COMPARISON OF METHODS FOR MEASURING CONCENTRATIONS OF SEMIVOLATILE PARTICULATE MATTER

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ABSTRACT
The purpose of this study was to compare methods for measuring concentrations of semivolatile particulate matter (PM) from indoor-environment, small, combustion sources. Particle concentration measurements were compared for methods using filters and a small electrostatic precipitator (ESP). Particle size distributions were measured using an electrical low-pressure impactor (ELPI). Semivolatile PM was produced from cigarette and incense smoke, and, for comparison, a relatively nonvolatile aerosol was produced from polyalphaolefin oil. Results showed that semivolatile PM concentrations measured using the ESP method were significantly higher than those measured using the filter method. The ESP method was shown to be a more effective means of measuring semivolatile PM under the test conditions.

INDEX TERMS
Particulate matter, Measurement methods, Semivolatile particles, Cigarette smoke, Incense smoke.

INTRODUCTION
Concentrations of PM in ambient and indoor environments are typically measured by gravimetric analysis of particles collected on filters. This method is suitable for measuring concentrations of nonvolatile PM, but may not be accurate for measuring concentrations of semivolatile PM. Semivolatile compounds have vapor pressures between 10^{-11} and 10^{-4} atm over the ambient temperature range, and these compounds may exist in both gas and particle phases in air. Semivolatile particles trapped in a filter matrix present a large surface area to the flowing airstream, and mass transfer between phases can occur. If gas-phase semivolatile concentrations are below equilibrium levels, mass may be transferred from the liquid particles collected on a filter to the gas phase, and concentrations may be underestimated (Volckens *et al.* 1999). If gas-phase semivolatile concentrations are above equilibrium levels, gas-phase semivolatiles may adsorb to the filter surface, and concentrations may be overestimated (McDow and Huntzicker 1990).

Methods for measuring concentrations of semivolatile PM have been developed that use denuders and filters, but these methods are cumbersome and are also subject to error from several sources (Volckens *et al.* 2000). An easier method of collecting semivolatile particles has been developed using a small ESP (Leith *et al.* 1996). As sampled air passes through the

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tubular ESP, particles are charged by ions generated by a corona with positive polarity, and charged particles are deposited on an aluminum foil substrate lining the wall of the ESP. The mass of particles collected on the substrate is determined by gravimetric analysis. Mass transfer between phases is minimized, because particles collected on the substrate present a smaller surface area to the flowing airstream, compared to particles collected on a filter, and the air velocity in the boundary layer near the substrate is less than the air velocity through a filter (Volckens *et al.* 2000).

In a previous study, PM emission rates for burning incense were determined using a filter method, an ESP method, and an ELPI method (Jetter *et al.* 2002). Emission rates determined by the ESP method were consistently higher than the other methods, most likely because the ESP captured and retained more semivolatile particle mass than the filters or the cascade impactor in the ELPI.

The objective of this study was to compare methods for measuring concentrations of semivolatile PM from indoor-environment, small, combustion sources. Particle concentration measurements were compared for the filter and ESP methods. Size distributions were determined using an ELPI. Semivolatile PM was generated from cigarette and incense smoke, and, for comparison, a relatively nonvolatile aerosol was generated from polyalphaolefin oil.

METHODS

A test system specifically designed for measuring PM emissions from indoor-environment sources was used for the experiments. Air flow through the system was automatically controlled with a proportional/integral/derivative (PID) controller, a variable-frequency drive that supplied electrical power to a blower, and an air-flow measuring station that provided feedback to the controller. Air from the blower passed through a plenum, prefilters, and ultra-low penetration air (ULPA) filters to a test chamber where aerosols were generated. Air flowed through the chamber, through a converging section, through a 180° bend, and then through a long, straight length of 25.4-cm (10-in.) diameter duct where isokinetic sampling probes were located. Air was exhausted through a stack to outside of the laboratory space. A detailed description of the test system, with a diagram and particle loss calculations, was included in a previous publication (Jetter *et al.* 2002).

For all tests, the target air-volume flow rate through the test system was 8495 L/min (300 cfm). The air flow rate was measured for each test, and the average flow rate for all tests, corrected to standard conditions, was 8463 L/min (298.9 cfm) with a standard deviation of 76 L/min (2.7 cfm). At this flow rate, the air velocity in the test section where the aerosol was generated was approximately 6 cm/s (12 fpm), an air velocity typically found in indoor environments with air circulation. The air velocity in the 25.4-cm (10-in.) nominal diameter duct was 253 cm/s (499 fpm), with turbulent flow, indicated by a Reynolds number of approximately 45000, for mixing of the air stream. A traverse of the cross-section of the duct at the location where the sampling ports were located with the sampling probe for the ELPI showed that particles were well-mixed in the air stream.

For each test, a sufficient amount of aerosol was generated to provide greater than 600 :g of particle mass collected on each filter and ESP substrate for accurate measurement. Cigarette and incense samples were placed on a remotely operated turntable, and a remotely operated lighter was used to ignite the samples to minimize particle generation not associated with the burning samples. Before the samples were ignited, the test chamber door was sealed, and

clean air was supplied to the test chamber for at least 15 minutes to reduce background concentrations of particles. Data were collected with the ELPI before each test to ensure that the background concentration of particles was less than 1 :g/m^3 and 1000 particles/cm^3. After each incense sample was ignited, a remotely operated air jet was used to blow out the flame so the samples smouldered as they would in normal use. During the lighting and burning of the cigarettes and incense, the samples were observed through a window in the test chamber. For comparison, a relatively nonvolatile aerosol of Emery 3004 polyalphaolefin oil was generated using a TSI Model 9302 atomizer.

Two University Research Glassware (URG) cyclone/filter assemblies were used to collect PM less than 2.5 :m in aerodynamic diameter ($PM_{2.5}$) and PM less than 10 :m in aerodynamic diameter (PM_{10}). Critical orifices were used to maintain the sampling flow rate for the cyclone/filter assemblies, and dry gas meters were used to measure the flows. A Dekati ELPI Model 97-2E real-time particle size spectrometer was used to measure particle size distributions. A data acquisition system was used to record output signals from the ELPI. An Aerosol Associates ESP was used to collect particles on aluminum foil substrates. A URG cyclone excluded particles larger than approximately 10 :m from the ESP, operating at a sampling flow rate of 3.0 L/min. A mass flow controller was used to control the sampling flow rate of the ESP. Filters and ESP substrates were weighed with a Sartorius MC-5 microbalance before and after experiments to determine the masses of particles collected.

Teflon® filters for the cyclone/filter assemblies and aluminum foil substrates for the ESP were equilibrated at 21.5 ± 0.3°C and 34 ±2% relative humidity for 24 hours in an environmental chamber, and tare weights were obtained before tests were performed. Following each test, filters and substrates were recovered and stored at a temperature of -40°C to reduce the loss of semivolatile particle mass. Filters and substrates were equilibrated for 24 hours at the same conditions before they were weighed again to determine the mass of PM collected.

As aerosol was generated, sampling pumps for the two cyclone/filter assemblies and the ESP were simultaneously activated, and sampling pumps were simultaneously deactivated at the end of the test period. The run time of the sampling pumps was measured and recorded. Data from the ELPI were recorded as 60-second averages before and during each test. Average PM concentrations were determined by dividing the measured mass of particles collected by the measured air sampling volume for each device. For each type of aerosol that was generated, five test replications were performed. Mean values and standard deviations were calculated for PM concentrations from the five replicates. For each replicate, the relative difference, D, between the PM_{10} concentration obtained by the ESP method, C_E, and the PM_{10} concentration obtained by the filter method, C_F, was calculated as: $D = C_E - C_F \; / \; [(C_E + C_F)/2]$. Statistical analysis was used to verify that differences in concentration measurements were due to the test methods rather than random error.

RESULTS

Table 1 shows measured PM concentrations in mg/m^3 for the three aerosol types and for the two test methods. Values are shown for the five replicates and for means and standard deviations of the replicates. Concentrations are shown for $PM_{2.5}$ and PM_{10} measured with the filters. For the cigarette and incense smoke, $PM_{2.5}$ and PM_{10} concentrations measured with the filters were similar, because the smoke consisted of particles less than 2.5 μm in aerodynamic diameter. However, for the polyalphaolefin aerosol, $PM_{2.5}$ and PM_{10} concentrations measured with the filters were not similar, because the aerosol contained some particles larger than 2.5 μm.

Table 2 shows relative differences between filter and ESP measurements of PM_{10} concentrations for the three aerosol types. Values are shown for the five replicates and for means and standard deviations of the replicates.

Figure 1 shows the filter versus ESP measurements of PM_{10} concentrations for the three aerosol types.

Table 1. Measured PM concentrations (mg/m^3)

Aerosol Type	Test Method	Replicate					Mean ± Std. Dev.
		1	2	3	4	5	
Polyalphaolefin aerosol (nonvolatile)	Filter, $PM_{2.5}$	6.8	6.7	6.6	6.6	6.6	6.6 ± 0.1
	Filter, PM_{10}	9.3	9.8	10.5	10.7	10.9	10.2 ± 0.7
	ESP, PM_{10}	8.8	9.5	9.1	9.4	9.3	9.2 ± 0.3
Cigarette smoke (semivolatile)	Filter, $PM_{2.5}$	12.1	10.1	10.3	11.0	9.6	10.6 ± 1.0
	Filter, PM_{10}	11.4	10.0	10.3	11.0	9.7	10.5 ± 0.7
	ESP, PM_{10}	15.2	12.1	13.0	14.0	12.5	13.3 ± 1.2
Incense smoke (semivolatile)	Filter, $PM_{2.5}$	2.3	2.8	3.2	3.3	2.8	2.9 ± 0.4
	Filter, PM_{10}	2.3	2.8	3.2	3.4	2.8	2.9 ± 0.4
	ESP, PM_{10}	2.6	3.1	3.6	3.7	3.0	3.2 ± 0.4

Table 2. Relative differences between filter and ESP measurements of PM_{10}

Aerosol Type	Replicate					Mean ± Std. Dev.
	1	2	3	4	5	
Polyalphaolefin aerosol	-0.05	-0.03	-0.14	-0.14	-0.16	-0.10 ± 0.06
Cigarette smoke	0.28	0.19	0.23	0.23	0.25	0.24 ± 0.03
Incense smoke	0.12	0.10	0.11	0.10	0.07	0.10 ± 0.02

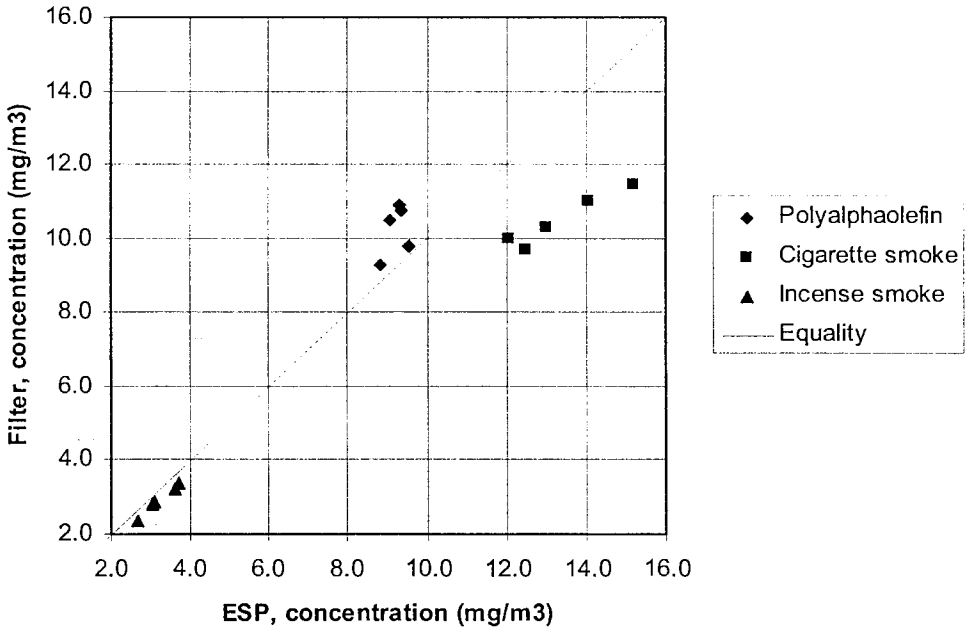

Figure 1. Filter versus ESP measurements of PM_{10} concentrations

Figure 2 shows the $PM_{2.5}$ size distributions by mass measured with the ELPI instrument for the three aerosol types. Mean values are shown with error bars representing plus or minus one standard deviation for the five values from replicated tests. The ELPI measurements, as well as the filter measurements, indicated that the polyalphaolefin aerosol contained particles larger than 2.5 μm in aerodynamic diameter, but the cigarette and incense smoke consisted of particles less than 2.5 μm. Size distributions were more consistent between replicates for the polyalphaolefin aerosol than for the cigarette and incense smoke. Size distributions for the incense smoke were consistent with those measured for incense smoke in a previous study (Jetter *et al.* 2002).

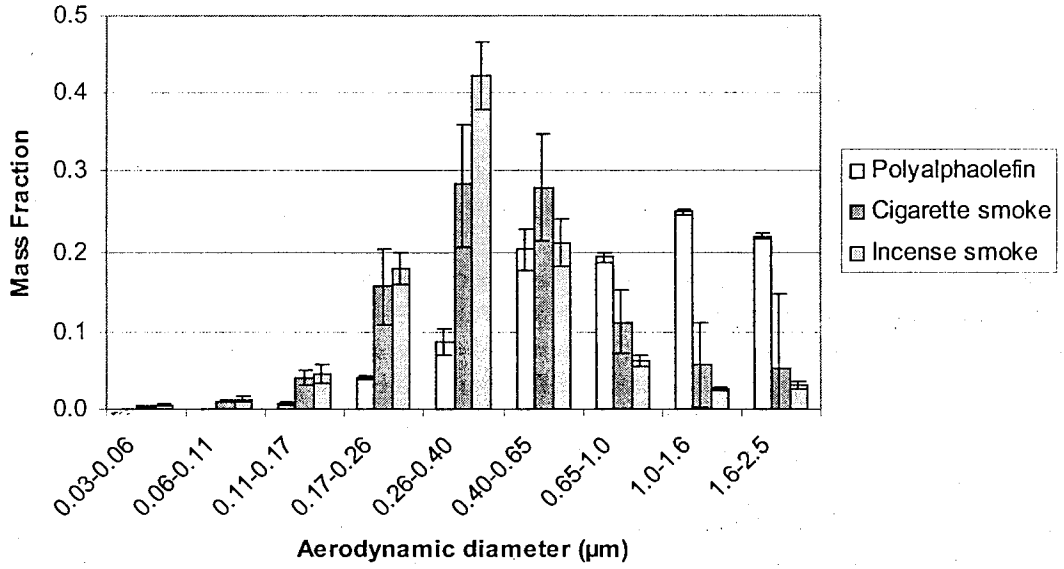

Figure 2. $PM_{2.5}$ size distributions by mass measured with ELPI

DISCUSSION

The data plotted in Figure 1 show that, for the nonvolatile polyalphaolefin aerosol, the concentrations measured with the ESP method were consistently lower than those measured with the filter method. However, for the semivolatile cigarette and incense smoke, the concentrations measured with the ESP method were consistently higher than those measured with the filter method. The relative difference in concentration measurements between the ESP and filter methods was greater for cigarette smoke than for incense smoke, possibly because the cigarette smoke contained more semivolatile matter than did the incense smoke.

The difference in concentration measurements between the ESP and filter methods for the polyalphaolefin aerosol may have been caused by a difference in sampling efficiencies at the sampling probes and/or cyclones, since this aerosol contained relatively large particles that are more susceptible to sampling issues. The larger particles also have a greater effect on gravimetric measurements. Conversely, the cigarette and incense smoke consisted of relatively small particles that are less susceptible to sampling issues, so differences in concentration measurements for the two test methods were less likely to be confounded by differences in sampling efficiencies. In previous tests, the ESP has been shown to have a collection efficiency of approximately 95% or greater for particles 0.02 to 1 μm and an efficiency of nearly 100% for particles in the 1 to 10 μm size range (Volckens *et al.* 2000).

Statistical analysis was performed on the PM_{10} data in Table 1. Differences in measured PM_{10} concentrations between the two test methods were analyzed with t-tests for paired data. Differences were calculated for each replicate by subtracting the PM_{10} concentration obtained by the filter method from the PM_{10} concentration obtained by the ESP method. For the polyalphaolefin aerosol, the mean difference was -1.0 mg/m^3 with a 95% confidence interval from -1.8 to -0.2 mg/m^3. For the cigarette smoke, the mean difference was 2.9 mg/m^3 with a 95% confidence interval from 2.1 to 3.6 mg/m^3. For the incense smoke, the mean difference was 0.3 mg/m^3 with a 95% confidence interval from 0.2 to 0.4 mg/m^3. Measurements with the ESP and filter methods were significantly different with observed significance levels (p-values) of less than 0.025 for the polyalphaolefin aerosol and less than 0.001 for both the cigarette and incense smoke.

CONCLUSIONS AND IMPLICATIONS

Results showed that semivolatile PM concentrations measured using the ESP method were significantly higher than those using the filter method. Although all methods for measuring concentrations have associated measurement error, the ESP method was substantially more effective than the filter method for capturing semivolatile PM in cigarette and incense smoke.

When PM concentrations are lower than those measured in this study, the ESP method may require a longer sampling time to collect sufficient PM mass for accurate gravimetric analysis. A possible drawback of the ESP method is that the corona produces ions that can react with the sampled air and form a metal oxide on the substrate surface over a long sampling period. However, gravimetric methods can correct for this phenomenon. To account for the metal oxide formation, a substrate with deposited PM is weighed, the PM is then removed from the substrate with solvents, and the clean substrate is weighed again. The difference in the two measurements provides an accurate indication of the collected mass, since the metal oxide is not removed from the substrate by the solvents. Another possible drawback of the ESP method is that the corona produces a small amount of ozone that can react with some compounds in sampled air. However, this does not appear to be a problem for PM measurements, since the particles are deposited on the substrate before coming into contact with the ozone plume inside the device.

Results from this study and from other studies have shown that the ESP method is an effective means of measuring PM in certain applications in the indoor environment, and the ESP method shows promise for other applications, such as in the ambient environment. Further testing and development of ESP methods are underway at U.S. EPA research laboratories and at the University of North Carolina at Chapel Hill.

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NRMRL-RTP-P-655

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECI
EPA/600/A-02/081		

4. TITLE AND SUBTITLE
Comparison of Methods for Measuring Concentrations of Semivolatile Particulate Matter

5. REPORT DATE

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) J.Jetter, Z.Guo (EPA); J.McBrian (ARCADIS); and M.Flynn (UNC)

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
ARCADIS Geraghty & Miller, Inc., RTP, NC.
Univ. of North Carolina, Chapel Hill, NC.

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Air Pollution Prevention and Control Division
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Published paper; 10/1/01-Pres.

14. SPONSORING AGENCY CODE
EPA/600/13

15. SUPPLEMENTARY NOTES APPCD project officer is J.J. Jetter, Mail Drop 54, 919/541-4830. For presentation at Indoor Air '02, Monterey, CA, 6/30-7/2-02.

16. ABSTRACT The paper gives results of a comparison of methods for measuring concentrations of semivolatile particulate matter (PM) from indoor-environment, small, combustion sources. Particle concentration measurements were compared for methods using filters and a small electrostatic precipitator (ESP). Particle size distributions were measured using an electrical low-pressure impactor (ELPI). Semivolatile PM produced from cigarette and incense smoke was compared with a relatively nonvolatile aerosol produced from polyalphaolefin oil. Results showed that semivolatile PM concentrations measured using the ESP method were significantly higher than those measured using the filter method. The ESP method was shown to be a more effective means of measuring semivolatile PM under the test conditions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Stationary Sources	13B
Tobacco	Particulate	06C,02D
Particles	Cigarettes	14G
Aerosols	Incense	07D
Smoke		21B
Measurement		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	6
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)