Instrumental Achievements

Rapid Analysis of Light Hydrocarbons and Carbon Dioxide in Air with Micro Thermal Conductivity Detector**Akira MACHINO, Hideo SUGIMOTO and Daijiro TERASAKI***Fundamental Technology Research Laboratory, Tokyo Gas Co., Ltd.,
Shibaura, Minato, Tokyo 105, Japan*

Light hydrocarbons, such as methane, ethane, propane and butane, are sometimes detected in air at concentrations of several ppm. Such amounts are thought to originate from fermentation gas, petroleum gas, or city gas. It is very important for identifying gas origin to be able to analyze minor components such as light hydrocarbons and carbon dioxide. In our previous study¹, a fully automated gas chromatograph system was developed to measure these compounds rapidly. This system was composed of packed columns and 7 detectors (TCD 4, FID 2, PID 1); it took 25–40 min to analyze one sample.

The last few years have seen dramatic developments in the application of capillary columns. Now the rapid analysis of light hydrocarbons can be accomplished using a capillary column with an FID. A TCD is generally used for the simultaneous analysis of light hydrocarbons and inorganic components such as carbon dioxide. However, it is seldom combined with capillary columns owing to the detector cell volume and sensitivity. A few years ago, Saadat and Terry² reported the development of a microchip TCD-GC, also known as the "GC on a chip". This micro-TCD was made by an etching technique called silicone micromachining and had a high sensitivity. A gas chromatograph such as a micro-TCD has recently been commercialized.^{3–5} Columns packed with alumina, molecular sieves, or porous polymers have been generally used for the analysis of inorganic gases and light hydrocarbons. In recent years, porous layer open tubular (PLOT) capillary columns coated with these materials have also become commercially available by new coating techniques.^{6,7} In this study, we combined the micro-TCD with PLOT-type capillary columns to accomplish the rapid analysis of light hydrocarbons and

carbon dioxide in air. We also investigated the optimum analytical conditions and developed the portable gas analyzer on the basis of these results.

Experimental

The characteristic features of the columns used in this study are listed in Table 1. The lengths of these columns ranged from 0.5–10 m. The capillary column was mounted in the splitless mode on an M-200 gas chromatograph (Nippon Tylan Co., Ltd.) equipped with a TCD. Helium was used as the carrier gas. Carbon dioxide and methane–butane gases were obtained from Takachiho Chemical Co., Ltd. These gases were arbitrarily mixed with air and used as the specimen gases.

Results and Discussion

Table 2 shows the results of the experiments on several capillary columns. Separation of inorganic gases and light hydrocarbons was unsatisfactory on a short capillary column coated with a liquid stationary phase like methylsilicone, even at lower column temperatures such as 303 K. With Al₂O₃/KCl PLOT and Molsieve 5A PLOT, the retention time of light hydrocarbons decreased after the analysis of air was repeated many times. This phenomenon must be caused by adsorption of water and carbon dioxide in air into the stationary particles, resulting in a change of adsorption characteristics. To reduce times for component analyses, either programmed temperature gas chromatography on sole column or isothermal gas

Table 1 Characteristic features of various columns

Stationary phase	Length/m	Inner diameter/mm	Film thickness/ μ m	Remarks
Porous polymer	0.5–10	0.32	10	PoraPLOT Q
Alumina	4	0.32	5	Al ₂ O ₃ /KCl PLOT
Molecular sieve	4	0.32	30	Molsieve 5A PLOT
Methylsilicone	4	0.10	10	DB-1

Table 2 Retention time of various components

Column	Analytical condition		Retention time/s								
	Column temperature/ K	Carrier gas velocity/ cm s ⁻¹									
			O ₂	N ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	CO ₂	H ₂ O
DB-1 (4 m)	303	20	21	21	21	21	21.5	22	24	21	22
Al ₂ O ₃ /KCl PLOT (4 m)	303	20	42	42	42	42	58	101	112	—	—
Molsieve 5A PLOT (4 m)	323	20	35	54	104	—	—	—	—	—	—
PoraPLOT Q (4 m)	303	20	41	41	43	92	—	—	—	54	157
	353	20	20	20	20	22	62	135	171	20	36

—: not eluted within 255 s.

chromatography on coupled columns for low and high boiling point gas fractions can be applied. But the former method takes a lot of time to adjust column over-temperature to an initial state at every zero hour of GC run. Therefore, the latter two column methods were examined. As shown in Table 2, methane, ethane and carbon dioxide could be separated on a PoraPLOT Q at 303 K within 100 s, and propane, isobutane, and butane could be separated at 353 K within 180 s. We decided to employ an analytical system in which one PoraPLOT Q column was used for analyzing methane, ethane and carbon dioxide at a low column temperature, while the analysis of propane, isobutane and butane was performed with another PoraPLOT Q column at a high column temperature.

In order to determine optimum flow rate for analyzing mixtures of light hydrocarbons and inorganic gases, we investigated the Van Deemter curves for methane, ethane and carbon dioxide. HETP becomes a minimum at 15 to 25 cm/s. The minimum values of HETP are about 1.2 mm.

Table 3 shows the relationship between column length and the resolution value, which was estimated by air (N₂+O₂) and methane. As shown in Table 3, a column length needs more than 8 m to separate air and methane completely. Figure 1 shows a typical chromatogram of air, methane, ethane and carbon dioxide. These components could be analyzed within 180 s and the minimum limit of detection of ethane ($S/N=3$) was 3 ppm under these conditions.

Detailed studies of the characteristics of the PoraPLOT Q column for hydrocarbons have already been reported by Zeeuw *et al.*^{8,9} However, data are not available on the separation of hydrocarbons and water. The effect of column temperature on the separation of propane and water was investigated in the range of 313–353 K. It was found that it was difficult to detect the trace hydrocarbons at lower temperatures because the tailing of the water peak became larger at such temperatures. However, the tailing was extremely small at 353 K. This phenomenon might have been due to the decrease in intermolecular forces between water and the surfaces of porous polymers. Table 4 shows the effect of column length on the resolution of water and

Table 3 Dependence of peak resolution of air and methane on column length

Column length/m	Resolution value
4	0.64
6	1.14
8	1.87
10	2.11

Column, PoraPLOT Q; temperature, 313 K; carrier gas velocity, 25 cm/s.

Fig. 1 Chromatogram of methane, carbon dioxide and ethane obtained with PoraPLOT Q column: column length, 8 m; temperature, 313 K; linear velocity, 25 cm/s.

propane. Propane was separated from water by a 2 m long column. Figure 2 shows a typical chromatogram of air, water, propane, isobutane and butane. These components could be analyzed within 100 s and the minimum limit of detection of propane ($S/N=3$) was 3 ppm under these conditions.

A portable gas analyzer was developed based on the above experimental results. It is small and compact (width: 430 mm, depth: 390 mm, and height: 120 mm); its weight is 9 kg. It has 2 independent analyzing

Table 4 Dependence of peak resolution of water and propane on column length

Column length/m	Resolution value
0.25	0
0.5	0.5
1	1.3
2	3.2
4	7.9

Column, PoraPLOT Q; temperature, 353 K; carrier gas velocity, 20 cm/s.

Fig. 2 Chromatogram of propane, isobutane and butane obtained with PoraPLOT Q column: column length, 2 m; temperature, 353 K; linear velocity, 20 cm/s.

systems into which gases are introduced simultaneously by the automatic sampling system. It takes only 3 min to analyze all compounds and the results are automatically displayed. The features of the analyzer are shown in Table 5.

The authors are grateful to Dr. Kanohta and the staff of

Table 5 Specifications of portable gas analyzer

Item	Specifications
Analytical time	3 min
Measurable component	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , <i>i</i> -C ₄ H ₁₀ , <i>n</i> -C ₄ H ₁₀ , CO ₂
Measurable range	5 ppm – 100% (CH ₄ 20 ppm – 100%)
Output form of analytical result	compositional values
Carrier gas cylinder	75 ml (100 kg/cm ²)
Power source	DC 12 V battery
Weight and size	9 kg, 430 mm×390 mm×120 mm

Nippon Tylan Co., Ltd. for their contributions to this study.

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(Received July 19, 1991)

(Accepted September 19, 1991)