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International Specialists in the Environment

MEMORANDUM

TO: Paul Doherty, RPO

THRU: John Caoile, FITOM sent for JC

FROM: Neal Hudson, E & E/FIT

DATE: March 22, 1988

SUBJECT: Field Analytical Screening Program (FASP):
Polynuclear Aromatic Hydrocarbon (PAH) Field Screening SOP
TDD #F-07-8711-051 PAN #F07Z104VA

Attached is the draft SOP for PAH field screening analysis of four late eluting compounds associated with coal gasification sites. The method has yielded results which correlate well with CLP data, but is expected to be further modified to compensate the matrix effects, column degradation, etc. This SOP has undergone E & E internal peer review at the Regional Office and Zone Project Management Office.

Any changes to the method are expected to be minor. The instrument response should remain constant for each compound. If major response changes are observed, the source(s) of the problem will be examined to determine if an instrument malfunction may be the cause.

CC: Robert D. Kleopfer, Chief, ENSV/Laboratory

SCREENING FOR POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL AT COAL GASIFICATION SITES

Field-screening analysis for polycyclic aromatic hydrocarbons (PAHs) in soil has been successfully performed by the procedure described here for a limited number of sites. Preliminary results have indicated that this method is useful in providing reliable data in a mobile support facility.

This method was designed to analyze for four PAH compounds associated with the wastes generated by coal gasification procedures. Instrument conditions described by this method favor the identification of the late eluting PAHs benzo(a)pyrene, benzo(k)fluoranthene, chrysene, and pyrene, thus minimizing the interferences caused by oils and tars. Quantitation objectives were established to provide the most reliable results at or near the Region VII EPA proposed action level of 13 ppm benzo(a)pyrene.

Elements of this method are subject to modification to accommodate new equipment, sample matrices, and data quality objectives.

Equipment

1. Tracor Model 540 Gas Chromatograph (GC) with flame ionization detector (FID) and 30 meter DB-5 megabore capillary column. Other GCs capable of creating the conditions described by this method may be substituted.

2. Top-loading balance: 0-100 g capacity; 0.01 g sensitivity.

3. Repipetor (0-10 ml) or 10 ml serial pipet.

4. 40-ml VOA vials with teflon septum cap.

5. Syringes - 5 or 10 ul Hamliton and;
   1 cc disposable for dilutions (Note 1)

6. Stock standard solutions of desired compounds.

Reagents

1. Methylene chloride, pesticide grade

2. GC gases
   - Nitrogen, ultrapure grade
   - Hydrogen, ultrapure grade
   - Compressed air, zero grade

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Instrument Conditions - Tracor 540

- Detector: FID
- Integrator: Spectraphysics SP4290
- Column: DB-5 megabore capillary (0.53 mm I.D.) 30 meter length
- Carrier Gas: Nitrogen, 40 cc/min. + 5 cc/min. makeup
- Detector Gases: Air 400 cc/min. Hydrogen, 30 cc/min.
- Oven Temperature: 100° C hold 2 min.; then ramp 8° C/min. to 310° C and hold for 2 min.
- Injector Temp.: 250° C
- Detector Temp.: 325° C

Sample Collection and Preparation

A special effort must be made by the samplers to insure adequate sample homogeneity. Due to the relatively small quantity of sample extracted during the screening process, homogeneity is crucial for obtaining reproducible analytical results. The following considerations should be observed during sample collection:

- Collect dry, fine particles whenever possible without sacrificing the representativeness of the sample
- Place the sample aliquots in a disposable container such as an aluminum pan, or a plastic bag;
- Rocks and other debris should be removed by passing the sample through a disposable 1/4 inch wire mesh prior to mixing;
- Homogenize the sample by thoroughly mixing and transfer to the sample jar
- Remove the screening aliquot from the sample jar which is to be submitted for CLP analysis.

Once the screening aliquot is obtained, it is extracted by the following procedure:

1. Accurately weigh 2 to 3 grams (± 0.01 gram) of sample into a 40-ml VOA vial.

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2. Add 10 ml methylene chloride to the vial using a pipet or repipetor.

3. Agitate the sample for one minute on a vortex mixer.

4. If particulate suspension exists, centrifuge the sample until the liquid extract is clear.

5. The extract is now ready for analysis. If high concentrations are anticipated (>200 ppm for any single constituent) or if an oily matrix has been extracted, dilution of the extract to 1:10 or 1:100 is recommended before injection.

Instrument Calibration

Standard Preparation -

Prepare three standard mixtures of the compounds of interest. Retention times for each component are established by injecting 5 to 10 ng of each compound separately. Working standards should be prepared by diluting commercially prepared stock standards to known concentrations for each component:

Solution 1. 1 ng/ul
Solution 2. 5 ng/ul
Solution 3. 10 ng/ul

The above concentrations provide a useful calibration curve for the stated objectives. The calibration range may be extended if the extended range meets current QA/QC criteria established for FASP calibrations. Where possible the printer parameters should be chosen to give at least 5 percent of full scale deflection at the lovest concentration of concern.

Prior to sample analysis, retention times and detector response factors (RF) are determined for each compound of interest. The prepared standard solutions are injected into the GC and RFs are calculated according to the following formula:

$$RF = \frac{\text{Peak Area (Std.)}}{\text{ng Std. Injected}}$$

During the initial calibration, RFs should be determined by generating three-point calibration curves of each standard to demonstrate detector response linearity. The average RF for each compound is used for quantification. The end points of the curve should bracket the expected sample extract concentration range. The integrator can be programmed to generate RF data at this point in the analysis. The percent Relative Standard Deviation (% RSD) for three RFs, as calculated by the following equation, should be less than 15 percent.

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$$\%RSD = \frac{\text{Standard Deviation}}{\text{Mean RF}} \times 100\%$$

Once the three point calibration curve has been developed, a single point concentration near the midpoint of the calibration range should be injected on subsequent days to check instrument response. The resulting RF must not deviate more than 20 percent from the established mean RF for each compound.

At least one sample of each soil type from a site should be spiked at a concentration near 10 ppm of benzo(a)pyrene, the prime constituent of concern. The spike concentration was selected to closely match the proposed action level. Spike recoveries should be in the range of 50 percent to 125 percent. Duplicate analyses should be performed on 5 percent of the samples unless otherwise stated in the data quality objectives (DQOs) of the work plan.

Analytical Procedures

After the method validation, an aliquot of the sample extract is injected into the GC. Each run takes 30 minutes to complete and approximately 10 additional minutes for the start temperature to re-equilibrate. The daily order of analysis is as follows:

1. Method Blank
2. Standards (as appropriate)
3. Samples (including spikes and duplicates)

A single mid-range standard is injected after every 10 samples. A method blank is injected after samples of high concentration to check for contaminant carry-over.

Calculation of Results

Each standard and sample chromatogram is printed on the integrator and peaks are tentatively identified as PAH compounds if their retention times are the same as those of the standards. The area of the peak is used to calculate the sample concentration by the following equation:

$$\text{PPM Conc.} = \frac{\text{Peak area} \quad \text{Extract Vol.(ul)} \quad \text{dilution factor}}{\text{RF(area/ng)} \quad \text{Injected. Vol.(ul)} \quad \text{sample wt(g)} \quad (1000 \text{ ng/ug})}$$

These computations may be performed by the analyst or the integrator may be programmed to make all or part of the calculations.

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Quality Assurance/Quality Control

Standard operating procedures for FASP QA/QC are described in the Regional SOP document and in the E & E SOP CHEM 3.10, dated September 1987. Included in the SOP are requirements for "screening" results which are less stringent than those for analytical results designed to generate more defendable results.

Data Quality Objectives (DQOs) for each site will provide the information required to establish QA/QC procedures for the project. Any variations from the procedures described in the QA/QC SOP will be stated in the work plan.

Attachments: 1. Sample chromatogram of the four PAH compounds referred to in the method.

2. Calibration curves for each of the above compounds using the conditions described by this method.

Note 1: The use of disposable syringes for dilutions is useful for screening since they minimize cross contamination and clean-up time. However, plastic syringes dissolve in methylene chloride. In order to minimize leaching and dissolution of syringes, dilutions must be made as rapidly as possible. No interferences from the plastic syringes have been noted to date.

Note 2: A single extraction without a cleanup and dehydration step appears reasonable for screening because it reduces the analysis time without measurable effects on the final results. A disposable hydrophobic filter will be placed over the injection part if high moisture levels appear to reduce the extraction efficiency.

Note 3: The attached chromatogram and calibration curves demonstrate that linear responses to the four PAH compounds were achieved for injected masses which ranged from 1-10 ng.

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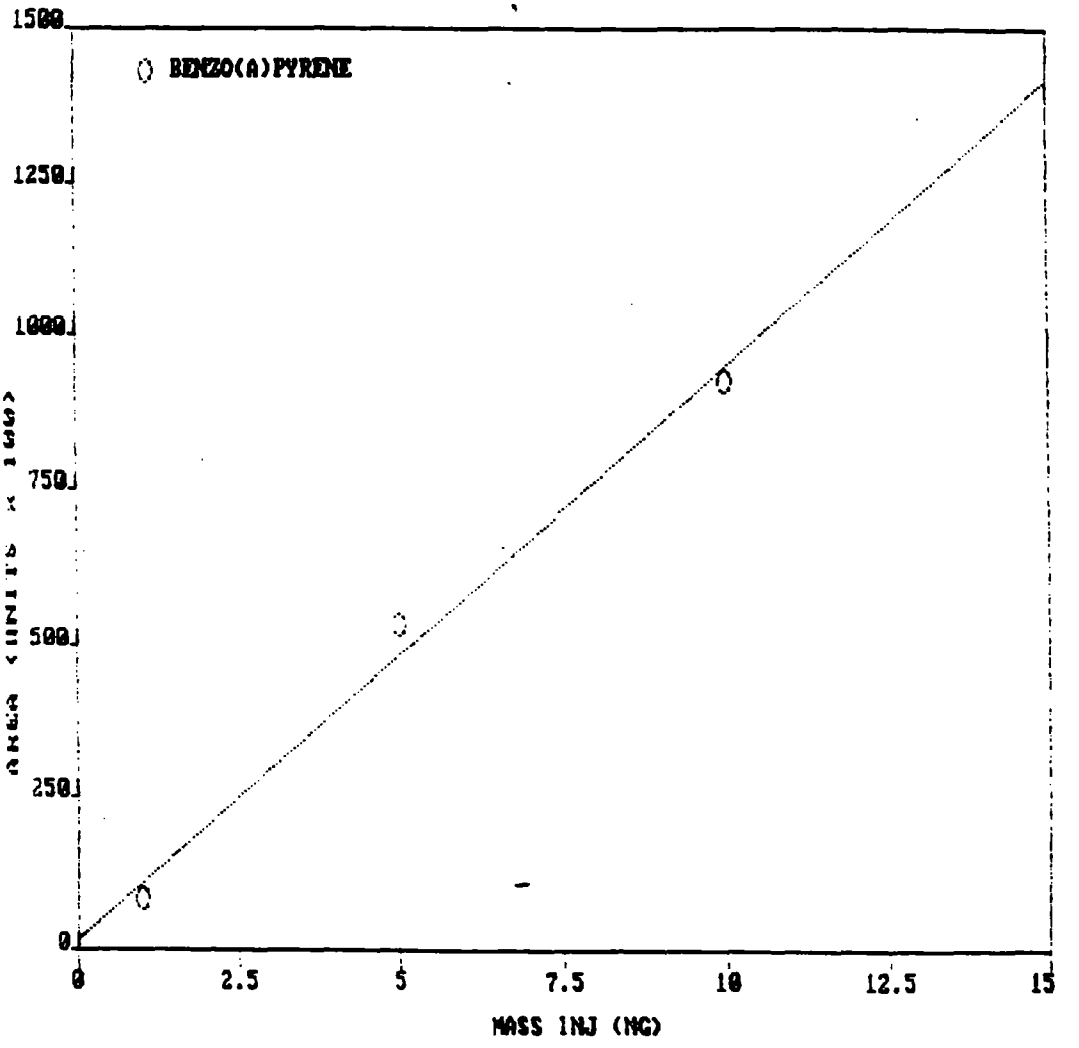
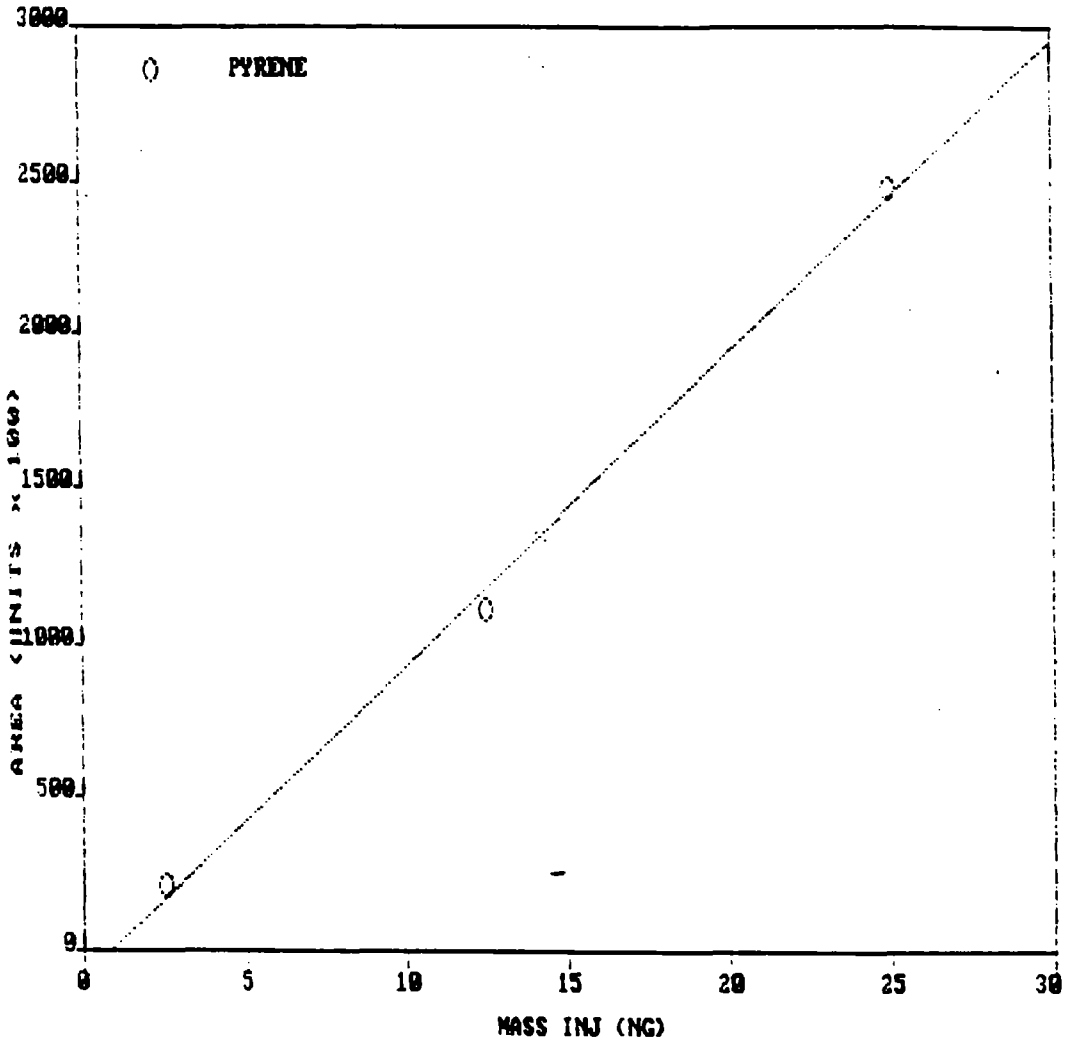
BENZO(A)PYRENE
CALIBRATION DATA



Amount Injected (ng)	Peak Area (Units)	Average	%RSD
1.0	8626	8412	2.6
"	8506		
"	8105		
5.0	60172	53436	8.9
"	49733		
"	50403		
10.0	101784	92690	7.2
"	90122		
"	86166		

Correlation Coefficient: 0.9946
ng injected = 1.064X10-4(Peak Area) + (-0.145)

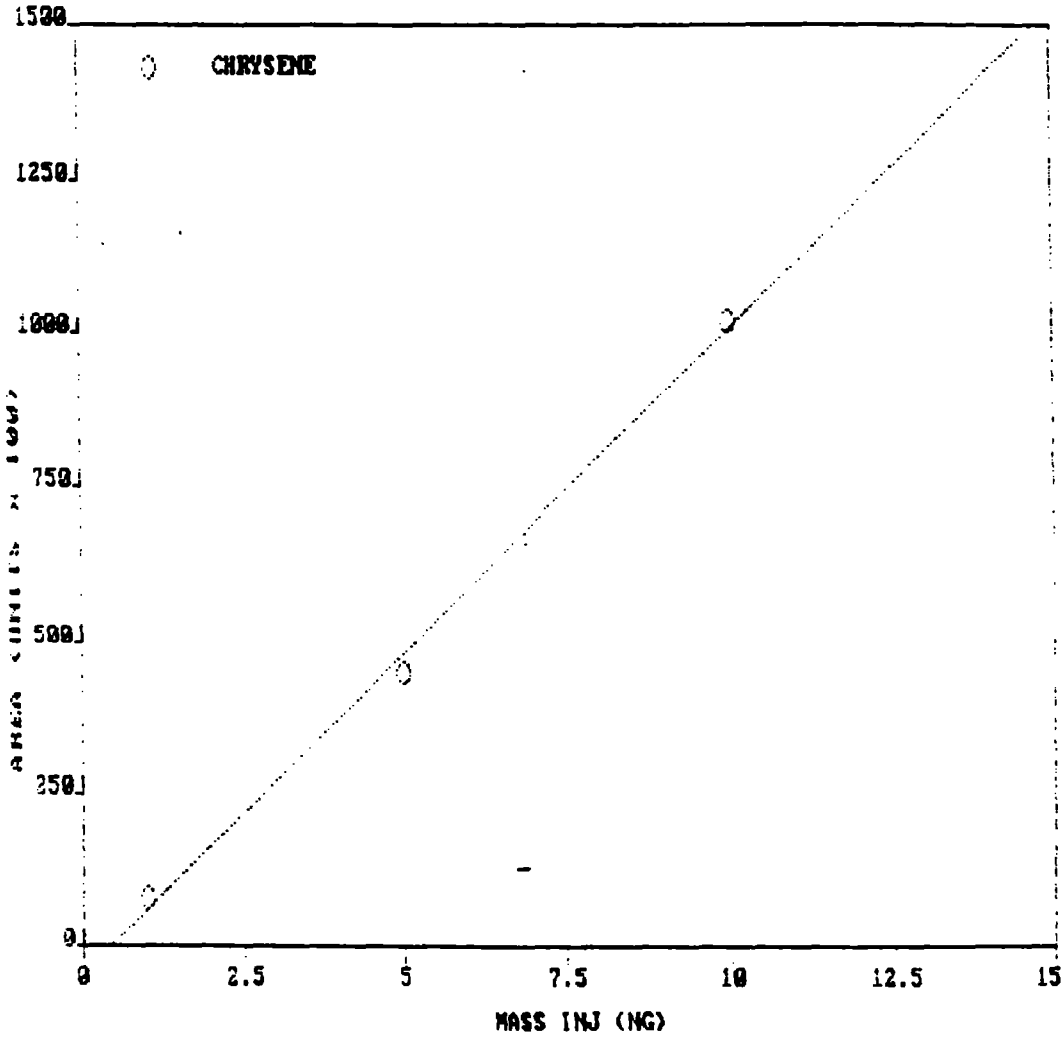
PYRENE
CALIBRATION DATA



Amount Injected (ng)	Peak Area (units)	Average	%RSD
2.5	19551	20754	6.9
"	22762		
"	19949		
12.5	115176	111176	1.5
"	114261		
"	104091		
25.0	258126	247794	3.1
"	245723		
"	239533		

Correlation Coefficient: 0.9986
ng injected = 9.85X10-5(Peak Area) + (0.867)

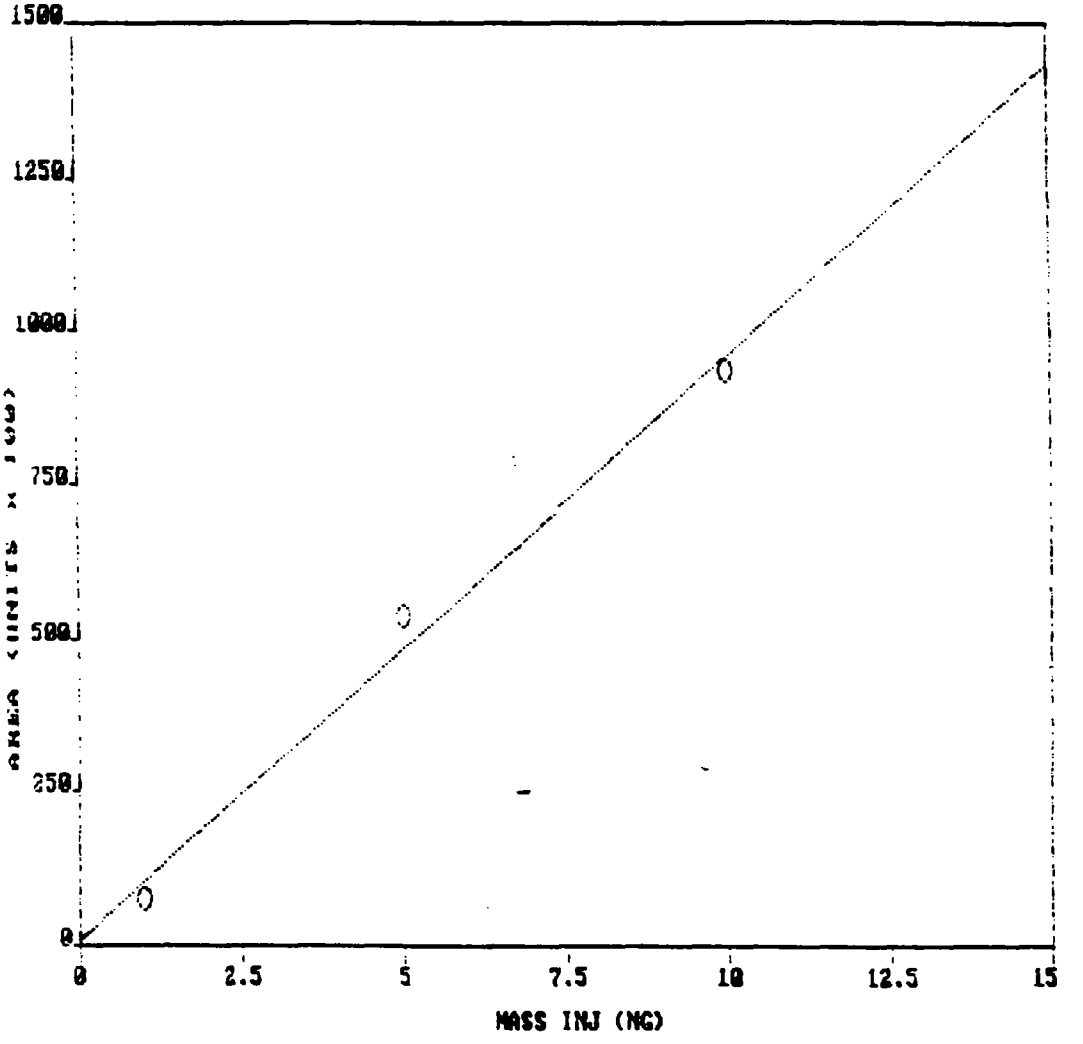
CHRYSENE
CALIBRATION DATA



Amount injected (ng)	Peak Area (Units)	Average	%RSD
1.0	7761	7986	2.0
"	8126		
"	8071		
5.0	42105	45050	8.4
"	42656		
"	50389		
10.0	94765	101888	5.1
"	106781		
"	104118		

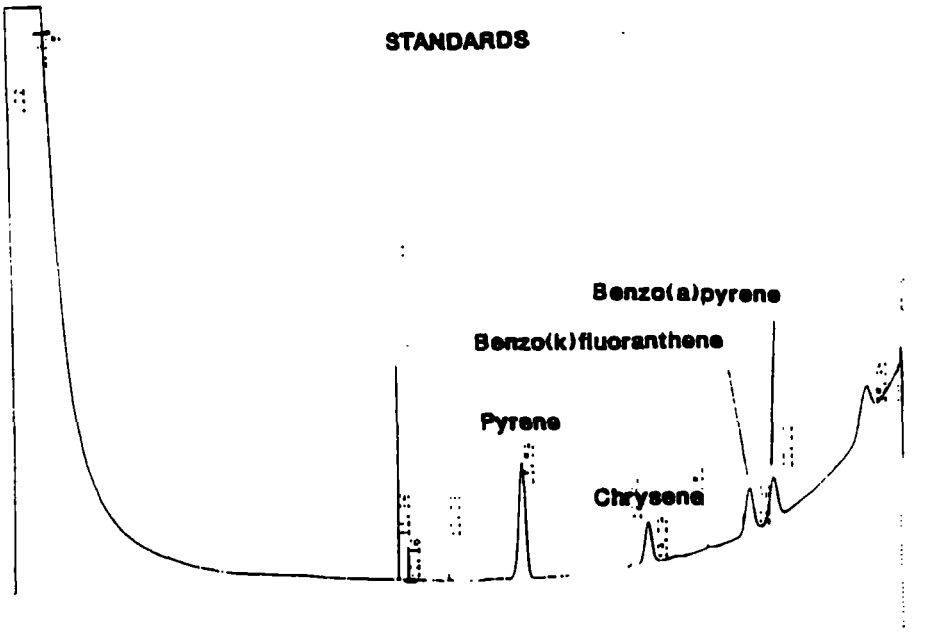
Correlation Coefficient: 0.9984
ng injected = 9.52X10-5(Peak Area) + (0.418)

BENZO(K)FLUORANTHENE
CALIBRATION DATA



Amount injected(ng)	Peak Area (units)	Average	%RSD
1.0	6983	7274	3.0
''	7522		
''	7317		
5.0	48231	53650	12.4
''	49667		
''	63054		
10.0	96127	93634	2.4
''	90621		
''	94155		

Correlation coefficient: 0.9943
ng injected = 1.037X10-4(Peak Area) + (-0.011)



PAHs IN SOIL

STANDARD OPERATING PROCEDURES

SAMPLE CHROMATOGRAM