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CAPILLARY GAS CHROMATOGRAPHIC ANALYSIS WITH THE FAR-UV ABSORBANCE DETECTOR

J. N. DRISCOLL*, M. DUFFY and S. PAPPAS

HNU Systems Inc., 160 Charlemont St., Newton, MA 02161 (U.S.A.)

SUMMARY

A far-ultraviolet detector is described which incorporates a novel UV photodiode having a narrow response range of 40 nm compared to conventional photodiodes. Since this detector is concentration sensitive, we have used it with capillary columns where the low optimum flow-rates enhance the sensitivity of the detector. The increased sensitivity of capillary columns for far-UV detection (FUVD) is demonstrated for a series of freons and gasolines. When FUVD was compared with flame ionization detection (FID) and photoionization detection (PID) (11.7 eV) for various hydrocarbon samples, the response was found to be slightly greater for FUVD than for FID. However, the absolute sensitivity of FID was greater because of its lower noise level. Similar results were obtained when FUVD was compared with PID (11.7 eV). FUVD yields responses to a number of organic compounds such as freons, that do not give a response in FID or PID. Water, oxygen, and inorganic gases can be detected at the same time as organic compounds.

INTRODUCTION

The use of far-UV absorbance detection (FUVD) is still relatively new in gas chromatography; it has been commercially available for less than one year. In contrast, the basic concepts for all the major detection methods currently used in gas chromatography were known and applied in the late 1950s or early 1960s¹. Even photoionization detection (PID) had been described at that time, although instruments were not produced commercially until 1976².

A number of papers have described FUVD^{3,4} along with several packed-column applications. A more recent paper⁵ described the improved performance, *i.e.* increased sensitivity of this method when used in conjunction with capillary columns. Middleditch *et al.*⁶ evaluated a number of detection methods, including FUVD in the analysis of trace organics in water by direct aqueous injection. The performance of FUVD was reported to be less than satisfactory in this particular application, due to the large response to water which obscured a number of hydrocarbon peaks of interest. Although they were able to detect lower levels by use of flame ionization detection (FID), they had to re-ignite the detector after the elution of the water peak.

FUVD had no such problem. In fact, we⁷ were able to develop a method for the analysis of low ppm levels of water and oxygen with the use of this detection method. Our data indicate that FUVD is one of the most universally sensitive detection methods available for the analysis of trace levels of water.

A schematic drawing of the far-UV detector is shown in Fig. 1. The detector consists of three components; a lamp which emits UV radiation in the far-UV region (124 nm), a 1-cm path length cell with an internal volume of 40 μ l, and a novel UV photodiode which has been described in detail elsewhere⁸. As was observed previously for PID⁹, which belongs to the class of concentration-sensitive detectors. The lower flow-rate used with capillary columns, coupled with the new 40- μ l cell signifi-

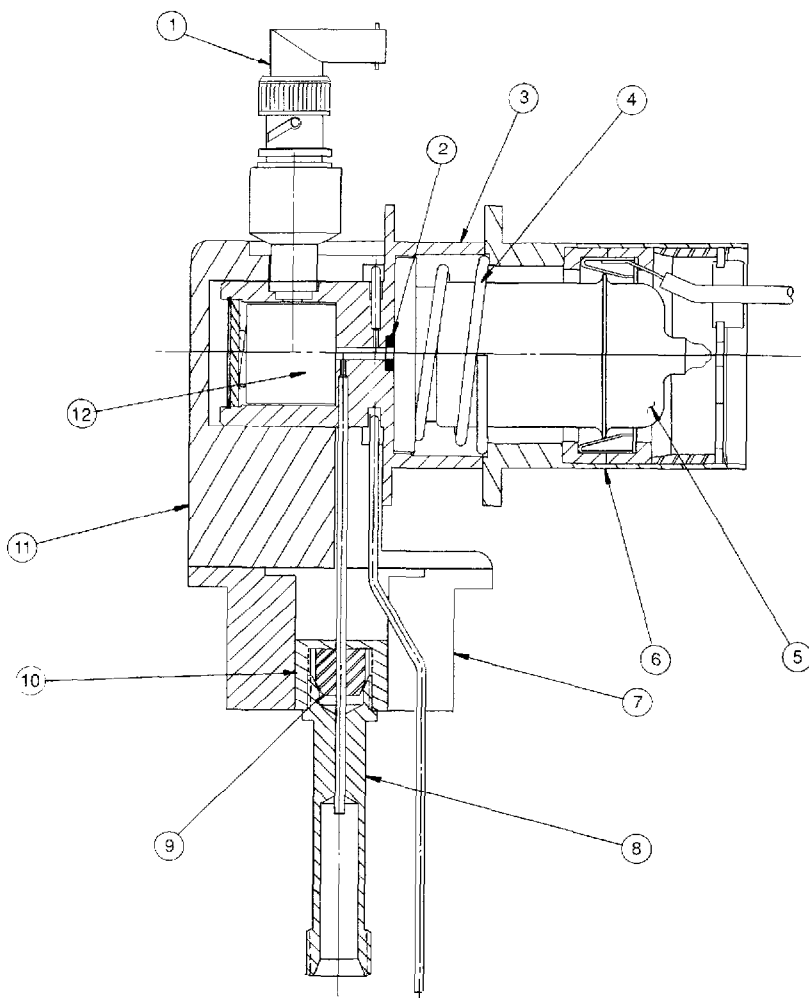


Fig. 1. Schematic drawing of the far-UV absorbance detector. 1 = BNC angle adapter, 2 = lamp seal, 3 = far-UV chamber assembly, 4 = lamp spring, 5 = lamp (10.2 eV), 6 = lamp cover assembly, 7 = FID body assembly, 8 = sample inlet (lower), 9 = graphite ferrule, 10 = sample inlet (top), 11 = UV detector base assembly, 12 = photodiode assembly.

cantly improved the sensitivity of PID. Since FUVVD belongs to the same class of methods as PID, and earlier data⁵ indicated greater sensitivity with capillary columns, it appeared logical to undertake a more detailed investigation of its use with capillary columns, including a recently developed porous layer open-tubular (PLOT) capillary column. The purpose of the present work was to investigate detection limits in capillary gas chromatography (GC) and compare FUVVD with other GC detection methods to determine some pertinent applications for this new technique.

EXPERIMENTAL

An HNU Systems (Newton, MA, U.S.A.) Model 321 gas chromatograph was equipped with an integrated Model 54 HNU far-UV detector, in-series with either an integral low dead volume photoionization detector having an 11.7-eV lamp, or with an flame ionization detector. The gas chromatograph was equipped with a packed column injector, a split/splitless injector and a HNU gas-sampling valve. Prepurified nitrogen or helium was used as the carrier gas. All chemicals were of ACS grade or its equivalent. The C₁-C₆ hydrocarbon gas standard contained 15 ppm of each compound (Scott Specialty Gases, Plumsteadville, PA, U.S.A.). The capillary columns (30 m × 0.53 mm, and 30 m × 0.32 mm with 3 and 1 μm film thickness respectively of 624 "halomatics" and a 10-m Poraplot Q column were purchased from Quadrex (New Haven, CT, U.S.A.) and Chrompack (Raritan, NJ, U.S.A.), respectively. Packed columns were: a HNU 6 ft. × 1/16 in. stainless-steel column packed with Haysep Q packing (Hayes Separations, San Antonio, TX, U.S.A.), or 6 ft. × 1/4 in. stainless-steel column packed with methyl silicone (1%) on Chromosorb WAW (John Mansville, CO, U.S.A.). A Spectra Physics (San Jose, CA, U.S.A.) Model 4270 integrator was used for plotting the chromatograms and determining the areas or peak heights in picoamperes. The typical integrator attenuation setting (1 pA amplifier, 10 mV full scale) was 16. A Tandy 3000 (IBM-compatible) computer was used with Lotus (Cambridge, MA, U.S.A.) 1-2-3 (Version 2.0) and a HNU Labpad, a statistical template which can be used within the Lotus 1-2-3 program for a number of statistical calculations.

RESULTS AND DISCUSSION

The HNU photodiode incorporated in the far-UV detector is considerably different from a conventional photodiode in that its spectral response is quite narrow, *ca.* 40 nm (magnesium fluoride cutoff to 150 nm) instead of 400 nm with the conventional photodiode¹⁰ (Fig. 2). The significance of this is that the HNU photodiode will only detect this narrow band of far-UV radiation from a UV light source which could also be emitting near-UV and visible radiation. As a result, for a conventional photodiode coated with alkali metals, the background current could be two orders of magnitude greater than the HNU photodiode if considerable UV and visible emission was present. In addition, the response to near-UV or visible radiation could reduce the dynamic range of the detector. Another characteristic of the HNU photodiode is its rugged construction (stainless steel), compared to the conventional photodiode which is constructed of glass. The only long-term maintainance of the HNU photodiode is the cleaning of the window. Since there is no vacuum inside the photodiode,

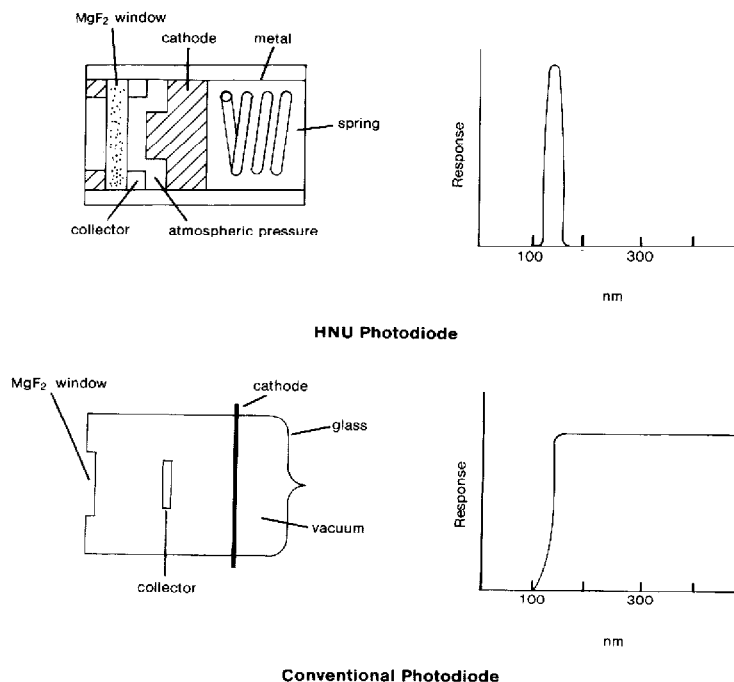


Fig. 2. Comparison of the structure and response characteristics of the HNU and a conventional photodiode.

as in a conventional photodiode, one cannot experience a catastrophic loss in performance if there is a leak.

One rather difficult application we investigated was the analysis of low levels of freons. Many of them are still used as propellants and as degreasing solvents. The ionization potentials for most of these compounds are too high to permit these species to be analyzed by PID, even with an 11.7-eV lamp. However, selected freons, such as genetron, can be analyzed with a 10.2-eV lamp. Furthermore, these fluorinated compounds produce a poor response in FID. It has been widely reported that freons are harmful to the environment and therefore it is essential to have available a sensitive method for their detection. For this application, we compared the results obtained on both packed (micropacked) columns and the recently developed Poraplot Q capillary column. The results are shown in Fig. 3. The chromatograms indicate nearly an order of magnitude improvement in detection limits when the Poraplot columns are used. The improvement in sensitivity is due mainly to a reduction in the column flow-rate (from 8 to 2.5 ml/min) and increased sharpness of the peaks from the capillary column.

We next investigated the effect of sample size on peak area and peak height with both the packed and capillary columns. The data are presented in Table I. For packed columns at 2 ml/min, both the peak height and peak area increase linearly, as expected, when the sample size is increased from 50 μ l to 4 ml, and, therefore, large samples can be chromatographed without any significant deterioration in performance. The data for the capillary column is, of course, somewhat different in that

TABLE I
 FUV D RESPONSE VS. SAMPLE SIZE

Sample: 100 ppm isobutylene.

Column and conditions	Amount injected (μ l)	Response	
		Area	Height
Micropacked Haysep Q; 20 ml/min, 100°C	50	30 813	964
	300	202 199	5 635
	405	265 958	6 584
	1000	668 846	16 983
	3000	1 724 129	40 892
	4000	2 644 977	58 272
Poraplot Q; 5 ml/min, 110°C	50	12 139	960
	300	86 804	5 025
	405	96 357	5 374
	1000	264 388	6 222
	3000	597 003	9 216
	4000	1 125 695	10 040

a linear relationship with peak height is seen only for the small sample sizes ($< 300 \mu$ l). As the sample size is increased, the sample loop is inadequately swept by the carrier gas, and the larger peak causes significant peak broadening. As the peak broadens, the change in peak area no longer shows the sharp break as seen with the peak height. Overloading of the capillary column also adds to the peak broadening, which increases the area but not the height. Thus, one trades some improvement in sensitivity for poorer chromatographic performance. In this instance, the optimum sample size for optimum capillary performance is 300μ l or less. Typical calibration curves (from 2.5 to 1000 ppm) for the three freons are very similar as shown by the following equations.

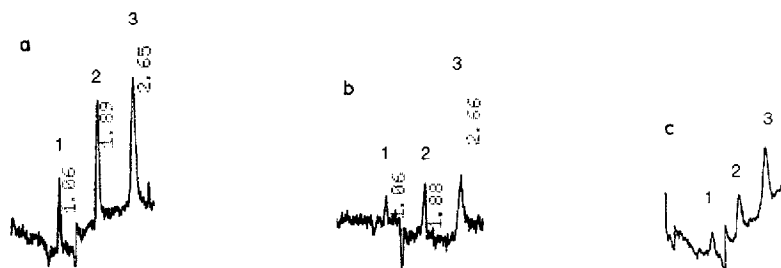


Fig. 3. Comparison of freon analysis by packed and capillary column chromatography (a) column, 10 m \times 0.32 mm I.D. Poraplot Q; carrier gas, nitrogen; flow-rate, 2.5 ml/min; sample, 100 μ l; oven temperature, 75°C; attenuation 1 \times 1; amounts injected: Freon 13 (1) 3.4 ng, Freon 22 (2) 2.8 ng, Freon 12 (3) 3.9 ng. (b) Same conditions as (a) except amounts injected: Freon 13 1 ng, Freon 22 0.9 ng, Freon 12 1.2 ng. (c) Column, 6 ft. \times 1/16 in. stainless-steel column packed with Haysep Q; carrier gas, nitrogen; flow-rate 8 ml/min; sample, 405 μ l; oven temperature, 150°C; attenuation, 1 \times 1.

Freon 13: response = $2.40 + 0.83 \log \text{concentration (ppm)}$; response factor = 0.94.

Freon 22: response = $2.65 + 0.81 \log \text{concentration (ppm)}$; response factor = 1.0.

Freon 12: response = $2.69 + 0.80 \log \text{concentration (ppm)}$; response factor = 1.0.

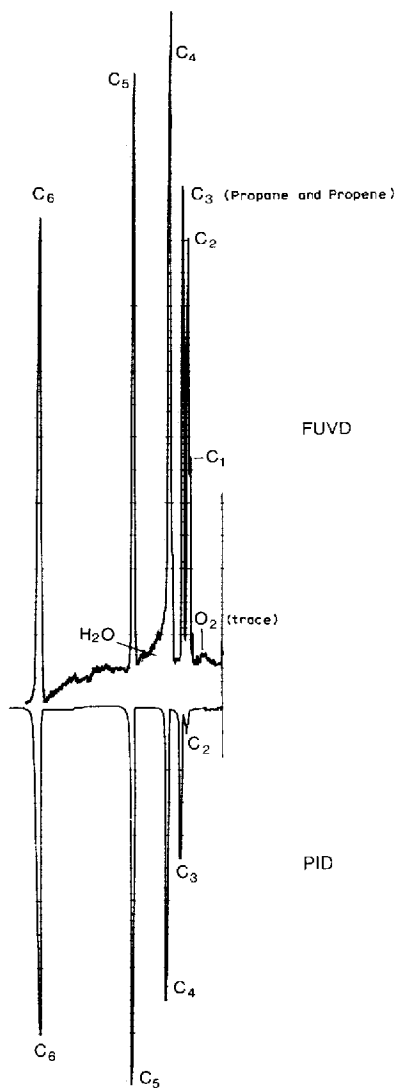


Fig. 4. FUVD responses *versus* low-dead-volume PID (11.7 eV) for C₁-C₆ hydrocarbons. (Top) FUVD attenuation 1×1 . (Bottom) PID (40 μl) with 11.7 eV lamp, attenuation 1×4 . Conditions: gas chromatograph, HNU Model 321; column, Quadrex 007-624-30(W)-1.0F; oven temperature, 35°C; detector temperature, 100°C; flow-rate, 2 ml/min; carrier gas, nitrogen; no make-up flow; sample, HNU gas sampling valve 300- μl loop.

Linearity was obtained for the three freons from 2.5 to 500 ppm. Also note the similarity in detector response for these three freons which have similar absorption coefficients in the far UV.

The response of the low-dead-volume photoionization detector (11.7 eV) and the far-UV detector are compared in Fig. 4 for a series of low-molecular-weight hydrocarbons (C_2 – C_6) at a concentration of 15 ppm each. The two detectors were operated in series with the low-dead-volume photoionization detector (40 μ l) downstream of the far-UV detector. The results are quite interesting in that PID starts with a strong response at C_3 (a small response is observed for C_2) which increases with increasing carbon number. In comparison, FUVd shows a similar response for C_1 – C_6 but provides additional information beginning with a small peak for trace oxygen in the cylinder and a response for trace water, which was found to be eluted together with the C_4 peak. The tailing of the water peak can be seen under the C_4 peak. Although these two species will be present in many samples, they are infrequently detected, since the most common gas chromatographic detectors either have poor sensitivity for them or do not respond at all. Many times, these compounds are the result of problems in chemical processes or products. Therefore, it is important to be able to detect traces of these compounds in a variety of sample matrices.

The responses in FID and FUVd were compared for an aqueous sample (0.2 μ l injected on-column) containing a hydrocarbon contaminant (light petroleum). The amplifier settings for the two detectors were similar and the integrator settings were kept constant. The three hydrocarbon peaks at 5.8, 7.8 and 8.5 min produce FUVd responses of 588 625, 341 522 and 138 268, respectively, which were 1.5 times greater than the FID responses of 345 939, 250 292, and 89 735, respectively, based on peak area. Since the noise level was lower for FID than for FUVd, the FID response could be amplified ten-fold via the integrator. Under these conditions, the sensitivity of FID is 3–5 times higher than that of FUVd. Differences in response time between the two amplifiers should be noted. The far-UV detector has a new high-impedance ultralow bias operational amplifier which produces improved specifications compared with conventional discrete field effect transistor/operational amplifier front ends. This allowed a reduction in the amplifier response time from 100–200 ms to its present 28 ms with only a small increase in noise. As a result, FUVd now has one of the fastest responses available for GC detection and is ideal for capillary chromatography. The FID amplifier has a response time of 100 ms. Clearly, we could increase the response time of the FUVd amplifier to reduce the noise further but this would compromise its superior applicability to capillary GC.

In order to demonstrate the greater sensitivity of FUVd compared to FID for capillary columns, we have chromatographed gasoline samples on packed, 0.53 and 0.32 mm I.D. capillary columns. The results are compared in Fig. 5. Note the dramatic improvement in response and resolution as one progresses from the packed to 0.32 mm I.D. capillary with FUVd. Again, this is mainly the result of the increase in response with the decreased flow-rate used for FUVd. Clearly capillary gas chromatography is the proper choice for analyses with FUVd. Further improvements in sensitivity might be expected with 0.18 mm I.D. capillary columns.

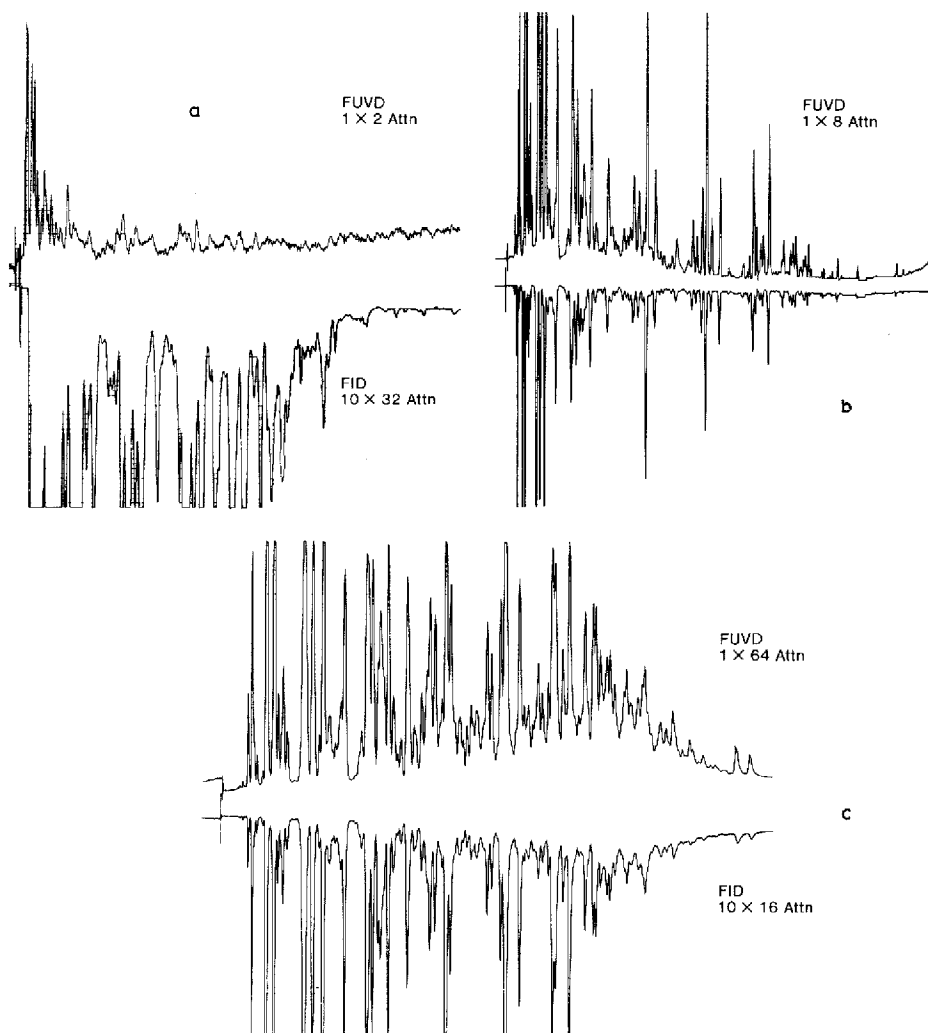


Fig. 5. Comparison of FUV and FID responses in gas chromatography of gasoline with packed and capillary columns. Conditions: (a) column, 6 ft. \times $\frac{1}{4}$ in. packed glass column packed with PermaBond methyl silicone 1% (w/w) OV-101; temperature, 30°C, hold for 5 min, then from 30 to 200°C at 10°C/min; carrier gas, helium; flow-rate, 25 ml/min; injection volume, 0.01 μ l (on-column). (b) Column, 30 m \times 0.53 mm I.D., 3.0 μ m film thickness Quadrex Halomatics 624; temperature, 30°C, hold for 1.5 min, then from 30 to 200°C at 10°C/min, hold at 200°C; split injection, 0.3 μ l; carrier gas, helium; flow-rate 19 ml/min. (c) Column, 30 m \times 0.32 mm I.D., 1.0 μ m film thickness Quadrex Halomatics 624; temperature, 30°C, hold for 1.5 min, then from 30 to 200°C at 10°C/min, hold at 200°C; split injection, 0.3 μ l; carrier gas, helium; flow-rate, 4 ml/min.

CONCLUSIONS

FUV gives responses to a number of organic compounds, such as freons, which cannot be detected by PID or FID. Water, oxygen, and other inorganic gases

can also be detected at the same time. Fused-silica capillary columns or Poraplot capillary columns improve the sensitivity of the detector, because the lower flow-rates (concentration-sensitive detector) give sharper peaks. The FUV D response to low-molecular-weight hydrocarbons is similar to the PID (11.7 eV) and FID responses. With some improvement in the signal-to-noise level in FUV D, the detection limit will also be similar. FUV D is ideal for capillary column gas chromatography of low- or intermediate-molecular-weight organic compounds.

With the recent introduction of the Poraplot columns, low-molecular weight organic, inorganic, or even fixed gases can be detected with FUV D at ng levels without experiencing the column overload conditions resulting from inadequate detector sensitivity. It is important to note that with FUV D, adequate detection limits can be attained by use of the small sample loops required for capillary columns.

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