

Development of Rapid Gas Chromatography System for Analyzing Individual Hydrocarbons in Automotive Exhaust Gas

Ayako Okawara, Environmental Analysis Lab.

The non-methane hydrocarbons (NMHCs) defined by the California Air Resources Board consist of about 200 types ranging from C2 to C12.¹⁾ Analysis of individual NMHCs has traditionally been performed after separating the NMHCs into light (C2-C4) and midrange (C5-C12) hydrocarbons (HCs). Problems with this analysis procedure include the complexity of the system requiring two gas chromatographs (GCs) or two capillary columns, and the very time-consuming nature of the analysis. The evaluation of new engines or exhaust after-treatment systems, however, requires a simple and rapid method of NMHC speciation.

We have developed a rapid gas chromatograph system for speciating NMHCs. In developing this system, the main tasks that we faced were (1) the elimination of water in the exhaust gas; (2) devising a means of concentrating the HCs into a narrow band; and (3) the rapid separation of the HCs using a single analytical column. **Figure 1** is a schematic diagram of the developed system. It consists of a water vapor remover, an HC trap, and an HC analyzer.

In the water vapor remover, the water in the exhaust gas was eliminated by two pre-columns (A and B). Without this remover, the water in the exhaust gas was frozen at the initial temperature of the gas chromatograph oven (-55°C) and the analytical column was plugged with ice. Consequently, the flow of carrier gas was obstructed and the elution of the C2-C3 HCs was delayed (**Fig. 2(a)**).

The HC trap has a cooled injection system (CIS) and a second cryotrap. Although the use of CIS caused a broadening and overlapping of the light HCs (**Fig. 2(b)**), the combination of CIS and the second cryotrap made it possible to concentrate

the HCs at the head of the analytical column as a narrow band (**Fig. 2 (c)**).

In the HC analyzer, the HCs were separated using an analytical column. A single narrow-bore capillary column was employed to simplify the system and achieve high resolution, and enabled to separate out 200 HC from the exhaust gas in only 10 minutes. Then, the separated HCs were detected by a flame ionization detector (FID) and a mass spectrometer (MS) (**Fig. 3**).

The analysis cycle of this rapid GC system required 18 minutes, and the detection limit was 5 ppb.

References

- 1) California Environmental Protection Agency, Air Resources Board, Method 102/103, "Procedure for the Determination of C2 to C12 Hydrocarbons in Automotive Exhaust Samples by Gas Chromatography," (1996)

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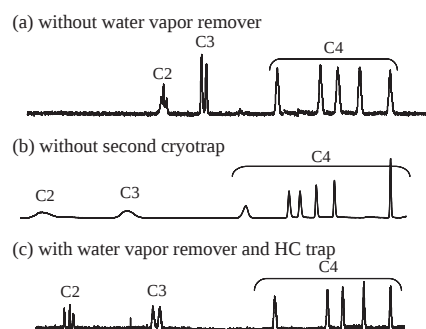


Fig. 2 Gas chromatograms of light hydrocarbons (C2-C4) standards.

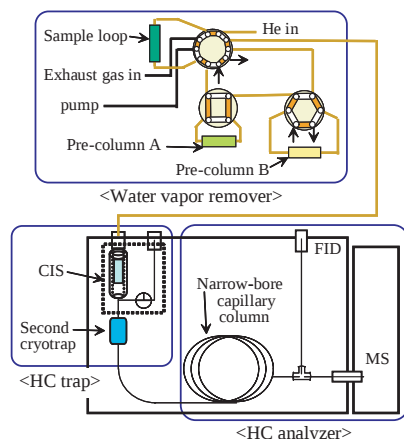


Fig. 1 Schematic diagram of rapid gas chromatography system.

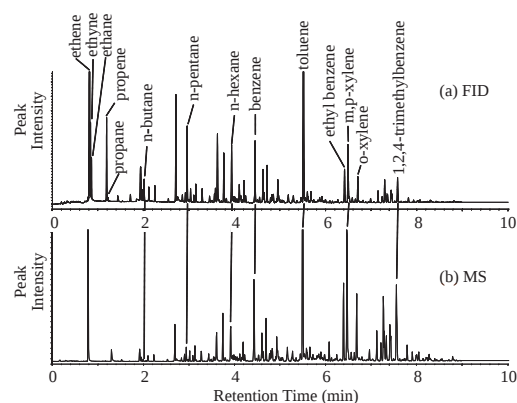


Fig. 3 Chromatograms of exhaust gas by simultaneous detection.