

Fine Particle Emissions from Residual Fuel Oil Combustion: Characterization and Mechanisms of Formation

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ABSTRACT

The characteristics of particulate matter (PM) emitted from residual fuel oil combustion in two types of combustion equipment were compared. A small commercial 732kW fire-tube boiler yielded a weakly bimodal particulate size distribution (PSD) with over 99% of the mass contained in a broad coarse mode, and only a small fraction of the mass in an accumulation mode consistent with ash vaporization. Bulk samples collected and classified by a cyclone indicate that 30 to 40% of the total particulate emissions were less than approximately $2.5\mu\text{m}$ aerodynamic diameter ($\text{PM}_{2.5}$). The coarse mode PM was rich in char, indicating relatively poor carbon burnout, although calculated combustion efficiencies exceeded 99%. This characteristic behavior is typical of this type of small boiler. Larger scale, utility units firing residual oil were simulated using an 82kW laboratory-scale refractory-lined combustor. PM emissions from this unit were in good agreement with published data including published emission factors. These data indicated that the refractory-lined combustor produced lower total but greater fine particulate emissions, as evident from a single unimodal PSD centered at approximately $0.1\mu\text{m}$ diameter. Bulk cyclone segregated samples indicated that all the PM were smaller than $2.5\mu\text{m}$ aerodynamic diameter, and loss on ignition (LOI) measurements suggested almost complete char burnout. These findings are interpreted in the light of possible mechanisms governing the release of organically bound refractory metals, and may have particular significance in considering the effects of fuel oil combustion equipment type on the characteristic attributes of the fine PM emitted into the atmosphere, and their ensuing health effects.

INTRODUCTION

Recently, airborne fine particulate matter (PM) has become the subject of considerable environmental interest due to the results of a number of studies correlating short term exposures of ambient levels of fine PM with acute adverse health effects[1-4]. Consequently, ambient concentrations and source emissions of fine PM, defined as less than $2.5\mu\text{m}$ in diameter ($\text{PM}_{2.5}$), face the possibility of increased regulation[5]. Numerous causative theories exist; however, health effect researchers have identified at least two properties of ambient particle composition that appear to exacerbate health damage. These are the presence of transition metals (e.g., Cu, Fe, V, Ni, and Zn)[6-8] and aerosol acidity. In addition to particle composition, another apparent factor influencing health impact is the presence of ultrafine particles ($<0.1\mu\text{m}$ in diameter)[2]. All three characteristics, transition metals, acidity, and ultrafine size, are exhibited by the PM generated from the combustion of residual fuel oils. Hence, one might hypothesize residual fuel oil combustion to be suspect, as far as emission of toxic fine particles are concerned. Therefore, while previous work[9] examined the effects of fuel oil compositions on the physical and chemical characteristics of fine PM, this paper describes the effects of different combustion equipment types. The results of both studies can be used as the basis for ultimately linking measures of acute pulmonary damage to combustion engineering variables.

EXPERIMENTAL

Particle characteristics and emissions are compared from two types of combustion systems. These can be considered to represent extremes of a range of practical conditions under which fuel oil is burned. Although they may not represent specific boilers in all respects, they are investigated here with a view to determining how this range of combustion conditions influence the characteristics of fine particles, and the mechanisms which form them. The first system is a small fire-tube boiler, in which combustion occurs in tubes surrounded by water or steam. These types of small boilers have large heat transfer surfaces, small volumes, relatively short residence times, cold walls, and high gas quenching rates, and often produce emissions with relatively high carbon contents due to unburned carbonaceous char. The second system is a laboratory-scale refractory-lined combustor designed to simulate the time/temperature

environments of larger utility boilers and incinerators. In large utility boilers the water or steam, rather than the combustion gases, is contained in tubes. These systems, including the refractory-lined combustor, operate at higher temperatures with lower quenching rates. As will be discussed later, particle emissions from this system contain very little unburned carbon and better approximate emissions from large oil-fired utility boilers as reported in the literature.

Fire-tube Boiler

Experiments were performed using the commercially available, North American, three-pass, fire-tube package boiler shown in Fig. 1. This unit is equipped with a 732kW North American burner with an air-atomizing oil nozzle. Oil temperature and oil and atomizing air pressures are independently controlled to ensure proper oil atomization. Figure 1 indicates the locations of several sampling ports. Temperatures at these locations ranged from 450 to 550K. Additional system details are presented elsewhere[9].

Refractory-lined Combustor

Experiments were also performed using the 59kW laboratory-scale refractory-lined combustor also shown in Fig. 1. This research unit was designed to simulate the time/temperature and mixing characteristics of practical gas- and oil-fired combustion systems. This unit is equipped with an International Flame Research Foundation (IFRF) moveable-block variable-air swirl burner which incorporates an air-atomizing oil nozzle positioned along its center axis and swirling air which passes through the annulus around the fuel injector to promote flame stability. The burner was configured for a high swirl flame (IFRF Type 2, swirl No.=1.48) with internal recirculation. Gas and aerosol samples were taken from stack locations at temperatures of approximately 670K. All experiments (fire-tube boiler and refractory-lined combustor) were performed at a stoichiometric ratio (SR) of 1.2 without secondary air preheat.

Particulate Sampling and Analysis

PM measurements were performed using several methods. Standard EPA Methods 5 and 60 sampling and analytical procedures were used to determine total particulate and metal concentrations[10-12] using inductively coupled plasma (ICP) mass spectrometry. Other metal analyses were determined by x-ray fluorescence (XRF) spectroscopy. Additional samples were analyzed by x-ray absorption fine structure (XAFS) spectroscopy, an element-specific structural analysis that is useful for determining trace element speciation and forms of occurrence in chemically and structurally complex materials like combustion ash[13,14].

PSDs were determined by three techniques: electrical mobility and inertial impaction for sampled aerosols; and light scattering for in-situ in-stack analyses. Extractive samples were taken for inertial impaction and electrical mobility analyses using an isokinetic aerosol sampling system described elsewhere[15,16]. These diluted samples were directed to a Thermo-Systems Inc. scanning mobility particle sizer (SMPS) configured to yield 54 channels evenly spaced (logarithmically) over a 0.01 to 1.0 μm diameter range. Extracted samples during the fire-tube boiler experiments were directed to an Andersen Inc. eight-stage, 25L/min, atmospheric pressure in-stack cascade impactor. An MSP Inc. ten-stage, 30L/min Micro-Orifice Uniform Deposit Impactor (MOUDI) was used during the refractory-lined combustor experiments. In-situ light scattering PSDs were obtained using an Insitac Inc. particle counter sizer velocimeter with a working range of approximately 0.3 to 100 μm diameter which slightly overlapped and extended the PSD data collected by the SMPS. Scanning electron microscope (SEM) samples were collected on silver membrane filters to minimize particle charging effects.

In order to collect larger quantities of size-segregated PM for parallel toxicological studies and XAFS analyses, a large dilution sampler capable of sampling 0.28 m^3/min of flue gas was used[17]. The extracted sample passed through a cyclone (50 and 90% collection efficiencies for 1.8 and 2.5 μm diameter PM, respectively) and was then diluted with clean filtered ambient air (2.8 m^3/min) to approximately ambient temperature (3s residence time). The resulting PM was collected on 64.8cm diameter Teflon-coated glass fiber filters, transferred to sampling jars, and made available for subsequent chemical, physical, or biological analysis.

The No. 6 oil used in both experimental systems contained 2.33% sulfur and 0.1% ash. Operational characteristics for both systems included similar oil temperatures (380-400K), atomizing air pressures (200-240kPa), and stoichiometries (SR=1.2). The droplet PSD produced using the Delavan Airo Combustion air-atomizing oil nozzle (model 30615-84) in the fire-tube boiler was relatively narrow with a mean diameter between 30 and 40 μ m. The refractory-lined combustor experiments used a similar Spraying Systems Co. (model Air Atom 1/4-JSS) air-atomizing oil nozzle and produced PSDs believed to be similar to those for the boiler studies. Therefore, any differences in carbon burnout may be attributed to differences in temperature history rather than in droplet size.

RESULTS AND DISCUSSION

Equilibrium Predictions

Although numerous previous studies report on equilibrium predictions in combustion environments, there are relatively few results for the inorganic ash species and concentrations pertinent to residual oil combustion. Thermochemical predictions were determined using the Chemical Equilibrium Analysis (CEA) computer code for calculating complex chemical equilibrium compositions[18] with thermochemical data taken from the literature[18-26]. Of interest is the thermodynamic partitioning between vapor and condensed phases, as well as the partitioning between various species. The fuel ultimate analysis and trace element concentrations were taken from Miller et al.[9]. However, only trace elements with concentrations greater than 1 μ g/g of oil were considered in the calculations.

Figure 2 presents the results for seven trace elements. Mass fractions of the elements (as indicated species) are plotted against temperature. The elemental dew points are calculated to range from 1800K for V to 900K for Cr. These predictions indicate that, at the concentrations present in fuel oil, all seven elements might vaporize within the combustion environment. The dew points are lower than those calculated for pulverized coal and incineration applications, because of the low ash and metal concentrations[27]. These calculations indicate possible vaporization of Cr, for example, which is usually considered to be nonvolatile. In fact, in

contrast to calculations performed for higher Cr concentrations (100 vs. 0.03ppm)[28], Fig. 2 indicates that $\text{Cr}_2\text{O}_3(\text{s})$ is not a predicted condensed species at intermediate temperatures. All seven elements are predicted to form sulfates at lower temperatures (700-1100K) and this may well affect the solubility and perhaps the bio-availability and toxicity associated with these trace elements.

Particle Size Distributions

Figure 3 presents representative particle volume distributions for the fire-tube boiler (open symbols) and refractory-lined combustor (shaded symbols) experiments. With extra detail shown in the inset, these electrical mobility and light scattering measurements span four decades of particle diameter (0.01-100 μm). The fire-tube boiler PSDs indicate that most of the particle volume is associated with large (coarse mode) particles greater than 10 μm diameter. However, the inset shows that even the fire-tube boiler (open symbols) produces a small accumulation mode with a mean diameter between 0.07 and 0.08 μm , which is notably smaller than that for the refractory-lined combustor (shaded symbols). Thus, both configurations produced an ultrafine mode, but only the fire-tube boiler produced a bimodal PSD with a very large and dominant coarse mode.

This type of bimodal PSD is consistent with a mechanism of metal vaporization/nucleation/coagulation/condensation and incomplete burnout of residual fuel cenospheres[9]. SEM images of oil char collected from the fire-tube boiler showed a sponge-like morphology that clearly suggests swelling and extensive pore formation. In general, the extent of ash (metal) vaporization is dependent on carbon burnout. For incomplete combustion, a substantial fraction of the trace metals remain trapped in the unburned char particles, and never escape into the vapor phase. However, as the combustion gases cool, those metals which have vaporized will condense on existing surfaces or, if supersaturation partial pressures are large enough, will nucleate to form new particles. The distinctive submicron peak (between 0.07 and 0.08 μm diameter) is clearly indicative of particles formed by nucleation, coagulation, and condensation of materials that have vaporized. Thus, when large portions of the metal

constituents fail to vaporize (open symbols), the accumulation mode will be very much smaller than when they do vaporize (shaded symbols).

The refractory-lined combustor volume PSD (shaded symbols) consists exclusively of a narrow submicron accumulation mode with a mean diameter of approximately $0.1\mu\text{m}$, and both light scattering measurements and the lack of any cyclone catch containing gray or black particles with measurable LOI support this. Clearly, as the oil char is consumed, the metals have vaporized almost completely and subsequently nucleated and grown to form the distinctive accumulation mode shown in Fig. 3. Comparison between the areas under the submicron volume PSD for the two types of equipment suggests that, while only a very small fraction ($<1\%$) of the metal trace elements are vaporized in the fire-tube boiler, well over 99% of these constituents vaporize in the refractory-lined combustor.

Comparison of Calculated and Measured Mass Concentrations

Total mass concentrations were calculated by integrating measured volume PSDs and applying assumptions on appropriate densities, and compared to mass concentrations measured independently (Table 1). Particle densities of 3.5 and $1.85\text{g}/\text{cm}^3$ were chosen for the accumulation (SMPS) and coarse (INSITEC) modes, respectively, based on average densities of trace element sulfates and oxides and activated carbons and oil chars taken from the literature. The calculated mass concentrations of 180 and $93\text{mg}/\text{m}^3$ for the boiler and combustor, respectively, agree remarkably well with the independently measured mass concentrations of 184 and $93\text{mg}/\text{m}^3$ for the boiler and combustor experiments, respectively.

Elemental Composition and Particle Size

As expected, trace element measurements showed similar mass emissions for both the fire-tube boiler and refractory-lined combustor experiments (data not reported here). However, PM from the fire-tube boiler had high values for LOI ranging from 60 to 85%, while the refractory-lined combustor samples did not. For the latter, the sum of V, Ni, Zn, Fe, Cu, Pb, and S, as elements, account for $21.6\text{mg}/\text{m}^3$ or 23% of the total mass emissions; whereas, when

counted as sulfates, they account for $67.1\text{mg}/\text{m}^3$ or approximately 72% of the total mass emissions. XAFS spectroscopy indicated that, while a large portion (40-60%) of the sulfur measured in the fire-tube boiler PM existed as unoxidized organic sulfur (predominantly thiophenic sulfur), essentially all (99%) of the particulate bound sulfur in the refractory-lined combustor samples was in the form of sulfates.

Figure 4 presents elemental mass fractions vs. particle diameter for six metals and sulfur from the refractory-lined combustor tests. Metals were analyzed by XRF and ICP spectroscopy while sulfur and sulfate were determined by XRF and ion chromatography (IC) analysis, respectively. In general, XRF and ICP analyses produce similar results, and the emissions of these elements are concentrated in particles between approximately 0.08 and $0.2\mu\text{m}$ diameter (i.e., the accumulation mode shown on Fig. 3). Sulfur and sulfates are present within particles of the same size. Note that Fig. 4 also indicates the presence of a distinct mode at approximately $1\mu\text{m}$ diameter for the “less-volatile” metals (V, Ni, Zn, and possibly Cu), but not for the semi-volatile metal Pb. These data are consistent with the conjecture that less-volatile metals are released very late during the final stages of heterogeneous char combustion, while more volatile metals may vaporize more easily from interior surfaces and diffuse away from the char particle earlier in the process. The “less-volatile” metals are vaporized primarily as a consequence of the oxidation of neighboring carbon structures to which they are inherently bound.

Model Predictions

Experimental results were compared to model predictions using a multi-component aerosol simulation code (MAEROS)[29]. The purpose of these calculations was to illustrate that the resulting PSDs for both systems could be predicted using the same modeling approach involving char particle burnout (or premature quenching) followed by homogeneous nucleation and coagulation of a portion of the PM mass. A secondary objective was to determine the extent to which differences in coagulation rates caused by large differences in vaporized mass and resulting number densities might account for the differences in the measured PSDs. Details regarding the application of MAEROS to combustion environments can be found elsewhere[30].

Figure 5 illustrates the predicted PSD evolution for both the fire-tube boiler and refractory-lined combustor. Coagulation was the only mechanism considered.

To examine particle evolution within the fire-tube boiler, 99.8% of the 180mg/m³ PM mass was distributed among 13 sections (within MAEROS) so as to simulate the coarse mode mass PSD illustrated in Fig. 3. The remaining 0.2% of this mass was assigned to section 2 (0.0021-0.0046μm diameter) to simulate the nucleation of a vapor fume (see Table 1). The initial number concentration was 1.5x10¹⁶/m³, with the nucleating vapor accounting for well over 99.99% of these particles. System pressure and temperature were maintained at 1.01x10⁵Pa and 810K, respectively, to simulate post-flame conditions. Following this initial distribution, Fig. 5 presents calculated mass PSDs at 0.1, 1.0, and 10s. While these three PSDs also represent 180mg/m³, number concentrations decline as coagulation proceeds. At 1.0 and 10.0s the coagulating nuclei have grown into the 0.01 to 0.1μm diameter range. These times represent a range of typical residence times within combustion systems. At 10s, number concentrations have fallen to 1.2x10¹⁴/m³, and the coagulating nuclei are accumulating in a mode with a mean diameter of approximately 0.02μm (see Fig. 5 insets). The distribution of the coarse mode PM is relatively unaffected by these processes.

In contrast to the boiler simulation, 100% of the 90mg/m³ PM mass measured in the refractory-lined combustor was assigned to section 2. Again, this initial distribution corresponds to the partitioning seen in Table 1, and indicates complete oxidation of the oil char and vaporization of the inorganic elements followed by homogeneous nucleation. The initial number concentration is 2.7x10¹⁸/m³. In comparison to the boiler simulation, Fig. 5 indicates that these nuclei tend to coagulate much more quickly, due to the much larger number concentration. At 1 and 10s, as number concentrations fall to 8.2x10¹⁴ and 7.6x10¹³/m³, respectively, coagulation slows considerably causing the aerosol to accumulate into a mode between approximately 0.07 and 0.2μm diameter. Coagulation processes predict that the accumulation mode produced from the refractory-lined combustor would have a larger mean diameter compared to the accumulation mode produced from the fire-tube boiler. This prediction is reflected in the measurements. The accumulation mode measured from the refractory-lined combustor matches the predicted PSD, while the predicted accumulation mode for the fire-tube boiler (0.02μm diameter) slightly under-

predicts the measured value ($\sim 0.07\mu\text{m}$ diameter). Heterogeneous condensation of a portion of the vapor on existing nuclei is a competing process and has been shown to increase particle growth rates[31]. Additionally, the coagulation mechanism does not include the effect of differing fractal properties of any agglomerates that may be formed. It has been assumed here that only spheres result from the coagulation process.

CONCLUSIONS

The effects of combustion configuration on fine particle emissions from residual fuel oil combustion were examined. A laboratory-scale refractory-lined combustor, which was shown to simulate combustion conditions of a large utility residual oil fired boiler (as far as particulate emission factors were concerned), produced fly ash particles with an essentially unimodal PSD with a mean diameter of approximately $0.1\mu\text{m}$. Conversely, a pilot-scale fire-tube package boiler produced particles with a weak bimodal size distribution, which included a small fraction ($\sim 0.2\%$) of the mass with particle diameters below $0.1\mu\text{m}$ and a large fraction ($\sim 99.8\%$) of the mass with particle diameters between 0.5 and $100\mu\text{m}$. Here the large particles were shown to consist of large porous carbonaceous cenospheres resulting from poor carbon burnout, and this characteristic is not uncommon for that class of equipment. Although the total particulate mass concentrations in the flue gas of the refractory-lined combustor were less than half of those of the fire-tube boiler, ultrafine particle concentrations of the refractory-lined combustor were notably larger than those measured for the fire-tube boiler. Volume PSDs obtained from two independent particle sizing instruments were, with only a few very reasonable assumptions, consistent with independently measured total mass emission rates, for both equipment types.

ACKNOWLEDGMENTS/DISCLAIMER

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REFERENCES

1. Wilson, R., and Spengler, J.D., eds., *Particles in Our Air: Concentrations and Health Effects*, Harvard Univ. Press, Cambridge, MA (1996).
2. U.S. Environmental Protection Agency, National Ambient Air Quality Standards for Particulate Matter: proposed decision, 40 CFR, Part 50 (1996).
3. Bachmann, J.D., Damberg, R.J., Caldwell, J.C., Edwards, C., and Koman, P.D., "Review of the National Ambient Air Quality Standards for Particulate Matter: Policy Assessment of Scientific and Technical Information," EPA-452/R-96-013 (NTIS PB97-115406), Office of Air Quality Planning and Standards, Research Triangle Park, NC (1996).
4. Wolff, G.T., Closure by the Clean Air Scientific Advisory Committee (CASAC) on the staff paper for particulate matter, EPA-SAB-CASAC-LTR-96-008, U.S. Environmental Protection Agency, Washington, DC, June 13, 1996.
5. Federal Register, 62 FR 38652, July 18, 1997.
6. Dreher, K., Costa, D., Hoffman, A., Bonner, J., and Osornio-Vargas, A., "Pulmonary Toxicity of Urban Air Particulate Matter (PM)," *Air & Waste Management Association Meeting on Measurement of Toxic and Related Air Pollutants*, Research Triangle Park, NC, 1996.
7. Dreher, K., Jaskot, R., Richards, J.H., Lehmann, J.R., Winsett, D., Hoffman, A., and Costa, D., *Amer. J. Respir. Crit. Care Med.*, 153(4:A15) (1996).
8. Dreher, K., Jaskot, R., Lehmann, J.R., Richards, J.H., McGee, J.K., Ghio, A.J., and Costa, D.L., *J. Toxicol. Environ. Health*, 50:285-305 (1997).
9. Miller, C.A., Linak, W.P., King, C., and Wendt, J.O.L., *Combust. Sci. Technol.*, 134:477-502 (1998).
10. Garg, S., EPA Method 0060 - Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes, in *Methods Manual for Compliance with the BIF Regulations: Burning Hazardous Waste in Boilers and Industrial Furnaces*, EPA/530-SW-91-010 (NTIS PB91-120006), pp.3-1 through 3-48, Office of Solid Waste and Emergency Response, Washington, DC, 1990.
11. EPA Test Method 1A-Sample and Velocity Traverses for Stationary Sources with Small Stacks or Ducts, in 40 CFR Part 60 Appendix A, Government Institutes Inc., Rockville, MD, 1994.
12. EPA Test Method 5 - Determination of Particulate Emissions from Stationary Sources, in 40 CFR Part 60 Appendix A, Government Institutes Inc., Rockville, MD, 1994.

13. Galbreath, K.C., Zygarlicke, C.J., Huggins, F.E., Huffman, G.P., and Wong, J.L., *Energy & Fuels*, 12:818-822 (1998).
14. Huggins, F.E., and Huffman, G.P., *J. Hazardous Materials*, in press (1999).
15. Scotto, M.A., Peterson, T.W., and Wendt, J.O.L., *Twenty-fourth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, pp.1109-1118, 1992.
16. Linak, W.P., Srivastava, R.K., and Wendt, J.O.L., *Combust. Sci. Technol.*, 101(1-6):7-27 (1994).
17. Steele, W.J., Williamson, A.D., and McCain, J.D., "Construction and Operation of a 10 cfm Sampling System with a 10:1 Dilution Ratio for Measuring Condensable Emissions," EPA/600-8-88-069 (NTIS PB88-198551), Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, 1988.
18. McBride, B.J., Gordon, S., and Reno, M.A., "Coefficients for Calculating Thermodynamic and Transport Properties of Individual Species," NASA Technical Memorandum 4513 (1993).
19. Chase, M.W. Jr., *JANAF Thermochemical Tables*, 3rd ed., parts 1&2. American Institute of Physics, New York, NY, 1986.
20. Barin, I., Knacke, O., and Kubaschewski, O., *Thermochemical Properties of Inorganic Substances*, Springer-Verlag, New York, NY, 1973.
21. Barin, I., Knacke, O., and Kubaschewski, O., *Thermochemical Properties of Inorganic Substances*, supplement, Springer-Verlag, New York, NY, 1977.
22. Barin, I., *Thermochemical Data of Pure Substances*, VCH Verlagsgesellschaft, New York, NY, 1989.
23. Barin, I., *Thermochemical Data of Pure Substances*, VCH Verlagsgesellschaft, New York, NY, 1993.
24. TAPP - Thermodynamic Properties Software, V2.2, ES Microwave Inc., Hamilton, OH (1995).
25. Ebbinghaus, B.B., *Combust. Flame*, 101:119-137 (1993).
26. Ebbinghaus, B.B., *Combust. Flame*, 93:311-338 (1995).
27. Linak, W.P., and Wendt, J.O.L., *Fuel Process. Technol.*, 39:173-198 (1994).
28. Linak, W.P., Ryan, J.V., and Wendt, J.O.L., *Combust. Sci. Technol.*, 116-117:479-498 (1996).

29. Gelbard, F. and Seinfeld, J.H., *J. Colloid Interface Sci.*, 78(2):485-501 (1980).
30. Linak, W.P., and Wendt, J.O.L., *Prog. Energy Combust. Sci.*, 19:145-185 (1993).
31. Davis, S.B., Gale, T.K., Wendt, J.O.L., and Linak, W.P., *Twenty-seventh Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, pp.1785-1791, 1998.

Table 1. Comparison of calculated mass concentrations determined from measured volume PSDs with measured mass concentrations determined by EPA Method 5[12].

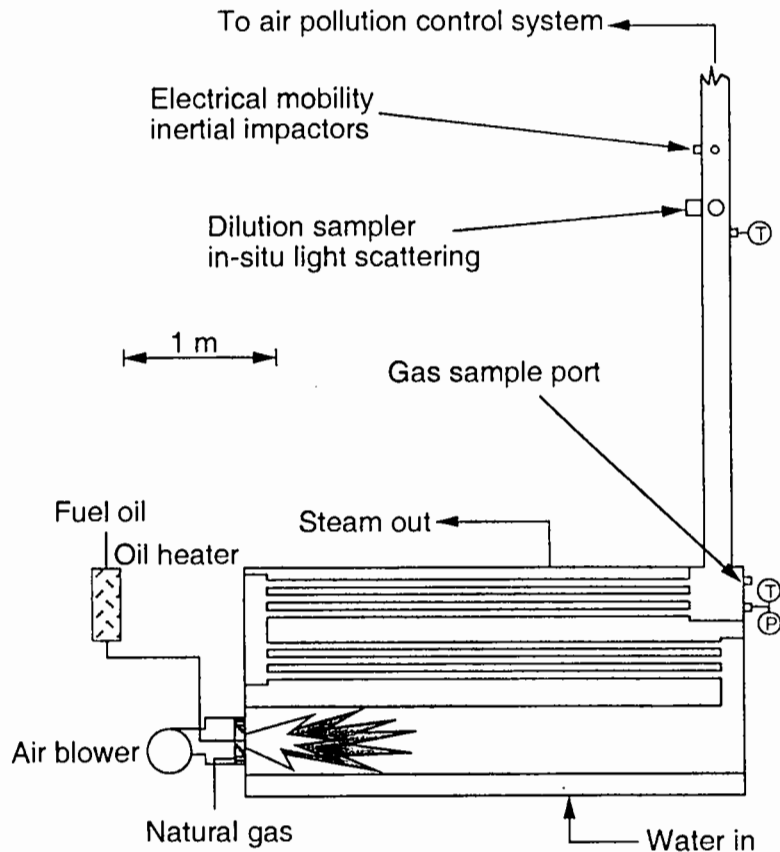
	VOLUME CONCENTRATIONS (MEASURED) ($\mu\text{m}^3/\text{cm}^3$)		MASS CONCENTRATIONS (CALCULATED) (mg/m^3) ¹		MASS CONCENTRATIONS (MEASURED) (mg/m^3) ²	
	BOILER	COMBUSTOR	BOILER	COMBUSTOR	BOILER	COMBUSTOR
SMPS	8.8e+1	2.7e+4	0.31	93	-	-
INSITEC	9.8e+4	1.9e+2	180	0.36	-	-
TOTAL	9.8e+4	2.7e+4	180	93	184 (6.2) ³	93

¹ Assumed fine mode particle density = $3.5\text{g}/\text{cm}^3$ based on typical densities for vanadium species. Assumed coarse mode particle density = $1.85\text{g}/\text{cm}^3$.

² Measured mass concentrations determined using EPA Method 5.

³ Number in parentheses indicated standard deviation based on multiple measurements.

Fire-tube boiler



Refractory-lined combustor

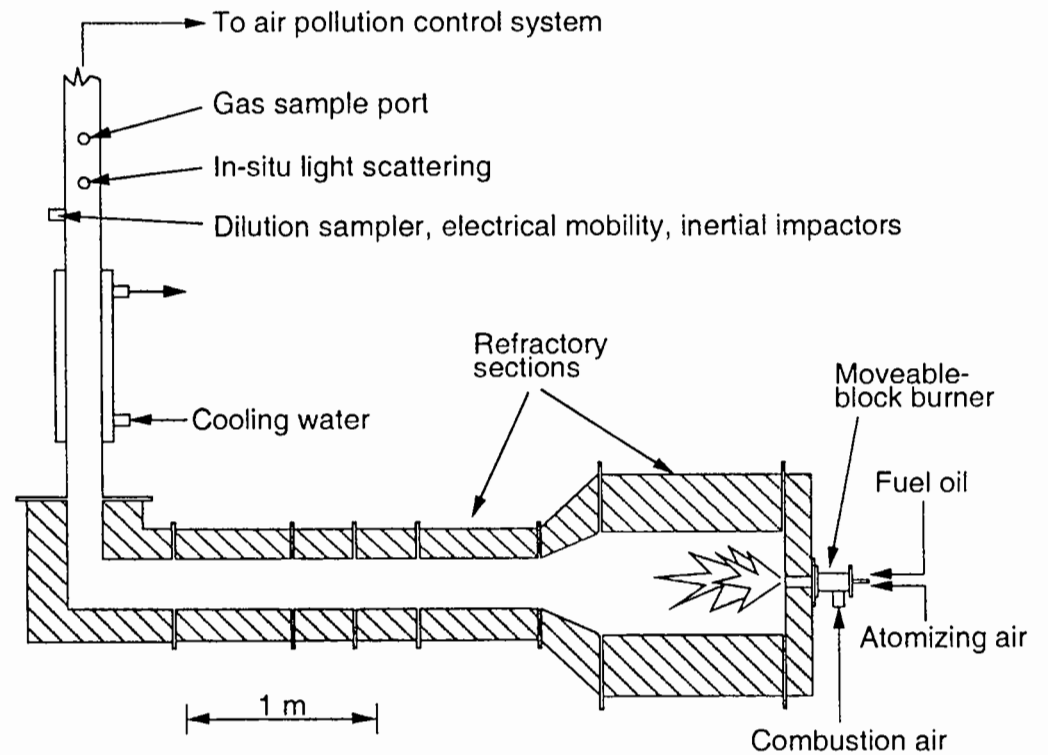


Fig. 1 - Two EPA combustion systems.

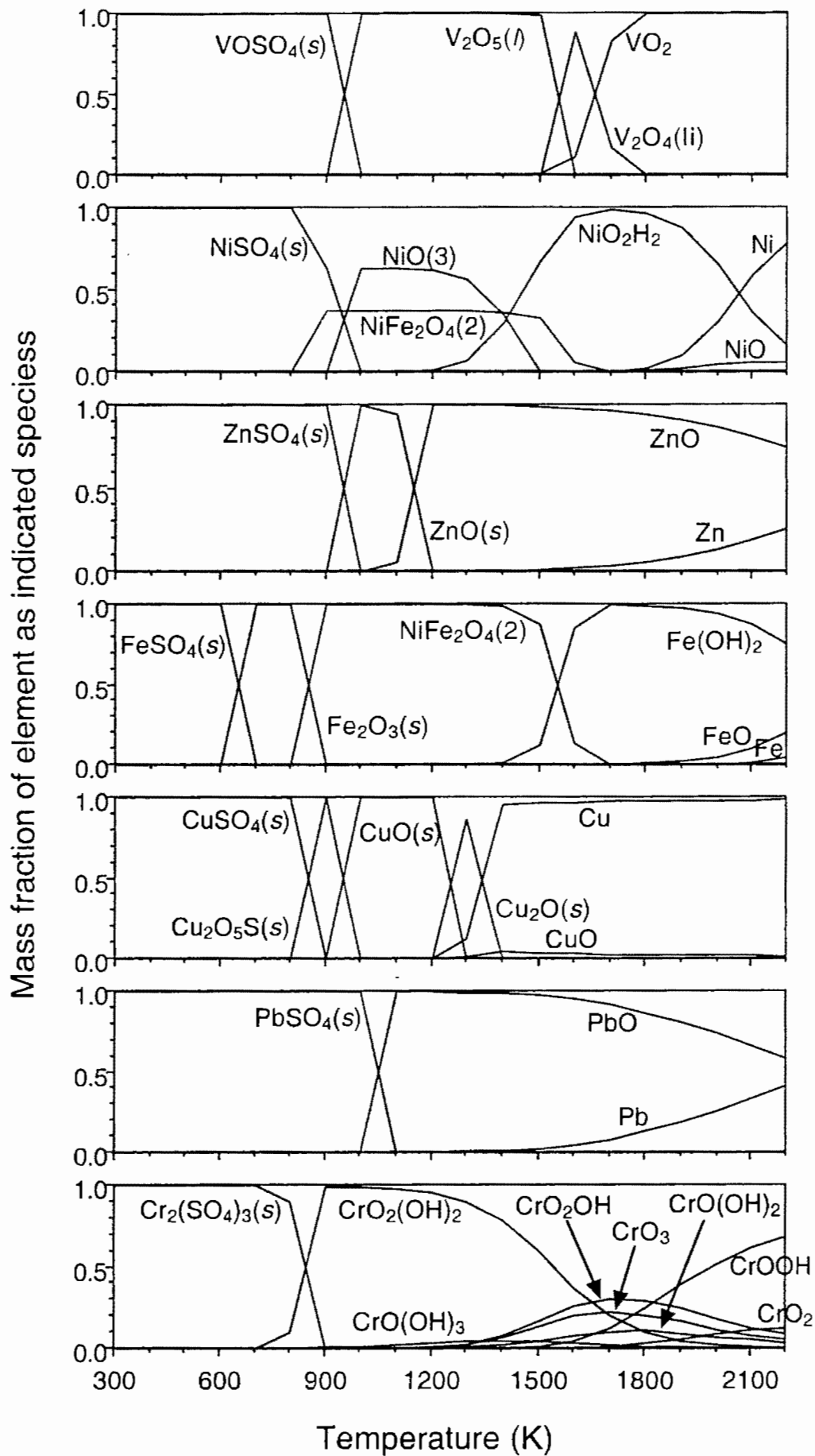


Fig. 2 - Residual fuel oil equilibrium predictions.

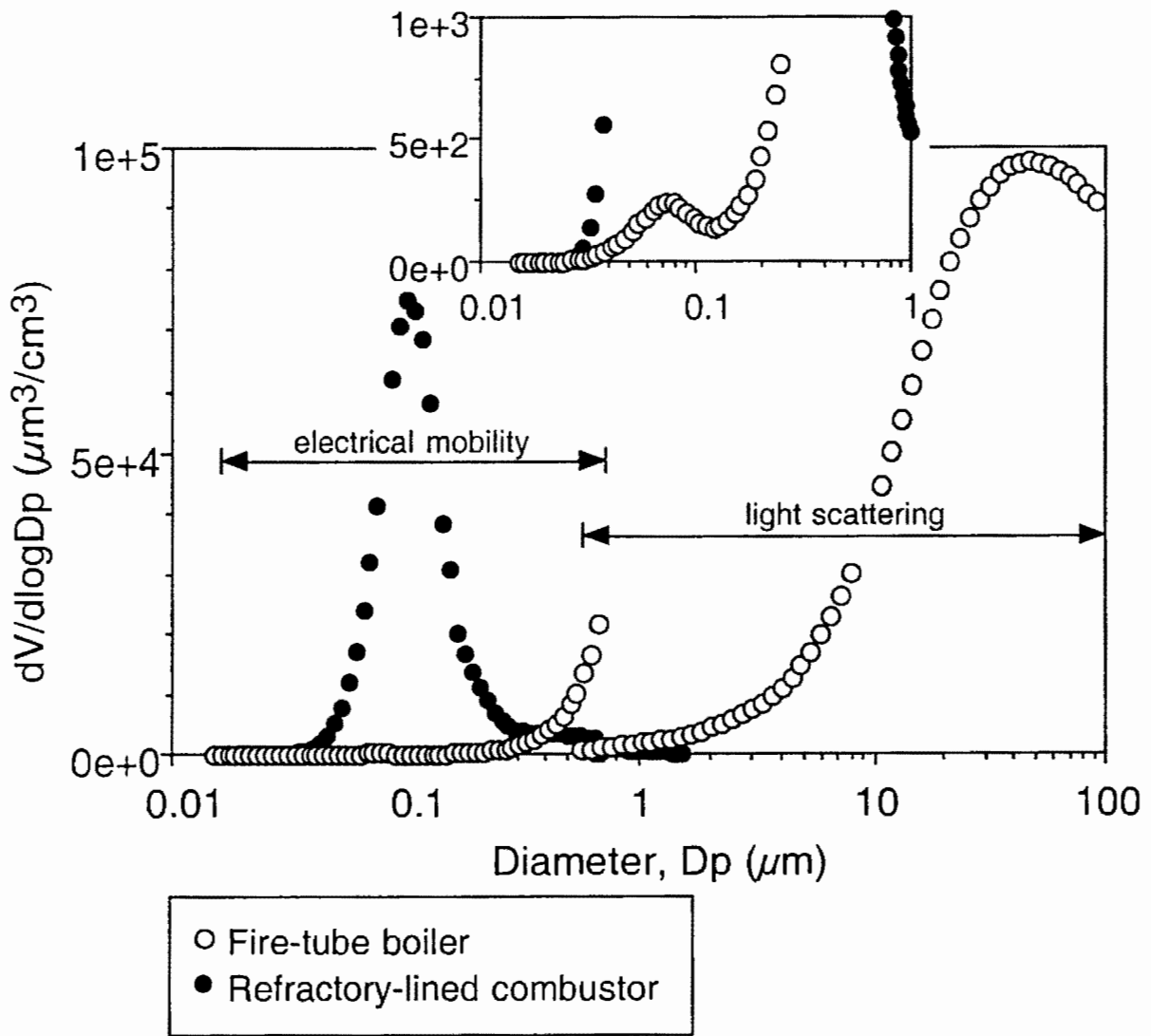


Fig. 3 - Measured volume PSDs.

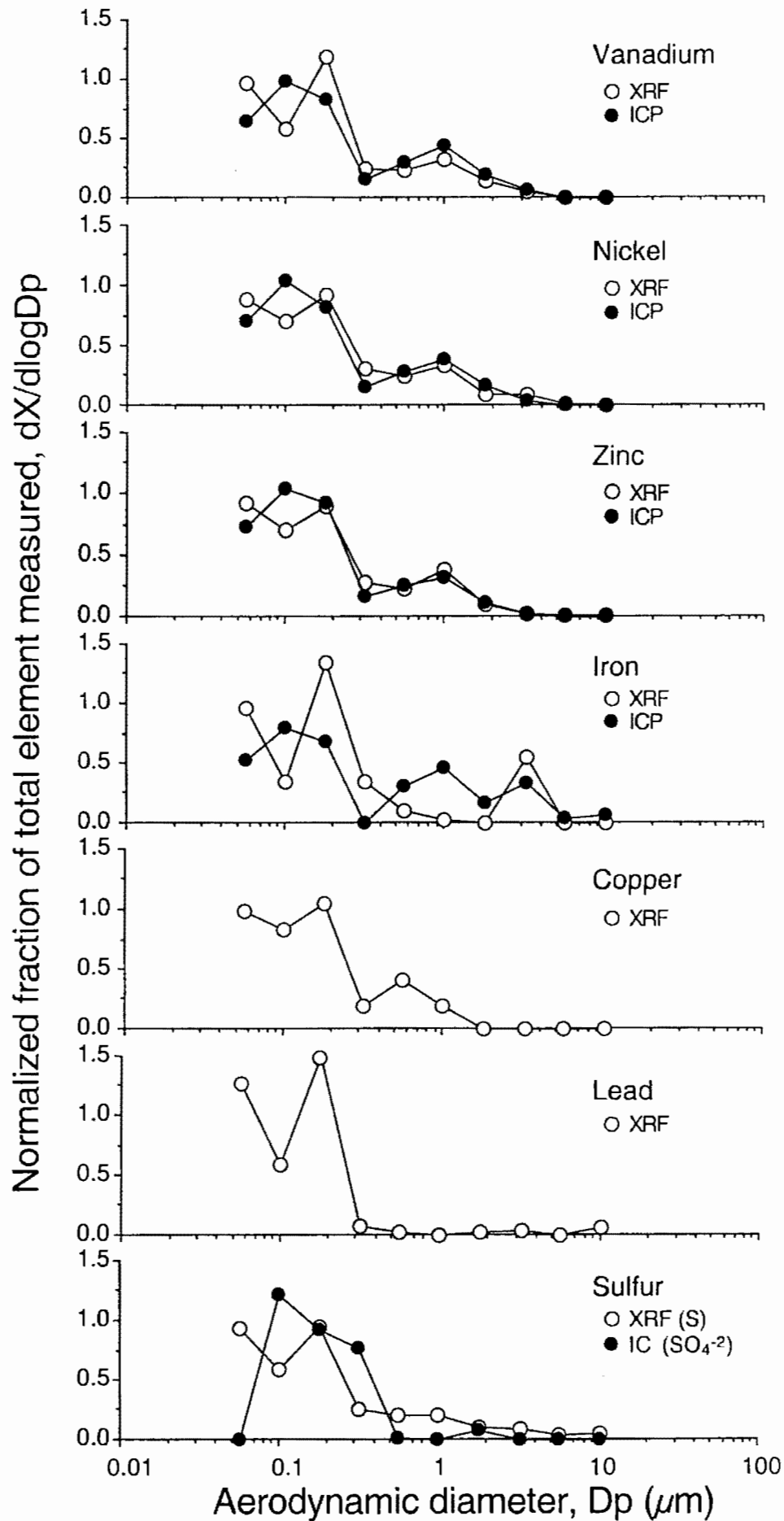


Fig. 4 - Elemental PSDs from the refractory-lined combustor.

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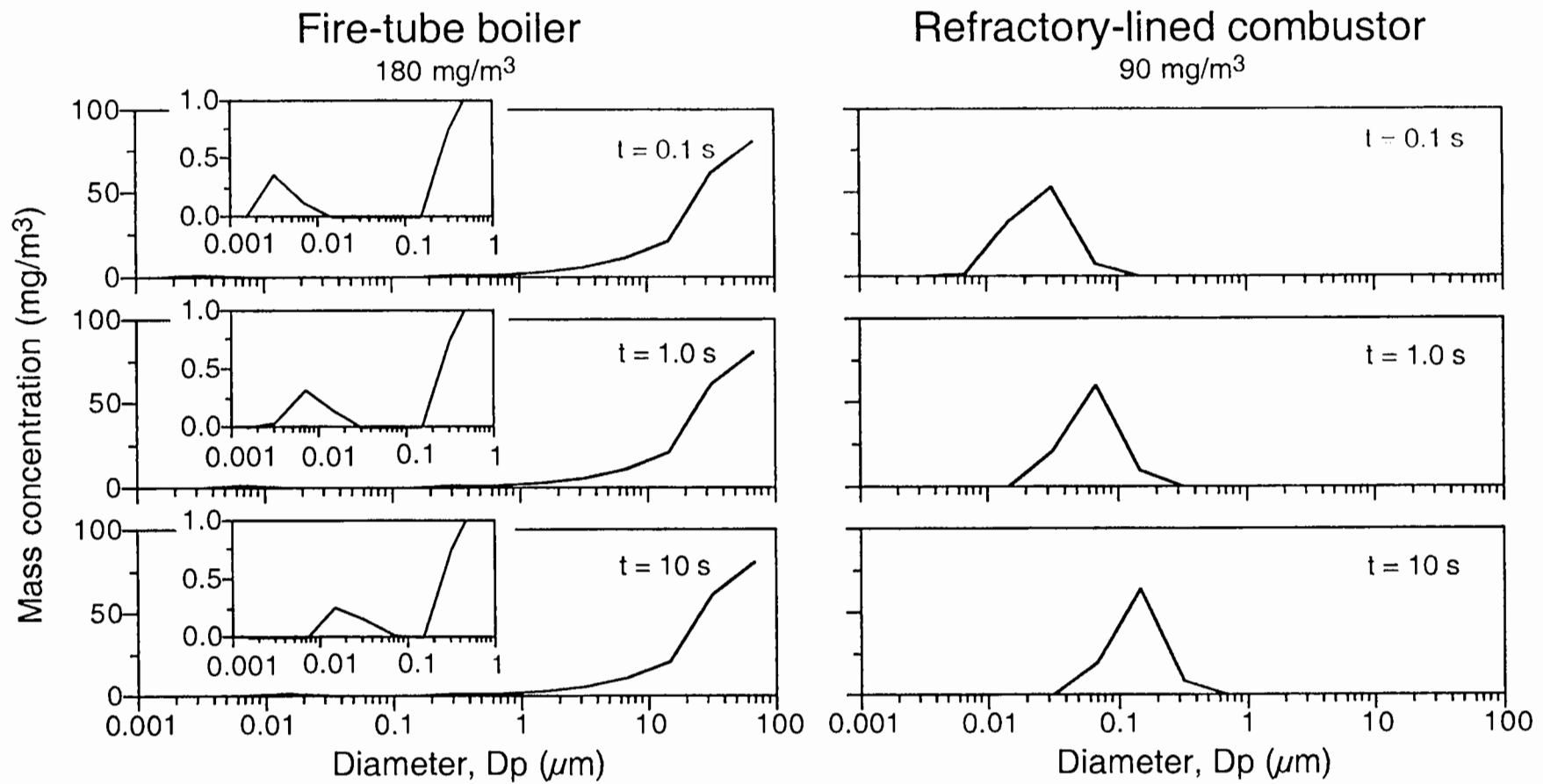


Fig. 5 - Predicted evolution of PSDs by coagulation.