Analysis of PAHs

in

Air and Precipitation Samples

IADN Project
PAH Procedure

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Introduction

This document outlines the instrumental analysis and quantitation of polycyclic aromatic hydrocarbons (PAH) collected in air and precipitation samples from five sites on the Great Lakes. This work is conducted at the School of Public and Environmental Affairs, Indiana University-Bloomington as a part of the Integrated Atmospheric Deposition Network (IADN).

PAH analyses are performed on a Hewlett-Packard (HP) 6890 gas chromatograph and a HP 5973 mass spectrometer (GC/MS). Chromatographic resolution is achieved with a 30 m × 250 µm DB-5 capillary column which has a 0.25 µm film thickness (J & W Scientific, Folsom, CA) with helium carrier gas. PAH are analyzed by GC-MS using selected ion monitoring (SIM) and quantitated using the method of internal standards. The PAH analyzed in this study are listed in Table I along with the quantitation and confirmation ions.

Table I: Target compounds and their monitored ions.

Retention Order	Compound	Quantitation Ion	Confirmation Ion
1	d10-Anthracene*	188	--
2	Acenaphthylene	152	151
3	Acenaphthene	153	154
4	Fluorene	166	165
5	d10-Phenanthrene**	188	--
6	Phenanthrene	178	176
7	Anthracene	178	176
8	Fluoranthene	202	101
9	d10-Pyrene**	212	
10	Pyrene	202	101
11	Retene	219	234
12	d12-Benz[a]anthracene*	240	--
13	Benz[a]anthracene	228	114
14	Chrysene	228	114
15	d12-Perylene*	264	--
16	Benzo[b]fluoranthene	252	126
17	Benzo[k]fluoranthene	252	126
18	Benzo[e]pyrene	252	126
19	Benzo[a]pyrene	252	126
20	Indeno[1,2,3,cd]pyrene	276	138
21	Dibenzo [a,h]anthracene	278	139
22	Benzo [g,h,l]perylene	276	138
23	Coronene	300	150

Performance Evaluation

Prior to analyzing a sample set, the GC-MS system performance and calibration are verified for all analytes. The mass spectrometer is tuned immediately before the running of a sample set using the system's operating software programs (AUTOTUNE) with perfluorotributylamine (PFTBA) calibration gas. Mass spectrometer parameters are adjusted so that masses 69, 219, and 502 and their respective isotopes meet the target mass-intensity criteria. A sample AUTOTUNE report is included on the following page.

Hexane is injected prior to the running of a sample set to insure the system is free from contaminants or interfering peaks. The Relative Standard Deviation (RSD) between a calibration standard and a performance standard should be within 20%.

Sample injections and system maintenance are recorded in the appropriate laboratory logbooks located near the instrument.

Instrumental Parameters

The GC oven temperature program is given in Table II. Other significant gas chromatographic parameters are:

Carrier gas:	helium (99.999 %; Liquid Carbonic, Chicago)
Injector:	Temp: 285°C
	Pulsed Splitless, 25.0 psi
	Constant Flow, 1.5 mL/min
Injection volume:	1 µL
Transfer line:	300°C

The mass spectrometer is operated in the electron ionization (EI) mode with ion source and quadrapole temperatures of 230ºC and 106ºC respectively.

Table II: GC oven temperature program for PAH analysis

Initial Temperature: 70ºC		
Initial Time: 3.00 min		
Rate (ºC/min)	**Final Temperature (ºC)**	**Final Hold Time (min)**
30.0	280	6.00
30.0	300	10.0
Total Run Time: 26.67 min		

Sample Analysis

The extracted samples, lab blanks and matrix spikes are stored in 4-mL amber vials at -20ºC until they are ready for analysis. They contain approximately 1 mL of solvent (hexane) and were previously spiked with 50 µL of the internal standard solution (see Table III).

Table III Internal standard solution.

Compound	Concentration (ng/µL)
d10-Anthracene	4.00
d12-Benz*[a]*anthracene	4.00
d12-Perylene	4.00

Standards and samples are brought to room temperature before they are injected. After the hexane blank is injected, a calibration standard (see Table IV) is injected followed by the samples. All injections are performed using a 6890 auto-injector with 1-µL volumes.

The mass spectrometer is turned on after a 6.5 minute solvent delay. Data is acquired in selected ion mode.   Windows and ion ranges are given in Table V.

Table IV. Calibration standard.

Retention Order	Compound	Concentration (ng/uL)
1	d10-Anthracene*	0.20
2	Acenaphthylene	0.20
3	Acenaphthene	0.20
4	Fluorene	0.20
5	d-10 Phenanthrene **	0.20
6	Phenanthrene	0.20
7	Anthracene	0.20
8	Fluoranthene	0.20
9	Pyrene	0.20
10	Retene	0.20
11	d12-Benzo[a]anthracene*	0.20
12	Benz[a]anthracene	0.20
13	Chrysene	0.20
14	d12-Perylene*	0.20
15	Benzo[b]fluoranthene	0.20
16	Benzo[k]fluoranthene	0.20
17	Benzo[e]pyrene	0.20
18	Benzo[a]pyrene	0.20
19	Indeno[1,2,3,cd]pyrene	0.20
20	Dibenz[a,h]anthracene	0.20
21	Benzo[g,h,I]perylene	0.20
22	Coronene	0.20

*internal standard
**surrogate standard

Table V. SIM windows for analyte detection.

SIM Window	Start Time (min)	Sim Mass (m/z)
1	6.50	76, 83, 151, 152, 153, 154, 165, 166
2	8.50	101, 202, 176, 178, 188, 204, 212, 219, 234
3	10.70	114, 126, 252, 228, 240, 264
4	15.00	138, 139, 150, 276, 278, 279, 300

Data Reduction and Analyte Quantitation

Data is collected and stored within the system's HP Chemstation (Windows NT). Mass chromatograms are generated, and their peaks are integrated with the accompanying software. Hardcopys of quantitation reports and total ion chromatograms are generated. Data files and quantitation results are stored electronically.

Quantitation is performed by Enviroquant using the method of internal standards. Relative response factors (RRFs) for each analyte are determined from the calibration standard's peak areas using equation 1,

$$\mathrm{RRF_{std}} = \left(\frac{\mathrm{mass_a}}{\mathrm{area_a}}\right)_{std} \div \left(\frac{\mathrm{mass_{istd}}}{\mathrm{area_{istd}}}\right)_{std} \qquad (1)$$

where $mass_a$ is the analyte's known mass in the injected amount of calibration standard, $area_a$ is the analyte's peak area, $mass_{istd}$ is the known mass of the appropriate internal standard, and $area_{istd}$ is that internal standard's peak area. With reference to Table I, the response factors for compounds 2-10, 12-13, and 15-22 are calculated relative to the internal standards d10-anthracene, d12-benz*[a]*anthracene, and d12-perylene respectively.

An analyte's mass in a sample ($mass_a$) is calculated from the RRF_{std} above and the internal standard response in the sample by the following equation:

$$\left(\mathrm{mass_a}\right)_{sample} = \left(\mathrm{area_a}\right)_{sample} \times \mathrm{RRF_{std}} \times \left(\frac{\mathrm{mass_{istd}}}{\mathrm{area_{istd}}}\right)_{sample} \qquad (2)$$

where $area_a$ is the analyte's peak area in the sample, $mass_{istd}$ is the mass of internal standard spiked into the sample, and $area_{istd}$ is the internal standard's peak area in the sample. The analyte concentrations are tabulated by Enviroquant and transferred to an Excel spreadsheet.

Quality Assurance

Each daily analytical batch includes at least one calibration standard, one performance standard, one instrument blank, one procedure blank, and one matrix spike. Acceptance criteria are summarized on the attached table. Refer to the IADN Quality Assurance Project Plan (QAPjP) for more details.

Instrumental Analysis and Quantitation of

Polycyclic Aromatic Hydrocarbons

prepared by

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