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Review

Use of full-spectrum absorbance and emission detectors in environmental analyses

John C. Fetzer* and Wilt R. Biggs

Chevron Research and Technology Company, P.O. Box 1627, Richmond, CA 94802-0627 (USA)

ABSTRACT

Several classes of environmentally important organic molecules can be both qualitatively and quantitatively analyzed through the use of HPLC with a full-spectrum detector. Specific attention will be paid to the polycyclic aromatic hydrocarbons (PAHs), since this compound class is not only important environmentally, but also provides an ideal example of the capabilities of this combination of analytical tools. The basic principles of these types of full-spectrum detectors, what makes this approach so useful in PAH analyses, and some environmental applications will be discussed.

CONTENTS

1. INTRODUCTION

High-performance liquid chromatography is commonly used in environmental analyses. The limitations of the detectors used in HPLC have, however, prevented its universal use. No detector for HPLC sensitive enough to detect all compounds, analogous to the flame-ionization detector in gas chromatography, is currently available [1]. The universal detectors, such as the refractive index, light scattering, and thermal conductivity detectors, do not have the sensitivity needed for environmental work. Detectors, such as monochromatic UV absorbance and fluorescence detectors, are very sensitive. These devices are too selective. When these detectors are used, many compounds are not

* Corresponding author.

observed because of the varying optimal wavelengths for different compounds. The recent development of full-spectrum UV absorbance and fluorescence detectors does somewhat overcome this limitation because all wavelengths are observed. Additionally, full-spectrum detectors provide information that helps identify the peaks.

Full-spectrum absorbance detectors first became commercially available in the early 1980s, and now a wide variety of different designs and features are available. These detectors are widely used, with applications in the analysis of petroleum and its refined products [2,3], pharmaceuticals [4], fullerenes [5], and many other areas, as well as in environmental areas. A general discussion of the strengths and disadvantages of full-spectrum detectors when applied to environmental problems will be made in this review. There are currently no commercially available full-spectrum fluorescence detectors, so this discussion will cover work performed on custom, in-house designed and made instruments. Some advantages and problems associated with this type of fluorescence detection will also be described.

2. FULL-SPECTRUM ABSORBANCE DETECTORS

Previously published reviews describe some of the more general features of full-spectrum absorbance detectors [1,6,7]. Full-spectrum detectors can be divided into two types, either fast-scanning or photodiode array-based optics. Photodiode array-based full-spectrum UV absorbance detectors are fundamentally different from either fast-scanning or monochromatic detectors. In the latter, a source produces broadband light which passes through a monochromator, yielding a beam of a single wavelength. This then passes through a flow cell. Only intensity at one wavelength is measured at a time. Fast-scanning detectors, as the name implies, rapidly change the wavelength passing through the flow cell. Their output is a spectrum "on the fly". In monochromatic detectors, sample absorbance at a sole wavelength is measured, yielding the familiar chromatograms.

2.1. Detector design: fast-scanning and photodiode-array detectors

The fast-scanning detectors operate using conventional optics. Design and electronics changes allow for very fast slewing rates for the diffraction gratings, acquisition times for the detector elements, storage of data, etc. The output of a fast-scanning detector can be effected by factors such as flow-rate and peak widths (and, therefore, column efficiency). The scanning rate must be sufficiently high so that changes in concentration as a peak passes through the detector flow cell do not result in distortions in individual spectra.

The second type of full-spectrum detector, the photodiode-array detector (PAD), passes the total light through the flow cell and then disperses it (usually with a diffraction grating). The dispersed light is measured by an array of photo-sensitive semiconductor material (the actual array of photodiodes). Alternatively this device is known as a diode-array detector (DAD).

Comparison of PADs to fast-scanning detectors shows they are usually less sensitive, 0.1 milliabsorbance unit (mA.U.) peak detection limit *versus* 0.02 mA.U. for fast-scanning detectors. They also have a shorter dynamic range, 0.5 mA.U. to 2 A.U. *versus* 0.1 mA.U. to 3 A.U. This is primarily due to the use of photo-multipliers in fast-scanning devices [6], which are more light-sensitive than photodiodes.

There is a spatial limit on the number of photodiodes that can fit in the sensing array. When the dispersed light is focused on the array, there is a tradeoff between spectral resolution, spectral range, and sensitivity. The balance between resolution and range results in two types of PADs, either higher-resolution instruments with an upper limit around 375 nm or lower resolution ones with a limit of 600 nm or more. For most classes of compounds, neither of the limits on resolution or range imposed by the array size are major problems. Most compounds absorb below 300 nm and have very little spectral fine structure.

For certain compound classes, however, balancing resolution and wavelength range can have limitations. Many polycyclic aromatic hydrocarbons (PAHs) of environmental concern, for example benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, and dibenzo[*b,def*]chrysene, have several bands above 375 nm [8,9]. Using an instrument with limited spectral range makes identification and quantitation difficult since only one part of the spectrum is used. Also as wavelength increases, fewer com-

pounds absorb. A limited wavelength range lowers selectivity of detection.

The absorbance spectra of most organic compounds have very few bands. These are usually broad, with little fine structure [10]. Normally a detector with higher resolution does not gather more useful information than one with lower resolution. Exceptions include differentiating unsubstituted and methyl- and other alkyl-substituted molecules, and the PAHs (see below).

2.2. Data analysis

Full-spectrum detectors, by monitoring all the wavelengths throughout a range, can also yield the traditional type of chromatogram and, additionally, either a contour map or three-dimensional (3-D) display showing all the data. An example of a 3-D chromatogram is shown in Fig. 1 [2]. It must be stated that this mode of data presentation is generally only used for esthetic impact. Much experience is needed in order to readily grasp the information in a 3-D format.

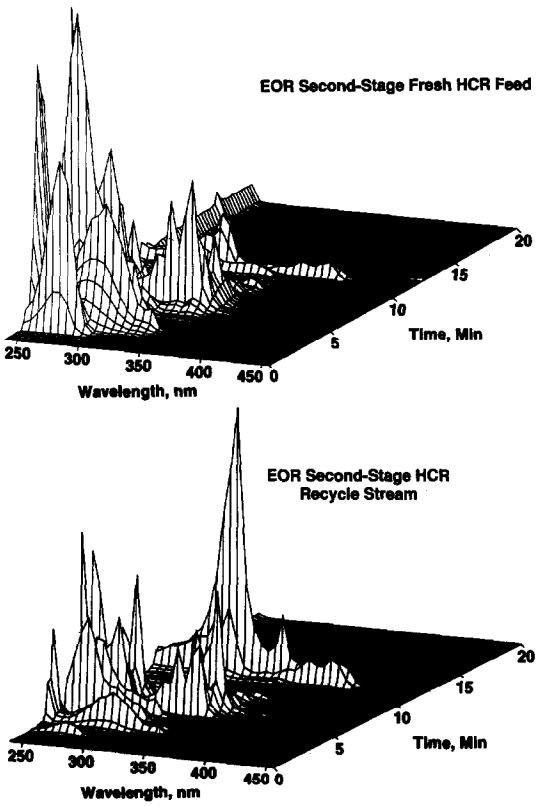

Fig. 1. Three-dimensional chromatograms of PAHs in refined petroleum products. From ref. 2.

Due to the much greater amount of data collected during a PAD run, as compared to single-wavelength detection, the amount of data storage is a key feature in PADs. If the detector is operated so that all spectra are stored at set intervals (as opposed to the mode where only certain spectra are stored, for example, at peak maxima), a run can easily take several megabytes of data storage. The chromatograms shown in Fig. 1 took over 1.5 megabytes of disk storage. PADs must have features which make storage of data and its manipulation and analysis easy.

Co-elution of peaks is not as severe a problem with PADs as with conventional detectors. If only two components co-elute, and the sampling rate of the PAD is set to be fast enough to discern a difference in retention time, spectral deconvolution techniques can be used [11–13]. With these, each component's contribution to the total series of spectra in the peak can be calculated by solving a series of algebraic equations. This allows both components to be identified and quantified. Analysis of peak data in this fashion also is used to determine purity of a peak. Deconvolution is a common method of data evaluation among PADs, since all spectral data points are collected simultaneously. There are potential problems in deconvolution of data from fast-scanning detectors. If any spectral skewing occurs due to the sequential collection of each wavelength in a spectrum, deconvolution is impossible.

Certain PADs can exhibit non-linear responses if wide bandwidths are used [14]. The non-linearity is a function of the bandpass and the shape of the analyte absorbance band, and arises because the algorithms used to reconstruct chromatograms from the original spectral data do not adequately account for the different molar absorptivity values of a compound at different wavelengths. The use of wider spectral ranges has been suggested to make the PAD a "universal" detector [15], which would greatly increase non-linearity.

The full-spectrum mode also makes peak identification possible. Commercial instruments commonly have the capability of matching unknown spectra to those of a previously collected library [16–18].

These comparisons yield "goodness of fit" or "purity of the peak" to show the reliability of the matches. As in the case of raw data collection, when building spectral libraries data storage is an important factor. For work with compound classes such as the PAHs (see below), a library of over a hundred spectra would be necessary [19].

3. FULL-SPECTRUM FLUORESCENCE DETECTORS

Full-spectrum fluorescence detectors are also divided along the lines of fast-scanning and diode array-based instruments. One major, fundamental difference exists between full-spectrum absorbance and fluorescence detectors [20–24]. There are currently no commercial instruments designed specifically to do full-spectrum fluorescence detection, so the only efforts have been with either modified fluorometers or in-house built systems. Their widespread use has, therefore, not occurred.

For fast-scanning optical systems, the low background inherent to right-angle viewing results in the usual very low detection limits common in conventional fluorescence spectrometry. For PAD-based systems, the lack of sensitivity to low light levels and the relatively high background signal require design changes. The light sources in most of these systems are lasers or special flashlamps which have extremely high intensities [22,23]. Cooled or intensified detector elements have been used [25,26].

Other work has relied on the higher concentrations inherent to peaks in micro-column HPLC, although signal averaging of spectra was also used to increase sensitivity [20,21]. These are acute problems since the intensity of fluorescence emission for most compounds is very weak. These limitations are true for most compound classes, but the PAHs, with their high quantum yields, do not usually require these steps.

One of the earliest reports of full-spectrum fluorescence detection was the use of an optical multichannel analyzer, a device similar to a television camera [27]. The optical element was a silicon-intensified target (SIT) imager.

The additional dimension of fluorescence lifetime has created an interesting variation on full-spectrum fluorescence detection [28]. This was made possible by the use of a novel modulated excitation source and PAD. More definitive identification of peaks in a complex sample and spectral separation of co-eluting analytes were obtained.

One limitation that full-spectrum fluorescence detectors have, even when they do become commercially available, that absorbance detectors do not is that emission spectra of some common PAHs change drastically with solvent [26,29]. The differences in the strengths of solvent interactions yield changes in the number of emission bands and their relative intensities. Pyrene and several other PAHs have been used as probes of solvent polarity because of this effect (less polar solvents only interact generally through Van der Waals forces and so have weak interaction with the PAHs, while more polar solvents interact by dipole–dipole forces which interact strongly with the π electrons in the aromatic rings). The spectra of benzo[*e*]pyrene and benzo[*ghi*]perylene in *n*-hexane and ethanol are shown in Fig. 2, reproduced from the GRAND spectral database [30]. These gross changes make identification in complex mixtures or when using solvent gradients difficult. Dual spectral libraries in a polar and a non-polar solvent have been suggested as solutions [30]. This would suggest a normal- and reversed-phase library when full-spectrum fluorescence is used.

There are no current comprehensive fluorescence spectral references that are aimed at compounds of environmental interest. One recent set covers the various types of spectra of PAHs, and similar hetero-atom containing molecules [9]. The PAHs are

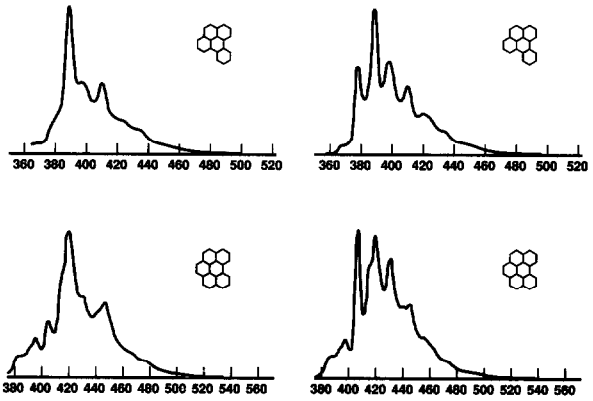

Fig. 2. Fluorescence spectra of benzo[*e*]pyrene and benzo[*ghi*]perylene. Spectral solvents: left, *n*-hexane; right, ethanol. From ref. 30. Scale in nm.

the most widely covered compound class in the literature, but spectra are widely scattered throughout many references.

As is the case with the full-spectrum absorbance detectors, data acquisition and storage are major concerns. In one system used for micro-column HPLC [21,22], only 375 spectra could be collected during a run. The narrowness of the peaks and their close elution times required hard wiring of the array output, rather than acquisition through a software-driven system, in order to rapidly collect the spectra.

4. ULTRAVIOLET–VISIBLE ABSORPTION SPECTROMETRY OF POLYCYCLIC AROMATIC HYDROCARBONS

The PAHs are very environmentally important molecules. The PAHs are produced by a wide variety of sources and are almost ubiquitous [31,32]. Several are potent carcinogens. They are also a unique class of compounds when UV–visible absorbance and fluorescence spectrometries are considered. The fluorescence excitation and UV absorbance spectra are almost always identical since they arise from the same electronic transitions [33]. The simplicity of structure yields very characteristic spectra. Each molecule is composed only of carbon and hydrogen atoms arranged in aromatic rings, and has a particular size and shape. For each aromatic ring arrangement, the numbers of bands, their locations, and their relative intensities form a unique fingerprint [34].

The most comprehensive spectral reference is still Clar's pair of books, published almost thirty years ago [8]. It contains hundreds of PAH absorbance spectra. Other collections of spectra have also been published [9,35], but many useful spectra of more recently synthesized PAHs are scattered throughout the literature [36–40]. Still, the amount of information in a PAH absorbance spectrum is sufficient enough that identification can be made using published spectra, when authentic standards are unavailable [41,42].

A set of UV absorbance spectra of several eight-ring isomers, molecular mass (M_r) 400, is shown in Figs. 3 and 4 as an example. Pairs of very structurally similar isomers were included to show the uniqueness of the absorbance spectra. The bands in these spectra are typical. The use of UV spectra, in combination with HPLC methods aimed at separating isomers, results in quantitative results with definitive identification [43,44]. This is very important for environmental PAH analyses since the degree of biological impact varies greatly among an isomer set.

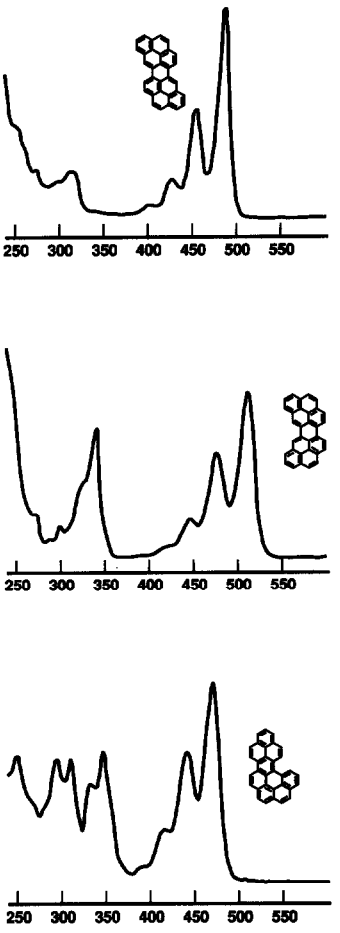

Fig. 3. UV absorbance spectra of M_r 400 PAHs. Scale in nm.

The pattern of bands in an alkyl-substituted PAH is very similar to that in the unsubstituted compound [35]. Red-shifts of a few nanometers occur for each linkage to the aromatic core of the molecule. Slightly larger shifts than expected from only two alkyl linkages are seen if the substitution is a saturated ring (typically 5–10 nm per ring). Fig. 5 shows spectra for several substituted pyrenes. The patterns of absorbance bands are extremely similar. Each spectrum has shifted incrementally. Note the

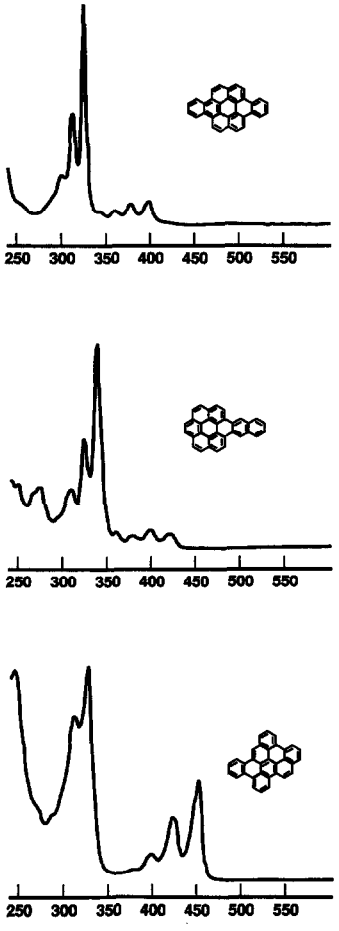

Fig. 4. UV absorbance spectra of M_r 400 PAHs. Scale in nm.

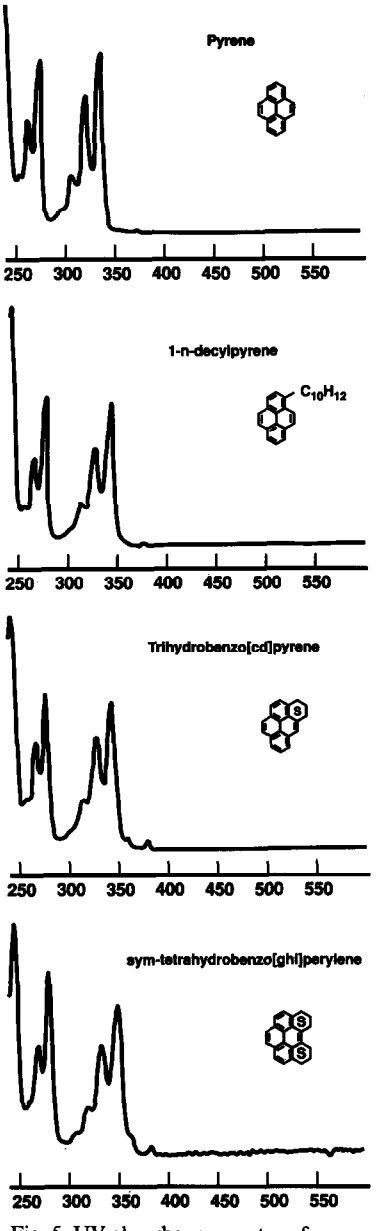

Fig. 5. UV absorbance spectra of pyrene and three alkylpyrenes. Scale in nm.

relatively large shift for the pyrene with two-ring substitution.

As can be seen in the figures, the spectral resolution necessary to perform spectral matching is only about 5 nm, much larger than that in commercial instruments. In fact, the nominal resolutions (spectral range divided by the number of diodes) of 1 nm or less commonly available in many commercial instruments are adequate. Even when the observation of small wavelength shifts are needed, such as with those in the alkyl PAHs, 1 or 2 nm resolution is sufficient.

The electronic transitions in the PAHs are π to π^* and so the molar absorptivities are usually 10^5 or greater [8,9]. This results in very high sensitivity for PAD methods. Spectra with 1 mA.U. intensity can be used to identify a peak. This corresponds to only a few nanograms of each PAH analyte per injection. The high quantum efficiencies of PAHs result in fluorescence detection limits usually a thousand

times lower than those of absorbance techniques [9].

5. ENVIRONMENTAL APPLICATIONS

The combination of HPLC with a PAD has been used to determine PAHs in carbon black and other soots [19–21], diesel exhaust [42], sediments in biomass reactors [43], and marine sediments [44]. However, the typically complex nature of samples obtained either directly from the environment (soil extracts, industrial wastewaters) or as extract from plants, fruits, or other biological systems represents a significant analytical challenge. While HPLC can provide significant resolution capabilities for these mixtures, the PAD contributes by allowing direct identification of a particular component, identification of a secondary metabolite, or provides information about peak homogeneity [45,46]. The promise [47] of enhanced analysis capabilities through the PAD usage has begun to be fulfilled. In 1987, the first review [48] of environmental analysis by HPLC and the PAD was published. The five references described therein foreshadowed the wide span of applications we are now beginning to see appear.

5.1. Analysis of herbicides and degradation products

With the exception of pharmaceutical applications, the determination of various herbicides (and algicides) and degradation products in water samples is the largest area of application at this time. Analysis for selected chlorophenoxy acid (dicamba and dinoseb) [49] and chlorotriazine-based herbicides [50] from water using various sample pretreatments are reported, as well as the linkage of HPLC–PAD with thermospray mass spectrometry for the detection [51] of atrazine, cyanazine, simazine, and other chlorotriazines. Several reports have also been published of analysis protocols for plant-protective agents and metabolites [52,53] and phenoxy-acid herbicides and bentazone (54–56].

5.2. Analysis of pesticides, insecticides, and metabolites

HPLC with a PAD has been applied to a broad variety of pesticides in drinking and surface water. Multi-residue analyses of both pesticides [57] and herbicides in drinking and surface water after solid-phase extraction [58] has been reported, as well as comparative studies between several multi-residue methods for eight pesticides common to regional agriculture (Spain) in citrus fruits [59]. Simultaneous determinations of 22 nitrogen-containing pesticides in drinking, ground, and surface water [60] and the extraction, clean-up, and determination of carbamate pesticides [61] in soil samples by HPLC–PAD are also reported.

5.3. Miscellaneous environmental applications

Searching the complex matrix of industrial wastewater for particular pollutants [62], identifying selected organic pollutants in river water [63], detecting phthalate esters in river waters [64], distinguishing various nitrophenols in rain-water [65], and detecting nitroaromatics [66] in surface water from the site of a former ammunition plant are all applications made either possible or much easier by photodiode-array detection of the related HPLC separation. Applications of environmental interest are not limited to water, plants, and soils. An example of using the PAD to confirm carbonyl structures in atmospheric chemistry studies has been reported [67], as well as the detection of more than 60 steroidal compounds in forensic analysis [68] of illegal preparations employed in cattle-breeding.

Lastly, HPLC–PAD has also found use in environmental applications of a more biological nature. A general method using HPLC–PAD for the analysis of mycotoxins and other fungal secondary metabolites has been reported [69], and the homogeneity of major fractions of aquatic fulvic acids from the Suwannee River as well as the presence of several repeated or similar structures within the fractions were demonstrated by the PAD [70].

6. CONCLUSIONS

Full-spectrum detectors give the chromatographer much more information than previously possible. By yielding both quantitative and qualitative information, their application to environmental problems is very powerful. This is especially true for analyses of PAHs, a classes of compounds with a uniquely high degree of spectral information.

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