Application Note: 341

# Low-Level PAH Analysis using the Finnigan Surveyor HPLC System with PDA Detection

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**Key Words**

- Finnigan™ Surveyor™ HPLC
- Environmental Application
- PAHs
- PDA Detection

## Overview

Polycyclic Aromatic Hydrocarbons (PAHs) occur naturally in fossil fuels and are a by-product of combustion practices involved in incineration and power generation. PAHs are classified as carcinogens and are closely monitored in the environment. Particularly in drinking and waste water, furnace emissions, soil, and hazardous waste.

This application of PAH resolution and quantitation is illustrated in this document using the Finnigan Surveyor HPLC System with a PDA detector. HPLC analysis coupled with PDA detection offers the ability to achieve detection limits that cannot be achieved by other analytical methods, including mass spectrometry.

## Introduction

Environmental testing labs are having to comply with increasingly lower detection limits for PAHs as municipal, industrial, and military entities are faced with ever more stringent waste and remediation discharge requirements. Environmental and municipal labs throughout the world have a need for a reliable HPLC method for separation and quantitation of PAHs.

This application uses EPA method 8310 which provides high performance liquid chromatographic conditions for ppb level detection of 16 different PAH molecules. However, a PAH chromatogram may incur interference from many unknown compounds that are in the waste samples used for PAH extraction. This "matrix effect" can severally limit PAH identification unless the compounds can be sufficiently resolved from each other. PAH resolution and quantitation works well as a stand-alone HPLC application using a PDA detector, which can be run in a manner that supports a production-like atmosphere that exists in many environmental labs. In addition, a PDA detector is much more sensitive than a UV/Vis detector used by many labs for this method.

## Method

EPA method 8310 is used to determine the concentration of PAHs in ground water and wastes. It is relatively close to EPA method 610, (for industrial and municipal wastewater) and EPA method 550 (for drinking water). Method 8310 provides high performance liquid chromatographic conditions for ppb level detection of 16 different PAH molecules. Some PAH molecules on the list co-elute, especially Acenapthene and Fluorene. This method was designed to provide as close to 100% resolution between peaks as possible, in a time frame that is suitable for production lab work and to provide the sensitivity needed to meet most laboratory detection limits.

## System Parameters

| | | |
|---|---|---|
| Flow Rate: | 2mL/min | |
| Mobile Phase: | A 99:1 (ACN:$H_2O$) | |
| | B 99:1 ($H_2O$:ACN) | |
| Gradient | A | B |
| Initial | 50 | 50 |
| 5.0 | 50 | 50 |
| 25 | 100 | 0 |
| 27 | 50 | 50 |
| 30 | 50 | 50 |
| Column Temp: | 30 °C | |
| Tray Temp: | 25 °C | |
| Syringe Flush Solvent: | 99:1 (ACN:$H_2O$) | |
| Injection Volume: | 1 uL | |
| Column: | Hypersil Green PAH 5 um, 100 × 4.6 mm | |
| Wavelength: | 254 nm, scan 200–400 | |
| Instruments: | Finnigan Surveyor LC Pump, Autosampler and PDA Detector | |

## Results and Discussion

All of the PAHs can be detected in the UV range of 190 to 360 nm. Even though the greatest response is around 190 nm, 254 nm gives more than adequate response with the least amount of interference from other molecules that may occur at the lower wavelengths.

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The Limit of Detection (LOD) established by this application, was defined as a peak whose signal to noise ratio is at least 3:1. A pre-mixed solution of all sixteen analytes was diluted in successive concentrations and analyzed until the desired peak characteristics were observed. Table 1 indicates the LOD in nanograms on-column for the analytes.

| Analyte | LOD (on-column) |
|---|---|
| Napthalene | 1.25 ng |
| Acenapthylene | 1.25 ng |
| Acenaphthene | 2.5 ng |
| Fluorene | 0.25 ng |
| Phenanthrene | 0.10 ng |
| Anthracene | 0.05 ng |
| Fluoranthene | 0.25 ng |
| Pyrene | 0.25 ng |
| Benzo(a)anthracene | 0.125 ng |
| Chrysene | 0.125 ng |
| Benzo(b)fluoranthene | 0.10 ng |
| Benzo(k)fluoranthene | 0.10 ng |
| Benzo(a)pyrene | 0.25 ng |
| Dibenzo(a,h)anthracene | 1 ng |
| Benzo(ghi)perylene | 0.4 ng |
| Indeno(1,2,3-cd)pyrene | 0.125 ng |

Table 1: Limit of detection values

The LODs in Table 1 support the reporting limits as published by many environmental labs. By back calculating from the LOD, the reporting limits match those of many environmental labs. The EPA published Method Detection Limits (MDL) for Method 8310 is provided for comparison. See Table 2.

| Analyte | EPA Method Detection Limit (µg/L) | Environmental Lab "X" (µg/L) | LOD Derived Reporting Limits (µg/L) |
|---|---|---|---|
| Napthalene | 1.8 | 0.5 | 0.25 |
| Acenapthylene | 2.3 | 1.0 | 0.25 |
| Acenaphthene | 1.8 | 0.5 | 0.5 |
| Fluorene | 0.21 | 0.1 | 0.05 |
| Phenanthrene | 0.64 | 0.05 | 0.02 |
| Anthracene | 0.66 | 0.05 | 0.01 |
| Fluoranthene | 0.21 | 0.1 | 0.05 |
| Pyrene | 0.27 | 0.05 | 0.05 |
| Benzo(a)anthracene | 0.013 | 0.05 | 0.025 |
| Chrysene | 0.15 | 0.05 | 0.025 |
| Benzo(b)fluoranthene | 0.018 | 0.1 | 0.02 |
| Benzo(k)fluoranthene | 0.017 | 0.05 | 0.02 |
| Benzo(a)pyrene | 0.023 | 0.05 | 0.05 |
| Dibenzo(a,h)anthracene | 0.030 | 0.2 | 0.2 |
| Benzo(ghi)perylene | 0.076 | 0.1 | 0.08 |
| Indeno(1,2,3-cd)pyrene | 0.043 | 0.05 | 0.025 |

Table 2: Reporting limits

## Conclusion

In Figure 1, all sixteen analytes for method 8310 are fully resolved from each other in less than 25 minutes. A shorter run time can be accomplished, but ground water samples typically contain other interfering components that could co-elute with PAHs. With almost 100% resolution between peaks, peak identification is easier since only the interference from the unknown compounds (if present) need to be addressed, instead of the neighboring PAH. This run time works well in production-type environments with high sample throughput. The fine line between productivity and resolution is a constant compromise in most labs, and a 25 minute run time with 100% resolution is quite achievable. This run time could be even shorter if matrix effects are at a minimum. Drinking water samples are typically much cleaner than ground water, and may have a shorter run time.

Many labs use a UV/Vis detector either by itself or coupled with a fluorescence detector. The UV/Vis is used for the analysis of the first four compounds on the list, and the fluorescence detector is used for the remainder. Although a fluorescence detector is more sensitive than a PDA detector, a PDA is more sensitive than a UV/Vis, and can help labs meet the reporting limits imposed by various regulatory bodies.

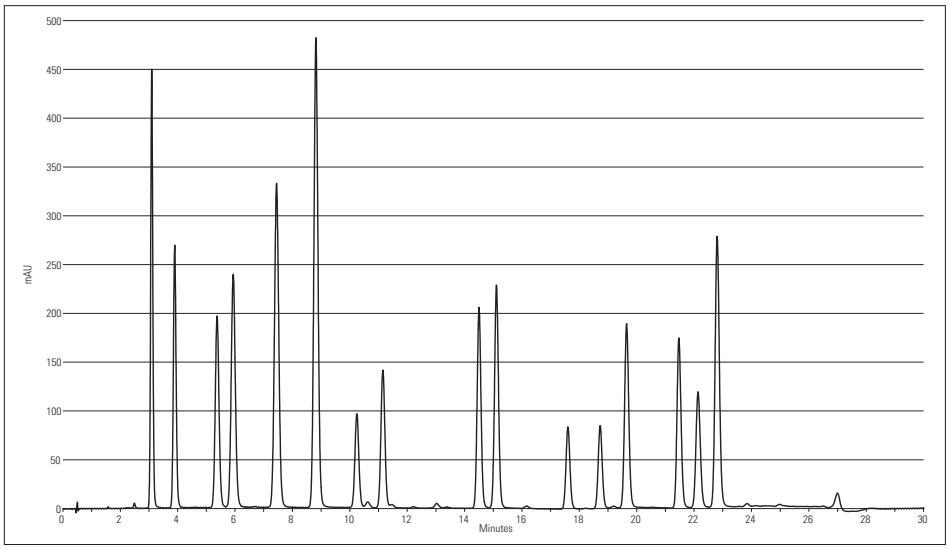


Figure 1: PAH chromatogram

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