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NITRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS
IN COAL COMBUSTORS AND EXHAUST STREAMS

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1. SUMMARY

During the period July 1, 1993 to September 30, 1993, the PAH preparation project at SRI International and the development of analytical methods for PAH proceeded at Stanford proceeded smoothly without any major obstacles. The PAH preparation project in Dr. Niksa's new laboratory at SRI International is now fully reactivated. New PAH samples from oxidative pyrolysis of the volatiles from various coals are now being acquired. Activity this quarter focused on upgrading the furnace and analytical equipment. A new coal feeder enables better control of the gas flows into the radiant coal flow experiment; hence, residence times will be assigned more accurately. We also reconfigured the induction power supply to achieve higher operating temperatures than before. The elemental analyzer for determinations of C/H/N in condensed phase samples, including PAH, benefitted from a major overhaul, and our new gas chromatographs are now being calibrated for the light hydrocarbons of interest. At this point, the only analytical instrument remaining to be reactivated is the on-line NDIR detector for water vapor, which will be evaluated in the next quarter.

Analytical activity this quarter focused on the HPLC separation procedure. Tests were conducted to determine the appropriate composition and flowrate of the HPLC eluent. Additional experiments utilizing standard mixtures allowed selection of the detection wavelength settings that optimized the sensitivity and specificity of PAH detection.

2. INTRODUCTION TO THE PROGRAM

Nitro-polynuclear aromatic hydrocarbons (nitro-PAH) are the predominant mutagens on respirable particles from coal-fired boilers. Since nitro-PAH are not primary products of coal devolatilization, their formation must involve secondary chemistry at elevated temperatures. However, it is not known where in the combustion or exhaust processes they form, which reaction species are involved, or how concentrations are influenced by operating conditions. Results from this study will help to relate the environmental impact of mutagenic emissions to boiler firing strategies.

The objectives of this three-year project are to (1) identify the conditions which promote the nitration of PAH during primary combustion, reburning, hot gas cleanup, and particulate removal; and (2) investigate the potential relationship between NO_x abatement and PAH nitration. A novel coal flow reactor burning actual coal products operates over the domains of heating rates, temperatures, fuel-equivalence ratios, and residence times in utility boilers. A fluidized bed will be built for studies of simulated hot gas cleanup at lower temperatures. Gas chromatography with chemiluminescence detection will measure the aggregate amount of nitro groups present, to determine when nitro-PAH first appear, and how nitration is affected by the operating conditions. Tars from primary and secondary pyrolysis and oxidative pyrolysis will be fractionated into chain hydrocarbons, polynuclear aromatics, oxygenated species, and a basic fraction, so that their ring number distribution can be monitored with high performance liquid chromatography.

3. FINDINGS

3.1 Introduction

Meeting the objective of this program involves two broad tasks: (1) Preparing the polynuclear aromatic hydrocarbons (PAH) under closely monitored pulverized fuel (p. f.) firing conditions; and (2) analyzing the PAH samples to monitor extents of nitration, ring number distributions, etc. While both activities are essential to this project, they involve scientific principles which are almost completely unrelated. So in this and all future reports, our findings will be segregated according to their relation to either sample preparation or sample analysis. In actuality, Dr. Niksa and Prof. Hildemann each have an associate working on these respective parts of this project.

Regarding activity on the PAH preparation side of the project, our technical progress has resumed now that almost all of the laboratory facilities are operating in Dr. Niksa's new laboratory at SRI International. While evaluating the performance of some major system components, we noticed that their performance had degraded considerably. Overhauls of the induction power supply for the radiant coal flow experiment and the elemental analyzer for C/H/N determinations of condensed phase samples have made these components perform better than ever. We also took the opportunity to redesign and fabricate a new coal feeder to improve the control of gas flows through the flow reactor. The remainder of the quarter was devoted to routine service on the new gas chromatograph, including calibrations for the light hydrocarbons. By the end of the quarter, the on-line NDIR meter for water detection was the only instrument remaining to be brought to good working order.

The main analytical goal for this quarter was to optimize the operating parameters for high performance liquid chromatography (HPLC) by injecting standard compounds.

Individual polycyclic aromatic hydrocarbons (PAH) as well as standard mixtures of PAH were injected separately to determine the appropriate eluent composition and flow rate, as well as the optimal detection wavelength. The preliminary results and further work planned are discussed in section 3.3.

3.2 Sample Preparation

3.2.1 Relocation to SRI International

Activity during this quarter focused on restoring the laboratory facilities used to prepare PAH for this project to working condition at SRI International. Regarding the radiant coal flow furnace, there were three modifications. First, the improved optical arrangement that ports the pyrometry signal into a cooled region was installed and shaken down, so there is no longer a heavy radiation load on any section of the housing. Second, the induction power supply was reconfigured, with the unexpected benefit that now there is more power available to heat the radiant furnace than ever. We are now able to continuously operate at temperatures to 1850 K, which is certainly adequate for this project. Third, the new housing for the coal feeder was completely shaken down. It is now leak tight over the range of gas flows of interest, so we expect better reproducibility of residence times and coal transport velocities. By the end of the quarter, Dr. Cho was running tests with coal to qualify his experimental techniques against our current database.

Regarding analytical equipment, an inspection of the circuitry in our elemental analyzer for C/H/N determinations of tars and chars revealed that several components had failed, and that the voltages delivered to the detectors were far off spec. A major overhaul restored the instrument to good working order, and all calibration tests have been satisfied. The instrument is again ready for routine service. Also, our group inherited a used gas

chromatograph at SRI that, unfortunately, was unable to hold calibrations. We traded it in for a rebuilt model that, so far, has satisfied all calibration trials. New calibration curves were acquired for CO, CO₂, O₂, NO, CH₄, and C₃H₈, leaving only the C₂ hydrocarbons to be done. Our on-line non-dispersive IR (NDIR) detector for water vapor is not functioning because of inordinate baseline drift. Unfortunately, its behavior is unlike any seen before by the manufacturer, although we suspect that the symptoms point to a moisture leak into the sample cell. This hypothesis will be pursued in the coming quarter.

3.3. Sample Analysis

3.3.1. Selection of Standards

Because coal tar consists of a complex mixture of organic chemicals, standard compounds must be utilized to initially identify the range of HPLC elution times corresponding to the different numbers of aromatic rings. The toluene fraction collected via gravity-flow column chromatography was chosen as the first target fraction to be analyzed by HPLC. Since the compounds recovered by toluene are expected to consist of 3- to 6-ring PAH, the standard PAH compounds were selected to span this range of ring numbers.

As a first step, four PAH standard compounds ranging in size from 2 to 6 rings were acquired: naphthalene (2 rings), anthracene (3 rings), benz(a)anthracene (4 rings), and benzo(ghi)perylene (6 rings). Separate HPLC injections of these four individual compounds allowed the elution times for each one to be accurately determined, and gave a preliminary idea of the time range over which elution of the toluene fraction was expected to occur. Then, a simple mixture of the four compounds was also injected. This allowed the reproducibility of the elution times and instrument response to be evaluated.

To more closely approximate the expected complexity the toluene fraction of the coal tars, a 16-PAH standard mixture was purchased from Chem Science, Inc. This standard suite, which contained PAH compounds ranging from 2 to 6 rings, is illustrated in Figure 1. It was prepared for use by dissolving in methanol at a concentration of 0.1 mg/ml.

3.3.2. HPLC Calibration Procedure

The calibration procedure for HPLC analysis this quarter started with testing the eluent composition, followed by selecting the optimal flow rate. The lower detection limit of sample concentration injected was also examined, in preparation for analyzing real tar samples via HPLC.

To examine the effect of eluent composition on sample elution, the flowrate of eluent in the HPLC system was initially set at 1.5 ml/min isocratically; that is, the composition of the mobile phase was held constant throughout the entire elution cycle. Although the mobile phase used by Lafleur et al. (1987) consisted of 92% hexane and 8% dichloromethane (DCM), heptane and DCM were initially chosen as the eluents for this project, in order to be consistent with the solvents used for gravity-flow column chromatography. In this initial set of experiments, we compared the effects of various eluent compositions on the ring number resolution. Eluent consisting of the following proportions of heptane and DCM were tested: 95% heptane/ 5% DCM, 90% heptane/10% DCM, and 80% heptane/ 20% DCM. Based on the resultant chromatograms, it was determined that the eluent with a higher proportion of DCM gave better separation. In addition, because the higher proportion of DCM resulted in stronger solubility of the larger PAH in the eluent, the compounds were carried through the analysis column more quickly. Thus, for a flow rate of 1.5 ml/min, the optimal proportion of heptane and DCM were 80%

Figure 1. A mixture of 16-Standard PAH

and 20%, respectively. However, the absorbance of ultraviolet/visible wavelengths for DCM was found to fall within the detection range (220 to 600 nm), and resulted in a strong solvent peak which overlapped with the absorbance for 2-ring-PAH (naphthalene). Because of this interfering absorbance, we replaced DCM with tetrahydrofuran (THF), since THF does not absorb as strongly in this range of wavelengths.

✓ Although THF is known to dissolve coal tar compounds more effectively than DCM, ^{ication of} verifying the optimal proportions of heptane and THF was still needed. At a flow rate of 1.5 ml/min, we found that the proportion of 80% heptane/20% THF gave better separation of the 16-PAH standard mixture than 90% heptane/10% THF or 95% heptane/5% THF. Thus an eluent composition of 80% heptane and 20% THF was utilized for the next set of experiments, in which the flowrate was varied.

Since the flow rate plays an important role in determining compound resolution and analysis time, three flow rates, 0.5, 1, and 1.5 ml/min, were tested with a fixed eluent composition. As we expected, the higher the flow rate used, the closer together the peaks eluted, but the less total elution time was needed. Thus, though the smallest flowrate tested, 0.5 ml/min, produced the most distinct separation among the peaks, the total time required for complete elution was more than 30 minutes, which was triple the time necessary at the flowrate of 1.5 ml/min. Therefore, to get adequate resolution within a reasonable period of time, 1 ml/min was chosen as the eluent flow rate.

In addition to testing the composition and flow rate of eluent, the minimum detection limit of concentrations for individual compounds was also examined. Absorbance could be observed only when the concentration for each compound was more than 1 ug/ml. On the other hand, because of the capacity of analytical column currently used, the maximum injected mass should not exceed 1 mg. Since typically, a sample

volume of 25 μ l is utilized for each injection, this maximum mass of 1 mg corresponds to an upper concentration limit of 40 mg/ml.

3.3.3. HPLC Results Utilizing Standards

To identify the optimal wavelength and bandwidth for detecting PAH, four individual compounds, naphthalene, anthracene, benz(a)anthracene, and benzo(ghi)perylene were injected, along with a mixture of these 4 compounds. Figure 2 shows the chromatograms of the 4-compound PAH mixture at wavelengths of 254 and 300 nm. Each of these chromatograms were measured with a bandwidth of 4 nm, using 80% heptane and 20% THF at a flow rate of 1 ml/min. The fact that one peak, corresponding to benzo(ghi)perylene, is missing in Figure 2.1 indicates that benzo(ghi)perylene did not absorb enough light between 252 and 256 nm to form a visible peak in the chromatogram. On the other hand, the chromatogram at wavelength 300 nm (Figure 2.2) shows the detection of all the compounds in the mixture, but has a relatively decreased peak height for anthracene. Figures 2.1 and 2.2 suggest that too narrow a bandwidth causes some PAH not to be detected; however, too broad a bandwidth loses the specificity and resolution desired for this project. Nevertheless, it was evident that a broader bandwidth than 4nm was needed to detect and quantify the PAH present in a complex mixture. After further testing using the more complex standard mixture of 16 PAH compounds, a wavelength of 300 nm with a bandwidth of 80 nm was chosen for quantifying the ring number distributions of real tar samples.

Figure 3 shows the chromatogram obtained for the standard mixture containing 16 PAH. The cutoff point between each ring-number group was determined by injecting individual standard compounds and comparing the corresponding elution times. Even in this complex mixture, the cutoff points between ring numbers are clearly observed, and are

Chromatograms of a standard mixture containing naphthalene, anthracene, benz(a)anthracene, and benzo(ghi)perylene

Figure 2.1. Chromatogram of 4-PAH mixture at wavelength 254 nm and bandwidth 4 nm.

Figure 2.2. Chromatogram of 4-PAH mixture at wavelength 300 nm and bandwidth 4 nm.

**Figure 3. Chromatogram of 16-PAH mixture at wavelength 300 nm and bandwidth 80 nm.
Flowrate - 1 ml/min. consisting of 80% heptane and 20% THF**

consistent with the results obtained for the individual standard compounds. Figure 3 shows that PAH with 3 rings or less elute before 5 min, 4-ring PAH elute between 5 and 8 minutes, 5-ring PAH elute between 8 and 14 minutes, and 6-ring PAH elute between 14 and 26 minutes. Since the goal of HPLC analysis in this project is to separate the PAH into groups by ring numbers, rather than identify every single compound in the sample, incomplete separation between individual PAH which contain the same number of aromatic rings is considered acceptable.

Because the peaks of the two 6-ring PAH (indeno[1,2,3,-cd]pyrene and benzo(ghi)perylene) shown in Figure 3 are very broad, it is suspected that these compounds have low solubility in the eluent currently used, 80% heptane and 20% THF. Thus, more tests involving the eluent composition are planned for the coming quarter.

4. SHORT RANGE OBJECTIVES

During the coming quarter, we will resume PAH sample collection. Tests will focus on oxidative pyrolysis conditions to supplement our existing data on primary devolatilization and secondary pyrolysis. Early in the quarter, Dr. Cho will fully qualify his experimental techniques against our current database, and define the operating conditions with various oxygen levels. Then he will acquire the samples for controlled oxidative pyrolysis of 3 or 4 coal types. Time permitting, he will also begin to monitor all gases present in significant quantities to close the elemental balances in his datasets.

Optimizing the operating conditions for the HPLC will be continued during the next quarter. First, compound separation using a gradient eluent (where the eluent composition is varied during an analysis) will be examined. Increasing the proportion of THF in the eluent should enhance the solubility of indeno[1,2,3,-cd]pyrene and benzo(ghi)perylene

and is expected to result in narrower peaks from the HPLC analyses. Miss Yu will also establish a preliminary universal calibration curve on the basis of ring numbers and elution time (minutes) by utilizing the suite of standard compounds used this quarter, the 16-PAH mixture. Finally, analysis will begin on the toluene fractions from two types of coal tars, Pittsburgh #8 and Dietz, to evaluate the applicability of the operation parameters and calibration curve for characterizing the real tar samples.

5. REFERENCE

Lafleur, A.L., Monchamp, P.A., Plummer E. F., Wornat, M.J., "Universal Calibration Method for the Determination of Polycyclic Aromatic Hydrocarbons by High Performance Liquid Chromatography with Broadband Diode-Array Detection", Analytical Letters, 20 (8), 1171-1192, (1987).

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