Notes

CHROM. 6001

The combination of gas chromatography and nuclear magnetic resonance spectroscopy

There has been a general attempt in the last few years to combine gas chromatography (GC) directly with spectroscopic methods, so that spectra are obtained at the time of elution of each chromatographic peak. There have been some reports on obtaining nuclear magnetic resonance (NMR) spectra of GC fractions after trapping the fractions[1-3].

The present paper describes the combination of GC and NMR spectroscopy.

Experimental

The flow diagram of the apparatus is shown in Fig. 1. The gas-lines that connected units 1, 2 and 3 were heated with tape heaters. Polyethylene tubing, of about 1 mm I.D., was used to connect units 3 and 5. The unit 2 consisted of a 500-ml flask and glass tubes, and nitrogen gas was bubbled into the solvent (carbon tetrachloride) which was maintained at 5-10° below the boiling point of the solvent. The flow-rate of organic vapour was determined by the temperature of the solvent and the flow-rate of nitrogen, and it was indicated by the amount (μl/min) of carbon tetrachloride vapour condensed by a small condenser. A small condenser of 3 mm I.D. and length 20 mm was used[3]. The flow-rate of carbon tetrachloride, about 100-200 μl/min, was selected to obtain a good NMR response and a suitable chromatogram in the combined procedure.

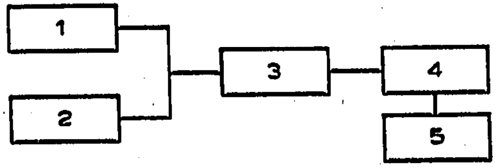

Fig. 1. Flow diagram of the apparatus. 1 = Gas chromatograph; 2 = generator of the gaseous mixture of organic vapour and nitrogen; 3 = small condenser; 4 = regulator of the flow-rate of the solution; 5 = NMR flow-cell.

The vapour of organic solvent was mixed with the effluent from the chromatograph, and the mixture was led into the condenser for the simultaneous condensation of the vapour and the sample component. Then the condensed liquid was fed continuously into the NMR flow-cell, of small volume, and its NMR spectrum was measured.

Three different flow-cells were used, as shown in Fig. 2. These flow-cells were placed in the NMR spectrometer and spun in the usual manner. The equipment used was a JNM-C-60 NMR spectrometer (Japan Electron Optics Laboratories).

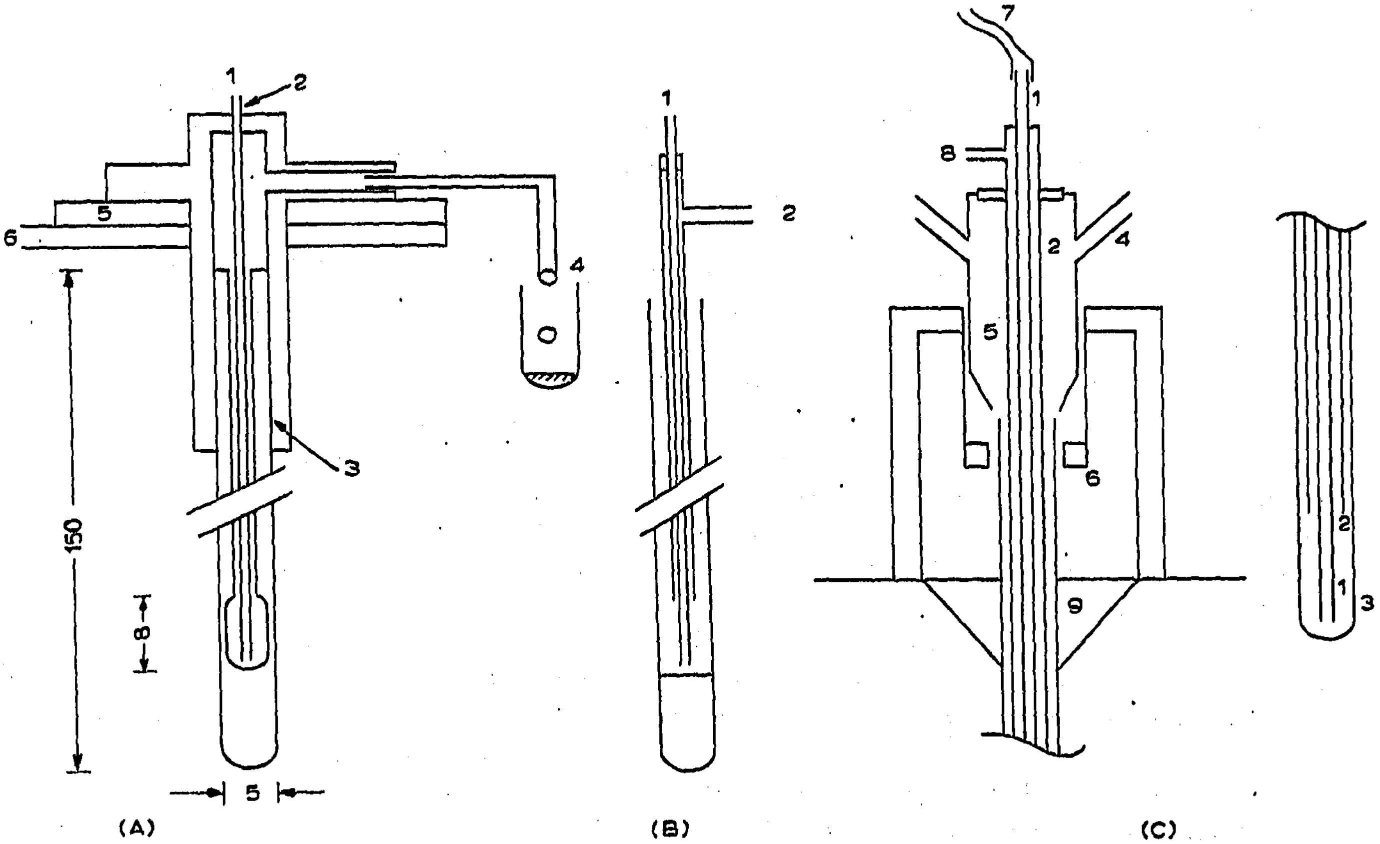

Fig. 2. NMR flow-cell. (A), Flow-cell of the ground-glass type. 1 = Inlet of the solution from the gas chromatograph; 2 = Teflon tube, I.D. 1 mm; 3 = ground-glass; 4 = outlet of the solution; 5 = sponge; 6 = aluminium holder. The flow-rate of the solution was adjusted by regulating the distance between the level of the solution in the condenser and the level of 4. (B), Flow-cell of the double-tube type. 1 = Inlet of the solution; 2 = outlet of the solution. The flow-rate of the solution was adjusted by a valve between a small condenser and the flow-cell. (C), 1 and 2 = Glass tubes; 3 = standard sample tube; 4 = inlet of air, blown by a compresser and dried over sodium hydroxide; 5 = holder for glass tubes; 6 = plastic stand; 7 = polyethylene tubing; 8 = outlet of the solution; 9 = spinner. The flow-rate of the solution was adjusted by the pressure of the blown air. The flow-rate of the air was 10–22 l/min.

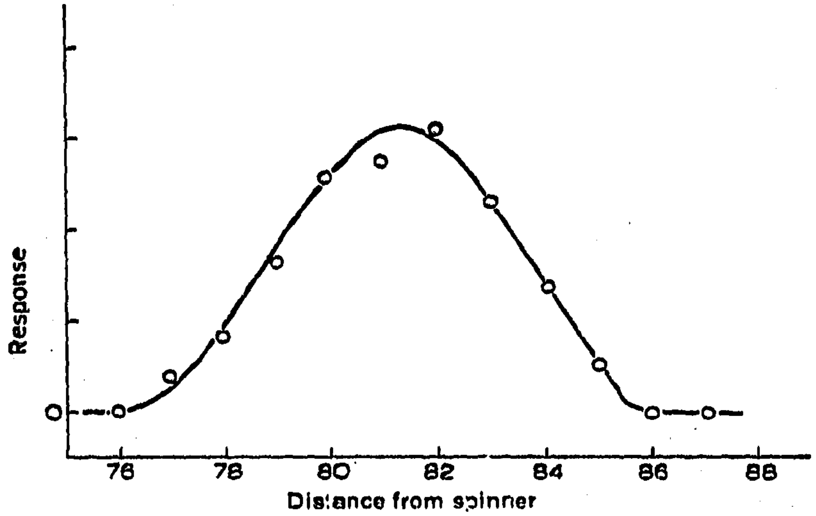

Fig. 3. Relation between the NMR response and the position of a 10% ethylbenzene–carbon tetrachloride solution in the standard sample tube.

Results and discussion

Sensitivity of NMR. To obtain good experimental conditions, we examined the relation between the NMR response and the position of a 10% ethylbenzene – carbon tetrachloride solution in the standard sample tube, as shown in Fig. 3. The volume of the solution was about 45 μl and its depth in the standard sample tube was 3.6 mm. The NMR spectrum was measured without spinning and the NMR response was shown by the peak height of the spectrum.

The maximum NMR response zone was 5.4 mm for the JNM-C-60 instrument. The relation between the response and the amount of solution in the sample tube is shown in Fig. 4. The peak height, which was measured without spinning, increased sharply at first and then more gradually. When a 50-μl volume of sample solution was taken, the response was half of that for a 300-μl volume. The NMR spectrum of a 2% ethanol solution, with a volume of about 50 μl, could be measured with good resolution with the JNM-C-60 instrument. In this experiment, it is preferable that the volume of the sample component itself is more than 1 μl when the volume of its solution in a solvent is about 50 μl, and the flow-cell is set at the position that gives the maximum response.

Comparison of the three different flow-cells. To avoid the presence of bubbles in the tubing and in the NMR cell, the rate of condensation of the organic vapour should be equal to the flow-rate of the solution at the outlet of the NMR cell. The flow-rate of the solution was therefore regulated by pressure difference, A and C in Fig. 2, or by operating a valve, B in Fig. 2. The ease with which the flow-rate of the solution could be adjusted decreased in the order C > A > B.

The flow-cell should be spun at a uniform speed. The inner tubes in each NMR cell must be set in the centre of the cell and must not touch the wall of the cell. As friction occurs in the glass–glass joints in A in Fig. 2, uniform spinning of A at high speed was difficult. The ease with which uniform spinning could be maintained decreased in the order C, B > A.

Performance of an NMR spectrometer connected to a gas chromatograph. The example of the combination of gas chromatograph and an NMR spectrometer is

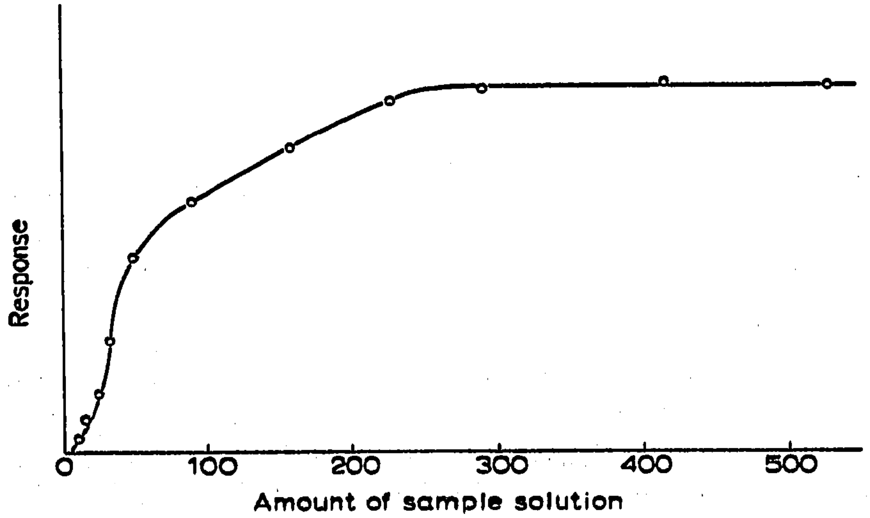

Fig. 4. Relation between the response and the amount of 10% ethylbenzene–carbon tetrachloride solution.

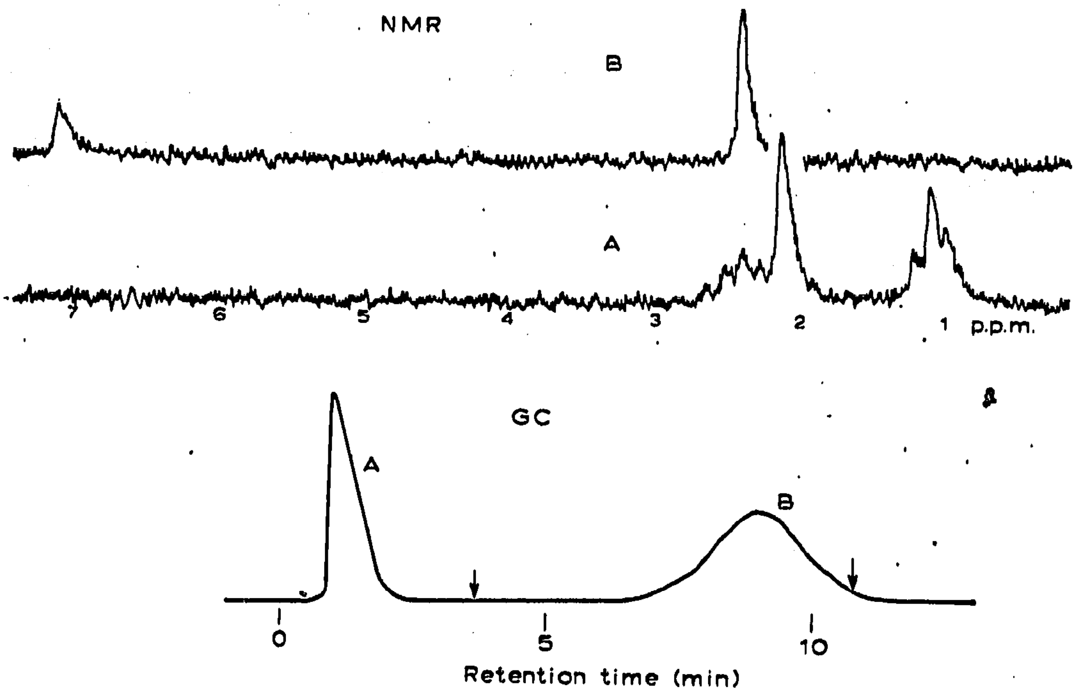

Fig. 5. Combination of GC and NMR spectroscopy. The sample was 20 μl of a mixture of methyl ethyl ketone and *p*-xylene. The arrows indicate the time at which the flow of sample–carbon tetrachloride solution was stopped and the NMR spectrum measured.

shown in Fig. 5. A mixture (20 μl) of methyl ethyl ketone and *p*-xylene was injected into the gas chromatograph. When the strong NMR response was observed, the flow of the methyl ethyl ketone–carbon tetrachloride solution was stopped and the NMR spectrum of A in Fig. 4 was measured. The sweep time was 2.5 min. After the spectrum had been obtained, the solution was allowed to flow and the next sample component was measured. Without interrupting the flow of the solution, consecutive scans between 2 or 3 p.p.m. were also taken. In this experiment, it was difficult to obtain a fine NMR spectrum with a 1-μl sample, possibly owing to non-uniform spinning of the NMR cell.

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