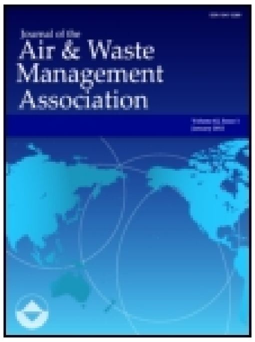

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Analysis of Complex Mixtures of Vapors in Ambient Air by Fast-Gas Chromatography

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The use of Fast-GC was investigated for the separation and analysis of mixtures of organic vapors in ambient air. Mixtures of up to 34 components were separated and total analysis times ranged from 8 to 100 seconds. Analyses were performed using both flame ionization and electron capture detectors. Up to 950 effective theoretical plates per second were produced when the flame ionization detector was used, and up to 300 per second when the electron capture detector was used. Theoretical predictions of optimal analysis conditions and of column performance matched experimental results.

Gas chromatography (GC) is one of the most widely used analytical techniques for monitoring contaminants in ambient air, especially for analysis of low and intermediate molecular weight organic vapors such as those included on the U.S. EPA list of 41 target compounds.[1] The method is popular because it is simple to use, sensitive and specific detectors are available, and the resolving power of GC systems is very high. One limitation of GC systems has been that each analysis normally takes several minutes, at a minimum. This is too long when a monitor is being used to warn of releases to the workplace, fenceline and/or community.

Starting in 1965, reports have appeared about the theory and practice of "high speed" or "fast" GC.[2–8] Recently, we have reported on the design and application of a Fast-GC system for air monitoring.[9–12] Information was given on instrument design, limits of detection for certain EPA target analytes taken individually, and the effect of changes in relative humidity. In this study, we report on the bases for choosing optimal conditions for use of Fast-GC in monitoring of complex mixtures of organic vapors in air.

Methods

The Fast-GC is based on the use of optimized components for each GC module: injector, column, detector and electronics. The injector is based on the use of a gas-cooled and electrically-heated capillary metal trap for focusing and reinjecting the sample as an extremely narrow band at the front of the column. A capacitive discharge was used for rapid heating.[13] The system design has been presented previously.[9–12]

Implications

The Fast-GC can be used to quantitatively monitor complex mixtures of organic vapors with great sensitivity and at high speed. This will provide information useful to regulators who are responsible for modeling or controlling VOC emissions, and to others who are responsible for the operation and use of VOC emission abatement systems. Because of the high speed of the system, it may be useful for monitoring changes in VOC composition and concentration as a function of rapidly changing atmospheric conditions or of location, as in use in a mobile laboratory or airplane.

A model 301 gas chromatograph (HNU Systems, Inc., Newton, Massachusetts) was modified to use both a standard HNU flame ionization detector (FID) and an HNU Systems-Nordien electron capture detector (ECD) which had a cell volume of 90 microliters.

The cold trap was mounted outside of the GC oven to permit more independent control of trap temperature. The samples were injected using a manual, six-port valve (Valco Instruments Co., Inc., Houston, Texas) fitted with a sampling loop. Loop sizes varying from 0.025 to 2 mL were used. After injecting, the sample was routed through a 50 cm long, 0.25 mm i.d. deactivated fused silica buffer column (Quadrex Corp., New Haven, Connecticut). Following the buffer column, the sample was focused on the inner wall of the cold trap tubing.

The cold trap was a 15 cm long, 0.25 mm i.d. × 0.625 mm o.d. Monel® 400 capillary tube which was cooled to −120 °C by a continuous flow of cold nitrogen gas that had passed through a copper tube immersed in liquid nitrogen. A needle valve on the cold nitrogen supply was used to adjust the trap temperature.

The frozen sample was rapidly vaporized to form a narrow injection band by running a pulse of current through the trap tubing. The current was provided by a capacitive discharge power supply which could raise the trap temperature by as much as 300 °C in less than 20 msec. A 10 to 30 second delay was used to ensure that quantitative purging of the injection loop had been accomplished before the trap heater was pulsed for injection. The computer-controlled trap heater circuit could achieve a very reliable zero-time reference for retention time measurements. Details of the inlet system design and performance characteristics have been presented elsewhere.[9–12]

All separations were performed using isothermal analysis at temperatures of 40 to 100 °C. Five, 10 and 30 meter 0.25 mm i.d. capillary columns were used with a 0.1 um bonded methyl silicone stationary phase (Quadrex). Hydrogen was used as the carrier gas for FID and operated at average linear velocities ranging from 60 to 175 cm/sec.

Hydrogen, or argon with 5 percent methane was used as the carrier gas for ECD. The velocity of argon was from 34 to 50 cm/sec and make-up gas of argon/methane was used at a flow rate of 120 ml/min.

A high-speed electrometer was developed specifically for this application by HNU Systems. Data were collected in an 80286-based personal computer which was equipped with a 12-bit A/D board (DT2801, Data Translation, Inc., Marlboro, Massachusetts). Data collection at a frequency of 200 Hz was controlled by the use of Labtech Notebook software (Laboratory Technologies Corporation, Wilmington, Massachusetts), and analysis was performed using software developed in our laboratory.

The mixtures of gas standards used in this study were obtained from the U.S. EPA (AREAL, Research Triangle Park, NC), and were delivered in Summa®-polished canisters. Those mixtures contained 41 compounds routinely analyzed in ambient air samples by the U.S. EPA Atmospheric Research and Environmental Assessment Laboratory (AREAL).

Results and Discussion

The significant advantage of Fast-GC is a 50 to 100-fold reduction in analysis time while maintaining resolution. The significant disadvantage is that all separations must be performed isothermally. Thus, it may be difficult to separate all components of a mixture if they vary widely in boiling point. This is a limitation that is shared by Fast-GC with all "traditional" GC-based multi-point air monitoring systems. However, laboratory-based GC instruments invariably are capable of performing temperature-programmed separations.

Because of this limitation (isothermal operation), it is important to consider those factors necessary for optimal operation, especially when separating components of complex mixtures. These factors include: column conditions (carrier gas velocity, column length, oven temperature) and detector operation. These are discussed below:

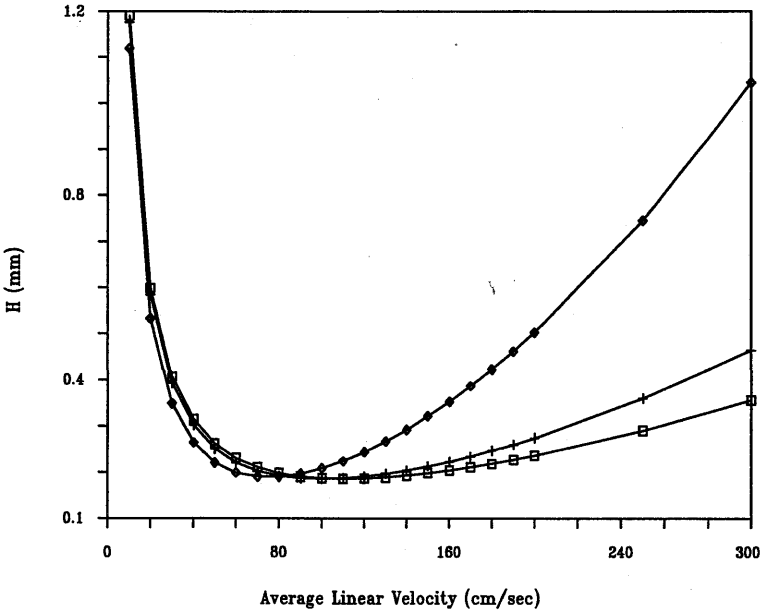

Figure 1. Relationship between H (height equivalent to a theoretical plate, in mm) and average linear carrier gas velocity (cm/sec) using hydrogen carrier gas. Key: □= 5 meter column length; + = 10 meters; ■= 30 meters.

Optimization of carrier gas velocity. The question of the relationship between carrier gas velocity and column efficiency has been well-developed.[14–16] In this study, the computer model written in our laboratory by Mouradian and Puig[17,18] was used. Figure 1 shows the results obtained with the computer model for a 0.25 mm i.d. column with a stationary phase film thickness of 0.1 micron. This combination of column diameter and film thickness was chosen as a compromise that would preserve much of the efficiency obtainable with a very small diameter capillary column, and at the same time, prevent overloading by very high concentration components frequently encountered in environmental ambient air samples.

The instrument dead-time values were chosen to be representative of those estimated for this system, as well as values reported in the literature for similar systems (about 1 ms).[9,16] A diffusion coefficient in the gas phase of 0.6 cm2/sec was used for hydrogen.[15] A liquid phase diffusion coefficient of 9 × 10–6 cm/sec was used.[19–21] The gas viscosity was estimated at 105 uP, which is characteristic of hydrogen gas at 100 °C.[22] A capacity factor of two (K = 2) was used to represent a "typical" analyte eluting in the middle of the chromatogram. Predicted optimum linear carrier gas velocities of 110, 85 and 60 cm/sec (3.2, 2.5 and 1.8 cm3/min) were obtained from the computer model for columns of 5, 10 and 30 meter lengths (Figure 1).

While these results would not be surprising to the experienced chromatographic scientist, it is important that the practitioner who uses Fast-GC for air monitoring applications also understands the use of these computer models. The choice of optimal flow rate is one of the critical steps in maintaining resolution while reducing analysis time.

Relationship of column length and resolution. Workplace or fenceline air samples taken near a single chemical process might contain only a limited number of analytes. However, a more typical situation is shown in Figure 2. In this case, the air mixture contained fourteen analytes in the low-ppm, high-ppb concentration range.

It is evident that, in order to baseline-resolve the most volatile components of the mixture (methyl chloride through trichloroethane), a 2 to 3 minute chromatographic analysis must be performed using a 30 meter column. On the other hand, if the principal components of interest are the peaks numbered "8" through "14" (carbon tetrachloride through chlorobenzene), then the separation can be accomplished in 20 seconds using a 5 meter column. Indeed, even components "3" through "7" are separated sufficiently under those conditions for a reasonable estimate of their concentration to be made.

This relationship between required separation, column length and analysis time can be more completely understood using the data in Table I, which were obtained using multiple runs of the chromatograms shown in Figure 2. Table I focuses on separation of two critical pairs of analytes: peaks "3" and "4" [1,1-dichloroethene (DCE) and 1,1,2-trichloro-1,2,2-trifluoroethane (F113)], and peaks "6" and "7" [1,2-

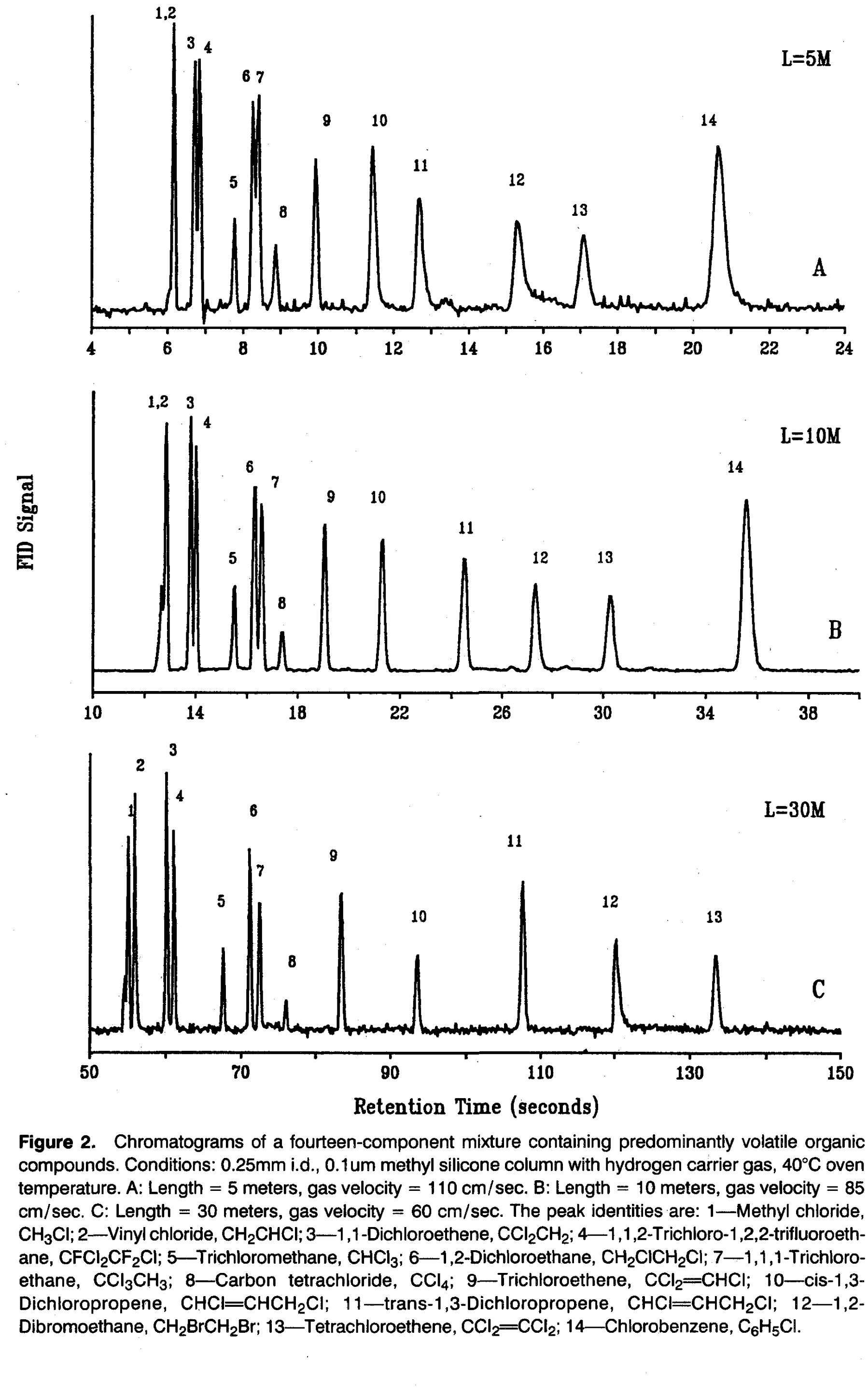

Figure 2. Chromatograms of a fourteen-component mixture containing predominantly volatile organic compounds. Conditions: 0.25mm i.d., 0.1um methyl silicone column with hydrogen carrier gas, 40°C oven temperature. A: Length = 5 meters, gas velocity = 110 cm/sec. B: Length = 10 meters, gas velocity = 85 cm/sec. C: Length = 30 meters, gas velocity = 60 cm/sec. The peak identities are: 1—Methyl chloride, CH_3Cl; 2—Vinyl chloride, CH_2CHCl; 3—1,1-Dichloroethene, CCl_2CH_2; 4—1,1,2-Trichloro-1,2,2-trifluoroethane, $CFCl_2CF_2Cl$; 5—Trichloromethane, $CHCl_3$; 6—1,2-Dichloroethane, CH_2ClCH_2Cl; 7—1,1,1-Trichloroethane, CCl_3CH_3; 8—Carbon tetrachloride, CCl_4; 9—Trichloroethene, $CCl_2{=}CHCl$; 10—cis-1,3-Dichloropropene, $CHCl{=}CHCH_2Cl$; 11—trans-1,3-Dichloropropene, $CHCl{=}CHCH_2Cl$; 12—1,2-Dibromoethane, CH_2BrCH_2Br; 13—Tetrachloroethene, $CCl_2{=}CCl_2$; 14—Chlorobenzene, C_6H_5Cl.

Table I. Resolution obtained for two critical pairs of analytes using three different column lengths.

Column length	W 1/2		Rt		Rs	
	Peak 3	Peak 4	Peak 3	Peak 4	Found	Increase
5 M	0.15	0.15	13.38	13.62	0.94	
10 M	0.16	0.17	20.55	20.96	1.32	1.404
30 M	0.26	0.28	60.06	61.11	2.29	2.436
	Peak 6	Peak 7	Peak 6	Peak 7		
5 M	0.22	0.22	16.45	16.74	0.78	
10 M	0.24	0.24	24.20	24.64	1.08	1.385
30 M	0.41	0.42	71.12	72.47	1.92	2.462

Note: Peak 3: 1,1-Dichloroethene. Peak 4: 1,1,2-Trichloro-1,2,2-trifluoroethane. Peak 6: 1,2-Dichloroethane. Peak 7: 1,1,1-Trichloroethane. W 1/2: Peak width at half height (seconds). Rt: Retention time (seconds). Rs: Resolution.

dichloroethane (DCA) and 1,1,1-trichloroethane (TCA)].

Note that for DCE and F113, the resolution of the peaks, calculated from the retention times and peak widths at half height, increases with column length from 0.94 to 1.32 to 2.29. This represents a factor of 1.404 for doubling of the column length from 5 to 10 meters, and 2.436 for increasing of the column length from 5 to 30 meters. For DCA and TCA, the factors of increase in resolution were 1.385 and 2.462 for those same length increases.

According to chromatographic theory, resolution is proportional to the square root of the column length at the optimal carrier gas flow condition. The increase in resolution when going from a 5 meter to a 10 meter column was predicted to be $\sqrt{2}$ or 1.414. The predicted increase in resolution when going from a 5 meter to a 30 meter column would be $\sqrt{6}$ or a factor of 2.45. These results represent very good agreement between theory and practice, and should guide the chromatographer in setting up the method to minimize analysis time and ensure the separation of critical pairs of analytes.

Relationship of column length and plate production. In addition to comparing the results obtained for critical pair resolution with column length to that predicted by theory, the efficiency of the system can be calculated for individual analytes. This is illustrated in Table II for the cases of carbon tetrachloride (CTC), tetrachloroethene (TCE) and mono-chlorobenzene (MCB).

The parameters most indicative of system performance are "NE" (number of effective plates) and "NE/second" or the number of effective plates "produced" per second. NE is equal to:

$$NE = 5.54\,(rt'/w_{1/2})^2$$

where:

rt' = "adjusted" retention time (retention time minus the retention time of a completely unretained peak)

$w_{1/2}$ = the peak width at half-height

In Fast-GC, a parameter of significance is how many effective plates are available in the short time of the analysis. Thus, if a 20 second analysis is performed, only a certain number of plates will be needed to provide the critical pair resolution described previously. A useful objective, given the experience with the instrumentation described in this paper, is the production of close to 1000 effective plates per second of analysis time. In Table II, it can be seen that NE/second of 778 to 953 was achieved. Had fewer been achieved using this system under these conditions, that would have been an indication of a problem with the system.

Theoretical calculations indicate that, for example, the case of TCE, NE/second should have been 981, 1301 and 805, for the 5, 10 and 30 meter column lengths. This represents a loss of 8.6 to 32 percent in rate of plate production between what was obtained in practice, and what was predicted by theory.

Choice of compromise conditions for chromatographic analysis of complex mixtures. In the example given in Figure 2, the rate of plate production was insufficient to separate the large number of volatile compounds at the start of the chromatogram. Therefore, a column longer than 5 meters was needed. In the case in which there are few very volatile compounds in a complex mixture of organic vapors in air, this may still be the case.

Figure 3 illustrates the situation in which all but one of the components of the mixture are less volatile than toluene. In this case, a 5 meter column and a 27 second analysis time may be adequate if estimated results can be accepted for the strongly overlapped components 1,1,2-trichloroethane + toluene, styrene + o-xylene, and 1,2,4-trimethylbenzene + benzyl chloride + m/p-dichlorobenzene. In many circumstances, in which a range-finding experiment is being performed, such approximations are acceptable. However, if baseline separation of all components is required, then a 30 meter column and a 100 second analysis time will be necessary. This is illustrated in Tracing C, Figure 3.

As stated before, a major limitation of the method is that temperature programming is not practical in the time scale of these analyses. Therefore, compromise conditions for complex mixtures must be met under isothermal column conditions. Given the objective of limiting analysis time to a few tens of seconds at most, optimal conditions must be set for each specific mixture. The fact that the experimental and theoretical results match closely simplifies the choosing of these optimal conditions.

Figure 4 illustrates the point that compromise conditions must be chosen to separate key components of complex mixtures. In this case, the figure illustrates a 36 component mixture of volatile organic compounds at the 0.2 ppm concentration level in air, separated using a 10 meter column. When the column temperature was 60 °C and the carrier gas velocity was 85 cm/sec, the primary tracing in the figure was obtained. Note the poor separation of the components in the first 16 seconds of the chromatogram. In order to attain adequate separation of most of the components at the beginning of the chromatogram, a column temperature of 40 °C was employed (inset Tracing). In order to obtain suitable chromatographic conditions for the last two components of the mixture (peaks 33 and 34, not shown on the tracing: 1,2,4-trichlorobenzene and hexachlorobutadiene), a column temperature of 100 °C was employed. In the tracings shown in the figure, at 40 and 60 °C, those two components were indistinguishable from the baseline. Once again, this illustrates the importance of understanding the limitations of an isothermal system, and choosing the correct compromise conditions.

Electron capture detector. For air monitoring applications, there are a significant number of analytes for which the FID will not be the detector of choice. The ECD is an alternative

Table II. The rate of effective separation plate production for three different column lengths.

	L	NE	NE/sec
CCl_4	5	3210	953
	10	4475	829
	30	18200	888
$CCl_2{=}CCl_2$	5	10581	897
	10	16225	882
	30	63507	791
C_6H_5Cl	5	11909	778
	10	19449	821

Note: L: Column length (meters). NE: Effective theoretical plates. NE/sec: Effective theoretical plates per second.

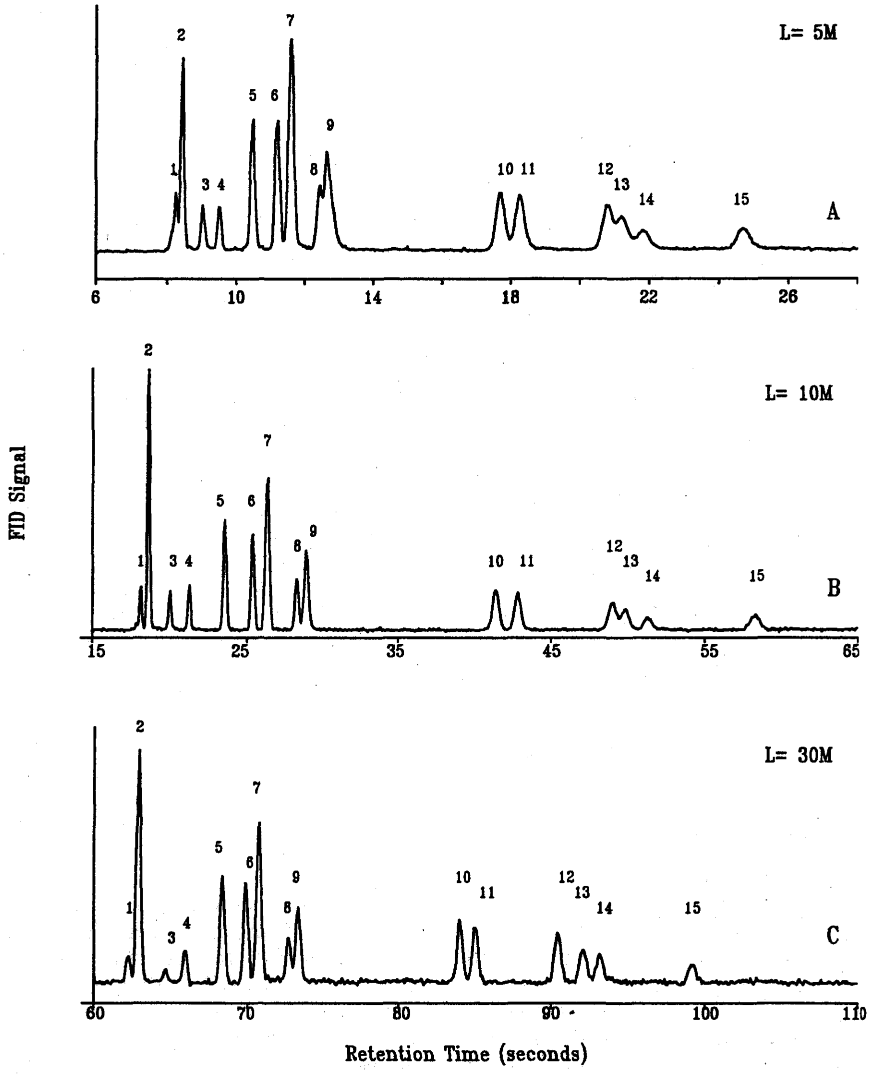

Figure 3. Chromatograms of a fifteen-component mixture, containing predominantly aromatic compounds. Conditions: 0.25mm i.d. 0.1um film methyl silicone column with hydrogen carrier gas. A: Length = 5 meters, oven temperature = 60°C, gas velocity = 110 cm/sec. B: Length = 10 meters, oven temperature = 60°C, gas velocity = 85 cm/sec. C: Length = 30 meters, oven temperature = 100°C, gas velocity = 60 cm/sec. The peak identities are: 1—1,1,2-Trichloroethane, $CH_2ClCHCl_2$; 2—Toluene, $C_6H_5CH_3$; 3—1,2-Dibromoethane, CH_2BrCH_2Br; 4—Tetrachloroethene, CCl_2CCl_2; 5—Chlorobenzene, C_6H_5Cl; 6—Ethyl benzene, $C_6H_5C_2H_5$; 7—m,p-Xylene, $(CH_3)_2C_6H_4$; 8—Styrene, $C_6H_5CHCH_2$; 9—o-Xylene, $(CH_3)_2C_6H_4$; 10—4-Ethyl toluene, $CH_3C_6H_4C_2H_5$; 11—1,3,5-Trimethylbenzene, $(CH_3)_3C_6H_3$; 12—1,2,4-Trimethylbenzene, $(CH_3)_3C_6H_3$; 13—Benzyl chloride, $C_6H_5CH_2Cl$; 14—m,p-Dichlorobenzene, $C_6H_4Cl_2$; 15—o-Dichlorobenzene, $C_6H_4Cl_2$.

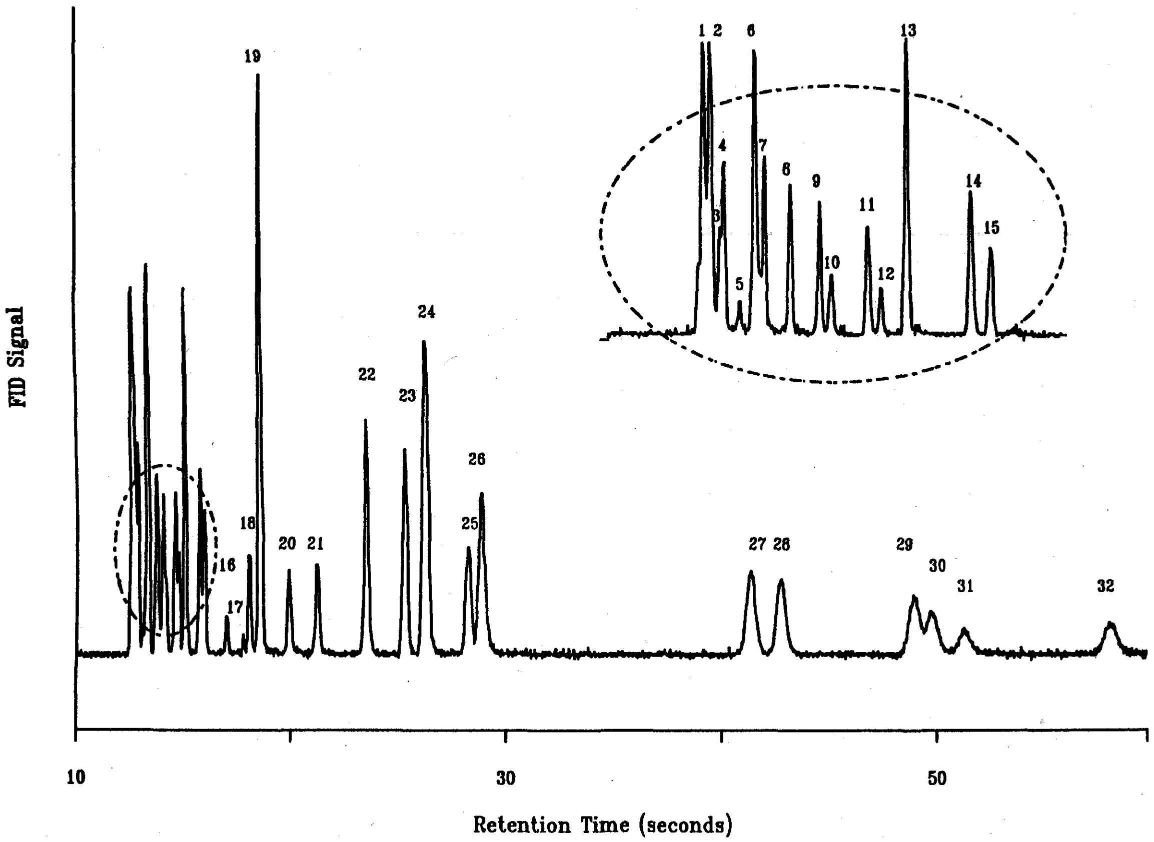

Figure 4. Chromatograms of a thirty-two component mixture of organic vapors in air. Conditions: 0.25 mm i.d., 0.1 um methyl silicone column with hydrogen carrier gas. Oven temperature is 60°C. Inset: oven temperature is 40°C. The peak identities are: 1—Methyl chloride; 2—Vinylchloride; 3—Methyl bromide; 4—Ethyl chloride; 5—Dichloromethane; 6—1,1-Dichloroethene; 7—1,1,2-Trichloro-1,2,2-trifluoroethane; 8—1,1-Dichloroethane; 9—cis-1,2-Dichloroethene; 10—Trichloromethane; 11—1,2-Dichloroethane; 12—1,1,1-Trichloroethane; 13—Benzene; 14—1,2-Dichloropropene; 15—Trichloroethene; 16—cis-1,3-Dichloropropene; 17—trans-1,3-Dichloropropene; 18—1,1,2-Trichloroethane; 19—Toluene; 20—1,2-Dibromoethane; 21—Tetrachloroethene; 22—Chlorobenzene; 23—Ethyl benzene; 24—m,p-Xylene; 25—Styrene; 26—o-Xylene; 27—4-Ethyltoluene; 28—1,3,5-Trimethylbenzene; 29—1,2,4-Trimethylbenzene; 30—Benzyl chloride; 31—m,p-Dichlorobenzene; 32—o-Dichlorobenzene; 33—1,2,4-Trichlorobenzene; 34—Hexachlorobutadiene.

detector that may be useful for compounds such as freons. The difficulty with using the ECD primarily centers around the fact that it is a "closed cell" type detector with internal "dead volume," as opposed to the FID, which is a zero volume detector.

This internal dead volume leads to peak broadening. The detector used in this study had an internal volume of 90 ul. Make-up gas is commonly used to reduce peak broadening when using closed cell detectors. Clearly, the more make-up gas that is used, the narrower the peak will get (up to a certain limit), but also the more diluted samples will be in the detector cell. Thus, the detector response will be reduced when more make-up gas is used. For this instrument configuration, a make-up gas volume of 120 cm3/min was optimal. This was also effective in eliminating peak tailing.

Even with the makeup gas, the performance of the system with the ECD did not match that with the FID. One of the reasons is that the response time of the FID electrometer was 5 msec, whereas the response time of the ECD amplifier was approximately 100 msec. This effectively limited the minimum peak width signal that can be output from the Fast-GC, and must be corrected with higher speed amplifiers. These amplifiers are being developed.

The second reason is that the argon-methane carrier gas used with the ECD will produce a less efficient separation than will hydrogen carrier gas. This is because of the higher viscosity of the argon-methane. Figure 5 illustrates the results of a separation of an 11 component mixture of halogenated organic vapors in ambient air using an argon-methane/ECD system. A visual comparison between these chromatograms and those shown in Figures 2 and 3 illustrates the loss of separating power. For an ECD, hydrogen carrier gas can be used as long as the argon-methane make-up gas is also used. For an equivalent separation, the retention times when using hydrogen carrier gas were reduced by a factor of two (Table III). As can be seen from the data in Table III, the number of plates for the critical separation of methyl chloroform and carbon tetrachloride were approximately equal. However, the rate of plate production, NE/second, is doubled when using hydrogen carrier gas. Even then, NE/second when using the ECD, is significantly lower than that obtained when using the FID.

Conclusions

In this study, the applicability of Fast-GC was tested for the analysis of components of complex mixtures of organic vapors in ambient air. The separation achieved for components of these mixtures correlated well with the separation predicted by theory.

In all cases tested, appropriate compromise conditions for separation of components could be established. This was important to the success of the method because of the limitations imposed by the requirement that isothermal conditions be used for these separations. Both FID and ECD systems were applied successfully.

These results, combined with results of a previous study in which a wide range of linearity, low limit of detection, and freedom from effects of atmospheric moisture were demonstrated, illustrate the potential utility of the method for air monitoring applications.

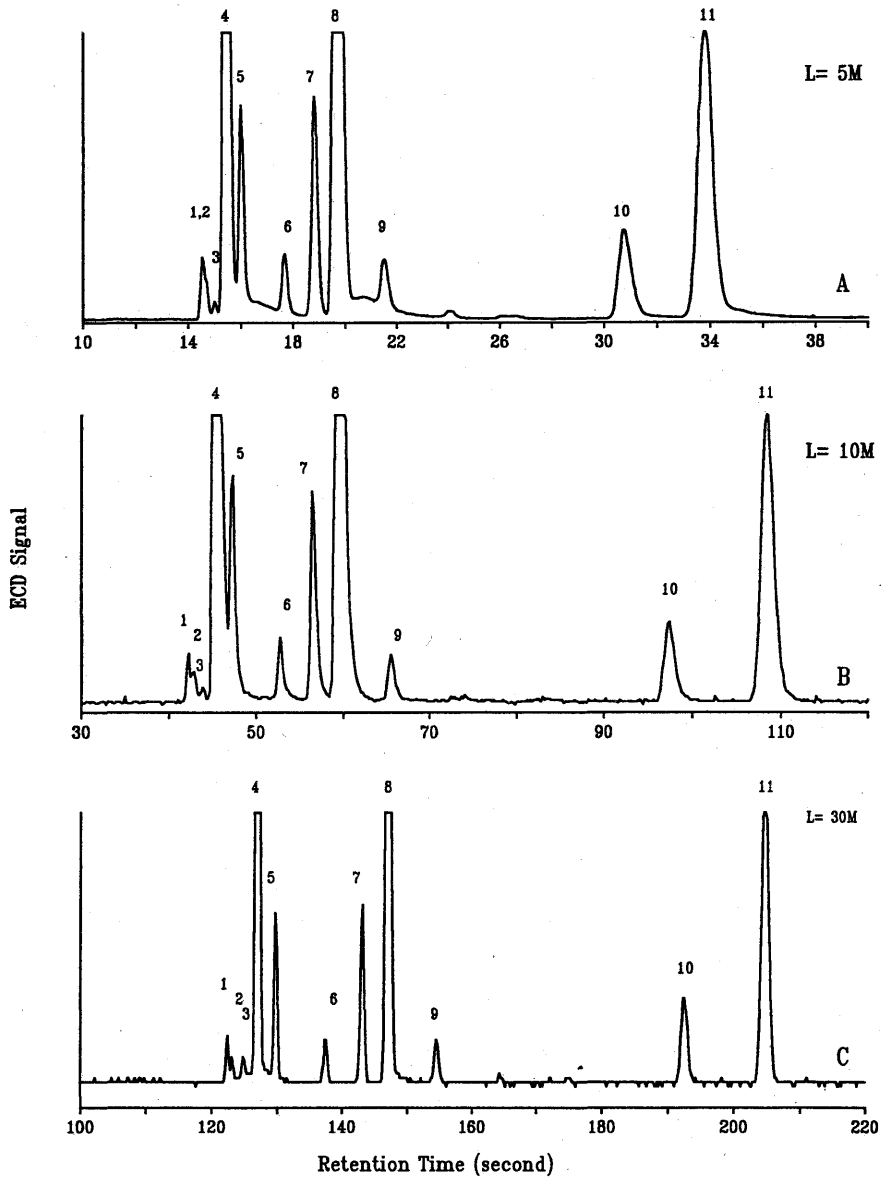

Figure 5. Chromatograms of an eleven-component mixture containing volatile organic compounds. Conditions: 0.25mm i.d., 0.1 um methyl silicone column with Argon-Methane (5%) carrier gas and make-up gas. A: Length = 5 meters, oven temperature = 40°C, gas velocity = 50 cm/sec. B: Length = 10 meters, oven temperature = 40°C, gas velocity = 40 cm/sec. C: Length = 30 meters, oven temperature = 60°C, gas velocity = 30 cm/sec. The peak identities are: 1—Dichlorodifluoromethane, CCl_2F_2; 2—1,2-Dichloro-1,1,2,2,-tetrafluoroethane, $CClF_2CClF_2$; 3—Vinyl chloride, CH_2CHCl; 4—Trichlorofluoromethane, CCl_3F; 5—1,1,2-Trichloro-1,2,2-trifluoroethane, $CFCl_2CF_2Cl$; 6—Trichloromethane, $CHCl_3$; 7—1,1,1-Trichloroethane, CCl_3CH_3; 8—Carbon tetrachloride, CCl_4; 9—Trichloroethene, CCl_2CHCl; 10—1,2-Dibromoethane, CH_2BrCH_2Br; 11—Tetrachloroethene, CCl_2CCl_2.

Table III. Resolution obtained for a critical pair of analytes using two different carrier gasses. Resolution between this critical pair was kept constant at 1.44. Conditions: Same as for Figure 8.

Analyte	CCl_3CH_3		CCl_4	
carrier gas	Ar	H_2	Ar	H_2
RT	12.56	6.62	13.08	6.9
$W_{(1/2)}$	0.24	0.12	0.26	0.125
NE	1745	1729	1872	2042
NE/second	139	261	143	296

Note: RT: Retention time (seconds). $W_{1/2}$: Peak width at half height (seconds). NE: Effective theoretical plates. NE/sec: Effective theoretical plates per second.

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