

III.

CHEMICAL AND PHYSICAL PROPERTIES OF ETS

This chapter presents the chemical and physical properties of ETS. Research shows that the combustion of tobacco products leads to the formation of thousands of particulate and gaseous constituents, each with their own physical properties. Among the various tobacco products consumed, cigarettes are the most common and therefore the main contributor to ETS (Jenkins *et al.*, 2000). According to the United States Department of Agriculture (USDA), 94 percent of the tobacco leaf production in United States was used for cigarettes (USDA, 2001). The discussion below summarizes the research, which has identified the various major components of ETS. The literature cited was produced since 1972.

A. ETS AS A COMPLEX MIXTURE

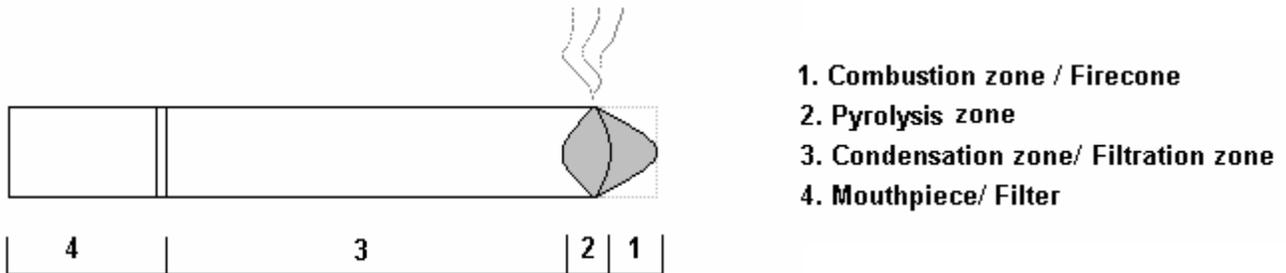
It is well established that ETS is a complex mixture of thousands of gases and particulate matter emitted by the combustion of tobacco products and from smoke exhaled by the smoker (NRC, 1986). Other minor contributors to ETS are from the smoke that escapes while the smoker inhales and some vapor-phase related compounds that diffuse from the wrapper of the tobacco product. The composition will vary depending on heat of combustion, tobacco content and additives present, and type of filter material used.

Of the thousands of substances that make up ETS, some are formed from combustion and some by atmospheric transformation. Appendix A includes a list of some of the compounds that have been detected in ETS.

Figure III-1 shows a cross section of a filtered cigarette, which illustrates the four zones in a burning cigarette. Cigarettes are comprised of a tobacco column (zone 3), which is housed in a paper, with a filter (zone 4) on one end. The combustion firecone (zone 1) and pyrolysis zone, where chemical decomposition occurs (zone 2), are located at the other end.

Figure III-1

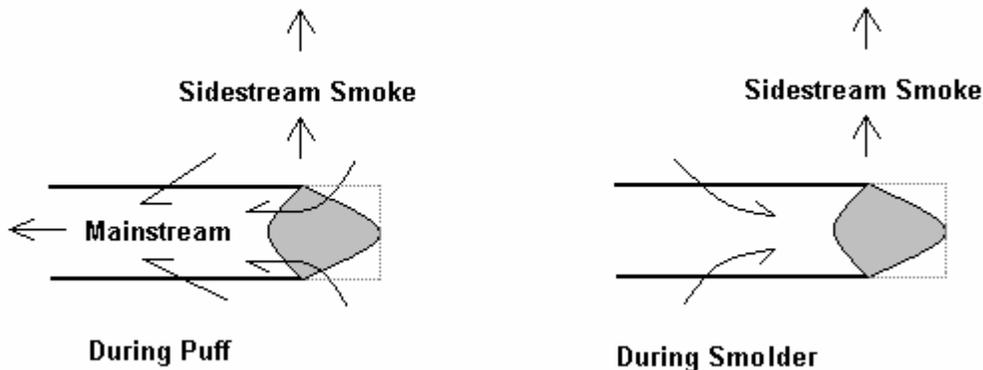
Diagram of a Filtered Cigarette



Researchers distinguish cigarette smoke as being comprised of two main components; mainstream and sidestream smoke. Figure III-2 illustrates the directions of airflow during smoking (Baker, 1980). Mainstream smoke is material that is drawn through the mouthpiece of a burning cigarette while sidestream smoke is material that is emitted from a smoldering cigarette between puffs. ETS is a combination of exhaled mainstream smoke, sidestream smoke, and compounds that diffuse through the cigarette paper.

Figure III - 2

Air Flux During Smoking



Ref: Baker, 1980

Similar chemical constituents have been found to be present in both mainstream smoke and sidestream smoke (USEPA, 1992). Differences in constituent quantities are due to variations in burning conditions, such as combustion temperature, differences in pH, and airflow rate. In general, sidestream smoke contains more ETS constituents on a per cigarette basis because more tobacco is consumed when it is smoldering between puffs, as compared to mainstream smoke.

Most tobacco crops grown in the U.S. are treated with pesticides during production. The U.S. Department of Health and Human Services has recorded the use of ethylene oxide as a common tobacco fumigant. However, pesticide residues in tobacco are likely to occur only in very low concentrations; typically as smaller, non-specific organic chemical components in ETS after decomposition during combustion (Fowles *et al.*, 2000).

1. Mainstream Smoke

Mainstream smoke is the smoke generated at the mouthpiece of a burning cigarette. More specifically, it is the exhaled smoke that was drawn in during puff and subsequently interacted with the lungs of a smoker. Modification of mainstream smoke occurs in the lungs as a result of absorption of some ETS constituents onto lung tissue, along with evaporation, particulate coagulation, and air dilution.

As a person draws in a puff from a cigarette, the airflow creates a lean burning condition with gas phase temperatures reaching 1562 °F (850 °C) at the core of the firecone and solid phase temperatures reaching 1472 °F (800 °C) at the firecone (Jenkins *et al.*, 2000). At the firecone, core temperatures are high enough to carbonize the tobacco and thus produce an oxygen deficient combustion zone. This region of the firecone contributes to the formation of constituents produced through reductive processes (Jenkins *et al.*, 2000). The gas phase and particulate matter constituents formed are cooled as the air stream passes through the tobacco column and is inhaled through the mouthpiece. The chemistry of the tobacco column changes as combustion products deposit on the remaining tobacco. The majority of ambient mainstream smoke is a result of the action of physically drawing a puff from a cigarette or cigar. However, the chemical characteristics of mainstream smoke changes as the mainstream smoke interacts in the lung, resulting in removal of some soluble organic gasses and some particulate matter.

2. Sidestream Smoke

Sidestream smoke is emitted from the burning end of a cigarette between puffs and is produced at generally lower temperatures, with a different airflow compared to mainstream smoke (Guerin *et al.*, 1987). The firecone temperatures are lower for sidestream smoke at 1112 °F (600 °C) (Jenkins *et al.*, 2000). Because the smoldering end requires airflow, a partial vacuum is created in the tobacco column, which acts to drive the flow of air from the filter end through the firecone (Jenkins *et al.*, 2000). Smoldering tobacco with lower temperatures leads to incomplete combustion, which in turn releases more quantity of compounds into the sidestream smoke as compared to mainstream smoke per cigarette (NCI, 1998).

3. Differences in the Composition of Mainstream and Sidestream Smoke

The result of the 1986 NRC report on ETS indicates that some compounds are emitted at up to more than ten times in sidestream smoke as compared to mainstream smoke (see Table III-1). Polycyclic aromatic hydrocarbons (PAHs) emissions are one example. In addition to several studies done previously measuring selected individual chemicals of PAHs in mainstream smoke, a recent study by Lodovici *et al.*, (2004) measured total PAH emissions in sidestream and mainstream smoke from different cigarettes purchased in Italy. Lodovici *et al.*, found that the PAH content in sidestream smoke is about ten fold higher compared with mainstream smoke. This study concludes that the contribution of PAHs derived from sidestream smoke is by far the most important factor in determining the PAH exposure of smokers and non-smokers.

Table III-1 also shows that ammonia emissions measured 40 - 170 times higher in sidestream smoke than in mainstream smoke. With few exceptions (e.g., hydrogen cyanide and organic acids), sidestream smoke contains greater mass emissions as compared to mainstream smoke (Jenkins *et al.*, 2000; NRC 1986). Sidestream smoke is quantitatively the major contributor to ETS since more cigarette is burned in between puffs as it smolders. The available data indicate that tobacco combustion results in the emissions of a large number of known toxic compounds and that many of these will be released at rates that are higher in sidestream than in mainstream smoke. Sidestream smoke may be more toxic per unit mass as compared to mainstream smoke (U.S. EPA, 1992).

Studies indicate that sidestream smoke mass emissions are relatively constant across various cigarette types, including filter, nonfilter, full flavor or low tar cigarettes (U.S. EPA, 1992; Jenkins *et al.*, 2000; Lodovici *et al.*, 2004; Leaderer and Hammond, 1991). Constituents of sidestream smoke are especially subject to phase changes because they are rapidly cooled and extensively diluted with ambient air (Jenkins *et al.*, 2000). Chapter VI contains a more detailed analysis of atmospheric persistence.

Table III - 1

Distribution of Constituents in Fresh, Undiluted Mainstream Smoke (MS) and Diluted Sidestream Smoke (SS) from Nonfiltered Cigarettes

Constituents	Amount in MS per Cigarette	SS/MS Ratio
Carbon monoxide	12 - 23 mg	2.5 - 4.7
Carbon dioxide	20 - 40 mg	8 - 11
Carbonyl sulfide	18 - 42 μ g	0.03 - 0.13
Benzene	12 - 48 μ g	5 - 10
Toluene	100 - 200 μ g	5.6 - 8.3
Formaldehyde	70 - 100 μ g	0.1 - ~50
Acrolein	60 - 100 μ g	8 - 15
Acetone	100 - 250 μ g	2 - 5

Constituents (cont.)	Amount in MS per Cigarette	SS/MS Ratio
Pyridine	16 - 40 µg	6.5 - 20
3-Methylpyridine	12 - 36 µg	3 - 13
3-Vinylpyridine	11 - 30 µg	20 - 40
Hydrogen cyanide	400 - 500 µg	0.1 - 0.25
Hydrazine	32 ng	3
Ammonia	50 - 130 µg	40 - 170
Methylamine	11.5 - 28.7 µg	4.2 - 6.4
Dimethylamine	7.8 - 10 µg	3.7 - 5.1
Nitrogen oxides	100 - 600 µg	4 - 10
<i>N</i> -Nitrosodimethylamine	10 - 40 ng	20 - 100
<i>N</i> -Nitrosodiethylamine	ND - 25 ng	< 40
<i>N</i> -Nitrosopyrrolidine	6 - 30 ng	6 - 30
Formic acid	210 - 490 µg	1.4 - 1.6
Acetic acid	330 - 810 µg	1.9 - 3.6
Methyl chloride	150 - 600 µg	1.7 - 3.3
Particulate matter	15 - 40 mg	1.3 - 1.9
Nicotine	1 - 2.5 mg	2.6 - 3.3
Anatabine	2 - 20 µg	< 0.1 - 0.5
Phenol	60 - 140 µg	1.6 - 3.0
Catechol	100 - 360 µg	0.6 - 0.9
Hydroquinone	110 - 300 µg	0.7 - 0.9
Aniline	360 ng	30
2-Toluidine	160 ng	19
2-Naphthylamine	1.7 ng	30
4-Aminobiphenyl	4.6 ng	31
Benz[a]anthracene	20 - 70 ng	2 - 4
Benzo[a]pyrene	20 - 40 ng	2.5 - 3.5
Cholesterol	22 µg	0.9
γ-Butyrolactone	10 - 22 µg	3.6 - 5.0
Quinoline	0.5 - 2 µg	8 - 11
Harman	1.7 - 3.1 µg	0.7 - 1.7
<i>N</i> '-Nitrososonronicotine	200 - 3000 ng	0.5 - 3
NNK	100 - 1000 ng	1 - 4
<i>N</i> -Nitrosodiethanolamine	20 - 70 ng	1.2
Cadmium	100 ng	7.2
Nickel	20 - 80 ng	13 - 30
Zinc	60 ng	6.7
Polonium-210	0.04 - 0.1 pCi	1.0 - 4.0
Benzoic acid	14 - 28 µg	0.67 - 0.95
Lactic acid	63 - 174 µg	0.5 - 0.7
Glycolic acid	37 - 126 µg	0.6 - 0.95
Succinic acid	110 - 140 µg	0.43 - 0.62

Source: NRC (1986).

Note: A ratio greater than 1 means that more of a substance is released in SS than in MS.

B. GAS PHASE COMPONENTS IN ETS

Experimental studies have found that cigarette smoke constituents are distributed between the particle phase and gas phase. The proportion of particle to gas components depends on the environmental conditions that affect the individual chemical constituent's volatility and solubility. This proportion could also be affected by conditions at the time of the sample collection and on the approach used for sampling and analysis. According to Pritchard *et al.* (1988), about 70 percent of particulate ETS evaporates into the gas phase as smoke is diluted and aged in the air. Although it is difficult to quantify because of differences in individual breathing and smoking pattern, some amount of gas phase ETS is deposited in the lung due to diffusion of gas (Pritchard *et al.*, 1988; Hiller *et al.*, 1982).

Some gas phase constituents are formed during tobacco combustion and are deposited downstream of the combustion zone in the tobacco column by filtration and condensation. Those components become part of the fuel for subsequent puffs as the firecone region advances along the tobacco column (Guerin *et al.*, 1987; Jenkins *et al.*, 2000). These processes result in the generation of some chemical constituents found in tobacco smoke that were not originally present in the tobacco plant (Ogden and Jenkins, 1999). Table III-2 shows some of the gas phase constituents, which have been detected in ETS and have known health impacts. There are other gaseous components of ETS that exhibit health impacts not categorized in Table III-2, such as carbon monoxide and nitrogen oxides that have effect on respiratory function and further contribute to tobacco related respiratory disease.

Table III - 2

Gas Phase Components in ETS with Known Health Effects

Constituent	TAC^{1/}	Prop 65^{2/}	IARC Class^{3/}	U.S. EPA Class^{4/}	Non-Cancer Health Effects^{5/}
1,3-Butadiene	Yes	Yes		B2	irritant ^{6/} , neurological effects
Acetaldehyde	Yes	Yes	2B	B2	irritant, dermatitis
Acetone				D	irritant, dizziness
Acetonitrile	Yes			D	irritant, cause vomiting
Acrolein	Yes		3	C	irritant, pulmonary edema
Benzene	Yes	Yes	1	A	CNS ^{7/} depressant, nausea
Carbon monoxide		Yes			headache, dizziness
Carbonyl sulfide	Yes				irritant, CNS depressant
Ethyl benzene	Yes			D	irritant, CNS depressant
Formaldehyde	Yes	Yes	2A	B1	irritant, induce asthma
Hydrazine	Yes	Yes			hepatotoxic, dermatitis
Methanol	Yes				neurotoxicant, irritant
Methyl chloride	Yes	Yes		D	CNS depressant, fatigue
N-Nitrosodiethylamine		Yes	2A	B2	
N-Nitrosodimethylamine	Yes	Yes	2A	B2	causes liver damage
N-Nitrosopyrrolidine	Yes	Yes	2B	B2	
Pyridine		Yes			irritant, dizziness
Styrene	Yes		2B		CNS depressant, irritant
Toluene	Yes	Yes		D	CNS depressant, irritant

Sources: NRC (1986); OEHHA (1997); CARB (1997).

Notes: 1/ Substances identified as Toxic Air Contaminants by California Health and Safety Code section 39655.

2/ Chemicals listed under Proposition 65 are known to the State to cause cancer or reproductive toxicity (California Health and Safety Code section 25249.5 *et seq.*).

3/ International Agency for Research on Cancer (IARC) Classification: 1-carcinogenic to humans; 2A-probably carcinogenic to humans with sufficient animal and inadequate or no human evidence; 2B-possible carcinogenic to humans with limited animal and no human evidence; 3-not classifiable as to its carcinogenicity to humans.

4/ U.S. EPA classification: A-human carcinogen; B1-probable human carcinogen with sufficient animal and limited human evidence; B2-probable human carcinogen with sufficient animal and inadequate or no human evidence; C-possible human carcinogen; D-not classifiable as to human carcinogenicity.

5/ Non-cancer health effects information from the Toxic Air Contaminant Identification Summaries List – September 1997 (CARB, 1997)

6/ "Irritant" may be classified as an eye, respiratory, and/or skin irritant

7/ CNS – central nervous system

C. PARTICULATE MATTER COMPONENTS IN ETS

ETS particles have been measured under various conditions and techniques by many researchers in the past. The relevance of particle size and composition to toxicological and epidemiological studies has prompted researchers to devote much attention to ETS particulate matter. ETS particles have been generally found to fall in the range of particles 2.5 µm or less.

Among the various studies reviewed by staff, it was apparent that ETS particle measurement is significantly affected by the test method used. For example, Jenkins *et al.* (2000) reported a particle size distribution, collected on standard Cambridge glass fiber filters, with a particle size of 0.2 μm or larger. In comparison, NRC (1986) measured a particle size of 0.1 μm or larger. The portion of the smoke that passed through a glass fiber filter that traps particles with a diameter of 0.1 μm or larger, was designated as the gas phase. Hence, the qualitative and quantitative composition of particulate phase to gas phase may vary depending on the specific sample condition, trapping systems, and analytic methods applied to characterize the mixture of ETS constituents (NRC, 1986; Ogden and Jenkins, 1999).

In general, highly concentrated mainstream smoke has constituents preferentially distributed in the particle phase region (Jenkins *et al.*, 2000). However, as the smoke ages and becomes diluted in ambient air, a large mass fraction of smoke particles evaporate to the vapor phase (Pritchard *et al.*, 1988). Table III-3 lists the particulate phase components found in ETS with known health effects. Besides the information presented in Table III-3, there are other adverse health effects associated with short and long term exposure to $\text{PM}_{2.5}$ and ultrafine particles, such as asthma and other respiratory diseases.

Table III - 3

Components found in ETS Particulate Matter with Known Health Effects

Constituent	TAC ^{1/}	Prop 65 ^{2/}	IARC Class ^{3/}	U.S. EPA Class ^{4/}	Non-Cancer Health Effects ^{8/}
2-Naphthylamine		Yes	1		irritant ^{9/} , dizziness
2-Toluidine	Yes	Yes	2B		CNS ^{10/} depressant
4-Aminobiphenyl	Yes	Yes	1		hematuria, lethargy
Aniline	Yes	Yes	3	B2	methemoglobinemia
Arsenic (inorganic)	Yes	Yes	1	A	hemolysis, neuropathy
Benz[a]anthracene	Yes	Yes	2A	B2	
Benzo[a]pyrene	Yes	Yes	2A	B2	dermatitis, irritant
Cadmium	Yes	Yes	2A	B1	bronchiolitis, irritant
Catechol	Yes		2B		methemoglobinemia
Chromium VI	Yes	Yes	1	A	renal toxicity, hemolysis
Dibenzo[a,i]pyrene	Yes	Yes	2B		
Dibenzo[a,l]pyrene	Yes	Yes	2B		
Hydroquinone	Yes		3		CNS excitation, tinnitus
Lead	Yes	Yes	2B/3 ^{5/}	B2	affects CNS, depression
N'-Nitrosornicotine		Yes	2B		
Nickel	Yes	Yes	1	A	immune alterations, irritant
Nicotine ^{6/}		Yes			
N-Nitrosodiethanolamine		Yes	2B	B2	
NNK ^{7/}		Yes	2B		
Phenol	Yes		3	D	cardiac arrhythmias
Quinoline	Yes	Yes		B2	irritant, nausea, coma

Ref: NRC (1986); OEHHA (1997); CARB (1997).

Notes: 1/ Substances identified as Toxic Air Contaminants by California Health and Safety Code section 39655.

2/ Chemicals listed under Proposition 65, known to cause cancer or reproductive toxicity (California Health and Safety Code section 25249.5 *et seq.*).

3/ International Agency for Research on Cancer (IARC) Classification: 1-carcinogenic to humans; 2A-probably carcinogenic to humans; 2B-possible carcinogenic to humans; 3-not classifiable as to its carcinogenicity to humans.

4/ U.S. EPA classification: A-human carcinogen; B1 probable human carcinogen with sufficient animal and limited human evidence; B2-probable human carcinogen with sufficient animal and inadequate or no human evidence; C-possible human carcinogen; D-not classifiable as to human carcinogenicity.

5/ Inorganic lead – 2B; organolead - 3

6/ Also found in gaseous form.

7/ NNK: 4-(N-methyl-N-nitrosamino)-1-(3-pyridyl)-1-butanone.

8/ Non-cancer health effects information from the Toxic Air Contaminant Identification Summaries List – September 1997 (CARB, 1997)

9/ "Irritant" may be classified as an eye, respiratory, and/or skin irritant

10/ CNS – central nervous system

1. ETS Particle Size and Distribution

Virtually all ETS particulate is comprised of respirable suspended particles (RSP). Various researchers define RSP differently. For example, occupational researchers define RSP as PM₄ or less. Likewise, more conservative researchers have defined RSP as PM₁₀ or PM₁₅. However, for purpose of this report, we consider most ETS particles to fall under PM_{2.5}, which are typically defined as particles 2.5 µm or less in diameter (NRC, 1986). RSP is also referred to as “fine” particles and can be inhaled into lungs posing health concerns (USEPA, 1992).

Of toxicological importance is the size fraction of ETS that could be deposited onto the lung. In general, particle sizes less than 0.1 µm in diameter have a high predicted deposition efficiency in the lungs (Chalupa *et al.*, 2004). Deposition efficiency of particles in the range of 0.5 µm is low because at this size, particles are too large to deposit to any great extent by diffusion and are too small to deposit by sedimentation or impaction (Hiller *et al.*, 1982). Particle deposition onto the lung is greatly dependent upon size. However, other factors also play an important role such as puff frequency, volume of air inhaled and duration of the pause between inhalation and exhalation. Therefore, a longer pause in the breathing cycle between inhalation and exhalation increases the deposition of particles for all size ranges from 0.1 to 10 µm (Hiller *et al.*, 1982; Hinds, 1998).

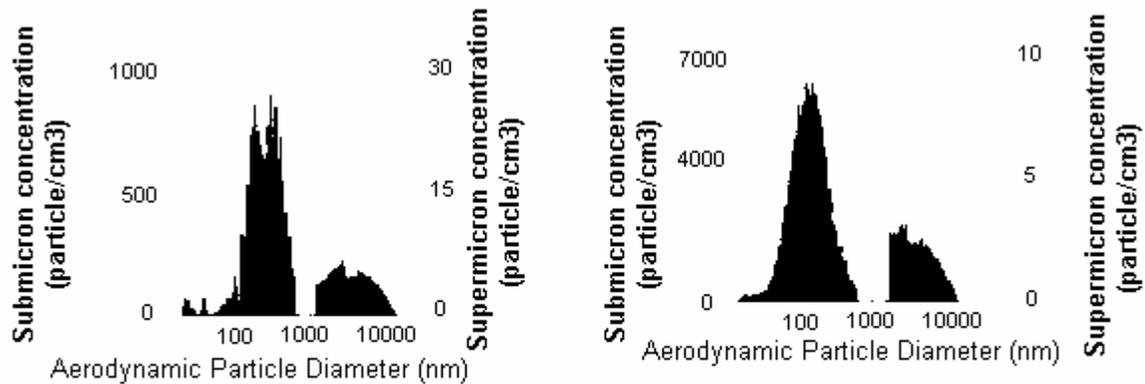
ETS particle size distribution and temporal effects have been investigated by several researchers under various controlled conditions. We found from the scientific literature that depending on the test conditions and the way ETS is generated, particle size distribution results vary. Researchers commonly report particle mass, diameter, length and particle number counts. Measured values are utilized to characterize overall ETS particle size distributions. ETS particle size distribution studies show that ETS exhibits a normal particle size distribution. Researchers typically report the mean and median peaks as measures of central tendency. The mean represents the average of particle size range, whereas the median represents the number at which half the number of particles fall above and below the value. The commonly used size distribution measurement techniques involve condensation nucleus counters, optical particle counters, aerosol electrometers and the cascade impactor.

Figure III-3 shows the distribution of ETS particle sizes in (a) mainstream and (b) sidestream smoke. Since ETS undergoes rapid chemical changes in the ambient environment, a chamber is generally used as a means to study ETS under controlled conditions. Morawska *et al.*, (1997) studied the distribution of ETS particles in the diameter range of 0.01 - 30 µm. A Scanning Mobility Particle Sizer (SMPS) and an Aerodynamic Particle Sizer (APS) were used to detect submicron particle levels ranging from 0.01 - 0.9 µm, and supermicron levels ranging from 0.5 - 30 µm, respectively. The measurements demonstrate that the distribution of ETS particles in both mainstream and sidestream smoke is bimodal. The vast majority of ETS particles were detected in the submicron range and an insignificant amount of ETS particles were in the supermicron range.

Figure III-3 shows the size distribution of ETS particles about 10 minutes after generation by a human smoker. The median diameter of the submicron peak of human-generated mainstream smoke was 0.238 μm (238 nm) with the geometric standard deviation 1.65. The median diameter of human-generated sidestream smoke was 0.136 μm (136 nm) with geometric standard deviation of 1.77.

Figure III - 3

Size Distribution of ETS Particles



(a) Size distribution of mainstream smoke produced by a human smoker.

(b) Size distribution of sidestream smoke produced by a human smoker.

Source: Morawska *et al.*, 1997

The measurements were performed independently by the SMPS (Scanning Mobility Particle Sizer) and the APS (Aerodynamic Particle Sizer) (1 μm = 1000nm).

Table III-4 lists some more notable particle measurement studies conducted by various researchers. Typically, sidestream smoke particles are in the broader size range 0.01 - 1.0 μm compared to mainstream smoke particles, which are in the range of size 0.1 - 1.0 μm (USEPA, 1992).

Table III-4

Reported ETS Particle Sizes

	Mainstream Smoke	Sidestream Smoke	Reference
Range in particle size	0.1-1.0 µm	0.01-0.8 µm	Carter and Hasegawa (1975); Hiller <i>et al.</i> (1982)
	0.1-1.0 µm	0.01-1.0 µm	U.S.EPA (1992)
Particle mean diameter ^{1/}	0.141µm	0.098 µm	Nelson <i>et al.</i> (1998)
	0.18 µm	0.1 µm	Guerin <i>et al.</i> (1987)
	0.41 µm	0.32 µm	Carter and Hasegawa (1975); Hiller <i>et al.</i> (1982)
Particle median diameter ^{2/}	0.21µm	0.185 µm	Nelson <i>et al.</i> (1998)
	0.23 µm	0.2 µm	Ogden and Jenkins (1999)
		0.14 µm	Morawska <i>et al.</i> (1997)
		0.16 µm	Ueno and Peters (1986)
		0.24 µm	Porstendorfer and Schraub (1972)
	0.235 µm	0.52-0.67 µm	McCusker <i>et al.</i> (1980)
0.44-0.43 µm		Chang <i>et al.</i> (1985)	
			McCusker <i>et al.</i> (1982)

Source: Morawska *et al.* (1997).

^{1/} Mean diameter: average diameter of all particle spectrum. (µm = 10⁻⁶ meter)

^{2/} Median diameter : equal number of particles counted in terms of diameter above and below this size.

Studies consistently show that sidestream smoke is comprised of smaller size particles as compared to mainstream smoke under the same test conditions (Ueno and Peters, 1986; Guerin *et al.*, 1987; Carter and Hasegawa, 1975; Hiller *et al.*, 1982; Jenkins *et al.*, 2000).

a. *Aging Process of ETS*

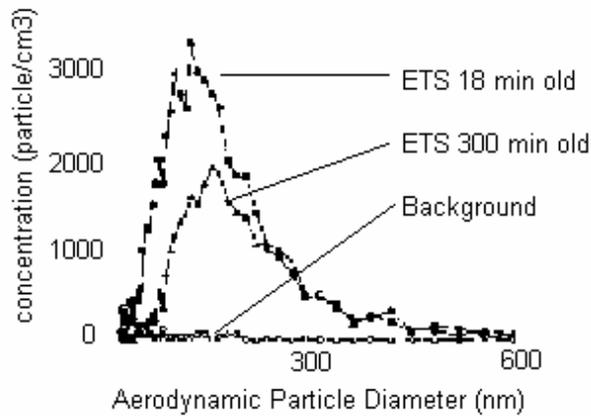
ETS undergoes a very dynamic aging process with several reactions observed such as coagulation, hygroscopic growth, evaporation, and condensation, among others.

Temporal Effect

The lifetime of ETS in ambient air depends mainly on dilution rates and environmental conditions. Yet, for indoor environments, ETS can be detected in the contained indoor environment long after it is first generated. Morawska *et al.* (1997) demonstrated the temporal effect on ETS particle size and concentration over time. As shown in Figure III-4, ETS concentrations are still well above background levels 300 minutes after the initial ETS generation. While particle concentration decreases, the particle mean and median diameter increased slightly. In chamber studies, decreases in ETS particle concentrations over time were mainly due to ventilation, wall deposition, coagulation, and evaporation of ETS particles (Morawska *et al.*, 1997; Pritchard *et al.*, 1988).

Figure III - 4

ETS Particle Concentration over Time



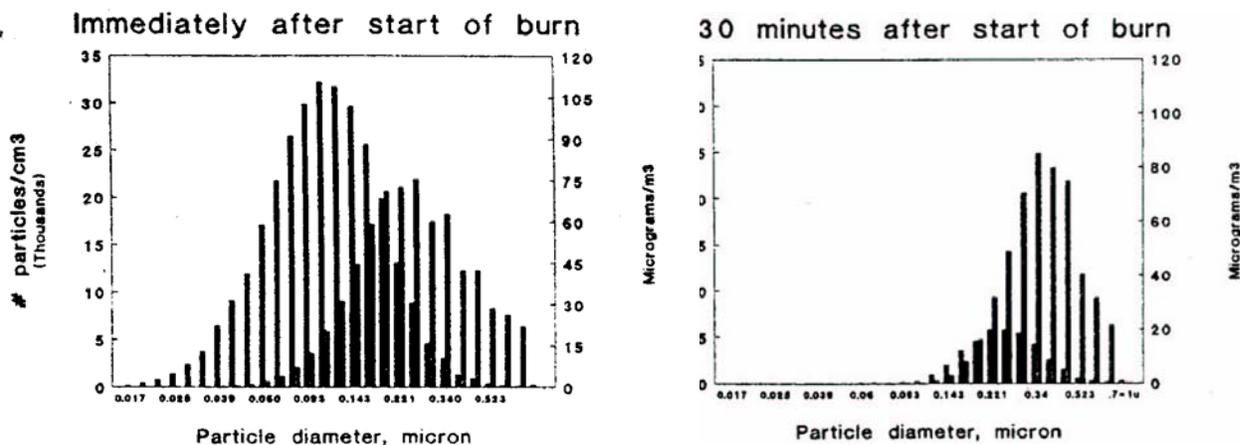
ETS size distribution at the beginning and at the end of the measurement period.

Source: Morawska *et al.* (1997).

Benner *et al.* (1989) also confirmed the prolonged-existence of ETS particles in the environment. ETS was generated in a 30-m³ Teflon® chamber and observed for four-hours. Observed results show that the number median diameter increased from 0.11 to 0.22 µm over the four-hour experimental period while the mass-median diameter increased from 0.26 to 0.34 µm. As shown in Figure III-5, the particle distributions remain normal over time while total concentration decrease. It is difficult to measure ETS removal rates in outdoor settings since outdoor conditions are highly variable and change rapidly.

Figure III - 5

ETS Particle Distribution Temporal Effect (0.015 - 0.75 μm size range)



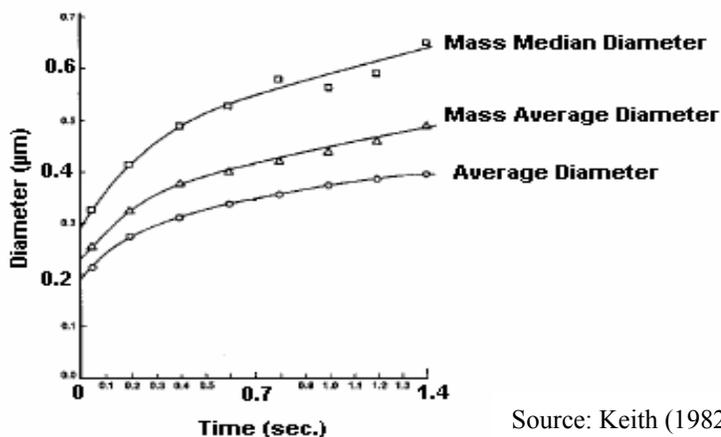
Source: Benner *et al.* (1989).

Coagulation

Coagulation of particles occurs when small particles collide into each other to form larger particles. Keith (1982) reported a doubling of particle diameter when undiluted smoke ages for 1.4 seconds (Figure III-6), consistent with coagulation theory. Coagulation mainly occurs in the lung during an active puff, as well as in indoor settings, where ambient ETS concentrations are elevated. For cigarette smoke under highly concentrated conditions (e.g., 10^9 particles per ml), coagulation of 0.1 - 1.0 μm diameter particles can occur in a fraction of a second (Keith 1982).

Fig III-6

Effect of Aging on Particle Size - Coagulation



Source: Keith (1982).

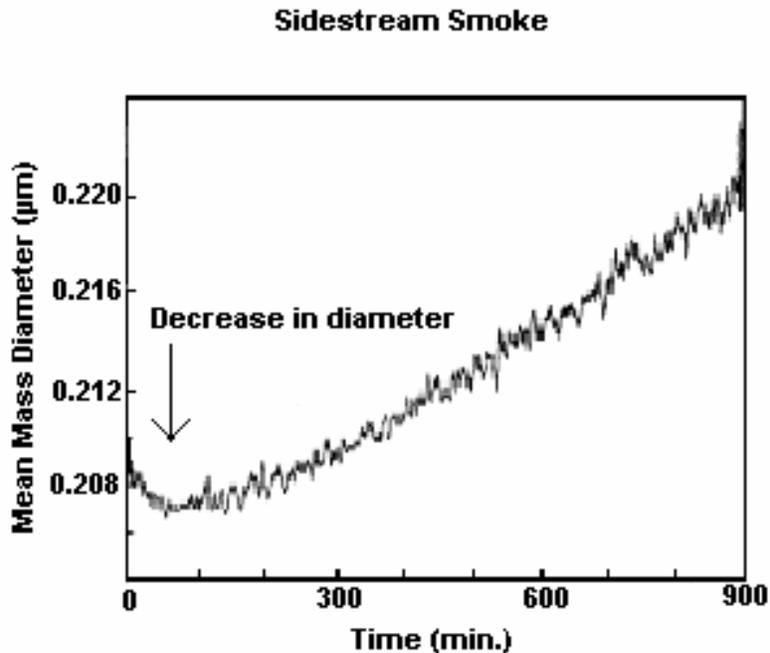
Hygroscopic Growth and Evaporation

In test chambers, Morawska *et al.* (1997) examined the effects of relative humidity on ETS particle growth. At high humidity (95 percent), total particle growth of up to 175 percent was observed, and postulated to result from hygroscopic growth (i.e., the hydration of dry particles). Studies have found that under high humidity, hygroscopic particles (such as those in ETS) can increase to the size of haze particles due to hydration (Seinfeld and Pandis, 1998). Coagulation and hygroscopic growth results in fine particle loss and faster settling of larger particles in the environment. Subsequently, the overall particle size distribution of ETS can be affected.

By contrast, a decrease in particle size has also been reported in other studies due to evaporation (Chang *et al.*, 1985; Ingebrethsen and Sears, 1989). In the work by Ingebrethsen and Sears (1989), sidestream smoke was diluted into a 0.45 m³ stainless-steel tank under controlled conditions of smoke concentration, air exchange and mixing rate. In the first 75-minutes, there was a strong indication of particle removal by evaporation. Figure III-7 shows the initial decrease in mass-mean diameter, indicating that evaporation had taken place. Elimination of smaller particles by evaporation and higher surface removal efficiencies may explain the increase in average diameter over time.

Figure III - 7

Evaporation of Particles in Sidestream Tobacco Smoke



Source: Ingebrethsen and Sears (1989).

Dilution

Of the physical reactions that occur to ETS, the most important is dilution. Certainly for ETS generated outdoors, dilution plays an important role in determining the actual ETS concentrations to which the public is exposed. As seen by our own testing, even modest winds reduced our measured nicotine concentrations (See Chapter V).

In a study by Chang *et al.* (1985), decreases in particle size were reported when machine-generated mainstream smoke was diluted. Machine-generated mainstream smoke was immediately diluted with laboratory air (humidity 45 - 75 percent) at dilution ratios of 6, 10, and 18 and introduced into the Cascade Impactor at 12.6, 5.1 and 4.4 seconds, respectively. The same dilution ratios were introduced to the Electrical Aerosol Size Analyzer (EAA) and Condensation Nuclei Counter (CNC) analyzers, at 23.3, 12.3, and 8.4 seconds. Table III-5 shows the decreases in particle size and number count resulting from the dilution of mainstream smoke with air. As ETS ages and mixes in air, water, volatile and semi-volatile components evaporate from the particles. Evaporation results in decreases in average particle size, and can shift overall particle size distribution curve and particle concentrations.

Table III - 5

Effects of Primary Dilution Ratio on the Number Concentration and Particle Size Distribution of Mainstream Cigarette Smoke

	Case 6	Case10	Case18
Primary Dilution Ratio	6	10	18
Mean Diameter (μm)	0.302	0.259	0.262
Standard Deviation of the Mean	1.27	1.18	1.26
Mean number conc. (particle/cm ³) ^a	4.2×10^9	3.6×10^9	7×10^8
Mean number conc. (particle/cm ³) ^b	2.4×10^9	2.1×10^9	4×10^8

^a Results from the Electrical Aerosol Size Analyzer (EAA).

^b Results from the Anderson Cascade Impactor.

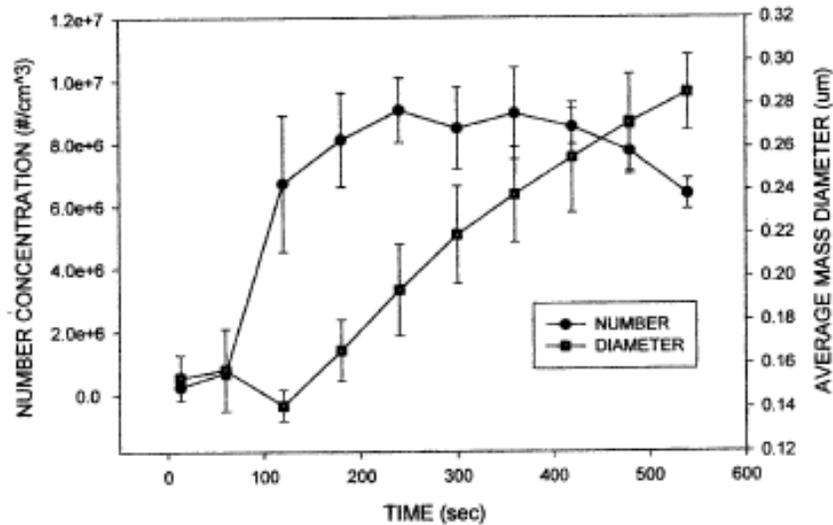
Particle Formation

Besides particle growth and shrinkage, particle formation and generation also affect ETS particle size distribution. Aerosol particle formation and growth has been observed in aging mainstream smoke from initially particle-free smoke vapor (Ingebrethsen and Lyman, 2002). In Ingebrethsen and Lyman (2002), 50 ml of particle-free filtered smoke was drawn from a cigarette attached to a filter holder. Particle formation and growth were measured using a light-scattering detection method as smoke aged over 500 seconds. Figure III-8 presents particle concentration and average particle size measurements over time on a log scale. The optical particle counter (OPC) detected particle formation and growth in average mass diameter in the first 500-seconds, most

likely due to condensation and coagulation. Beyond 500-seconds, particle number concentration began to decline from peak levels, but average mass diameter continued to increase. These results provide evidence that some fraction of filtered, particle-free mainstream smoke does not remain in the gas-phase for long before undergoing varying degrees of particle formation.

Figure III – 8

Particle Formation in Cigarette Smoke Gases



Source: Ingebrethsen and Lyman (2002).
 Error bars are ± one standard deviation.

Particles in the diameter range of 0.005 - 0.05 μm can be formed by condensation of hot vapor during the combustion process and by droplet formation of atmospheric species, and contain most of the toxic compounds in ETS. In comparison, particles in the diameter range of 0.05 - 2 μm are among the most stable, and are formed by gas-to-particle conversion, chemical reaction, condensation and coagulation (Hinds, 1998).

In conclusion, the particle-size composition of ETS changes dynamically. Changes result from growth and shrinkage of particles by coagulation, hygroscopic growth, evaporation, condensation and formation among others. From a toxicological perspective, it should be noted that even after ETS undergoes complex reactions, the majority of ETS particles are still in the fine particulate range between 0.1 and 1.0 μm diameter.

D. SEMI-VOLATILE COMPONENTS IN ETS - NICOTINE

In addition to gas and particle phases, ETS also has constituents that are detected as in both phases to the degree determined by their volatility and the environmental conditions. These compounds are referred to as being “semi-volatile,” and include substances such as nicotine, 3-ethenylpyridine, alkanes, and selected PAHs and PCBs.

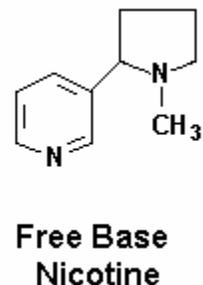
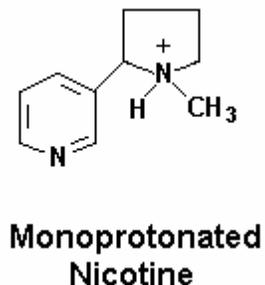
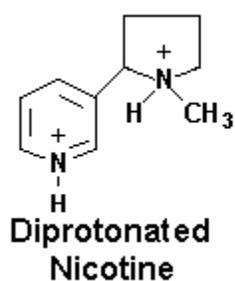
Semi-volatile compounds with lower vapor pressure may be adsorbed to the surrounding surfaces and may reenter the gas phase through desorption (Van Loy *et al.*, 2001). This dynamic behavior of semi-volatile compounds prolongs its availability in the environment, particularly in the indoor environment. Therefore, one may be exposed to semi-volatile constituents, such as nicotine, for a longer period after the active smoking has ceased.

Of the various semi-volatile components in ETS, nicotine deserves some discussion because of its use as a marker in the ARB’s monitoring study and because of its use as a surrogate for exposure (See Chapter V, Section E). As mentioned earlier, nicotine exists mainly in the particle phase in mainstream smoke, but exists primarily in the gas phase in sidestream smoke (Jenkins *et al.*, 2000; Van Loy *et al.*, 2001). Nicotine is one of the most commonly used indicators to detect ETS in the environment because it is unique to tobacco smoke (Ogden and Jenkins, 1999).

To enhance the generation of gas phase nicotine during smoking, ammonia-forming compounds are sometimes added to the tobacco. The presence of ammonia promotes nicotine existence in the gas phase rather than adsorbed to particles (Pankow *et al.*, 1997). Figure III-9 shows three forms of nicotine -- mono, diprotonated, and free-base nicotine. The diprotonated and monoprotonated forms of nicotine do not exist in the gas phase and reside essentially in the particle phase. In contrast, free-base nicotine can exist in both the particle and gas phases. Unlike the protonated forms of nicotine, the free-base nicotine particles can be converted to the gas phase, and readily absorbed into the lung and into the blood stream.

Figure III-9

Three Forms of Nicotine



The semi-volatile constituents of ETS exhibit different dynamic behaviors depending on temperature, dilution and other environmental conditions. For example, some components of fine particles and volatile aerosols also may exhibit semi-volatile behavior under controlled conditions. As the volatile aerosols on the outer layer of a particle evaporate, either partially or entirely (Kunh *et al.*, 2004), particle diameters may decrease until the non-volatile core is reached.

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