

951061

NOTES

ENVIRONMENTAL

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Enhanced Detection of PAHs

951061-01

Polyaromatic hydrocarbons (PAHs) are among the most frequently monitored environmental contaminants. Standard and official methods for the analysis of PAHs are found in compendia for air, waste water, drinking water, solid waste, and food analysis'. Many of these methods specify HPLC, usually with UV and fluorescence detection, as the recommended analytical procedure. Continuing developments in HPLC detector capabilities serve a dual purpose: to increase sensitivity and achieve more reliable identification, especially considering the complex nature of many samples where PAH contamination is a concern.

PHOTODIODE ARRAY DETECTION FOR PAH ANALYSIS

More essential information about the constituents of a sample can be obtained by using a photodiode array (PDA) detector rather than a single wavelength UV detector. By simultaneously monitoring absorbance vs time over a full range of specified wavelengths, the PDA detector provides spectral information about each peak. Recent advances in optical design now enable the analyst to achieve detection levels with PDA which were previously achieved only with fixed or variable wavelength UV/VIS detectors. New algorithms have been developed to process the spectral data into peak purity and peak identity information with unprecedented accuracy and reliability.

The only detector that offers the versatility of PDA detection without

compromising spectral resolution, sensitivity or linearity is Waters™ 996 Photodiode Array Detector. This powerful detector automatically detects UV/VIS absorbing compounds anywhere within the 190-800 nm range at a sensitivity of 1.5×10^{-5} AU noise. With its true optical resolution of 1.2 nm and linearity up to 2.0 AU, the 996 PDA Detector provides superior spectral resolution and quantitation. As part of an HPLC system, the 996 PDA Detector can be controlled by a single keyboard with Waters Millennium® Chromatography

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A Comparison of 951061-02 Capillary Ion Analysis to Wet Chemical Methods and Ion Chromatography for Environmental Water Analysis

CAPILLARY ION ANALYSIS—AN EMERGING TECHNIQUE FOR FAST AND HIGH

RESOLUTION ION ANALYSES

Capillary Ion Analysis (CIA) is a separation mode of capillary electrophoresis (CE) pioneered by Waters™ beginning in 1990. It is finding more and more applications within the realm of environmental analysis. CIA is a technique for separating ionic compounds that is unique compared with other techniques for measuring ions. It rapidly measures low molecular weight inorganic and organic anions and cations in a variety of environmental matrices^{1,2}.

HOW CIA WORKS

Unlike traditional ion chromatography where ions are separated based upon interactions with stationary phases in a packed column, CIA separates ions according to their mobility as they travel through a small diameter capillary filled with an electrolyte solution^{3,7}. As a voltage is applied across the capillary the ions in the capillary begin to move toward the detector. The more conductive ions migrate through the

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Manager software. In addition to controlling the 996 detector and other components of the HPLC system, the Millennium Chromatography Manager acquires the data and applies patented algorithms to assess the purity of the peak and performs rigorous library matches for peak identification².

Waters 996 PDA Detector achieves high performance in a variety of situations³. A commercial testing laboratory adds value for its customers by spectrally confirming the identity of regulated PAHs before reporting its HPLC results. A researcher studying the relationship of lung cancer and PAHs caused by combustion can distinguish compounds with virtually identical spectra by acquiring them at the 1.2 nm resolution provided only by the 996 PDA Detector. Other uses include screening for PCB congeners in marine biota⁴ and nitroaromatic and nitramine explosives in groundwater⁵.

Table 1: Detection Modes

Detection mode

Concentration A: UV @ 254 nm

Concentration B: Fluorescence with time-programmed wavelength changes

Instrument method

Autosampler: 717plus

Pump: 616 Solvent Delivery System

Detectors:

996 PDA: start-200 nm, end-415 nm

Scan Rate: 1.0 spectra/sec.

Resolution: 1.2 nm

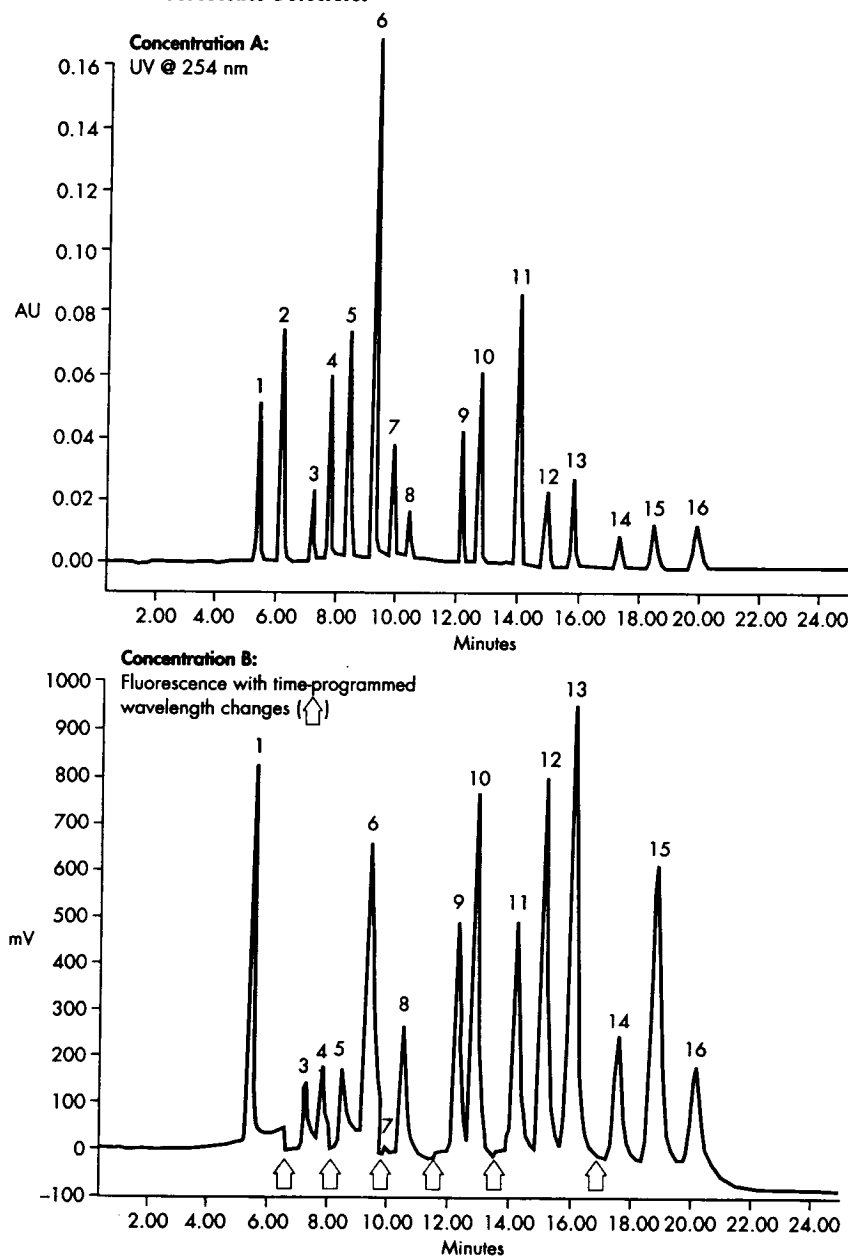
474 Fluorescence: Acquisition

Rate, 1 pt/sec.

Fluorescence Program Table

Step	Time	Ex	Em	Gain
Initial		224	330	1
1	6.5	270	323	—
2	6.5	—	—	1
3	6.9	—	—	1
4	8.0	260	380	—
5	8.2	—	—	10
6	9.7	270	400	—
7	11.5	270	385	—
8	13.5	280	410	—
9	16.8	270	466	—
10	16.9	—	—	100
11	25.0	Program end		

Figure 1: Chromatogram of common environmental PAHs detected with both Waters 996 PDA and 474 Fluorescence Detectors.



Peak ID's	Concentration A	Concentration B
1. Naphthalene	20 ppm	2000 ppb
2. Acenaphthylene	40 ppm	4000 ppb
3. Acenaphthene	20 ppm	2000 ppb
4. Fluorene	4 ppm	400 ppb
5. Phenanthrene	2 ppm	200 ppb
6. Anthracene	2 ppm	200 ppb
7. Fluoranthene	4 ppm	400 ppb
8. Pyrene	2 ppm	200 ppb
9. Benzo(a)anthracene	2 ppm	200 ppb
10. Chrysene	2 ppm	200 ppb
11. Benzo(b)fluoranthene	4 ppm	400 ppb
12. Benzo(k)fluoranthene	2 ppm	200 ppb
13. Benzo(a)pyrene	2 ppm	200 ppb
14. Dibenzo(a,h)anthracene	4 ppm	400 ppb
15. Benzo(g,h,i)perylene	4 ppm	400 ppb
16. Indeno(1,2,3-cd)pyrene	2 ppm	200 ppb

Conditions:

Column: Supelcosil™, LC PAH, 4.6 mm x 15 cm

Eluent A: Water/methanol (35/65)

Eluent B: Acetonitrile

Pump: 616 Solvent Delivery System—Spurge 30 mL/min.

Gradient:

Time	Flow	% A	% B	Curve
Initial	1.5	100	0	—
11.0	1.5	0	100	6
18.0	1.5	100	0	11

Injection volume: 20 microliters



IMPROVEMENTS IN FLUORESCENCE DETECTION FOR PAH ANALYSIS

Advanced detector designs that offer more effective analyses of PAHs are not limited to the UV/VIS PDA instruments. Waters new 474 Scanning Fluorescence Detector features sophisticated electronics and an optical design for enhanced sensitivity. Simple programming steps let you take advantage of the advanced wavelength programming capability of the 474 detector. For complex multicomponent analysis, time-based programs can be applied to utilize each analyte's emission and excitation wavelength maxima. Table I demonstrates the fluorescence wavelength switching program used to achieve maximum response.

Figure 1 shows a chromatogram of the 16 PAH compounds, listed as priority pollutants by the U.S. EPA, detected with both Waters 996 PDA and 474 Fluorescence Detectors. Acenaphthylene is not present in the 474 detector chromatogram since it does not fluoresce and is only detected by the 996 PDA detector.

To check peak purity and determine whether a seemingly homogeneous peak contains hidden impurities, the Spectral Contrast routine is applied to

the selected peak. In Figure 2 the Spectral Contrast routine was applied to the naphthalene peak in the original chromatogram (see underlaid window). Spectral Contrast compares the spectrum at the peak apex to the spectra at every other point on the naphthalene peak to confirm peak purity. This comparison ensures confidence in the match to the library of spectra for peak identification.

The regulated target analyte benzo(a)pyrene was identified in a sample containing PAH's using the same library matching routine displayed in Figure 3.

When this sample of polyaromatic hydrocarbons (PAH) was separated, the spectrum of the peak was found to match the library spectrum of benzo(a)pyrene. Even at a 40-fold absorbance level difference, the spectral comparison is excellent.

Advanced PDA and fluorescence detection capabilities in Waters HPLC systems are providing environmental analysts with comprehensive information to meet increasingly demanding PAH detection and compound identification requirements.

On the enclosed reply card, please check box 17 to receive a reprint of the article about using PDA for PAHs

Waters HPLC systems provide environmental analysts with comprehensive information to meet increasingly demanding PAH detection and compound identification requirements.

and PCB congeners.

Check box 18 to receive a reprint of the article about detection and analysis of explosives. Check box 3 for more information on Waters 996 Photodiode Array Detector and box 6 for a Waters 474 Fluorescence Detector brochure.

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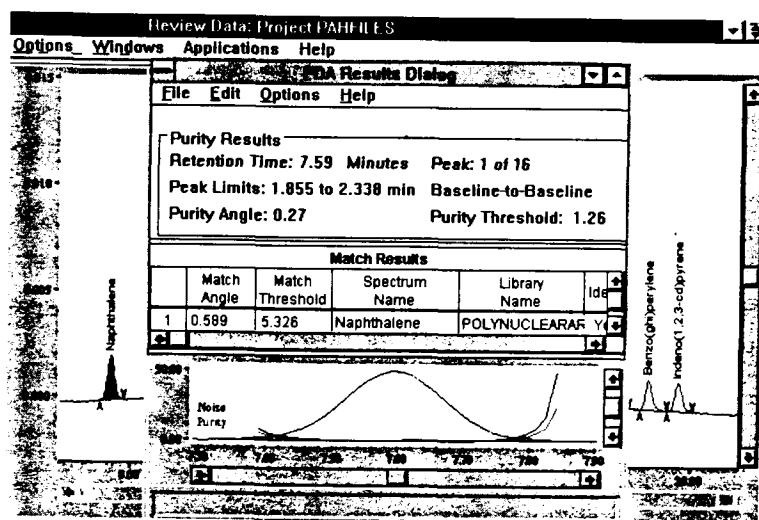


Figure 2: Millennium PDA Software's Windows environment makes it easy to check the purity of specific peaks and confirm their identity even at sub-ppm levels.

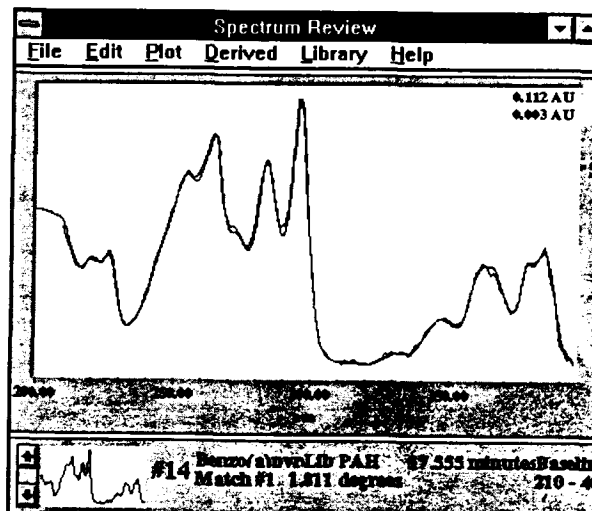


Figure 3: Even at a 40-fold absorbance level difference, peak identification is practical since spectra are normalized.