MASTER

**QUARTERLY REPORT
January 1-March 31, 1979**

**Prepared for
Pollutant Characterization
and Safety Research Division**

**Office of Health
and Environmental Research
Department of Energy**

**AMES LABORATORY, DOE
IOWA STATE UNIVERSITY
AMES, IOWA**

Date Transmitted: July 1979

**PREPARED FOR THE DEPARTMENT OF ENERGY
UNDER CONTRACT W-7405-eng-82**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

QUARTERLY REPORT
January 1 - March 31, 1979

Prepared for

Pollutant Characterization and
Safety Research Division

Office of Health and
Environmental Research
Department of Energy

by

AMES LABORATORY
IOWA STATE UNIVERSITY
AMES, IOWA

Under Contract W-7405-eng-82

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Available from: National Technical Information Service
U. S. Department of Commerce
P.O. Box 1553
Springfield, VA 22161

Price: Microfiche	\$3.00
Printed	\$5.25

Table of Contents

POLLUTANT CHARACTERIZATION AND SAFETY RESEARCH

	<u>Page</u>
I. Characterization of Organic Pollutants Emitted by the Co-combustion of Refuse Derived Fuel and Coal	1
II. Environmental Effects of Using Municipal Solid Wastes as a Supplementary Fuel	3
III. Microbiological Air Quality at the Ames Municipal Solid Waste Recovery System	9
IV. Solid Waste to Methane Environmental Study	11
V. X-Ray and Ultraviolet Excited Optical Luminescence (XEOL, UVEOL) of Carcinogens - Analytical Possibilities	14
VI. Laser Pumped Luminescence (LPL) Spectroscopy	47
VII. Multielement Characterization of Air Particulates	56

I. Characterization of Organic Pollutants Emitted by Fossil Fuel Processing and Energy Generating Plants (G. Junk, H. Svec)

A. Progress

Interpretation of past analytical data has shown that the burning of refuse (RDF) combined with coal at a local power plant has little effect on the amount of polychlorinated biphenyls (PCB's) and other organic components present in the vapor phase and sorbed on the particulate matter. The most reliable quantitative data are for the PCB's. These compounds were present even when no refuse was added to the coal fuel. These observations of PCB's in the emissions when refuse was absent in the fuel were confirmed: for fly ash and grate ash from a power plant where only coal has been burned; for residues from chimneys of wood burning fireplaces; and for fly and grate ash from both hard and soft wood fires. These data suggest the formation of PCB's in the combustion process, because no PCB's were measured in any of the fuels other than the refuse. All the fuels did, however, contain from 0.02 to 0.6% total chlorine. All attempts to verify the formation of PCB's by laboratory combustions of chlorine doped fuels have been inconclusive so far.

Preliminary experiments were run on the fly ash collected at a local power plant to determine the possible presence of chlorinated dibenzodioxins and chlorinated dibenzofurans. The former could be produced in the combustion process and the latter are documented emissions during the incineration and heat treatment of chlorinated phenols, dioxins and PCB's. Literature procedures were used for the class separation of the dioxins and furans from the PCB's and other possible interferences. Methylene chloride was shown to be superior to benzene for extraction of these materials from fly ash. No conclusive evidence about the absence, presence or amounts of dioxins and furans is available from interpretation of our preliminary data.

Standard procedures for confirming the PCB's at picogram levels have been developed and employed for most of our environmental extracts. These capillary gas chromatograph/mass spectrometer techniques are very useful for positive confirmations.

Other standard procedures for separating and identifying the EPA priority pollutants are also being developed. These techniques allow for both qualitative confirmation and quantitation of preselected

pollutants in the extracts from stack emissions and our other environmental programs.

B. Status

The furan and dioxin investigation has been hampered by a lack of the various isomers necessary for positive characterization. Efforts to obtain these standards are in progress with due regard to the safety hazard of these highly toxic materials.

The formation of many of the chlorinated organic components are expected to be influenced by combustion conditions which exist in commercial boilers and which are difficult to simulate in the laboratory. Thus the tests with doped fuels may take longer than anticipated.

Future extractions of particulates will be accomplished with the mixed solvents of benzene and methanol or benzene and methylene chloride to increase the efficiency of the removal of the dioxins and furans. Appropriate class separations will be used to obtain two fractions, one containing the PCB's and related non-polar components and the other containing the dioxins and furans.

II. Environmental Effects of Using Municipal Solid Wastes as a Supplementary Fuel (H. R. Shanks, J. L. Hall, A. W. Joensen)

A. Progress

With the completion of the installation of the dump grate in the suspension fired boiler, it is now possible to perform emission evaluations on Unit 7. In this report, observation on the emissions of NO_x and PCBs, and on the PCBs, Cl^- , F^- , PO_4^{3-} , NO_3^- , and SO_4^{2-} species immobilized on the stack particulates will be discussed.

Twelve or more measurements of the stack NO_x level were made at each boiler load for 0, 10 and 20% RDF fuel added. Figure 1 shows the average NO_x level for each load and fuel ratio. The bars on the individual points represent the variability among the samples and do not indicate error in the determinations. The data are suggestive of a slight decrease in NO_x emission, both with respect to the higher loading and RDF heat input percentages. If the decreases in NO_x emission are indeed real, they would be consistent with the expected lower flame temperatures for higher fuel loading and RDF input percentages.

Figures 2, 3, 4 show, respectively, the concentration of PCBs measured in the vapor phase before and after the electrostatic precipitator and in the fly ash. The data points represent the average of three or more determinations and the bars on the data points indicate the variation among individual samples. If the large variation among the samples is considered, there appears to be no significant trends that can be related to boiler load or fuel composition.

Ion chromatography has been used to determine the leachable Cl^- , F^- , PO_4^{3-} , NO_3^- and SO_4^{2-} ions occurring in the stack particulates. For strong NaCO_3 leaching solutions, no leachable Cl^- or NO_3^- were found.

Leachable sulfate levels are near 30% for particulates from burning coal only but decrease to about 8% for 20% RDF. Surface analysis with SIMS indicates high sulfur levels on the surface of the particles. Leachable fluorides and phosphates are present at 1 to 2% and 0.5% respectively but show no trend with amount of RDF burned.

B. Status

There is little doubt that the combustion of RDF results in an increase in the emission of volatile metals, particularly lead. Data from a number of studies on coal fired plants show that the lead and other volatile metals are concentrated on the smaller particulates.

Our analysis of fly ash and stack particulates obtained when RDF is cogenerated with coal support these findings. There is, however, a general lack of data on the concentrations of lead and other trace elements of concern in the various constituents of the burnable fraction of solid waste. Our analysis of RDF from the Ames facility indicates that overall, lead is present in the range of 500 to 1000 ppm. Because this level is higher than those found in coal and, for some other sources of RDF, we are attempting to identify the major contributing materials within the burnable fraction. Samples of local newsprint, magazines, computer paper, cardboard, etc. have been prepared and will be analyzed for lead content as well as several other trace elements.

Additional methods for the characterization of the particulates and fly ash are being evaluated, including the determination of the leachable fraction of various trace elements and their concentration as a function of depth within the individual particulates.

Our strategy for attacking the difficult characterization and quantitation problem, especially for the trace organic molecules, has evolved from an approach based on the identification and quantitation of specific classes of compounds to one based on first fractionating the samples into compound classes followed by assaying the toxicity and mutagenicity of the fractions. Toward this end, we are adding staff who are competent in performing the Ames mutagenicity and other toxicity tests. The determination of toxic organic molecules on fly ash is assuming additional significance because of the increasing interest in the introduction of fly ash into the working environment as a filler in concrete.

Figure 1. Uncorrected NO_x emissions determined as NO₂ for 80 and 100% load.

Figure 2. Concentration of PCB's in the vapor phase before the electrostatic precipitator.

Figure 3. Concentration of PCB's in the vapor phase in the stack.

Figure 4. Concentration of PCB's on the fly ash as a function of % RDF.

III. Microbiological Air Quality of the Ames Municipal Solid Waste Recovery System (R.N. Kniseley)

A. Progress

Microbiological sampling has been continued in and around the Ames Solid Waste Recovery System (ASWRS) and at ambient locations in Ames. The installation of the dust control equipment at the processing plant started in mid-October and was completed in mid-December. Therefore, during this quarter, we had our first opportunity to evaluate the impact of dust control equipment on the microbial air quality in the processing plant. Data collected during the six-week period prior to the implementation of dust control show that the air in the processing plant contained an average of 130,000 non-respirable (NR) colony-forming units (CFU)/m³ and 103,000 respirable (R) CFU/m³. The averages of the three-month period after installation of the dust control equipment were 10,000 NR CFU/m³ and 120 R CFU/m³. However, this decrease cannot be entirely attributed to dust control, because the average temperature during the January-March period was about 20°C lower than the average for September and October. Our data for FY 78 show that this temperature decrease should have decreased the number of CFU/m³ by about a factor of three. Therefore, dust control apparently provided a factor of three to four decrease in the number of CFU/m³ in the processing plant.

As mentioned in previous reports, difficulties have developed during the cold weather because of freezing of the liquid media used in the standard all-glass impingers and the gel media in the six-stage Andersen 2000 Air Samplers. The freezing of the media has a definite effect on the collection efficiency of both the impingers and of the Anderson 2000 Air Sampler. Won and Ross (1) have suggested that the addition of cornstarch and additional agar to the media used in the Anderson 2000 can minimize this problem. Won and Ross have also reported higher microbial recoveries with this modified media as compared with conventional media when the air temperatures are below 0°C. Our preliminary results agree with those observations.

The use of 5% sheep blood agar (SBA) was initiated this quarter because preliminary results indicated that these media sustained more total growth than TSA while recovering the same number of coagulase-positive staphylococci and fecal streptococci. A side by side comparison showed a 15% higher recovery of nonrespirables and 30% higher recovery of respirables for SBA than for TSA.

Status and Plans

Bacterial sampling will continue in and around the ASWRS to determine the seasonal effect on microbiological air quality with the dust collectors installed. Concurrently, continuing efforts will be directed towards improving sampling techniques for all microbiological species.

More extensive identification of the fungi in the plant and upwind and downwind are required before the full environmental impact of the ASWRS can be assessed. A search for a qualified mycologist to continue these identifications is underway.

- (1) Won, W.D. and Ross, H., Cryobiology, 3, No. 2, 1966.

IV. Solid Waste to Methane Study (C. Chriswell)

A. Progress

The objectives of this work include the identification and quantification of molecular and elemental species in the effluents from the Pompano Beach anaerobic digester. Priority was initially given to the development of effective techniques for isolating organic compounds from effluents. This work has progressed to the stage where emphasis is now being placed on the identification of compounds in the process filtrate.

Pesticides and polychlorinated biphenyls (PBC's) were extracted from the filtrate and determined by gas chromatography using an instrument equipped with a halogen sensitive electron capture detector. Approximately 4 ppb ($\mu\text{g/L}$) of PCB's in the form of Arochlor 1248 were found in the process filtrate. The source of the Arochlor was found to be approximately 2,300 ppb ($\mu\text{g/Kg}$) of PCB's in the refuse fed into the digester. Tests were also performed for the pesticides listed in Table 1. Of these only dieldrin was detected at approximately 0.015 ppb in the process filtrate.

Table 1. Pesticides Tested For In The Process Filtrate

<u>Pesticide</u>	<u>Detection Limit</u>	<u>Pesticide</u>	<u>Detection Limit</u>
aldrin	0.002 ppb	p,p'-DDD	0.005 ppb
dieldrin	0.005	α -endosulfan	0.005
endrin	0.005	β -endosulfan	0.005
heptachlor	0.002	α -BHC	0.001
heptachlor epoxide	0.002	β -BHC	0.001
p,p'-DDT	0.005	γ -BHC	0.001
p,p'-DDE	0.005	δ -BHC	0.001

Anion exchange procedures have been shown to be relatively effective for isolating those phenols which have been classified as priority pollutants. As shown by the data in Table 2, the recovery ranges from 67 to 93%.

Table 2. Anion Exchange Recovery of Phenols

<u>Compound</u>	<u>Recovery</u>	<u>Compound</u>	<u>Recovery</u>
2,4-dichloro-phenol	67%	4-nitrophenol	86%
2,4,6-trichloro-phenol	96	2,4-dinitro-phenol	81
pentachloro-phenol	91	2,4-dinitro-o-cresol	93
2-nitrophenol	90		

When this separation procedure was applied to the process filtrate, no priority phenols were detected in the anion exchange extract but several other acidic compounds were identified. These are listed in Table 3.

Table 3. Acidic Compounds Recovered from Process Filtrate

3-methylbenzoic acid	phthalic acid
3-chlorobenzoic acid	palmitic acid
3,5-dimethylbenzoic acid	stearic acid
benzoic acid	oleic acid
myristic acid	

Neutral and basic organic compounds were also extracted from the process filtrate and examined by gas chromatography-mass spectrometry. The compounds identified to date are listed in Table 4.

Table 4. Base-Neutral- Compounds Identified in Filtrate

<u>Compound</u>	<u>Approximate Concentration</u>
diethylphthalate	500 ppb
dibutylphthalate	30
diisobutylphthalate	10
butyl,benzylphthalate	1
naphthalene	2
diethylphthalate	10

The listed compounds account for approximately 90% of the total peak area of all compounds present in this extract. With the exception of one as yet unidentified compound, no other constituents of this fraction are present at concentrations approaching the ppb level.

B. Status

Although the presently used isolation procedures appear effective, efforts will continue to be directed towards improving and refining them. In addition, efforts will continue to be directed towards the identification of more components in the process filtrate. The concentration of those constituents already identified will be determined in future samples.

Trace metal determinations and mutagenicity assays have been delayed until more samples are accumulated. Although these tests are considered extremely important, their nature makes it more convenient and cost effective to run a large number of samples at a single time.

In the immediate future the highest priority will be given to identification of components present in filter cake samples. To date relatively few components have been determined in filter cake samples, but this has been primarily due to low concentrations. This problem is readily overcome by processing larger samples.

V. X-Ray and Ultraviolet Excited Optical Luminescence (XEOL, UVEOL) of Carcinogens - Analytical Possibilities (A. P. D'Silva and V. A. Fassel)

A. Progress (C. S. Woo)

The application of reversed phase TLC to the isolation and identification of several PAH compounds present in a shale oil distributed by the National Bureau of Standards as a surrogate reference material (#352) was evaluated. A 0.5 gm. sample of the shale oil was dissolved in 100 ml of cyclohexane and sequentially partitioned with 1.5N NaOH and 1N HCl to remove the acidic and basic compounds. The neutral fraction was then loaded onto an alumina column (acidic, 10% H₂O, 30 gm) and on eluting with cyclohexane, the PAH fraction was obtained. The cyclohexane eluate was evaporated to dryness and the residue was dissolved in 0.5 ml methylene chloride.

The reversed phase TLC plate (octadecylsilane bonded on silica gel) was spotted at the point marked X in Figure 1 with a 4 μ l aliquot of the above methylene chloride extract. The plate was developed in the 1st dimension (denoted by 1) with methanol - H₂O (95:5) and subsequently in the 2nd dimension (denoted by 2) with cyclohexane. The compounds indicated as 1, 2 and 3 on the two dimensional chromatogram were identified as pyrene, benz [a] anthracene and benz [a] pyrene by comparison with the reference chromatograms. Here R₁ and R₂ are the origins of the reference TLC developed along dimensions 1 and 2 respectively. The shaded areas represent unresolved components. The small spots adjacent to the shaded area along dimension 1 have been tentatively identified as carbazoles. The spots in the center of the TLC plate are PAH compounds not identified at present.

A paper titled "Characterization of Environmental Samples for Polynuclear Aromatic Hydrocarbons by an X-Ray Excited Optical Luminescence Technique" has been submitted for publication to Analytical Chemistry. A copy of the same is attached.

B. Status

Studies on the application of reversed phase TLC and HPLC for the isolation of PAH compounds as well as N and S heterocyclics will be continued. A N₂ laser fluorometric system designed for scanning of both one and two dimensional TLC plates will be utilized to quantitate the compounds separated on TLC plates. The system will also be used to identify and quantitate aflotoxins isolated from refuse derived fuels.

Figure 1. Reversed phase TLC of PAH compounds obtained from the neutral fraction of the NBS shale oil surrogate material #352.

CHARACTERIZATION OF ENVIRONMENTAL SAMPLES FOR
POLYNUCLEAR AROMATIC HYDROCARBONS BY AN
X-RAY EXCITED OPTICAL LUMINESCENCE TECHNIQUE

C. S. Woo,^{††} A. P. D'Silva and V. A. Fassel^{*}

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-7405-eng-82. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so for U.S. Government purposes.

CHARACTERIZATION OF ENVIRONMENTAL SAMPLES FOR
POLYNUCLEAR AROMATIC HYDROCARBONS BY AN
X-RAY EXCITED OPTICAL LUMINESCENCE TECHNIQUE[†]

C. S. Woo,^{††} A. P. D'Silva and V. A. Fassel*

Ames Laboratory, USDOE
and Department of Chemistry
Iowa State University
Ames, Iowa 50011

BRIEF

The x-ray excited optical luminescence technique has been utilized to obtain profiles of the polynuclear aromatic hydrocarbon content of some products of the combustion and conversion of coal, and of shale and fuel oils.

ABSTRACT

The x-ray excited optical luminescence (XEOL) of a concentrate in n-heptane of the neutral fraction isolated from byproducts of coal combustion and conversion, and from shale and fuel oils has been utilized to obtain profiles of their polynuclear aromatic hydrocarbon content. The advantages of observing the XEOL of these compounds in Shpol'skii solvents to differentiate isomeric compounds are documented.

[†] Based on papers presented at the following conferences: Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1978; Ninth Materials Research Symposium, "Trace Organic Analysis: A New Frontier in Analytical Chemistry", National Bureau of Standards, Washington, DC, April 1978; International Symposium on the Analysis of Hydrocarbons and Halogenated Hydrocarbons in Aquatic Environment, Hamilton, Ont., Canada, May 1978; Polynuclear Aromatic Hydrocarbons, Third International Symposium on Analysis, Chemistry and Biology, Columbus, Ohio, October 1978.

^{††} Chemistry Department, University of Northern Iowa, Cedar Falls, Iowa.

INTRODUCTION

A substantial increase is predicted in the utilization of coal for power production and in coal gasification-liquifaction technologies. The products of coal combustion or conversion to gaseous or liquid fuels are known to contain substantial quantities of polynuclear aromatic hydrocarbons (PAHs), nitrogen heterocyclics, sulfur heterocyclics (thiophenes) and oxygen heterocyclics (furans). Several constituents in the above classes of compounds are known to be carcinogens, co-carcinogens and oncogens (1). Thus, the increased utilization of coal will substantially increase the environmental load of the above compounds through particulate and other fugitive emissions. Because the carcinogenicity of such emissions has been found to be enhanced through synergistic effects (1), the cumulative effects on environmental degradation and occupational health of these emissions are expected to be of substantial complexity and magnitude. To evaluate the potential impact of this environmental loading, a large number and variety of environmental samples consisting of particulates and products of coal conversion technologies should be characterized. As a result, there is increasing interest in new analytical concepts that may prove useful for the efficient detection, quantitation, and monitoring of the potentially hazardous compounds at trace levels.

There have been recent significant advances in the application of new analytical techniques and methodologies to the quantitation of PAHs in environmental samples (2-12). In the discussion that follows, only typical "state of the art" technologies and methodologies

are cited, and the references are not exhaustive. In recent years the principal techniques utilized are: thin layer chromatography (TLC), capillary column gas chromatography followed by flame ionization detection (GC) or mass spectral characterization (GC-MS), gas liquid chromatography using nematic liquid crystal columns (GLC) and high performance liquid chromatography with fluorescence detection (HPLC). A critical test for any of these analytical techniques is the capability to identify and/or quantitate isomeric species, because the PAHs contained in environmental samples usually consist of several isomeric groups, having widely varying carcinogenicity. Typically, an analytical technique should be able to resolve the four-ring isomers, chrysene, benz[a]anthracene (B[a]A), pyrene, triphenylene and the near isomeric compound fluoranthene. Another group of isomers, namely benz[a]pyrene (B[a]P), benz[e]pyrene (B[e]P), and perylene is often found in environmental samples. The individual members of this group are known to have widely varying carcinogenicity, but often are not adequately resolved by the analytical techniques cited above. Thus, chrysene and triphenylene are not adequately resolved by the GC technique (5), and the HPLC technique cannot adequately resolve mixtures of either chrysene and B[a]A or perylene and B[e]P (9,10). If fluorescence detection is used, the overlapping elution bands of these isomeric mixtures can be resolved spectroscopically via a careful programming of the excitation and emission wavelengths. Success has been reported in separating the isomeric species discussed above, as well as others, by GLC when nematic liquid crystal columns are employed (11,12). Unfortunately, the limited stability of the

liquid crystal phases at the moderately high temperatures ($\sim 250^{\circ}\text{C}$) utilized in such separations often results in column bleed. Thus, several samples cannot be processed through such columns. A major disadvantage shared by all the analytical techniques cited above is the necessity of employing time-consuming prior isolation of the individual compounds including isomers. Thus, some prior separation of the PAH fraction from complex samples will be necessary.

In a recent communication we reported the observation of the sharp-line luminescence of a selected group of PAH compounds in a Shpol'skii type solvent solidified at 90 K and irradiated by x-rays (13). The application of this technique to the identification of several PAHs in coal samples has also been reported (14). In this communication we report further observations that portend an increasing use of this technique for the qualitative identification and quantitative estimation of a broad range of PAHs and aromatic heterocyclics including isomers of these compounds. For the results reported in this communication, prior isolation of the individual components was not required, although our observations show that some prior separations will be necessary on complex samples if more complete screening is desired on the PAH fraction of complex samples.

EXPERIMENTAL FACILITIES AND PROCEDURES

Apparatus The relatively simple XEOL spectrometric instrumentation used in these studies has been described (13).

Extraction and Identification of PAH compounds The procedure described by Giger and Blumer (15) was modified (14) and used to isolate the neutral fraction of PAHs in environmental samples; the

three-step separation procedure used is presented in an abbreviated form in Table 1. An aliquot of the PAH concentrate in n-heptant is subjected to XEOL examination. Shale oils consist of an extremely complex mixture of organic compounds, and the isolation of the PAH fraction from shale oils is a singularly difficult analytical task (16). In our studies a modified procedure was adopted to isolate the PAH fraction from a shale oil sample distributed by the National Bureau of Standards as a surrogate reference material. A 0.5 gm samples of the shale oil was dissolved in 100 ml of cyclohexane and sequentially partitioned with 1.5 N NaOH and 1 N HCl to remove the acidic and basic compounds. The neutral fraction was then loaded on to an alumina column (acidic, 10% H₂O, 30 g) and on eluting with cyclohexane, the PAH fraction was obtained. The cyclohexane eluate was evaporated to dryness. The residue was dissolved in 1 ml of methanol and then subjected to the fractionation procedure shown in Table 1, except that the second 50 ml of eluant was collected in 5 ml subfractions. Except for the investigation of solvent effects on the XEOL of dibenzothiophene, all other spectra were obtained in a n-heptane solvent at 90 K.

RESULTS AND DISCUSSION

It has been emphasized that one of the basic limitations of several analytical techniques used to characterize the PAH content of samples is the difficulty encountered in identifying isomers, which generally have widely ranging carcinogenecity. In Figure 1, the characteristic sharp-line luminescence spectra observed on the x-ray irradiation of the two groups of isomers are reproduced. The differentiation of isomeric species is clearly seen in the top portions of Figure 1, which shows the composite spectrum of a mixture of 200 ng

Table 1. Separation procedure for the isolation of PAH's from environmental samples.

each of the four isomers chrysene, pyrene, B[a]A, triphenylene and the near isomer fluoranthene. All the five compounds can be easily identified in contrast to the difficulties associated with resolving chrysene and B[a]A by HPLC, or chrysene and triphenylene by GC. The lower spectrum in Figure 1 shows the distinct features of carcinogenic B[a]P, the mildly carcinogenic B[e]P, and the noncarcinogenic perylene. In this context, the difficulties experienced in separating and identifying the isomeric perylene and B[e]P by HPLC should be recalled (9,10). Of special interest are the distinct features shown by B[a]P and B[e]P. Under UV excitation, the emission band at 390 nm has usually been employed for the identification of B[e]P. Under x-ray excitation, B[e]P exhibits both fluorescence at 390 nm as well as phosphorescence at 536 nm. The phosphorescence emission is more intense and also occurs in a spectral region where relatively little interference is expected from the luminescence of other PAH compounds.

The B[a]P and benzo[k]fluoranthene (B[k]F) are known to have similar UV excited fluorescence spectra with their optimum emission at ~400 nm. Figure 2 clearly shows that the two compounds can easily be identified.

Because environmental samples often contain a large number of PAH compounds, the feasibility of identifying as many compounds as possible by the XEOL technique was demonstrated by examining a mixture of 12 PAH compounds. In addition to other compounds, this mixture contained the three isomeric groups: B[a]P, B[e]P, perylene; B[a]A, chrysene, triphenylene; and anthracene, phenanthrene. Fluoranthene was also present in these mixtures at 20 µg/ml and the concentration of the remainder varied from 2 to 10 µg/ml. The XEOL spectrum of this mixture is presented in Figure 3. In the figure all the isomeric compounds can be readily identified.

Because the major goal of our present study was to obtain the PAH profiles of environmental samples utilizing the XEOL technique, a variety of environmental samples were examined. The PAH profile of a fly ash sample collected in the city of Ames power plant stack is shown in Figure 4. The spectrum represents PAH compounds present in a 1/5 fraction of a n-heptane concentrate obtained on processing of a 10 gm sample. The presence of a relatively strong peak for benz[a]pyrene should be noted. A second sample consisted of air particulates collected at a site within three blocks of the Ames City power plant, while the stack plume impinged the ground. The sample was collected on a 20 cm x 25 cm quartz fiber filter fitted to a high volume sampler, which was operated for two hours. The spectrum shown in Figure 5 represents PAH compounds present in less than 1/20 of the air particulate sample.

For quantitative determinations in complex mixtures, as represented by those discussed above, the method of standard additions is preferred (17) so that artifacts induced by energy transfer processes or by inner filter effects can be minimized (18). The effect of the additions of increasing amounts of a mixture of B[a]P, perylene, triphenylene, and coronene to aliquots of the air particulate sample discussed above is shown in Figure 6. The analytical calibration curves obtained from a least square fit are shown in Figure 7. The results of this quantitation study indicate the presence of a relatively large amount of benz[ghi]perylene and coronene in the air particulate sample. Although the original purpose of collecting this sample was to characterize the power plant stack plume that impinged the ground in the vicinity of the plant site, the fact that the sample was collected several blocks away from the plant site suggested that

automobile and truck exhausts contributed to the PAH content. This contention was confirmed by earlier observations of relatively high levels of benz[ghi]perylene and coronene in automobile exhausts (19), in contrast to the levels detected in byproducts of coal combustion (20).

The profile of PAHs extracted from a sample of solvent refined coal (SRC) process solvent and a sample of gas stream condensate from a coal gasification plant at the Morgantown Energy Technology Center are shown in Figures 8 and 9 respectively. The separation of the PAHs present in the SRC process solvent was a relatively easy task. A known amount of the sample was directly loaded on the Sephadex LH20 column and subjected to further processing as indicated in Table 1 to obtain the PAH fraction. The presence of three known carcinogens, B[a]A, B[a]P and 3-methylcholanthrene in the SRC process solvent is indicated in the spectrum shown in Figure 6. The presence of a large amount of organic matter in the gas stream condensate made the isolation of the PAH fraction a difficult task, as is indicated by the broad background observed in the spectrum of this sample in Figure 9. To obtain a better separation of the PAH fraction, a more elaborate fractionation procedure would have to be adopted.

PAH Profiles of Shale and Fuel Oil Samples The diversity of organic compounds present in shale oil samples, as indicated by the work of Hurlubise et al (16), makes the isolation of a reasonably pure PAH fraction a difficult task. The spectrum shown in Figure 10 represents the PAHs detectable in the sixth and seventh, five-ml subfractions of the second 50-ml eluate from the separation procedure outlined in this communication. The broad spectral background underlying the sharp peaks suggests the presence of other organic compounds not adequately separated from the PAHs in the separation procedure used.

The problems associated with oil spill characterization and the diverse analytical methodology required for unequivocal identification of the source of an oil spill has recently been reviewed (21). Recent studies have demonstrated that the improved spectral structure observed with ultraviolet excited low temperature luminescence in contrast to room temperature luminescence is a more effective way of fingerprinting fuel oils (22). Because the spectra observed by Fortier and Eastwood are typical of those observed for PAH compounds which are known to be present in petroleum products, we were led to evaluate the potential of XEOL in Shpol'skii matrices as an alternate approach. Five mg fuel oil samples were loaded on Sephadex LH20 columns (Sigma Chemical Company) and subjected to permeation chromatography. The PAH fraction present in the benzene-methanol (1:1) eluant was further processed as outlined earlier to obtain the PAH concentrate. The PAH profiles of four different fuel oil concentrates obtained in this way are shown in Figure 11. There do not appear to be significant differences in the number 2 fuel oils shown on the left of the figure, but identifiable differences are observed between the number 2, 4, and 6 oils. Thus, the technique described in this communication may provide an alternate avenue for characterizing oil spills.

XEOL of Other Organics in Shpol'skii Solvents The XEOL spectrum of the carcinogen benzene is shown in Figure 12, and the spectra of the carcinogenic carbazoles are shown in Figure 13. The spectral differences observed in Figure 13 should facilitate the identification of the two isomers present in a mixture. As shown in Figure 14, dibenzothiophene, a carcinogenic compound presumed to be a major

component of the organic sulfur compounds in coal, exhibits sharp line spectra in the n-heptane Shpol'skii host but not in either tetrahydrofuran or cyclohexane solvents. To the best of our knowledge, the spectrum of dibenzothiophene in a n-heptane host is the first report of a Shpol'skii spectrum of this compound.

CONCLUSION

One of the criteria in the UICC/IARC specifications for an acceptable analytical method for PAH determination is the capability to identify several components that may be present in mixtures isolated from a sample. The components which should be unequivocally identified and measured are B[a]A, B[a]P, B[e]P, benzo[ghi]perylene, pyrene, B[k]F and coronene (23,24). In this communication we have demonstrated that XEOL of PAHs in Shpol'skii solvents can meet the identification criterion, in contrast to most other analytical techniques cited. To obtain reliable quantitative data on "real world" samples, significant improvements in the analytical methodology to isolate PAH fractions or subfractions will no doubt be necessary. This task has been shown to require a substantial effort (25,26). The potential advantages of utilizing the Shpol'skii effect to simultaneously detect several PAHs present in fractions isolated by improved analytical methodology, e.g., HPLC, has been recently demonstrated (27).

ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy, contract No. W-7405-Eng-82, Division of OHER budget code GK-01-02-04 GK-01-02-04-3. The authors thank Dr. Delyle Eastwood, Mr. Scott Fortier and the United States Coast Guard R & D Center for the supply of fuel oil samples characterized in this investigation.

REFERENCES

1. "Environmental, Health and Control Aspects of Coal Conversion: An Information Overview", Ed., H. M. Braunstein, E. D. Copenhaver and H. A. Pfuderer, ORNL/EIS-95, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, 1977.
2. Pierce, R. C.; Katz, M. Anal. Chem. 1975, 47, 1743.
3. Novotny, M.; Lee, M. L.; Bartle, K. D. J. Chromatog. Sci. 1974, 12, 606.
4. Bjørseth, A.; Lunde, G. Am. Inc. Hyg. Assoc. J. 1977, 38, 224.
5. Giger, W.; Schaffner, G. Anal. Chem. 1978, 50, 243.
6. Doran, T.; McTaggart, N. C. J. Chromatog. Sci. 1974, 12, 715.
7. Dong, M.; Locke, D. C. Anal. Chem. 1976, 48, 368.
8. Dark, W. A.; McFadden, W. H.; Bradford, D. L. J. Chromatog. Sci. 1977, 15, 454.
9. Fox, M. A.; Staley, S. W. Anal. Chem. 1976, 48, 992.
10. Das, B. S.; Thomas, G. H. Anal. Chem. 1978, 50, 967.
11. Janini, G. M.; Muschik, G. M.; Schroer, J. A.; Zielinski, W. L. Jr. Anal. Chem. 1976, 48, 1879.
12. Janini, G. M.; Shsikh, B.; Zielinski, W. L. Jr. J. Chromatog. 1977, 132, 136.
13. D'Silva, A. P.; Oestreich, G. J.; Fassel, V. A. Anal. Chem. 1976, 48, 915.
14. Woo, C. S.; D'Silva, A. P.; Fassel, V. A.; Oestreich, G. J. Environ. Sci. & Technol. 1978, 12, 173.
15. Giger, W.; Blumer, M. Anal. Chem. 1974, 46, 1663.
16. Hurtubise, R. J.; Schabron, J. F.; Feaster, J. D.; Therkildsen, D. H.; Poulson, R. E. Anal. Chim. Acta 1977, 89, 377.
17. Shpol'skii, E. V. J. Appl. Spect. 1967, 7, 336.
18. Kirkbright, G. F.; DeLima, C. G. Analyst 1974, 99, 338.
19. Grimmer, G.; Bohnke, H.; Glaser, A. Zbl. Bkt. Hyg., I. Abt. Orig. B. 1977, 164, 218.
20. Natusch, D. F. S.; Wallace, J. R.; Evans, C. A. Science 1974, 183, 202.

21. Bentz, A. P. Anal. Chem. 1978, 50, 655A.
22. Fortier, S. H.; Eastwood, D. Anal. Chem. 1978, 50, 334.
23. UICC Technical Report Series, Vol. 4, 1970.
24. IARC Internal Technical Report, No. 71/002, 1971.
25. Wise, S. A.; Chesler, S. N.; Hertz, H. S.; Hilpert, L. R.; May, W. E. Anal. Chem. 1977, 49, 2306.
26. Guerin, M. R.; Epler, J. L.; Griest, W. H.; Clark, B. R.; Rao, T. K. in "Carcinogenesis - A Comprehensive Survey", P. W. Jones and R. I. Freudenthal, ed.; Raven Press, New York, 1978; pp. 21-33.
27. Colmsjö, A.; Stenberg, U. Anal. Chem. 1979, 51, 145.

FIGURE CAPTIONS

- Figure 1. X-ray excited optical luminescence of isomeric polynuclear aromatic hydrocarbons in n-heptane.
- Figure 2. A comparison of X-ray excited optical luminescence of benz[a]pyrene and benz[k]fluoranthene in n-heptane.
- Figure 3. X-ray excited optical luminescence of a mixture of 12 PAHs in n-heptane
 1) 2-methylnaphthalene 2) Chrysene 3) Benz[a]anthracene
 4) Benz[e]pyrene 5) 3-Methylcholanthrene 6) Benz[a]pyrene
 7) Anthracene 8) Fluoranthene 9) Coronene
 10) Perylene 11) Triphenylene 12) Phenanthrene
- Figure 4. X-ray excited optical luminescence of PAHs extracted from 10 gms of particulates collected at the City of Ames power plant stacks.
 1) Dibenz[ah]anthracene 2) Benz[a]pyrene
 3) Benz[ghi]perylene 4) Anthracene 5) Dibenz[ai]pyrene
 6) Perylene 7) Triphenylene 8) Phenanthrene
 9) Fluoranthene
- Figure 5. X-ray excited optical luminescence of PAHs extracted from air particulates.
 1) Chrysene 2) Dibenz[a,h]anthracene 3) Benz[a]pyrene
 4) Benz[ghi]perylene 5) Anthracene 6) Dibenz[ai]pyrene
 7) Coronene 8) Perylene 9) Triphenylene
 10) Phenanthrene 11) Benz[e]pyrene
- Figure 6. Spectral profiles resulting from the addition of increasing amounts of PAHs to aliquots of a particulate sample extract.
 1) Benz[a]pyrene 2) Coronene 3) Perylene
 4) Triphenylene
- Figure 7. Calibration curves for coronene, perylene, benz[a]pyrene and triphenylene obtained using the standard addition procedure. The amounts of PAHs present in the original sample are represented by the symbol x.
- Figure 8. X-ray excited optical luminescence of PAHs extracted from 250 mg of solvent refined coal-process solvent. The spectrum represents PAHs present in only 3 mg of the sample.
 1) Chrysene 2) Benz[a]anthracene 3) Benz[e]pyrene
 4) 3-Methylcholanthrene 5) Benz[a]pyrene
 6) Benz[ghi]perylene 7) Dibenz[ai]pyrene
 8) Triphenylene 9) Perylene 10) Phenanthrene
 11) Fluoranthene

Figure 9. X-ray excited optical luminescence of PAHs extracted from 1.7 mg of a tarry residue obtained during an experiment conducted at Morgantown Energy Research Center, Morgantown, West Virginia. The spectrum represents PAHs present in only 1/200 of the processed sample.

- 1) Chrysene 2) Pyrene 3) Benz[a]anthracene
- 4) Benz[e]pyrene 5) Dibenzo[a,h]anthracene 6) Anthracene
- 7) Benz[a]pyrene 8) Benz[ghi]perylene 9) Dibenzo[a,i]pyrene
- 10) Perylene 11) Triphenylene 12) Dibenzo[a,h]pyrene
- 13) Phenanthrene 14) Fluoranthene

Figure 10. X-ray excited optical luminescence of PAHs extracted from shale oil.

- 1) Pyrene 2) Chrysene 3) Benz[e]pyrene 4) Benz[a]pyrene
- 5) Anthracene 6) Triphenylene 7) Perylene
- 8) Phenanthrene 9) Fluoranthene

Figure 11. X-ray excited optical luminescence spectra of fuel oils (each sample represents 0.2 ml of 5 mg/ml fuel oil in n-heptane).

- 1) Phenanthrene 2) Chrysene 3) Pyrene
- 4) Dibenzoanthracene 5) Anthracene 6) Perylene
- 7) Triphenylene 8) Benz[e]pyrene 9) Fluoranthene

Figure 12. X-ray excited optical luminescence of 20 ppm benzene in n-heptane.

Figure 13. X-ray excited optical luminescence of two isomeric carbazole. Each compound was 20 ppm in n-heptane.

Figure 14. Effects of solvents on the structure of dibenzothiophene spectrum under X-ray irradiation. Dibenzothiophene was present at 20 ppm in each solvent.

Figure 1. X-ray excited optical luminescence of isomeric polynuclear aromatic hydrocarbons in n-heptane.

Figure 2. A comparison of X-ray excited optical luminescence of benz[a]pyrene and benz[k]fluoranthene in n-heptane

Figure 3. X-ray excited optical luminescence of a mixture of 12 PAHs in n-heptane

1) 2-methylnaphthalene	2) Chrysene	3) Benz[a]anthracene
4) Benz[e]pyrene	5) 3-Methylcholanthrene	6) Benz[a]pyrene
7) Anthracene	8) Fluoranthene	9) Coronene
10) Perylene	11) Triphenylene	12) Phenanthrene

Figure 4. X-ray excited optical luminescence of PAHs extracted from 10 gms of particulates collected at the City of Ames power plant stacks.

1) Dibenz[ah]anthracene	2) Benz[a]pyrene
3) Benz[ghi]perylene	4) Anthracene
5) Dibenz[ai]pyrene	6) Perylene
7) Triphenylene	8) Phenanthrene
9) Fluoranthene	

Figure 5. X-ray excited optical luminescence of PAHs extracted from air particulates.

1) Chrysene	2) Dibenz[a,h]anthracene	3) Benz[a]pyrene
4) Benz[ghi]perylene	5) Anthracene	6) Dibenz[ai]pyrene
7) Coronene	8) Perylene	9) Triphenylene
10) Phenanthrene	11) Benz[e]pyrene	

Figure 6. Spectral profiles resulting from the addition of increasing amounts of PAHs to aliquots of a particulate sample extract.
 1) Benz[a]pyrene 2) Coronene 3) Perylene
 4) Triphenylene

Figure 7. Calibration curves for coronene, perylene, benz[a]pyrene and triphenylene obtained using the standard addition procedure. The amounts of PAHs present in the original sample are represented by the symbol x.

Figure 8. X-ray excited optical luminescence of PAHs extracted from 250 mg of solvent refined coal-process solvent. The spectrum represents PAHs present in only 3 mg of the sample.

1) Chrysene	2) Benz[a]anthracene	3) Benz[e]pyrene
4) 3-Methylcholanthrene	5) Benz[a]pyrene	
6) Benz[ghi]perylene	7) Dibenzo[a]pyrene	
8) Triphenylene	9) Perylene	10) Phenanthrene
11) Fluoranthene		

Figure 9. X-ray excited optical luminescence of PAHs extracted from 1.7 mg of a tarry residue obtained during an experiment conducted at Morgantown Energy Research Center, Morgantown, West Virginia. The spectrum represents PAHs present in only 1/200 of the processed sample.

1) Chrysene	2) Pyrene	3) Benz[a]anthracene
4) Benz[e]pyrene	5) Dibenzo[a,h]anthracene	6) Anthracene
7) Benz[a]pyrene	8) Benz[ghi]perylene	9) Dibenzo[a,i]pyrene
10) Perylene	11) Triphenylene	12) Dibenzo[a,h]pyrene
13) Phenanthrene	14) Fluoranthene

Figure 10. X-ray excited optical luminescence of PAHs extracted from shale oil.

1) Pyrene	2) Chrysene	3) Benz[e]pyrene	4) Benz[a]pyrene
5) Anthracene	6) Triphenylene	7) Perylene	
8) Phenanthrene	9) Fluoranthene		

Figure 11. X-ray excited optical luminescence spectra of fuel oils (each sample represents 0.2 ml of 5 mg/ml fuel oil in n-heptane).

1) Phenanthrene	2) Chrysene	3) Pyrene
4) Dibenanthracene	5) Anthracene	6) Perylene
7) Triphenylene	8) Benz[e]pyrene	9) Fluoranthene

Figure 12. X-ray excited optical luminescence of 20 ppm benzene in n-heptane.

Figure 13. X-ray excited optical luminescence of two isomeric carbazoles. Each compound was 20 ppm in n-heptane.

Figure 14. Effects of solvents on the structure of dibenzothiophene spectrum under X-ray irradiation. Dibenzothiophene was present at 20 ppm in each solvent.

VI. Laser Pumped Luminescence (LPL) Spectroscopy (G. Small)

A. Progress

Fluorescence Line Narrowing Spectroscopy (FLNS)

To optimize the resolution of FLNS for organic impurities dissolved in organic glasses, two improvements in the previously described apparatus were made:

- (i) Addition of a N₂-pumped tunable dye laser (both the National Research Corporation PTL-2000 and Molelectron DL-200 systems are being used).
- (ii) Addition of a gated detection system and LSI-11 microprocessor.

Improvement (i) was essential for selective excitation, time resolution and optimum line narrowing capabilities. Figures 1 and 2 demonstrate the latter. Figure 1 is the absorption spectrum of perylene in a glycerol: water glass associated with the fluorescent state. In a previous report it was noted that high energy laser excitation of perylene near 27,500 cm⁻¹ resulted in no appreciable line narrowing at 4.2 K. The spectra in Figure 2 clearly demonstrate fluorescence line narrowing for three different excitation frequencies ($\nu_A^{EX}, \nu_B^{EX}, \nu_C^{EX}$ in Figure 1). The simplest spectrum results for $\nu_C^{EX} = 23,150$ cm⁻¹ because excitation is into a less vibrationally congested region. Finally, excitation into the (0,0) band at 22,750 cm⁻¹, Figure 1, results in an even simpler fluorescence spectrum with only one origin rather than three (0₁,0₆,0₅) as in trace C of Figure 2. These data along with others demonstrate that excitation tunability allows for facile generation of simple narrow line fluorescence spectra suitable for resolving geometric isomers.

Improvement (ii) allows one to take advantage of the pulsed (~ 10 ns pulse width) excitation from the dye laser for time resolution of mixtures of PAHs or, for example, nitrogen heterocycles. The gated detection system is based on two Evans Associates model 4130 gated integrator modules. An Evans Associates model 4141 programmable time delay module and locally fabricated circuits based on 74121 integrated circuit chips allow for controlling both the time delay and gate width for synchronous detection of the pulsed signals based on the same trigger that fires the N₂ laser. Positioning of the gate width from 28 ns up to several μ s is possible at any time prior to, during or after the signal pulse. The synchronization circuitry for this detection system and firing of the laser are controlled by an LSI-11 microprocessor. Spectra normalized for laser pulse

intensity jitter can be generated. Initial experiments on an anthracene ($\tau_{fl} = 5\text{ns}$)/fluoranthene ($\tau_{fl} = 50\text{ns}$) mixture have shown that the anthracene fluorescence spectrum can be totally suppressed leaving only the portion due to fluoranthene.

GC-Rotationally Cooled Fluorescence Spectroscopy

The goal of this project is to obtain narrow line fluorescence from aromatic hydrocarbons in the vapor phase present in the effluent of a gas chromatograph. The fluorescence from these hot molecules will be narrowed by cooling rotational and vibrational degrees of freedom through a supersonic expansion with helium carrier gas. The supersonic expansion nozzle source is in operation and its performance under conditions of temperature and carrier gas pressure compatible with gas chromatograph interfaces is being assessed. Two different methods of detecting fluorescence are currently being used. They are excitation spectra in which the total fluorescence from the beam is collected as a function of laser excitation wavelength; and dispersed fluorescence which is scanned by a spectrometer while maintaining a fixed excitation wavelength. It is the dispersed fluorescence (eventually to be collected by a rapid scan spectrometer) which is intended to be used for GC detection. At present, however, both types of detection are needed to determine different characteristics of the expansion. Figure 3 shows an example of the dispersed fluorescence from I_2 in a supersonic helium expansion. The fluorescence was excited continuously by the 5145Å line of an Ar^+ laser. This wavelength excites I_2 from the zero vibrational level of the ground state to vibrational level 43 of the B state (43-0). In the figure the strongest lines are due to transitions from vibrational level 43 to vibrational levels 1, 2,, of the ground state. That is, no vibrational relaxation occurs in the excited state before emission for these bands. Several weaker bands, some of which are labelled in the figure, are due to relaxation from level 43 to lower lying levels 42, 41, 40, followed by emission to levels 1, 2, 3 of the ground state. The relative amount of relaxed fluorescence is dependent upon the distance from the nozzle at which the excitation laser crosses the beam and also upon the pressure of the helium carrier gas. At short distances and high pressures an increase in relaxed emission is observed.

In Figure 4 a portion of the excitation spectrum of I_2 is

shown. The laser bandwidth for this case was 3 cm^{-1} . Three vibrational bands, 0-7, 1-9, and 2-11 (the first number labels the ground vibrational level, the second the excited vibrational level) are shown. The effective vibrational temperature of the beam may be determined from the relative intensity of these bands and the Frank Condon factors for these transitions. At three atmospheres of helium, and with a 100μ diameter nozzle orifice a temperature of 85-100K was determined. At five atmospheres with the same nozzle the temperature was 60-75K.

Figures 5 and 6 show excitation spectra of naphthalene in a supersonic expansion. The width of the 438 cm^{-1} band shown in Figure 6 is laser limited but some rotational structure is apparent. An important question regarding these large aromatic molecules is what happens to the fluorescence spectrum when the excitation energy is several thousand wavenumbers above the origin of the first electronic state. In order to answer this question the dispersed fluorescence must be obtained. Research to accomplish this is now in progress.

B. Status

Fluorescence Line Narrowing Spectroscopy (FLNS)

Since the building plan of this project is essentially complete, we plan to establish the resolution capability of FLNS for complex mixtures of organic pollutants imbedded in the glycerol:water glass. Both laboratory prepared and real samples will be utilized.

GC-Rotationally Cooled Fluorescence Spectroscopy

One reason why difficulty in observing the dispersed fluorescence from PAHs has been encountered is that the temperatures required to obtain a sufficient vapor pressure of these molecules are rather high ($100\text{-}300^\circ\text{C}$). This temperature must be maintained along the entire nozzle length. Otherwise, the compounds tend to condense in and plug the narrow nozzle orifice. Although it was realized that this nozzle heating problem would have to be solved when the apparatus was interfaced to a GC, it was hoped that the question of the extent of excited state vibrational relaxation could be considered before addressing the nozzle heating problem. However, this was not the case and several methods of nozzle heating are being tried. Progress has been made on this problem and it should be possible to consider the vibrational relaxation problem shortly.

Figure 1. Electronic absorption spectrum of perylene.

Figure 2. Line narrowed fluorescence spectra of perylene for different excitation frequencies.

Figure 3.

The dispersed fluorescence of I_2 in a supersonic beam of helium. Excitation at $5145 \text{ \AA}$ corresponds to the level $43-0$. The strong bands in the spectrum are fluorescence from vibrational level 43 in the upper state to vibrational levels 1, 2, 3, etc. in the lower state. The weaker bands, some of which are labelled, represent vibrational relaxation in the excited state prior to emission.

Figure 4. The fluorescence excitation spectrum of I_2 in a supersonic helium beam in the region of the 0-7, 1-9, and 2-11 bands

Figure 5. The fluorescence excitation spectrum of the origin region of naphthalene in a supersonic helium beam.

Figure 6. A higher resolution excitation spectrum of the 438 cm^{-1} band of naphthalene. The arrows indicate the laser bandwidth, 0.7 cm^{-1} .

VII. Multielement Characterization of Air Particulates. (E. DeKalb, B. Bear)

A. Progress

Comparison data have been obtained and correlated for the determination of various elements on 24 air particulate filters by two independent analytical techniques, induction-coupled plasma - atomic emission spectroscopy (ICP-AES) and x-ray fluorescence spectroscopy (XRF). Calibration of the XRF instrument was accomplished by using reference air particulate filters as prepared on the Air Filter Calibration Facility (AFCF). The ICP-AES instrument was calibrated using reference solution mixtures of known concentrations. The sample filters were first analyzed non-destructively by XRF, and then dissolved in H_2SO_4 plus a few drops of 50% H_2O_2 for the ICP-AES determinations.

The filters analyzed consisted of the following:

10 filters	Ambient sampling in vicinity of municipal power plant,
4 filters	Non-respirable particulates - welding shop
4 filters	Respirable particulates - welding shop
2 filters	Non-respirable particulates - auto exhaust
2 filters	Respirable particulates - auto exhaust
1 filter	Non-respirable particulates - leaf burning
1 filter	Respirable particulates - leaf burning

Comparison data are shown in Tables 1-11. The values are given for both μg per filter loading and μg per volume of air filtered. Twenty or more elements were determined by each of the analytical techniques, but only 15 were determined by both, and for many of those elements, comparisons were not possible because the values were at or below detection limits for one or both techniques.

The values show good agreement for Ca, Fe, Mn and Ti. Some unresolved discrepancies remain for Al, Cu, Ni, Si and Zn. For Al and Si, the ICP-AES values were consistently lower than those obtained by XRF, which was probably caused by incomplete dissolution of some of the particulates. The Cu and Zn values were either satisfactory or somewhat low as determined by ICP-AES, which could also reflect incomplete dissolution. The ICP-AES analyses for Ni were consistently higher than those determined by XRF. No explanation for this disagreement has been developed.

As stated in a previous report, the AFCF is capable of loading 12 filters simultaneously with a relative standard deviation of better than $\pm 3\%$. Various observations have lead to the conclusion that this residual non-reproducibility is caused by the flow resistant characteristics of the individual Nucleopore membrane filters. According to James Robinson, Nucleopore Corporation, filter-to-filter non-reproducibility, within a lot, will be in the range of 2 to 3 percent. It thus appears that the AFCF is functioning in a satisfactory way.

B. Status

Further efforts to improve the AFCF are not anticipated. If desired, a complete redesign should make it possible to balance the flow resistance of the 12 sampling ports prior to particulate deposition.

To resolve the problems of incongruent values for particular elements, additional air particulate samples must be collected and analyzed. A two-stage, virtual impactor, air particulate sampler (Sierra model 244) has been purchased and will be used to collect the needed samples from various environments. The preparation of several sets of standard filters specifically formulated to approximate real-life samples is also anticipated.

Research will continue on developing filter holders and preservation techniques so that standard filters can be transported and distributed without the loss of a portion of the particulate load.

Table 1

Analysis of Welding Particulates

	μg		$\mu\text{g}/\text{l}$	
	XRF	ICP	XRF	ICP
Al (Respirable)	2.6	< 1	.14	< .05
(")	2.7	< 1	.11	< .04
Cu (Non-respirable)	< .81	.20	< .043	.011
(")	1.1	.25	.025	< .003
(Respirable)	.47	< .05	.043	.010
(")	.54	< .05	.022	< .002
Fe (Non-respirable)	120	120	6.3	6.3
(")	140	150	5.7	5.8
(Respirable)	.41	.25	.022	.013
(")	2.7	1.4	.11	.054
Mn (Non-respirable)	12	12	.63	.62
(")	16	16	.64	.64
(Respirable)	.36	.35	.014	.014
Ni (Non-respirable)	< .2	.40	< .011	.021
(")	< .15	.45	< .008	.024
(Respirable)	< .2	.65	< .008	.026
(")	< .2	~.45	< .008	~.018
Si (Non-respirable)	67	< 2	3.6	< .11
(")	< .4	< 2	.021	< .11
(Respirable)	98	< 2	3.9	< .08
(")	3.9	< 2	.21	< .08
Ti (Non-respirable)	4.8	4.9	.26	.26
(")	6.5	6.5	.26	.26
Zn (Non-respirable)	< .74	.30	< .039	.016
(")	~.06	< .10	~.003	< .005
(Respirable)	.90	.45	.036	.018
(")	~.14	< .10	~.006	< .004

Table 2

Auto Exhaust

	μg		$\mu\text{g}/\ell$	
	XRF	ICP	XRF	ICP
1969 Car (Non-respirable)	5.2	5.3	.21	.21
(Respirable)	17	17	.68	.70
1977 Car (Non-respirable)	1.7	~ 1.3	.068	$\sim .05$
(Respirable)	1.5	~ 3.9	.059	$\sim .16$

Table 3

Determination of Al in Air Particulates Near
Ames Municipal Power Plant

Sample No.	μg		$\mu\text{g}/\text{m}^3$	
	XRF	ICP	XRF	ICP
1	6.7	3.0	1.1	.48
2	8.5	2.6	3.3	1.0
3	26	20	6.4	4.9
4	15	5.6	5.7	2.1
5	44	38	13	11
6	15	6.2	3.4	1.4
7	11	4.1	2.5	.92
8	8.9	2.8	1.3	.40
9	47	46	14	14
10	7.6	4.6	1.2	.73

Table 4
Determination of Ca in Air Particulates Near
Ames Municipal Power Plant

Sample No.	μg		$\mu\text{g}/\text{m}^3$	
	XRF	ICP	XRF	ICP
1	11	12	1.8	2.0
2	7.2	7.3	2.8	2.9
3	190	190	46	46
4	29	28	11	11
5	360	350	110	110
6	28	29	6.4	6.6
7	17	21	3.8	4.8
8	11	13	1.6	1.8
9	420	410	130	120
10	19	19	3.0	3.0

Table 5
Determination of Cu in Air Particulates Near
Ames Municipal Power Plant

Sample No.	μg		$\mu\text{g}/\text{m}^3$	
	XRF	ICP	XRF	ICP
1	.51	.50	.082	.080
2	3.0	3.3	1.2	1.3
3	.71	.75	.18	.19
4	1.8	1.7	.68	.66
5	1.1	1.2	.33	.35
6	.43	.45	.097	.10
7	.49	.25	.11	.056
9	1.8	1.7	.53	.51
10	.29	.15	.046	.024

Table 6
Determination of Fe in Air Particulates Near
Ames Municipal Power Plant

Sample No.	μg		$\mu\text{g}/\text{m}^3$	
	XRF	ICP	XRF	ICP
1	2.5	2.6	.40	.41
2	2.0	3.2	.79	1.3
3	36	28	8.8	7.0
4	4.8	4.9	1.8	1.8
5	61	61	18	18
6	4.9	5.4	1.1	1.2
7	3.2	3.5	.72	.79
9	76	77	23	23

Table 7
Determination of Mn in Air Particulates Near
Ames Municipal Power Plant

Sample No.	μg		$\mu\text{g}/\text{m}^3$	
	XRF	ICP	XRF	ICP
3	1.1	1.1	.26	.26
5	1.9	1.9	.57	.57
6	.17	.20	.038	.045
9	2.1	2.1	.62	.63

Table 8
Determination of Ni in Air Particulates Near
Ames Municipal Power Plant

Sample No.	μg		$\mu\text{g}/\text{m}^3$	
	XRF	ICP	XRF	ICP
1	< .15	.35	< .024	.056
2	< .15	.80	< .059	.31
3	< .15	.35	< .037	.087
4	< .15	.45	< .057	.17
5	< .15	.45	< .045	.14
6	< .15	.30	< .034	.068

Table 9
Determination of Si in Air Particulates Near
Ames Municipal Power Plant

Sample No.	μg		$\mu\text{g}/\text{m}^3$	
	XRF	ICP	XRF	ICP
1	23	< 2	3.7	<.3
2	24	< 2	9.4	<.8
3	148	< 2	37	<.5
4	60	< 2	23	<.7
5	240	< 2	72	<.6
6	55	< 2	12	<.4
7	33	< 2	7.4	<.4
8	22	< 2	3.1	<.3
9	250	< 2	75	<.6
10	25	< 2	4.0	<.3

Table 10
Determination of Zn in Air Particulates Near
Ames Municipal Power Plant

Sample No.	μg		$\mu\text{g}/\text{m}^3$	
	XRF	ICP	XRF	ICP
1	.42	<.1	.067	<.016
2	.37	<.1	.15	<.04
3	.52	.55	.13	.14
5	.63	.55	.19	.17
7	.28	11.4*	.063	2.6*
8	.23	<.1	.033	<.01
9	.78	.40	.24	.12

* Probable contamination

Table 11

Discription of Sampling Stations
For Collection of Filters of Tables 3-10

<u>Sample No.</u>	<u>Location from Power Plant</u>	<u>Wind Speed (mph)</u>	<u>Location Characteristics</u>
1	Up Wind	8	Paved city street
2	Down Wind	8	Cemetery
3	Up Wind	6-8	Busy unpaved road
4	Down Wind	6-8	City Park
5	Up Wind	10	Busy unpaved road
6	Down Wind	8	Residential street corner
7	Down Wind	10	Residential street corner
8	Down Wind	10	Busy unpaved road
9	Down Wind	Variable	Busy unpaved road
10	Up Wind	Variable	Residential street corner

OTHER Quarterly Report Mailing List - July, 1979

Dr. Joseph Duckett
National Center for Resource Recovery
1211 Connecticut Avenue, NW
Washington, D.C. 20011

Mr. Donald Knowles
Industrial Hygienist
Environmental Investigations Branch
NIOSH (Room 117)
944 Chestnut Ridge Road
Morgantown, W. Virginia 26505

Mr. Douglas W. Boehm
Environmental Control Technology
Office of Environment
Mail Station E-201
U.S. Department of Energy
Washington, D.C. 20545

Dr. Subrata Sengupta
Department of Mechanical Engineering
University of Miami
P.O. Box 248294
Coral Gables, Florida 33124

Mr. Terry Sprengel
City Manager
City Hall
Ames, Iowa 50010

Mr. Bill Rosenkranz
OALWU (RD-682)
Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460

Dr. Robert A. Olexesy
Energy Systems Environmental
Control Division
Industrial Environmental Research
Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Mr. Alden Christianson/George Huffman
Solid & Hazardous Waste Research
Laboratory
U.S. Environmental Protection Agency
National Environmental Research Center
Cincinnati, OH 45268

Mr. Carlton A. Wiles
Solid & Hazardous Waste Research
Laboratory
U.S. Environmental Protection Agency
National Environmental Research Center
Cincinnati, Ohio 45268

Mr. Douglas Fiscus
Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

Dr. Gerald Goldstein
Office of Health and Environmental
Research
Office of Environment
Mail Station E-201
U.S. Department of Energy
Washington, D.C. 20545

Dr. Robert L. Butenhoff
Office of Health & Environmental Research
Environment, Mail Station E-201
U.S. Department of Energy
Washington, D.C. 20545

Mr. Donald K. Walter
Branch Chief
Urban Waste Technology Branch
Office of Conservation and Solar
Applications
Mail Station 2221C
Department of Energy
Washington, D.C. 20545

Dr. Charles E. Carter
Manager, Biomedical Programs
Office of Health & Environmental
Research, M.S. #-201
Office of Environment
U.S. Department of Energy
Washington, D.C. 20545

Dr. Walter H. Weyzen
Deputy Manager
Physical & Technological Programs
Office of Health & Environmental
Research, M.S. E-201
Office of Environment
U.S. Department of Energy
Washington, D.C. 20545

OHER Quarterly Report Mailing List - July, 1979
Page 2

Dr. Jeff Swinebroad
Asst. Director for Regulator Liaison &
Deputy Assoc. Dir. for Research &
Development Programs
Office of Health and Environmental
Research, M.S. E-201
U.S. Department of Energy
Washington, D.C. 20545

Dr. Robert W. Wood
Director, Pollutant Characterization
and Safety Research
Office of Health and Environmental
Research
Mail Station E-201
Department of Energy
Washington, D.C. 20545

Dr. Nathaniel Barr
Asst. Dir. for Special Programs
Office of Health & Environmental
Research, M.S. E-201
Office of Environment
U.S. Department of Energy
Washington, D.C. 20545

Dr. Charles W. Edington
Assoc. Director for Research &
Development Programs
Office of Health & Environmental
Research, M.S. E-201
Office of Environment
U.S. Department of Energy
Washington, D.C. 20545

Dr. W. W. Burr, Jr.
Acting Director
Office of Health & Environmental
Research, M.S. E-201
Office of Environment
Department of Energy
Washington, D.C. 20545

Howard Shanks
A207 Physics

R. Kniseley
6 Spedding Hall

H. Svec
21 Gilman Hall

G. Small
6 O&L

Jerry Hall
217 Mech. Engr.

J. O'Toole
123 Reactor

C. Chriswell
316 Metallurgy