Characterization of Volatile Organic Compounds associated with Environmental Tobacco Smoke

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Abstract

In this study, a wide range of volatile organic constituents of environmental tobacco smoke (ETS) were determined using an environmental chamber, where ETS is the sole source of target compounds. ETS was generated in an environmental chamber by a number of different cigarettes, including the Kentucky reference cigarette and eight different commercial brands. More than 30 compounds were measured simultaneously for a total of twelve experimental runs. The target compounds are classified into three major classes, i.e. vapor phase ETS markers including 3-ethnylpyridine (3-EP) and nicotine, carbonyl compounds including formaldehyde, and volatile organic compounds (VOCs). The results from the chamber study were used to generate characterized ratios of selected VOCs to 3-EP, a vapor phase ETS marker. Emission factors for VOCs associated with ETS were also estimated. The characteristic ratios appeared to be generally in good agreement with published data obtained by environmental chamber studies similar to this study. This implies that the ratios may be useful for identifying and quantifying the impact of ETS as a source of target compounds in 'real world' indoor environments, which is affected by a complex mixture of multi-sources. The environmental chamber method described here provides a direct and reliable method to compare the ETS generated by different cigarettes. The method can also be applied to the simultaneous determination of many different ETS components.

Key words : Environmental Tobacco Smoke (ETS), Volatile Organic Compounds (VOCs), Nicotine, 3-Ethnlypyridine, Benzene, Environmental Chamber

1. INTRODUCTION

Environmental tobacco smoke (ETS) is defined as an aged and diluted mixture of sidetream smoke, that produced by direct combustion of a tobacco product, and exhaled mainstream smoke (Guerin et al., 1992). The term 'ETS' has often been used interchangeably with other terms, such as 'second hand smoke' , 'involuntary smoking' , and 'passive smoking' . Health significance of human exposure to ETS has been of great concern for several years since ETS is believed to contain many of the same hazardous constituents as mainstream smoke (USEPA, 1992; NRC, 1986; Wald et al., 1986; Repace and Lowrey, 1980). In early 1990's, ETS has been determined by U.S. environmental and occupational health authorities to be a human carcinogen (USEPA, 1992; NIOSH, 1991). However, the degree to which human exposure to ETS represents an adverse health effect still remains a point of contention (Lee and Thornton, 1998; Smith et al., 1992; Lebowitz, 1989; Wells, 1988; Surgeon General, 1986). This is principally because it is generally known that relative

quantities of many individual constituents present in ETS are considerably different from those found in mainstream smoke (Guerin et al., 1987), and also because it is difficult to quantitatively estimate the excess exposure due solely to tobacco smoking in environments most frequently encountered by the general population (Baker and Proctor, 1990; Eatough et al., 1989).

ETS related trace constituents of currently greatest concern in the air of indoor environments are volatile organic compounds (VOCs). Some of these constituents are known to be carcinogenic and thus remain of public health concern (Hodgson et al., 1996; Wallace et al., 1987). In general, VOCs are contributed to the indoor environment by a variety of sources, including motor vehicle exhaust, solvent evaporation, tobacco smoke, and any other combustion processes involving fossil fuels. Most studies of the trace organic constituents of ETS have not thoroughly considered the impact of such other sources, principally because of the lack of characteristic information on the occurrence of these compounds associated with ETS.

Identification and apportionment of sources of a specific constituent in indoor air is of great importance in developing regulatory/technological controls for indoor air quality management. In order to characterize air quality in a variety of indoor environments with respect to ETS, two factors must be taken into consideration: one is the absolute levels of specific constituents of ETS, and the other is the sources of these constituents. Despite the complexities and difficulties, a large numbers of studies have been undertaken to determine the chemical compositions of ETS (Nelson et al., 1998; Heavner et al., 1992; Eatough et al., 1989; Löfröth et al., 1989; Jenkins et al., 1983). Measurement of ETS requires a marker which would need to be unique for tobacco smoke and present in sufficient quantity in the smoke to be detected even at very low smoking rates. A number of criteria for a tracer or marker for ETS have been well documented in the literature (NRC, 1986). No such ideal marker exists, but nicotine has been historically used as a marker for

ETS. Nicotine can be relatively easily analyzed, and it is present in both the vapor phase and particulate phase. However, problems associated with its use as an ETS marker have been recently demonstrated by several studies (Eatough, 1989; Ogden and Maiolo, 1989). It was then suggested that 3-ethenylpyridine (3-EP), which has been known to be a major pyrolysis product of nicotine, would be a better marker of ETS constituents in the vapor phase (Hodgson et al., 1996; Heavner et al., 1992; Eatough, 1989). Heavner et al. (1992, 1996) further suggested and demonstrated a technique of ETS apportionment to assess the effect of smoking activity on specific VOC concentrations using the ratio of 3-EP to other VOCs found in ETS. For particulate phase measurements, the best marker known so far is solanesol, a tobacco specific compounds, which can be measured by HPLC or GC (Ogden and Maiolo, 1989).

The chemical characterization of ETS has frequently been carried out in environmental chambers (Nelson et al., 1998; Hodgson et al., 1996; Heavner et al., 1992; Löfröth et al., 1989). The controlled environmental chamber provide a number of advantages for determining the trace constituents of ETS. First, concentrations of ETS constituents in the chamber can be increased by generating smoke in a reproducible manner to levels that is practically impossible to be found in 'real world' settings. Second, background levels of target components present in ETS can be minimized by cleaning the air supplied to the chamber. As a result, the availability of consistent experimental conditions based on a chamber equipped with advanced facilities enables to obtain highly reliable and reproducible experimental results.

The purpose of this study is threefold: (i) to characterize the occurrence of a wide range of volatile organic constituents of ETS, including aromatics, carbonyls, and nitrogen containing compounds; (ii) to investigate the characterized ratios of selected VOCs to 3-EP, a vapor phase ETS marker, and to compare the ratios with those reported in the literature; and finally (iii) to determine average and variability of VOC emission

factors (micrograms per cigarette) for ETS. In this study, ETS was generated in an environmental chamber by a number of different cigarettes, including the Kentucky reference cigarette and eight different commercial brands.

2. EXPERIMENTAL METHODS

2. 1 Environmental Chamber

All experiments were performed in an indoor environmental chamber at the Oak Ridge National Laboratory (ORNL) in Tennessee, USA. The ORNL environmental chamber is a 27 m³ room (3 m by 3.6 m, 2.5 m height), and consists of fully automated air processing equipments for temperature, humidity, and slightly sub-ambient pressure control at air circulation flow rates up to 14 m³/min. The chamber is constructed with low-emitting materials, and its interior surface is clad with stainless steel. Air supplied to the chamber is dehumidified and then filtered through activated charcoal and high-efficiency particulate air (HEPA) filters to provide low-background concentrations of airborne contaminants. Temperature inside the chamber is controlled by heating and cooling coils located within a recirculation system, and relative humidity (RH) is controlled by addition of steam to recirculated air. The steam is generated through a reverse osmosis water purification system. The chamber has a wide access door, dual pane windows, and several access ports for instrumental cables, sampling lines, and external power.

For the experiments of this study, the chamber was operated in the 'static' mode (i.e., no mechanical ventilation). The only air exchange was due to removal of air for sampling, which was estimated to be 0.02 air exchanges per hour. Since the chamber is isolated both from the supply air system and the recirculation system, temperature and RH tended to be drift during the chamber experiments depending on the heat load inside the chamber. In order to maintain the temperature and RH in the range of 20~25°C and 45~55% during the sampling period, the temperature and RH were controlled at 20°C and 55%, respectively, prior to the start of each experiment.

2. 2 Generation of ETS

A University of Kentucky reference cigarette (1R4F) and eight commercial cigarette brands were tested for this study. The commercial cigarettes are all filtered brands in regular size (83 mm long), including four 'low-tar', two 'ultra-low-tar', and two 'full-flavor' brands. Two of the 'low-tar' brands were Asian cigarettes; one from Korea and the other from Japan. The other cigarettes were all U.S. brands. Before conducting the experiments, all cigarettes were conditioned for a week at 50~55% relative humidity and room temperature over a solution of saturated sodium bromide in a desiccator.

A total of twelve experimental runs were carried out, and details of each run are given in Table 1. In each run, six cigarettes were smoked in the chamber, except Run #3 and Run #4, in which three and nine reference cigarettes were smoked, respectively. The number of cigarettes for Run #3 and #4 were controlled to investigate the proportionality of the amount of ETS generated with the number of cigarettes smoked. Three smoking machines (ADL/II smoking system, Arthur D. Little, Inc., MA, USA) were used simultaneously for generating the smoke (i.e., two cigarettes in sequence per machine for six cigarettes smoking). The machine smoking was under a standard condition of 35 cm³ puff, 2 second duration, and one puff per minute (ISO, 1986). Each cigarette was smoked for 8~9 minutes, and approximately 5 cm in length was consumed. The sidestream smoke was emitted into the chamber to simulate ETS, while the mainstream was vented to the outside of the chamber.

The smoking machine were placed in the center of the chamber, about 1 m from the floor, surrounded by sampling equipments for ETS constituents. Since the air recirculation system of the chamber was off, it was necessary to use a fan, located in one corner of the chamber, to keep good mixing of the chamber air during the smoke generating period. After finishing the

Table 1. Operating conditions for each run of environmental chamber experiments.

Experiment	Tested cigarette	Number of cigarettes	Temp. (°C)	RH(%)	ACH (h⁻¹)
Run 1	Reference IR4F	6	20~23	48~55	0.02
Run 2	Reference 1R4F	6	20~24	48~55	0.02
Run 3	Reference 1R4F	3	20~23	49~55	0.02
Run 4	Reference 1R4F	9	20~23	48~55	0.02
Run 5	Korean - low tar	6	20~24	47~55	0.02
Run 6	Japanese - low tar	6	20~23	49~55	0.02
Run 7	USA - low tar (I)	6	20~23	48~55	0.02
Run 8	USA - low tar (II)	6	20~23	48~55	0.02
Run 9	USA - ultra low tar (I)	6	20~24	48~55	0.02
Run 10	USA - ultra low tar (II)	6	20~24	45~55	0.02
Run 11	USA - full flavor (I)	6	20~24	46~55	0.02
Run 12	USA - full flavor (II)	6	20~24	45~55	0.02

* air changes per hour

machine smoking, the chamber was left for 5 minutes before sampling started in order to allow the smoke to be completely diluted and mixed in the chamber. ETS sampling then started and continued for an additional 120 minutes. The fan was switched off during the sampling phase to avoid any substantial deposition of ETS onto the surface of the fan blades.

Once an experimental run was completed, the chamber was cleaned by supplying air at air exchange rate of 30 per hour (14 m³/min) for at least 24 hours prior to a subsequent run. Each run was preceded by a background monitoring run for 2 hours to ensure the cleanliness of the chamber.

The operating conditions for the background monitoring run were exactly same as the main run, except for the smoke generation. The background levels of any target analytes were then subtracted from the measured levels for the main run.

2. 3 Sampling and Analysis

2. 3. 1 Target Compounds

More than 30 compounds were measured simultaneously during each experimental run. These compounds can be classified into three major classes: (i) vapor phase ETS markers including 3-EP, nicotine, and myosmine; (ii) carbonyl compounds including formaldehyde and acetaldehyde, etc.; and (iii) VOCs includ-

ing BTEX and nitrogen containing compounds such as pyridine and picolines, etc. The criteria for the selection of target compounds were based on a number of factors such as the prevalence of a compound in the air of indoor environments, the frequency of a compound reported in previous researches, the occurrence of a compound found in other sources apart from ETS such as vehicle exhaust and consumer products, and the potential for adverse health effect.

2. 3. 2 Vapor Phase ETS Markers

For the measurement of vapor phase ETS markers such as 3-EP, nicotine, and myosmine, the chamber air was drawn through glass sorbent tubes containing XAD-4 resin (SKC Inc., PA, USA) using SKC personal pumps at a flow rate of 1 L/min for two hours. Two sample tubes were collected for each run, and stored in a freezer at −15°C prior to extraction. The entire content of the XAD-4 sorbent tube was transferred to a 4 ml vial, and then extracted with 2 mL of ethyl acetate containing 0.01% triethylamine and a known amount of quinoline as an internal standard. An aliquot of the extract was injected by an autosampler on a Hewlett-Packard 5890A GC system equipped with a nitrogen selective detector and a J&W DB-5 capillary column (30 m × 0.32 mm, 1.0 μm). The column oven temperature was initially 50°C for 1 min, and increased to 215°C at a rate of 10°C/min, and then

to 275°C at a rate of 20°C/min. The injector and detector temperatures were set at 220°C and 300°C, respectively. Carrier gas (He) flow was 3.5 mL/min (15 psi). Peaks for 3-EP, nicotine, and myosmine were determined with one assay and compared to standards of known concentration. 4-ethnylpyridine (4-EP) was used as a surrogate standard for 3-EP since a standard material for the 3-EP is not commercially available. Precision and method detection limits estimated for the ETS markers analyzed in this study are given in Table 2.

2. 3. 3 Carbonyl Compounds

Carbonyl compounds were collected on Sep-Pak DNPH-silica cartridges (Waters, Milford, USA) using personal pumps (Du Pont, DW, USA) at a flow rate of 1 L/min for 2 hours. Duplicate samples were obtained for each experimental run. After sampling, the cartridges were capped and stored in a refrigerator prior to extraction. The carbonyl compounds were extracted with 4 mL of acetonitrile, and then analyzed by HPLC with UV detection (Risner, 1995). The HPLC system consisted of a Rheodyne 7125 injector with 100 μL sample loop, a Shimadzu SCL-6B system controller, a LC-9A pump, a CTO-6A column temperature controller, a SPD-6AV UV detector, and a CR-4A data integrater.

Chromatographic separations were carried out using a solvent gradient elution at a flow rate of 1 mL/min on two Waters Nova-Pak C_{18} analytical columns (150 × 3.9 mm, 5 μm particle size), which were connected in series. The analytical columns, preceded by a Waters Guard-Pak column containing a C_{18} insert, were placed in a column oven at a constant temperature of 30°C. The mobile phase consisted of two parts, A (60% water, 30% acetonitrile, and 10% tetrahydofuran) and B (40% water and 60% acetonitrile). The gradient elution was programed from 100% A to 100% B over 20 min, and then followed by column washing with 100% B for 5 min. The system was equilibrated for 10 min prior to the next injection. A total of seven carbonyl compounds were analyzed in this study, and

Table 2. Precision and method detection limits for vapor phase ETS markers and carbonyl compounds.

Compound	Repeatability[a]	Method detection limit[b]		Mean duplicate precision[c]
		ng/cartridge	μg/m³	
3-EP	4.3%	20	0.17	8.1%
Nicotine	6.3%	40	0.33	7.0%
Myosmine	6.8%	·5	0.04	10.9%
Formaldehyde	2.9%	5	0.04	7.4%
Acetaldehyde	3.0%	7	0.06	7.0%
Acetone + Acrolein	4.5%	10	0.08	32.3%
Propionaldehyde	5.1%	10	0.08	22.9%
Methyethyketone	3.7%	20	0.17	26.5%
Bezaldehyde	4.6%	40	0.33	14.2%

a) Repeatability was estimated as a relative standard deviation of ten replicate analysis of a standard solution.

b) Method detection limit (MDL) was estimated as following; MDL = t $(n-1, 0.99) \times SD$, where $t(n-1, 0.99)$ is the student-t value for $n-1$ degree and 0.01 significance level, while SD is standard deviation of n replicate analysis of a standard solution at a low level concentration (n=5 in this study). The MDL in concentration unit was estimated for a typical sampling volume of $0.12 \, m^3$.

c) Mean duplicate precision is defined as $\sum_{i=1}^{n} | X_i - Y_i | / Z_i$, where X_i and Y_i are the concentrations of first and second samples of ith measurement, respectively. while Zi is the average concentration of the first and second samples (n=12 in this study).

results of analytical performance evaluation for these compounds are summarized in Table 2.

2. 3. 4 Volatile Organic Compounds

VOCs were collected on triple sorbent traps (TSTs, 6 mm OD, 76 mm × 4 mm ID stainless steel tubing) for 2 hours at a flow rate of 80 mL/min using Alpha-2 personal pumps (Du Pont, DW, USA). A total of four VOC samples were collected for each run. The traps were plugged at the upstream end of the sampling flow with approximately 15 mm of silanized glass wool and filled with 14 mm lengths of each of three carbonaceous adsorbents (Supelco, PA, USA) in order of increasing absorbency: Carbotrap C (20~40 mesh, 120 mg), Carbotrap (20~40 mesh, 50 mg), and Carbosieve S-III (60~80 mesh, 140 mg). Another 15 mm plug of silanized glass wool was inserted in the downstream end. Swagelok stainless steel caps and nuts and Vespel /Graphite ferrules (1/4″ ID) were used to seal the traps. Prior to use, each TST was conditioned by ther-

mal desorption on a manifold inside a GC oven. The traps were heated at 385°C overnight (ca. 16 hours) with highly purified helium flowing opposite to the sampling direction at a rate of $10 \sim 60$ mL/min. One trap was randomly selected from each batch of 10 traps and analyzed by a thermal desorption followed by gas chromatography/mass spectrometry (TD/GC/MS) method (Ma *et al.*, 1997) prior to standard spiking and/ or sample collection to ensure the cleanliness of the batch.

TD/GC/MS analysis was performed on a Hewlett-Packard 5972A GC/MS system. A modified injector port was used to adapt an in-house manufactured short -path desorber to transfer desorbed VOCs directly into a cryofocusing loop in a splitless mode, as shown in

Fig. 1. A male Swagelok 1/4″ nut was welded on the septum retainer nut for direct connection of TST traps. A section of aluminum clad fused silica capillary tubing (0.53 mm ID, 5 cm long) was inserted through the septum to serve as a transfer line to the glass liner in the injector port. A capillary inlet adaptor with a 1/16″ Swagelok male fitting was installed at the base of the injector port. A cryogenic loop, made with 15 cm of stainless steel tubing (0.04″ ID, 1/16″ OD), was connected to the inlet adaptor with a 1/16″ Vespel /graphite ferrule. A capillary fused silica column (Rtx - 5, 0.32 mm ID, 60 m, 5 μm film thickness) was connected to the stainless steel cryofocusing loop via a Valco 3-way ZDV switching valve. A flash heating tube furnace, capable of heating TSTs to 400°C in 1.5

Thermal Desorption/Gas Chromatography/Mass Spectrometry System
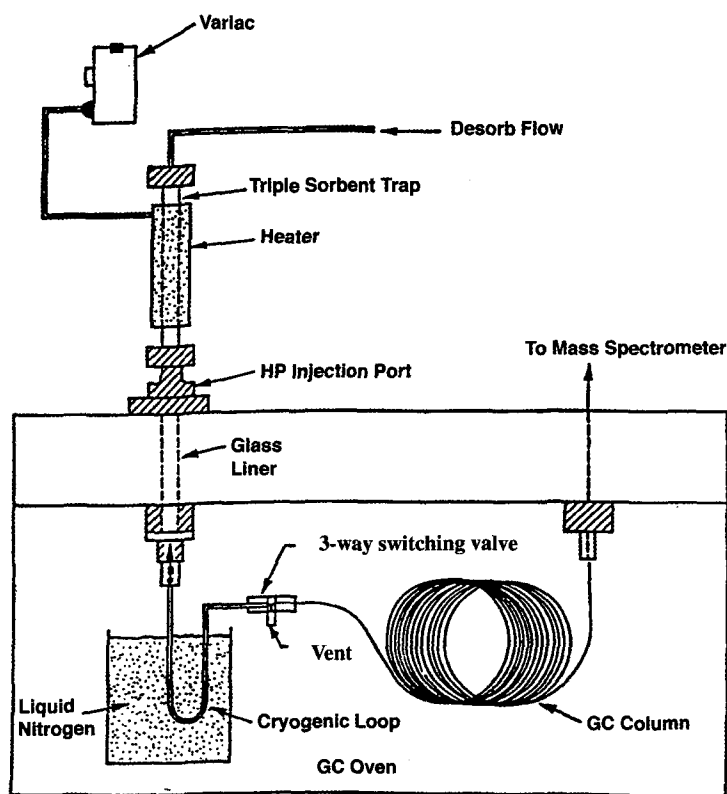

Fig 1. Schematic diagram of thermal desorption/gas chromatography/mass spectrometry system used for the analysis of VOCs.

min, was constructed from a coiled resistor cable heater (50 mm × 7 mm ID, 240 W, Watlow Cable Heater Co., MO, USA) encased in a ceramic tube using high temperature cement.

In a typical analysis, the cryogenic loop was first immersed in a liquid nitrogen bath. A TST was then placed in the tube furnace and connected to the modified septum retainer with the upstream end of the trap

nearest the injector. During the flash desorbing process, the carrier gas (He) flow was increased by switching the three-way valve to the 'vent' position, and the trap was purged at a flow rate of 50 mL/min for seven min in the direction opposite to the sampling flow. The liquid nitrogen bath was removed from the cryofocusing bath and oven temperature program (10 °C for 10 min, 5°C/min to 230°C, hold for 20 min at

Table 3. Precision, method detection limits (MDL), and characteristic ions used for identification of each target VOCs analyzed in this study.

No.	Target compound	Retention time (min)	Characteristic ions (m/z)			Repeat-ability[a]	Linearity (R)	MDL[b]		Mean multiplicate precision[c]
			1st	2nd	3rd			ng/tube	μg/m³	
1	Furan	13.62	68	39	42	10.3%	0.97~0.99	15	1.5	26.0%
2	2-Methyl-1,3-butadiene	14.27	67	53	67	8.8%	0.93~0.96	11	1.1	23.8%
3	1-Hexene	19.25	56	84	41	12.5%	0.95~0.98	11	1.1	27.2%
4	2-butanone	19.80	43	72	57	12.3%	0.95~0.99	13	1.3	20.9%
5	2-Methylfuran	20.10	82	81	53	10.5%	0.96~0.99	15	1.5	31.2%
6	2-Methyl-1,3-pentadiene	22.02	67	82	39	13.4%	0.92~0.98	6	0.6	53.0%
7	d₆-Benzene (IS)[d]	23.43	84	56	54	NA[e]	NA	NA	NA	NA
8	Benzene	23.56	78	51	52	5.5%	0.98~1.00	9	0.9	8.3%
9	1,3-Cyclohexadiene	24.02	79	80	77	7.8%	0.85~0.92	7	0.7	ND[f]
10	1-Heptene	24.91	41	56	98	6.5%	0.96~0.99	11	1.1	28.7%
11	Heptane	25.37	43	71	100	4.3%	0.95~0.99	11	1.1	50.4%
12	2,5-Dimethylfuran	25.82	96	95	81	5.5%	0.94~0.98	7	0.7	41.9%
13	Pyridine	27.83	79	52	51	12.8%	0.96~0.98	20	2.0	20.6%
14	d₈-Toluene (IS)	28.61	98	100	70	NA	NA	NA	NA	NA
15	Toluene	28.90	91	92	65	6.5%	0.97~0.99	9	0.9	7.5%
16	2-Picoline	31.06	93	66	39	14.5%	0.98~0.99	19	1.9	16.0%
17	d₁₀-Ethylbenzene (IS)	32.80	98	116	70	NA	NA	NA	NA	NA
18	3- & 4-Picolines	32.97	93	66	39	13.7%	0.97~0.99	38	3.8	20.7%
19	Ethylbenzene	33.00	91	106	77	6.3%	0.97~1.00	9	0.9	6.9%
20	m- & p-Xylenes	33.40	91	106	77	4.5%	0.99~1.00	17	1.7	6.3%
21	Styrene	34.16	104	103	78	6.7%	0.98~1.00	9	0.9	7.5%
22	o-Xylene	34.37	91	106	77	7.4%	0.98~0.99	9	0.9	9.8%
23	d₅-Bromobenzene (IS)	36.00	161	163	82	NA	NA	NA	NA	NA
24	1,3,5-Trimethylbenzene	37.14	105	120	77	12.8%	0.95~0.98	4	0.4	20.4%
25	Benzonitrile	38.07	103	76	50	5.5%	0.97~0.99	10	1.0	7.8%
26	1,2,4-Trimethylbenzene	38.26	105	120	91	10.8%	0.96~0.99	4	0.4	12.9%
27	Limonene	38.85	68	93	121	5.2%	0.96~0.99	9	0.9	6.2%
28	1-Methylnaphthalene	49.18	142	141	115	13.5%	0.99~1.00	10	1.0	24.6%

a) Repeatability was estimated as a relative standard deviation of five replicate analysis of a standard solution.

b) Method detection limit estimated as following; MDL=t(n-1, 0.99)×SD, where t(n-1, 0.99) is the student-t value for n-1 degree and 0.01 significance level, while SD is standard deviation of n replicate analysis of a standard solution at a low level concentration (n=5 in this study). The MDL in μg/m³ was estimated for a typical sampling volume of 10 l of air.

c) Mean multiplicate precision is defined as a relative standard deviation of measured levels of three or four samples collected simultaneously for each run in this study

d) internal standard

e) not applicable

f) not detected

final temperature) was initiated immediately. The three-way valve was switched back to the injection position to transfer the desorbed VOCs from the cryogenic loop to the head of the column. The flow rate of carrier gas was held at 1.0 mL/min throughout the GC run by an electronic pressure controller with vacuum compensation. The injector temperature was held at 250°C, and the GC/MS transfer line temperature was held at 280°C. Electron impact spectra were obtained

with an electron energy of 70 eV, and mass spectral data were acquired with a scan rate 1.6 scan/ sec over a mass range of 29～300 amu. The integrated area of the total ions or of a selected ion (Table 3) was obtained for each component for data manipulation. Prior to analysis of the TST samples, the traps were dried by passing approximately 2 L of dry helium through the trap, to prevent water vapor from freezing in the cryogenic loop. The sample traps were then spiked with a
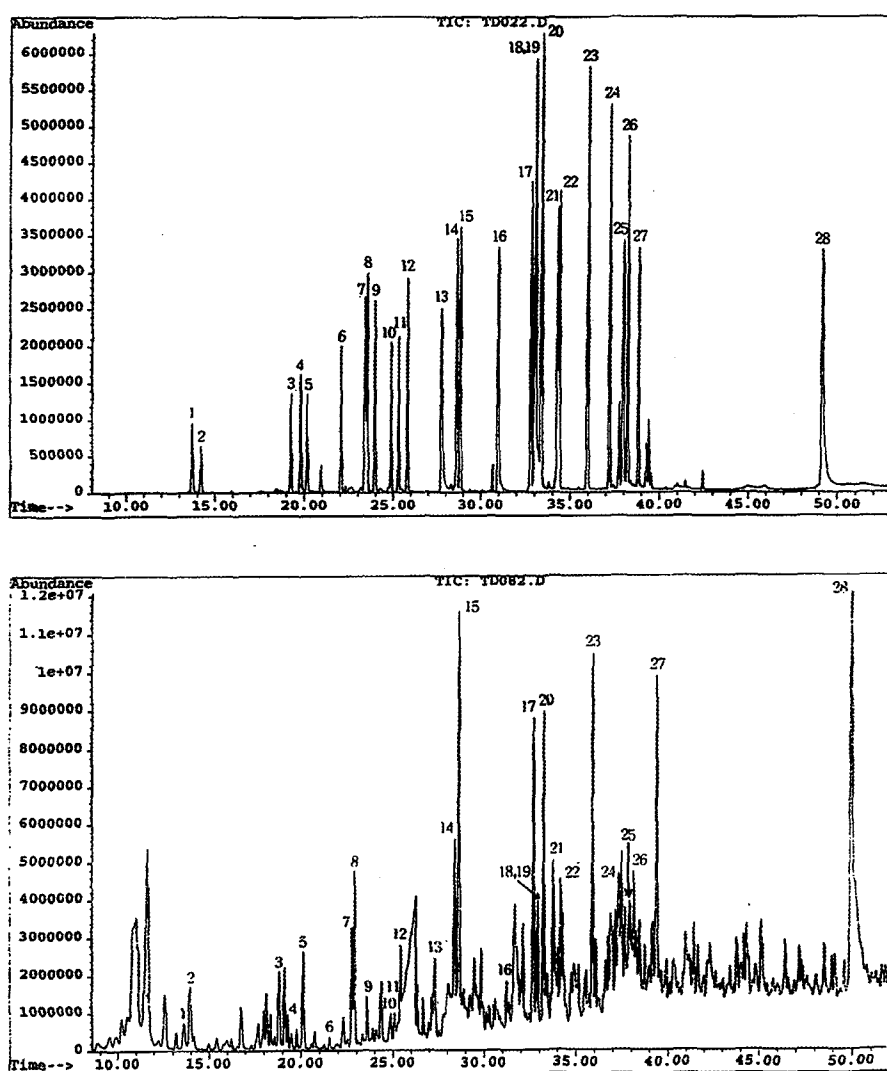

Fig 2. Typical VOC chromatograms for a standard gas mixture (above) and an ETS sample (below) analyzed by thermal desorption/GC/MS system.

vapor phase mixture of four internal standards (Table 3) for quantification of target analytes by the internal standard method. All target analytes were quantified using a validated software package (Hewlett Packard EnviroQuant™, Version C.00.02).

The methodology for VOC standard generation used in this study is similar to those described in USEPA Methods TO-1 and TO-2 (Winberry et al., 1988), except for differences in analytes and the standard bottle. Table 3 lists the gas standard mixture used for this study which was generated from a mixture of neat liquid standards in a concentration range of 67.3 mg/mL (for 1-hexene) to 126.3 mg/mL (for benzonitrile). Gas standards were generated by injecting 2 μL of neat liquid standard mixture through a Mininert™ valve into a 250 mL preheated (70°C) gas tight glass bottle. The mixture was stirred with a magnetic stirring bar and glass beads for 30 min to ensure complete vaporization of the liquid. Aliquots (0.1 mL, 0.2 mL, 0.5 mL, and 1.0 mL) of this gas standard mixture were spiked onto TSTs via a preheated (70°C) injector to obtain a concentration range of ca. 50 to 1000 ng/trap.

The injector consisted of a 1/4″ stainless steel Swagelok tee; the TST was attached to one end of the tee, while helium flowed through it from the opposite end at 200 mL/min. Using a preheated (70°C) syringe, gas standard was slowly injected into the stream of helium through a septum attached to the third end of the tee (at a 90° angle to the trap). A total of 400 mL of helium was passed through the trap after the injection to ensure even distribution of the VOCs on the trap.

Each of the TSTs used either for standard spiking or sampling was spiked in the same manner with a vapor phase mixture of four deuterated internal standards (Isotec, Inc., OH, USA) at a nominal concentration of 1000 ng/trap. A four-point calibration curve was constructed for each target analyte with concentrations ranging from ca. 50 to 1000 ng/trap. The area ratios (target analyte to internal standard) of a selected ion were measured at each concentration. A linear regression curve was fitted to the data to construct a target analyte calibration curve. Five calibration curves were

constructed for each target analyte over a period of the VOC analysis. The correlation coefficient for all of the target analytes fell in a range of 0.92 to 1.00 (Table 3), except 1,3-cyclohexadiene which was not detected in ETS samples. Typical GC/MS chromatograms for standard and ETS samples are shown in Fig. 2, while precision and method detection limits are summarized in Table 3. Performance evaluation of the TD/GC/MS method used in this study was intensively carried out in a separate study, and details can be found elsewhere (Ma et al., 1997).

3. RESULTS AND DISCUSSION

During the last three decades, a large number of studies have been conducted for the physical and chemical characterization of tobacco smoking, but they are almost all for mainstream or sidestream smoke (Smith et al., 1992). The sidestream smoke is defined as the smoke freshly emitted by the smoldering end of a cigarette between puffs, while the mainstream smoke is the smoke from the cigarette that is directly inhaled by the smoker. ETS is the smoke to which nonsmokers are exposed when they are in an indoor environment where smoking occurs. ETS is composed largely of sidestream smoke, with minor contributions from exhaled mainstream smoke and any smoke that escapes from the burning part of the tobacco during puff-drawing by the smoke. ETS differs from mainstream and sidestream smoke in that it is highly diluted and dispersed within an indoor environment, and undergoes 'againg'. As a result, physico-chemical characteristics of ETS may be substantially different from those of mainstream and sidestream smoke. Strictly speaking, the cigarette smoke tested in this study can not be regarded as the 'real ETS' since only sidestream smoke was generated and diluted in an environmental chamber. However, it is generally well known that major part of ETS (approximately 85%) is contributed by sidestream smoke (CIAR, 1995). Therefore, results obtained from experiments carried out in this study may still be useful to provide quantitative infor-

mations on the chemical characteristics of ETS, particularly with respect to volatile organic constituents.

Concentrations of vapor phase ETS markers and carbonyl compounds measured for the reference ciga-

Table 4. Concentrations (in μg/m³) of vapor phase ETS markers and carbonyl compounds measured in a 27 m³ environmental chamber for each run (see Table 1 for details of each run)

Compound	Kentucky reference cigarette (1R4F)				Commercial cigarettes							
					Low tar				Ultra low tar		Full flavor	
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12
Number of cigarette smoked	6	6	3	9	6	6	6	6	6	6	6	6
3-Ethnylpyridine	55	57	34	96	53	57	55	54	52	61	65	60
Nicotine	128	135	67	209	91	112	89	88	103	114	130	131
Myosmine	6.4	7.4	4.0	10.5	5.7	6.9	5.7	5.9	6.7	7.9	8.4	8.1
Formaldehyde	247	278	124	354	216	244	208	192	246	253	246	259
Acetaldehyde	495	430	241	615	452	488	467	428	456	462	485	460
Acetone+Acrolein	116	128	77	192	128	133	121	108	111	142	131	144
Propionaldehyde	32	33	17	46	43	37	30	32	44	28	32	28
Methylethylketone	48	50	23	74	56	54	46	36	45	60	48	57
Bezaldehyde	22	24	12	30	28	28	23	22	29	19	29	23

Note: each concentration is the mean of duplicate samples.

Table 5. Concentrations (in μg/m³) of VOCs measured in a 27 m³ environmental chamber for each run (see Table 1 for details of each run)

| VOC	Kentucky reference cigarette (1R4F)				Commercial cigarettes							
					Low tar				Ultra low tar		Full flavor	
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12
Number of cigarette smoked	6	6	3	9	6	6	6	6	6	6	6	6
Nunmber of samples collected	3	4	4	4	3	3	3	4	4	3	4	4
Furan	39(5)	34(16)	21(3)	83(20)	34(15)	45(27)	28(6)	36(7)	30(5)	48(5)	47(13)	51(8)
2-Methyl-1,3,-butadiene	276(51)	366(121)	176(15)	562(72)	349(127)	383(163)	271(58)	357(109)	342(151)	442(47)	384(77)	385(27)
1-Hexene	22(6)	24(8)	12(3)	36(12)	23(6)	26(11)	17(4)	21(3)	19(5)	25(3)	28(14)	28(5)
2-Butanone	35(12)	35(9)	18(4)	60(15)	40(3)	36(10)	25(5)	26(8)	24(3)	39(1)	39(9)	38(8)
2-Methylfuran	39(20)	32(13)	15(3)	55(12)	39(17)	51(16)	33(5)	26(14)	28(7)	43(7)	52(20)	37(5)
2-Methyl-1,3-pentadiene	1.8(0.7)	2.8(0.9)	0.9(0.9)	7.6(0.7)	1.5(1.1)	1.5(0.9)	1.4(1.1)	2.6(1.0)	2.6(0.9)	3.7(1.3)	4.4(2.1)	1.2(1.0)
Benzene	46(9)	53(2)	35(2)	82(3)	54(8)	51(3)	54(6)	46(3)	48(4)	54(3)	50(3)	61(5)
1-Heptene	12(3)	15(5)	9(4)	25(5)	7(1)	9(6)	11(2)	11(4)	11(2)	17(2)	18(7)	17(4)
Heptane	21(15)	35(18)	16(10)	53(12)	10(6)	25(10)	36(7)	51(21)	22(10)	9(5)	24(18)	24(14)
2,5-Dimethylfuran	9(4)	10(6)	4(2)	23(5)	10(6)	16(7)	12(7)	11(4)	10(3)	13(4)	19(7)	11(5)
Pyridine	69(15)	56(7)	35(3)	84(10)	50(21)	61(23)	62(2)	50(11)	46(16)	51(8)	50(12)	62(9)
Toluene	107(17)	107(6)	64(2)	151(9)	117(21)	101(2)	101(11)	91(4)	96(4)	101(9)	102(7)	108(4)
2-Picoline	21(4)	24(2)	13(2)	32(4)	17(6)	13(4)	20(4)	23(2)	18(4)	22(2)	30(3)	22(3)
3-Picoline + 4-Picoline	82(36)	88(10)	49(3)	98(11)	48(9)	50(22)	76(28)	82(18)	75(18)	70(7)	89(10)	76(7)
Ethylbenzene	28(1)	27(1)	15(2)	46(5)	23(1)	21(3)	23(3)	23(1)	21(2)	24(1)	25(2)	25(2)
m-Xylene + p-Xylene	65(7)	60(3)	37(3)	83(7)	56(3)	56(3)	58(3)	52(4)	53(3)	55(2)	57(3)	53(2)
Styrene	32(3)	29(1)	16(2)	37(5)	29(2)	24(1)	26(3)	25(1)	23(4)	26(1)	28(2)	27(1)
o-Xylene	18(2)	17(1)	9(1)	26(2)	12(2)	14(1)	14(2)	14(1)	14(2)	16(2)	16(2)	15(1)
1,3,5-Trimethylbenzene	17(7)	16(2)	8(1)	24(15)	21(7)	12(2)	11(4)	13(1)	12(1)	13(1)	14(1)	12(1)
Benzonitrile	19(2)	17(1)	11(0.5)	20(3)	18(2)	15(1)	16(1)	17(1)	16(1)	14(2)	19(2)	16(0.4)
1,2,4-Trimethylbenzene	10(3)	9(1)	5(0.4)	12(3)	9(1)	8(1)	9(1)	8(1)	8(1)	7(1)	9(1)	8(1)
Limonene	62(4)	63(2)	38(2)	86(5)	64(8)	59(3)	61(2)	56(4)	61(10)	53(1)	65(6)	54(1)
1-Methylnaphthalene	3.2(0.5)	3.1(0.2)	1.2(0.3)	5.4(1.7)	2.4(1.6)	3.3(0.3)	2.5(0.5)	2.5(0.6)	3.0(0.4)	3.1(0.7)	3.4(1.3)	3.3(0.8)

Note: number in parethesis indicate a standard deviation
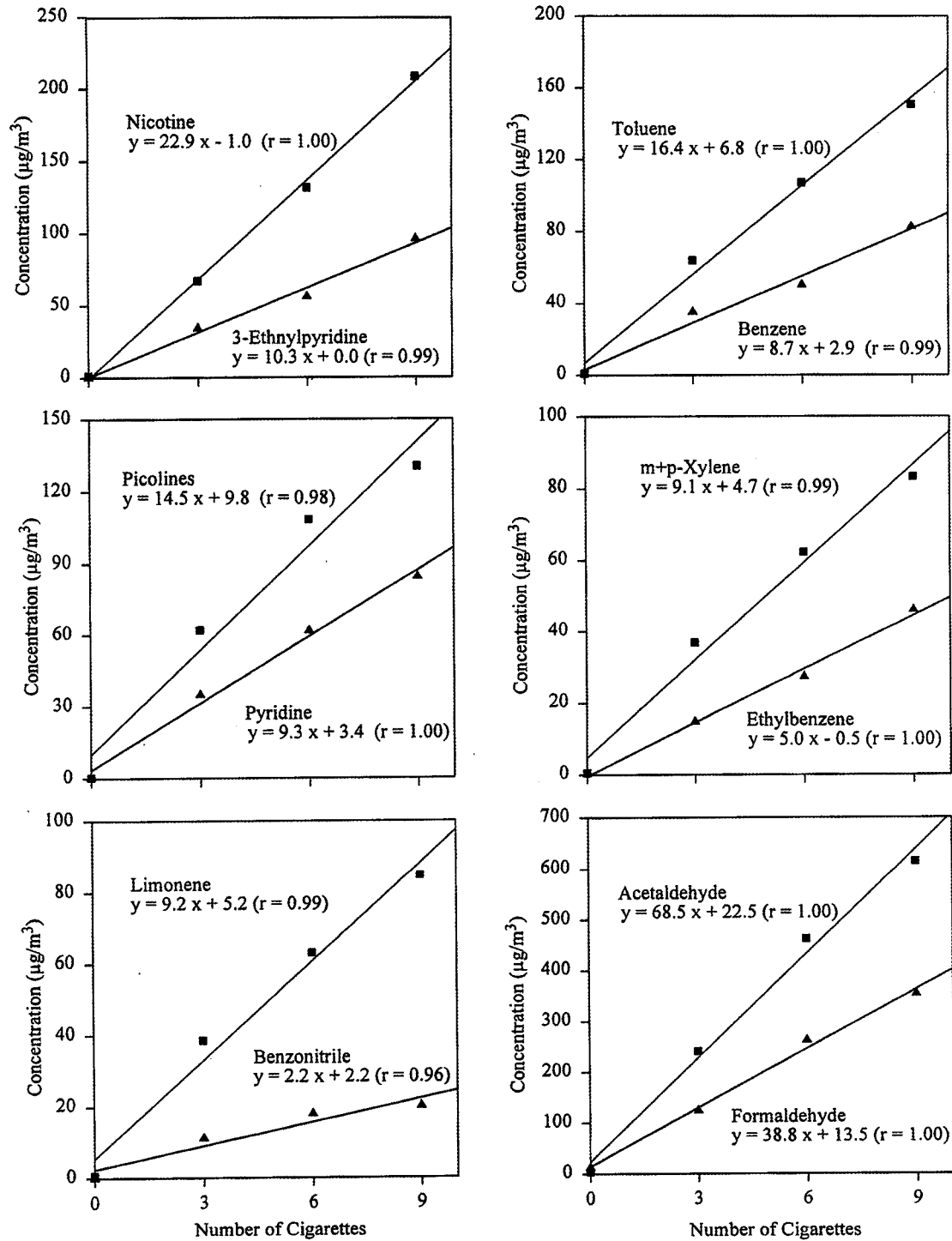
Fig. 3. Relationships between the concentrations of selected VOCs and the number of cigarettes smoked in a 27 m³ environmental chamber.

rette and commercial cigarette brands are presented in Table 4, while VOC concentrations for each run are included in Table 5. All values have been corrected for background air concentrations. Although the number of VOC samples collected for each run is four, some samples were unexpectedly lost during the thermal desorption stage due to an instrument malfunction. As a result, the number of samples analyzed were three for Run #1, #5, #6, #7, and #10. On the basis of measured levels of nicotine and 3-EP, the smoke concentrations in the chamber was approximately 100 or more times greater than is typically encounted in the 'real world' (Jenkins et al., 1996; Holcomb, 1993; Guerin et al., 1992). Such high ETS levels were necessary to ensure reliable quantitation of trace ETS components. Among the target analytes, the ETS constituent of the highest concentration was found to be acetaldehyde, followed by 2-methyl-1, 3-butadiene, and formaldehyde. It is interesting to note that there is a relatively constant ratio of benzene to toluene, approximately 1 : 2. In typical indoor and ambient air of urban areas, the benzene to toluene ratios were reported to be in the range of 1 : 4 ~ 1 : 6 (Baek et al., 1997), while a ratio of 1 : 1.5 was consistently found for the tunnel air where vehicle exhaust is the dominant source of VOCs (Lonneman, 1986). Differently from other runs, three and nine reference cigarettes were smoked for Run #3 and #4, respectively. The measured concentrations of target analytes for these runs were then plotted together with average levels of Run #1 and #2, for which six cigarettes were smoked. Results of regression analysis for selected components of ETS are shown in Fig. 3, which clearly indicates a good linearity of ETS levels depending on the number of cigarettes smoked in the chamber.

Table 6 summarized the measured concentrations of ETS constituents with respect to the type of cigarettes, i.e. reference, low-tar, ultra-low-tar, and full-flavor. Tar and nicotine are presently the common parameters used to ascribe the strength of a cigarette brand. Substantial variation in the concentrations of ETS components among commercial cigarettes has been reported previously in a study for 50 different commercial cigarette brand styles (Martin et al., 1997). However, among the more limited brand styles tested in this study, it appeared that ETS concentrations of most analytes do not differ greatly among the commercial cigarettes and also from the reference cigarette. For many of the measured components, the rank order of ETS component generation was 1R4F≒full-flavor> ultra-low-tar>low-tar cigarettes. This is somewhat an unexpected finding since ultra-low-tar cigarettes appeared to generate more ETS levels than low-tar. Such results may be associated with the fact that despite its containing less tobacco, the ultar-low-tar cigarette is more highly ventilated than the full-flavor and low-tar cigarettes (Nelson et al., 1998). As a result, the amount of tobacco burned between puffs might have been increased slightly, relative to the other commercial cigarettes. However, it was also reported that tar and nicotine levels in sidestream smoke are comparable regardless of whether they come from medium-, low-, or ultar-low-tar cigarettes (Rickert et al., 1984). Hence, it can not be concluded from table 6 that whether or not statistically significant differences existed among the different cigarettes in terms of 'tar content' for each target analyte, since each of the three groups of commercial cigarettes were consisted of different brands. In addition, the number of experimental runs were too limited to give any statistically meaningful result. For these reasons, no further attempt was made in this study to test the null hypothesis that the difference between the ETS levels for each group of four types of cigarettes (reference, low-tar, ultra-low-tar, and full-flavor) is no greater than the difference within groups.

In order to apportion sources in any complex mixture of anlytes, a marker or tracer for a given source must be identified. As summarized in a review by U.S. National Research Council (1986), a suitable tracer for quantifying ETS concentrations should be (i) unique or nearly unique to tobacco smoke; (ii) present in sufficient quantities to permit detection even at low smoking rates; (iii) similar in emission rate for a vari-

Table 6. Summary of concentrations of ETS markers and VOCs associated with tobacco smoke generated by six cigarrettes in 30 m³ chamber.

VOC	Kentucky reference cigarette* (1R4F)			Commercial cigarettes								
				Low tar			Ultra low tar			Full flavor		
	N	Mean(S.D.)	Range	N	Mean(S.D.)	Range	N	Mean(S.D.)	Range	N	Mean(S.D.)	Range
3-Ethnylpyridine	8	61(6)	54~67	8	55(2)	50~59	4	57(7)	47~63	4	63(3)	59~65
Nicotine	8	134(5)	126~151	8	95(11)	86~112	4	109(11)	94~121	4	130(2)	127~132
Myosmine	8	7.2(0.7)	6.2~8.1	8	6.1(0.6)	5.5~7.1	4	7.3(1.1)	5.9~8.5	4	8.3(0.4)	8.0~8..8
Furan	15	42(13)	23~68	13	36(15)	23~77	7	38(11)	23~51	8	49(10)	33~61
2-Methyl-1,3,-butadiene	15	347(75)	231~544	13	341(112)	210~559	7	385(122)	235~561	8	384(54)	307~482
1-Hexene	15	24(6)	16~36	13	22(7)	12~38	7	22(5)	15~29	8	28(10)	12~40
2-Butanone	15	37(9)	25~48	13	31(9)	21~45	7	30(8)	21~40	8	39(8)	28~48
2-Methylfuran	15	34(11)	22~61	13	36(15)	17~65	7	35(10)	24~51	8	44(16)	29~69
2-Methyl-1,3-pentadiene	15	2.9(1.7)	0.5~5.4	13	1.8(1.0)	0.5~3.7	7	3.1(1)	1.5~5.2	8	2.8(2)	0.5~6.8
Benzene	15	57(10)	39~74	13	51(6)	42~63	7	51(5)	42~57	8	55(7)	48~65
1-Heptene	15	16(5)	10~30	13	9.6(4)	4~18	7	14(4)	9~19	8	18(5)	9~24
Heptane	15	32(15)	10~61	13	32(20)	3~77	7	17(11)	4~36	8	24(15)	14~52
2,5-Dimethylfuran	15	11(5)	4~18	13	12(6)	5~22	7	11(3)	7~17	8	15(7)	5~25
Pyridine	15	62(10)	46~86	13	55(15)	36~79	7	48(12)	35~69	8	56(12)	36~74
Toluene	15	111(13)	89~131	13	102(14)	87~139	7	98(7)	92~111	8	105(6)	92~111
2-Picoline	15	23(3)	18~30	13	19(5)	10~26	7	20(3)	15~23	8	26(5)	18~33
3-Picoline+4-Picoline	15	83(20)	45~116	13	66(24)	33~98	7	73(13)	52~92	8	83(11)	67~97
Ethylbenzene	15	29(7)	20~53	13	23(2)	19~26	7	22(2)	19~25	8	25(2)	23~28
m-Xylene + p-Xylene	15	63(8)	48~81	13	55(4)	47~61	7	54(3)	49~57	8	55(3)	51~61
Styrene	15	29(4)	20~35	13	26(3)	22~31	7	24(3)	18~26	8	27(1)	25~29
o-Xylene	15	17(2)	14~20	13	14(2)	8~17	7	15(2)	12~18	8	16(1)	13~17
1,3,5-Trimethylbenzene	15	16(5)	9.4~30	13	14(5)	6.5~29	7	13(1)	11~13	8	13(1)	11~15
Benzonitrile	15	18(4)	11~23	13	16(2)	15~20	7	15(1)	13~17	8	17(2)	15~22
1,2,4-Trimethylbenzene	15	9(2)	6~12	13	8(1)	7~10	7	8(1)	7~10	8	9(1)	7~10
Limonene	15	65(8)	53~81	13	60(5)	51~73	7	58(8)	52~75	8	59(7)	53~73
1-Methylnaphthalene	15	3.0(0.8)	1.7~5.2	13	2.7(0.8)	0.8~3.9	7	3.0(1)	2.5~3.8	8	3.3(1)	2.5~5.3
Formaldehyde	8	252(18)	232~288	8	215(22)	188~253	4	255(19)	234~278	4	253(15)	232~268
Acetaldehyde	8	454(41)	405~499	8	459(32)	418~509	4	459(33)	426~488	4	473(21)	458~504
Acetone+acrolein	8	132(23)	97~158	8	123(45)	68~178	4	127(23)	95~147	4	138(20)	111~154
Propioaldehyde	8	33(3)	29~35	8	36(11)	26~54	4	36(11)	27~52	4	30(3)	27~34
Methylethylketone	8	48(6)	40~58	8	48(15)	26~66	4	53(15)	40~72	4	53(7)	47~62
Benzaldehyde	8	23(5)	19~26	8	25(5)	20~37	4	24(6)	18~29	4	26(4)	23~32

ety of tobacco brands; and (iv) in constant proportion to compounds in ETS that affect human health for a wide range of cigarette brands and environmental conditions. In addition to these criteria, the tracer should be easily, accurately and cost-effectively measured. Nicotine is one of the major components of ETS, and has been widely used as a marker for ETS in past studies. However, it decays very rapidly, as well as is reactive in the presence of UV light (Eatough et

al., 1989). Furthermore, nicotine can be easily deposited on fabrics and surfaces from which it is subsequently released. 3-EP is also unique to tobacco smoke, and is second only to nicotine in concentration. This compound has been evaluated to be a more suitable marker of vapor phase ETS than nicotine since it is more stable under UV irradiation, and is present in the vapor phase exclusively (CIAR, 1995). Myosmine can also be easily measured, unique to tobacco smoke, and may

be a conservative vapor phase tracer of ETS. However, it is present at only 2～7% of the vapor phase nicotine concentration of ETS (Guerin et al., 1992). Another potential marker for ETS is pyridine. Since pyridine is unreactive, it can be used as a constant against which the reactivity of compounds such as nicotine and myosmine can be measured. However, more studies should be conducted to determine if pyridine is unique to ETS or if significant concentrations due to other sources are present in indoor environments.

Based on analytical results from a number of field and chamber studies, Heavner et al. (1992, 1996) suggested a method for the ETS apportionment of selected analytes by calculating their ratios to the 3-EP concentration. The percentage of any analyte attributable to ETS might be expressed as below;

$$\% \text{ analyte due to ETS} = \frac{C_{analyte}/C_{3-EP}}{F_{analyte}/F_{3-EP}} \times 100$$

where the denominator is the ratio of any analyte to 3-EP determined from the field measurements, and the numerator is the ratio of same analyte to 3-EP determined in the chamber, where ETS is the sole source of the target analyte. Using the analytical results from the chamber experiments (Table 6), concentration ratios of target analytes to 3-EP were calculated, and the results are given in Table 7. The ratios for published values obtained by other chamber studies were also recalculated and compared with the results of this study. A ratio of nicotine to 3-EP appeared to be relatively consistent among different brands, ranging from 1.73 ～2.20, and generally in good agreement with published values (Nelson et al., 1998; Heavner et al., 1992).

Table 7. Comparison of concentration ratios of target analytes to 3-EP for various type of cigarettes tested by environmental chamber studies.

Compound (μg/m³)	Reference cigarette (1R4F)		Low tar cigarette			Ultra low tar cigarette		Full flavor cigarette	
	This study	Heavner et al. (1992)	This study	Nelson et al. (1998) 100 mm	Nelson et al. (1998) 83 mm	This study	Nelson et al. (1998)	This study	Nelson et al. (1998)
3-Ethnylpyridine	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Nicotine	2.20	N.A*	1.73	2.07	2.25	1.91	1.53	2.06	2.16
Myosmine	0.12	N.A	0.11	0.13	0.14	0.13	0.13	0.13	0.14
Benzene	0.93	0.89	0.93	1.25	0.96	0.89	1.03	0.87	1.16
Pyridine	1.02	0.81	1.00	1.11	0.96	0.84	0.85	0.89	1.12
Toluene	1.82	N.A	1.85	2.71	2.29	1.72	2.21	1.67	2.76
2-Picoline	0.38	0.24	0.35	0.36	0.31	0.35	0.23	0.41	0.36
3- & 4-Picolines	1.36	0.47**	1.20	0.75	0.69	1.28	0.63	1.32	0.78
Ethylbenzene	0.48	N.A	0.42	0.31	0.28	0.39	0.27	0.40	0.32
m- & p-Xylenes	1.03	N.A	1.00	1.01	0.91	0.95	0.84	0.87	1.01
Styrene	0.48	0.34	0.47	0.32	0.28	0.42	0.28	0.43	0.32
o-Xylene	0.28	N.A	0.25	0.21	0.19	0.26	0.19	0.25	0.22
1,3,5-Trimethybenzene	0.26	N.A	0.25	0.03	0.04	0.23	0.03	0.21	0.04
Benzonitrile	0.30	N.A	0.29	N.A	N.A	0.26	N.A	0.27	N.A
1,2,4-Trimethylbenzene	0.15	N.A	0.15	0.12	0.13	0.14	0.10	0.13	0.13
Limonene	1.07	N.A	1.09	1.54	1.25	1.02	1.00	0.94	1.40
3-Ethylpyridine	N.A	0.10	N.A	0.19	0.17	N.A	0.16	N.A	0.20
Formaldehyde	4.13	N.A	3.91	5.46	5.04	4.47	3.85	4.02	5.68
Acetaldehyde	7.44	N.A	8.35	13.64	10.75	8.05	9.21	7.51	12.52
Acetone & Acrolein	2.16	N.A	2.24	N.A	N.A	2.23	N.A	2.19	N.A
Propionaldehyde	0.54	N.A	0.65	N.A	N.A	0.63	N.A	0.48	N.A
Methylethylketone	0.79	N.A	0.87	N.A	N.A	0.93	N.A	0.84	N.A
Bezaldehyde	0.38	N.A	0.45	N.A	N.A	0.42	N.A	0.41	N.A
Air changes per hour	0.02	0.05	0.02	0.10	0.10	0.02	0.10	0.02	0.10

* N.A = not available; ** 3-picoline data only

The ratios of benzene and toluene to 3-EP were also found to be fairly constant, ranging from 0.87~0.93, 1.67~1.82, respectively. Some discrepancies in the normalized ratios of each analyte to 3-EP between different studies might be resulted from a difference in the type of cigarettes tested and also from a difference in the air exchange rate for each experiment.

Table 8 summarized the emission factors (in micrograms per cigarette smoke) determined for ETS markers, VOCs, and carbonyl compounds associated with ETS from the commercial brands and from the 1R4F

reference cigarette. The emission factors were estimated by multiplying the chamber volume to the measured concentrations of target analytes for each run, and then normalized to the number of cigarettes smoked. The average emission factors for nicotine and 3-EP for commercial cigarettes were 483±79 and 257±21 μg/cigarette, respectively, which are slightly lower than those for the reference cigarette. Multiplicate chamber experiments (n=4) were conducted for the reference cigarette, as shown in Table 1. The variabilities in the multiplicate chamber measurements for most target

Table 8. Estimated emission factors[a] (μg/cigarette) for VOCs in sidestream tobacco smoke.

VOC	Kentucky reference cigarette (1R4F)	Commercial cigarette			
		Low tar	Ultra low tar	Full flavour	Average
Number of Test	4	4	2	2	8
3-Ethnylpyridine	274 ± 27[b]	247 ± 9	256 ± 31	283 ± 13	257 ± 21
Nicotine	603 ± 22	427 ± 49	490 ± 49	585 ± 9	483 ± 79
Myosmine	32 ± 4	28 ± 3	33 ± 5	38 ± 2	31 ± 5
Furan	189 ± 58	162 ± 67	171 ± 49	220 ± 45	180 ± 40
2-Methyl-1,3-butadiene	1561 ± 337	1534 ± 504	1732 ± 549	1728 ± 243	1639 ± 220
1-Hexene	108 ± 27	99 ± 31	99 ± 22	126 ± 45	105 ± 19
2-Butanone	166 ± 40	139 ± 40	135 ± 36	175 ± 36	150 ± 31
2-Methylfuran	153 ± 49	162 ± 67	157 ± 45	198 ± 72	174 ± 44
2-Methyl-1,3-pentadiene	13 ± 8	8 ± 4	13 ± 4	13 ± 9	11 ± 5
Benzene	256 ± 45	229 ± 27	229 ± 22	247 ± 31	234 ± 17
1-Heptene	72 ± 22	43 ± 18	63 ± 18	81 ± 22	57 ± 19
Heptane	144 ± 67	144 ± 90	76 ± 49	108 ± 67	113 ± 61
2,5-Dimethylfuran	49 ± 22	54 ± 27	49 ± 13	67 ± 31	58 ± 14
Pyridine	279 ± 45	247 ± 67	216 ± 54	252 ± 54	241 ± 33
Toluene	499 ± 58	459 ± 63	441 ± 31	472 ± 27	457 ± 22
2-Picoline	103 ± 13	85 ± 22	90 ± 13	117 ± 22	94 ± 12
3- & 4-Picolines	373 ± 90	297 ± 108	328 ± 58	373 ± 49	324 ± 36
Ethylbenzene	130 ± 31	103 ± 9	99 ± 9	112 ± 9	104 ± 11
m- & p-Xylenes	283 ± 36	247 ± 18	243 ± 13	247 ± 13	246 ± 13
Styrene	130 ± 18	117 ± 13	108 ± 13	121 ± 4	116 ± 8
o-Xylene	76 ± 9	63 ± 9	67 ± 9	72 ± 4	69 ± 5
1,3,5-Trimethybenzene	72 ± 22	63 ± 22	58 ± 4	58 ± 4	65 ± 5
Benzonitrile	81 ± 18	72 ± 9	67 ± 4	76 ± 9	75 ± 5
1,2,4-Trimethylbenzene	40 ± 9	36 ± 4	36 ± 4	40 ± 4	38 ± 3
Limonene	292 ± 36	270 ± 22	261 ± 36	265 ± 31	275 ± 13
1-Methylnaphtahlene	13 ± 4	13 ± 4	13 ± 4	15 ± 4	13 ± 1
Formaldehyde	1134 ± 81	967 ± 99	1147 ± 85	1138 ± 67	1048 ± 110
Acetaldehyde	2043 ± 184	2065 ± 144	2065 ± 148	2128 ± 94	2081 ± 85
Acetone & Acrolein	594 ± 103	553 ± 202	571 ± 103	621 ± 90	573 ± 59
Propionaldehyde	148 ± 13	162 ± 49	162 ± 49	135 ± 13	155 ± 29
MEK	216 ± 27	216 ± 67	238 ± 67	238 ± 31	227 ± 36
Bezaldehyde	103 ± 22	112 ± 22	108 ± 27	117 ± 18	113 ± 17

a) The emission factors were estimated by multiplying the chamber volume (27 m³) to the measured concentrations of VOCs, and then normalized to the number of cigarettes smoked.
b) Uncertainty is one standard deviation.

analytes appeared to be less than or similar to the uncertainties estimated for the sampling and analytical method (Tables 2 and 3). This indicates that the variations in the chamber experiments introduced very little additional uncertainty. These data on the emission rate of ETS may be useful to studies on the mathematical modeling of indoor air quality management regarding tobacco smoke as a source of interest, or to studies on the assessment of human exposure to ETS in indoor environments. As an example, if the number of smoked cigarettes and the volume of indoor spaces are known, the ventilation rate needed to attain a less toxic level or a comfort level can be approximately calculated.

4. CONCLUSIONS

In this study, a wide range of organic constituents of ETS were determined using an environmental chamber where ETS is the sole source of VOCs. The environmental chamber method described here provides a direct and reliable method to compare the ETS generated by different cigarettes. The method can also be applied to the simultaneous determination of many different ETS components.

Results from the chamber experiments were used to generate characteristic ratios of selected VOCs to 3-EP, a known vapor phase ETS marker, and to estimate emission factors for ETS constituents. The characteristic ratios appeared to be generally in good agreement with published data obtained by environmental chamber studies similar to this study. This implies that the ratios may be useful for identifying and quantifying the impact of ETS as a source of target compounds in 'real world' indoor environments, which is affected by a complex mixture of multi-sources.

However, additional researches both using the chamber and in the field are further required in order to determine the characteristic ratios of VOCs to 3-EP across a large number of commercial cigarette brands, and also to demonstrate the capability of apportioning the contribution of ETS to target VOC levels in 'real

world' indoor environments, using the characteristic ratios

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