Journal of Chromatography, 331 (1985) 77–82
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17 867

LONG PATHLENGTH ULTRAVIOLET ABSORBANCE DETECTION FOR GAS CHROMATOGRAPHY WITH CONCURRENT FLUORESCENCE MEASUREMENT

DEBRA L. VAN ENGELEN, ANTHONY K. ADAMS and LAWRENCE C. THOMAS*
Department of Chemistry, Oregon State University, Corvallis, OR 97331 (U.S.A.)
(Received May 2nd, 1985)

SUMMARY

Multimode gas-phase spectrometric measurements of gas chromatography (GC) eluates are made concurrently in a long pathlength cell. The 167-mm cell resulted in up to ten-fold improvements in limits of detection of GC eluates by UV absorbance relative to previous detectors. The concurrent measurement of UV fluorescence in the same cell provides highly selective detection for multi-ring polynuclear aromatics in addition to the selectivity of the absorbance measurement. Limits of detection for aromatic compounds range to low nanogram levels for the multimode detector.

INTRODUCTION

Although conventional UV absorbance and fluorescence detectors are routinely used with liquid chromatography, few UV spectrometric detectors have been developed for gas chromatography (GC). In previous work, we described two spectrophotometric detectors which measure gas-phase samples directly as they elute from the GC column[1,2]. Gas-phase spectrometric detectors require special considerations for interfacing the separation and detection systems. Aside from bulkiness, which is often a problem, there are conflicting requirements for detector temperatures, sample mass and cell volume.

Several couplings of GC with fluorescence detection have been developed[1–3]. For example, a UV fluorescence detector has been developed by modification of a flame photometric GC detector to make selective and sensitive measurements of polynuclear aromatic compounds (PNAs) in the gas phase[1]. For that detector, interfacing problems were resolved by adding make-up gas to the heated detector cell and by using quartz fiber optics bundles to thermally isolate optical components.

Long pathlengths can be helpful for GC spectrophotometric measurements. For example, absorbance detectors for GC have primarily utilized radiation in the IR region. These systems have the advantages that a fixed waveband may be chosen to detect a specific vibrational transition or, as in the case of Fourier transform IR, many spectra may be generated for eluates[4–6]. In order to improve sensitivities, IR

0021-9673/85/$03.30

measurements of GC effluents are sometimes made in long light pipes of 0.5 m or more in length which are coated with metals which efficiently reflect IR light. However, long light pipes may deteriorate chromatographic resolution if the volume of the detector cell is incompatible with the chromatographic band volume[7,8]. Similarly, total reflection through long capillary cells has been used with visible light to improve absorption sensitivities for measurements in solution[9].

UV absorbance measurements often exhibit much greater sensitivities than measurements made at longer wavelengths. The good sensitivity of UV detection makes it potentially useful for GC and compatible with trace analyses because the cell columes and sample sizes can be small.

UV absorbance may also be quite selective for certain classes of compounds. Virtually all compounds absorb in the vacuum UV and a detector has been designed using short-wavelength UV light which is essentially a universal detector[10]. Due to the extremely high absorptivities in this region, this detector has limits of detection comparable to a flame ionization detector. At longer wavelengths, *e.g.* 180–240 nm, UV light is selectively absorbed primarily by unsaturated substances and low-molecular-weight aromatic compounds. Gas-phase absorbance detectors which use radiation in this region of the spectrum have been described[11,12]. However, these systems transported GC effluents to the spectrometer via cumbersome heated transfer lines.

At still longer wavelengths, *e.g.* 250–300 nm, high UV absorbance of GC effluents is limited to extended π-conjugated compounds. Conveniently, many of the polycyclic aromatic compounds which absorb well at these longer wavelength also fluoresce efficiently[13]. We have previously described a dual-mode GC detector for simultaneous UV absorbance and fluorescence measurements[2]. In the system described herein, UV wavebands have been chosen which are selectively absorbed by aromatic substances with some showing strong fluorescence. The selectivity of this system, when combined with the resolving power of GC separations is advantageous for measurements of PNAs from complex environmental or biological samples. The long pathlength detector cell increases absorbance sensitivities. Considerations in the design included the low reflectivity of UV light, maintaining the cell volume compatible with the chromatographic band volumes, and striking a compromise between the advantages of a long absorbance pathlength and a large viewed volume for the fluorescence measurement.

EXPERIMENTAL

Reagents

PNAs were obtained from Aldrich (minimum guaranteed purities are indicated in Table I). Solutions were prepared using reagent grade methylene chloride. Nitrogen carrier gas was 99.5% pure.

A solution of aromatics was prepared and diluted to determine sensitivities, ranges of linearity, and limits of detection. The composition of this solution was as follows: aniline, 0.07 μg/μl; dibenzofuran, carbazole, 2-phenylindole, pyrene, 9-phenylcarbazole, 1,2-benzanthracene, benzo[*e*]pyrene and 13H-dibenz[*a,i*]carbazole, each 0.11 μg/μl.

Apparatus

Details of the optical components and instrumentation are similar to a pre-

viously described system[2]. GC separations were performed on a Tracor Instruments Model 565 gas chromatograph. Light from a deuterium source was passed via a condensing mirror through a 260-nm bandpass optical filter onto the tip of a 1 m × 3 mm Welch Allyn high-temperature quartz fiber optics bundle. Light emitted from this fiber optics bundle illuminates the eluate flowpath through the long pathlength detector cell (see Fig. 1). Fluoresced light is detected through a Suprasil quartz window perpendicular to the cell flowpath. Emitted light is filtered by 340-nm long pass and 380-nm bandpass filters prior to detection by the fluorescence photomultiplier tube (PMT) 1. Transmitted light for the absorbance signal is collected at the eluate entrance end of the cell by a 250 × 1 mm Maxlight high-temperature fused-silica fiber optics bundle. Subsequently, the light is filtered by a 240-nm bandpass filter and detected by PMT 2. The transmittance signal is converted to an absorbance signal by an electronic logarithmic amplifier.

The long UV absorbance pathlength detection cell was milled from a solid aluminium block (see Fig. 1) and was heated to 250°C. The absorbance pathlength is 167 mm and has a volume of 320 µl. Upon elution from the GC column, the sample flows into a 151-mm length of the detector cell which is lined with a 1 mm I.D. glass tube. Following this, it continues in a linear direction into a 16-mm section which is lined with a 4 mm I.D. Suprasil tube. The fluorescence measurement is made through a side-window which views this larger volume cavity. The entire absorbance pathlength is 167 mm. PTFE fittings keep the cell gas-tight and ensure alignment of the liner tubes.

Procedure

Dilutions of the PNA test solution were separated by GC. A temperature program was used with an initial temperature of 150°C for 2 min, then increased at 10°C/min to a final temperature of 250°C, held for 20 min. Nitrogen was used as the carrier gas with a flow-rate of 30 ml/min.

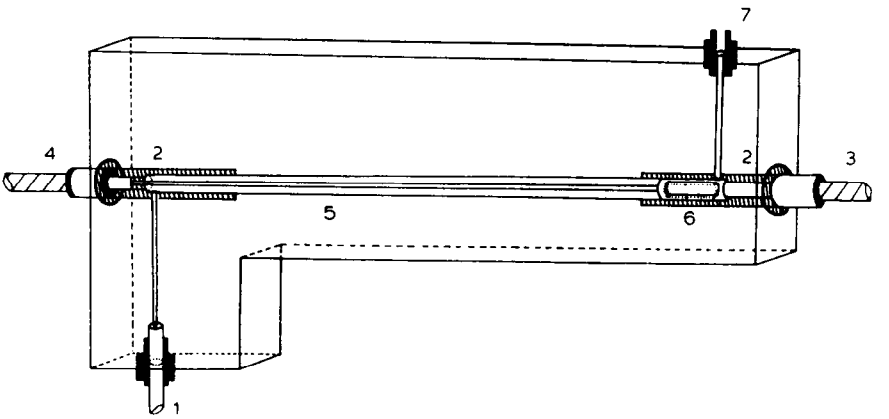

Fig. 1. Heated, flow-through detector cell with volume of 230 µl and absorbance pathlength of 167 mm: 1 = GC column; 2 = PTFE sleeves; 3 = source fiber optics bundle; 4 = absorbance fiber optics bundle; 5 = 1 mm I.D. glass tube; 6 = 4 mm I.D. Suprasil tube with Suprasil side window; 7 = exhaust.

RESULTS AND DISCUSSION

Preliminary measurements were made prior to constructing the long pathlength cell to determine the length of 1 mm I.D. glass tube which would transmit sufficient UV light for adequate absorbance measurements. As the length was increased, the peak-to-peak noise remained nearly constant. However light intensity, measured by the difference between the dark current and zero absorbance signals, diminished approximately as to the inverse square of the distance. A glass tube length of *ca.* 150 mm was found to allow sufficient UV light transmittance, and resulted in a total cell volume of 320 μl when combined with the larger volume cavity for the fluorescence measurement. The full absorbance pathlength is 10.4 times longer than a previous design[2], yielding significant improvements in sensitivities.

Fig. 2 shows chromatograms from absorbance and fluorescence measurements of aromatic eluates. Sensitivities and limits of detection were determined for the nine

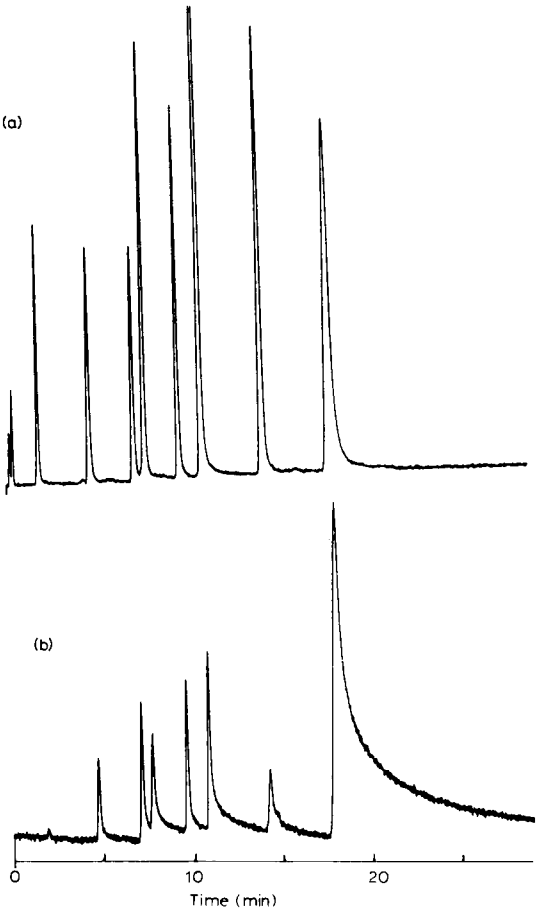

Fig. 2. Chromatograms of PNA solution produced by simultaneous (a) absorbance and (b) fluorescence detection, containing 345 ng aniline, and 550 ng each of dibenzofuran, carbazole, 2-phenylindole, pyrene, 9-phenylcarbazole, 1,2-benzanthracene, benzo[*e*]pyrene, 13H-dibenz[*a,i*]carbazole.

TABLE I

GAS PHASE LONG PATHLENGTH ABSORBANCE–FLUORESCENCE GC DETECTION OF SELECTED AROMATIC COMPOUNDS

LOD = limits of detection, S = sensitivity.

*Compound**	t_R *(min)*	*Absorbance detection*		*Fluorescence detection*	
		LOD (ng)	*S (absorbance units ng^{-1})*	*LOD (ng)*	*S (ng^{-1})***
Aniline (99)	0.18	25	$0.12 \cdot 10^{-4}$	ND***	ND***
Dibenzofuran (98)	1.60	10	$0.34 \cdot 10^{-4}$	370	$0.13 \cdot 10^{3}$
Carbazole (96)	4.47	13	$0.35 \cdot 10^{-4}$	65	$0.77 \cdot 10^{3}$
2-Phenylindole (95)	6.93	16	$0.35 \cdot 10^{-4}$	50	$0.99 \cdot 10^{3}$
Pyrene (99)	7.54	8	$0.67 \cdot 10^{-4}$	62	$0.81 \cdot 10^{3}$
9-Phenylcarbazole (97)	9.47	11	$0.57 \cdot 10^{-4}$	46	$1.1 \cdot 10^{3}$
1,2-Benzanthracene (99)	10.78	4	$1.79 \cdot 10^{-4}$	42	$1.2 \cdot 10^{3}$
Benzo[*e*]pyrene (99)	14.18	8	$0.99 \cdot 10^{-4}$	83	$0.61 \cdot 10^{3}$
13H-Dibenz[*a,i*]carbazole (98)	18.00	5	$1.66 \cdot 10^{-4}$	3	$1.60 \cdot 10^{3}$

* Values in parentheses denote the minimum guaranteed purities by Aldrich.
** Sensitivity for fluorescence calculated according to a method described in ref. 1.
*** Compound not detected at levels tested.

compounds. The differences in sensitivities and selectivities effected by the two modes provide additional qualitative information relative to single measurement modes. The results of these measurements are summarized in Table I. The range of eluted masses tested for the compounds was 13–550 ng and non-linearities were not observed within this range. The figures-of-merit for fluorescence measurements are nearly identical to those for a previous detector[2] and show the greatest sensitivity for PNAs containing three or more fused rings.

The absorbance sensitivity shows an eight-fold improvement for benzo[e]pyrene and is fourteen times better for 13H-dibenz[*a,i*]carbazole than the sensitivities for a shorter pathlength cell. The improvements for limits of detection are five- and ten-fold for benzo[*e*]pyrene and 13H-dibenz[*a,i*]carbazole, respectively. Improvements for limits of detection are less dramatic than for sensitivity due to an increase in the relative background noise level accompanying decreased total transmitted light.

Fig. 3 shows a GC separation of an acetone extract of used motor oil which illustrates advantages of this dual-mode detection system. The complex sample was dissolved in acetone, filtered, and the filtrate injected on the GC column. In order to illustrate overall sensitivities and selectivities for aromatic compounds in the sample, 400 ng of pyrene was coinjected with the sample, and an elution time of 13.0 min for each chromatogram. The absorbance detector responds to a solvent peak, and detected low-molecular-weight unsaturated and aromatic compounds in addition to larger polycyclic aromatics. The fluorescence mode characteristically detects only the larger polycyclic aromatic compounds. The simplicity and speed of GC separation along with subsequent selective detection allows for quantitation of these compounds with little sample clean-up. The information available from the relative absorbance and fluorescence intensities may enhance identification of the eluted compounds.

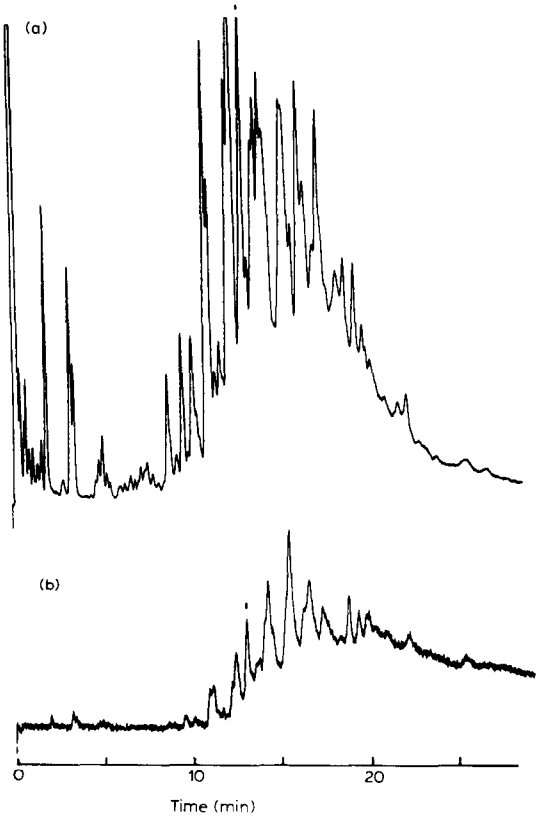

Fig. 3. Chromatograms of an acetone extract of used motor oil plus 400 ng pyrene: (a) absorbance, (b) fluorescence. GC temperature program: 100°C for 2 min, from 100 to 280°C at 10°C/min and at 280°C for 20 min.

REFERENCES

1 L. C. Thomas and A. K. Adams, *Anal. Chem.*, 54 (1982) 2597.
2 A. K. Adams, D. L. van Engelen and L. C. Thomas, *J. Chromatogr.*, 303 (1984) 341.
3 P. Froelich and E. L. Wehry, in E. L. Wehry (Editor), *Modern Fluorescence Spectroscopy*, Plenum Press, New York, 1981, p. 35.
4 M. D. Erickson, *Appl. Spectrosc. Rev.*, 15 (1979) 261.
5 P. R. Griffiths, J. A. de Haseth and L. V. Azarraga, *Anal. Chem.*, 55 (1983) 1361A.
6 K. S. Chiu, K. Biemann, K. Krishnan and S. L. Hill, *Anal. Chem.*, 56 (1984) 1610.
7 P. R. Griffiths, *Appl. Spectrosc.*, 31 (1977) 284.
8 G. N. Giss and C. L. Wilkins, *Appl. Spectrosc.*, 38 (1984) 17.
9 K. Fuwa, W. Lei and K. Fujiwara, *Anal. Chem.*, 56 (1984) 1640.
10 J. N. Driscoll, B. Towns and P. Feriolli, *Res./Develop.*, Sept. (1984) 104.
11 W. Kaye, *Anal. Chem.*, 34 (1962) 287.
12 M. Novotny, F. J. Schwende, M. J. Hartigan and J. E. Purcell, *Anal. Chem.*, 52 (1980) 736.
13 H. H. Jaffe and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962.