CHROMSYMP. 2681

Sensitive flame ionization detector for the determination of traces of atmospheric hydrocarbons by capillary column gas chromatography

Yoshio Tsujino* and Kazuhiro Kuwata

Environmental Pollution Control Centre, 3-62, 1 Chome, Nakamichi, Higashinari-ku, Osaka 537 (Japan)

ABSTRACT

A sensitive flame ionization detector was developed for capillary column gas chromatography. The detector used no make-up gas and lower flow-rates of hydrogen and air to suppress detector noise and to achieve maximum response. The detector was responsive down to the 10^{-13} g level for C_2–C_{11} hydrocarbons. Atmospheric hydrocarbons could be determined at parts per billion or parts per trillion levels by using gas chromatography with the detector via cryogenic concentration of a small volume of air sample.

INTRODUCTION

Flame ionization detection (FID) has been usually employed for gas chromatographic (GC) determination of atmospheric hydrocarbons in studies of air pollution [1–14]. In such cases, a large volume of air sample has been often sampled by using cryogenic or adsorptive concentration techniques to compensate the detector response, thus lowering the GC performance because of contamination of analytical columns and the detector. On the other hand, water vapour in the sample may be condensed to clog the sampling tubes in the cryogenic process. Use of a large amount of dehydration agent could cause an unsuccessful determination of polar or unstable components owing to their adsorption or reactivity.

In this study, a sensitive flame ionization detection (FID) system was developed for capillary column GC analysis and successfully applied to the determination of trace levels of atmospheric C_2–C_{11} hydrocarbons via a cryogenic concentration of a small volume of air sample.

---

* Corresponding author.

EXPERIMENTAL

Reagents and materials

All the reagents used for calibration were of special grade from Wako (Osaka, Japan). Tedlar bags (10 l) were used to prepare a standard sample and to sample an air sample.

The 50 ppb (v/v) toluene standard sample was prepared as follows. A 23.7-μl aliquot of toluene was diluted with 100 ml of hexane and 10 μl of the solution were placed into a 1-ml glass ampoule. The ampoule was sealed by fusing its end, then placed into a 1000-ml glass flask. The flask was evacuated, the ampoule broken by shaking the flask, and the flask heated at 80°C for 10 min in a oven. Nitrogen was introduced into the flask to atmospheric pressure, 10 l of nitrogen were passed through the flask at room temperature and the gas sample was collected into a 10-l Tedlar bag.

Apparatus

A Varian (Walnut Creek, CA, USA) 1400 gas chromatograph equipped with a Hewlett-Packard (Avondale, PA, USA) 3380A integrator was employed. The analytical columns used were a 42 m × 0.25 mm I.D. stainless-steel squalane capillary col-

TABLE I

RESPONSES OF S-FID FOR HYDROCARBONS AND RELATIVE RESPONSES OF HYDROCARBONS TO TOLUENE

No.	Hydrocarbon	Detection limit[a] (pg)	Sensitivity[b] (pg/s)	Relative response[c]
1	Ethylene	0.5	0.036	0.953
2	Acetylene	0.5	0.034	1.00
3	Propylene	0.5	0.036	0.953
4	Propane	0.5	0.037	0.916
5	Isobutane	0.3	0.021	1.02
6	Isobutene + 1-butene	0.3	0.022	0.953
7	*n*-Butane	0.3	0.021	1.02
8	*trans*-2-Butene	0.3	0.022	0.953
9	*cis*-2-Butene	0.3	0.022	0.953
10	3-Methyl-1-butene	0.2	0.011	0.953
11	Isopentane	0.2	0.011	0.972
12	1-Pentene	0.2	0.011	0.953
13	2-Methyl-1-butene	0.2	0.011	0.953
14	*n*-Pentane	0.2	0.011	0.972
15	*trans*-2-Pentene	0.2	0.011	0.953
16	*cis*-2-Pentene	0.2	0.011	0.953
17	2-Methyl-2-butene	0.2	0.011	0.953
18	Cyclopentane	0.2	0.011	0.972
19	2,3-Dimethylbutane	0.1	0.008	0.963
20	2-Methylpentane	0.1	0.008	0.963
21	3-Methylpentane	0.1	0.008	0.963
22	*n*-Hexane	0.1	0.008	0.963
23	Methylcyclopentane	0.1	0.008	0.963
24	2,4-Dimethylpentane	0.1	0.008	0.963
25	Benzene	0.1	0.008	1.05
26	Cyclohexane	0.1	0.008	0.963
27	2-Methylhexane	0.1	0.008	0.963
28	2,3-Dimethylpentane	0.1	0.008	0.963
29	3-Methylhexane	0.1	0.008	0.963
30	*n*-Heptane	0.1	0.008	0.963
31	Methylcyclohexane	0.1	0.008	0.963
32	Toluene	0.1	0.008	1.00
33	2-Methylheptane	0.1	0.009	0.907
34	4-Methylheptane	0.1	0.009	0.907
35	3-Methylheptane	0.1	0.009	0.907
36	*n*-Octane	0.1	0.009	0.907
37	Ethylbenzene	0.1	0.008	0.953
38	*p*-Xylene	0.1	0.009	0.935
39	*m*-Xylene	0.1	0.008	0.972
40	*o*-Xylene	0.1	0.008	0.953
41	*n*-Nonane	0.1	0.009	0.916
42	Isopropylbenzene	0.1	0.009	0.907
43	*m*-Ethyltoluene	0.1	0.008	0.944
44	*p*-Ethyltoluene	0.1	0.009	0.935
45	*o*-Ethyltoluene	0.1	0.008	0.953
46	1,3,5-Trimethylbenzene	0.1	0.009	0.916
47	1,2,4-Trimethylbenzene	0.1	0.009	0.907
48	*n*-Decane	0.1	0.009	0.915
49	1,2,3-Trimethylbenzene	0.1	0.009	0.916
50	*n*-Undecane	0.1	0.009	0.915

[a] Absolute detection limit at three times the noise level on the squalane capillary column (which showed an excellent performance for simultaneous separation of the aliphatic and aromatic hydrocarbons).
[b] Calculated by using a chromatogram of the hydrocarbons simultaneously separated on the squalane column.
[c] Relative response of hydrocarbon to toluene (w/w).

umn (Hitachi, Tokyo, Japan) and a J&W Scientific (Folsom, CA, USA) 30 m × 0.2 mm I.D. DB-1 fused-silica bonded-phase capillary column system. A two-stage concentration technique was employed for air sampling. The first cryogenic trap was a 30 cm × 2.1 mm I.D. stainless-steel tube packed with Flusin GU 60–80 mesh (GL Science, Tokyo, Japan). For making the second trap, a 300 cm × 0.25 mm I.D. stainless-steel squalane capillary column (Hitachi) was deactivated at 300°C for 120 min under a nitrogen stream, spiralled and covered with glass-fibre ribbons 1 mm thick. The GC analytical conditions were as follows: carrier, nitrogen 0.6 ml/min; column temperature, (1) 0°C for 10 min, raised rapidly to 30°C and programmed from 30 to 90°C at 1°C/min for the squalane column and (2) 0°C for 10 min and programmed from 0 to 150°C at 4°C/min for the DB-1 column; sensitive FID, hydrogen 25 ml/min, air 200 ml/min (no make-up gas was used).

Sampling and analytical procedure

Air was sampled at 300 ml/min for 30 min into a Tedlar bag by using a lung-type pneumatic sampler. A 50–1000-ml volume of the sample was passed at 200 ml/min through the first sampling trap at liquid oxygen temperature. The condensed components were then moved into the second trap at liquid oxygen temperature by heating the first trap at 100°C and by passing the carrier for 15 min in the opposite direction to that used in sampling. The retrapped substances were released by exposing the second trap at room temperature. When the second trap was exposed at room temperature, GC analysis was started. Hydrocarbons with C_2–C_{11} were identified by their retention times and quantified by the peak areas. The concentration of the hydrocarbons was determined by using 50 ml of 50 ppb toluene and the relative responses to toluene shown in Table I.

RESULTS AND DISCUSSION

Sensitive FID

A Varian 1400 FID assembly was modified so as to insert a capillary column outlet to the hydrogen path in the manner to keep the hydrogen flow streamlined (see Fig. 1). No make-up gas was used in the capillary GC analysis to avoid turbulent flow owing to mixing with the hydrogen and the carrier gases. The flow-rates of hydrogen and air were re-
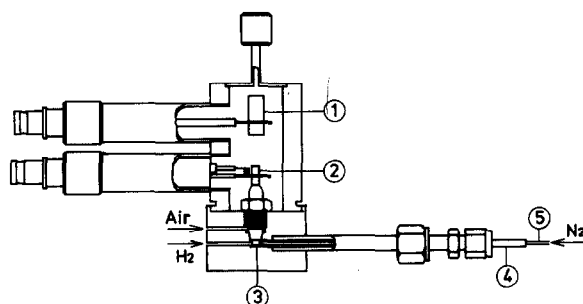

Fig. 1. Sensitive FID system. 1 = Electrode, ion collector; 2 = jet flame tip (orifice diameter, 0.51 mm); 3 = gas confluent cell; 4 = stainless-steel tube (1.5 mm I.D.); 5 = analytical column.

duced to 25 and 200 ml/min, respectively, to minimize the noise. The position of the column outlet was adjusted by using a screw nut to minimize detector noise. The best position of the outlet was just at the inner wall of the gas confluent cell of the detector (see Fig. 1). A too deep or too shallow position resulted in a highly noisy output. These conditions made the flame stable and minimized the noise output. The more turbulent flow in the flame seemed to produce more noise in the detector output. Fig. 2 shows plots of detector output under both flame-on and flame-off conditions. The noise observed was approximately $1 \cdot 10^{-14}$ A/mV, being at the same level as inherent in one of the electronic circuits. Little noise derived from the flame was detected. Once the detector conditions were set, the noise level and the analytical response were very constant whenever the detector was used throughout a year.
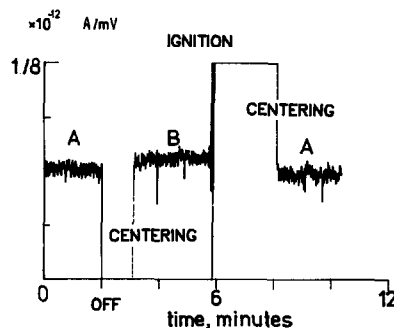

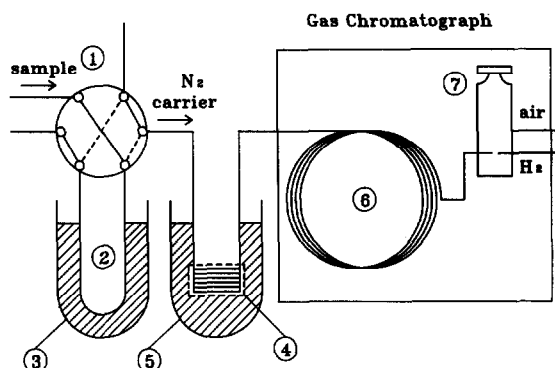Fig. 2. Noise level of the detector output. (A) Flame-on; (B) flame-off.

Fig. 3. Analytical system of air sample. 1 = Six-way switching valve; 2 = first cryogenic trap; 3 = liquid oxygen bottle (− 183°C) or hot water bottle (100°C); 4 = second trap (squalane-coated 300 cm × 0.25 mm I.D. stainless-steel capillary tube spiralled and covered with 1-mm-thick glass-fibre ribbon); 5 = liquid oxygen bottle (− 183°C); 6 = analytical column; 7 = sensitive FID system.

Detection of hydrocarbons

The above modification was for minimizing the FID noise under the flame-on condition and not for maximizing an absolute response output to hydrocarbons. Table I indicates the detection limits and the sensitivities of typical C_2–C_{11} hydrocarbons as observed in the atmosphere. As a result of suppress-

ing the detector noise, the sensitivities were 20–100 times better than those of conventional FID assemblies [15–18]. The linear dynamic range was 10^{-12} to 10^{-4} g for the hydrocarbons. Bleeding-free capillary columns and the sensitive FID system may be useful to determine ultra-traces of such hydrocarbons at the low noise level.

Determination of atmospheric hydrocarbons

A 50–1000 ml volume of air sample, subjected to the cryogenic concentration, was enough for determination of the atmospheric hydrocarbons. In this case, no clogging due to water vapour occurred in the packed column and the capillary tubes during the concentration. The water vapour and other substances coexisting in the sample had little effect on the separation efficiency of the analytical columns and the detector performance. In this case, two-stage concentration was used to determine simultaneously a number of C_2–C_{11} hydrocarbons.

The second trap was exposed at room temperature after retrapping the organics at a liquid oxygen temperature (see Fig. 3). When the C_2–C_4 hydrocarbons were eluted from the analytical column, the temperature-programmed GC analysis was started. In this way, the C_2–C_{11} hydrocarbons were simultaneously separated and determined at ultra-trace levels.
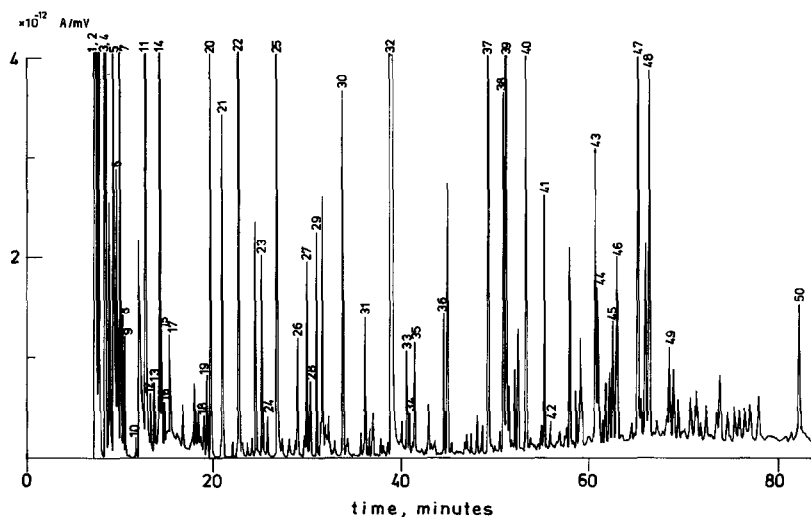

Fig. 4. Typical chromatogram of the determination of trace levels of atmospheric hydrocarbons: the sample volume was 1000 ml; the analytical column used was the squalane capillary column; see Table II for the hydrocarbons.

TABLE II

TYPICAL ANALYSIS OF ATMOSPHERIC HYDROCARBONS AT THE ENVIRONMENTAL POLLUTION CONTROL CENTER, OSAKA CITY

Sample volume, 200 ml; analytical column used, squalane capillary column. Concentration (v/v) in parts per American billion (10^9).

No.	Hydrocarbon	Concentration (ppb)	No.	Hydrocarbon	Concentration (ppb)
1	Ethylene	23.3	26	Cyclohexane	0.8
2	Ethane + acetylene	24.3[a]	27	2-Methylhexane	1.5
3	Propylene	6.1	28	2,3-Dimethylpentane	0.6
4	Propane	8.9	29	3-Methylhexane	1.7
5	Isobutane	5.1	30	n-Heptane	2.0
6	Isobutene + 1-butene	3.6	31	Methylcyclohexane	0.7
7	n-Butane	11.0	32	Toluene	31.1
8	trans-2-Butene	1.1	33	2-Methylheptane	0.6
9	cis-2-Butene	0.9	34	4-Methylheptane	0.3
10	3-Methyl-1-butene	0.2	35	3-Methylheptane	0.7
11	Isopentane	10.6	36	n-Octane	0.6
12	1-Pentene	0.4	37	Ethylbenzene	3.8
13	2-Methyl-1-butene	0.7	38	p-Xylene	2.3
14	n-Pentane	7.7	39	m-Xylene	5.4
15	trans-2-Pentene	0.7	40	o-Xylene	2.8
16	cis-2-Pentene	0.3	41	n-Nonane	0.7
17	2-Methyl-2-butene	0.5	42	Isopropylbenzene	0.1
18	Cyclopentane	0.4	43	m-Ethyltoluene	2.0
19	2,3-Dimethylbutane	0.8	44	p-Ethyltoluene	1.1
20	2-Methylpentane	3.9	45	o-Ethyltoluene	0.7
21	3-Methylpentane	3.1	46	1,3,5-Trimethylbenzene	1.2
22	n-Hexane	5.5	47	1,2,4-Trimethylbenzene	2.9
23	Methylcyclopentane	1.7	48	n-Decane	0.9
24	2,4-Dimethylpentane	0.3	49	1,2,3-Trimethylbenzene	0.6
25	Benzene	5.1	50	n-Undecane	0.4

[a] The value was obtained by using the relative response of acetylene in Table I because ca. 90% of the peak was occupied by acetylene.

Table II indicates an example of determination of hydrocarbons in the atmospheric environment by using the squalane column and sensitive FID, and Fig. 4 shows a typical chromatogram of the atmospheric hydrocarbons. The hydrocarbons could be determined at ultra-trace levels without any problems, such as column-clogging, column/detector contamination and disappearance of polar or reactive components, as often seen in conventional analyses of atmospheric samples.

CONCLUSIONS

The proposed sensitive FID was useful to determine sensitively hydrocarbons in the atmospheric environment without effects of water vapour and other coexistent substances. A more sensitive detector signal could be available if a modern electronic data-processing system is applied. In any case, sensitive FID may be useful for trace analysis of many other types of samples on bleeding-free capillary columns.

REFERENCES

1 J. H. Raymer, E. D. Pellizzari and S. D. Cooper, Anal. Chem., 59 (1987) 2069.
2 W. A. McClenny, J. D. Pleil, M. W. Holdren and R. N. Smith, Anal. Chem., 56 (1984) 2947.
3 W. Nutmagul, D. R. Cronn and H. H. Hill, Jr., Anal. Chem., 55 (1983) 2160.
4 P. F. Nelson and S. M. Quigley, Environ. Sci. Technol., 16 (1982) 650.

5 C. V. Hampton, W. R. Pierson, T. M. Harvey, W. S. Updegrove and R. S. Marano, *Environ. Sci. Technol.*, 16 (1982) 287.

6 S. Coppi, A. Betti and M. Ascanelli, *J. Chromatogr.*, 390 (1987) 349.

7 P. Ciccioli, E. Brancaleoni, A. Cecinato, C. Dipalo, A. Brachetti and A. Liberti, *J. Chromatogr.*, 351 (1986) 433.

8 R. R. Arnts, *J. Chromatogr.*, 329 (1985) 399.

9 M. Termonia and G. Alaerts, *J. Chromatogr.*, 328 (1985) 367.

10 R. S. Hutte, E. J. Williams, J. Staehelin, S. B. Hawthorne and R. E. Sievers, *J. Chromatogr.*, 302 (1984) 173.

11 A. Zlatkis, L. Ghaoui, S. Weisner, H. Weisner and H. Shanfield, *Chromatographia*, 20 (1985) 343.

12 A. I. Clerk, A. E. Mcintyre, J. N. Lester and R. Perry, *Int. J. Environ. Anal. Chem.*, 17 (1984) 315.

13 K. Sexton and H. Westberg, *Atoms. Environ.*, 18 (1984) 1125.

14 P. F. Nelson and S. M. Quigley, *Atoms. Environ.*, 18 (1984) 79.

15 M. M. Thomason and W. Bertsch, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 690.

16 R. K. Simon, Jr., *J. Chromatogr. Sci.*, 23 (1985) 313.

17 P. L. Patterson, *J. Chromatogr. Sci.*, 24 (1986) 466.

18 K. J. Hyver and P. Sandra, *High Resolution Gas Chromatography*, Hewlett-Packard, Avondale, PA, 3rd ed., 1989, Ch. 4, pp. 6–23.