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THE COMBINATION OF AN ULTRAVIOLET AND A THERMAL CONDUCTIVITY DETECTOR IN GAS CHROMATOGRAPHY

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SUMMARY

An ultraviolet (UV) detector with a liquid cell, which is usually used as a detector in liquid chromatography, was used as a selective detector in gas chromatography. Ethanol vapour was mixed with the effluent from the gas chromatograph, the gaseous mixture was led into a small condenser for the simultaneous condensation of the vapour and sample components, and then the condensed solution was led to the UV detector. The sensitivity for a substance that contains one benzene ring is nearly the same as that with a thermal conductivity detector (TCD), but for a substance such as naphthalene it is about ten times that with a TCD.

At each sample injection, two chromatograms from the UV detector and the TCD are obtained, and the structure of a sample component is indicated by comparison of the two chromatograms.

INTRODUCTION

Gas chromatography (GC) with the use of an ultraviolet (UV) detector has been reported by several workers[1–4], the detector consisting of a UV spectrometer with a specially designed gas cell[1–3]. Recently, a UV detector and a refractive index detector for liquid chromatography have been developed[5]. These detectors are provided with a liquid cell with a small volume and they are also applicable as detectors for GC if the gaseous effluent from the column is converted into a liquid.

In our previous work, the vapour of organic solvent was mixed with the GC effluent, the gaseous mixture was led into the condenser for the simultaneous condensation of the vapour and sample components and the condensed solution was led to an IR liquid cell[6,7] or a fraction collector[8].

This paper describes the combination of a UV detector and a thermal conductivity detector (TCD) in GC. The UV detector has a liquid cell and is usually used as the detector in liquid chromatography.

EXPERIMENTAL

Generation of vapour

A pump that delivered liquid at a constant flow-rate was utilized to pump the effluent liquid into a vaporizing unit for the purpose of converting it into vapour. The pump (Type PHR-1A, Tamaseiki Kogyo, Tokyo, Japan) consisted of a stainless-steel syringe (40 ml) and a screw-rod which pushed the plunger of the syringe at a rate varying from 0.5 to 0.05 mm/min, while the pumping flow-rate ranged from 280 to 28 μl/min. This pump is able to compress liquids to a pressure of 100 atm, but in this work compression to about 3 atm was used. One of the sample injection ports of the gas chromatograph was employed as a vaporizing unit, maintained at 200–250° by an electric furnace. In this work, ethanol vapour was used and in order to obtain steady flow of vapour, a resistant (2 m × 3 mm I.D.) tube packed with glass beads was connected to the port. The vapour and the column effluent were mixed in the tube of a three-way joint. The noise level of the TCD was about 7 μV owing to the pressure variations during mixing there. A schematic flow diagram is shown in Fig. 1.

Condenser and UV detector

The gaseous mixture of ethanol vapour and the GC effluent were led into a small condenser, shown in Fig. 2, which has a small capillary gas inlet. The gaseous

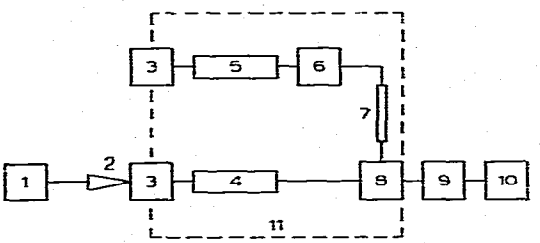

Fig. 1. Schematic flow diagram. 1 = Pump; 2 = needle; 3 = sample injection; 4 = stainless-steel tube packed with glass beads (30–60 mesh); 5 = column; 6 = TCD; 7 = stainless-steel capillary tube, length 1 m and I.D. 0.3 mm; 8 = three-way joint; 9 = small condenser; 10 = UV detector; 11 = gas chromatograph. The line between 8 and 9 was heated with a tape heater. The line between 9 and 10 was a stainless-steel tube of length 4 cm and I.D. 0.5 mm.

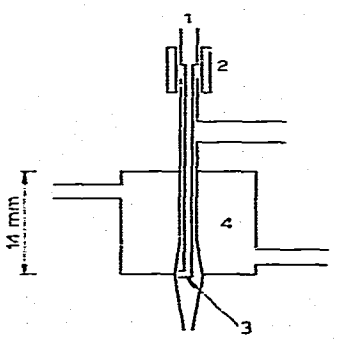

Fig. 2. Condenser. The condenser is made of glass and cooled with water. 1 = Inlet of the gaseous mixture of GC effluent and ethanol vapour; 2 = silicone tube; 3 = capillary tube, O.D. 1 mm; 4 = water jacket.

mixture was passed through the capillary gas inlet and came into contact with the cold glass walls; almost all of the condensable vapour condensed around the outlet of the capillary.

The condensed liquid was led into the liquid cell of a UV absorption detector (Laboratory Data Control, Riviera Beach, Fla., U.S.A.), which has a cell volume of 8 μl and a pass length of 10 mm and measures UV absorption at 254 nm.

In order to prevent bubbles from entering the liquid cell of the detector, the level of the surface of the condensed liquid in the lower part of the condenser was adjusted by regulating the level of the end of the tube from which the liquid fell after passing through the detector[5,6]. If the amount of ethanol that entered the vaporizing port and the flow-rate of the helium carrier gas remained constant, it was not necessary to change the level of the end of the tube. It was simple to maintain the level of the surface of the liquid in the condenser.

The head of the capillary was bent to the wall of the condenser and its head was attached to the wall, as shown in Fig. 2. The capillary tube was made in the following manner. The centre part of a glass tube, about 6 cm in length, was heated in a town gas–oxygen flame, then drawn out in the outer part of the flame, so that each end retained its original diameter while the centre part became a capillary with an O.D. of about 1 mm. One end was then held and the capillary part was heated in the flame for a short time so that the capillary part bent at a right-angle as a result of the weight of the other end. This condenser is superior to other types[5–7] because the condensing area on the wall of this condenser is smaller than that of others and no condensed liquid remains on the head of the capillary.

Gas chromatograph

A Shimazu 4BPT gas chromatograph with a TCD (Shimazu Seisakusho, Kyoto, Japan) was used. Two electric recorders were used: a Model B-361, which was furnished with 3 pens (Rigakudenki Kogyo, Tokyo, Japan) and a Model LER 91S (Yokogawa Electric Works, Tokyo, Japan), with minimum inputs at full scale of the chart of 10 mV for the former and 1 mV for the latter. Stainless-steel columns, I.D. 3 mm, were used.

Materials

All chemicals used were of extra pure grade or analytical reagent grade. The columns contained 20% (w/w) dioctyl phthalate on Chromosorb W AW (80–100 mesh) and 5% (w/w) diethylene glycol sebacate on C-22 (60–80 mesh), each column length and I.D. being 1 m and 3 mm, respectively.

RESULTS AND DISCUSSION

The sample components that have been separated in the column first pass through the TCD, and then the vapour of the sample components is condensed simultaneously with ethanol vapour to give an ethanolic solution, which passes through the UV detector. Two chromatograms are obtained for each sample injection. As there is some distance between the two detectors, the peak of a chromatogram from the UV detector (UV chromatogram) is delayed by about 8 sec from the identical peak of the chromatogram from the TCD (TCD chromatogram).

When the sample component changes from the gaseous state into the liquid state, its volume is reduced about 300 times. If the sample component in the gaseous state is condensed smoothly to give an ethanolic solution and is led into the UV detector without flow disturbance, the peak widths of the TCD and UV chromatograms at half-height should be nearly equal. Table I gives the ratios of these peak widths at half-height (RPW).

TABLE I

RATIO OF PEAK WIDTHS AT HALF-HEIGHT (RPW) OF UV AND TCD CHROMATOGRAMS

Amount of sample injected: 0.015 μl.

Flow-rate of ethanol vapour (mg/min)	*Sample*			
	Toluene		*o-Xylene*	
	UV peak width at half-height (sec)	*RPW*	*UV peak width at half-height (sec)*	*RPW*
223	10.4	1.3	15	1.1
198	10.4	1.5	17	1.2
153	10.4	1.4	18	1.3
103	13.6	1.8	23	1.6

When the flow-rate of ethanol vapour and the peak width at half-height of the UV chromatogram become larger, the RPW becomes smaller. When the peak width at half-height of the UV chromatogram is about 15 sec and the flow-rate of ethanol vapour is about 200 mg/min the RPW is 1.1–1.2 and the patterns of the TCD and UV chromatograms are nearly identical. In this experiment, the flow-rate of ethanol was set at 198 mg/min and the flow-rate of helium carrier gas at 40 ml/min.

The linearity of the UV detector response was examined. A 0.04–0.80-μl

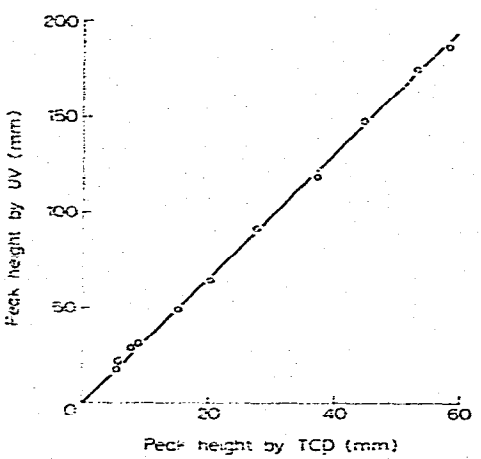

Fig. 3. Relationship between peaks heights by UV detector and TCD. Sample: 1.58% solution of toluene in ethanol; amount injected, 0.04–0.80 μl. Ranges of UV detector and TCD: 0.16 optical density unit and 10 mV, respectively. Flow-rates of ethanol vapour and helium carrier gas: 198 mg min and 40 ml min, respectively.

volume of a 1.6% (v/v) solution of toluene in ethanol was injected and the peak heights of toluene recorded by the TCD and UV detectors were measured and plotted against each other (Fig. 3). The relationship between these peak heights was linear.

The sensitivity of the UV detector depends on the absorbance of the sample. The sensitivity for a sample component that contains one benzene ring is nearly the same as that in the TCD, but for a component that contains fused benzene rings, such as naphthalene, it is about ten times that in the TCD. The minimum detectable amount of sample with this detector is 10–100 ng. A comparision of the sensitivities of the two detectors is shown in Fig. 4.

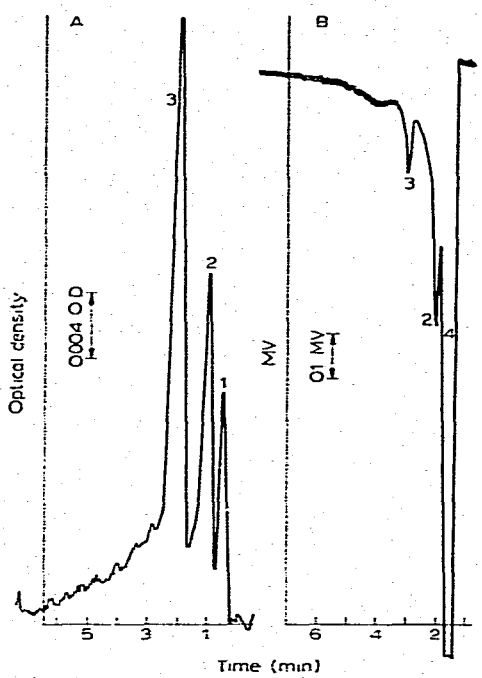

Fig. 4. Comparison of sensitivities of UV detector (A) and TCD (B). Sample: ethanolic solution containing 3% (v/v) each of (1) *o*-xylene, (2) methyl benzoate and (3) quinoline; amount injected, 0.01 μl. Peak 4 is a mixture of ethanol and *o*-xylene. Filament current of TCD: 115 mA. Column: diethylene glycol sebacate polyester; temperature, 215°.

Combination of TCD and UV detectors

Some typical examples are shown in Figs. 5–7, which indicate that the peak shapes of the UV chromatograms are nearly the same as those of the TCD chromatograms, confirming that the sample components in helium carrier gas are led smoothly into the UV detector after passing through the TCD.

The UV detector detects only those substances which have some absorbance in the UV region, in this case at 254 nm, and is therefore a selective detector. In Fig. 5, ethanol and octane are not detected by the UV detector, while in Fig. 6, two unknown substances, which may have large absorbances, are detected, although they give only small peaks in the TCD chromatogram. If the solvent used in a sample solution has

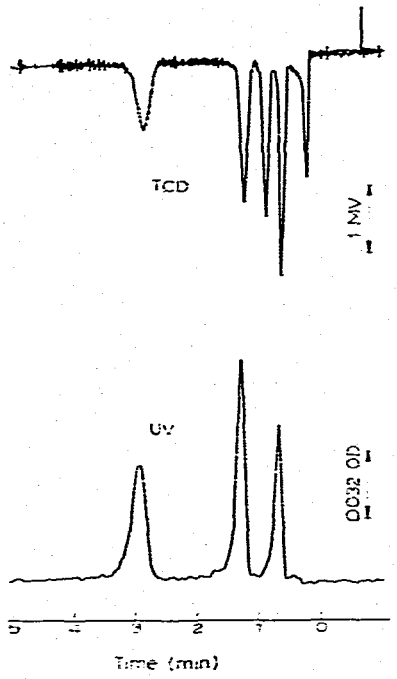

Fig. 5. Combination of the two detectors. The peaks on the TCD chromatogram are identified as ethanol, benzene, octane, toluene and *o*-xylene, from right to left. Amount injected: 0.07 μl of a mixture containing equal amounts of the five components. Column: 20% (w/w) dioctyl phthalate; temperature, 120°.

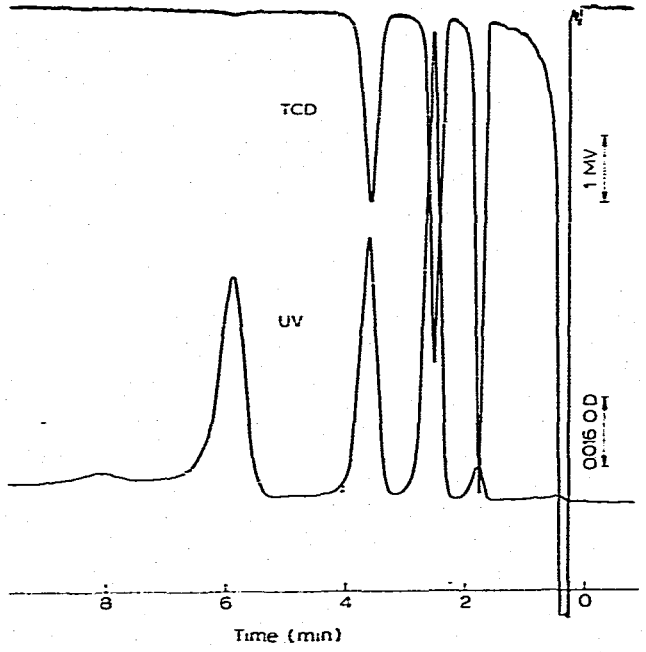

Fig. 6. Combination of the two detectors. The peaks on the UV chromatogram are methyl isobutyl ketone, with a retention time of 1.8 min, ethylbenzene, isopropylbenzene and two unknowns, from right to left. Amount injected: 0.1 μl of an ethanolic solution containing 10% (v/v) of methyl isobutyl ketone, ethylbenzene and isopropylbenzene. Column: 20% dioctyl phthalate; temperature, 120°. The peaks of the two unknowns show strong UV absorbances.

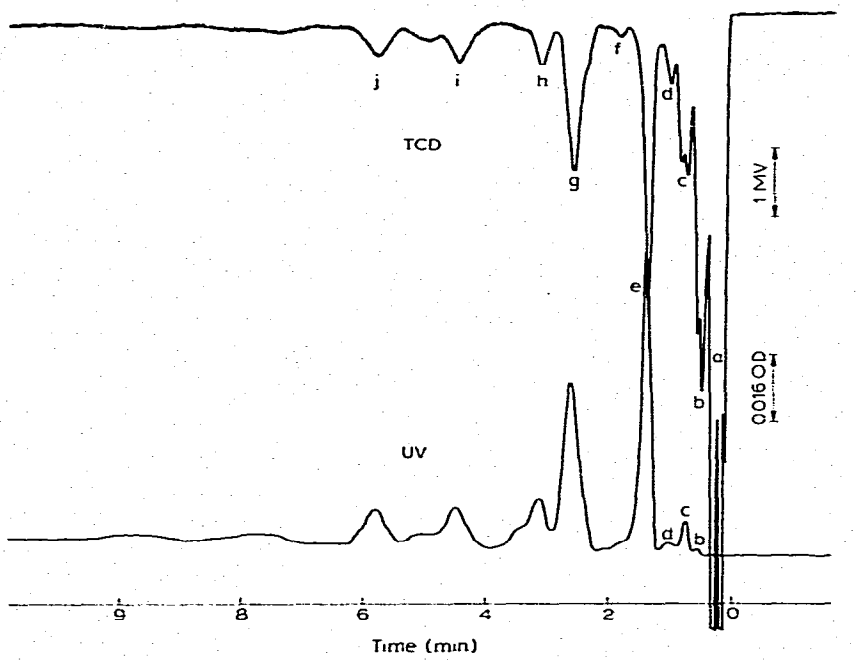

Fig. 7. Combination of the two detectors. Sample: 0.2 ml of gasoline. Column: 20% (w/w) dioctyl phthalate; temperature, 120°.

no absorbance in the UV region, the UV chromatogram shows no solvent peak. Hence, by using a UV detector, a component present in small amounts but with a large absorbance, and a substance that has the same retention time as that of the solvent, can be detected.

The chromatograms of gasoline are shown in Fig. 7. The peak ratios of the UV and TCD chromatograms are 1.4, 0.1 and 15 for derivatives of benzene, olefins or ketones, and naphthalene, respectively. Hence peaks b, d and f are identified as olefins or ketones, peaks c, e, g, h, i and j are benzenes, and peak a is saturated hydrocarbons. Comparison of the two chromatograms of polychlorinated biphenyls also indicates the structures of many sample components.

The qualitative information obtained by GC is only the retention volume of a sample when it is analyzed with a gas chromatograph using a non-selective detector. When two or more detectors are used, one of which is non-selective and the other selective, we can obtain much more information about a sample by means of GC. If the UV detector can detect many different wave numbers simultaneously, the use of such a detector is much more valuable. Although in the present work the UV detector detects only one wavelength, its combination with a TCD is very useful.

When a UV detector is used with a liquid cell, the window of the cell does not become dirty as it is washed continuously with the solvent. Hence a liquid cell is superior to a gas cell, which becomes dirty as a result of condensation of a sample.

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