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Continuous determination of volatile organic compounds in the atmosphere by an automated gas chromatographic system

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Abstract

A fully automated gas chromatographic system has been developed for the continuous determination of trace levels of 54 selected volatile organic compounds (VOCs) in the atmosphere, with a short time resolution. The method is based on the preconcentration of an air sample using a multibed collection tube (Carbotrap B, Carboxen 1000, Carboxen 1001) at ambient temperature, by thermal desorption, and analysis of the VOCs using a capillary gas chromatograph equipped with a photoionization detector and an electrolytic conductivity detector connected in series. The detection limit of 0.01 ppb for each compound was obtained using a 1-l air sample. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

A large number of man-made volatile organic compounds (VOCs) are routinely emitted into the ambient environment in industrialized countries. Atmospheric concentrations of these VOCs are sub-ppb and are subject to rapid temporal variations. The demand for accurate, sensitive and simple techniques for the monitoring of low levels of VOCs in the atmosphere has increased tremendously in recent years [1–10]. However, the analysis of ppt–ppb levels of VOCs in the atmosphere requires special instrumentation.

The aim of this work was to develop a continuous measurement system that is capable of determining trace levels of VOCs in the atmosphere with a short time resolution. For this purpose, a gas chromato-

graphic system with photoionization detection (PID) and electrolytic conductivity detection (ELCD) systems connected in series was combined with a preconcentration device using an adsorbent tube and a thermal desorption apparatus. Considering the prospect of a large number of tests and repetitions, we designed an automated continuous sampling and analysis system. The method is based on the preconcentration of an air sample using a multibed tube (Carbotrap B, Carboxen 1000, Carboxen 1001) at ambient temperature, followed by thermal desorption, and analysis of 54 selected VOCs by capillary gas chromatography with PID and ELCD, connected in series (Table 1).

The aromatic and unsaturated compounds are selectively detected by PID, then the halogenated compounds are selectively detected by ELCD [11,12].

These specific detectors were highly sensitive to

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Table 1
List of target VOCs

Num-ber	Compound	Detection		M_r	b.p. (°C)	Num-ber	Compound	Detection		M_r	b.p. (°C)
		PID	ELCD					PID	ELCD		
1	1,1-Dichloroethene	x	x	96.9	31.7	28	Ethylbenzene	x		106.2	136.2
2	Methylene chloride		x	84.9	40.2	29	<i>m</i> -Xylene	×		106.2	139.1
3	<i>trans</i> -1,2-Dichloroethene	x	x	96.9	47.5	30	<i>p</i> -Xylene	x		106.2	138.2
4	1,1-Dichloroethane		x	99.0	57.3	31	<i>o</i> -Xylene	x		106.2	144.4
5	<i>cis</i> -1,2-Dichloroethene	x	x	96.9	60.3	32	Styrene	×		104.2	145.2
6	2,2-Dichloropropane		x	113.0	70.5	33	Bromoform		x	252.7	149.6
7	Bromochloromethane		x	129.4	67.0	34	Isopropylbenzene	x		120.2	152.4
8	Chloroform		×	119.4	61.2	35	1,1,2,2-Tetrachloroethane		x	167.9	147.0
9	1,1,1-Trichloroethane		x	133.4	73.9	36	Bromobenzene	x	x	157.0	156.2
10	Carbon tetrachloride		x	153.8	76.7	37	1,2,3-Trichloropropane		x	147.4	156.9
11	1,1-Dichloropropene	x	x	111.0	77.2	38	<i>n</i> -Propylbenzene	x		120.2	159.2
12	Benzene	x		78.1	80.1	39	2-Chlorotoluene	x	x	126.6	158.9
13	1,2-Dichloroethane		x	99.0	83.4	40	1,3,5-Trimethylbenzene	x		120.2	164.7
14	Trichloroethene	x	x	131.4	86.6	41	4-Chlorotoluene	x	x	126.6	162.0
15	1,2-Dichloropropane		x	130.0	96.4	42	<i>tert</i> -Butylbenzene	x		134.2	169.5
16	Dibromomethane	x	x	173.6	97.0	43	1,2,4-Trimethylbenzene	x		120.2	170.0
17	Bromodichloromethane		x	168.3	87.0	44	<i>sec</i> -Butylbenzene	x		134.2	183.4
18	<i>cis</i> -1,3-Dichloropropene	x	x	111.0	103.3	45	1,3-Dichlorobenzene	x	x	147.0	173.0
19	Toluene	x		92.1	110.6	46	<i>p</i> -Isopropyltoluene	x		134.2	177.1
20	<i>trans</i> -1,3-Dichloropropene	x	x	111.0	112.2	47	1,4-Dichlorobenzene	x	x	147.0	174.1
21	1,1,2-Trichloroethane		x	133.4	113.3	48	<i>n</i> -Butylbenzene	x		134.2	183.4
22	Tetrachloroethene	x	x	165.8	121.2	49	1,2-Dichlorobenzene	x	x	147.0	180.5
23	1,3-Dichloropropane		x	130.0	120.5	50	1,2-Dibromo-3-chloropropane		×	236.4	196.0
24	Dibromochloromethane		x	208.3	116.0	51	1,2,4-Trichlorobenzene	x	x	181.4	213.0
25	1,2-Dibromoethane		x	187.9	131.4	52	Hexachloro-1,3-butadiene	x	x	260.8	215.0
26	Chlorobenzene	x	x	112.6	132.0	53	Naphthalene	x		128.2	218.0
27	1,1,1,2-Tetrachloroethane		×	167.9	130.2	54	1,2,3-Trichlorobenzene	x	x	181.4	218.0

the VOCs, giving good precision and a wide linear range. This system has been used successfully to determine hourly variations in environmentally important VOCs at ppt–ppb levels in the urban atmosphere of Yokohama.

2. Experimental

2.1. Standard samples

Standard samples for the 54 VOCs were prepared by diluting the liquid standard containing a mixture of the 54 VOCs (Tokyo Kasei Kogyo, Japan) with high purity nitrogen.

2.2. Analytical instrumentation

Fig. 1 shows the instrumental arrangement used

for the transfer, preconcentration, thermal desorption and GC analyses of the VOCs in the sampled air.

The air sample was preconcentrated using a modified concentration system (GAS-30, DKK, Japan) attached to the GC system. The air sample was drawn through a PTFE prefilter into the sampling line at a flow-rate of 50 ml/min. The PTFE filter was used as an inlet filter to remove particulates from the sampled air. The air sample was then preconcentrated by passing it through the collection tube at ambient temperature. When the sampling transfer was completed, the valves were switched to the dry purge position and a nitrogen purge was used to remove any water vapor from the sampled air (2 min with high purity nitrogen gas) prior to the thermal desorption procedure. Valve 2 was then turned to the injection mode. Simultaneously, the collection tube was rapidly heated to 280°C and maintained at that temperature for 8 min. The trapped sample was desorbed and introduced into the

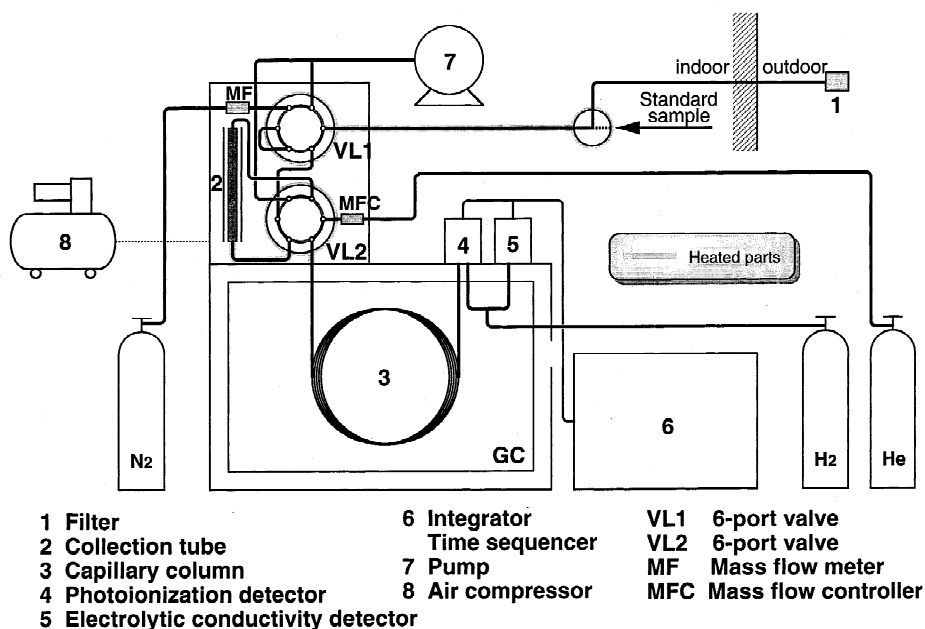


Fig. 1. Schematic diagram of the GC-PID/ELCD system.

capillary column by back-flushing with the carrier gas at a flow-rate of 10 ml/min. At this point, the GC temperature program is started automatically. During subsequent analysis, the collection tube was refreshed at 280°C by a nitrogen purge. At the end of the purge time, the valves were switched to the sampling mode and temperature program analysis was started. The collection tube and the column were connected to the valve by stainless steel tubes (1.6 mm O.D.). All transfer components (tubing, valves) were heated, to avoid the adsorption of components in the sample air, using ribbon heaters at about 90°C. The instruments' operating conditions are listed Table 2.

The GC work was performed using a Hewlett-Packard 5890 gas chromatograph equipped with a PID system (SRI, USA) and a Hall 700A ELCD system (Tracor, USA) or a dry ELCD system (SRI, USA), connected in series.

Capillary column separation was done using a 3- μ m film thickness [75 m \times 0.53 mm I.D. DB-624 (J&W Scientific)]. The GC operating conditions are listed in Table 2. For the repetitive operations of sampling and analysis, the switching valves, sampling pump, mode of heating and several time sequences and integrators were regulated by a

Shimadzu chromatopack C-R2 (Shimadzu, Japan). The time program for sequential analyses is shown in Fig. 2.

2.3. Collection tube

The multibed collection tube (15 cm \times 2.1 mm I.D., stainless steel) was packed with a combination of 112 mg of Carbotrap B (60–80 mesh, Supelco), 83 mg of Carboxen 1000 (60–80 mesh, Supelco) and 17 mg of Carboxen 1001 (60–80 mesh, Supelco). The adsorbents were held in place by a small amount of quartz wool. Prior to sampling, the collection tube was conditioned by a nitrogen purge at 280°C. The sampling temperature was empirically determined at ambient temperature. Typically, the sampling flow-rate was 50 ml/min, with a sampling period of 20 min.

2.4. Calibration

The standards for the 54 VOCs were established by spiking 2–50 ng of each compound of the liquid standards with high purity nitrogen. The standards

Table 2
Operating conditions of the GC–PID/ELCD system

Collection tube		15 cm×2.1 mm I.D.
Adsorbent		Carbotrap B, 60–80 mesh (112 mg) Carboxen 1000, 60–80 mesh (83 mg) Carboxen 1001, 60–80 mesh (17 mg)
Sampling temperature		Ambient
Sampling flow-rate		50 ml/min
Sampling volume		1000 ml
Heating temperature		280°C
Desorption time		8 min
Dry purge		30 ml/min, 2 min
Gas chromatography		Hewlett-Packard 5890
Column		DB-624 75 m×0.53 mm, 3 μm
Temperature program		40°C (5 min), 6°C/min, 200°C (10 min)
Carrier gas		He, 10 ml/min
Detection		
PID	Lamp	10.2 eV
	Range	10·2 ⁸
ELCD	H ₂ flow-rate	30 ml/min
	Reactor temperature	850°C
	Solvent	<i>n</i> -Propanol, 0.3 ml/min
	Range	10·2 ⁵
Dry ELCD	Air flow-rate	10 ml/min
	Reactor temperature	1000°C
	Range	10·2 ⁶

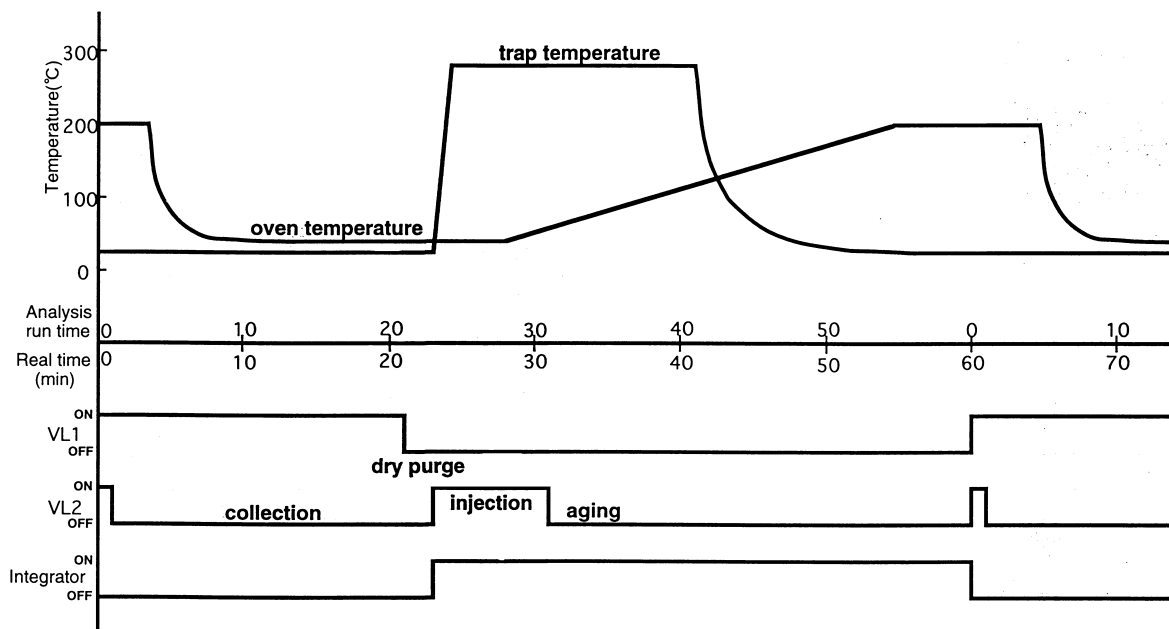


Fig. 2. Event sequencing and temperature profiles for a typical repetitive operation of the GC–PID/ELCD system.

were collected in the collection tube, then desorbed in the usual way.

2.5. Atmospheric measurement

The proposed system was used for the hourly automatic measurement of the VOCs at Hiyoshi, in the urban atmosphere of Yokohama, located about 20 km southwest of the center of Tokyo and about 10 km from the Keihin industrial zone. The air sample was collected through a PTFE tube (2 mm O.D.), outside the window of the laboratory, 5 m above ground. In order to reduce the loss of the compounds in the air sample due to adsorption onto the internal surfaces of the PTFE tube, atmospheric air was allowed to flow through the tube prior to the sampling and to pre-equilibrate. The stability of the system was checked using the standard sample of 54 VOCs at the beginning and the end of the continuous measurement. The analytical conditions were the same as those already described.

3. Results and discussion

3.1. Breakthrough volume

The breakthrough volume of the collection tube must have a large capacity, but there must also be qualitative recovery from the adsorbents by thermal desorption. The most commonly used adsorbents, such as Tenax, do not have an adequate adsorption capacity for most volatile organic compounds at ambient temperature. Even though cooling the collection tube during sampling increases the sampling efficiency, particularly for the lighter compounds, the trapping of water interferes with subsequent GC analysis. Therefore, the temperature of the collection tube was determined at ambient temperature. The collection efficiency of the collection tube was evaluated by comparing the peak area values for the substances that were determined from the tube with those of the unpurged standard gas. The measurements were carried out by sampling the standard of 54 VOCs at a flow-rate of 50 ml/min at ambient temperature. A standard containing 20 ng of each compound and a known volume of nitrogen (for purging) were allowed to flow through the collection

tube, then the GC analysis was conducted. The breakthrough volumes for the 54 volatile organic compounds were over 4 l at a flow-rate of 50 ml/min and ambient temperature (20°C), and the collection efficiencies were almost 100%. For practical purposes, a 20-min sampling time at a flow-rate of 50 ml/min was used. The collection tube had sufficient capacity to adsorb the VOCs at ambient temperature.

3.2. Recovery efficiency

Recovery efficiencies for the standards from the collection tube were determined, using a standard gas containing 20 ng/l of each compound, by changing the thermal desorption time at 280°C for the collected standards on the multibed collection tube. It was found that 2 min was sufficient to desorb all of the compounds at 280°C. The recovery efficiencies for all of the compounds were 100%, when the time allotted for thermal desorption was over 2 min at 280°C; therefore, an 8-min desorption time, including the refreshing time, was selected for use. Quantitative recovery was also confirmed by comparison with a direct injection of the liquid standards onto the capillary column.

3.3. Calibration, reproducibility and the detection limit

These specific detectors were highly sensitive for the VOCs, giving good precision and a wide linear range.

The calibration curves were automatically made by purging the standards into the collection tube using high-purity nitrogen under the given experimental conditions. The calibration curves of the 54 VOC standards were linear over the range of 2–50 ng (regression coefficient of 0.998–1.000). The detection limits of the 54 VOC standards for PID and ELCD, with a signal-to-noise ratio of three, are shown in Table 3.

The relative standard deviations of these compounds were better than 5% for a 1-l air sample.

3.4. System performance

The responses of PID and ELCD for the standard

Table 3
Detection limits for PID and ELCD of VOCs

Number	Compound	M_r	b.p. (°C)	Detection limit ($S/N=3$)				Number	Compound	M_r	b.p. (°C)	Detection limit ($S/N=3$)			
				PID		ELCD						PID		ELCD	
				(pg)	(ppt) ^a	(pg)	(ppt) ^a					(pg)	(ppt) ^a	(pg)	(ppt) ^a
1	1,1-Dichloroethene	96.9	31.7	–	–	19.8	4.6	28	Ethylbenzene	106.2	136.2	4.8	1.0	–	–
2	Methylene chloride	84.9	40.2	–	–	15.7	4.1	29	<i>m</i> -Xylene	106.2	139.1	4.3	0.9	–	–
3	<i>trans</i> -1,2-Dichloroethene	96.9	47.5	–	–	12.8	3.0	30	<i>p</i> -Xylene	106.2	138.2	4.3	0.9	–	–
4	1,1-Dichloroethane	99.0	57.3	–	–	9.4	2.1	31	<i>o</i> -Xylene	106.2	144.4	5.4	1.1	–	–
5	<i>cis</i> -1,2-Dichloroethene	96.9	60.3	7.3	1.7	13.2	3.6	32	Styrene	104.2	145.2	5.3	1.1	–	–
6	2,2-Dichloropropane	113.0	70.5	–	–	15.4	3.6	33	Bromoform	252.7	149.6	–	–	18.7	1.7
7	Bromochloromethane	129.4	67.0	–	–	9.8	1.7	34	Isopropylbenzene	120.2	152.4	5.8	1.1	–	–
8	Chloroform	119.4	61.2	–	–	9.0	1.6	35	1,1,2,2-Tetrachloroethane	167.9	147.0	–	–	17.2	2.3
9	1,1,1-Trichloroethane	133.4	73.8	–	–	10.3	1.7	36	Bromobenzene	157.0	156.2	4.1	0.6	16.1	2.2
10	Carbon tetrachloride	153.8	76.1	–	–	14.1	2.0	37	1,2,3-Trichloropropane	147.4	156.9	–	–	15.1	2.0
11	1,1-Dichloropropene	111.0	77.2	10.7	2.2	10.1	1.5	38	<i>n</i> -Propylbenzene	120.2	159.2	5.9	1.1	–	–
12	Benzene	78.1	80.1	3.9	1.1	–	–	39	2-Chlorotoluene	126.6	158.9	4.7	0.8	23.4	4.1
13	1,2-Dichloroethane	99.0	83.4	–	–	6.4	1.4	40	1,3,5-Trimethylbenzene	120.2	164.77	4.6	0.9	–	–
14	Trichloroethane	131.4	86.6	6.8	1.2	13.7	2.3	41	4-Chlorotoluene	126.6	162.0	4.8	0.9	16.9	3.0
15	1,2-Dichloropropane	130.0	96.4	–	–	11.7	2.0	42	<i>tert</i> -Butylbenzene	134.2	169.5	7.5	1.3	–	–
16	Dibromomethane	173.8	97.0	44.1	5.7	10.2	1.3	43	1,2,4-Trimethylbenzene	120.2	170.0	–	–	–	–
17	Bromodichloromethane	168.3	87.0	–	–	7.3	1.0	44	<i>sec</i> -Butylbenzene	134.2	183.4	7.0	1.2	–	–
18	<i>cis</i> -1,3-Dichloropropene	111.0	103.3	14.8	3.0	8.2	1.7	45	1,3-Dichlorobenzene	147.0	173.0	10.4	1.6	31.4	4.8
19	Toluene	92.1	110.6	4.2	1.0	–	–	46	<i>p</i> -Isopropyltoluene	134.2	177.1	9.5	1.5	–	–
20	<i>trans</i> -1,3-Dichloropropene	111.0	112.2	40.5	2.1	11.5	2.3	47	1,4-Dichlorobenzene	147.0	174.1	5.1	0.8	17.5	2.7
21	1,1,2-Trichloroethane	133.4	113.3	–	–	10.6	1.8	48	<i>n</i> -Butylbenzene	134.2	183.4	6.7	1.1	–	–
22	Tetrachloroethene	165.8	121.2	8.2	1.1	15.4	2.1	49	1,2-Dichlorobenzene	147.0	180.5	7.4	1.2	20.0	3.1
23	1,3-Dichloropropene	130.0	120.5	–	–	12.1	1.6	50	1,2-Dibromo-3-chloropropane	236.4	196.0	–	–	16.5	1.6
24	Dibromochloromethane	208.3	116.0	–	–	13.7	1.5	51	1,2,4-Trichlorobenzene	181.4	213.0	9.8	1.2	29.0	3.6
25	1,2-Dibromoethane	187.9	131.4	–	–	9.8	1.2	52	Hexachloro-1,3-butadiene	260.8	215.0	11.2	1.0	9.2	0.8
26	Chlorobenzene	112.6	132.0	4.2	0.8	39.2	7.8	53	Naphthalene	128.2	218.0	6.9	1.2	–	–
27	1,1,1,2-Tetrachloroethane	167.9	130.2	–	–	7.9	1.1	54	1,2,3-Trichlorobenzene	181.4	218.0	9.3	1.1	22.9	2.8

^a Sampling volume, 1 l.

compounds were generally stable for 24 h. The standard deviations for 20 ng of the 54 standard compounds, which were measured continuously over 24 h, were under 10% for PID and ELCD. Fig. 3 presents typical chromatograms for the 54 standard VOCs.

The analytical procedure described is potentially useful for volatile organic compounds with boiling points approximately in the range of 31–218°C.

The performance of the automated GC system was demonstrated by a daily calibration check of the system using ppb levels of the standard components. The standard deviations of the retention time for the continuous measurements were under 0.01 min for 24 runs.

3.5. Measurements of VOCs in the atmosphere

Continuous measurement of the 54 VOCs was carried out automatically for 24–48 h at a 1-h cycle using this system from December 1995 to July 1997 at Hiyoshi in the urban atmosphere of Yokohama and the field study results were obtained. Fig. 4 presents typical chromatograms for the VOCs in the atmosphere, which were obtained using this system. Good chromatographic resolution was preserved and sharp peaks were obtained for the continuous measurements. As an example, the diurnal variations in the VOCs are shown in Fig. 5 Table 4. The concentrations of benzene, ethylbenzene, *m,p*-xylene, *o*-xylene and 1,2,4-trimethylbenzene were at ppt–ppb

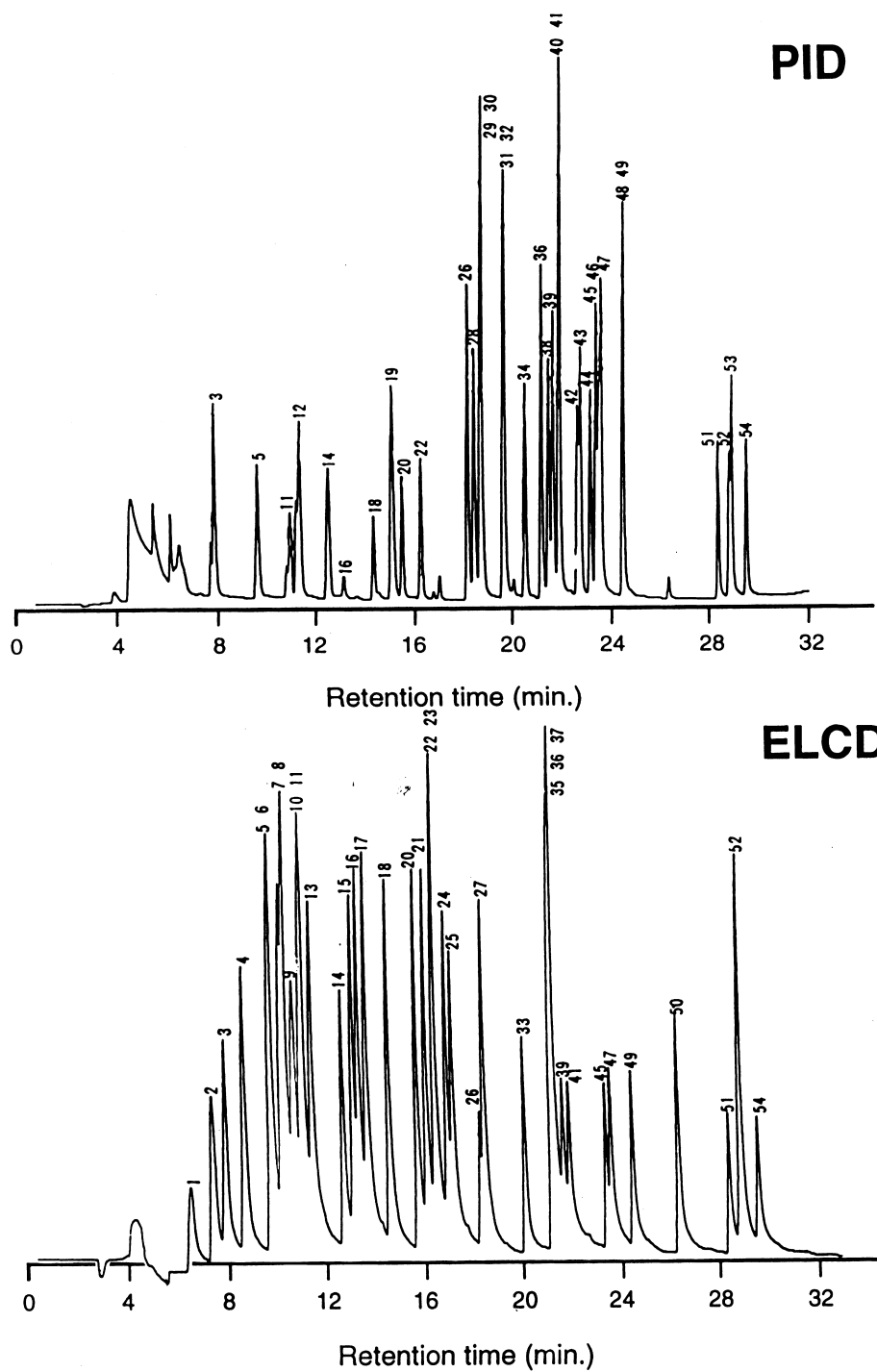


Fig. 3. Chromatograms of the standard gas containing the VOCs. For peak identification, see Table 1.

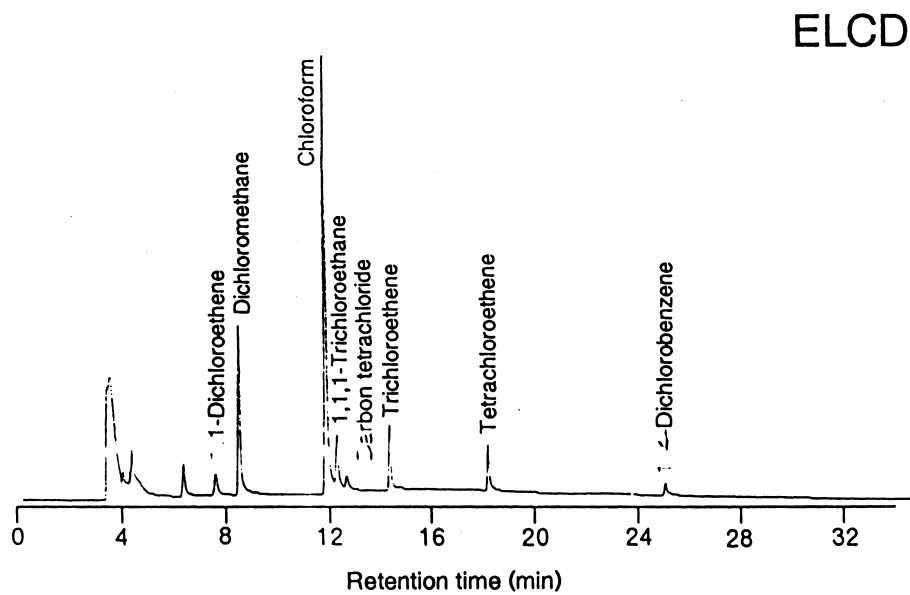
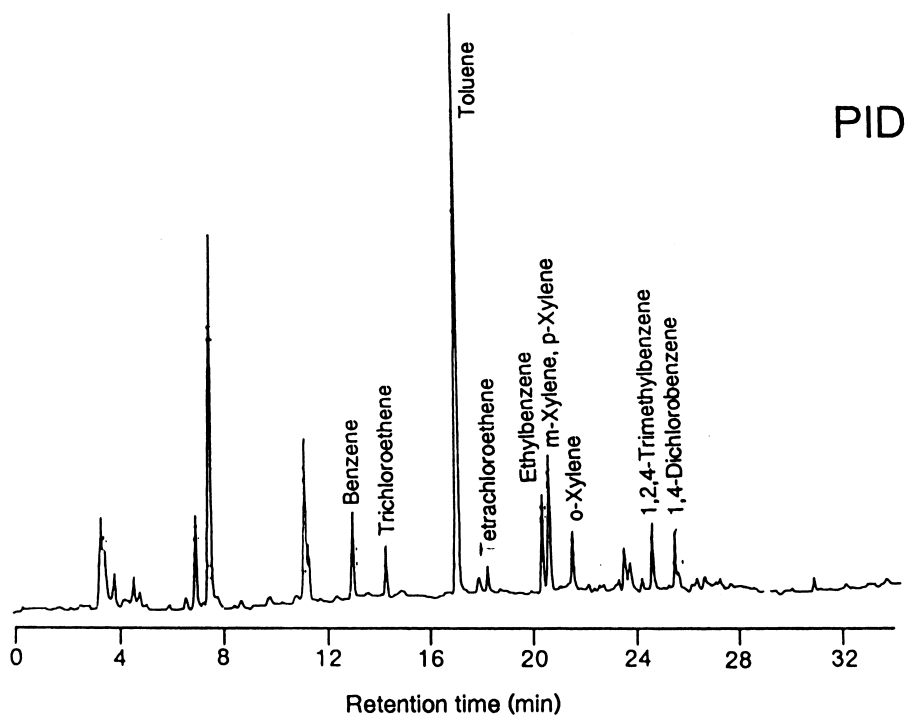


Fig. 4. Chromatograms of VOCs in the urban atmosphere in Yokohama on 13–14 December 1995. For peak identification, see Table 1.

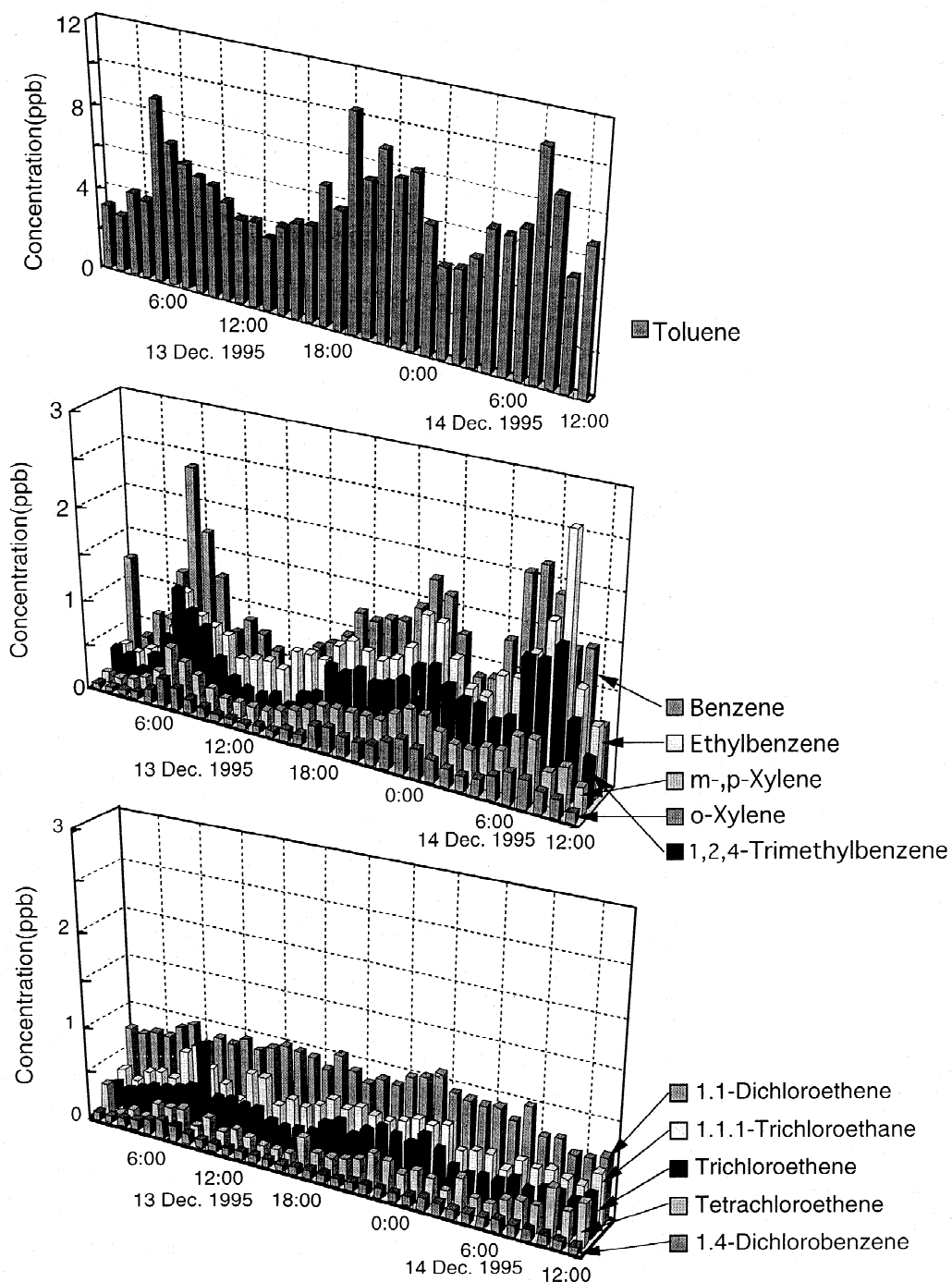


Fig. 5. Diurnal variation of VOC concentrations in the atmosphere at Hiyoshi in Yokohama on 13-14 December 1995.

Table 4
Average and range of VOC concentrations in the urban atmosphere in Yokohama on 13–14 December 1995

Compound	Average (ppb)	Range (ppb)
1,1-Dichloroethene	0.86	0.62–1.09
Methylene chloride	2.03	1.08–6.30
Chloroform	2.55	0.35–13.07
1,1,1-Trichloroethane	0.52	0.27–0.82
Carbon tetrachloride	0.45	0.25–0.68
Benzene	1.13	0.36–2.53
Trichloroethene	0.41	0.24–0.94
1,2-Dichloroethane	0.22	<1.89
Toluene	5.82	2.72–10.54
Tetrachloroethene	0.24	0.04–0.51
Ethylbenzene	0.88	0.24–2.63
<i>m</i> -Xylene, <i>p</i> -xylene	0.35	0.09–0.64
<i>o</i> -Xylene	0.18	0.05–0.37
1,2,4-Trimethylbenzene	0.66	0.16–1.56
1,4-Dichlorobenzene	0.10	0.07–0.19

levels, and the concentrations of these aromatic compounds showed similar diurnal variations. On the other hand, the concentrations of 1,1-dichloroethene, 1,1,1-trichloroethane, trichloroethene and 1,4-dichlorobenzene were at ppt levels, and were lower than those for the aromatic compounds. The precise study of the variations in these compounds will be reported elsewhere.

4. Conclusion

We have described an automated preconcentration–GC–PID–ELCD system for the continuous measurement of ambient atmospheric VOC levels.

The combination of preconcentration using a multibed collection tube and analysis with an extremely sensitive GC allows the determination of the 54 VOCs at levels as low as ppt levels for a 1-l air sample. This system has been demonstrated to be capable of measuring the diurnal variations of the 54 VOCs with a time resolution of 60 min. This sensitive, simple and affordable analytical system is effective for obtaining sequential and repetitive measurements for the continuous determination of trace levels of VOCs with a short time resolution.

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