

1.0 PURPOSE/APPLICABILITY

This method describes the analysis of semi-volatile organic compounds (SVOC) in air. The SVOCs include non-polar analysis of Polycyclic Aromatic Hydrocarbons (PAH), Aliphatic Hydrocarbon Analysis (Alkanes), Hopanes and Steranes, and Polar analysis. The method uses a sampling train consisting of a Teflon-impregnated glass fiber (TIGF) filter backed up by a PUF/XAD/PUF sandwich solid adsorbent. The separate portions of the sampling train are extracted and combined dependent on analyses. The analysis method is gas chromatography/mass spectrometry (GC/MS). Mass spectrometry provides definitive identification of SVOCs.

This method follows the procedure described in EPA Method TO-13 (June 1988, EPA/600-4-89/017). The exceptions are that 1) the DRI procedure uses a PUF/XAD-4/PUF sandwich adsorbent trap where TO-13 recommends either PUF or XAD-2, and 2) the DRI procedure calls for more rigorous cleaning than the EPA method.

2.0 MATERIALS/APPARATUS

2.1 Sampling Substrates

100 mm TIGF filters (Pall Gellman, ultrapure quality), PUF, and XAD-4 (Fisher Scientific) are obtained. Cleaning is as per Section 4 below. All solvents are Fisher Scientific Optima or HPLC grade.

2.2 GC/MS

The chromatographic system consists of a Varian CP-3800 gas chromatograph equipped with an 8200 CX Autosampler and interfaced to a Vairan Saturn 2000 Ion Trap Mass Spectrometer. The alternative system consists of a Varian CP-3800 gas chromatograph with a model CP-8400 Autosampler and interfaced to a Saturn 2000 Ion Trap Mass Spectrometer. Column is a CP-Sil8 30mx0.25 mmX025XX (Chrompack).

3.0 PERSONNEL QUALIFICATION

This SOP assumes that personnel performing the procedures are familiar with basic laboratory practice and operation of Dionex Accelerated Solvent Extractor (ASE), rotary evaporators, and the Varian GC/MS system and Saturn Workstation 5.2 computer software. Specific requirements for these instruments are found in the appropriate manuals.

4.0 SUBSTRATE CLEANING PROCEDURE

4.1. Filters

Teflon-impregnated glass fiber (TIGF) filters are cleaned by sonication for 10 minutes in dichloromethane (CH_2Cl_2) twice, with the solvent replaced and drained, and sonicated for 10 minutes in methanol twice with the solvent replaced. Filters are then dried in a vacuum oven at -15 to -20 in Hg for minimum of 24 hours, weighed (if necessary), placed in Uline metallic ZipTop static shielding bags, stored in aluminum cans in freezer .

If quartz filters (Pall Gellman, ultrapure quality), are used, they are baked at 900 °C for 4 hr before use.

4.2 PUF Plugs

PUF plugs are cleaned by first washing with distilled water, followed by Dionex ASE extraction for 15min/cell with ~ 170 mL acetone at 1500 psi and 100°C , followed by Dionex ASE extraction for 15min/cell with ~ 170 mL of 10% diethyl ether in hexane under the same conditions. The extracted PUF plugs are dried in a vacuum oven at -15 to -20 in Hg, 50°C for approximately 3 days or until no solvent odor is detected . If storage is necessary, PUF plugs are stored in clean 1L glass jars with Teflon lined lids wrapped in aluminum foil. Powder-free nitrile gloves are worn at all times when handling PUF plugs.

4.3 XAD-4

If new XAD-4 is used, it is placed in a Buchner funnel and rinsed with distilled water three times followed by technical grade methanol 3-4 times, and again three times with distilled water. It is then put into clean nylon stockings and further cleaned by Soxhlet extraction for 48 hours with methanol. For new and recycled XAD-4, it is then Dionex ASE extracted for 15min/cell with ~ 170 mL of dichloromethane (CH_2Cl_2) at 1500 psi and 100°C , followed by acetone. The XAD-4 is then dried in a vacuum oven at -15 to -20 in Hg and 50°C . Cleaned XAD-4 is transferred to clean 1L glass jars and stored in aluminum cans with activated charcoal.

4.4 Certification of Substrate

An aliquot of each batch of cleaned XAD-4, PUF, and TIGF (or glass fiber) filters has to be extracted as per Section 6.0 below, and checked by GC/MS for purity. Any batch determined to have excessive impurities (more than $10\ \mu\text{g}$ of naphthalene) will not be re-cleaned and checked again for purity.

4.5 Assembly of PUF/XAD/PUF Cartridge

Powder-free nitrile gloves are worn at all times during the cartridge assembly. One PUF plug is put at the bottom of a clean glass cartridge followed by 10 g of XAD-4 and a second PUF plug. The PUF/XAD/PUF cartridge is then placed in Uline ZipTop metallic static shielding bags and stored in aluminum cans at room temperature.

5.0 SAMPLE RECEIPT AND STORAGE

In the field, exposed samples are stored at 0°C in a freezer or ice chest, and are shipped to DRI overnight delivery at 0°C in ice chest (DRI's original shipping containers). Upon receipt by the laboratory, the samples are logged into the Laboratory Information Management System (LIMS) by Project Media Identification (PMI) number, and field data is recorded (sampling location, date, and start and stop time, elapse timer, and flow rate). If the time span between sample login and extraction is greater than 24 hours, the samples must be kept cold at 0-4°C in a freezer or refrigerator. The exposure of the sample media to ultraviolet light emitted by fluorescent lights must be minimized.

6.0 EXTRACTION OF SUBSTRATE

6.1 Addition of Internal Standards

6.1.1 Polycyclic Aromatic Hydrocarbon (PAH), non-polar

Prior to extraction, the following deuterated internal standards are added to each sample (filter, PUF/XAD/PUF):

naphthalene-d ₈	9.486	ng/μl
biphenyl-d ₁₀	7.008	ng/μl
acenaphthene-d ₁₀	5.997	ng/μl
phenanthrene-d ₁₀	5.991	ng/μl
anthracene-d ₁₀	5.000	ng/μl
pyrene-d ₁₂	4.993	ng/μl
benz(a)anthracene-d ₁₂	2.004	ng/μl
chrysene-d ₁₂	1.997	ng/μl
benzo[k]fluoranthene-d ₁₂	1.000	ng/μl
benzo[e]pyrene-d ₁₂	0.700	ng/μl
benzo[a]pyrene-d ₁₂	0.703	ng/μl
benzo[g,h,i]perylene-d ₁₂	0.600	ng/μl
coronene-d ₁₂	0.500	ng/μl

The amount of internal standards added should correspond to the expected range of concentrations found in real samples and the final volume of extracts during analysis.

6.1.2 Hopane and Sterane, non-polar

Prior to extraction, the following deuterated internal standards are added to each sample (filter, PUF/XAD/PUF):

cholestane- d6	0.375	ng/μl
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The amount of internal standards added should correspond to the expected range of concentrations found in real samples.

6.1.3 Aliphatic Hydrocarbon Analysis (Alkanes), non-polar

Prior to extraction, the following deuterated internal standards are added to each sample (filter, PUF/XAD/PUF):

dodecane-d26	10.9	ng/μl
hexadecane-d34	2.36	ng/μl
eicosane-d42	1.88	ng/μl
octacosane-d58	4.9	ng/μl
tetracosane-d50	1.89	ng/μl
hexatriacontane-d74	10.2	ng/μl

The amount of internal standards added should correspond to the expected range of concentrations found in real samples.

6.1.4 Polar Organic Compounds, polar

Prior to extraction, the following deuterated internal standards are added to each sample (filter-sorbent pair):

cholesterol-2,2,3,4,4,6-d6	9.85	ng/μl
levoglucosan-u-13C6	31.25	ng/μl
hexanoic-d11 acid	4.5	ng/μl
benzoic-d3 acid	4.5	ng/μl
decanoic-d19 acid-	4.5	ng/μl
palmitic-d31 acid	4.5	ng/μl
heptadecanoic-d33 acid	4.4	ng/μl
myristic-d27 acid	3.3	ng/μl

succinic-d4 acid	2.55	ng/μl
phthalic 3,4,5,6-d4 acid	4.6	ng/μl

The amount of internal standards added should correspond to the expected range of concentrations found in real samples and the final volume of extracts during analysis.

6.2 Extraction of PUF, XAD-4, and Filter

Depending on analyses, PUF, XAD-4 and Filter will be extracted in the following combinations. Solvents are selected to optimize the polarity range desired for analyses.

6.2.1 Non-Polar Analysis Only

Filters and are extracted twice with approximately ~170 mL of dichloromethane (CH_2Cl_2) using the Dionex ASE for 15 min/cell at 1500 psi and 100°C.

Since PUF media degrades when extracted with dichloromethane, the PUF/XAD/PUF are extracted twice with ~170 mL of acetone using the Dionex ASE for 15 min/cell at 1500 psi and 100°C. This method gives good recovery for PAH, aliphatic hydrocarbons (alkanes), and hopanes and steranes.

6.2.2 Polar and Non-Polar Analyses

Filters and XAD-4 are extracted together with ~170 mL dichloromethane (CH_2Cl_2) using the Dionex ASE for 15 min/cell at 1500 psi and 100°C followed by ~170 mL acetone extraction under the same conditions.

Since PUF media degrades when extracted with dichloromethane, the PUF/XAD/PUF are extracted twice with ~170 mL of acetone using the Dionex ASE for 15 min/cell at 1500 psi and 100°C. This method gives good recovery for PAH, aliphatic hydrocarbons (alkanes), hopanes and steranes, and polar organic compounds.

6.3 Treatment of Extracts

6.3.1 Non-Polar Analysis Only

Extracts are concentrated to ~1ml by rotary evaporation at 35 °C under gentle vacuum, and filtered through a 0.2 μm AnotopTM 10 Whatman leuc-lock filter on 4 mL glass syringe), rinsing the flask 3 times with 1 ml dichloromethane and acetone (50/50 by volume) each time. Filtrate is collected in a 4 mL amber glass vial for a total volume of ~4 mL.

Approximately 200 μL of acetonitrile is added at this time and the extract is split into two fractions. Each fraction is then concentrated using a Pierce Reacti-Therm under a gentle stream of ultra-high purity (UHP) nitrogen with a water trap (Chrompack CP-Gas-Clean moisture filter 17971) to 100-200 μL . The final extract volume is adjusted to 100 μL with acetonitrile.

6.3.2 Polar and Non-Polar Analyses

Extracts are concentrated to $\sim 1\text{ml}$ by rotary evaporation at 35 $^{\circ}\text{C}$ under gentle vacuum, and filtered through a 0.2 μm PTFE disposable filter device (Whatman Pura discTM 25TF), rinsing the flask 3 times with 1 ml dichloromethane and acetone (50/50 by volume) each time. Filtrate is collected in a 4 mL amber glass vial for a total volume of $\sim 4\text{ mL}$.

Approximately 200 μL of acetonitrile is added at this time and the extract is split into two fractions. Each fraction is then concentrated under a gentle stream of ultra-high purity (UHP) nitrogen with hydrocarbon and water traps to 100-200 μL . The final extract volume is adjusted to 100 μL with acetonitrile.

6.4 Cleanup of Samples (non-polar analysis)

For complex samples that contain analytical interference, the following method is used to clean up the sample using silica gel semi-prep Solid Phase Extraction (SPE 6-mL 0.5-g LC-SI, Supelco Silica).

1. Assuming SVOC in 100 μL acetonitrile, concentrate to 25 μL and add 25 μL dichloromethane and 150 μL hexane.
2. Condition SPE-Silica cartridge with 1.5 mL hexane/benzene (1:1), followed by 1.5 mL hexane.
3. Transfer sample into the SPE-Silica cartridge.
4. Elute sample with 1.5 mL hexane, followed by 3 mL hexane/benzene (1:1) in separate 4 mL vials.
5. Concentrate to 100 μL (only hexane should remain) and transfer to GC vial insert and concentrate to 20 μL .
6. Rinse original vial with 100 μL dichloromethane and concentrate to 40 μL (hexane/DCM (1:1)) and dilute to total volume of 100 μL with acetonitrile.

The hexane fraction contains the non-polar aliphatic hydrocarbons (alkanes), and hopanes and steranes, and the hexane/benzene fraction contains the PAH and N-PAH.

6.5 Silylation of Polar Organic Compounds (polar analysis)

If extracts have been split for polar and non-polar analysis, the fraction for the polar analysis is derivatized using a mixture of bis(trimethylsilyl)trifluoroacetamide and pyridine to convert the polar compounds into their trimethylsilyl derivatives for analysis of organic acids, cholesterol, sitosterol, and levoglucosan. Depending upon the expected range of analytes, it is recommended to split the second fraction into two equal fractions, thus providing a second opportunity for a clean silylation reaction.

1. The extract is reduced to a volume of 50 μ L using a Pierce Reacti-Therm under a gentle stream of ultra-high purity (UHP) nitrogen with a water trap (Chrompack CP-Gas-Clean moisture filter 17971).
2. 50 μ L of silylation grade pyridine is added to vial.
3. 150 μ L of bis(trimethylsilyl)trifluoroacetamide is added slowly to each vial and immediately capped.
4. The sample is then placed into thermal plates (custom) containing individual vial wells with the temperature maintained at 70°C for 3 hours.
5. The samples are then analyzed by GC/MS within 18 hours.

7.0 ANALYSIS

7.1 Instrument Method

The samples are analyzed by the electron impact (EI) GC/MS technique, using a Varian CP-3800 gas chromatograph equipped with a 8200 CX Autosampler and interfaced to a Varian Saturn 2000 Ion Trap Mass Spectrometer or Varian CP-3400 gas chromatograph with a model CP-8400 Autosampler and interfaced to a Saturn 2000 Ion Trap Mass Spectrometer

Injections are 1 μ l in size in the splitless mode onto a 30m long 5% phenylmethylsilicone fused silica capillary column (J&W Scientific type DB-5): CP-Sil8 Chrompack (30m x 0.25mm x 0.25 mm) for PAH, hopanes and steranes, alkanes and polars; and CP-Sil24 Chrompack (30m x 0.25mm x 0.25 mm) for N-PAH.

Identification and quantification of the analytes are made by Selected Ion Storage (SIS), by monitoring the molecular ions of each analyte and each deuterated analyte.

7.2 Preparation Stage

- A. The instrument (GC/MS) preparation steps are as follows:
- 1) Check for air and water in the system (Ion Time = 100, a total ion current (TIC) below 700 is preferred).
 - 2) Adjust calibration gas pressure for Ion Trap instrument (75% preferred).
 - 3) Check calibration gas pressure ~ 75%.
 - 4) Perform autotune for electron multiplier setting, mass calibration, and RF ramp.

Identification and quantification of the analytes are made by Selected Ion Storage (SIS), by monitoring the molecular ions of each analyte and each deuterated analyte.

7.3 Calibration

Calibration curves are made by the molecular ion peaks of the analytes using the corresponding deuterated species as internal standards. If there is no corresponding deuterated species, the one most closely matching in volatility and retention characteristics is used.

National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1647 (certified PAH), with the addition of the internal standards listed in Section 6.1.1-6.1.4 and the targeted PAH not present in this mixture, is used to make calibration solutions. Six concentration levels for each analyte of interest are employed. Table 1 lists the concentration levels of standard compounds in calibration solutions. The calibration curve for each calibrated compound is constructed; Figures 1 through 6 show examples of acceptable calibration curves. After the calibration is completed, a standard solution is injected to perform calibration checks. If deviations from the true values exceed $\pm 20\%$, the calibration procedure is repeated or new calibration levels must be prepared. One replicate analysis and one calibration check is performed for every 10 injections of samples. If difference between true and measured concentrations exceeds $\pm 20\%$, the system is recalibrated. During batch processing, calibration is performed before each batch.

8.0 REPORTING

Each sample is reported initially in terms of mass per sample ($\mu\text{g}/\text{sample}$). Ambient concentrations in terms of mass per volume (i.e., ng/m^3 or other units if requested) are reported based upon the sample volume adjusted for ambient temperature and pressure, or reported as "standard" volume.

All information for the sample is recorded and combined into both a printed report and an Excel file for inclusion in the database (see Appendix).

8.1 Method Detection Limits (MDLs)

Method detection limits are 0.01-0.03 ng/ μ l for PAH, hopane and sterane, and alkane compounds, and 0.03-0.04 ng/ μ l for polar compounds.

8.2 Measurement Uncertainty

Measurement uncertainty is reported as one-sigma standard deviation between replicate tests (when 3 tests conducted under same conditions) or the combined root mean square of the analytical measurement uncertainty, which is defined by the following equation:

$$\sqrt{(\text{replicate precision} * \text{analyte concentration})^2 + (\text{analyte detection limit})^2}$$

This equation incorporates the analyte detection limit for each compound so when concentrations approach zero the error is reported as the analyte detection limit. When multiple samples are pooled the difference between samples is typically greater than the precision of any of the analytical techniques employed. Most data has relatively small reported measurement uncertainty's which shows the reproducibility of the samples. When larger errors (>30% of reported concentration) are observed, it is typically because the concentrations of the analyte were close to the detection limit of the measurements.

Table 1. Calibration Levels for PAH analysis (bold compounds co-elute and are quantified together)

Compound	Level 1 (ng/uL)	Level 2 (ng/uL)	Level 3 (ng/uL)	Level 4 (ng/uL)	Level 5 (ng/uL)	Level 6 (ng/uL)
1-ethylnaphthalene	0.359	0.718	1.436	2.873	11.491	45.965
1,2-dimethylnaphthalene	0.361	0.722	1.444	2.887	11.548	46.193
1,4-chrysenequinone	0.240	0.479	0.958	1.917	7.667	30.667
1,6 + 1,3 dimethylnaphthalene	0.719	1.438	2.876	5.753	23.012	92.047
1,8-dimethylnaphthalene	0.240	0.481	0.962	1.924	7.695	30.781
1-methylfluorene	0.298	0.596	1.192	2.383	9.533	38.133
1-methylphenanthrene	0.200	0.400	0.799	1.598	6.392	25.568
1-methylpyrene	0.240	0.481	0.961	1.922	7.688	30.752
1-phenylnaphthalene	0.199	0.398	0.796	1.591	6.365	25.461
2-ethylnaphthalene	0.357	0.714	1.428	2.856	11.424	45.696
1,4+1,5+2,3-dimenaephene	1.078	2.156	4.313	8.625	34.501	138.005
2,6-dimethylnaphthalene	0.352	0.704	1.408	2.817	11.267	45.067
2-methylbiphenyl	0.360	0.720	1.441	2.881	11.525	46.102
2-methylphenanthrene	0.246	0.492	0.983	1.967	7.867	31.467
2-phenylnaphthalene	0.358	0.716	1.433	2.866	11.463	45.853
3,6-dimethylphenanthrene	0.203	0.406	0.813	1.625	6.500	26.000
3-methylbiphenyl	0.361	0.721	1.442	2.884	11.537	46.149
4H-cyclopenta(def)phenanthrene	0.000	0.000	0.000	0.000	0.000	0.000
4-methylbiphenyl	0.369	0.738	1.475	2.950	11.800	47.200
4-methylpyrene	0.240	0.479	0.958	1.917	7.667	30.667
5+6 methylchrysene	0.559	1.119	2.237	4.475	17.899	71.595
7-methylbenz(a)anthracene	0.279	0.558	1.117	2.233	8.933	35.733
7-methylbenzo(a)pyrene	0.290	0.579	1.158	2.317	9.267	37.067
9,10-dihydrobenzo(a)pyren-7(8H)-one	0.281	0.561	1.122	2.244	8.976	35.904
9-anthraldehyde	0.371	0.742	1.483	2.967	11.867	47.467
9-fluorenone	0.280	0.560	1.120	2.240	8.961	35.845
9-methylanthracene	0.239	0.479	0.958	1.916	7.663	30.653
acenaphthene*	0.201	0.402	0.804	1.609	6.435	25.739
acenaphthenequinone	0.202	0.404	0.808	1.617	6.467	25.867
acenaphthylene	0.200	0.400	0.800	1.600	6.400	25.600
anthrone	0.277	0.554	1.108	2.217	8.867	35.467
BaP*	0.160	0.321	0.642	1.283	5.133	20.533
benz(a)anthracene*	0.200	0.400	0.799	1.599	6.395	25.579
benz(a)anthracene-7,12-dione	0.279	0.558	1.117	2.233	8.933	35.733

benzanthrone	0.360	0.720	1.440	2.880	11.518	46.073
anthracene*	0.159	0.319	0.638	1.276	5.103	20.411
anthraquinone	0.280	0.559	1.119	2.237	8.949	35.795
benzo(k+j)fluoranthene*	0.397	0.794	1.587	3.174	12.697	50.789
benzo(g,h,i)perylene*	0.200	0.400	0.800	1.600	6.401	25.602
benzo(c)phenanthrene	0.200	0.400	0.800	1.601	6.403	25.613
benzonaphthothiophene	0.240	0.479	0.958	1.917	7.667	30.667
BeP*	0.202	0.403	0.807	1.613	6.453	25.813
chrysene*	0.190	0.379	0.758	1.517	6.067	24.267
coronene*	0.160	0.320	0.640	1.280	5.118	20.474
dibenz(ah+ac)anthracene	0.323	0.645	1.291	2.582	10.327	41.307
dibenzofuran	0.278	0.556	1.111	2.223	8.890	35.560
fluorene	0.241	0.481	0.963	1.925	7.700	30.800
fluoranthene	0.252	0.503	1.006	2.013	8.050	32.200
indeno(1,2,3-cd)pyrene	0.161	0.321	0.642	1.284	5.136	20.544
perinaphthenone	0.279	0.558	1.116	2.232	8.928	35.712
perylene	0.200	0.400	0.800	1.600	6.400	25.600
phenanthrene*	0.201	0.401	0.802	1.604	6.417	25.667
pyrene*	0.196	0.392	0.783	1.567	6.267	25.067
retene	0.277	0.555	1.109	2.219	8.875	35.499
2,3,5-trimethylnaphthalene	0.199	0.399	0.797	1.594	6.378	25.511
2,4,5-trimethylnaphthalene	0.277	0.554	1.108	2.217	8.867	35.467
1,4,5-trimethylnaphthalene	0.239	0.478	0.957	1.914	7.654	30.616
xanthone	0.240	0.481	0.961	1.923	7.691	30.763
1-methylnaphthalene	0.361	0.723	1.446	4.338	17.351	69.403
2,7-dimethylnaphthalene	0.300	0.599	1.198	3.594	14.377	57.507
bphenyl*	0.360	0.720	1.440	4.319	21.597	107.983
bibenzyl	0.362	0.724	1.448	4.345	21.723	108.617
2-methylnaphthalene	0.430	0.860	1.720	5.160	25.800	129.000
nphthalene*	0.359	0.717	1.435	5.739	34.432	206.592

*deuterated forms of these compounds are added to samples prior to extraction as surrogate for quantitation

Table 2. Calibration Levels for Hopanes and Steranes Analysis

Compound	Level 1	Level 2	Level 3	Level 4	
	ng/uL	ng/uL	ng/uL	ng/uL	ng/uL
cholestane-d6*	0.750	0.750	0.750	0.750	0.750
cholestane	0.250	0.500	1.000	2.000	4.000
17 α -21 β (H) Hopane (19)	0.250	0.500	1.000	2.000	4.000
17 β (H)-30-Norhopane (17a)	0.250	0.500	1.000	2.000	4.000
17 β (H)-21 β (H) Hopane (23)	0.250	0.500	1.000	2.000	4.000

*deuterated forms of these compounds are added to samples prior to extraction as surrogate for quantitation

Table 3. Calibration Levels for Aliphatic Hydrocarbon Analysis (Alkanes), bold compounds co-elute and are quantified together

Compounds	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8
	ug/uL							
2,6,10-trimethylundecane_(norfarnesane)	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-heptylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
2,6,10-trimethyldodecane_(farnesane)	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tetradecane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-pentadecane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-octylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-nonylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-heptadecane + 2,6,10,14-tetramethylpentadecane_								
pristane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-hexadecane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
2,6,10-trimethylpentadecane_norpristane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-decylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-undecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-nonadecane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-octadecane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
2.6.10.14-	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000

tetramethylhexadecane_phytane

n-dodecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tridecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tetradecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-heneicosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-eicosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-pentadecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-docosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tricosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tetracosane-d50*	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-heptadecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-octadecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tetracosane* + n-hexadecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-pentacosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-nonadecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-heptacosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-eicosylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-hexacosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-octacosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000

*deuterated forms of these compounds are added to samples prior to extraction as surrogate for quantitation

Table 4. Calibration Levels for Polar Organic Compounds Analysis

Compound	Level	Level	Level	Level	Level	Level
	1	2	3	4	5	6
	ng/uL	ng/uL	ng/uL	ng/uL	ng/uL	ng/uL
4-pentenoic	0.323	2.155	6.464	10.773	15.083	18.315
hexanoic acid	0.300	2.400	7.199	12.960	18.144	21.384
heptanoic	0.334	2.228	6.685	11.142	15.598	18.941
me-malonic	0.321	2.570	7.710	12.850	17.990	21.203
guaiacol	0.268	2.680	7.370	15.075	20.100	25.125
benzoic acid	0.300	2.400	7.199	12.960	18.144	21.384
octanoic	0.314	2.091	6.272	10.453	14.635	17.771
glycerol	0.348	2.320	6.960	11.600	16.240	19.720
maleic	0.328	2.620	7.860	13.100	18.340	21.615

DRI STANDARD OPERATING PROCEDURE

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Title: Analysis of Semi-Volatile Organic
Compound by GC/MS

Number: 2-750.5

Revision: 05

succinic acid	0.300	2.400	7.199	12.960	17.820	21.060
4-methylguaiacol	0.385	3.851	10.591	21.664	28.885	36.106
methylsuccinic acid	0.300	2.400	7.199	12.960	17.820	21.060
o-toluic	0.313	2.500	7.500	12.500	17.500	20.625
picolinic acid	0.300	2.400	7.199	12.960	18.144	21.384
m-tolic	0.327	2.613	7.840	13.067	18.293	21.560
1,2,4-butanetriol	0.300	2.400	7.199	12.960	18.144	21.384
nonanoic	0.318	2.120	6.360	10.600	14.840	18.020
p-toluic	0.169	1.128	3.384	5.640	7.896	9.588
3-methylpicolinic	0.321	2.568	7.704	12.840	17.976	21.186
6-methylpicolinic	0.319	2.550	7.650	12.750	17.850	21.038
2,6-dimethylbenzoic	0.269	2.150	6.450	10.750	15.050	17.738
4-ethylguaiacol	0.260	2.598	7.146	14.616	19.488	24.360
syringol	0.266	2.655	7.301	14.934	19.913	24.891
glutaric acid	0.300	2.400	7.199	12.960	17.820	21.060
2-methylglutaric	0.319	2.550	7.650	12.750	17.850	21.038
2,5-dimethylbenzoic	0.260	2.080	6.240	10.400	14.560	17.160
3-methylglutaric	0.261	2.085	6.256	10.427	14.597	17.204
2,4-dimethylbenzoic	0.263	2.100	6.300	10.500	14.700	17.325
3,5-dimethylbenzoic	0.256	2.050	6.150	10.250	14.350	16.913
2,3-dimethylbenzoic	0.272	2.172	6.516	10.860	15.204	17.919
n-decanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
4-allylguaiacol	0.284	2.843	7.817	15.990	21.320	26.650
4-methylsyringol	0.283	2.832	7.788	15.930	21.240	26.550
3,4-dimethylbenzoic	0.269	2.153	6.460	10.767	15.073	17.765
adipic acid	0.300	2.400	7.199	12.960	17.820	21.060
t-2-decenoic	0.318	2.123	6.368	10.613	14.859	18.043
cis-pinoic acid	0.300	2.400	7.199	12.960	17.820	21.060
3-methyladipic	0.328	2.623	7.868	13.113	18.359	21.637
4-formylguaiacol	0.283	2.832	7.788	15.930	21.240	26.550
undecanoic	0.315	2.523	7.570	12.617	17.663	20.818
isoeugenol	0.300	3.000	8.250	16.875	22.500	28.125
pimelic acid	0.300	2.400	7.199	12.960	17.820	21.060
acetovanillone	0.266	2.655	7.301	14.934	19.913	24.891
lauric acid	0.300	2.400	7.199	12.960	17.820	21.060
phthalic acid	0.300	2.400	7.199	12.960	17.820	21.060
levoglucosan	0.300	2.400	7.199	12.960	18.144	21.384
syringaldehyde	0.266	2.655	7.301	14.934	19.913	24.891
tridecanoic acid	0.300	2.400	7.199	12.960	17.820	21.060

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Title: Analysis of Semi-Volatile Organic
Compound by GC/MS

Number: 2-750.5

Revision: 05

suberic acid	0.300	2.400	7.199	12.960	17.820	21.060
isophthalic acid	0.300	2.400	7.199	12.960	17.820	21.060
azelaic acid	0.300	2.400	7.199	12.960	17.820	21.060
myristoleic	0.307	2.046	6.138	10.230	14.322	17.391
myristic acid	0.300	2.400	7.199	12.960	17.820	21.060
sebacic	0.165	1.098	3.294	5.489	7.685	9.332
pentadecanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
undecanedioic	0.165	1.099	3.296	5.493	7.691	9.339
palmitoleic	0.318	2.120	6.360	10.600	14.840	18.020
palmitic acid	0.300	2.400	7.199	12.960	18.144	21.384
isostearic	0.312	2.080	6.240	10.400	14.560	17.680
dodecanedioic acid	0.165	1.099	3.296	5.493	7.691	9.339
heptadecanoic	0.323	2.585	7.756	12.927	18.097	21.329
1,11-						
undecanedicarboxylic	0.171	1.141	3.424	5.707	7.989	9.701
oleic acid	0.300	2.400	7.199	12.960	18.144	21.384
elaidic acid	0.300	2.400	7.199	12.960	17.820	21.060
stearic acid	0.300	2.400	7.199	12.960	18.144	21.384
1,12-dodecanedioic	0.166	1.105	3.315	5.525	7.735	9.393
nonadecanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
dehydroabietic acid	0.300	2.400	7.199	12.960	17.820	21.060
eicosanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
pentadecanedioic acid	0.166	1.105	3.315	5.525	7.735	9.393
abietic acid	0.300	2.400	7.199	12.960	18.144	21.384
heneicosanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
docosanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
tricosanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
tetracosanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
cholesterol	0.750	5.999	17.998	32.400	44.550	52.650
b-sitosterol	0.750	5.999	17.998	32.400	44.550	52.650

APPENDIX

SVOC Program Information

I. Before Running

A. Each project must be listed in the database "H:\db_prg\oalproj.dbf.". Fill in the following columns:

Column	Value
NUM	Use the next number in sequence
PROJ_NAME	A short description you will recognize
PROJ_CODE	The two-digit project code MUST be unique
ROOT_DIR	The directory where the project data are stored
STATUS	"c" for current, or "o" for old
SVOC	enter 1 to run the SVOC programs, 0 otherwise.

B. For each project, there is a list of target compounds for analysis. This list is in the directory "H:\db_calib\svoc\" and it is called AAcmpd.dbf, where AA is the project code in the oalproj.dbf database. In this same directory is a database called "Template.dbf" which is a template you can copy to make the new ones. The fields you must fill in are:

Column	Description
Field_Name	The mnemonic for the PAH or PAH uncert.
Field_Type	ignore this
Field_Len	ignore this
Field_Dec	ignore this
Compound	The long name for the compounds only, enter nothing for uncert. This MUST exactly match the way it is in the mass spec calibration file.
Type	Enter "c" for a compound, nothing for uncert.

C. If you intend to import GCMS data, you must use Lantastic to attach the GC/MS computer's c: (hard) drive to a drive on the local machine.

II. Running

A. Run the genbatch program and follow inputs.

B. IF this is the first time you have worked on this project, you must first run the option "N" which creates a new set of files. This will make the files you will need.

C. You now can quit the programs and enter samples into the 'lab' database. This is the database the import program uses to determine what to import.

D. If the sample is run diluted, that file name and process status are also noted. When there is no diluted sample, just leave the name blank and set the dil_f_proc bit to zero. After the samples are imported, the program automatically enters a 2 for the proc bit.

Column	Description
PID	Standard ID
XMSFLAG	Mass Spec flag
F_NAME	Mass Spec file name for main analysis
F_PROC	Process bit for main (0=do nothing, 1= import normally, 2=import done).
DIL_F_NAME	Mass Spec file name for diluted analysis (if done)
DIL_F_PROC	Process bit for diluted (0=do nothing, 1= import normally, 2=import done).
SAMPLNO	Sample number
LOT	Lot numbers
ANALDATE	Date of analysis
COMMENTS	Notes

E. Once the import is done, AND the field data have been entered, you may continue with the rest of the processing, simply by following the sequence.

F. For the first batch of any project, the menu looks like:

```
** FILE CREATING FOR BATH 1 ONLY **  
N FOR Creating New Project Files  
6 FOR Importing XMS data.  
** Copying files from current Batch \data to \report  
3 FOR Copying Field data.  
4 FOR Copying analysis (xms) data.  
** Continue Processing Field  
5 FOR Processing Field data file.  
** Continue Processing Analysis (xms) file.  
7 FOR Running REP.  
8 FOR Merge FLD and XMS files to CHM file.  
9 FOR Calculate blank values and blank uncertainty.  
10 FOR Convert chm file to con file (ug/m3).
```

Simply follow the sequence through. Note, before going to Step 3 and beyond, you must first make sure the field and xms data are all input.

III. Continuing a Project: Batch 2 and Following.

A. The menu for batch 2 and following looks like:

- ** Copying files from previous Batch \report to current \data directories**
 - 1 FOR Copying Field data from Batch (prev) to (current).**
 - 2 FOR Copying analysis (xms) and LAB data from Batch (prev) to (current).**
 - 6 FOR Importing XMS data.**
- ** Copying files from current Batch \data to \report**
 - 3 FOR Copying Field data.**
 - 4 FOR Copying analysis (xms) data.**
- ** Continue Processing Field**
 - 5 FOR Processing Field data file.**
- ** Continue Processing Analysis (xms) file.**
 - 7 FOR Running REP.**
 - 8 FOR Merge FLD and XMS files to CHM file.**
 - 9 FOR Calculate blank values and blank uncertainty.**
 - 10 FOR Convert chm file to con file (ug/m³).**

This is basically the same as before, except you simply want to copy the previous Field, lab and xms files.

SVOC2 - The Sequel

Background

We have to analyze for more than just the PAH species, so a second processing program has been written. This program follows the PAH analysis program sequence with a number of exceptions.

Exceptions

The second SVOC program uses the same lab and field files as the regular program and thus these need to be finished at the same time.

The option exists in this program to define which compounds will be imported from the regular samples and which from diluted ones. This must be the same for all compounds in a project, although some adjustments can be made if necessary. In any case, all compounds must be imported the first pass through and then a sub-group can be imported from a second (called diluted) on file.

Everything is case sensitive, especially the compound names.

Steps

1. Tell the Data Processing Manager which projects need this so the OALProj database and the other necessary files can be updated.
2. Update the compound list file. This file is project-specific and it is located in the

H:\db_calib\svoc\ directory in the general form xx2cmpd.dbf, where xx is the project code. The template is nf2cmpd.dbf. This needs to be filled out in the following format:

Field_name This is the mnemonic that will become the field name. Each compound must be followed by its associated uncertainty, just as in the example.

Field_type Leave alone

Field_len Leave alone

Field_dec Leave alone

Compound For the compound only (not the uncert.), insert the compound name EXACTLY as it is in the HP GC/MS calibration file. If this is not spelled EXACTLY as it is in the calibration file on the HP GC/MS nothing will work. Do not put in anything for the uncertainties.

Type Put in "c" for compounds, nothing for uncertainties. EVERY compound in the list MUST have a "c" in this field.

Dil Put in "d" for compounds that will be imported from diluted files, nothing otherwise.

3. Update the Lab database. There are five new fields in the lab database for the second SVOC files. These are:

F2_name Mass spec file name for primary analysis

F2_proc Process status for above (1= ready to import, 2= done)

Dil_f2_nam MS file name for diluted run

Dil_f2_pro Process status for above (1= ready to import, 2= done)

Date2 Analysis date for second compound list.

This should follow the conventions used in the normal data processing for PAH species.

4. Do genbatch and follow the instructions. When you select a project you will be prompted to select either SVOC or Additional SVOC compounds. Selecting the latter (option 7) will take you to the SVOC2 programs. First use the "N" option to build new files and then continue by importing the mass spec data and continuing the processing. This will create XM2 (the raw mass spec data), the CH2 file, and the CN2 (ng/m3) file.

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.999
1,7-dimethylphenanthrene Compound: 45 of 83 Standard Deviation: 0.028
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard)) (Lin|Lin)
[$y = 0.000000 \text{ E}0 \text{ x}^2 + 1.269278 \text{ E}0 \text{ x} + -4.631979 \text{ E}-3 \text{ } 1$]

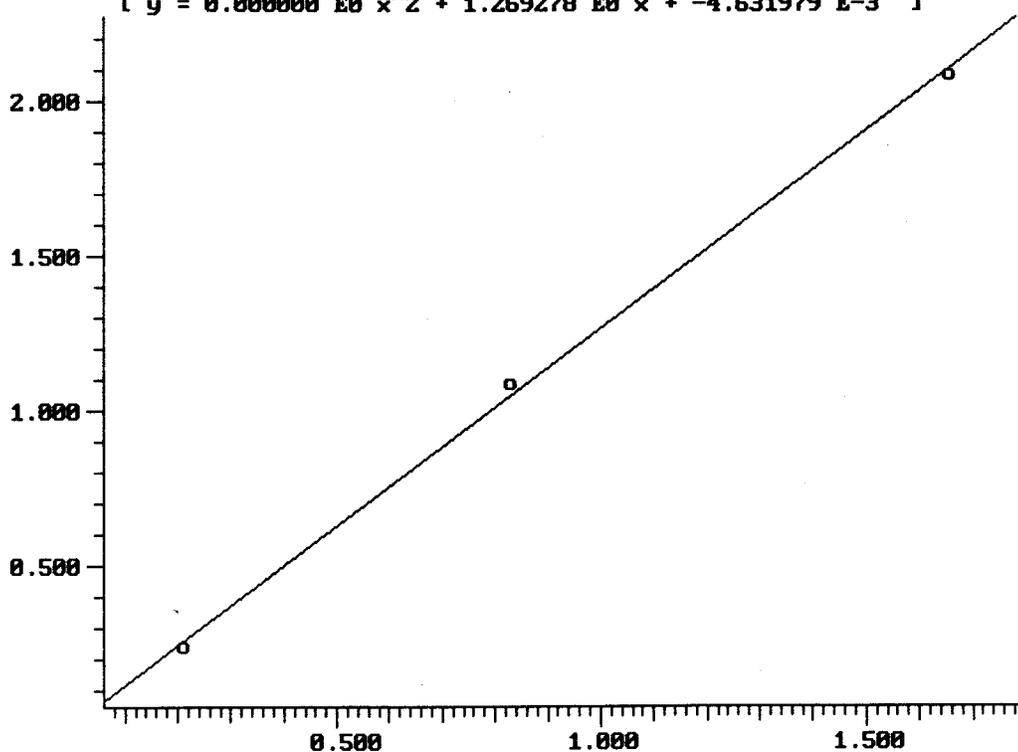


Figure 1

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.999
C-dimethylphenanthrene Compound: 44 of 83 Standard Deviation: 0.028
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard)) (Lin/Lin)
[$y = 0.000000 \text{ E}0 \text{ x}^2 + 1.269930 \text{ E}0 \text{ x} + -4.550553 \text{ E-}3$]

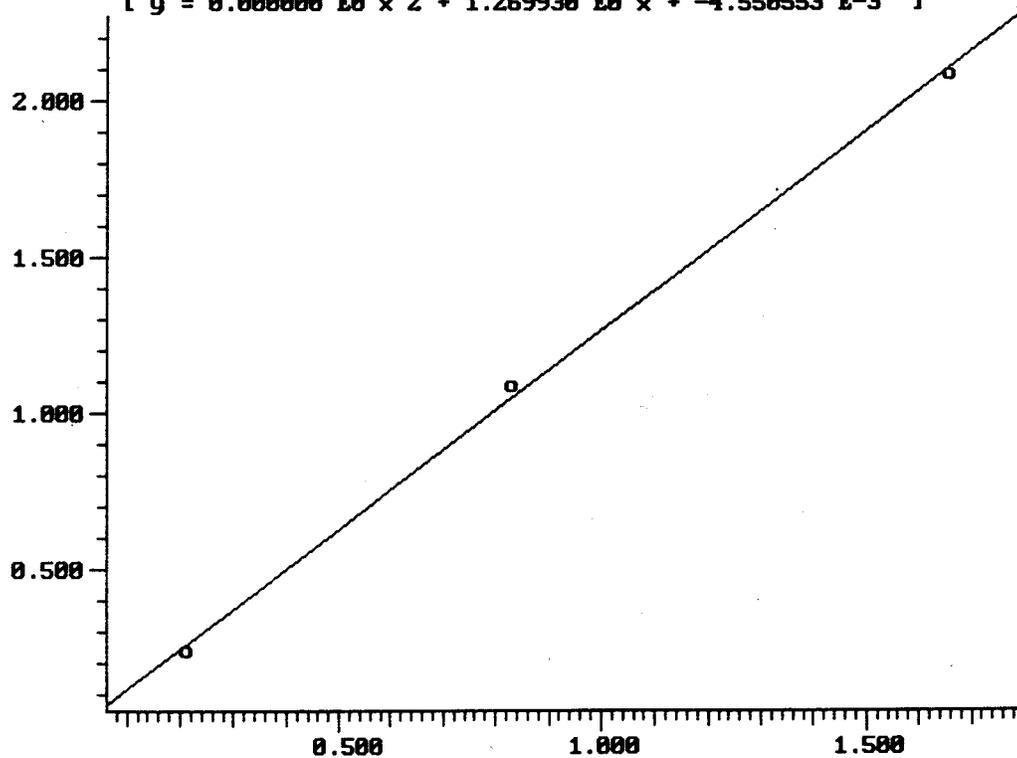


Figure 2

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.999
B-dimethylphenanthrene Compound: 43 of 83 Standard Deviation: 0.026
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard))
[$y = 0.000000 \text{ E}0 \text{ x}^2 + 1.272932 \text{ E}0 \text{ x} + -6.577547 \text{ E-}3$]

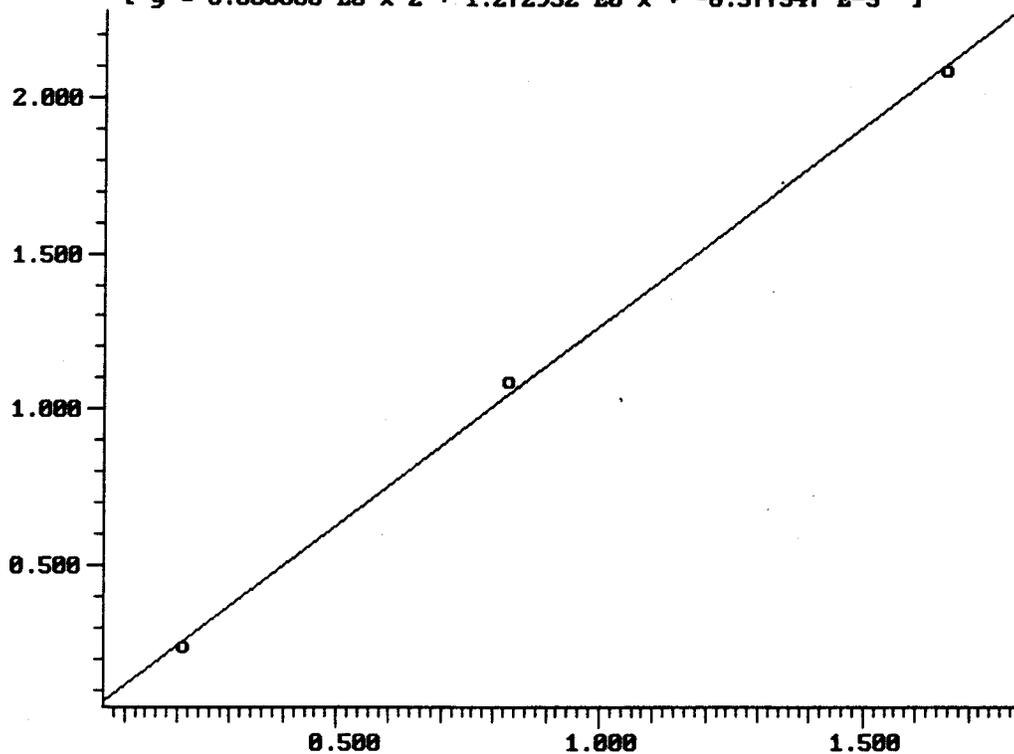


Figure 3

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.999
A-dimethylphenantherene Compound: 42 of 83 Standard Deviation: 0.026
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard)) (Lin/Lin)
[$y = 0.000000 \text{ E}0 \text{ x}^2 + 1.272866 \text{ E}0 \text{ x} + -6.185425 \text{ E-}3$]

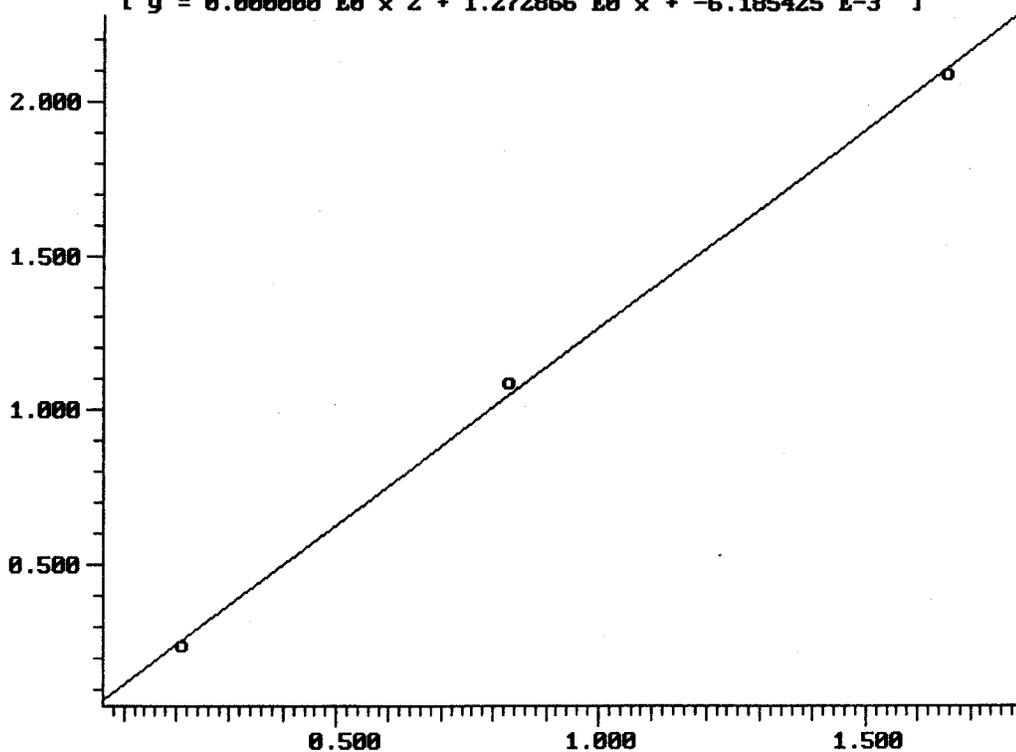


Figure 4

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.997
2,6+2,7-dimethylnaphthalene Compound: 7 of 83 Standard Deviation: 0.053
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard)) (Lin/Lin)
[$y = 0.000000 E0 x^2 + 5.571070 E-1 x + 8.442393 E-2$]

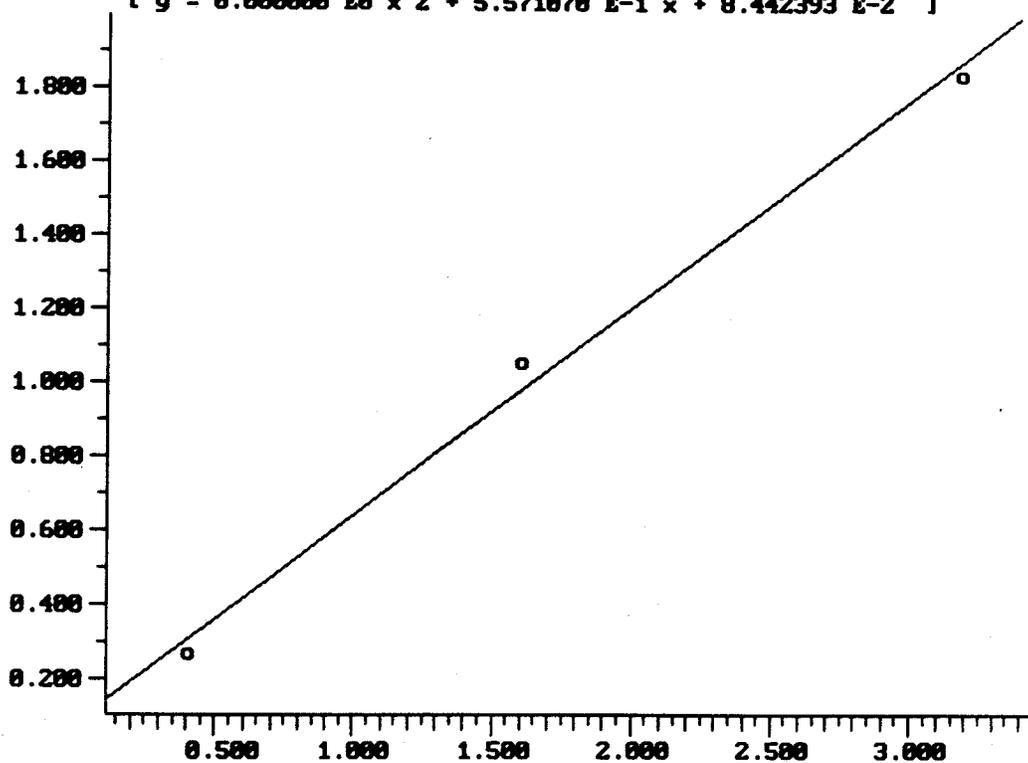


Figure 5

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.996
Biphenyl Compound: 6 of 83 Standard Deviation: 0.022
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard)) [Lin|Lin]
[$y = 0.000000 \text{ E}0 \text{ x}^2 + 0.520552 \text{ E-1 x} + 3.587838 \text{ E-2}$]

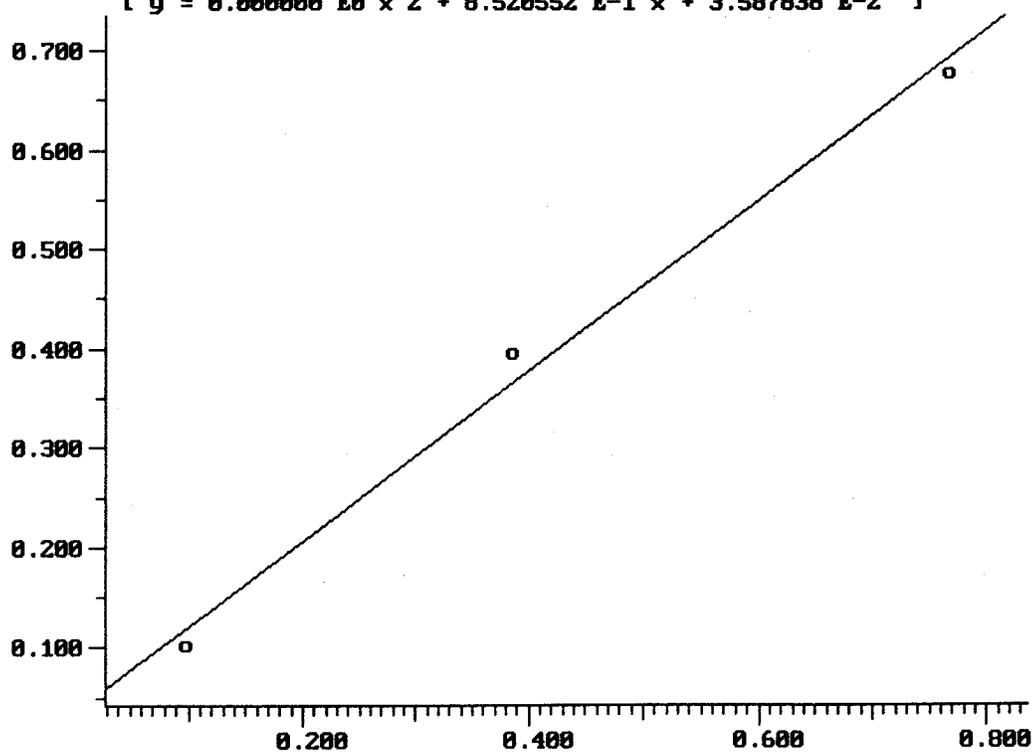


Figure 6