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Short Communication

ULTRAVIOLET-VISIBLE DIODE-ARRAY SPECTROPHOTOMETER AS A DETECTOR FOR GAS CHROMATOGRAPHY

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Summary. An ultraviolet-visible diode-array spectrophotometer is used as a detector for gas chromatography. This detector can provide a full u.v.-visible spectrum of each compound as it elutes from the column, thus enhancing discrimination between incompletely separated components. A discrimination of ca. 1:5000 could be achieved for a mixture of toluene and benzene. The detection limit is comparable to that of the thermal conductivity detector, i.e., about 0.5 μg for the various components. The detector is particularly useful when gases other than helium are used because the sensitivity does not depend on the gas used.

Chromatographic techniques serve as powerful means of separating compounds. However, because gas and liquid chromatography are usually limited to the use of retention times for the identification of compounds, identification is often enhanced by interfacing these techniques to detection systems such as mass spectrometry or Fourier transform infrared spectrometry that provide additional qualitative information. In this study, a u.v.-visible diode-array spectrophotometer is used to aid in the identification of components. The advantage is that the diode-array device can provide an almost continuous monitoring of the whole spectrum from 200 to 800 nm. Most large polyatomic molecules have broad spectra at room temperatures; however, the range of molecules that are volatile below 300°C and are easily studied in gas chromatography generally have distinctive features which allow unambiguous identification of molecules. These features may allow not only identification but also enhanced discrimination between molecules by optical means which may not be easily achieved by gas chromatography [1—5]. The sensitivity in this technique depends very strongly on such parameters as the path length and the absorptivity (ϵ).

The sensitivity demonstrated herein may not be better than existing methods of detection, but in many cases the problem is one of rapid identification rather than of sensitivity. This would be especially true in situations involving bulk samples from chemical waste disposal sites. Moreover, in pyrolysis experiments, in which rapid sampling and identification is essential, this technique would be useful. In such problems, the ability to identify each component in a rapid and simple manner is the crucial point.

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Experimental

The experimental system is shown in Fig. 1. A Gow-Mac Model 69-1000 gas chromatograph was used. The column (0.25-in. diameter, 6 ft. long) was packed with a bonded phase of 5% SP-1200 and 1.75% bentone-34. A typical flow rate of 60 ml min^{-1} helium and a column temperature of 90°C were used. This unit contained a thermal conductivity detector which could be used to monitor the effluent independently of the optical experiments. The effluent was connected to the absorption cell. The cell (12.5-cm long and 1.5-cm internal diameter; total volume about 30 ml) was made of glass except for the windows, which were of Suprasil quartz for transmission down to 200 nm. Helium was continuously flushed through the cell at a rate of about 150 ml min^{-1}; this was done to minimize cell dead volume, because otherwise residual material from one peak would remain in the cell for an extended period thus significantly broadening the detected peak width. The flow of gas allowed peak widths almost as sharp as those obtained from the thermal conductivity detector. The cell was heated, usually at about 70°C (chromel-alumel thermocouple), with a heating tape to prevent the components from condensing onto the cell windows.

A Hewlett-Packard 8450A diode-array spectrophotometer was used. This spectrophotometer is microprocessor-controlled and can be programmed to display only a given portion of the spectrum. For most volatile aromatic compounds of interest, the 500—200 nm region is generally most useful.

For sensitivity studies, one of the pure components (e.g., benzene) was diluted with one of the other components (e.g., toluene). The detection limit was defined as the point at which the S/N ratio for the benzene peak was 2. Samples (typically, 0.2—0.5 μl) were injected from a Hamilton 701 microliter syringe. For these measurements, the diode-array spectrophotometer can be programmed to monitor the absorption at one wavelength as a function of time to obtain a chromatogram for each concentration of sample injected. The wavelength for each compound was selected and optimized experimentally by first studying the spectrum of pure components. In addition to obtaining an absorption chromatogram, the detector could be pro-

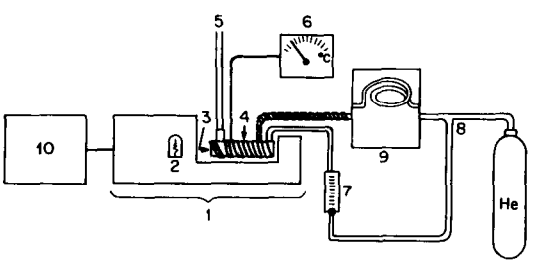

Fig. 1. Experimental set-up of the diode array/gas chromatographic detector: (1) Hewlett-Packard u.v.-visible diode-array spectrophotometer; (2) excitation lamp; (3) optical gas absorption cell; (4) heating tape; (5) gas outlet; (6) thermocouple readout; (7) regulator for helium flow to purge cell; (8) helium tank; (9) gas chromatograph; (10) printer.

grammed to obtain a full spectrum of the contents of the cell as a function of time, e.g., every 3 s. Thus, as each peak eluted from the chromatograph, a spectrum was displayed providing an aid in the identification of each component. In this manner, a three-dimensional plot of wavelength vs. time could be constructed for identification and as a means of discriminating compounds in a mixture.

Results and discussion

One point illustrated by this work is that simple volatile organic compounds can be identified by their u.v.-visible spectra. In Fig. 2 are shown the spectra of five compounds recorded for single-component samples passed through the column; only the portion of the spectra between 226 to 350 nm is displayed because these compounds do not absorb visible radiation. Although the u.v. bands are generally broad because of the Boltzmann population of states at room temperature, the spectra are still different enough that even xylene isomers can be identified. For equal amounts of the five components in a mixture, it was shown that three components are resolved completely and two (*p*- and *m*-xylene) are incompletely resolved with a resolution of 0.7. The u.v. spectra of the eluent can be used to resolve the two components. In Fig. 3, the peaks at 264, 266 and 272 nm in the spectrum taken at 383 s show clearly that it is the spectrum of *p*-xylene. The spectrum taken 24 s later shows that the relative intensities of the peaks at 264 and 266 nm have changed and the peak at 272 nm has been shifted 1 to 2 nm toward shorter wavelengths, thus indicating that the peak is *m*-xylene.

The limits of discrimination obtainable from g.c. alone vs. the combination of g.c. and diode-array detector were further compared for mixtures of

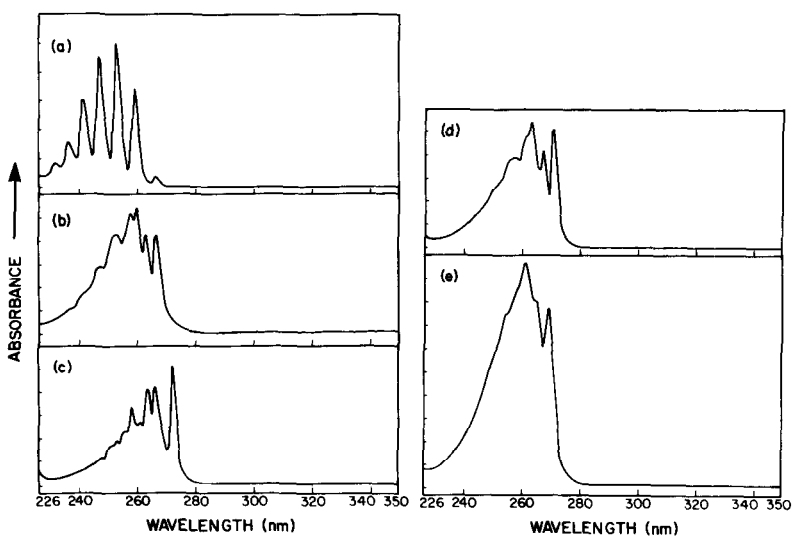

Fig. 2. Absorption spectra of five compounds taken as each eluted from the column: (a) benzene; (b) toluene; (c) *p*-xylene; (d) *m*-xylene; (e) *o*-xylene.

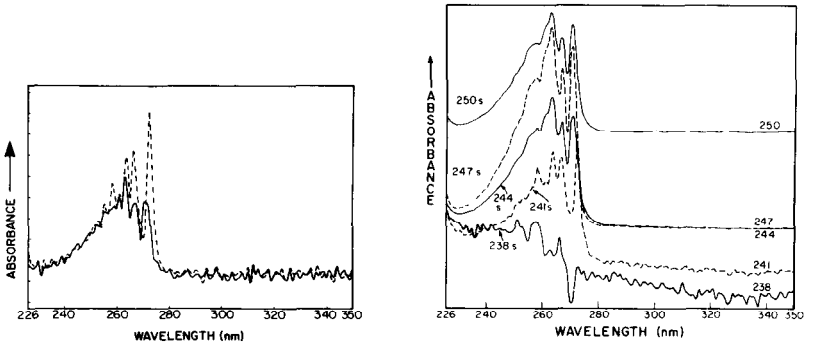

Fig. 3. Ultraviolet absorption spectra of *p*-xylene and *m*-xylene in an unresolved mixture: (- - -) spectrum taken at 383 s; (——) spectrum taken at 407 s.

Fig. 4. Ultraviolet spectra of a 1:50 mixture of *p*- and *m*-xylene eluted from the chromatograph as a function of time.

toluene in benzene and *p*-xylene in *m*-xylene. The thermal conductivity detector could discriminate toluene in a 1:600 toluene/benzene mixture in a 0.4-μl sample; however, it could not discriminate toluene in a 1:1200 mixture. In the second mixture, the injection sample was doubled to 0.8 μl so that the amount of toluene would remain the same because its detection limit in this technique was approached. With the diode-array detector (260 nm), it was possible to discriminate a 1:5000 toluene/benzene mixture but not a 1:10 000 mixture. Further, g.c. alone can barely resolve *p*- and *m*-xylene peaks even in a 1:1 mixture. The diode-array detector, however, can detect *p*-xylene in a 1:50 mixture of *p*- and *m*-xylenes (see Fig. 4). Even though *m*-xylene absorbs in the same wavelength range as *p*-xylene, the shift between the two spectra is sufficient to allow such discrimination. The thermal conductivity detector cannot discriminate the components in this mixture. Of course, there are high-resolution chromatographic techniques that can discriminate between such mixtures, but the advantage herein is the capability for rapid separation and identification of simple mixtures.

The limits of detection were evaluated for the five components of Fig. 1. Table 1 shows the detection limits for both detectors. At the optimum

TABLE 1

Limits of detection for the diode-array and thermal conductivity detectors

Compound	Limit of detection (μg)		Compound	Limit of detection (μg)	
	Diode array	Thermal cond.		Diode array	Thermal cond.
Benzene	0.53	0.53	*o*-Xylene	0.88	0.44
Toluene	0.52	0.31	*m*-Xylene	0.29	0.29
			p-Xylene	0.43	0.43

wavelength for each compound, the detection limits were comparable to the thermal conductivity detector.

Azulene was studied briefly. The molar absorptivity of the s_2 state of azulene is about 100 times that of the s_1 state of benzene and a detection limit in the low nanogram range would be predicted. However, the azulene peak is broadened even under optimum column conditions and thus the relative peak height is lower than if the peak were sharp like that of benzene. A limit of detection of about 100 ng was found for azulene when separated from benzene.

There are many problems associated with the use of different gases with thermal conductivity detectors. The diode-array detector should not be affected by the use of different carrier gases, because most do not absorb in the 200—800 nm region. With the thermal conductivity detector, there are significant differences in the limits of detection of benzene in various carrier gases; the ratio for $He:N_2:Ar:CO_2$ was found to be 1:0.05:0.04:0.04 under useful conditions for each gas. No significant change was observed in sensitivity for the optical detector as a function of carrier gas and the spectra of benzene and toluene were exactly the same when these carrier gases were used.

One problem inherent in the use of the diode-array detector is that small changes in the position of the cell may cause changes in the observed absorbances. Thus, the optical cell must be firmly mounted in position and not changed between experiments. However, in this study, the change in the absorbance of benzene in the detector was less than 25% over an average of many measurements using the same and different carrier gases.

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