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Quarterly Report
January 1, 1983 - March 31, 1983

Prepared for
Pollutant Characterization
and Safety Research Division

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

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Date Transmitted: June 1983

Ames Laboratory
Iowa State University
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Prepared For
The U. S. Department of Energy
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Identification and Characterization of Pollutants

QUARTERLY REPORT

January 1 - March 31, 1983

Prepared for the

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Office of Health
and Environmental Research
Office of Energy Research
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Under Contract W-7405-eng-82

by the

AMES LABORATORY, DOE

IOWA STATE UNIVERSITY

AMES, IOWA

Date Transmitted: June 1983

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MEASUREMENT AND DOSIMETRY

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I. High Resolution, High Sensitivity Luminescence and
Other Spectroscopic Techniques

1. Laser Excited Shpol'skii Spectroscopy (LESS)
(A. D'Silva, V. Fassel)

A. Progress (A. Elsaid, M. Iles)

A holder accommodating four samples was fabricated and tested successfully. With the new holder only 25 μ l samples are required for analysis. The instrument was also modified to obtain spectra with a vidicon detector. With this detector spectra can be obtained within 30 seconds, which facilitates the observation of spectra from samples that photodegrade very easily.

It is well known that 3-hydroxy-benzo[a]pyrene is formed in significant amounts during metabolic activation of benzo[a]pyrene by the enzyme aryl hydrocarbon hydroxylase found in lung tissue. In the past, this compound could be detected by its room temperature fluorescence only after separation from other metabolites by HPLC. A characteristic quasiline Shpol'skii effect fluorescence spectrum of 3-hydroxy-benzo[a]pyrene dissolved in n-octane is shown in Fig. I-1-1. This is presumably the first reported spectrum of a hydroxy compound obtained by utilizing the Shpol'skii effect.

B. Status

We will attempt to obtain the fluorescence spectra of phenolic compounds that are found in significant quantities in coal liquids such as SRC-II. Attempts will be made to obtain the LESS spectra of other metabolites of B[a]P such as dihydrodiols and quinones. DNA adducts of PAHs found "in vivo" are known to exhibit intense fluorescence. Thus, we will also attempt to examine their fluorescence spectra in Shpol'skii solvents.

Figure I-1-1. Quasiline Shopol'skii spectrum of 3-hydroxybenzo[a]pyrene.

2. Laser Induced, Tunable Molecular Ionization with TOF Mass Spectrometry (A. D'Silva, V. Fassel)

A. Progress (R. Dobson)

The nude ion source has not yet been received, hence the time-of-flight mass spectrometer has not been tested. The laser beam handling system was redesigned and currently no laser scatter within the instrument is observed. A 50°C pulse valve was added to the jet assembly. The electronics for the operation of the pulse valve had to be modified to facilitate operation with the laser system. The fluorescence spectrum of the NO₂ probe gas is shown in Fig. I-2-1. The highly resolved spectrum indicates that the jet assembly is working satisfactorily and is ready to be mated to the TOF mass spectrometer.

B. Status

The studies on NO₂ will be completed and the TOF mass spectrometer will be assembled and tested.

Figure I-2-1. Fluorescence spectrum of NO₂ probe gas at 5% in air.

3. Fluorescence Line Narrowing Spectroscopy (FLNS)
(G. Small, J. Hayes)

A. Progress (M. McGlade)

The principal thrust of this project was redirected towards the problem of PAH metabolism and carcinogenicity in biochemical systems. The water containing glasses e.g., EtOH-glycerol-water, that are utilized in FLNS, are ideal solvents for biological samples. Benzo(a)pyrene [B(a)P] is widely recognized for its carcinogenicity and as a result has been studied quite extensively. There is evidence which suggests that B(a)P modification of DNA precedes tumor induction. Modification is known to proceed through the metabolism of 7-methylbenzo(a)pyrene to the 7,8-dihydrodiol with binding to the DNA apparently occurring via a 7,8-dihydrodiol 9,10-epoxide. There is also evidence which suggests that one of the four diastereomeric 7,8-dihydrodiol-9,10-epoxides preferentially binds to the amino group of guanine. FLNS may provide a sensitive and selective method for the analysis of PAH metabolites in biochemical systems without recourse to the generally applicable methods. These methods involve extensive chromatographic clean-up to remove all noncovalently bonded metabolites prior to fluorescence analysis at 77°K. Preliminary work showed that it was very easy to produce FLN spectra of two model metabolites. Figures I-3-1 and 2 are the FLN spectra for 7,8,9,10-tetrahydroxybenzo(a)pyrene (Tetrol) and the benzo(a)pyrene dihydrodiol epoxide (BPDE) - guanosine adduct.

B. Status

It is important at this stage to establish the generality of FLN for model metabolites. To this end, the following compounds will be studied: 7,8,9,10-tetrahydro-benzo(a)pyrene, 7-hydroxytetrahydrobenzo(a)pyrene, 10-hydroxytetrahydro-benzo(a)pyrene and 4,5-dihydroxy-9-methoxybenzo(a)pyrene. Inter-comparison of these spectra will be important for evaluation of selectivity. An important goal is to obtain FLN spectra for covalently bound B(a)P in actual DNA samples.

Figure I-3-1. FLN spectrum of 7, 8, 9, 10-tetrahydroxybenzo(a)pyrene (Tetrol)

Figure I-3-2. FLN spectrum of benzo(a) pyrene dihydrodiol epoxide (BPDE)-guanosine adduct

4. Rotationally Cooled Fluorescence Spectroscopy (RCFS) (G. Small, J. Hayes)

A. Progress

Previous attempts to obtain the RCF spectrum of phenanthrene were unsuccessful due to clogging of the nozzle when operated at a temperature high enough to produce an adequate phenanthrene vapor pressure. This problem has been overcome in the new metal nozzle. Unfortunately, the phenanthrene emission is still quite weak. Only two bands in the spectrum have been observed, presumably, the origin and a $\sim 1400\text{ cm}^{-1}$ vibration. The low intensity is quite puzzling since photophysical properties of phenanthrene (benzonaphthalene) in solution are quite similar to those of naphthalene.

RCF-GC analysis of α -aminonaphthalene was attempted. Two difficulties were encountered. The first is a relatively trivial problem with the method of inserting the GC column into the nozzle oven. Because of the flow resistance of the column, most of the sample flowed around rather than through the column. This problem can be easily solved in future work. A more difficult problem is that concentrations of α -aminonaphthalene, easily detected in laboratory prepared solutions, could not be detected in doped samples of solvent refined coal (SRC-II).

B. Status

The problems encountered in both phenanthrene and α -aminonaphthalene will be further investigated. The most obvious approach would be to investigate phenanthrene by multi-photon ionization. This would easily distinguish between a low absorption cross section and a low fluorescence quantum yield. At present, the equipment required to do this experiment is not available.

Regarding the aminonaphthalene analysis, the approach has not yet been decided. The problem is more involved than just being able to analyze aminonaphthalenes. In analysis of complex mixtures of unknown composition, such as SRC-II samples, differences between results obtained by direct analysis and those obtained following preseparation call into question the role of reactions (e.g. complex formation and protonation) that may occur in the sample.

Also, in the coming quarter, the use of RCF-GC for analysis of organics in water by trapping on organic resins will be evaluated.

II. Advanced Methodologies for Measurement of Toxic Effluents from Energy Processes

1. Measurement of Vapor, Liquid and Particle Effluents from Energy Processes (G. Junk)

A. Progress (J. Richard, M. Avery)

The development and complete testing of our simplified method for the determination of polycyclic aromatic hydrocarbons (PAHs) present on particulate matter has been completed. In summary, we can obtain quantitative data for selected PAHs present on urban dust and other particles using a simplified procedure consisting of: sonic probe extraction with cyclohexane; clean-up with Florisil and XAD-4; and measurement with high resolution gas chromatography and flame ionization detection (HRGC/FID). The analysis can be further simplified by eliminating the clean-up step if HRGC/electron impact mass spectrometer (MS) is available. Both the FID and the MS methodology give results consistent with those obtained by time-consuming standard procedures. The direct HRGC/MS procedure, combined with chemical ionization can also be applied to the determination of polycyclic organic materials present in solvent refined coal, shale oil and crude oil. The results of these studies are currently being collated for presentation at scientific meetings and as part of a manuscript dealing with the determination of PAHs.

Steam distillation, solvent extraction, anion exchange and cation exchange were investigated as analytical techniques for isolating and concentrating low molecular weight and soluble organic compounds from water solutions. The test waters were synthetic solutions and shale oil process water. The synthetic solutions were prepared by adding organic acids and bases to organic free water. The shale oil process water was obtained from the National Bureau of Standards. These solutions were used to evaluate the four different analytical techniques for trace amounts of organic compounds in energy related waste waters.

With the exception of acetic and propionic acids, the recoveries listed in Table II-1-1 are all satisfactory. However, the acids required such a lengthy distillation for recovery that no concentration was achieved.

Preliminary studies showed that the acids and bases could be readily separated into individual fractions by controlling the pH of the distillation. Equivalent amounts were recovered regardless of the order of the distillation. Thus the acids can be removed first along with the neutral components by adjusting the pH to ~2 before the first

distillation. The pH is adjusted to ~11 for the second distillation which isolates the bases. If the order is reversed the bases and neutrals are isolated in the first distillation and the acids in the second.

Several polar compounds were identified in the steam distillates of the shale oil process water. Quantitative data are listed in Table II-1-II. The data for the identified acids are given in Table II-1-III. To obtain quantitative data for acetic and propionic acids, an anionic exchange procedure, developed previously in this program, was used. The data for standard solutions and the shale oil process water are given in Tables II-I-IV and V, respectively.

B. Status

The results for the PAHs analyses are now complete and the collated data will be incorporated into a manuscript to be submitted to Talanta. Some of our PAHs analytical data will also be presented at the Boston MA, May 8-13, 1983 meeting of the American Society for Mass Spectrometry. A copy of a preprint proceedings of this talk is attached as Appendix A.

The results of our study of polar organic compounds in the process water from retorting oil shale will be interpreted fully and collated. A report of these investigations will be written and submitted for publication possibly during the next quarter.

TABLE II-1-I. Recovery of Acids and Bases from Standard Aqueous Solutions Using Steam Distillation.

Cmpd.	PPM Added	Percent Recovery							
		Acid Fraction		Acid/Neutral Fraction		Base Fraction		Base/Neutral Fraction	
		1st 50 mL	2nd 50 mL	1st 50 mL	2nd 50 mL	1st 50 mL	2nd 50 mL	1st 50 mL	2nd 50 mL
Acetic Acid	200	18	13	18	15				
Butanoic Acid	100	73	22	79	21				
Heptanoic Acid	100	99	--	100	--				
Decanoic Acid	50	50	35	50	20				
Tetradecanoic Acid	50	--		--					
Phenol	25	70	25	68	24				
Methyl Amine	46					77		68	
Ethyl Amine	56					86		93	
Pyridine	10					97		105	
2,6-Lutidine	20					95		99	
Aniline	2					96		90	
Isoquinoline	2					94		89	
Acetonitrile	20							89	

TABLE II-1-II. Recovery of Nitrogen Compounds from 50 mL of NBS Shale Oil Process Water Using Steam Distillation.

N-Compd.	$\mu\text{g/gH}_2\text{O}$			
	Base/Neutral Fraction		Base Fraction	
	1st 25 mLs	2nd 25 mLs	1st 25 mLs	2nd 25 mLs
Methyl Amine	10	--	9	--
Ethyl Amine	9	--	8	--
Propyl Amine	4	--	4	--
Butyl Amine	2	--	2	--
Acetonitrile	21	--	--	--
Propionitrile	5	--	--	--
Butyronitrile	1	--	--	--
Benzonitrile	3	--	--	--
Pyridine	5	--	5	--
2-Methyl Pyridine	5	--	5	--
2,4-Dimethyl Pyridine	3	--	3	--
2,6-Dimethyl Pyridine	15	--	15	--
2,4,6-Trimethyl Pyridine	20	--	18	--
Aniline	2	--	2	--
Isoquinoline	1	--	1	--

TABLE II-1-III. Recovery of Acids from 50 mL of NBS Shale Oil Process Water by Steam Distillation

Acid	$\mu\text{g/gH}_2\text{O}$			
	Acid/Neutral		Acid	
	1st 25 mLs	2nd 25 mLs	1st 25 mLs	2nd 25 mLs
Acetic	206	125	187	100
Propanoic	78	23	74	15
Methyl Propanoic	31	3	30	6
Butanoic	50	8	47	5
2-Methyl Butanoic	32		29	
3-Methyl Butanoic	21		20	
Pentanoic	108	12	93	14
Hexanoic	124		125	
Heptanoic	157		143	
Phenol	13	2	12	2

TABLE II-1-IV. Recovery of Acidic Compounds from Standard Solutions Using Anion Exchange

Acid	PPM Added	Percent Recovered
Acetic	100	96
Propanoic	100	98
Methyl Propanoic	100	99
Butanoic	100	100
3-Methyl Butanoic	100	97
Pentanoic	100	98
4-Methyl Pentanoic	100	96
Hexanoic	100	95
Heptanoic	100	102
Phenol	25	92

TABLE II-1-V. Recovery of Acids from Shale Oil Process Water Using Anion Exchange and Direct Injection

Acid	$\mu\text{g/gH}_2\text{O}$	
	Direct Injection	Anion Exchange
Acetic	160	156
Propanoic	170	190
Methyl Propanoic	69	64
Butanoic	116	130
2-Methyl Butanoic	60	65
3-Methyl Butanoic	26	34
Pentanoic	185	207
Hexanoic	139	159
Heptanoic	187	203
Phenol	21	19

Appendix A

SIMPLIFIED METHODOLOGY FOR PAHs ON SUSPENDED PARTICLES
Michael J. Avery, John J. Richard, and Gregor A. Junk,
Ames Laboratory-USDOE, Iowa State University, Ames, IA 50011

Presented at the American Society of Mass Spectrometry,
May 8-13, 1983, Boston, MA

SUMMARY

Accurate quantitative data for selected polycyclic aromatic hydrocarbons present on urban dust can be obtained by using a simple procedure consisting of: sonic probe extraction with cyclohexane; clean-up with Florisil®-XAD-4®; and measurement with high resolution gas chromatography and flame ionization detection (HRGC/FID). The analysis can be further simplified by eliminating the clean-up step if HRGC/electron impact mass spectrometry (MS) is available. Both the FID and MS methods give results consistent with those obtained by time-consuming standard procedures. The direct HRGC/MS procedure, combined with chemical ionization, can also be applied to the determination of polycyclic organic materials present in solvent refined coal, shale oil and crude oil.

EXPERIMENTAL

Extraction. An Artex-Sonic Dismembrator equipped with a 3/4" probe and operated at 240 watts was used to extract 0.25 g samples with 30 mL of solvent. Sonication time was 10 minutes after which the solu-

tion was filtered and the sample extracted two more times with fresh solvent. The three extracts were combined and reduced to 1 mL.

Clean-up. The extract was transferred to a 0.5 cm I.D. glass column containing 1 g of Florisil®, and then eluted with 15 mL benzene. The collected benzene was concentrated to 0.5 mL and transferred to a 1.4 cm I.D. glass column containing 9 g of XAD-4® wetted with ethanol. A clean PAH fraction was obtained using a modification of the procedure reported by Spitzer¹. Eluates of the XAD-4® column with 25 mL ethanol and 25 mL pentane were discarded. The PAHs were then eluted with 25 mL benzene. The collected benzene was reduced to 1 mL.

Equipment. The HRGC analysis were performed on a Carlo Erba Fractovap equipped with a 30 m DB-5 fused silica capillary column and a FID. The HRGC/MS analyses were performed on a Finnigan 4000 GC/MS equipped with a 30 m DB-5 fused silica capillary column and operated in the multiple-ion-monitoring mode. Ionization was accomplished with electron impact or chemical ionization with isobutane reagent gas and ion source pressure of 0.3 Torr. External standards were used for quantitation. All solvent reductions were performed with a rotary evaporator.

RESULTS AND DISCUSSION

The NBS has issued certified values for the concentrations of five PAHs in SRM 1649, a time-integrated, homogenized sample of Washington DC urban dust. The results of our analyses of this SRM are compared to these NBS certified values in Table 1. The average difference between

values is 8%. Comparable reproducibilities were obtained by the two methods. These results are used as validation of the simple and rapid methodology for the determination of selected PAHs in samples as complex as urban dust.

The simplified procedure was applied to other PAHs in SRM 1649 and to PAHs on particles from other sources. The results of these analyses are listed in Table 2. Quantitative values for five additional PAHs in SRM 1649 are given in columns 2 and 3. The PAH content of St. Louis urban dust was also measured and the values are given in column 4. For comparison, the NBS uncertified values for this same dust are listed in column 5. The PAHs measured in a sample of fly ash from a coal-fired power plant and flue tar from a wood burning stove are shown in columns 6 and 7.

If GC/MS instrumentation is available, the analytical procedure for PAHs can be made even simpler. The increased selectivity of the mass spectrometer operated in the multiple-ion-monitoring mode enables the analyst to bypass the Florisil®-XAD-4® clean-up. Direct HRGC/MS analysis, using electron impact (EI), of a cyclohexane sonic probe extract of SRM 1649 was performed and the results agree to within 15% of the results, obtained using a clean-up procedure and HRGC/FID.

The direct HRGC/MS procedure, using chemical ionization (CI) and isobutane as the reagent gas, has also been applied to the analyses of polycyclic organic materials (POMs) in other complex mixtures. Samples of solvent refined coal, shale oil and crude oil were diluted 100/1 in hexane and analyzed directly for selected POMs. The results of these

analyses listed in Table 3 agree with those obtained in an interlaboratory study.

CONCLUSION

The simplified procedures used to determine twelve PAHs and three POMs on urban dusts and in process streams can certainly be extended to determine other organic compounds. In each case, the additional compounds need only be tested and the procedure finely tuned to obtain quantitative results.

The simple Florisil®-XAD-4® chromatography is not applicable to class separation of all the components present in complex mixtures. The reasons for this conclusion are the known irreversible adsorption of some components on the Florisil® and the insufficient documentation of the separating capability of the XAD-4®.

¹T. Spitzer, J. Chromatogr., 1982, 237, 273.

Table 1. Comparison of the Analysis of SRM 1649.

Compound	Concentration in $\mu\text{g/g}$	
	NBS	This
	Certified	Study
Fluoranthene	7.1 ± 0.5	7.6 ± 0.5
Benz(a)anthracene	2.6 ± 0.3	2.9 ± 0.4
Benz(a)pyrene	2.9 ± 0.5	2.7 ± 0.6
Indeno(1,2,3-cd)pyrene	3.3 ± 0.5	3.1 ± 0.6
Benz(ghi)perylene	4.5 ± 1.1	5.0 ± 1.1

Table 2. HRGC/FID Measurement of PAHs in Cleaned-up Extracts from Various Particle Samples.

COMPOUND	Concentration in $\mu\text{g/g}$					
	St. Louis Urban Dust		Washington Urban Dust SRM 1649		Power Plant Fly Ash ^a	Wood Stove Tar ^b
	This Study	NBS Uncertified	This Study	NBS Uncertified		
Phenanthrene	4.5	NR ^c	4.5	3.0	ND ^d	70
Fluoranthene	7.1	7.9	e	e	0.3	143
Pyrene	5.9	7.4	5.8	6.3	0.7	178
Benz(a)anthracene	2.6	2.8	e	e	ND	170
Chrysene	6.9	6.6	4.3	5.4	ND	225
Benz(a)pyrene	2.4	2.6	e	e	0.07	115
Benz(e)pyrene	3.6	NR	3.3	3.3	ND	75
Indeno(1,2,3-cd)pyrene	3.6	4.8	e	e	ND	91
Benz(ghi)perylene	5.6	5.5	e	e	ND	74
Dibenz(ah)anthracene	ND	NR	0.4	0.4	ND	ND

^aElectrostatic precipitator ash from a coal-fired power plant.

^bTaken from the chimney of an air-tight wood burning stove.

^cNR = Not reported.

^dND = Not detected at detection limit of 0.05.

^eCertified values given and compared in Table 1.

Table 3. Analyses of Polycyclic Organic Materials Present in Complex Samples by Direct HRGC/CIMS.

Compound	Concentration in $\mu\text{g/g}$		
	Solvent-Refined Coal	Wilmington Crude Oil	Shale Oil
Pyrene	200	11	161
Benz(a)pyrene	250	1	14
Benz(e)pyrene	250	0.5	NA ^a
Dibenzthiophene	1064	41	NA
Acridine	158	13	NA
Carbazole	1913	6	NA
1-Methylnaphthalene	NA	0.6	NA
2-Methylnaphthalene	NA	0.3	NA

^aNA = Not analyzed.