Hygroscopic Growth of Assorted Indoor Aerosols

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ABSTRACT. The hygroscopic growth of particles produced from four different kinds of oils during deep frying, from sausages during grilling, and from burning wood in a stove was studied using a Tandem DifferentialMobility Analyzer. The size distributions and the soluble fractions of the particles were also measured. The median diameters of the particles from the oils were in the range of 168–200 nm and those from the sausages and the wood in the range of 55–80 nm. The median diameter and the geometric standard deviation of the particles from wood depended on wood burning with or without a flame. The soluble fractions of the particles from the oils were between 8% and 22%, and those from wood between 70% and 92%. The soluble fraction for particles from the sausages was 46%. The particles of the oil and sausage smokes did not grow and those of the wood smoke showed a significant growth. AEROSOL SCIENCE AND TECHNOLOGY 24:151–160 (1996)

INTRODUCTION

Aerosols are generated during various household activities such as cooking, wood burning, etc. Cooking oils, cooking meat, and wood burning result in a release, in fine particles size (diameter ≤ 2.5 μm), of a number of organic compounds (Hildemann et al. 1991, 1994), including n-alkanoid acids, carboxylic acids, oleic and palmitoleic acids, amides, cholesterol and polycyclic acids (Rogge et al. 1991, 1993; Osten et al. 1994). The knowledge of aerosol composition is essential for determining the source of the aerosol material. It also serves as a guide to the studies of their associated health effects. Many organic species found in fine aerosol are known to be carcinogenic and/or mutagenic (Daisey et al. 1980; Pitts 1983; Schuetzle 1983; Gundel 1993). Inhalation of wood smoke leads to increased incidence of pulmonary infection (Zelikoff 1994).

Another important factor that has bearing on the health effects is the hygroscopicity of the inhaled particles. Depending on their nature some of these particles may grow in the humid environment of the respiratory tract and attain a size larger than their dry particle size. The site and the quantity of material that deposits in the various compartments of the respiratory tract depends on the size of the depositing particles and hence will depend on whether they do or do not grow at the high relative humidity in the respiratory tract. Thus the knowledge of the hygroscopic growth of the particles is necessary for determining their inhalation effects. In their studies on aerosol in Los Angeles and Grand Canyon, Zhang et al. (1993) found that particles of a given size had distinctly different hygroscopic characteristics, which they termed "more" and "less" hygroscopic. They re-

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ported that on an average 60%–70% of the particle carbon was associated with the less hygroscopic particles and the balance with the more hygroscopic particles.

The aim of the present study is to measure the hygroscopic growth of the particles emitted from oils in a simulated cooking operation, from a high fat meat (sausages), and from wood burning.

HYGROSCOPIC GROWTH MODEL

The growth model for soluble salt particles was given by Ferron (1977). To describe the behavior of partially soluble components, Li and Hopke (1993, 1994) developed a semiempirical model by introducing a parameter, χ, defined as the mass ratio of the insoluble to the soluble materials. Dua et al. (1995a) have simplified the expression for the growth ratio. According to this model the hygroscopic growth ratio can be described by

$$\frac{d_1}{d_0} = \left[1 + \beta \frac{M_w H}{R_1 - H} \right]^{1/3} \qquad (1)$$

where

$$\beta = \frac{\rho_0 i}{(1 + \chi) M_s}, \qquad (2)$$

$$R_1 = \exp\left[\frac{4 \sigma_1 M_w}{R T \rho_1 d_1} \right], \qquad (3)$$

$$\rho_1 = 1 + (\rho_0 - 1)\left(\frac{d_0}{d_1} \right)^3, \qquad (4)$$

where d_1 and d_0 are the diameters of grown and dry particles respectively; ρ_1 and ρ_0 are their respective densities relative to water; M_w is the molecular weight of water; M_s is the apparent average molecular weight of soluble component; H is the relative humidity in the system; i is degree of dissociation of the soluble component in water, which equals the number of molecule or ions into which a dissolved molecule is dissociated in water. R_1 is the ratio of the

partial pressure on the surface of a droplet of diameter d_1 to that on the flat surface and is defined by the Kelvin equation. σ_1 is the surface tension of solution, R is the gas constant and T is the absolute temperature. σ_1 can be assumed to be equal to the surface tension of water. For the particles that grow, d_1 and d_0 are measured experimentally. Under the assumption that $\rho_1 = 1$, all quantities in Eq. 1, except β, are either measurable or known. Therefore, by employing the least squares method to fit the experimental data to this model, the value of β can be estimated. Using the estimated value of β and the measured soluble fraction, an estimate of the molecular weight of the material can be made if ρ_0 and i are known.

EXPERIMENTAL

Particles from oils used in a simulated frying operation, the grilling of high fat meats (sausages), and combustion of wood (commonly found in houses), were produced, and their hygroscopic growth, size distribution, and soluble fraction were measured. Oil particles are often formed in cooking when water evaporates forming a bubble of oil that bursts at the surface, producing droplets. To simulate this process, oil of a particular kind was placed in a deep frying pan. The pan was placed in a Lucite chamber and heated electrically. Water droplets from a pipette were directed onto the oil. These water droplets were produced with a nebulizer (Leong et al. 1982) whose drain line was plugged and whose outlet line was inverted and connected to the pipette. This nebulizer produces droplets with volume median diameter of about 400 nm. In order to have a nearly steady concentration of the oil droplets in the chamber the flow of water entering the nebulizer was controlled by controlling the water feed rate and the nebulizer air flow rate. The temperature of the oil measured by immersing a thermometer in the oil, without touching the bottom of the pan, was in the range 195°–220°C. The top of the chamber was

loosely covered with a Lucite plate and the samples were drawn from the chamber using a pump.

The smoke from sweet Italian sausages was emitted when they were heated on a domestic electric grill (Jenn Aire). Adjacent to the grill, the smoke was pulled into a ventilation duct with an exhaust fan. The sample was taken from the duct through a hole drilled into it.

The wood smoke was emitted during burning hard wood (mostly maple) in a wood stove (Vermont Casting Resolute). Since the experiments were done in a private house, no hole was drilled in the chimney. The sample was drawn from the top of the firebox through a tube placed inside the stove through the open stove door in order to obtain a high concentration of the particles that could subsequently leak from the firebox.

A Tandem Differential Mobility Analyzer (TDMA) was used for the hygroscopic growth study. The TDMA, its humidifier system, the method of measurement of the relative humidity and the hygroscopic growth have been reported earlier (Li et al. 1992; Li and Hopke 1993, 1994; Dua et al. 1995a). The TDMA was used in the over pressure mode and a metal bellows pump was used for drawing the particles and delivering them to the first differential mobility analyzer (DMA). This line included a heated copper tube, a silica gel diffusion dryer and a charge neutralizer to dry and charge the particles. The output of this DMA was a monodisperse aerosol of the selected size which was humidified in a wetted water reactor and scanned in the second DMA coupled to a condensation nuclei counter (CNC) and a personal computer. There was no charge neutralizer in line with the second DMA. The dimensions of the wetted water reactor and the air flow rate were such that the passing aerosol attained a relative humidity of nearly 100%. Using thermostated baths, the relative humidity and the temperature of the sheath air in the second DMA were maintained as close as possible to those of the aerosol air (> 99%). The sheath air flow rate was 6

LPM in the first DMA and 3 LPM in the second DMA. The aerosol air flow rate was 10% of the sheath air and the excess air flow rate was equal to the sheath air. The particle size distribution after the second DMA was obtained by matching the distribution curves of the voltage ramp-up and of the voltage ramp-down (Wang and Flagan 1990). The ramp-up and ramp-down scan times were about 200 s. The sources and magnitudes of errors of the hygroscopic measurements with TDMA system have been previously discussed (Li et al. 1992). It was reported that an 8% error in determining the values of the growth ratio is possible due to uncertainty in humidity mainly and other factors.

To measure the size distribution of the emitted particles, the first DMA and the wetted water reactor were bypassed and the output of the charge neutralizer was connected directly to the second DMA. The size distribution of the particles in a living room which was being heated by the wood stove was also measured. This will be useful for the assessment of the inhalation exposures. During the measurements in the living room, a ceiling fan was kept on to achieve an efficient mixing of the room air.

The soluble fraction of the particles was determined by the method described earlier (Li and Hopke 1993, 1994; Dua et al. 1995a). The sample was collected on a filter and the soluble fraction was extracted by placing the filter on the surface of water in a petri dish. By weighing the filter before sample collection and after collection and extraction, the soluble fraction was determined from the change in the mass.

RESULTS AND DISCUSSION

Figures 1–4 show the size distribution of smoke particles emitted from Hollywood Peanut Oil, Mazola Corn Oil, Wesson Canola Oil, and Wesson Vegetable Oil, respectively. For each oil different spectra were taken sequentially at a time intervals of about 4 min. Each circle shows the mean of the data points and the error bars represent the standard deviation of the data
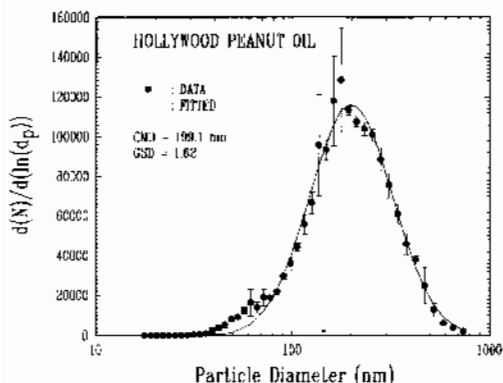
FIGURE 1. Size distribution of Hollywood Peanut Oil particles. Different spectra were taken sequentially at a time interval of about 4 min. Each circle shows mean of the data points corresponding to a size and the error bars represent the standard deviation of the data points from the mean. The solid line represents the log-normal fit to the data points.
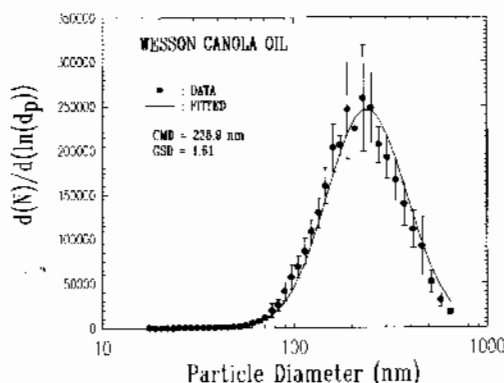

FIGURE 3. Size distribution of Wesson Canola Oil particles. Different spectra were taken sequentially at a time interval of about 4 min. Each circle shows mean of the data points corresponding to a size and the error bars represent the standard deviation of the data points from the mean. The solid line represents the log-normal fit to the data points.

points from the mean. The solid lines represent the log-normal fits to the data points. The size distributions of the particles presented in Figs. 5–7 correspond to the sausages, wood burning with a flame and wood burning without a flame, respectively. Table 1 provides their characterization. It is

seen that the median diameters of the oil particles are in the range 168–240 nm with a geometric standard deviation of about 1.6. The median diameters of the smoke particles of sausages and wood are lower than those of the oils. The wood-combustion particles sampled at different phases
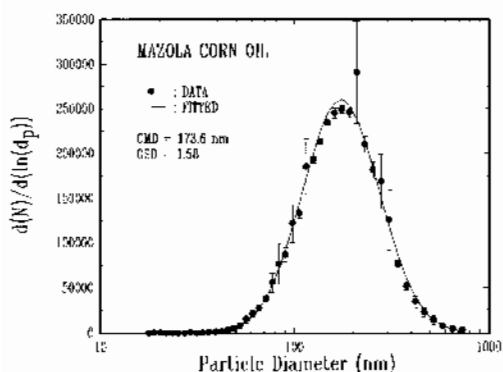

FIGURE 2. Size distribution of Mazola Corn Oil particles. Different spectra were taken sequentially at a time interval of about 4 min. Each circle shows mean of the data points corresponding to a size and the error bars represent the standard deviation of the data points from the mean. The solid line represents the log-normal fit to the data points.
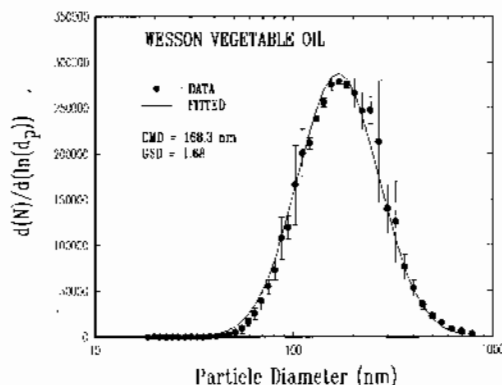

FIGURE 4. Size distribution of Wesson Vegetable Oil particles. Different spectra were taken sequentially at a time interval of about 4 min. Each circle shows mean of the data points corresponding to a size and the error bars represent the standard deviation of the data points from the mean. The solid line represents the log-normal fit to the data points.
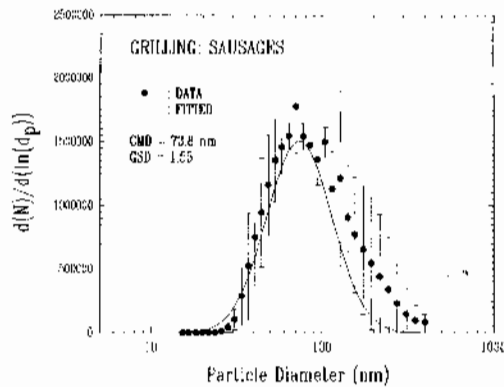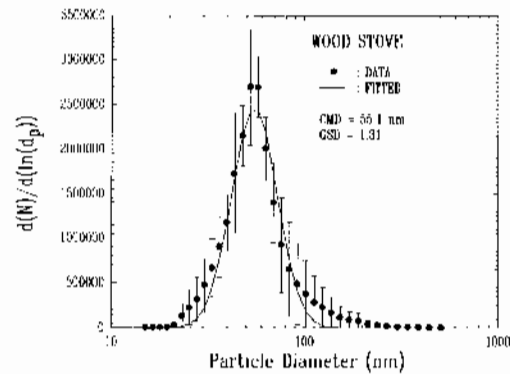
FIGURE 5. Size distribution of smoke particles from sweet Italian sausages. Different spectra were taken sequentially at a time interval of about 4 min. Each circle shows mean of the data points corresponding to a size and the error bars represent the standard deviation of the data points from the mean. The solid line represents the log-normal fit to the data points.

FIGURE 7. Size distribution of smoke particles emitted during wood burning without a flame. Different spectra were taken sequentially at a time interval of about 4 min. Each circle shows mean of the data points corresponding to a size and the error bars represent the standard deviation of the data points from the mean. The solid line represents the log-normal fit to the data points.

of burning showed distinctly different size distributions. The median diameter and geometric standard deviation of the particles in the living room with wood burning in the wood stove were 97 nm and 1.8, respectively (Fig. 8). Figure 9 corresponds to size
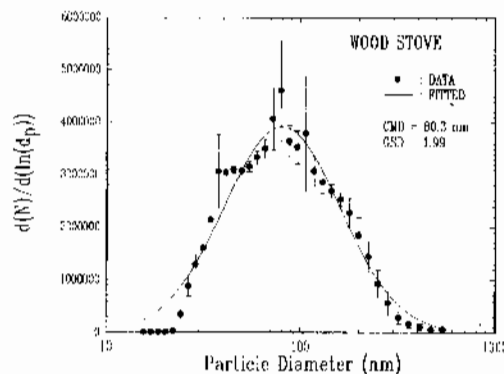

FIGURE 6. Size distribution of smoke particles emitted during wood burning with a flame. Different spectra were taken sequentially at a time interval of about 4 min. Each circle shows mean of the data points corresponding to a size and the error bars represent the standard deviation of the data points from the mean. The solid line represents the log-normal fit to the data points.

distribution of room particles without wood burning.

Figures 10–13 show the hygroscopic growth of particles from the four kinds of oils studied. Generally, oils used for deep frying are heated for few hours before they are replaced with fresh oil. Since many oils are specifically produced to be polyunsaturated, the nature of the oil constituents may change with the heating time. The oils could become oxidized and the change in unsaturated character might have a bearing on their hygroscopicity. To determine the influence of the oil heating time on the hygroscopicity of the generated particles the growth measurements, for each of the four oils, were done at two different heating times. These are marked in the Figs. 10–13.

Figure 14 presents the hygroscopicity of smoke particles from the sweet Italian sausages during grilling. Figure 15 exhibits the growth curve of particles emitted during wood burning with a flame. The growth curve in Fig. 16 corresponds to the condition of wood burning down to embers, where the wood is burned out to coke which glows or is covered with ash and there is no

TABLE 1. Characterization of Various Smoke Particles[a]

Product	CMD (nm)	GSD	Soluble Fraction
Hollywood Peanut Oil	199.1	1.62	0.076 ± 0.026
Mazola Corn Oil	173.6	1.58	0.164 ± 0.008
Wesson Canola Oil	238.9	1.61	0.203 ± 0.045
Wesson Vegetable Oil	168.3	1.68	0.128 ± 0.033
Sweet Italian sausages	73.8	1.55	0.456 ± 0.087
Wood burning with flame	80.3	1.90	0.714 ± 0.022
Wood burning without flame	55.1	1.31	0.924 ± 0.098
Particles in living room (wood burning in the wood stove)	96.7	1.81	

[a] CMD = Count median diameter; GSD = Geometric standard deviation.

flame or visible smoke. It is observed that the smoke particles from oil and sausages show practically no growth whereas those from the wood embers show significant growth.

The oil particles show small values (0.08 to 0.22) for the soluble fractions. The particles from the sausages have a soluble fraction of 0.46. The soluble fractions of wood vary between 0.71 and 0.92, depending upon whether the wood is burning with or without a flame.

The oils are expected to be hydrophobic and would not be expected to show any growth. The small values of the soluble fractions (0.08 to 0.22) of the oil particles is compatible with their lack of observable growth. Their is no influence of oil heating times on their hygroscopicity. The smokes from sausages show no growth although their soluble fraction is 0.46. This value is relatively high for no growth. This result suggests that the particles from sausages form micelles, as had been previously seen in hair spray (Li and Hopke 1994). These droplets can disperse in liquid water by the interaction of the polar end of the fatty acids. Thus, the long chain fatty acids, which form a significant component of the aerosols emitted from charbroiling of meats
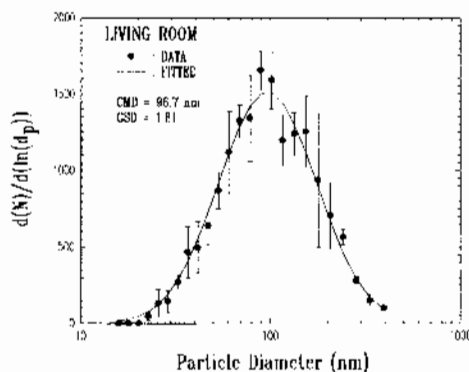

FIGURE 8. Size distribution of the particles in the living room during wood burning in a wood stove. Different spectra were taken sequentially at a time interval of about 4 min. Each circle shows mean of the data points corresponding to a size and the error bars represent the standard deviation of the data points from the mean. The solid line represents the log-normal fit to the data points.
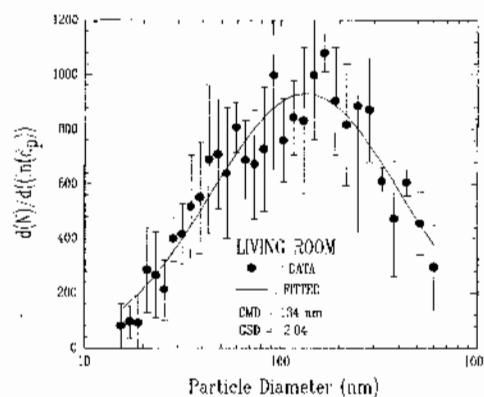

FIGURE 9. Size distribution of the background particles in the living room. Different spectra were taken sequentially at a time interval of about 4 min. Each circle shows mean of the data points corresponding to a size and the error bars represent the standard deviation of the data points from the mean. The solid line represents the log-normal fit to the data points.
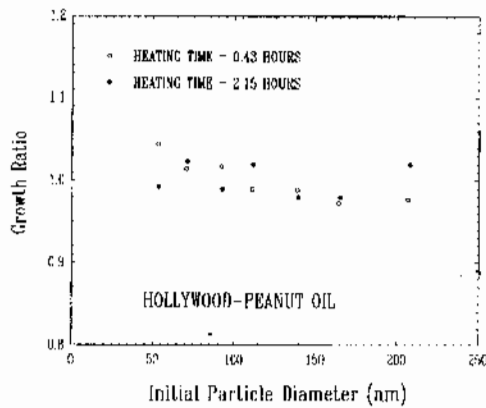
FIGURE 10. Hygroscopic growth of smoke particles from Hollywood Peanut Oil. The heating time is the time for which the oil was heated before making the measurements.
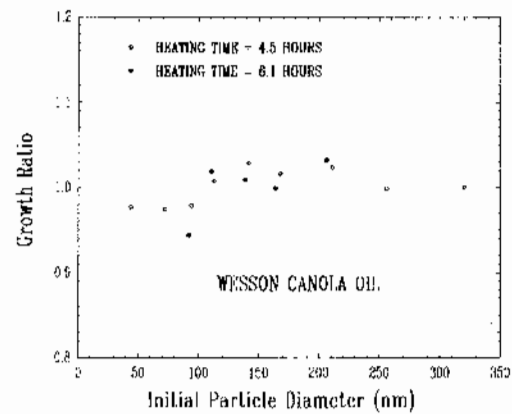

FIGURE 12. Hygroscopic growth of smoke particles from Wesson Canola Oil. The heating time is the time for which the oil was heated before making the measurements.

(Rogge et al. 1991), do not exhibit hygroscopic growth at a relative humidity of ~ 99%.

Under some conditions of wood burning, practically no growth was observed whereas in the other (embers) a significant growth was seen. These results suggest that the constituents of the wood smoke change during the different phases of wood combustion. McKenzie et al. (1994) have quan-

tified the major compounds emitted from the smoldering combustion of wood. These are mixture of ash, char, some unburnt fuel, tar, condensed compounds and condensible gases. Hüglin et al. (1994) reported the emitted compounds differ with the phase of combustion. Cachier et al. (1994) observed that the aerosols produced by African Savanna biomass burning were characterized by their organic matter (black
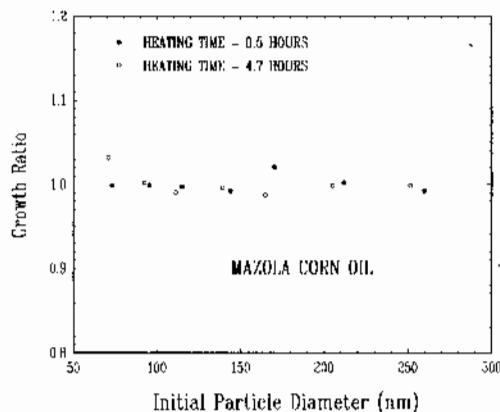

FIGURE 11. Hygroscopic growth of smoke particles from Mazola Corn Oil. The heating time is the time for which the oil was heated before making the measurements.
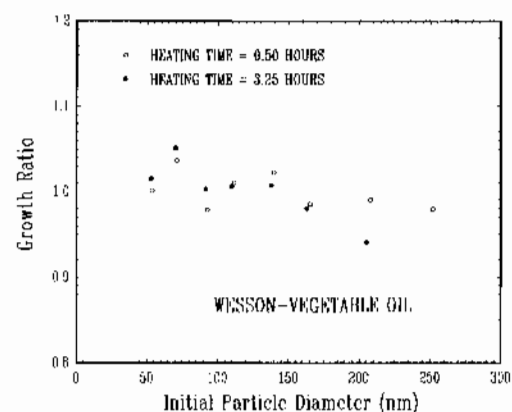

FIGURE 13. Hygroscopic growth of smoke particles from Wesson Vegetable Oil. The heating time is the time for which the oil was heated before making the measurements.
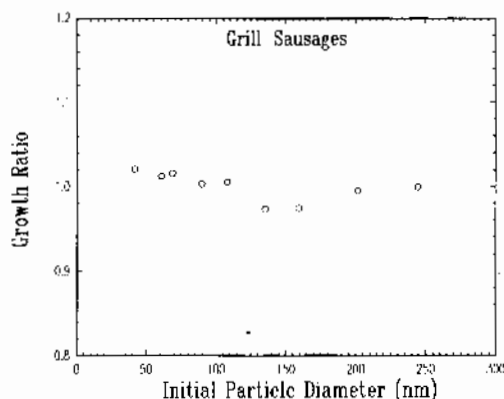
FIGURE 14. Hygroscopic growth of smoke particles from sweet Italian sausages.

FIGURE 16. Hygroscopic growth of smoke particles from wood embers. Lines represent the growth curves based on the model presented in Eq. 1 for the fractional relative humidities of 0.998, 0.990, and 0.995.

carbon to total carbon ratio in the range 3%–25% and their potassium content (potassium to black carbon ratio ~0.6). They also reported variability of the total suspended matter and CO_2 during the various flaming and smoldering phases of the combustion. Echalar et al. (1994) have reported that the relative abundance of potassium to total particle matter varies according to the phase of fire (flaming/smoldering) of biomass in Africa and Brazil. Potassium compounds are known to be generally soluble and thus, highly hygro-
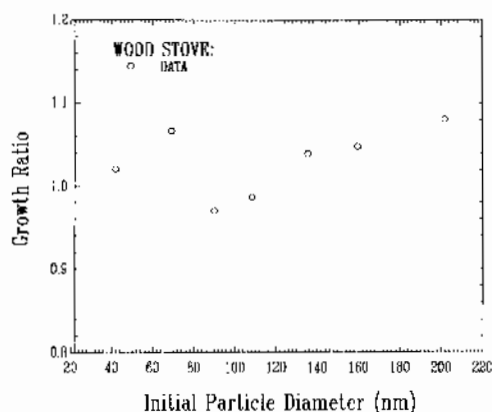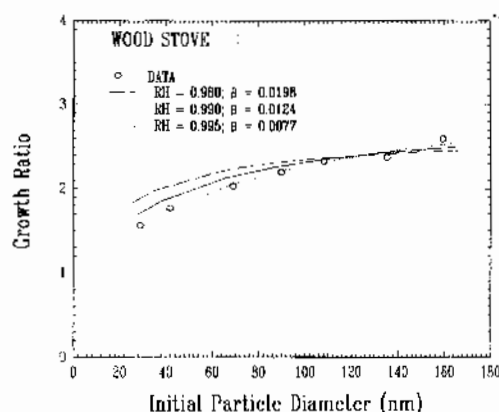

FIGURE 15. Hygroscopic growth of smoke particles from wood burning with a flame.

scopic. The presence of potassium in wood smoke may be responsible for the high value of the soluble fraction and of the growth of the particles from wood.

The hygroscopicity studies shows that although the value of the soluble fraction has a bearing on the hygroscopic growth of the particles, it may not be the only variable to use when predicting hygroscopic potential. Our previous studies (Dua et al. 1995a) have shown that the hygroscopic growth, for various materials, can be generally expressed by the parameter β given in Eq. 1. An alternative method of knowing the hygroscopic fraction for particles of a preselected size (with DMA) is to measure their critical supersaturation in a cloud chamber and compare the number of particles counted in an optical counter with the total number measured with the condensation nuclei counter for the same initial size.

For the particles that grow, the growth model (Eq. 1) can be used to estimate the value of β and to obtain grow curves as at various relative humidities (Fig. 16). The model calculations were performed at more than one humidity because it was impossible in these experiments to either measure or control the humidity as accurately as 0.1%. The humidity in the system was found

to be between 99% and 99.5% by measuring the hygroscopic growth of NaCl particles. It is not unreasonable to assume $\rho_1 = 1$ for the purpose of simplification of the exponential term (Eqs. 1 and 3). It does not introduce much error. $\rho_1 = 1$ implies that either the growth ratio is large or $\rho_0 = 1$ or both. If, instead $\rho_0 = 1.5$, and growth ratio = 2, ρ_1 works out to be 1.0625. For $d_1 = 100$ nm, this introduces an error of 2.6% in the value of the denominator in Eq. 1 for $H = 0.990$ and 3.0% for $H = 0.995$. The error for the growth ratio will be lower than these values.

As defined in Eq. 2, β is a combined parameter that shows the total effect of the degree of dissociation, soluble fraction $(1/(1 + \chi))$, average molecular weight of the soluble components and their average density. Since smoke particles are assumed to contain mostly organic components, and organic components are usually weakly dissociated in water, the value of i can be assumed close to unity except for potassium. Because the value of β, at a constant humidity, is inferred from one set of measurements, it is not possible to extract values of i, ρ_0, and M_s, as the system is underdetermined. However, if the product $\rho_0 i$ in Eq. 1 is assumed to be 1, the value of the molecular weight can be estimated. The estimated values of M_s for growing wood aerosols are 74.2 and 120 for the relative humidities of 0.990 and 0.995, respectively. The actual value may be higher by value of the product $\rho_0 i$. The molecular weights cannot be directly related to species chemical constituents in the mixture of materials in the smoke particles, but can be used to estimate the growth for further deposition modeling and dosimetry estimation.

The median diameter and of the geometric standard deviation of wood smoke were observed to vary with the condition of wood burning. Hüglin et al. (1994) have also found a change in the shape and position of the maximum of the particle distribution during the different phases of wood burning.

Cooking in oils, meat cooking, and wood burning are the major sources of organic aerosol emission to the atmosphere. The chemical composition of the various organic compounds and their hygroscopic behavior are useful for the identification of their source, prediction of the concentration in the atmosphere, and for the assessment of the health effects.

CONCLUSIONS

The size of the oil particles produced in a simulated frying operation was higher than those of the particles produced from grilling of sausages and from wood burning. The size distribution of the wood smoke changed with the phase of the wood burning. The soluble fraction of the wood smokes was higher than those of oils or sausages. The particles from four cooking oils and sweet Italian sausages showed no growth, whereas particles from wood embers showed a significant growth at a high relative humidity ($\sim 99\%$). From these results, it is possible to estimate the change in lung deposition of particles that occurs from the hygroscopic growth within the respiratory tract. For example, the effect of the changes in deposition on the dose from attached radon decay products can be estimated (Dua et al. 1995b).

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