

CHAPTER

4

FAR-UV IONIZATION (PHOTOIONIZATION) AND ABSORBANCE DETECTORS

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High-resolution chromatography has become more important during the past decade as a result of the development of fused silica capillary columns that change the average column resolution in gas chromatography (GC) from several thousand to more than 20,000 plates. The photoionization detector (PID) has emerged over the past decade as a versatile detector for a variety of organic compounds and has applications in capillary GC, high-performance liquid chromatography (HPLC), and supercritical fluid chromatography (SFC). Application of the PID to the latter techniques is possible because of the high ionization potential of many of the solvents used as the mobile phases.

The far-ultraviolet absorbance detector (FUVAD) is of a more recent vintage (about 1987) but has shown some promise for the detection of low-molecular-weight organic compounds, and low- or sub-ppm levels of inorganic materials such as water and oxygen after separation by GC. No applications of this detector are apparent in HPLC or SFC since most solvents used as mobile phases strongly absorb in the far-UV range, thus eliminating the possibility of trace level detection.

The PID and FUVAD are concentration sensitive detectors with a response that varies inversely with flow rate of the carrier gas:

$$C = 1/F$$

where C is the solute concentration and F is the carrier gas flow rate. This concentration sensitivity is particularly important for high resolution GC,

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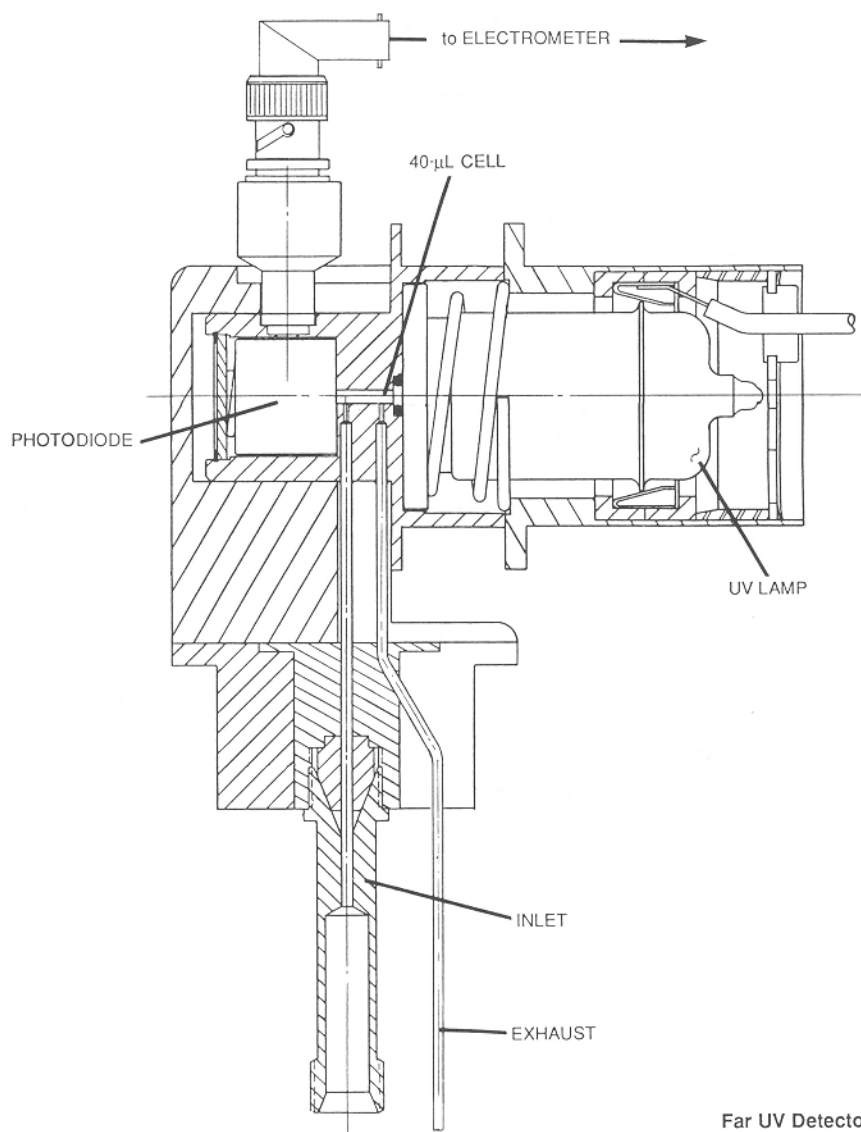


Figure 4.20. Schematic drawing of far-UV absorbance detector.

2. FAR-UV ABSORBANCE

2.1. Introduction

The far-UV absorbance detector (FUVAD) is still fairly new to GC compared with typical GC detectors. This detector has emerged as a result of the recent development of a novel UV photodiode (35) and the availability of stable UV sources more than a decade ago (7). This detector, shown in Figure 4.20, was optimized for capillary column usage and has a 40- μ L dead volume cell.

2.2. UV-Absorbing Species/Spectra

Most organic and inorganic species strongly absorb in the far-UV. Notable exceptions are the inert gases and nitrogen, which weakly absorb. Certain diatomic species (O_2 , CO, etc.) that have absorption minima in the region of the lamp energy (124 nm) will have a poor response, but low-ppm levels can still be detected. A typical far-UV absorption spectrum is shown in Figure 4.21.

2.3. Applications

The far-UV detector is new to gas chromatography and frequently is compared with the thermal conductivity detector because it will respond to any compound that absorbs in the far- or vacuum-UV. The latter name is a misnomer since a carrier gas flows through the cell and a vacuum is not

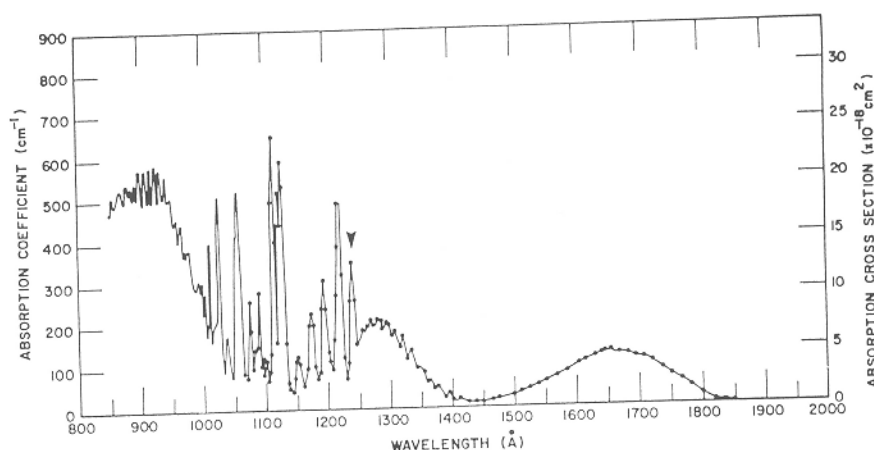


Figure 4.21. Far-UV absorption spectrum of water.

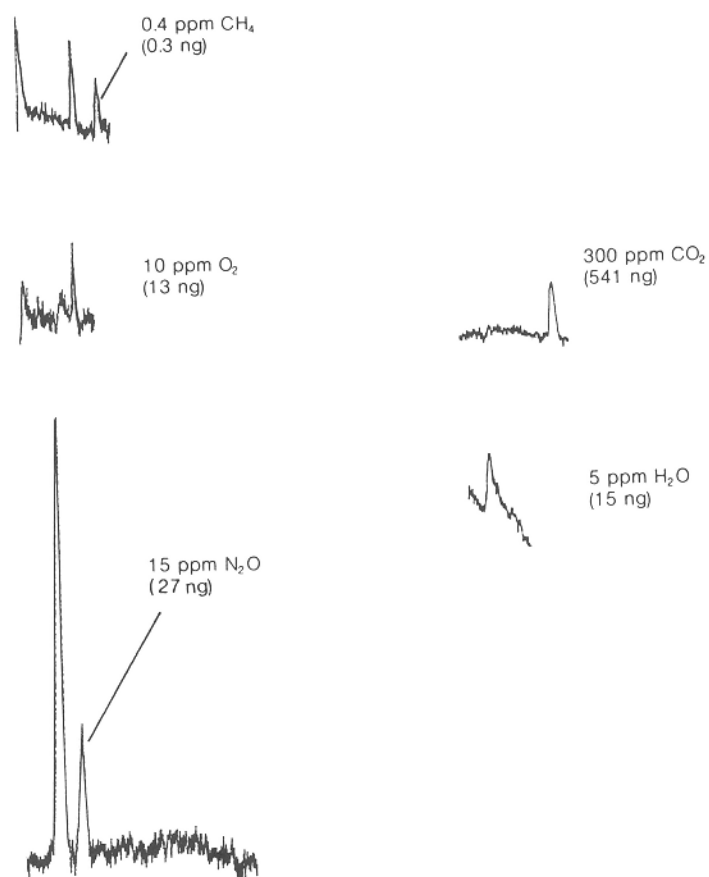


Figure 4.22. Detection of low-ppm levels of various gases by FUVAD.

needed. There are few species, notably the noble gases such as xenon, krypton, and argon, which do not absorb in this region. Thus, the detector has a response that is nearly universal, a low dead volume (40 μ L), and a fast electrometer time constant (25 ms). The primary emission from this lamp is the line at 124 nm. Although there are visible lines, the photodiode is unresponsive to any long-wavelength UV or visible emission. Only the absorption at 124 nm needs to be considered. The photodiode has been described in detail elsewhere (36, 37).

Typical chromatograms for the FUVAD are shown in Figure 4.22. The detector has an excellent response to organic compounds such as methane

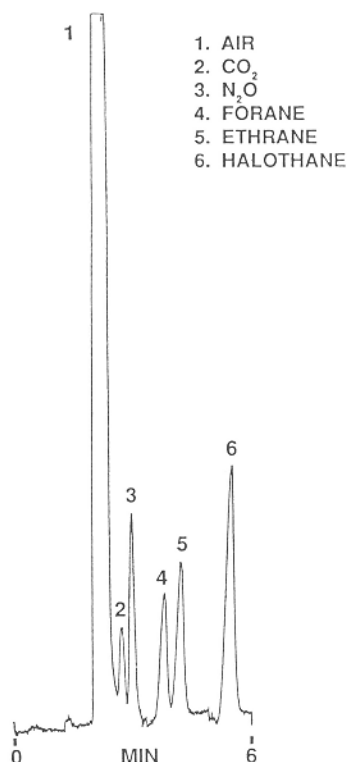


Figure 4.23. Detection of nitrous oxide and halo-
thanes in air.

that absorb strongly in the far-UV. The sub-nanogram detection limit for methane is better than that achieved with the FID. For higher-molecular-weight organic compounds, the response of the FUVAD will be within a factor of 2 or 3, whereas the response of the FID increases more rapidly so that the FID detection limits will be lower than the FUVAD for high-molecular-weight hydrocarbons. This detector will still be excellent for the analysis of hydrocarbons using capillary GC where the characteristics of the FUVAD are optimized.

The data in Figure 4.22 show that at a value of two times the signal-to-noise ratio, the detection limit for oxygen is approximately 7 ppm (9.2 ng). The FUVAD is a concentration sensitive detector with a response that is inversely proportional to the flow rate of the carrier gas ($C = 1/F$, where F is the carrier gas flow rate). Low levels (ppm) of O_2 and water in gases, pharmaceuticals, and process streams are potential applications for this detector.

Low levels of atmospheric constituents such as N_2O and CO_2 can be detected. Triatomic gases such as these have band spectra in the far-UV. If a

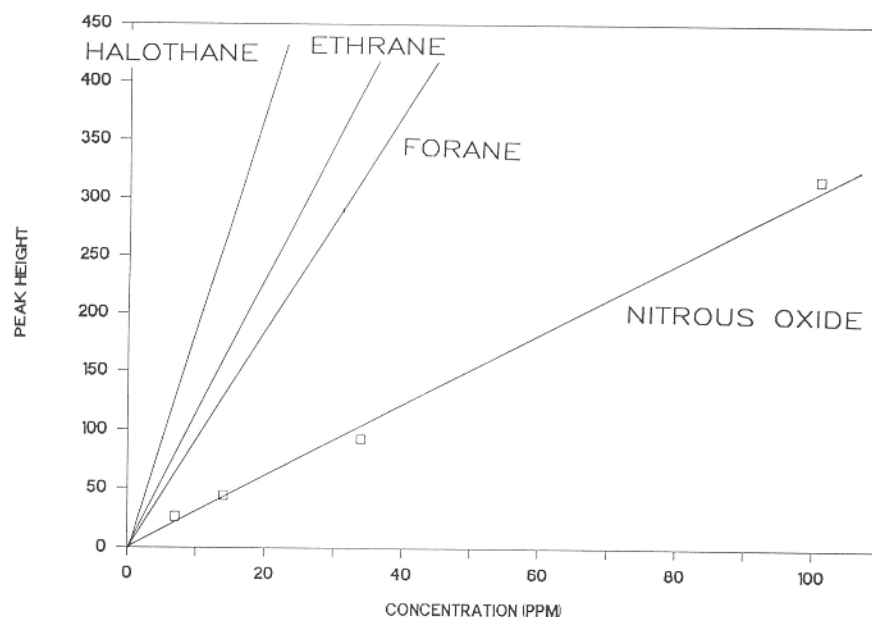


Figure 4.24. Response curves and linear range for nitrous oxide and haloethanes.

minimum occurs at 124 nm, there can be several orders of magnitude difference in the observed detection limits, as seen for CO_2 and N_2O .

As expected, the chromatography of water was considerably more difficult than that of oxygen. As the first injections of 180 ppm of water on this column did not produce any sizable peaks (36), we conditioned the column for several hours with the calibration gas (180 ppm water in nitrogen). From the accumulated data, we estimate that an order of magnitude was lost because of the need to use a carrier gas flow rate of 60 mL/min. Reproducibility was good, with a coefficient of variation (CV) of 8% for the three replications. As the data in Figure 4.22 indicate, it is still possible to detect 5 ppm of water (CV = 21%), even at a carrier flow of 60 mL/min (with the 4-mL sample loop = 121 ng).

One typical application for the FUVAD involves the monitoring of anesthetic gases in operating room atmospheres. These gases have been shown to cause problems in pregnant women and, in fact, may be carcinogenic. The threshold limit values are in the low-ppm range. The only instrument currently capable of detecting these gases is the mass spectrometer, which is quite complex, expensive, and nonportable. A typical chromatogram of low-ppm levels of anesthetic gases with far-UV detection is shown in Figure 4.23. These compounds represent the majority of anesthetic gases used at present. Note

that all are baseline separated and detected adequately at low-ppm levels by the FUVAD. Typical calibration curves for these species are shown in Figure 4.24. All were found to be linear over nearly three decades. This new detector appears to have many applications for the analysis of trace gases in a wide variety of sample matrices.

3. FUTURE DEVELOPMENTS

Future developments undoubtedly will involve improvements needed for capillary GC and environmental analysis. Both require improved sensitivity, faster response, and even improvements in selectivity. Such requirements could be met for the PID and FUVAD with the development of a low-cost, compact laser light source with sufficient energy to achieve two-photon absorption in the far-UV region.

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