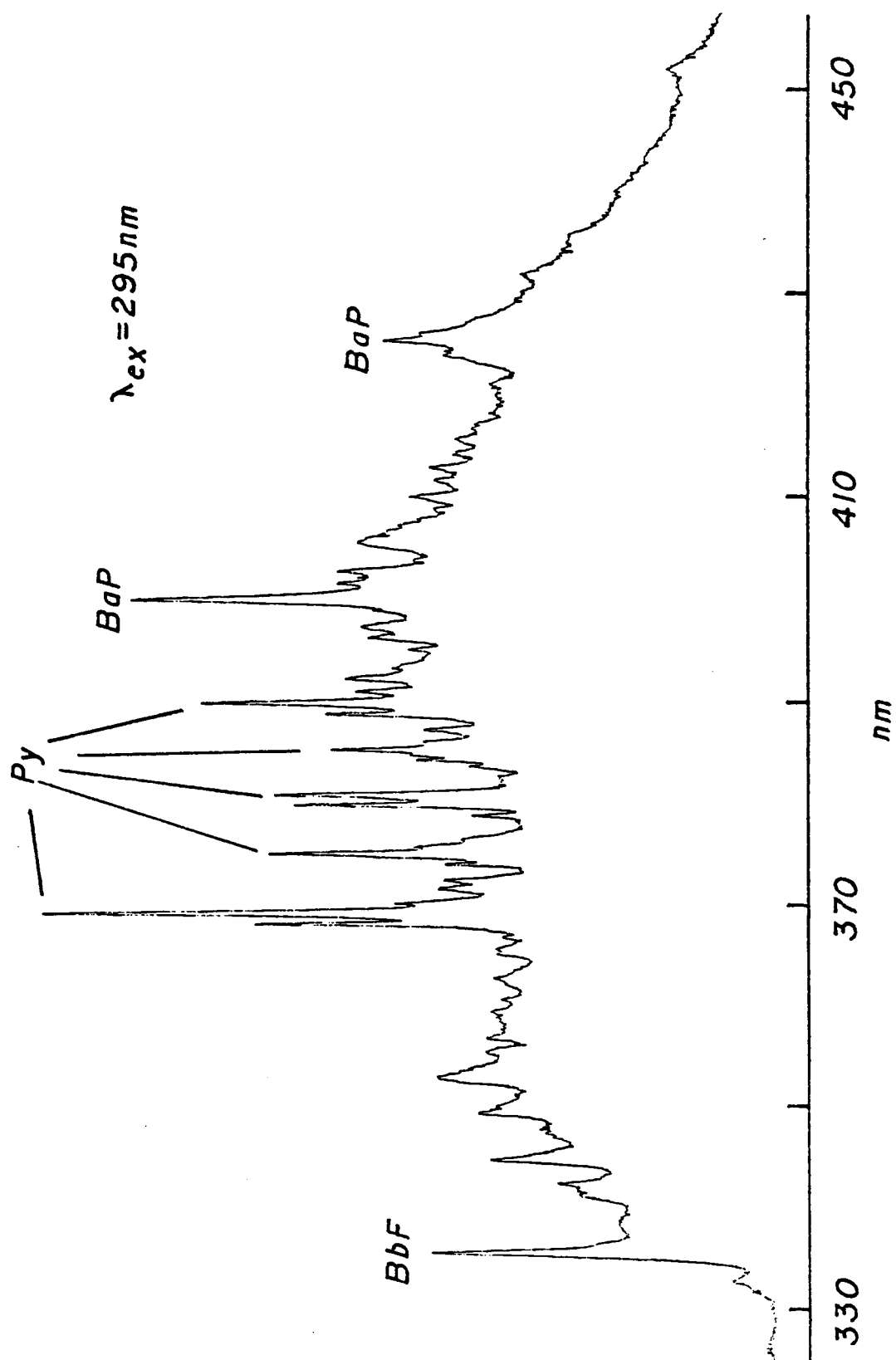


Figure 8. SRC I Spectrum in Nitrogen Matrix.

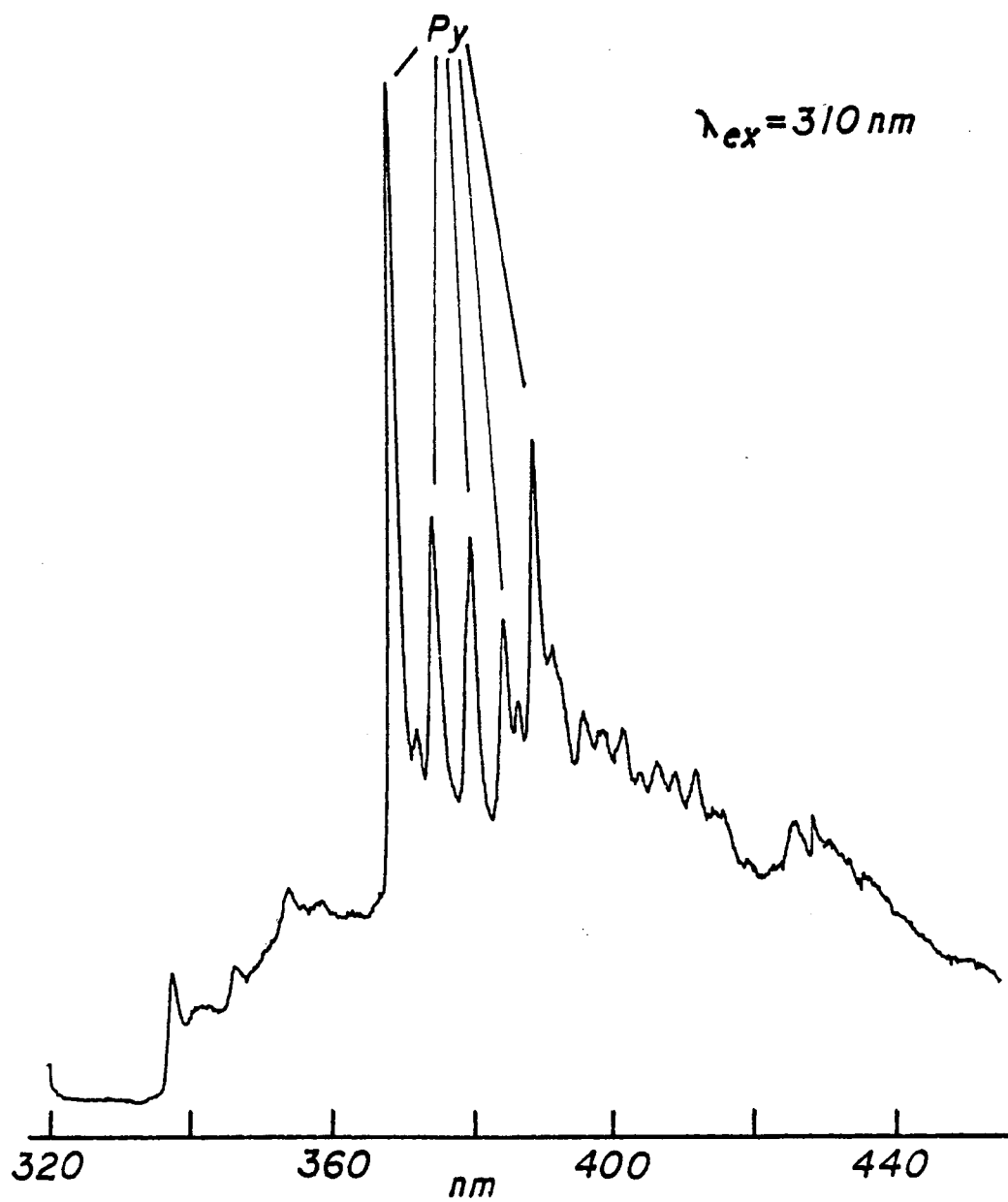


Figure 9. SRC I Spectrum in Argon Matrix.

gases to be used for analysis of SRC I and SRM 1580. The multiplets observed in n-heptane served as an excellent fingerprint for identification (Figure 10A), while the singlets observed in n-octane (Figure 10B) were considered more useful for quantitation.

C. LIMITATIONS IN SIGNAL ACQUISITION AND PROCESSING

The steady-state fluorescence spectrometer (p 30) was used to survey deposits of SRC I for PAH content preliminary to analysis with the dye-laser spectrometer (p 31). Problems encountered when using xenon-lamp excitation of fluorescence (background, spectral overlap, and photodecomposition) were largely overcome by using the dye-laser spectrometer. Background contributions to lamp-excited fluorescence spectra were reduced to some extent by using a narrower range of temperature rather than the full capacity of the Knudsen oven (Figure 11). Spectral overlap was a problem with xenon-lamp excitation as evidenced by the inability to resolve BaA from pyrene at any excitation wavelength. Because of the narrow-band nature of the dye-laser source, selective excitation was much more feasible with the laser spectrometer than with the xenon lamp spectrometer. Finally, photodecomposition of some PAHs was observed with both excitation sources; however, since the laser beam is so small (≈ 2 mm in diameter) with respect to the sample deposit (≈ 1 cm), the sample could be raised or lowered and fresh sample could thus be illuminated. In contrast, the image of the xenon lamp virtually filled a sample deposit, so that photolysis occurred across virtually an entire deposit when the lamp spectrometer was used.

BaP in SRC I

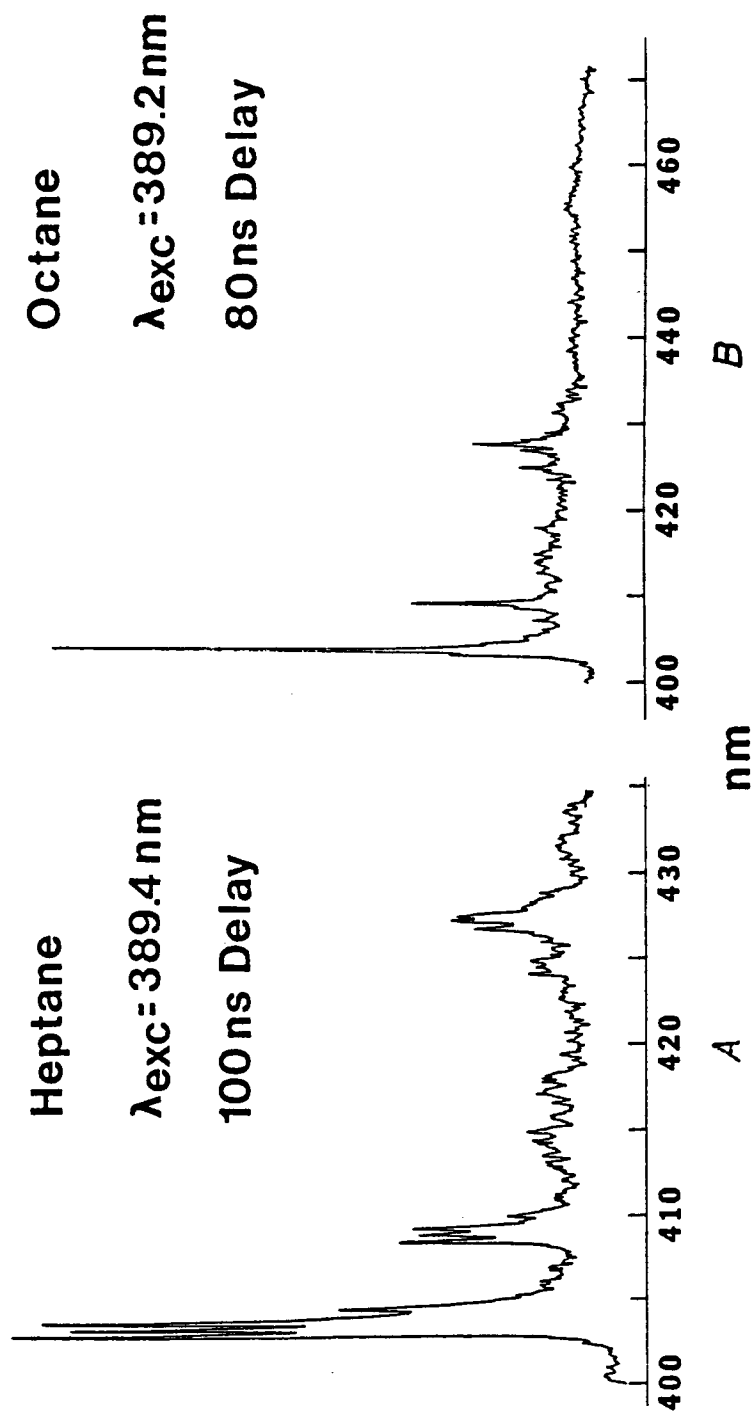


Figure 10. Fluorescence Spectra of BaP Selectively Excited in SRC I.

Effect of Temperature on Xe Lamp Spectra

SRC I in Heptane

$\lambda_{ox}=305\text{nm}$

20° - = 190°C

20° - = 90°C

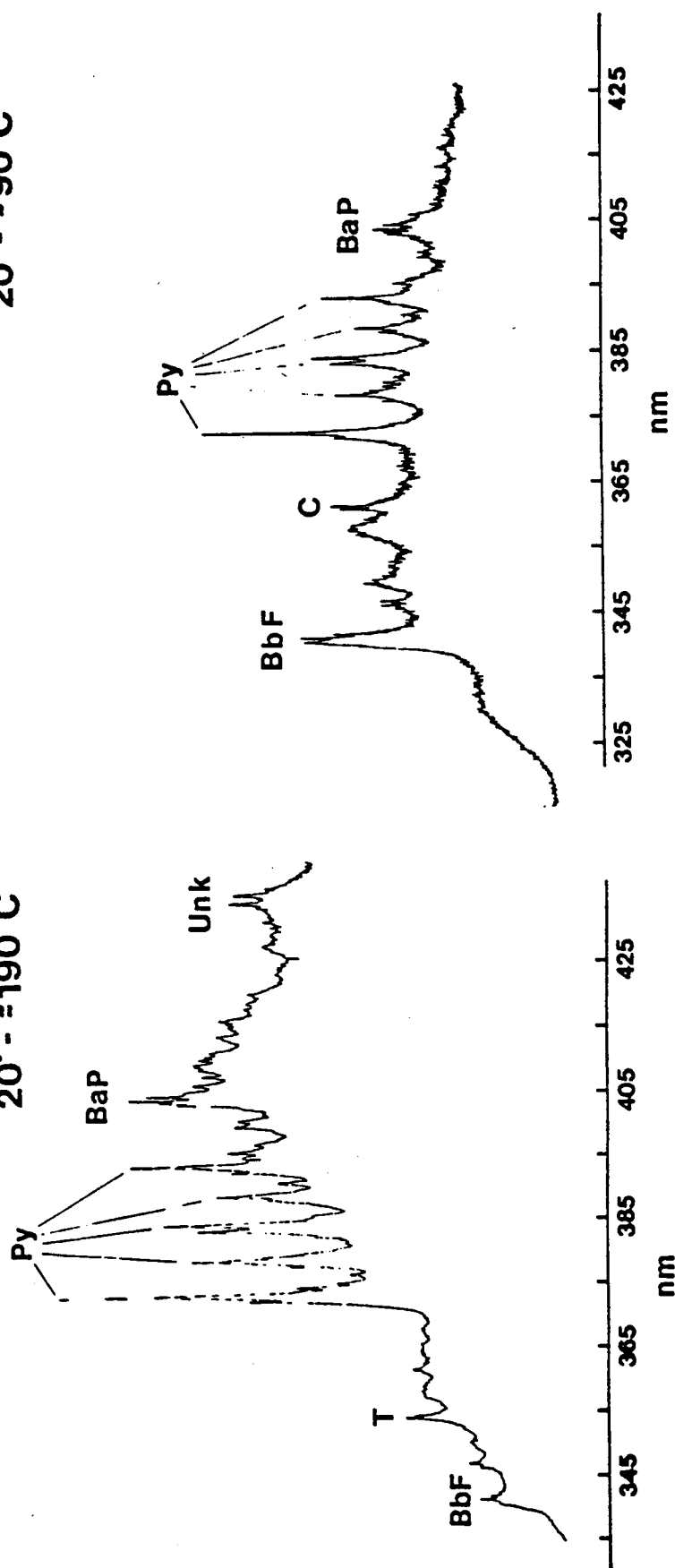


Figure 11. Effect of Temperature of Knudsen Oven on Lamp Spectra of SRC I.

Problems associated with the use of the dye-laser spectrometer were described earlier (Chapter 1, pp 14-15). More specifically, they may be summarized as follows:

1. Use of several different dyes was necessary for the analysis of real samples, requiring frequent re-tuning of the dye laser.
2. It was necessary to minimize scattered dye fluorescence to prevent its interference with sample emission at wavelengths near the excitation wavelength, an especially significant problem for weak fluorescence signals. Placing a piece of polarizing film between the oscillator and amplifier dye cells, and narrowing the laser aperture, generally minimized scattered dye fluorescence.
3. Frequency doubling of the dye laser output, with a concurrent decrease in laser power (optimum frequency doubling efficiency was about 7 %), was necessary to observe several PAHs in SRC I.
4. The sampling oscilloscope was set up to take measurements through a relatively narrow time "window" (350 picoseconds), negating the possibility of acquiring phosphorescence spectra at a reasonable signal-to-noise ratio.
5. Pulse-to-pulse variations in laser power, tolerable when exciting with the fundamental, were considerably more severe when frequency doubling was used.

In spite of the problems cited, the dye-laser spectrometer was highly dependable and the laser required little maintenance.

D. STEADY-STATE LAMP-EXCITED FLUORESCENCE RESULTS

Several PAHs were identified in SRC I using xenon-lamp excitation of fluorescence (Figures 12 and 13). The capability of sampling the phosphorescence signal as well as the fluorescence signal permitted verification of the presence of phenanthrene in SRC I; phenanthrene exhibits fluorescence bands in a congested region in SRC I spectra.

Deposits of SRM 1580 yielded no distinct spectral bands which could be assigned to PAHs. Instead, lamp-excited fluorescence spectra were very broad (Figure 14); therefore, no PAHs were identified in SRM 1580 under these conditions. There are two possible causes for this situation. First, the shale oil may have been a more complex sample than SRC I. SRM 1580 contained large amounts of polar compounds which have been shown to exhibit broad spectral features even under MI conditions with lamp excitation.⁶⁹ Alternatively, vacuum sublimation from the Knudsen oven may have been less effective at simplifying the shale oil deposits. SRC I had been subjected to treatment with solvents and high temperatures and probably retained relatively little volatile material, whereas the shale oil liquid was probably replete with volatile components. Probably both situations apply.

E. DYE-LASER EXCITED FLUORESCENCE SPECTRA

When Shpol'skii matrices are used, the emission bands of most PAHs are very narrow (typically $1-10\text{ cm}^{-1}$); absorption bands are similarly narrowed. By selecting an excitation wavelength which is coincident with a narrow absorption band of a particular PAH, that compound can be excited selectively in the presence of other PAHs which have nearby

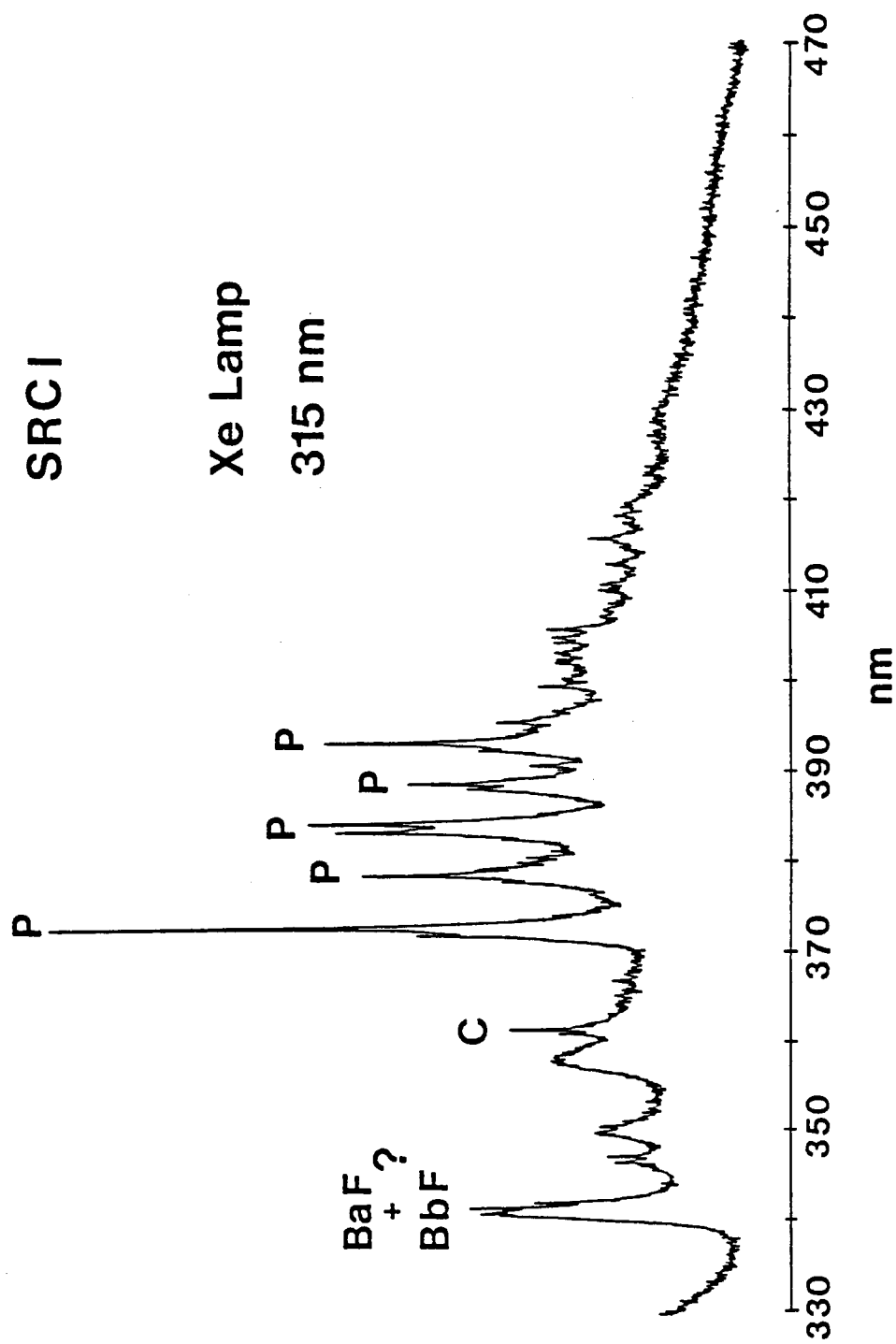


Figure 12. Lamp Spectrum of SRC I in Heptane.

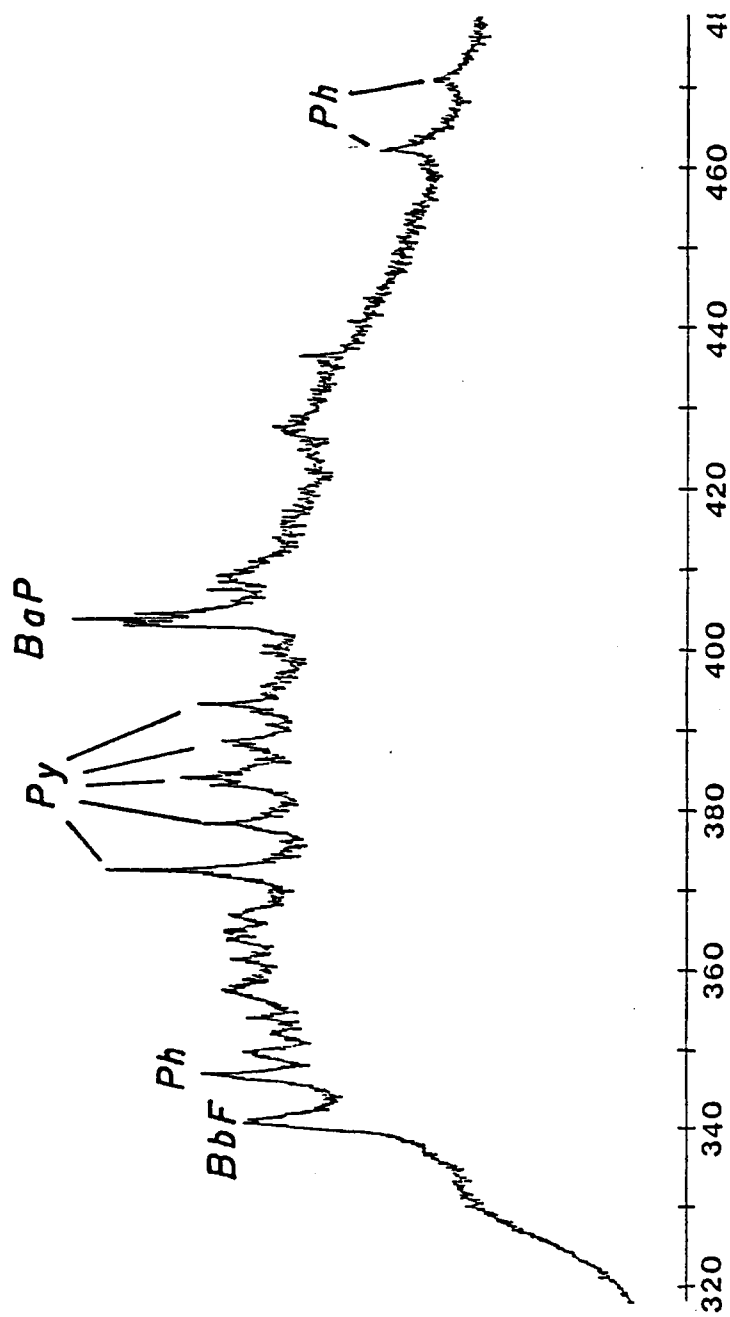


Figure 13. Phenanthrene Confirmed from Phosphorescence Bands in Lamp Spectrum of SRC I in Heptane at $\lambda_{\text{exc}} = 300 \text{ nm}$.

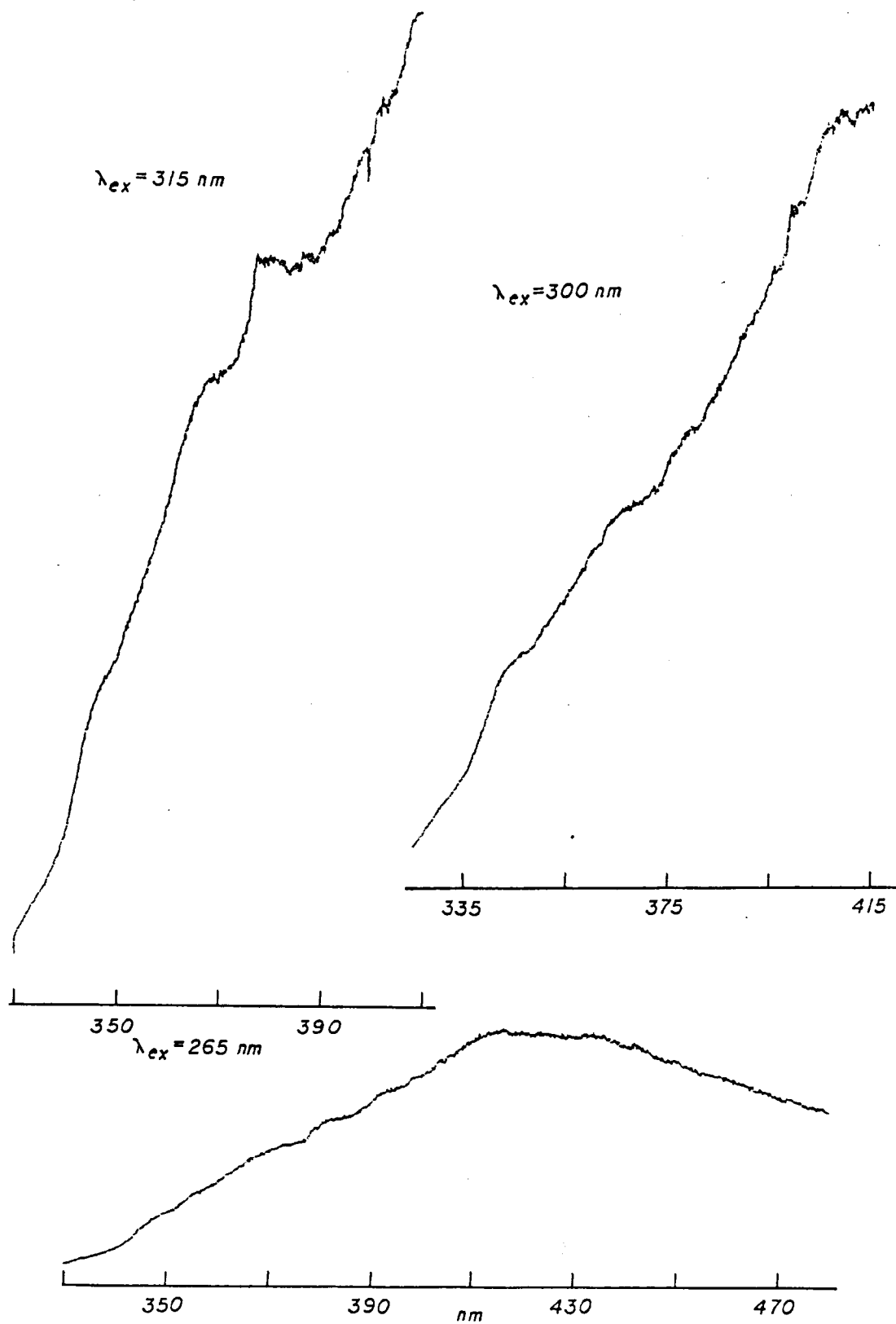


Figure 14. Lamp Excited Spectra of SRM 1580.

(but not enveloping) absorption bands. Most PAHs have several absorption bands which can be accessed. The probability of spectral interference from other PAHs with overlapping absorption bands decreases as the excitation wavelength approaches the emission wavelength until, in the limit, only molecules of that PAH occupying certain sites in the matrix will be excited to fluoresce (site-selection conditions).

However, molar absorptivities of PAHs decrease as the excitation wavelength approaches the near UV (Table VI) and limits of detection consequently increase. Laser power is higher in this region where the lasing fundamental can be used. BaP (Figure 15), 7,10-DM BaP (Figure 16), and perylene (Figure 17) were identified in SRC I using selective excitation.

Time resolution was used extensively throughout this work. The time-resolution capability of the dye-laser spectrometer was highly effective in reducing background in spectra of real samples. This was clearly demonstrated for spectra of BaA in SRC I (Figure 18). The time resolution capability proved to be useful in confirming the identities of BbF and BaF in SRC I after observing the temporal behavior of a mixture of the two compounds (Figure 19).

BaP has been shown to be time-resolved in the presence of a large excess of BkF,⁶³ but the identification of BkF in the presence of BaP in real samples is a more difficult problem. BkF was identified in SRC I using selective excitation and short time delays (Figure 20). Since BkF has a much shorter fluorescence lifetime than BaP, at increasing time delays BaP was found to interfere with BkF even at this excitation wavelength.

TABLE VI
MOLAR ABSORPTIVITIES FOR SEVERAL PAHS IN ISOCTANE
AT ROOM TEMPERATURE⁷³

Compound	Excitation Wavelength (nm)	Molar Absorptivity (M ⁻¹ cm ⁻¹)
Triphenylene	341.5	113
	290.1	9,305
	257.6	174,646
Benz(a)anthracene	383.4	850
	358.6	5,075
	299.1	9,978
	287.6	95,000
Tetracene	473.7	9,160
	295.1	24,399
	276.8	292,019
Benzo(e)pyrene	372.3	200
	326.6	4,900
	294.6	12,900
	281.1	97,900
Pyrene	371.1	125
	334.7	59,800
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	240.6	91,700
Chrysene	360.8	700
	319.8	13,700
	267.7	163,700

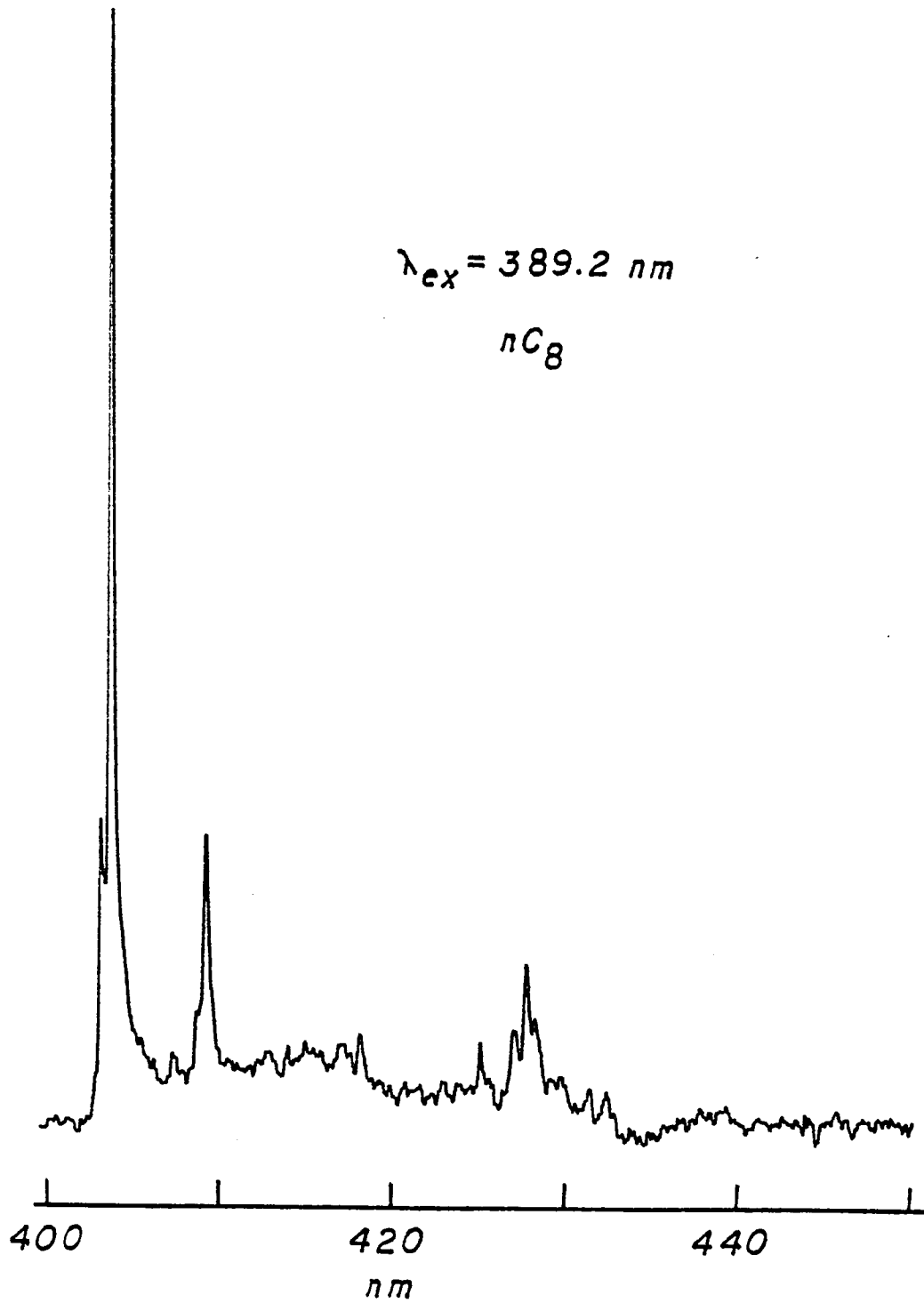


Figure 15. BaP Identified in SRC I.

Laser
 $\lambda_{\text{exc}} = 365.0 \text{ nm}$
60 ns Delay

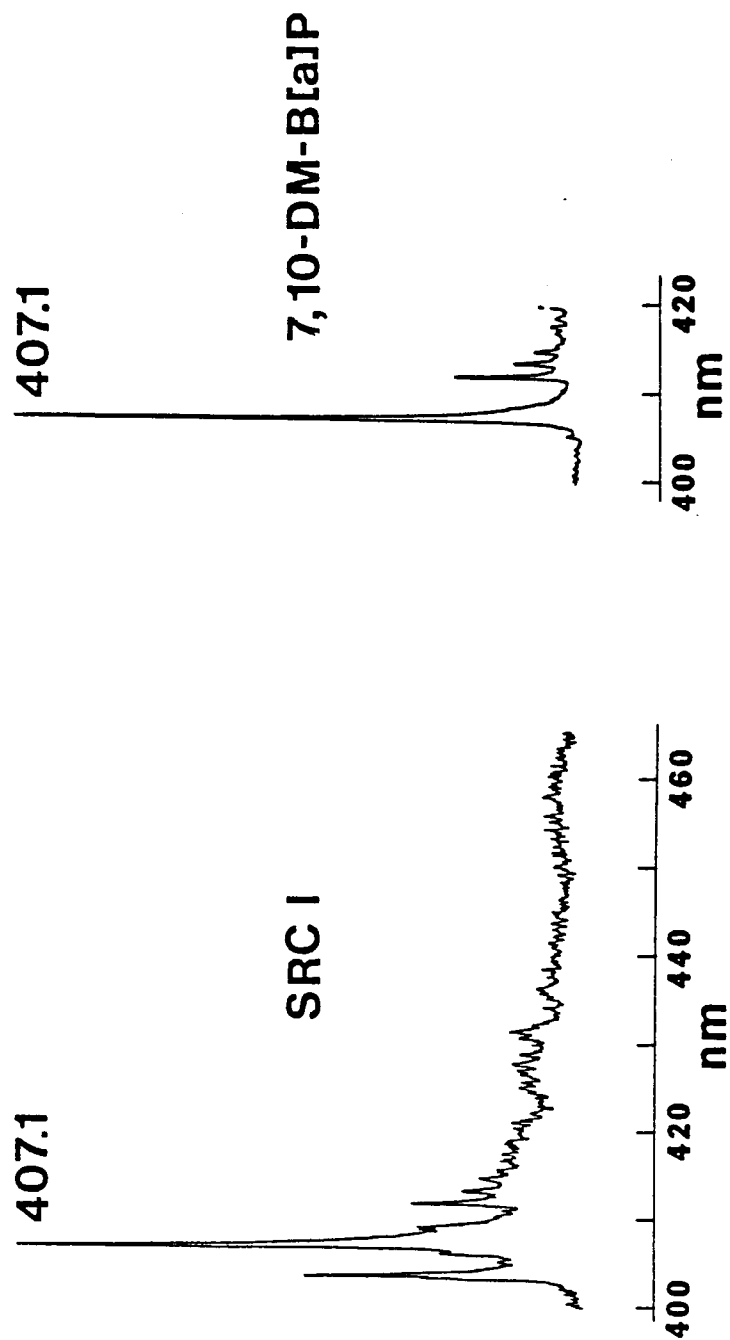


Figure 16. 7,10-Dimethylbenzo[a]pyrene Identified in SRC I.

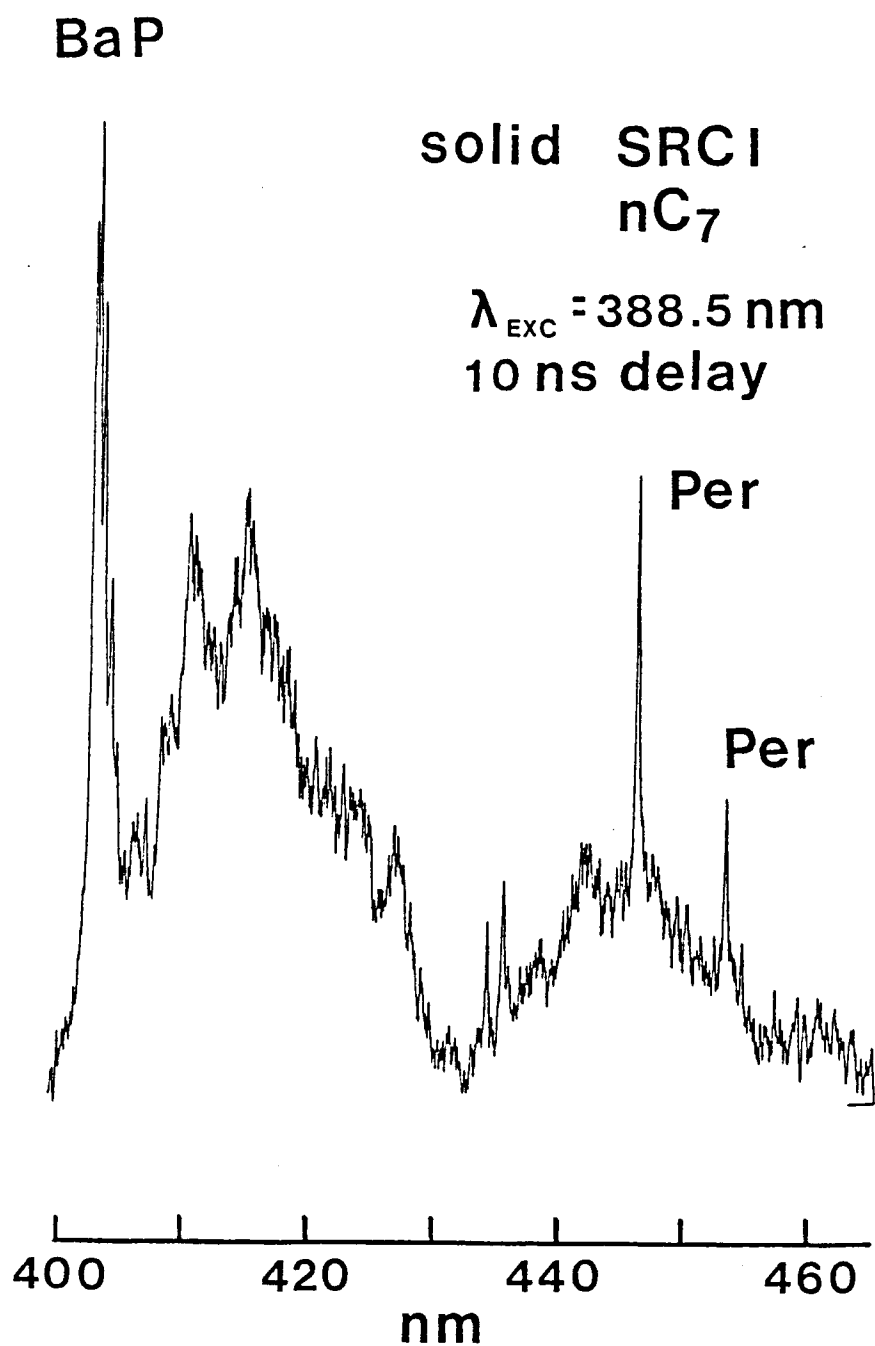


Figure 17. Perylene Identified in SRC I.

SRC I in nCg: Background Suppressed

with Time Delay

$\lambda_{EX} = 283.0\text{nm}$

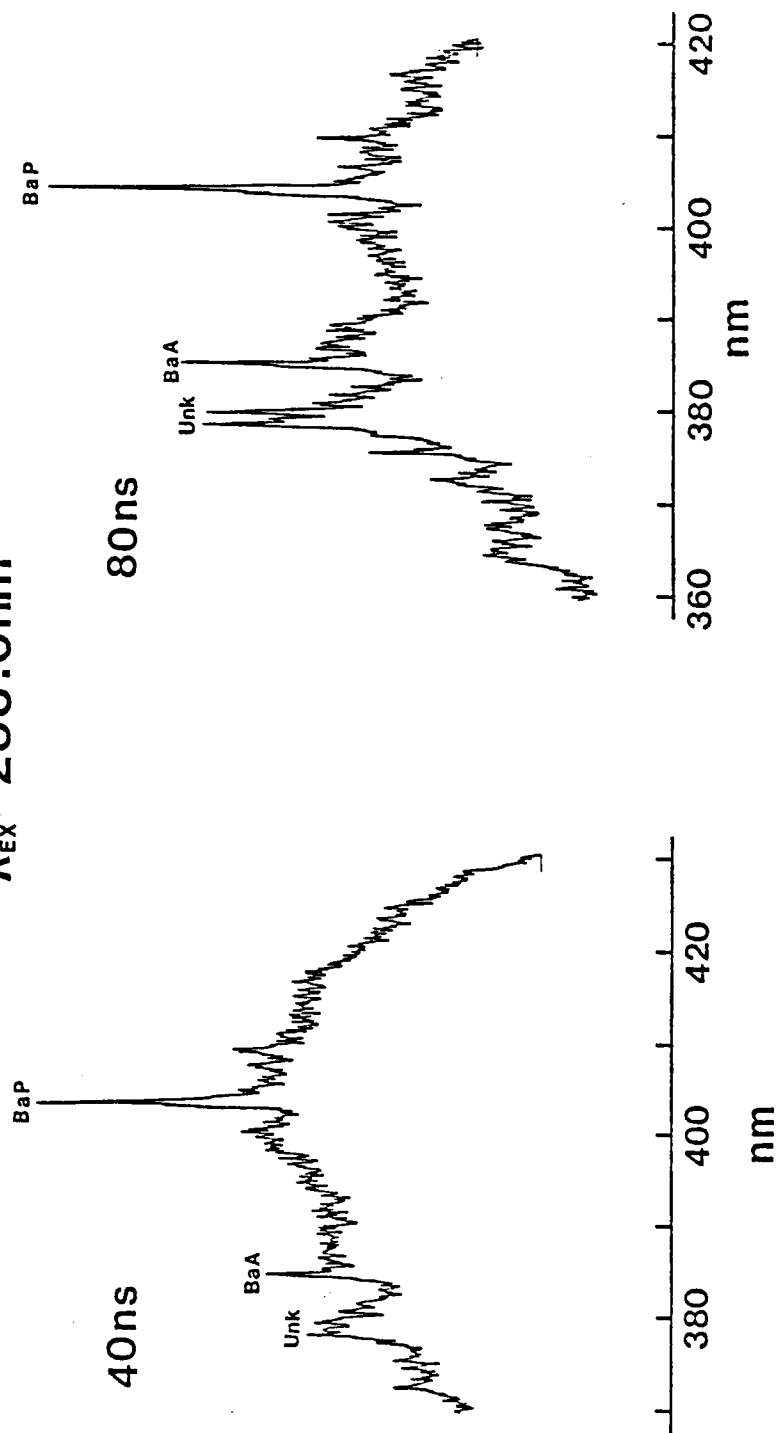


Figure 18. Effect of Using Time Delay in Reducing Background.

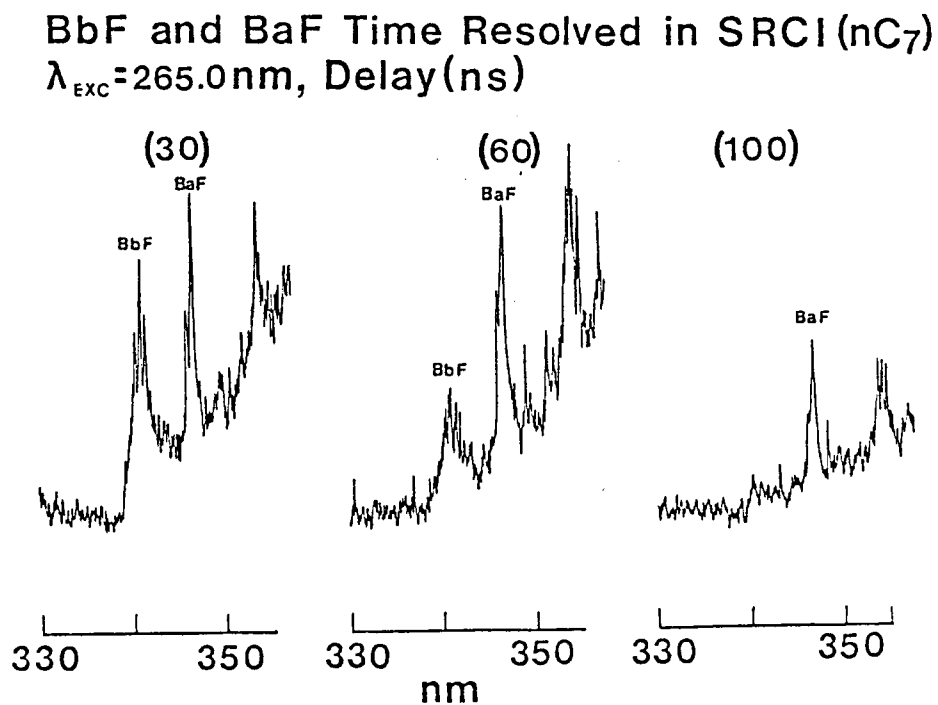
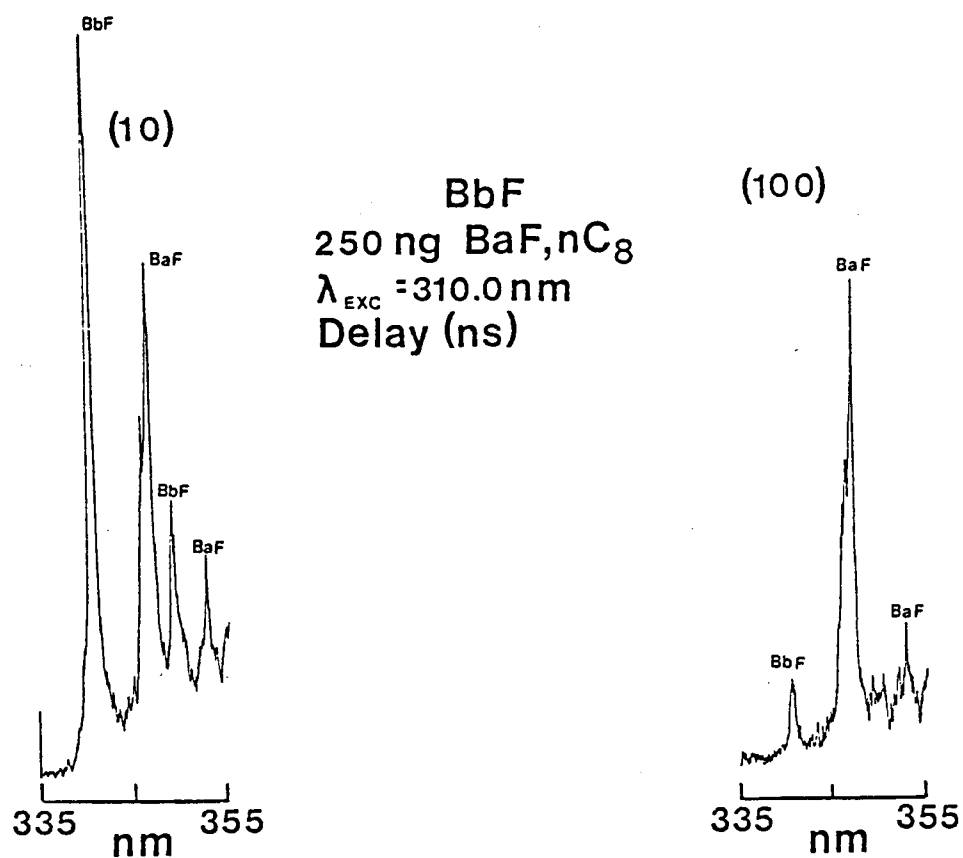


Figure 19. Temporal Behavior of a Mixture of BaF and BbF, and SRC I.

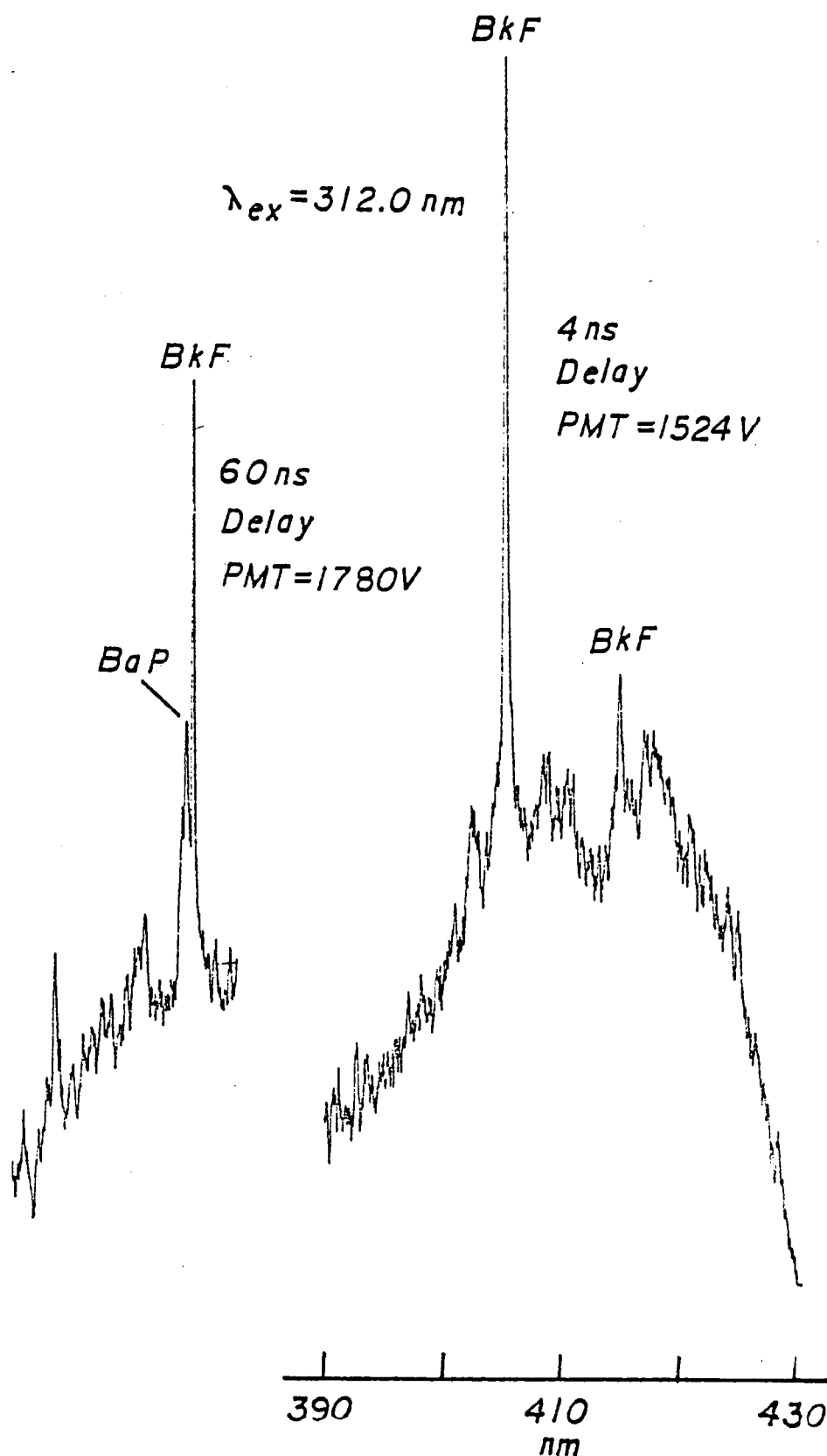


Figure 20. Benzo[k]fluoranthene Identified in SRC I.

Spiking the sample with a solution of a pure PAH suspected to be present in the sample was often useful for identifying unknown peaks in spectra of SRC I deposits. As shown for chrysene (Figure 21) and benz[a]anthracene (Figure 22), a peak was first noted in the spectrum of SRC I. If that peak matched, in $\lambda_{\max}$, a major peak in the library spectrum of a pure PAH, a second deposit was prepared which was spiked with the suspected compound. An increase (without shift in band location or production of a spectral multiplet) in the intensity of the suspected peak, with regard to the remainder of the spectrum, verified the identity of the suspected compound. The time delay was kept constant. Evaluation of the temporal behavior of the suspected compound and of the spectral feature in question would have yielded further support for identification of unknowns.

The PAHs identified in SRC I by the techniques described above are compiled in Table VII.

F. QUANTITATION OF PAHS IN REAL SAMPLES

Quantitative results for the direct analysis of real samples by MIF have not been previously reported. Mohan⁷¹ reported results for the quantitation of BaP in a PAH fraction (HPLC) of shale oil. A quantitative analysis of SRC I and SRM 1580 using the dye-laser spectrometer was undertaken in this work.

Several problems associated with the dye-laser spectrometer which may have been innocuous for qualitative work were of special significance for quantitative work:

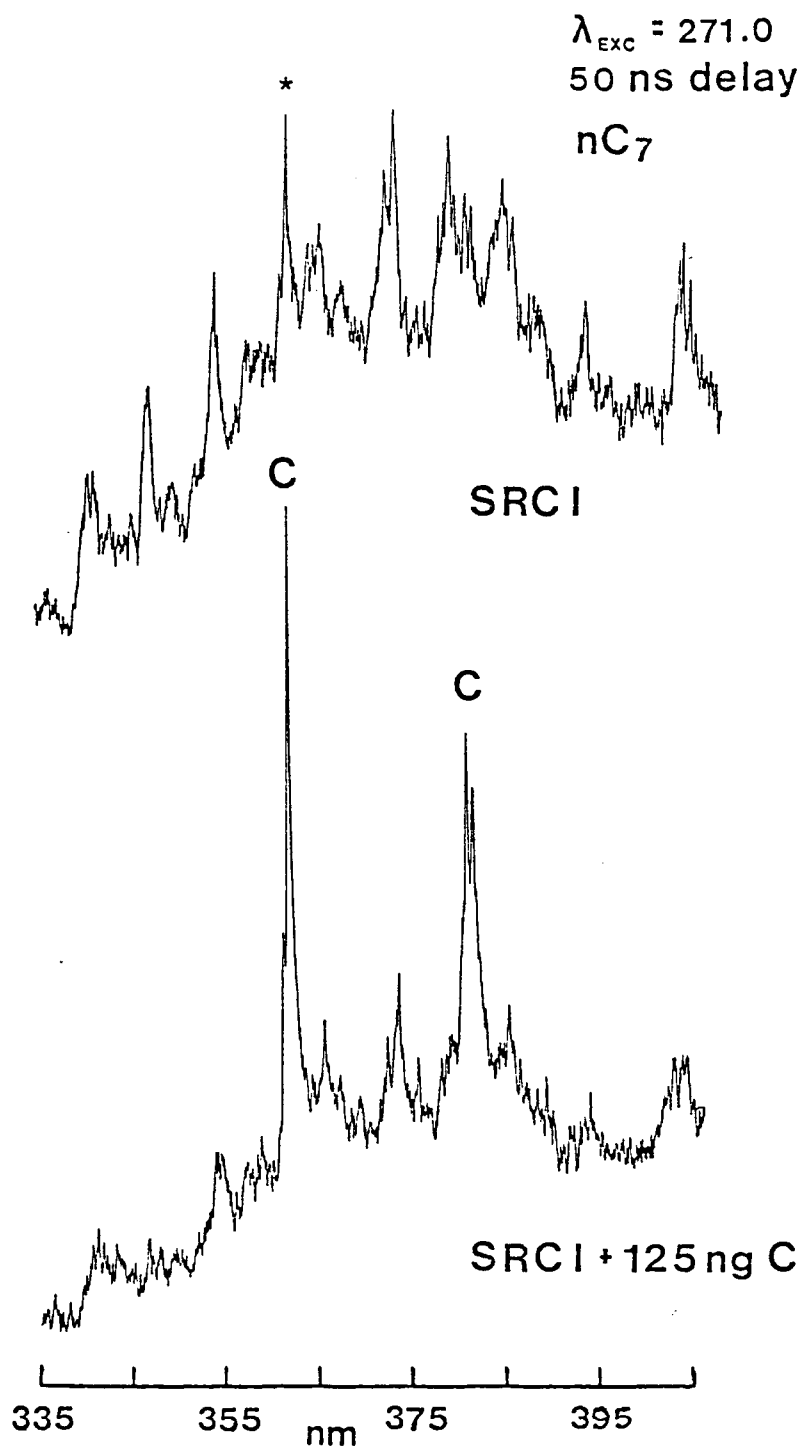


Figure 21. Chrysene Identified in SRC I.

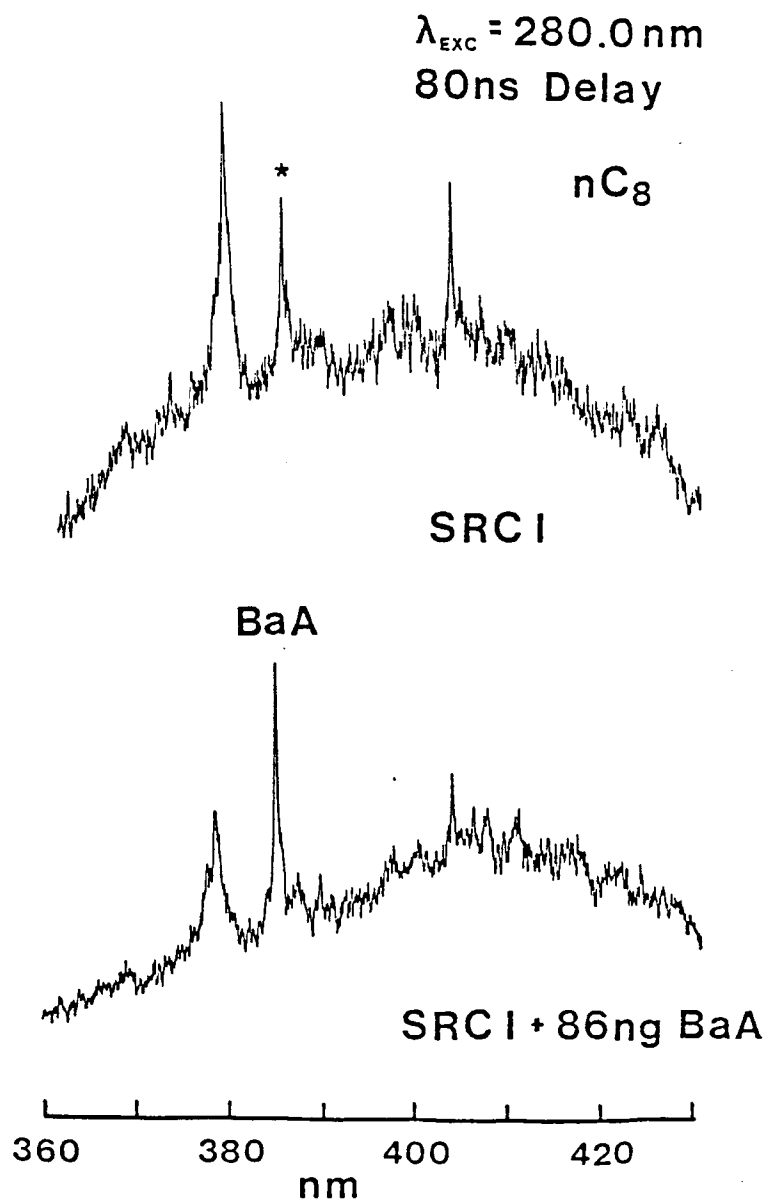


Figure 22. Benz[a]anthracene Identified in SRC I.

TABLE VII
POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IDENTIFIED IN SOLVENT REFINED COAL

Compound	Abbr.	Matrix	Laser, λ_{exc} (nm)	Delay(ns)	Lamp, λ_{exc} (nm)	SRC I, λ_{em} (nm)	Pure Compd., λ_{em} (nm)
Benz[a]anthracene	BaA	octane	280.0	80		385.1	385.1
Benzo[a]fluorene	BaF	heptane	265.0	30		347.1	347.1
Benzo[b]fluorene	BbF	heptane	265.0	60		340.3	340.3
Benzo[b]fluorene	BbF	octane	275.0	20	260,315	340.5	340.5
7,10-Dimethylbenzo[a]pyrene 7,10-DMBaP		octane	365.0	60		407.1	407.1
Benzo[a]pyrene	BaP	octane	389.2	80		403.9	403.9
Benzo[a]pyrene	BaP	heptane	389.4	100	300	403.7	403.7
Benzo[k]fluoranthene	BkF	octane	312.0	4		404.3	404.3
Chrysene	C	heptane	271.0	50	305	361.5	361.5
Perylene	Per	heptane	388.5	10		445.9	445.9
Perylene	Per	octane	389.4	0		445.6	445.6
Pyrene	Py	octane	275.0	120		372.9	372.9
Pyrene	Py	heptane			315	372	372
Phenanthrene	Ph	heptane			300	347	347
Triphenylene	T	heptane			305	352.6	352.6

1. The spectral composition of the excitation beam had to be maintained throughout a quantitative experiment. Re-tuning the dye, adjusting the beam aperture, and adjusting the polarizing film in the course of the experiment were undesirable.
2. The excitation wavelength used for both the analyte and the internal standard had to fall within the range of a single dye; in the most favorable cases both could be excited at the same laser wavelength.
3. Since sample deposits were not necessarily homogeneously distributed over the sample surface, it was important that the laser beam interrogate the same portion of the surface for each point of a quantitative plot.
4. It was important that the PMT be operated at a voltage well within its linear response range. Errors produced in the measurement of strong signals at low PMT voltages have been noted.⁷⁴ Throughout this work the PMT was operated between 1200V and 2000V. The signal strength impinging on the PMT was easily controlled by adjusting the slit widths of the emission monochromator.
5. Saturation of the oscilloscope resulted in non-linear signal response. When saturation occurred, peaks were flattened or rounded by varying degrees. Reducing the voltage on the PMT or using a less sensitive scale on the oscilloscope restored peak symmetry.
6. The time delay function of the oscilloscope had to be zeroed for each start of the laser. This was especially important if spectral intensities of the analyte and internal standard were measured at

different time delay settings and the fluorescence lifetimes were significantly different. In this case, the zero time delay was referenced to the maximum fluorescence intensity of the signal exhibiting the shorter lifetime. The oscilloscope was allowed to warm up. The reference signal was maximized by setting the emission monochromator at λ_{max} . The "scan" was then used to center the signal one division from the extreme left side of the oscilloscope graticule, and the "time delay mult." setting was adjusted to maximize the signal at this location on the graticule.

7. Ratios of peak intensities for two compounds, BaP and perylene, in a single deposit were found to vary with dye-laser power (Figure 23). Measurements at different values of output power of the dye laser were made by defocusing the beam of the amplifier cell with the "dye cell translation" thumbscrew. The measurement variation was most severe for low power values (less than 200 mV for BBQ). The experiment was not repeated for other compounds, and general conclusions concerning the reason for the observed behavior could not be reached without further investigation. Therefore, all measurements for a quantitative plot were made before there was significant deterioration of the lasing dye.

It was standard procedure in this laboratory that, once an operator began a determination, the dye-laser spectrometer was dedicated to that experiment until its conclusion; thus, many of the problems cited above could be avoided.

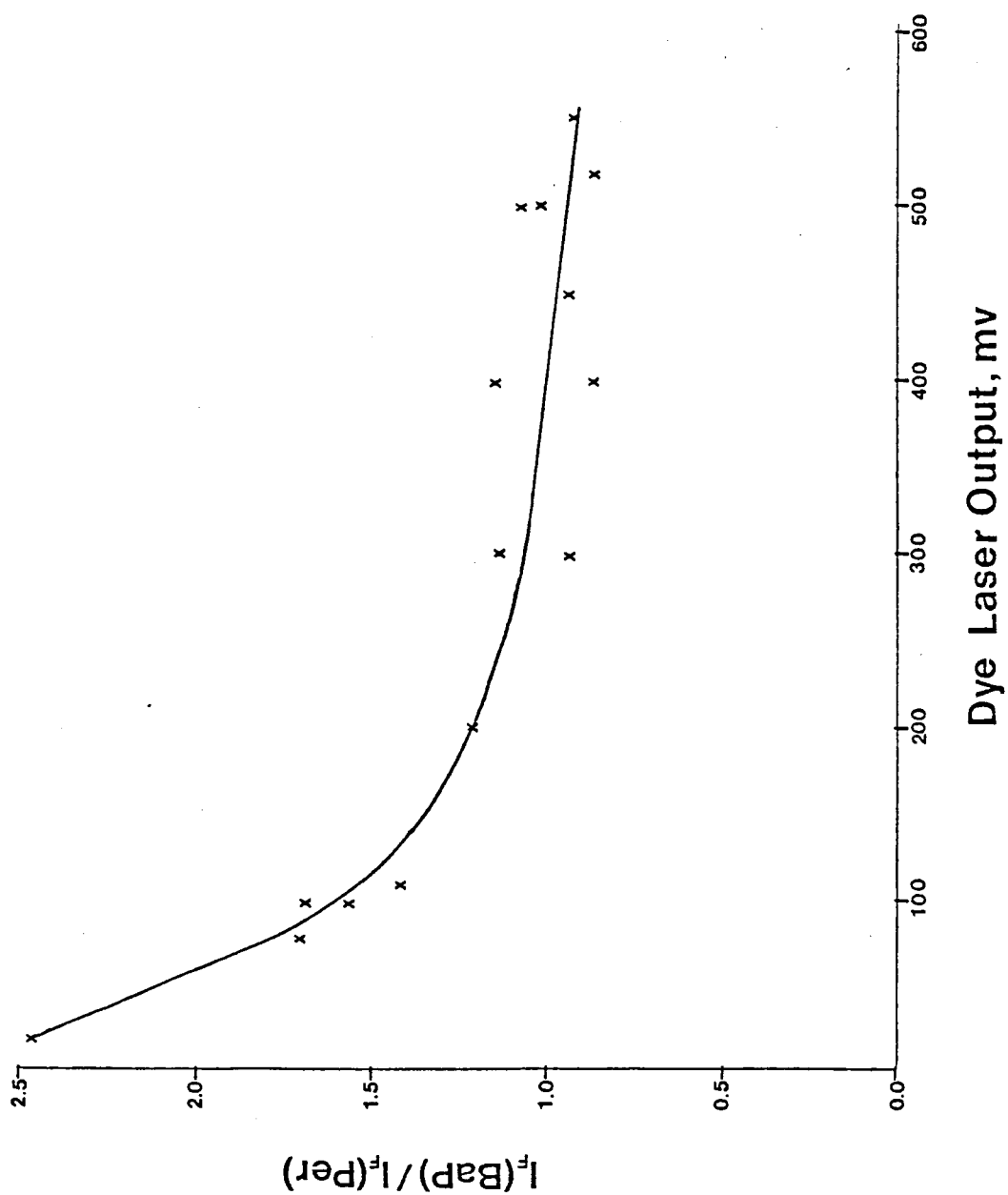


Figure 23. Measurement of Peak Ratios of BaP and Perylene Found to vary with Laser Power.
 (Laser Power (millijoules) = $V / 3.36 \text{ V mJ}^{-1}$)

1. Quantitative Precision

Experiments were performed to evaluate the reproducibility of data within a single deposit, and from deposit to deposit. The experiments were performed under frequency-doubling conditions, in which imprecision was expected to be most severe. Pulse-to-pulse variations in the laser output were more severe under these conditions. Since the power of the dye-laser output was considerably lower than when operated in the fundamental, the intensity of the signal was decreased, placing additional demands on conditions required for data acquisition (generally, wider slits on the emission monochromator and higher PMT voltages were required under frequency-doubling conditions).

In these experiments, four deposits containing 50 ng each of BaP and BaA were prepared in n-octane. Spectra were taken for both compounds at $\lambda_{\text{ex}} = 291.8$ nm and 60 ns time delay (relative to the peak intensity of BaP at $\lambda_{\text{em}} = 403.9$ nm). Measurements were collected in pairs, a BaA peak at $\lambda_{\text{em}} = 385.1$ nm and a BaP peak at 403.9 nm. The data ($I_{\text{F,BaP}}/I_{\text{F,BaA}}$) were taken from all parts of the sample surface to evaluate the homogeneity of the sample deposit, and to determine a good signal sampling procedure for quantitative experiments. The results of those experiments evaluating precision are given in Table VIII.

The precision of the data within a single deposit was improved when the beam interrogated the same portion of the sampling surface, as compared with the precision observed for sampling the entire surface (Figure 24).

The quantitative results from deposit to deposit showed the smallest variability (Table VIII) when the entire surface was sampled

TABLE VIII

REPRODUCIBILITY STUDY: THE MEASUREMENT (I_F , BaP/I_F , BaA) MADE OVER DIFFERENT PARTS OF THE SAMPLE SURFACE (50 ng EACH OF BaP AND BaA IN n -OCTANE)

	Bottom	Low Mid	Mid	High Mid	Top	Mean Value	Three measurements made at mid sampling surface			Mean Value
Deposit 1	0.809	0.922	0.874	1.018	1.086	$0.942 \pm 11.8\%$	0.874	0.907	0.909	$0.898 \pm 2.53\%$
Deposit 2	0.839	0.865	0.908	0.938	1.0596	$0.922 \pm 9.32\%$	0.908	0.914	0.872	$0.896 \pm 2.21\%$
Deposit 3	0.867	0.946	0.807	0.865	0.902	$0.877 \pm 5.85\%$	0.807	0.752	0.792	$0.784 \pm 3.63\%$
Deposit 4	1.003	0.799	0.891	1.013	0.980	$0.937 \pm 9.71\%$	0.891	0.885	0.870	$0.882 \pm 1.23\%$
Mean Value	$0.880 \pm 9.7\%$	$0.883 \pm 7.4\%$	$0.870 \pm 5.1\%$	$0.959 \pm 7.5\%$	$1.007 \pm 8.3\%$	$0.920 \pm 3.2\%$				$0.865 \pm 6.3\%$

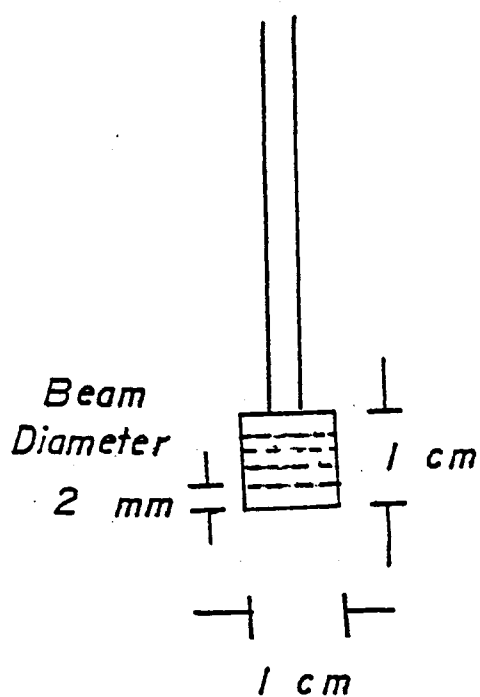


Figure 24. Possible Orientations of the Dye-Laser Beam with Respect to the Sampling Surface.

by moving the deposit with respect to the laser beam and thus illuminating five distinct regions of the deposit (Figure 24), and averaging the results for the five illuminated regions.

Since this set of data represented a worst case (for reasons mentioned earlier, p 65), and since a single deposit was used to define a point on the quantitative plot, a signal sampling procedure was chosen which yielded good precision within a single deposit and reasonable precision from deposit to deposit. Specifically, for each quantitation, the same portion of the sample surface (Figure 24) was interrogated for each deposit throughout the experiment. The mean of five measurements for a single sample deposit defined a point (for which the imprecision was small, 2-3 % r.s.d.), and four such points defined the quantitative plot. This standard addition plot was then subjected to a linear regression analysis for line fitting and the unknown value (concentration of analyte) was obtained by extrapolating that line to the abscissa. A total of 20 x-values and 20 y-values were used in performing linear regression analyses as described by Larsen, *et al.*⁷² An example set of data employing this procedure is shown in Table IX. In this way, 18 degrees of freedom were permitted (rather than 2 d.f. for one measurement per deposit) for calculation of the precision of the value predicted at the abscissa.

2. Quantitative Accuracy and Results of Determinations

The determination of three PAHs known to be present in SRM 1580 was attempted. Pyrene was chosen because it is generally present at relatively high concentrations in samples known to contain PAHs. Benzo[a]pyrene was chosen because it is an important carcinogen.

TABLE IX

DATA SET FOR DETERMINATION OF BaP IN SHALE OIL USING
FOUR MI DEPOSITS IN OCTANE*

x = ng of BaP added to 1.5 μ l of SRM 1580	y = $I_F(\text{BaP})/I_F(\text{Per})$
0.5	0.813, 0.887, 0.844, 0.879, 0.816
5.0	1.006, 0.9904, 1.047, 1.0331, 1.000
10.0	1.1129, 1.0903, 1.1195, 1.1346, 1.0658
15.0	1.3219, 1.3228, 1.3016, 1.22597, 1.2461

* Linear regression analysis performed according to Larsen, et al.⁷²
for standard addition: $n = 20$; $t_{95} = 2.101$; slope = 0.02793884; ordinate
intercept = 0.8533072; standard error of regression = 0.0374021;
predicted value for x, when y = 0, is 31.03 ± 5.22 at 95% C.L.

Benzo[e]pyrene was chosen because it is isomeric with benzo[a]pyrene. Certified values for the concentrations of these PAHs in SRM 1580 had been determined by NBS.

The results for pyrene obtained in this laboratory are given in Figure 25. The signal-to-noise ratio appeared to be limiting for small spikes of pyrene, and deviations of the "standard-addition" plot from linearity occurred for larger spikes of pyrene. Sampling the signal at time delays longer than 80 ns produced no improvement in the signal-to-noise ratio. The deviations from linearity which occurred for large spikes of pyrene were also observed for large spikes of analyte in other determinations. Energy transfer mechanisms have been evoked in past studies⁹ to explain this behavior. The deviation from linearity may simply result from non-quantitative transfer in the vacuum sublimation of increasingly larger samples, implying that longer deposition times would extend the linear plot to larger spikes of analyte. This apparent artifact is not considered crucial to quantitative determinations, however, since an adequate linear range can be established by addition of suitably small spikes of analyte. The low signal-to-noise ratio for small spikes of pyrene seems to be the limiting factor in the determination of pyrene in SRM 1580.

The optimum excitation wavelength for benzo[e]pyrene was ascertained to be 363.6 nm by depositing 57 ng of the pure compound in octane. A deposit of 1.5 μ l of SRM 1580 yielded no detectable fluorescence signal for this compound. In a subsequent experiment, 1.5 μ l of SRM 1580 spiked with 57 ng of benzo[e]pyrene was deposited in n-octane; no fluorescence from benzo[e]pyrene could be detected. Apparently, the

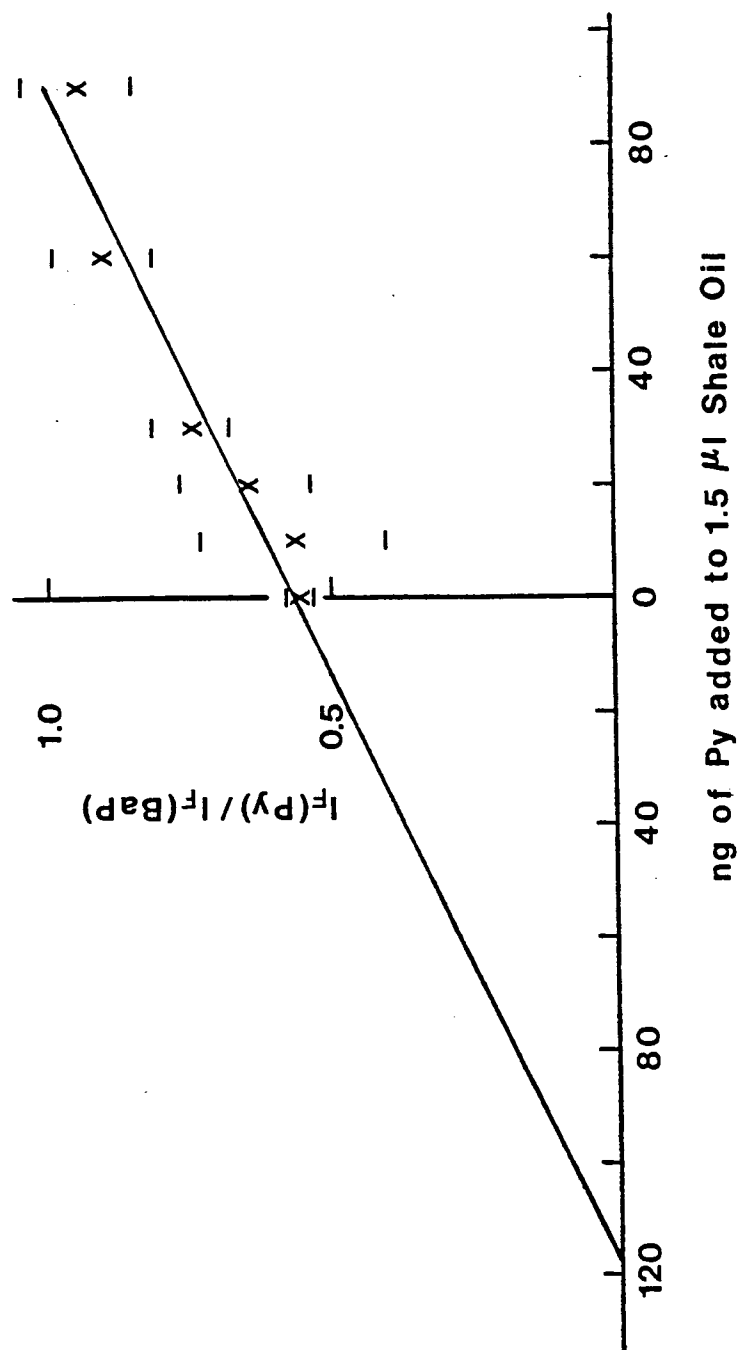


Figure 25. Determination of Pyrene in SRM 1580.

signal for benzo[e]pyrene in SRM 1580 deposits is masked, presumably by inner-filter effects (i.e., absorption of the fluorescence by other sample constituents). Attempts to verify this speculative conclusion by obtaining absorption spectra of deposits of SRM 1580 failed, due to the highly scattering character of the deposits.

The presence of benzo[a]pyrene was confirmed in SRM 1580 by preparing deposits in heptane and in octane (Figure 26). The quantitative results for BaP in SRM 1580 were more encouraging than those obtained for pyrene; the results are shown in Figure 27. A density of 0.895 mg/ μ l for the shale oil sample was used to convert weight/volume measurements to a weight/weight basis (μ g/g or ppm). The quantitative results for BaP in SRM 1580 (23 ± 4 μ g/g) compared favorably with the NBS certified value (21 ± 6 μ g/g).

Determination of four PAHs (benzo[a]pyrene, perylene, benz[a]-anthracene, and benzo[b]fluorene) was attempted in SRC I. The results are given in Figures 28-31. The value predicted at the abscissa and its standard deviation were normalized to 1 mg of sample and reported as μ g/g. Because this sample has not previously been characterized, the accuracy of these results cannot be assessed.

Sources of possible error which have not been previously addressed include the following considerations:

- a. Measurement of the sample - an estimate of the error in measuring 1.5 μ l of SRM 1580 was approximately 1%; whereas as much as 3% error could have occurred in weighing 360 μ g of SRC I.

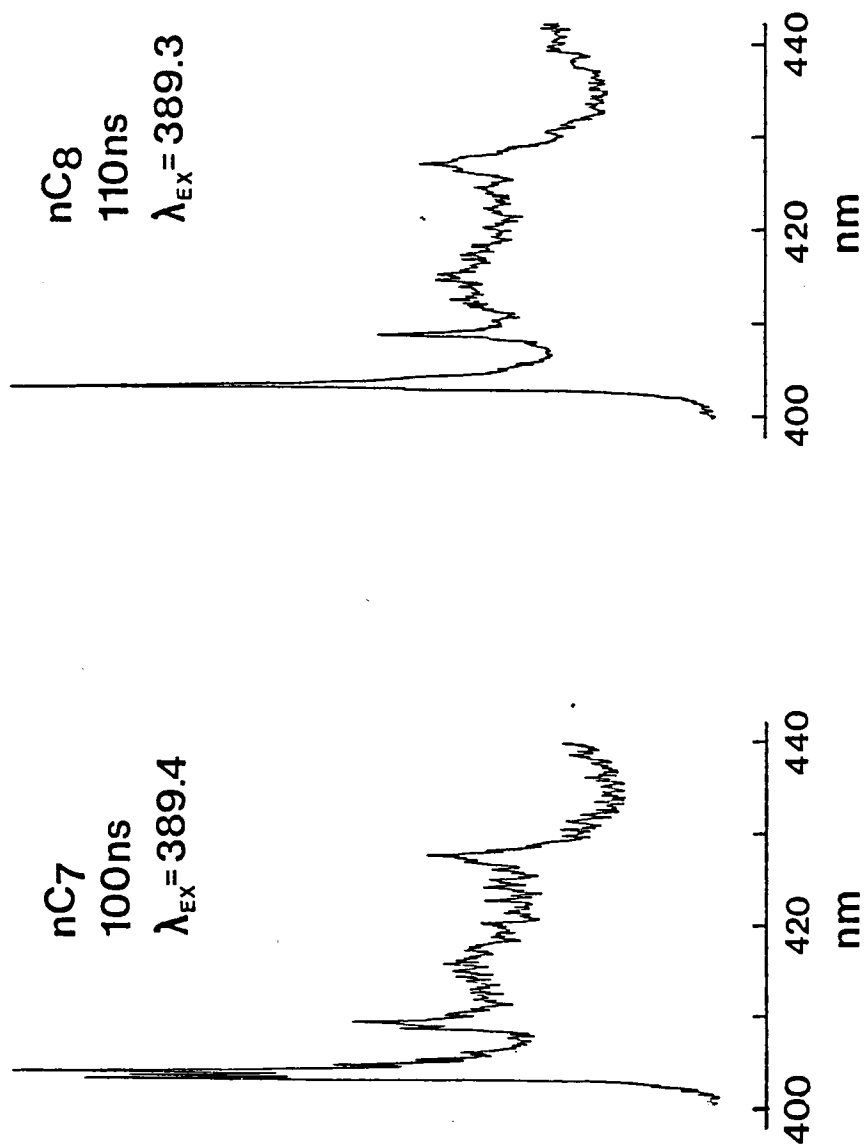


Figure 26. BaP Confirmed in SRM 1580.

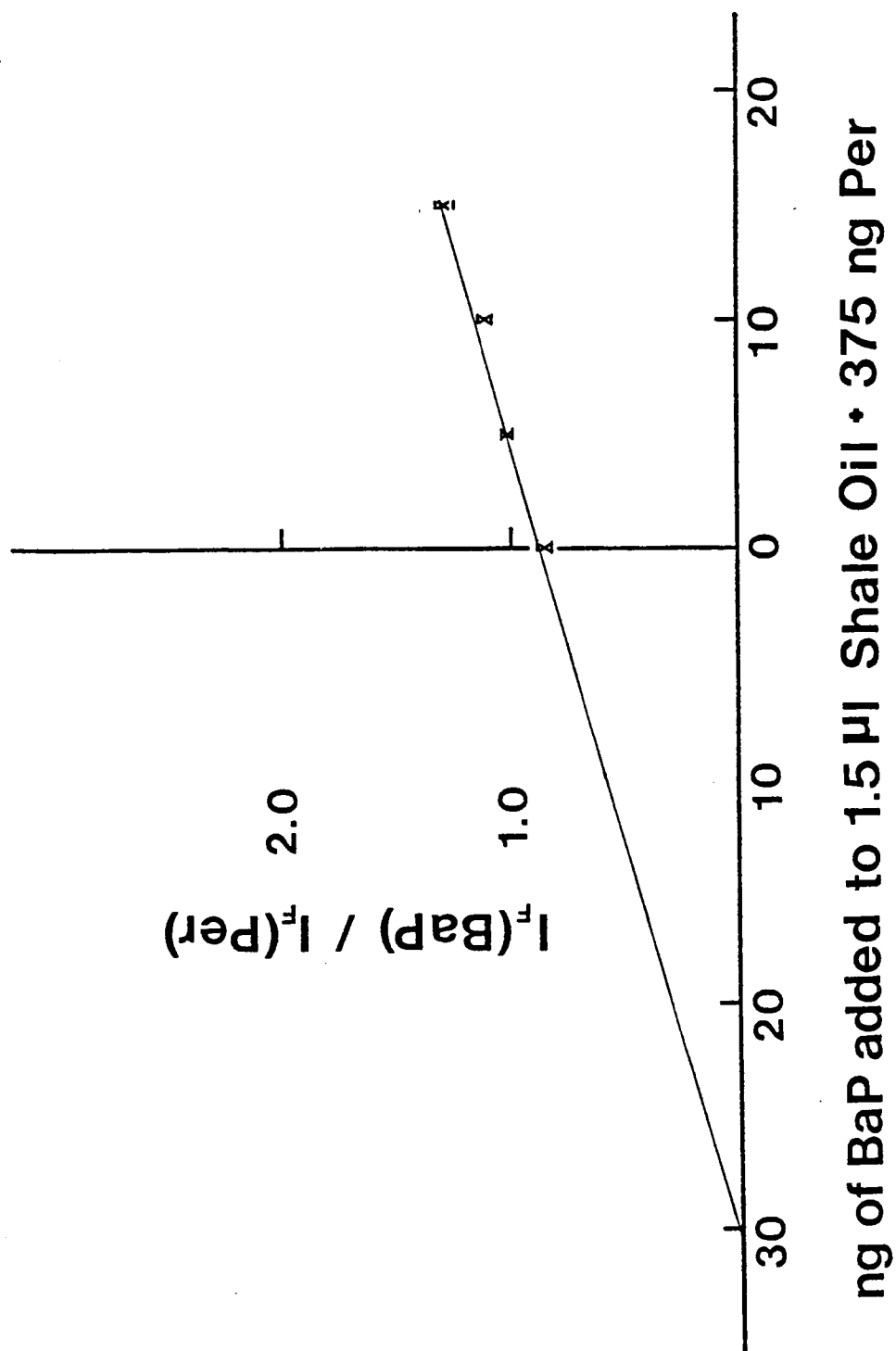


Figure 27. Quantitation of BaP in SRM 1580.

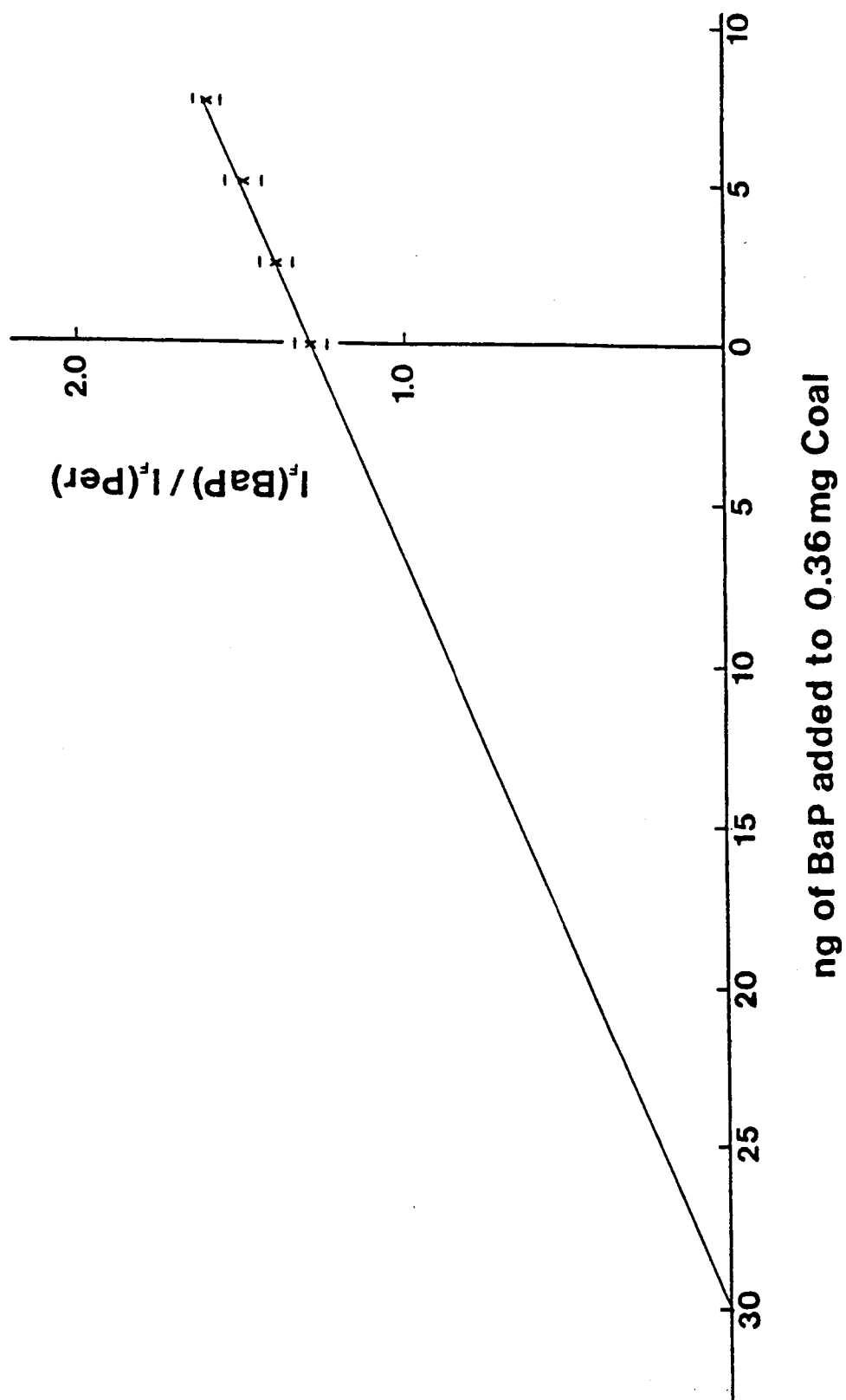


Figure 28. Quantitation of BaP in SRC I.

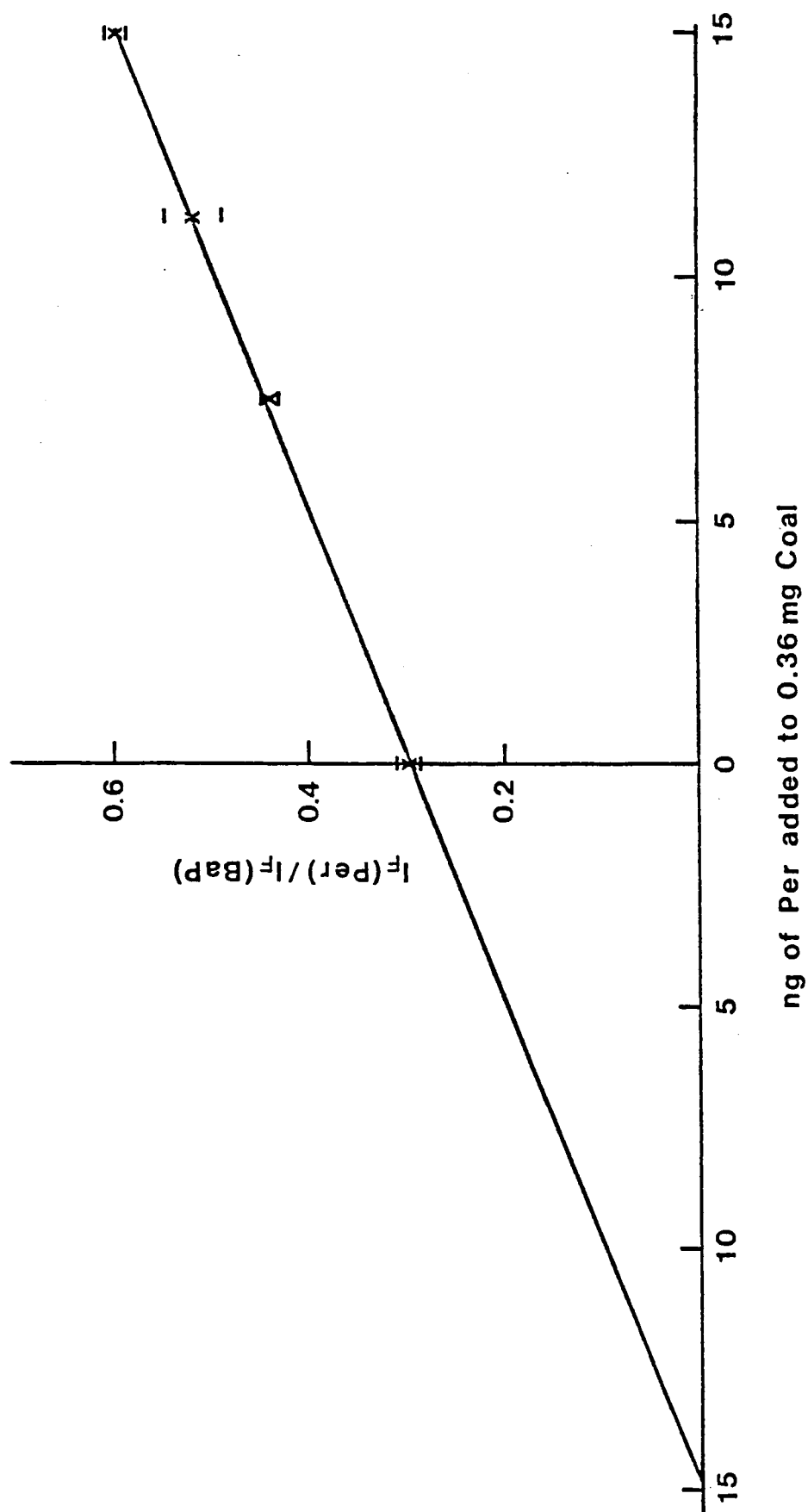


Figure 29. Quantitation of Perylene in SRC I.

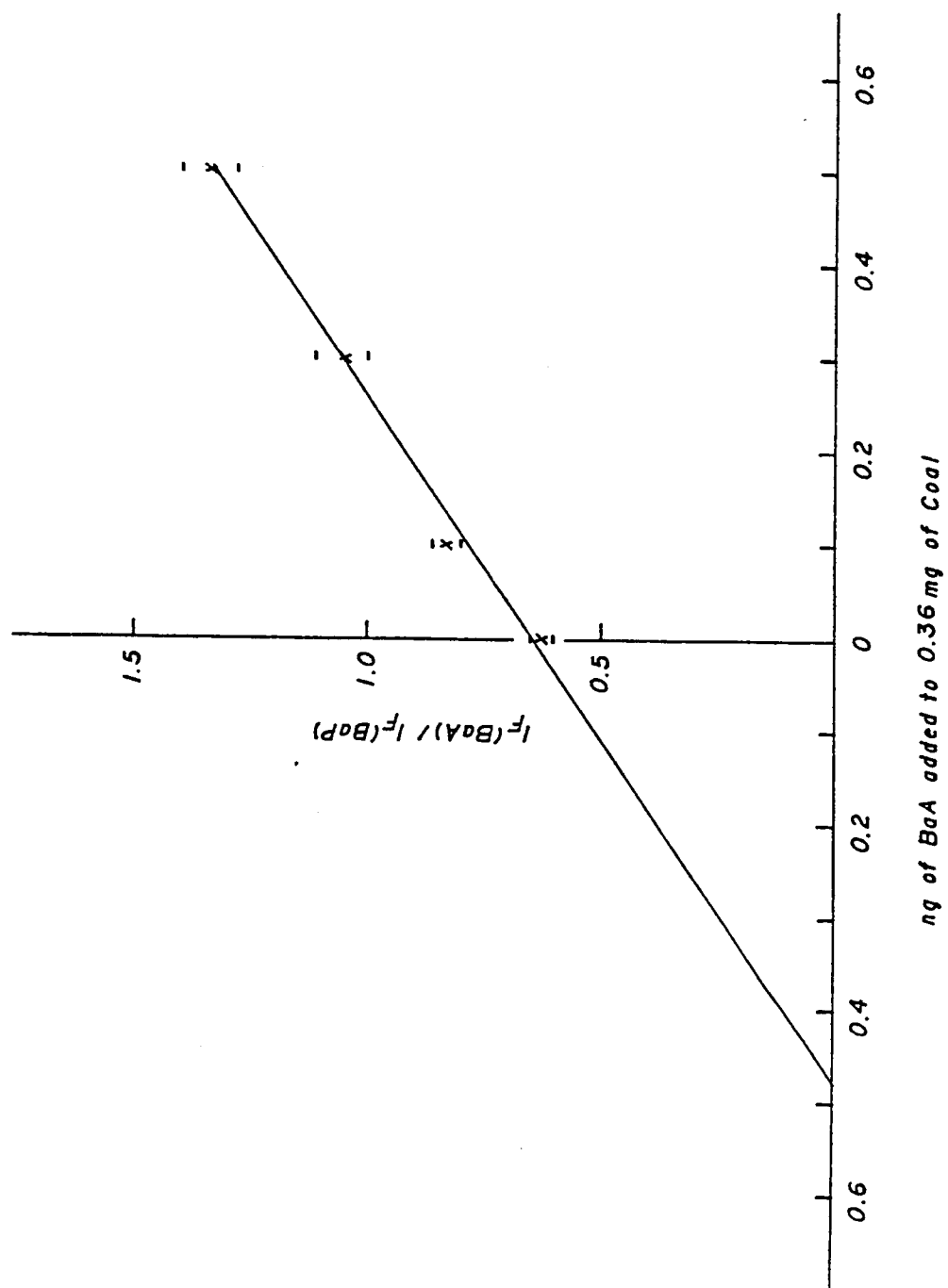


Figure 30. Quantitation of BaA in SRC I.

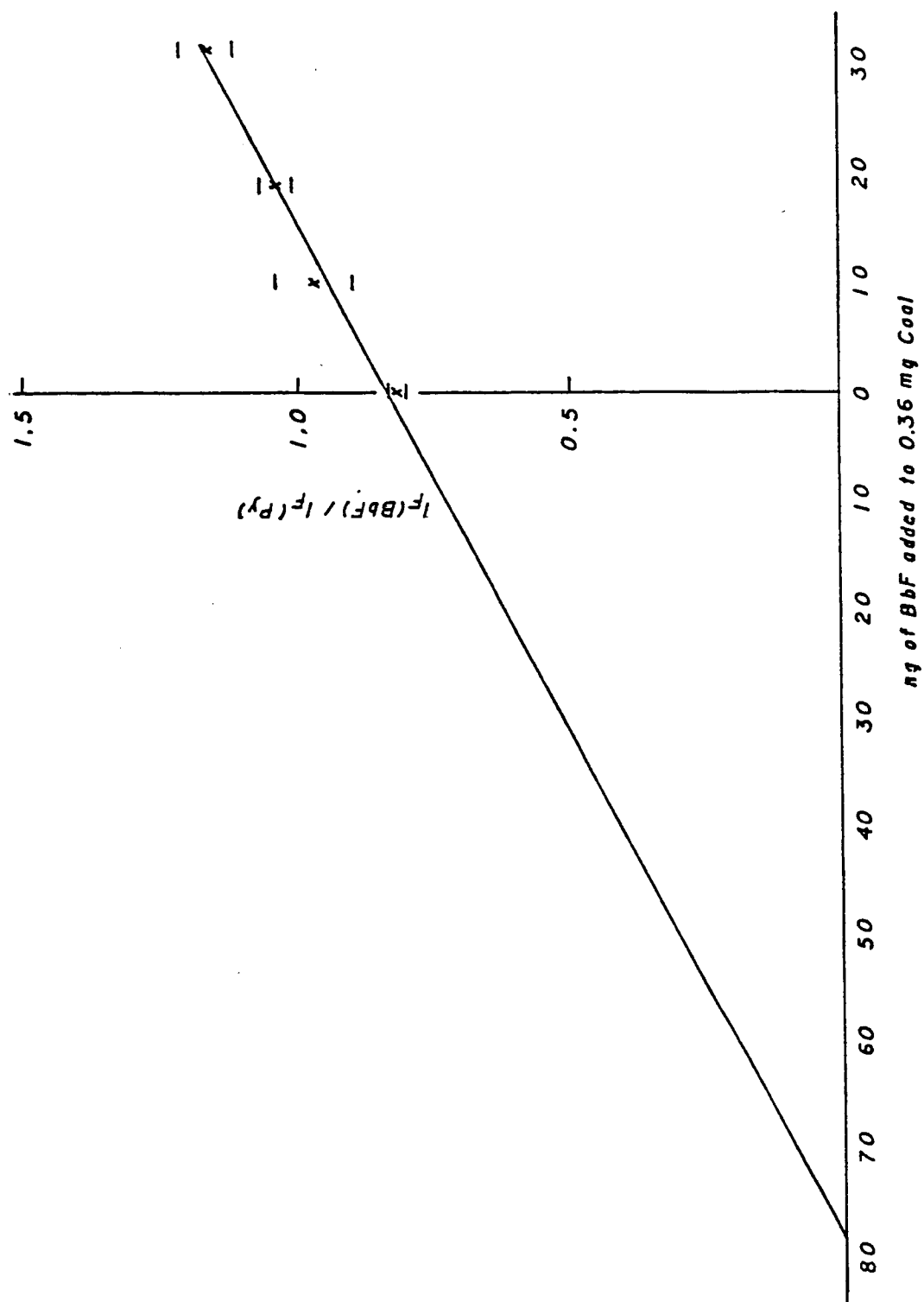


Figure 31. Quantitation of BbF in SRC I.

- b. efficiency of the vacuum sublimation - the assumption that the analyte spike mimicked the behavior of the PAH in the sample was based on the initial assumption that the vacuum sublimation was highly efficient. It was assumed that, if the point from an unspiked sample fell on the line for spiked samples, then the vacuum sublimation was virtually 100% efficient for that determination. With the exception of pyrene in SRM 1580, the correlation coefficient was greater than 0.99 for all determinations in this investigation.

The results of these determinations have been summarized in Table X. Parameters used in these determinations (excitation wavelength, delay time, etc.) have been compiled in Chapter 2 (Table V, p 34).

The direct determination of BaP in SRM 1580 by MIF has been shown to be both accurate and precise. The precision of quantitative results for SRC I is encouraging. The disparity in the number of PAHs which could be determined in SRM 1580 and in the SRC I is undoubtedly due to the greater complexity of the former sample.

TABLE X
RESULTS OF DETERMINATIONS

<u>Sample</u>	<u>Analyte</u>	<u>Correlation Coefficient</u>	<u>Certified</u>	<u>Found ($\mu\text{g/g}$)</u>
SRM 1580	Pyrene	0.9689	104 ± 18	87 ± 64
SRM 1580	BaP	0.9926	21 ± 6	23 ± 4
SRC I	BaP	0.9991		83 ± 19
SRC I	Perylene	0.9997		41 ± 7
SRC I	BaA	0.9959		1.3 ± 0.2
SRC I	BbF	0.9906		220 ± 63

CHAPTER IV

SUMMARY AND CONCLUSIONS

Development of the MIF procedure for analysis of SRC I was lengthy and tedious, but progressed well after optimization of sample deposition conditions and re-alignment and optimization of the dye laser. Reasonable spectra could be obtained with the xenon-lamp spectrometer, and the capability for simultaneously scanning phosphorescence was advantageous. The bulk of the qualitative analysis of SRC I required the selective excitation capability of the dye-laser spectrometer. Through judicious use of the time delay capability of the laser spectrometer, background could often be suppressed to obtain a reasonable signal-to-noise ratio. In many cases, identification of peaks in SRC I spectra was relatively straight-forward. Benzo[a]pyrene, perylene, pyrene, and 7,10-dimethylbenzo[a]pyrene were identified simply by finding an excitation wavelength and time delay which produced a spectrum which matched existing library spectra. Whenever uncertainty existed in the identity of a fluorescence peak, the sample was spiked with the suspected compound; in this way benz[a]anthracene and chrysene were identified in SRC I.

Undoubtedly there were PAHs present in SRC I which were not identified in this study. It was not the purpose of this investigation, however, to catalog the PAH composition of the sample, but rather to assess the utility of MIF for analysis of PAHs in complex samples.

It had been anticipated that SRM 1580 might prove to be a suitable standard reference material for assessing the quantitative

accuracy of MIF results of SRC I analyses. However, by comparing lamp-excited spectra of SRM 1580 with those obtained for SRC I, it became obvious that SRM 1580 was a much more complex sample than SRC I. SRM 1580 probably contains a much larger fraction of volatile compounds; it is known to contain relatively high concentrations of nitrogen heterocycles which usually exhibit broad absorption and emission bands even at low temperature. The background was much more intense in spectra of SRM 1580, limiting the capability of the laser spectrometer for improving the signal-to-noise ratio by time resolution. This difficulty proved to be the limiting factor in the determination of pyrene in SRM 1580. Quantitative results for BaP in SRM 1580 were precise and accurate, comparing favorably with the NBS certified value.

In conclusion, MIF has been shown to be a promising technique for direct analysis of PAHs in "real" samples. The precision of the quantitative results for PAHs in SRC I was most encouraging. Results of quantitative determinations appeared to be highly reliable, but the accuracy of those determinations could not be adequately assessed due to the lack of suitable reference standards. The greatest success of MIF should be realized for solid samples containing PAHs in the ppm range. Samples such as SRM 1580, which contain relatively high concentrations of heterocyclic compounds, will probably always pose problems for the MIF analyst attempting a direct sample characterization.

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VITA

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