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A Personal Particle Speciation Sampler

Susanne Hering, Nathan Kreisberg, and Walter John





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STATEMENT

Synopsis of Research Report 114

A Personal Particle Speciation Sampler

Particulate matter (PM) in ambient air is a complex mixture containing particles of different sizes and chemical composition. Characterizing the composition of particles and linking it to toxicity may help reveal the underlying biological mechanisms of health effects, and in turn that information may point the regulatory community to the types of particles most likely associated with toxic effects. In addition, characterizing particles may help to trace particles back to their sources.

Epidemiology studies often use area measures of exposure as surrogates for personal exposure measurements. Exposure of individuals reflects local conditions and time-activity patterns that can vary greatly from exposure measured by the centrally based monitors. Personal monitors can better represent such actual individual exposure and thus have been incorporated into some studies examining PM. Because the components of PM responsible for adverse health effects are not always evident, however, personal monitors are needed that can collect information on different aspects of PM, including physical and chemical constituents—both organic and inorganic. This information is important both to complement epidemiology studies and to understand how different sources contribute to an individual's overall exposure. However, no single method allows determination of all characteristics of PM, and different sampling substrates are needed for assessing the presence and concentrations of the PM constituents of interest. The Health Effects Institute funded the study described in this report to design a personal monitor that addresses these needs.

APPROACH

Dr Susanne Hering of Aerosol Dynamics Inc and her colleagues set out to design and validate a personal sampler for particles smaller than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$) that is suitable for subsequent chemical speciation work. Specifically, the sampler was intended to meet the measurement needs for $\text{PM}_{2.5}$ mass concentration and several of its major constituents (including elemental carbon, organic carbon, sulfates, and nitrates). To

allow personal monitoring, the device had to be portable and capable of battery operation for 8 continuous hours. In developing the personal particle speciation sampler, Dr Hering and her colleagues selected and tested individual components of the sampler and then performed limited field tests of a prototype that incorporated the selected components.

The overall design of the personal particle speciation sampler consists of a size-selective inlet to remove all particles larger than $2.5\ \mu\text{m}$ in aerodynamic diameter, 2 sampling channels, a flow controller, and a pump. An oilless, greaseless, size-selection inlet allows precise measurement of organic carbon without the contamination problems that often occur when oil or grease is used. The 2 sampling channels allow use of quartz and Teflon filters so that PM mass concentrations and specific chemical constituents can be determined by applying a variety of filter-based analytic methods. The investigators decided to use a single pump to keep weight and noise to a minimum. Design of the personal particle speciation sampler also included the option for a denuder (a device used to remove interfering vapors) and for recapture of semivolatile components of the particles, such as nitrate. Finally, to allow detection of mass in the small sample volume obtained by the personal samplers, the personal particle speciation sampler design was made compatible with β gauge determination of PM mass, a technique that measures the attenuation of β particles through a blank-loaded and PM-loaded filter and associates the measured difference in β attenuation to PM mass.

RESULTS

Investigators evaluated several designs for each of these objectives and ultimately selected the most appropriate components. Three types of size-selective PM inlets were tested: microtrap, spiral, and compact cyclone—a modification of the cyclone impactor. Of these, the compact cyclone inlet was chosen because it performed closest to the federal reference method and provided the best exclusion of larger particles.

Research Report II4

To measure the total mass and chemical components of PM in their sampler, Dr Hering used 2 sampling channels: one with quartz filters used to measure elemental and organic carbon and one with Teflon filters to measure particle mass and inorganic anions (such as sulfate, nitrate, and ammonium). A cellulose backup filter impregnated with sodium chloride was included downstream from the Teflon filter to capture volatile nitrate that might be stripped from the primary filter.

Of the two denuders evaluated, the activated carbon honeycomb denuder was chosen because it was more compact and more effective at removing nitric acid than the aluminum denuder coated with magnesium oxide. The only disadvantage of this denuder was that it required periodic regeneration (heating to 100°C for at least 1 hour) to prevent release of nitric acid. Four systems for using the β gauge technique were assessed for stability, precision, and effects of loading and unloading filter cassettes. Investigators chose the AT100 β source and an integrated solid-state detection system because of its strong β source (providing good counting statistics) and long-term stability.

IMPLICATIONS

For analysis of personal PM exposure, it is increasingly important to get speciation data from personal

monitors. The careful attention to the weight and size elements, and the ability to measure PM_{2.5} mass concentration, elemental carbon, organic carbon, sulfates, and nitrates in the same instrument, may make the personal sampler described by Dr Hering and colleagues a valuable addition to personal monitoring tools. Once validated, this sampler could allow measurement of personal exposures to fine PM over relatively short periods of time (ie, 8 hours) and could measure important PM characteristics such as size and chemical constituents. The lightweight, compact design makes it suitable for widespread use, including personal monitoring for children and the elderly.

The study met the 5 design requirements that it set: 2-channel sampling; an oilless, greaseless inlet; provision for denuders; compatibility with β gauging; and single-pump operation. However, issues such as saturation still need to be addressed (as in environments high in tobacco smoke, ammonia, or nitric acid). Before being used widely, the sampler needs more comprehensive laboratory and controlled field testing, as is currently underway. This sampler therefore holds promise but is not yet ready for population studies.



CONTENTS

Research Report 114

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HEI STATEMENT

This Statement is a nontechnical summary of the Investigators' Report and the Health Review Committee's Critique.

INVESTIGATORS' REPORT

When an HEI-funded study is completed, the investigators submit a final report. The Investigators' Report is first examined by three outside technical reviewers and a biostatistician. The Report and the reviewers' comments are then evaluated by members of the HEI Health Review Committee, who had no role in selecting or managing the project. During the review process, the investigators have an opportunity to exchange comments with the Review Committee and, if necessary, revise the report.

| | | | |
|---|---|---|----|
| Abstract | 1 | Selection of Filter Media, Spot Size, and Sampler Flow Rate | 8 |
| Introduction | 1 | Inlet Evaluation | 9 |
| Specific Aims | 2 | Denuder Performance | 11 |
| Methods | 3 | β Attenuation Experiments | 12 |
| Overall Approach for PPSS Development | 3 | Prototype Design | 14 |
| PM _{2.5} Inlet Tests of Particle Penetration | 3 | Prototype Field Evaluation | 15 |
| Denuder Tests of Nitric Acid | | Discussion | 18 |
| Capture Efficiency | 5 | Acknowledgments | 19 |
| Filter Selection Tests | 5 | References | 19 |
| Aerosol Mass Determination | 6 | Appendix A. Other β Gauge Systems | 20 |
| Prototype Testing | 7 | About the Authors | 27 |
| Results | 8 | Abbreviations and Other Terms | 27 |

CRITIQUE Health Review Committee

The Critique about the Investigators' Report is prepared by the HEI Health Review Committee and Staff. Its purpose is to place the study into a broader scientific context, to point out its strengths and limitations, and to discuss remaining uncertainties and implications of the findings for public health.

| | | | |
|------------------------------------|----|--|----|
| Introduction | 29 | Assays for PM Mass Determination | 31 |
| Scientific Background | 29 | The Prototype PPSS | 32 |
| Technical Evaluation | 30 | Discussion | 32 |
| Aims and Objectives | 30 | Denuder | 32 |
| Study Design and Results | 30 | Assays for PM Mass Determination | 32 |
| Inlets | 31 | The Prototype PPSS | 32 |
| Sampling Channels | 31 | Conclusion | 32 |
| Denuder | 31 | Summary | 33 |
| Filters | 31 | Acknowledgments | 33 |
| Filter Area | 31 | References | 33 |

RELATED HEI PUBLICATIONS

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ABSTRACT

Fuller understanding of personal exposures to particulate matter with aerodynamic diameters below 2.5 μm ($\text{PM}_{2.5}^*$) requires a personal sampler suitable for assaying not only $\text{PM}_{2.5}$ mass but also its major chemical constituents: elemental carbon, organic carbon, sulfates, and nitrates. The goal to measure these constituents simultaneously imposes several constraints on personal sampler design. The aim of this project was to develop a sampler within these constraints that would be suitable for personal monitoring over 8 hours. In addition, with the intent to improve the precision of mass measurements, we investigated offline use of β attenuation.

The personal particle speciation sampler (PPSS) includes an inlet to remove particles larger than 2.5 μm , 2 sampling channels, and a pump with flow control. One channel serves for measuring particle mass and inorganic ions; the other, for measuring organic carbon and elemental carbon. Denuders can be placed in either channel or both channels. A backup filter can be placed on the denuded channel to collect volatilized particulate nitrate. Two prototype PPSS units were built and tested. The results of both laboratory testing of key PPSS components and a limited field study of the prototype in comparison to an AIHL (Air and Industrial Hygiene Laboratory) cyclone-based sampler are reported.

* A list of abbreviations and other terms appears at the end of the Investigators' Report.

This Investigators' Report is one part of Health Effects Institute Research Report 114, which also includes a Critique by the Health Review Committee and an HEI Statement about the research project. Correspondence concerning the Investigators' Report may be addressed to Susanne Hering, Aerosol Dynamics Inc, 2329 Fourth St, Berkeley CA 94710.

Although this document was produced with partial funding by the United States Environmental Protection Agency under Assistance Award R82811201 to the Health Effects Institute, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency, and no official endorsement by it should be inferred. The contents of this document also have not been reviewed by private party institutions, including those that support the Health Effects Institute; therefore, it may not reflect the views or policies of these parties, and no endorsement by them should be inferred.

INTRODUCTION

Personal monitoring has long been recognized as a critical aspect of exposure assessment. An important constituent of environmental exposure is $\text{PM}_{2.5}$, which is associated with combustion sources and photochemical processes. These fine particles have been implicated in health effects and are currently regulated by the US Environmental Protection Agency (EPA). Yet technical constraints have limited most personal monitoring of particle exposures to measures of either particle mass or mass and ionic constituents. As the parameter subject to environmental regulation, mass is certainly of interest, but it is an incomplete characterization of airborne particles.

$\text{PM}_{2.5}$ comprises many chemical constituents including sulfates, nitrates, organic carbon, soot-like carbon, and metals, and they vary in size and morphology. Which of the many particle parameters are important to human health is not known (EPA 1996). For example, some research has suggested that the smallest particles, those below 0.1 μm , are important to health effects (Peters et al 1997). Other research has implicated particle acidity (Dockery et al 1996; Spengler et al 1996). Morphology may play a role, as in cases of asbestos exposure, and the hypothesis that chemical composition affects toxicity is certainly plausible.

Apart from its possible health implications, particle chemistry is a valuable tool for identifying sources of particle exposure. For many years chemical mass balances have been used to trace the sources of particles found in ambient air. Similar methods can be applied to indoor air or personal exposure samples. For example, sulfate has very few indoor sources, and in many homes it is a good tracer for outdoor particles. Soot-like carbon results from combustion processes, including outdoor sources such as vehicular exhaust and indoor sources such as cooking fumes. With chemical information one can begin to assess the fraction of particle exposure attributable to outdoor ambient particles.

To understand the exposure of individuals to the particular constituents of $\text{PM}_{2.5}$, a personal monitor suitable for assaying all of its major chemical constituents, as well as its mass, is necessary. In current personal samplers particles

are collected onto a single Teflon filter. The samples may be assayed gravimetrically for mass and extracted for analysis of inorganic ions such as sulfate, but it is not possible to determine their complete chemistry. Specifically, these samples are not suitable for accurate assay of particulate nitrate or carbon.

Techniques for measuring the different chemical constituents of $PM_{2.5}$, including semivolatile species such as nitrate compounds, have been developed through many sampling programs (Fitz and Zwicker 1988; Solomon et al 1988, 1989; Chow et al 1993). These studies have shown that different types of filters and sampling approaches are required for assaying different chemical constituents of $PM_{2.5}$.

Gravimetric mass is measured on Teflon filters because they are not hygroscopic, do not adsorb sulfur dioxide or other vapors, and are mechanically stable. In contrast, analysis of carbon requires a noncarbonaceous substrate such as quartz, which can be cleaned before sampling by baking at 500°C. Quartz filters are analyzed by thermal evolution of the deposited aerosol with direct nondispersive infrared detection of carbon dioxide, or flame ionization detection after conversion of evolved carbonaceous vapors to methane. Because of their mechanical instability, quartz filters cannot be used to determine gravimetric mass.

Teflon filters do not efficiently retain volatile species such as ammonium nitrate. Sampling systems for nitrate consist of a denuder to strip out vapor-phase nitric acid followed by an absorbing filter medium that retains nitrate and nitric acid (Forrest et al 1982; Possanzini et al 1983; Appel et al 1984; Ferm 1986; Allegrini et al 1987; Ferm et al 1988). The wall of the denuder has an adsorbing coating that captures nitric acid by diffusion while allowing particles to penetrate (by virtue of their lower diffusion coefficient). The particles are then collected on the filter. An adsorbing filter medium can be selected such that any nitrate that disassociates during sampling is immediately recaptured. The Harvard personal sampler (Koutrakis et al 1988; Brauer et al 1989) uses a denuder filter system for accurate collection of particle nitrate and associated gases (ammonia, nitric acid, and sulfur dioxide).

Another issue for particle sampling is the inlet. All $PM_{2.5}$ samplers have an inlet to exclude particles above 2.5 μm in diameter. For its pre-cut device, the $PM_{2.5}$ federal reference method (FRM) sampler uses a well impactor consisting of a heavily oiled filter that sits in a cup upon which the incoming airstream impinges. Other samplers such as the personal environmental monitor (PEM, MSP Corp, Minneapolis MN) and the Harvard personal sampler (Brauer et al 1989) use a flat-plate impactor with an oiled impaction surface. The oil is used to prevent rebound and subsequent penetration of coarse particles to the fine particle sample.

Yet possible contamination by the oil is a concern in measurements of organic constituents.

The small volume of air that is obtained by personal samplers makes precise measurements at low levels of exposure difficult. One of the more challenging parameters to measure with precision is the gravimetric mass. Filter stability and weight capability limit the precision of mass measurements to within several micrograms. For personal sampling, with sample sizes of 1 to 2 m^3 , this translates to a few micrograms per cubic meter of air. An alternative method for assaying mass is β gauging. This method has been used for many years for real-time mass measurement of ambient air samples. These gauges measure the attenuation of β particles (energetic free electrons) through the filter sample. The β particles are scattered by the electron cloud of the filter and particle deposit. The scattering response is largely independent of the sample's chemical composition. The method is sensitive to the particle mass per unit area and can be adapted to very small samples. As such, offline β gauging is an attractive alternative to gravimetric mass determinations, but its use requires that the personal sampler be configured to ensure consistent orientation of the filter during gauging.

For these reasons, currently available personal samplers are not well suited for measurement of both the carbonaceous and inorganic ion fractions of $PM_{2.5}$. First, current samplers collect onto a single filter, and no single filter medium is suitable for all analytes. For example, the quartz filter media required for carbon analysis are too friable for gravimetric mass determinations. Second, only the Harvard personal sampler provides for retention of volatile constituents through a denuded adsorbing filter such as is used for ambient measurements of nitrates. Third, the commonly used oiled inlets are not desirable for carbon analysis because of the potential for contamination. Finally, even mass measurement is difficult because of the uncertainties imposed by the small sample sizes inherent with personal monitoring.

SPECIFIC AIMS

The objective of this project was to develop a personal monitor to meet measurement needs for each of the major parameters of $PM_{2.5}$: mass and content of elemental carbon, organic carbon, sulfates, and nitrates. The goal of simultaneously measuring all of these species as well as mass imposes several constraints on the sampler design. The aim of this project was to develop a sampler within these constraints while suitable for personal $PM_{2.5}$ monitoring over 8 hours. The specific design requirements for a PPSS, and the reasons for them are as follows:

- *Two-channel sampling* is required because no single filter medium is compatible with every analyte detection method. Determination of total organic carbon can only be done using quartz filters, which are friable and thus not compatible with gravimetric mass determinations (or with β attenuation owing to their thickness). Measurement of both carbon and particulate mass requires parallel collection on a Teflon filter and a quartz filter.
- *An oilless, greaseless $PM_{2.5}$ inlet* is desirable for precise measurements of organic carbon. Many of the commonly used inlets, such as the FRM sampler or single-stage impactors, use oil or grease to prevent particle rebound. When organic carbon is measured, this potential source of contamination should be avoided.
- *Provision for incorporating denuders* on each channel is required for accurate measurement of semivolatile constituents such as ammonium nitrate. A denuder is used to remove interfering vapors, and the primary filter (or alternatively a backup filter) usually consists of a reactive or adsorbing filter medium to prevent evaporation of deposited particles during sampling. Denuder filter methods are well developed for nitrate and are evolving for organic measurements as well.
- *Compatibility with β gauging* is necessary because precise mass measurements are difficult with the small sample volumes collected by personal samplers, especially for samplers with flow split between 2 channels. The ability to gauge the attenuation of β particles in samples used for mass determination offers a potentially more precise alternative to gravimetric mass measurements.
- *Single-pump operation* of both flow channels is dictated by size, weight, and noise limitations for personal samplers. All the components must be packaged in a sampler small enough to be worn, and permit 8-hour operation with a battery-powered personal sampling pump.

To address precision and accuracy, specific performance objectives were defined for the PPSS: independent tests for inlet function, denuder function, and β gauging as well as side-by-side precision testing and comparison with a reference sampler. Specific performance objectives incorporated goals for accuracy and precision: penetration efficiency within 5% of the published $PM_{2.5}$ FRM cutpoint for both liquid and solid particles; removal of more than 95% of the nitric acid upstream of the filters used for nitrate; detection limit defined at a 2 SD level of $1 \mu\text{g}/\text{m}^3$ for mass, at $0.3 \mu\text{g}/\text{m}^3$ for sulfate and nitrate, and at $0.5 \mu\text{g}/\text{m}^3$ for organic carbon

and elemental carbon; and precision of 8% for side-by-side sampling at levels above the detection limit.

METHODS

OVERALL APPROACH FOR PPSS DEVELOPMENT

The individual components of the PPSS are an inlet to remove particles above $2.5 \mu\text{m}$, 2 sampling channels, and a pump with flow control (Figure 1). One channel serves for measurement of mass and inorganic ions; the other, for organic carbon and elemental carbon. Denuders can be placed above either channel or both channels. A backup filter on the denuded channel collects the volatilized particulate nitrate. This basic scheme fulfills the design constraints outlined above.

The first step in the PPSS development was to select and test the individual components. These tests focused on inlet, nitric acid denuder, filter media, filter deposit area, and β gauge technology. In the second step the components were incorporated into a complete prototype PPSS. The precision and accuracy of the prototype were tested through field measurements with comparison to a reference sampler. The final step, field testing by an independent investigator, is being addressed in an ongoing study at Johns Hopkins University.

The experimental methods for testing each component and assessing the prototype performance are described in the next section.

$PM_{2.5}$ INLET TESTS OF PARTICLE PENETRATION

Performance of the $PM_{2.5}$ inlets was evaluated for both liquid and solid particles generated in the laboratory. Both types of tests are necessary to assess inlet efficiency. Solid particles are prone to bounce and reentrainment, leading to penetration of particles larger than the $2.5\text{-}\mu\text{m}$ cutpoint.

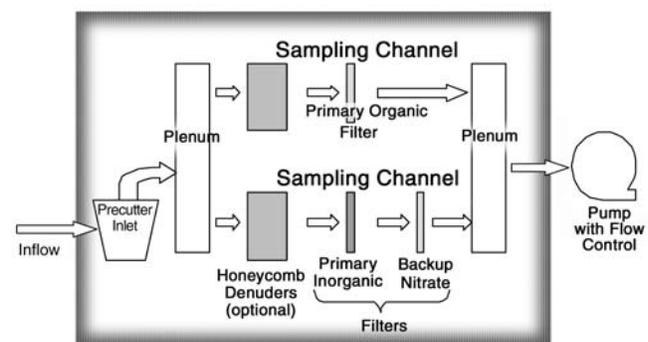


Figure 1. PPSS components.

These larger particles are then collected on the sample filter, leading to artifactual oversampling. Liquid particles are most likely to be lost during transport, and liquid particles smaller than the 2.5- μm cutpoint may be lost in the inlet. These losses lead to undersampling. Reliable performance of the inlet requires nearly equal performance for liquid particles and solid particles.

For candidate inlets, laboratory measurements were made of the penetration as a function of particle aerodynamic diameter using polydisperse and monodisperse test particles and an aerodynamic particle sizer (APS; model 3320, TSI, St Paul MN), as described by John and Kreisberg (1999). The size-dependent penetration efficiency was determined by comparing particle-size distributions measured before and after particles passed through the inlet being tested.

Solid particle tests were done using polydisperse polystyrene latex (Duke Scientific, Palo Alto CA) and polydisperse aluminum oxide (Micro Abrasives Corp, Westfield MA). The latex particles were in the form of a dry powder with particle diameters ranging from 1 to 20 μm . The aluminum oxide was also a dry powder. These powders were aerosolized using a fluidized bed constructed in our laboratory. A flanged tube sealed to the back half of a standard Gelman filter holder (Pall Corp, Ann Arbor MI) formed the chamber of the fluidized bed. The tube was clear to permit visual observation. The fluidized bed particles were glass beads 320 to 420 μm in diameter (sieve size 60/80; part 5420, Alltech, Deerfield MI). These beads are normally used for gas chromatography; they are clean and relatively free of fine particles. The glass beads, which were less massive than the large metallic beads that are typically used in fluidized beds and could damage the latex particles, were still capable of deagglomerating the test particles. The bed held approximately 17 g of the beads, which were supported by a 47-mm etched stainless steel screen supporting a glass fiber filter. The support screen and filter were reversed from the normal mounting to provide protection against breakage of the filter. For particle generation approximately 20 mg of the latex or aluminum oxide was added as a batch to the bed, and the fluidized bed was slightly shaken to mix with the particles. The bed airflow was increased until the bed had the appearance of boiling. Flow rates through the fluidized bed varied from 1 to 5 L/min.

Liquid aerosol tests were performed using oleic acid particles generated by direct nebulization or as a monodisperse aerosol generated by a vibrating-orifice aerosol generator (VOAG; model 3350, TSI). To maximize the resulting particle size, no solvent was used in the nebulization solution. To enhance the concentration of larger particles, output flow from the nebulizer was passed through a virtual impactor fashioned from a tee and 2 thin-walled brass tubes with 0.25-inch outside diameter and

separated by approximately 0.125 inch. The particle flow entered the tee through the first thin-walled tube at 1.1 L/min and exited through the second thin-walled tube at 0.1 L/min, with the excess being dumped through the side of the tee. Because of inertia, the larger particles were concentrated in the 0.1 L/min exit flow.

The particle penetration test system was configured such that aerosol flowing upward from the aerosol generator turned 90° to enter a horizontal tube (Figure 2). After passing a pair of polonium-210 (^{210}Po) charge-neutralizer strips, the flow was diluted with air and introduced to a plenum. The plenum had a large volume, 120 L, to stabilize the aerosol concentration. A pair of fans symmetrically stirred the aerosol in the plenum. The aerosol was sampled from the plenum by 2 vertical, parallel tubes. One sampled the aerosol in the plenum directly (bypass aerosol); the other sampled the aerosol after it had passed through the sampler's particle-size selector (sampler aerosol).

The cyclone inlet was tested within the personal sampler body, which was placed inside the plenum, whereas the microtrap and spiral inlets were sampled as isolated inline components. The personal sampler filter channels were left empty, and only one side was tested at a time. The exhaust of the channel being tested was coupled directly to the APS. To maintain the proper flow split and total inlet flow to the sampler, 2 L/min makeup flow was maintained for the other filter channel. Care was taken to match the aspiration efficiencies of the sampler aerosol and bypass aerosol lines in all cases.

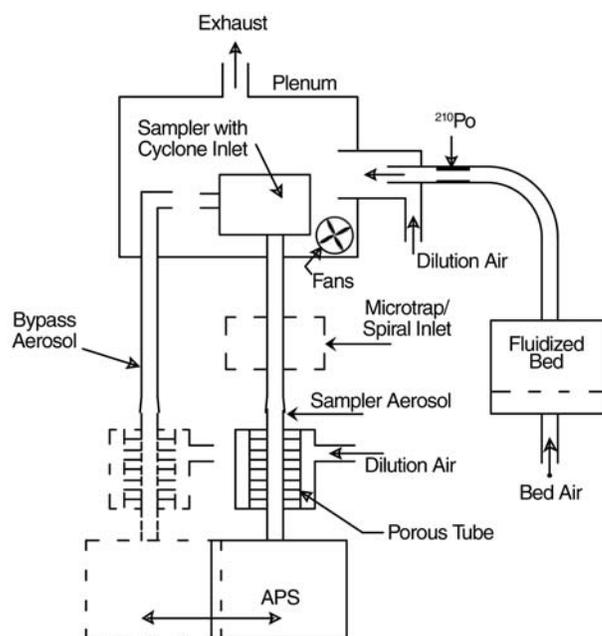


Figure 2. Particle penetration test system.

An APS was used to measure the particle size distributions. To avoid losses and possible biases associated with valves and tube connections, APS collection was simply switched between the 2 sampling lines. A short piece of conducting silicone tubing was used to enable fast connections. Because the APS sampled at a fixed flow rate of 5 L/min, it was necessary to augment or dilute the aerosol flow, depending on the flow rate of the sampler being tested. This flow compensation was achieved by introducing flow of 1 to 3 L/min from a porous tube surrounding the inlet of the APS (see Figure 2).

A measurement consisted of taking a 1-minute count of the bypass aerosol, followed by a 1-minute count of the sampler aerosol, and then another 1-minute count of the bypass aerosol. The 2 counts of bypass aerosol were averaged to compensate for changes in aerosol concentration (in each particle-size bin) during the measurements. The measurement was discarded if the change was more than approximately 15%. The sampling efficiency was obtained by dividing the sampler aerosol counts by the averaged bypass aerosol counts in each particle-size increment.

Penetration tests for ultrafine aerosols were made on the prototype personal sampler using a condensation particle (nuclei) counter (CPC; model 3760, TSI). Flow was drawn through the sampler equipped for normal operation minus filters and into the CPC to measure total particle counts. The penetration of particles below approximately $0.1 \mu\text{m}$ (the ultrafine mode that dominates particle counts in atmospheric sampling) was measured by comparing the particle counts emerging from the prototype sampler with those from directly drawn room air. The outlet of one channel of the sampler was configured to couple directly to the CPC through a short conducting tube that was alternately disconnected from the sampler and used to sample room air directly. The rated lower limit of detection of this CPC was $0.014 \mu\text{m}$, and the estimated loss to diffusion of particles of this size through the inlet tubing used for sampling was a mere 1.1% (but sharply decreased as particle size increased). The flow drawn by the CPC was 1.5 L/min, so 2.5 L/min makeup flow was drawn through the second channel to produce the normal total sampler inlet flow. The lower channel flow used by the CPC ensured that the measured diffusion losses within the sampler were at the upper limit of those expected during normal operation.

DENUDER TESTS OF NITRIC ACID CAPTURE EFFICIENCY

Two types of multitube denuders were tested for nitric acid penetration. One type of denuder was a magnesium oxide coating on an aluminum lattice manufactured by Hexcel (Dublin CA). The aluminum material was provided

in 2 lengths: 6 mm and 25 mm, with 216 and 271 cells, respectively, after being cut to mount in Teflon collars. The magnesium oxide coating was created by pressing 12 g magnesium oxide through a 150-mesh screen into 25 mL of ethanol, dipping the denuder into the resulting slurry, and drying it with compressed air. One day later compressed air was used to blow excess magnesium oxide out of the denuder.

The other denuder type consisted of an activated carbon honeycomb manufactured by Mast Carbon Ltd (Guildford, UK). The carbon honeycombs required no preparation other than mounting in a Teflon collar. This material is produced in monoliths, 29 mm in diameter and upward of 25 cm long, that can be cut to different lengths. Lengths of 1 cm with approximately 200 cells each were used in all of the tests. The manufacturer activated the surface of the samples through heating.

Laboratory testing was done using nitric acid generated by a permeation tube (VICI Metronics, Santa Clara CA), evolving into a scrubbed, dry airflow. A mass flow controller regulated the source flow. Catalyst-equipped chemiluminescent nitrogen oxide analyzers were used to detect the nitric acid upstream and downstream of the denuder (Figure 3). The denuder was mounted in a Teflon-lined chamber, and Teflon gas transport lines were used throughout. Cross comparisons between the 2 analyzers were performed with no denuder in place to correct for biases. An allowance of 60 minutes per configuration was used to reach internal equilibrium. Collection efficiency was determined by comparison of upstream and downstream readings on the nitrogen oxide analyzers.

FILTER SELECTION TESTS

For both carbon analysis and β gauging, detection limits depend on the amount of sample deposited per unit area of

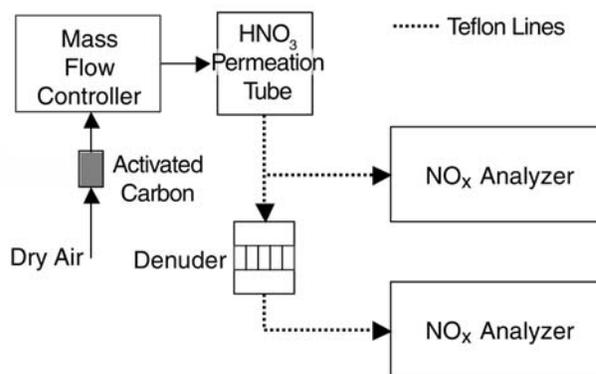


Figure 3. Test system for measuring denuders' HNO₃-capture efficiency. HNO₃ = nitric acid.

filter. Confining the deposit increases sensitivity, but results in a greater pressure drop across the filter. The optimal trade-off between filter medium, deposit area, pressure drop, and attainable flow rate was evaluated through direct measurements of different filter media and personal sampling pumps.

Pressure drops were measured as a function of filter face velocity using a magnehelic differential pressure gauge (Dwyer, Michigan City IN). Flow control was provided by personal sampling pumps (Air-Chek-2000, SKC, Eighty Four PA). Volumetric flow rates were verified using a flowmeter (Dry-Cal, Bios, Pomton Plains NJ). Stainless steel masks placed on either side of the filters were used to determine filtration areas. The masks were fabricated from 0.010-inch stainless steel shim stock using a hole punch to define the exposed area. For each of 4 types of filters, measurements were made at 3 flow rates (1, 2, and 3 L/min) and at 4 filtration areas (0.495, 0.710, 0.968, 1.26, and 3.60 cm²).

AEROSOL MASS DETERMINATION

β Attenuation Technique

The use of β -radiation attenuation to measure aerosol mass collected on a surface by filtration or impaction dates back to the early 1970s (Lilienfeld 1970; Lin et al 1973; Macias and Husar 1976). The β particles are high-energy electrons that are scattered by the electron cloud in matter. This scattering depends on the electron cloud density and is largely independent of the chemical composition of the matter (Jaklevic et al 1981). Transmitted intensity of β particles follows a simple exponential attenuation of the form

$$I = I_0 e^{-\mu x},$$

where I and I_0 are the transmitted and incident β -particle count rates, x is the areal mass density of the absorber, and μ is the mass absorption factor for the absorber, which is constant at approximately 0.26 cm²/mg.

The β penetration is measured first through the blank filter and then again after aerosol collection. The deposited mass depends logarithmically on the ratio of initial β intensity to final β intensity. The β gauges are calibrated using standard absorption strips and comparing the results with gravimetric measurements to obtain the effective value of μ for ambient aerosol. Linear approximations of the logarithmic ratio are acceptable for narrow ranges of density measurements as would be the case with small additions of aerosol mass to a filter.

Four β attenuation systems were tested in an effort to extend this method of aerosol mass determination to light

filter loads: (1) a commercial instrument called the β attenuation monitor (BAM-1020, Met One Instruments, Grants Pass OR); (2) a custom β gauge built by Aerosol Dynamics; (3) a custom system built by University of California (Davis CA); and (4) a commercial β gauge called the AT100 (Adaptive Technologies Inc [ATI], Rockville MD). Table A.1 summarizes the specifications for these different systems.

Test methods varied depending on the particular system. In general, the limit of precision was tested by monitoring the β attenuation of a static filter in place between the source and detector for more than 12 hours. Intervals for averaging were then selected to provide adequate counting accuracy (based on Poisson statistics) to judge the inherent stability of a given system. The level of precision for active gauging of filters, with the necessary repeated insertion and removal of filters, can only equal or fall below the precision level for this base case. Of the 4 systems, only the AT100 β gauge proved sensitive enough to approach our detection limit goal of 1 $\mu\text{g}/\text{m}^3$ for a 1-m³ sample. Details of the test methods and results for the rejected systems are described in Appendix A.

AT100 β Gauge

The AT100 β gauge is a commercial unit sold for monitoring thin film thickness in a manufacturing environment. Because rapid measurements are required to provide accurate thickness readings of film passing between rollers, this system's activity source (3 mCi of promethium-147 [¹⁴⁷Pm], half-life of 2.5 years) is higher than those of the other β gauge systems by a factor of 3000. ¹⁴⁷Pm is a pure β emitter like ¹⁴C but with slightly higher mean energies. The detection system consists of a proprietary silicon diode combined with an integrated pulse counter, all housed in a well-shielded case. A digital serial communication line connects with a computer to complete the system. ATI lent us a demonstration unit for evaluation during our PPSS development.

The gauge and custom filter-mounting jig were placed inside a custom-built clear plastic glove box (100-L capacity) built to provide sufficient thermal insulation from the room and human operator (a significant source of heat and humidity). This thermally decoupled arrangement allowed gauging of pairs of filters with shifts of less than 0.2°C or 0.1% relative humidity for the time needed to recalibrate the gauge and to gauge a pair of filters.

Tests performed with this system included precision tests on static filters, tests of repeatability in gauging reinserted filters (with and without aerosol loads), and tests comparing measurements of sampled ambient aerosol masses obtained by β gauging and by gravimetry.

Ambient samples were collected with a single PPSS sampler loaded with 2 Fiberfilm filters (T60A20, Pall Corp) for a mass measurement method comparison. By utilizing both channels of a single sampler, we could avoid the small uncertainties introduced by the passive flow split (previously shown to be less than 1%) because the 2 Fiberfilm filters should load similarly. To provide a gravimetric comparison, the filters were first weighed using a microbalance (model MC-5, Sartorius, Edgewood NY) before being loaded in the PPSS filter cassettes. To reduce filter shifting from compression within the PPSS, the cassettes were first loaded and then unloaded into the PPSS filter channel before the first gauging.

PROTOTYPE TESTING

Field performance of the PPSS was tested through ambient sampling in the area of Berkeley, California. Most samples were collected inside our laboratory directly beneath a ceiling air vent through which outdoor air could be drawn into the laboratory space. Two sets of samples were collected inside the Caldecott Tunnel, a freeway commuter tunnel to the east of Berkeley.

To evaluate precision, samples were collected with a pair of collocated prototype PPSSs. To evaluate accuracy, comparison was made with reference samples collected simultaneously using 47-mm Gelman filter holders with the AIHL cyclone providing the 2.5- μm precut. The AIHL cyclone is used in the IMPROVE monitoring network, the Caltech sampler, and the EPA speciation sampler marketed by Thermo Andersen (Smyrna GA). As such, this inlet has had extensive field evaluation and serves as a good reference standard for particle-size selection.

Because of delays in development of the β gauge system, mass measurements for comparing β gauging and gravimetry were made on a separate set of ambient samples (described as part of laboratory testing previously) taken after the field sampling was completed.

PPSS Sampling

For the PPSS the samples for mass determinations and inorganic ion analysis were collected on Fiberfilm filters. These were used as provided by the manufacturer. The backup filter used to capture of volatilized nitrate was a Whatman 41 cellulose filter impregnated with a 2% solution of sodium chloride in 50:50 water-methanol dried in a low-temperature oven. Samples for organic analysis were collected on Tissuquartz filters (2500QAT, Pall Corp). These were cleaned before sampling by prefiring at 500°C to 600°C for 2 or more hours. The total flow through the PPSS and the flow split between the 2 channels were checked at the beginning and end of each sampling period. The parts of the PPSS in contact with filter medium were

cleaned between each run by rinsing in isopropanol and distilled water.

AIHL Cyclone Sampler

For the AIHL cyclone sampler, mass and ions were collected on preweighed Teflo filters provided by Desert Research Institute (Reno NV). This was followed by a cellulose filter (Whatman 31ET) impregnated with 2% sodium chloride in water-methanol. Samples for organic analysis were collected on a pair of quartz filters operated in series. These were prefired in the same manner as for the PPSS. The cyclone was configured with a tee that split the flow between the 2 sampling lines. The flow through each sampling line was indicated by an inline rotameter downstream of each filter set. These were calibrated to provide accurate readings at the reduced pressure downstream of the filters, and differential pressure readings were obtained at the beginning and end of each run with magnehelic differential pressure gauges (Dwyer). The AIHL cyclone sampler used filters that were 47 mm in diameter and operated at approximately 6 times the flow rate of the PPSS. These quartz filters were masked to a diameter of 20 mm so that the face velocity would match the face velocity for the quartz filter of the PPSS to within 5%.

Fiberfilm filters were weighed in our laboratory using a microbalance (Sartorius MC-5) with a sensitivity of 1 μg .

Treatment of Samples

All samples were refrigerated before shipment to laboratories for analysis. Quartz filters for carbon analysis were stored in petri dishes lined with aluminum foil that had been baked at 300°C. Samples were shipped for analysis in containers with blue ice via priority overnight carrier.

Mass was determined gravimetrically after equilibration to 35% relative humidity and 22°C for 24 hours in accordance with EPA specifications. Sulfate and nitrate ions were measured by ion chromatography. Desert Research Institute performed all of the mass and inorganic chemical analyses and the carbon analysis for the first 5 of the 10 filter sets. Because of scheduling constraints at Desert Research Institute, Sunset Laboratories (Forest Grove OR) performed the carbon analysis for the remaining filter sets. Both laboratories use thermal desorption from the quartz substrate with analysis of the evolved carbon dioxide. Differences in methods led to systematic differences in the allocation of carbon mass as organic carbon or elemental carbon. Because each set of quartz filter samples was analyzed at one laboratory, however, precision tests for differences within a given set were not affected by these systematic differences in methods.

β Gauge Sampling

Six samples were taken in a separate evaluation of the β gauge method. A single prototype PPSS was used with both channels configured to collect mass on Fiberfilm filters. This approach eliminated uncertainties arising from differential filter loading in the channels and consequent changes in flow split. Each filter was weighed before and after sampling using the microbalance and the AT100 β gauge. Both the balance and the β gauge were housed in a clear polycarbonate box that was constantly purged with dry, filtered air. A small filter/blower maintained good circulation of dust-free air within the box. Relative humidity and temperature were monitored using a Humitter probe (Vaisala, Woburn MA). Static charge effects were minimized using polonium strips (NRD, Grand Islands NY) inside the box.

RESULTS

SELECTION OF FILTER MEDIA, SPOT SIZE, AND SAMPLER FLOW RATE

The first step in the design of the PPSS was to examine the detection limits, analyze the compatibility of filter media, and evaluate the gain that might be expected from concentrating the sample in a collection area on the filter. These analyses determined not only the sampling media but also the flow rate of the PPSS. As the inlet performance and denuder performance both depend on flow rate, these steps had to be resolved first.

Analytic detection limits for the filter analysis, mostly taken from the guidance document for PM_{2.5} speciation (Chow and Watson 1998), are listed in Table 1, which

shows that detection limits are better for inorganic ions than for mass or organic and elemental carbon. Because detection limits for organic and elemental carbon depend on the sample deposited per unit area of filter, we investigated the approach of concentrating the sample. Similarly, the sensitivity of β gauge methods for particle mass depends on the areal density of the particle deposit. Thus detection limits can be improved by concentrating particle samples onto a smaller deposit area than is the current usual practice. However, pressure drop considerations limit the extent to which sample size can be reduced.

Pressure drop was measured as a function of face velocity for 4 types of filters: 0.6- μ m pore size Nuclepore, Tissuequartz, and Fiberfilm; and 3- μ m Teflo. Nuclepore filters are attractive for β attenuation measurements because they have low areal density and are mechanically stable (ie, they are not easily compressed). Tissuequartz filters are used for carbon measurement. The Teflo and Fiberfilm filters may be useful for mass and inorganic ion analyses in that the Teflon substrate of these filters avoids gas-phase adsorption artifacts.

The pressure drop was plotted as a function of the face velocity, defined as the volumetric flow rate divided by the spot area (Figure 4). Although highly uniform and therefore attractive for β attenuation purposes, Nuclepore filters were quickly eliminated for displaying an excessively large pressure drop. Teflo filters are the standard for mass measurements. They resulted in small pressure drops but were too uneven in areal density for use in a β gauge.

The β gauges were capable of assaying spots with diameters on the order of 1 cm. This diameter translated into a face velocity of 20 to 60 cm/sec for the range of the SKC pump, 1 to 3 L/min (see vertical dashed lines in Figure 4).

Table 1. Analytic Detection Limits

| Species | Analytic Method | Method Limit of Detection ^a | Detection Limit for (1 m ³ air)/(1-cm ² filter) ^b |
|------------------|--------------------------|--|--|
| Mass | Gravimetry ^c | 3.5 μ g/filter (47-mm diameter) | 3.5 μ g/m ³ |
| | BAM-1020 β gauge | 2.0 μ g/cm ² | 2.0 μ g/m ³ |
| Nitrate | Ion chromatography | 0.05 μ g/mL | 0.2 μ g/m ³ |
| Sulfate | Ion chromatography | 0.05 μ g/mL | 0.2 μ g/m ³ |
| Ammonium ion | Autocolorimetry | 0.05 μ g/mL | 0.2 μ g/m ³ |
| Organic carbon | Thermal optical analysis | 0.8 μ g/cm ² | 0.8 μ g/m ³ |
| Elemental carbon | Thermal optical analysis | 0.2 μ g/cm ² | 0.2 μ g/m ³ |

^a From Chow and Watson (1998).

^b Corresponds to 2 L/min flow through 1 cm² for 8 hours.

^c Improvements in microbalances have reduced these limits by approximately a factor of 4, substituted here, compared with the original published values of 15 μ g per filter.

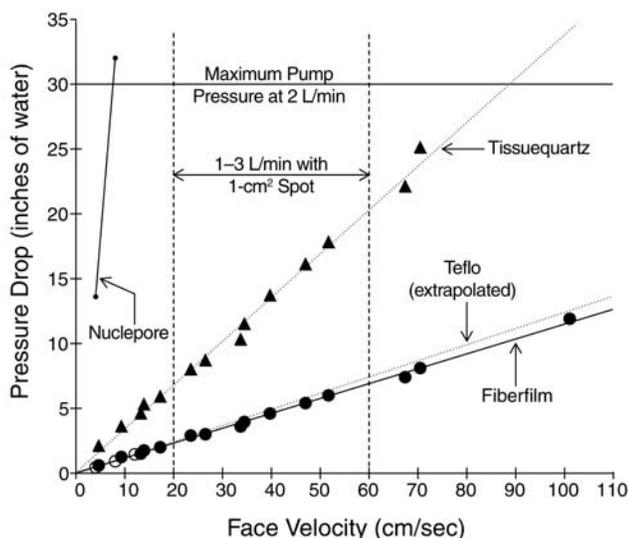


Figure 4. Pressure drop of unloaded filters versus face velocity.

Both Fiberfilm, best for β gauging, and Tissuequartz, best for analysis of organic and elemental carbon, had pressure drops well within the limits of the SKC pump for sampling rates of 2 L/min. At 3 L/min, the Tissuequartz pressure drop exceeded the water limit of 15 inches for this particular pump although the Fiberfilm remained at half that level. The SKC pump is representative of current personal sampling pumps in its limitations.

The effect of loading on these pressure drops was tested using a 25-mm Fiberfilm filter loaded with aluminum oxide particles generated by a dust-disperser system. A total mass of 167 μg was collected, which is equivalent to an areal density of 46 $\mu\text{g}/\text{cm}^2$. This density is conservatively high for that likely to be encountered by a personal sampler with a flow rate of 2 L/min through a 1-cm spot for 8 hours, for a total sample volume of roughly 1 m^3 . The pressure drop before and after collections was measured to be 3.0 inches of water, indicating no measurable change.

On the basis of these tests, we selected Fiberfilm and Tissuequartz filters with collection diameters of 7 and 8 mm, respectively, and with 2 L/min flow through each channel. The result was a deposit area of 0.38 and 0.50 cm^2 for inorganic and carbon samples, respectively, and the sample volume for an 8-hour collection was 1 $\text{m}^3/\text{channel}$. The corresponding detection limits expected from the values given in Table 1 were 0.1 $\mu\text{g}/\text{m}^3$ for elemental carbon, 0.4 $\mu\text{g}/\text{m}^3$ for organic carbon, and 0.8 $\mu\text{g}/\text{m}^3$ for mass determined by β attenuation.

INLET EVALUATION

Three types of inlets were examined for use in the PPSS: particle microtrap, spiral, and cyclone. The first 2 types were new and thus untested but offered the advantage of compactness. The cyclone was more difficult to package in a compact sampler but had repeatedly been shown to provide good cutpoints for both liquid and solid particles.

Microtrap Inlet

An existing microtrap particle collector was modified for use as a prospective precut device for the PPSS. The microtrap collector consists of a staggered array of circular jets stationed above a second array of receiving cups or microtraps. The particle-laden airstream passes through the jets and makes a sharp turn over the microtraps. As a result of the particles' inertia, particles above a well-defined aerodynamic size, the cutpoint, are deposited into the collection microtraps situated directly beneath each jet orifice. The resulting penetration of solid, polydisperse polystyrene latex particles at a total flow rate of 2 L/min using 24 jets was determined. The average of 2 runs is shown by the dotted line in Figure 5, with error bars indicating ± 1 SD according to Poisson counting statistics. The 50% aerodynamic cutpoint is at 2.5 μm as desired, but approximately 5% penetration is indicated for particles above roughly 4 μm in diameter. Without further refinements or the addition of a second precut device upstream of the microtrap

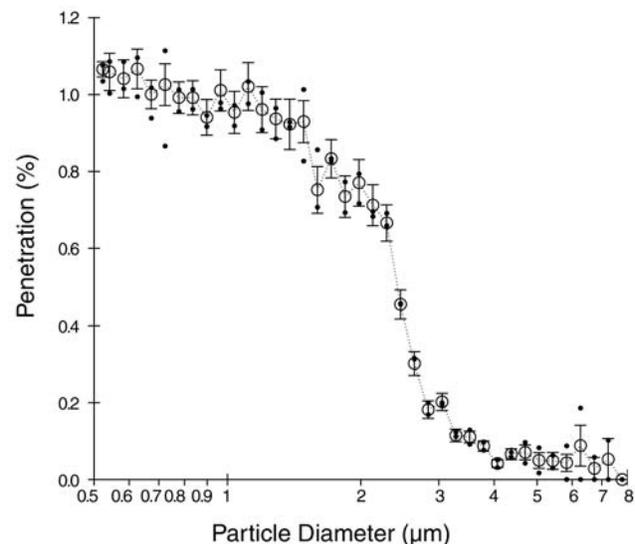


Figure 5. Laboratory measurements of penetration of solid, polydisperse polystyrene latex spheres through a particle microtrap at 2 L/min flow rate. Each circle is the average of 2 runs (points) and circles are shown with ± 1 SD Poisson error bars based on raw counts in each APS size bin.

targeting particles of 4 μm or larger, the microtrap could not reliably provide 100% collection of these larger particles. Significant impact on $\text{PM}_{2.5}$ mass collected can result with even a low but finite penetration of large particles. Therefore, the microtrap in its current configuration does not satisfy the PPSS design goal for mass.

Spiral Inlet

The spiral inlet consists of a curving spiral channel that provides inertial removal of large particles with relatively gentle impact to avoid bounce and disaggregation. Extensive laboratory tests had shown the spiral inlet to be effective at removing both liquid and solid bouncy particles and its performance to be equivalent to the EPA FRM $\text{PM}_{2.5}$ standard. However, ambient field tests we performed with the spiral inlet in certain locations (eg, Phoenix AZ) showed the presence of soil dust elements and larger masses than were obtained by collocated cyclone sampling, indicating coarse particle penetration. Although this effect was never reproduced in the laboratory owing to the difficulty in producing large enough particles, this consistent field observation indicated the necessity of taking precautionary measures.

Preliminary work was started on testing a precut device based on a virtual cyclone designed by Walter John following the work of Torczynski and Rader (1997), with the objective to eliminate large-particle penetration. Chen et al (1999) reported on a virtual cyclone for personal sampling that provided a respirable (4- μm) particle cutpoint. This virtual cyclone could be placed ahead of the spiral or microtrap to exclude the largest particles. Laboratory measurements indicated that the use of a virtual impactor precut device eliminated coarse particle penetration without influencing the cutpoint characteristics of the spiral inlet. With the addition of a second precut device, however, the advantage of compactness was lost. Therefore the spiral inlet was no longer satisfactory for use in the PPSS.

Cyclone Inlet

While the filter channel design was under development, it became clear that a parallel, cylindrical precut device would best complement the evolving PPSS design. The use of a compact cyclone approach, suggested by Walter John and following the design of Kenny and Gussman (1997) was therefore adopted. Using Kenny's proportions and design criteria, we built a cyclone to provide a 2.5- μm cutpoint at 4 L/min (the combined flow for the 2 channels of the PPSS).

Two operating configurations for the sampler were evaluated: one direct and the other with inlet tubing. In the direct configuration the PPSS was placed inside the test chamber, and the challenge aerosol was aspirated directly into the inlet port on the face of the sampler. This configuration is

analogous to the PPSS being worn on the subject's torso. In the second configuration particles were sampled through a 46-cm-long, flexible, electrically conducting tube attached to the PPSS inlet. This second configuration mimics placement of the PPSS in a small waist pouch or backpack with a tube extending to the vicinity of the breathing zone.

The collection efficiency of the cyclone inlet was tested with the cyclone mounted inside the sampler. The 2 filter channels were empty, enabling measurement of particle penetration through the cyclone and plenum into the filter chamber. Calibration tests were done with solid, polydisperse polystyrene latex particles and with liquid, monodisperse oleic acid particles. Owing to limitations of the APS, calibration with polydisperse oleic acid could not be performed, as described in the Methods section.

Calibration results are shown in Figure 6. Each set of points represents the average of 6 individual penetration curves for samples obtained using the direct configuration or 5 individual curves for samples obtained using the configuration with inlet tubing. For direct sampling the cutpoint (the diameter of particles collected with 50% efficiency) was 2.55 μm . The geometric standard deviation (GSD), given by the square root of the ratio of particle diameters for collection efficiencies of 84% and 16%, was 1.24. No difference was evident between liquid and solid particles. Sampling with inlet tubing resulted in a cutpoint of 2.50 μm with a GSD of 1.25. Within the accuracy of the

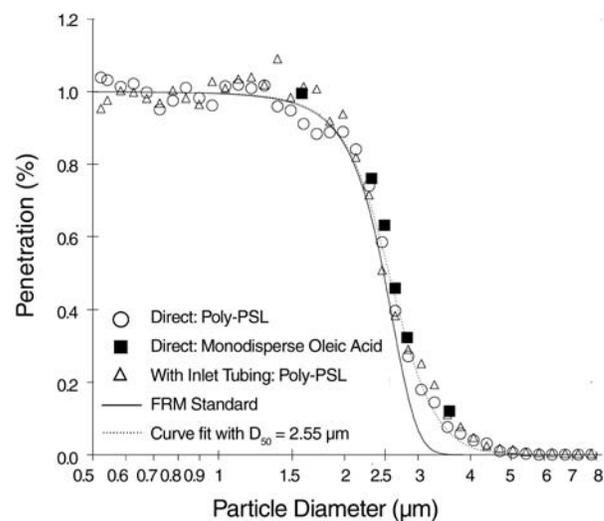


Figure 6. Penetration of solid, polydisperse polystyrene latex (poly-PSL) spheres and liquid, monodisperse oleic acid particles through the compact cyclone inlet and empty PPSS body at 4 L/min. Direct sampling and sampling through a conducting, flexible inlet tube were tested. Curve fit to the direct polydisperse polystyrene latex case is shown in comparison with the FRM $\text{PM}_{2.5}$ penetration standard. D_{50} is the particle diameter collected with 50% efficiency.

measurements, these 2 cyclone inlet configurations were equivalent. For comparison, the solid line in Figure 6 shows the FRM standard curve for $PM_{2.5}$ sampling, which has a cutpoint of $2.5\ \mu\text{m}$ and a GSD of 1.18 (Peters et al 2001). By comparison with the FRM curve, the PPSS cyclone allowed somewhat more penetration of particles in the aerodynamic diameter range of 3 to $4\ \mu\text{m}$.

The degree of agreement with the FRM standard for $PM_{2.5}$ sampling was quantified following the procedure outlined in *US Code of Federal Regulations* (40 CFR, Part 53, Subpart F). The code defines 3 bimodal size distributions, labeled *coarse*, *typical*, and *fine*, for which the fraction of particle mass that penetrates through the idealized FRM inlet is 13.8%, 34.3%, and 78.5%, respectively, of the total. A cutpoint curve is considered equivalent to the FRM curve if, for each of these 3 distributions, the mass that penetrates falls between 95% and 105% of that which penetrates the FRM inlet, and if the cutpoint is between $2.3\ \mu\text{m}$ and $2.7\ \mu\text{m}$. To test the PPSS cyclone, the polydisperse polystyrene latex penetration data for direct sampling (circles in Figure 6) were fit to an equation of the same form used by Peters and colleagues (2001) to describe the FRM curve. The resulting fit (dotted line in Figure 6) was then evaluated at the 43 discrete sizes defined in the Federal Registry, multiplied by the particle mass listed for that size and distribution, and summed. For the 3 idealized distributions, coarse, typical, and fine, the calculated mass penetrating to the collecting filters was 1.045%, 1.015%, and 1.007%, respectively, of that calculated for the FRM sampler. In each case the bias in penetrating mass relative to the FRM standard was within the allowed 5%.

Because the liquid particle tests were limited to a few particle sizes, the possibility of inertial losses was investigated further. The most likely location for inertial losses was the upper plenum surface where the exit flow from the cyclone had to make a sharp turn to enter the filter chambers. To test for losses at the cyclone exit, we greased the interior plenum surface and measured the penetration of Arizona road test particles through the cyclone and into the filter chambers. Results were compared with those obtained from a sampler without greased surfaces. These tests were done at the end of the project with a newly fabricated, plastic-body PPSS, containing an aluminum cyclone of the same dimensions as that used to obtain the data in Figure 6. No systematic difference was seen in the penetration curves. Fits to the data, with and without grease on the plenum, gave equivalent cutpoints to within 0.6% and identical GSD values. These differences are within the margin of experimental error.

Finally, we investigated the efficiency of transport of ultrafine particles through the inlet and into the filter chambers. Ultrafine particles are subject to diffusional

losses, which are larger at low sampling flow rates. Penetration of ultrafine particles was measured with the prototype sampler configured for normal sampling operation that included the compact cyclone, Teflon denuder holder, filter support rings, and channel screw caps, but without filters. Room air, which had a maximum in the number distribution below $0.1\ \mu\text{m}$, was used as the challenge aerosol. The PPSS was operated at a flow rate of 4 L/min through the cyclone, but only 1.5 L/min through the test channel, so as to match the flow rate of the CPC. Alternate sampling for 20-second periods of room air and at the exit of the filter channel of the prototype resulted in average concentrations of 4410 particles/cm³ and 4320 particles/cm³, respectively. The average penetration was 98% with an SE of 1.6%. Addition of the carbon denuder reduced penetration of ultrafine particles to $93\% \pm 1.8\%$ SE.

Selection of Cyclone Inlet

On the basis of measurements for the microtrap, spiral, and cyclone inlets, the cyclone was selected as the $2.5\text{-}\mu\text{m}$ precut device for the PPSS. Of the 3 inlets tested, its penetration curve was closest to that of the FRM fine particle standard. In addition, it offered the advantage of being the most-tested approach for exclusion of coarse particles. This was important because laboratory evaluation of the effectiveness of the test inlets for excluding very large particles was difficult. The one disadvantage of the cyclone, its size, was circumvented through the compact design for the sampler proposed by Walter John. The penetration curve for the cyclone met the criteria defined in the *Federal Register* for $PM_{2.5}$ samplers. Performance was equal for both liquid and solid particles. Explicit tests for penetration of ultrafine particles placed lower penetration limits of 98% for operation without the denuder and 93% with the denuder. Finally, we found that the PPSS inlet could be operated with flexible, electrically conducting tubing attached to the inlet with no degradation in the size selection characteristics. This offers the opportunity for the sampler to be placed in a small waist pouch or backpack, rather than worn directly.

DENUDER PERFORMANCE

Nitric acid capture efficiency was measured in the laboratory for 2 types of denuders (Table 2). In these tests the activated carbon denuder was more efficient at removing nitric acid than the magnesium-oxide-coated aluminum denuder, requiring less than half the length to achieve the same level of efficiency. The relevant control parameter for gas capture by diffusion within laminar tube flow is the flow rate per unit length. Thus the carbon denuder has the advantage of being more compact. After prolonged use the carbon

denuder had released a fraction of nitric acid that was collected. The manufacturer states that the carbon honeycomb denuder will desorb vapors after some period of exposure but that heating for 1 hour at 100°C or higher readily reactivates this material. To avoid degradation in effectiveness, these denuders should be reactivated after each use.

Field tests had been run on the coated aluminum denuder prior to this study. Sampling filtered ambient air (Pasadena CA) allowed assessment of nitric acid vapor penetration through the denuder onto the backup filter. For accurate measurement the denuder must be at least as efficient as the adsorbing filter in capturing and retaining vapor nitrite and compounds containing nitrate. Similar tests still need to be performed with the carbon honeycomb denuder, but this would require obtaining measurements in the summer when nitric acid concentrations are relatively high. Such results are not available for presentation in this report.

In view of these considerations, the carbon honeycomb denuder was selected mostly because of its smaller size. It also has the potential capability of providing denuding for the organic leg of the sampler if necessary. The only drawback of carbon-based denuders is the need to regularly regenerate them through heating.

β ATTENUATION EXPERIMENTS

Four different β attenuation systems were tested. The first 3 systems tested did not meet our measurement goals, which led us to pursue other methods. In this section we primarily describe the results with the final selected system. Details of the test results on the rejected systems can be found in Appendix A.

All 4 β gauge systems suffered from 2 major sources of error: (1) inherent drifts due to temperature changes, and (2) registration shifts of mounted filters relative to a rigid source-detector configuration. Temperature effects were sometimes directly correlated to air density effects (AT100 system) but could also be indirectly related through effects on electronics stability (BAM-1020 system and probably the UC Davis system). The 2 simplest ways to address this first limitation are to (1) introduce temperature control of the entire detection system and (2) increase the detection rate through a stronger radiation source to provide commensurately shorter counting periods. Ultimately both approaches were adopted in the final AT100-based system. A design feature of the PPSS ultimately solved the second effect, lack of proper realignment of the filter inside the gauge, by mounting each filter securely inside a metal cassette. This arrangement protected the filter from handling effects and allowed a keying system to be used to positively align the filter inside the gauge.

Table 2. Capture Efficiency by Two Denuders at Single-Channel Flow Rate of 2 L/min^a

| Denuder | Length (mm) | Flow/Cell (cm ³ /min) | No. of Tests | HNO ₃ Collection Efficiency (%) ^b |
|--------------------------------------|-------------|----------------------------------|--------------|---|
| Laboratory Testing in Dry Air | | | | |
| MgO-coated Al | 6 | 7.4 | 1 | 80 |
| MgO-coated Al | 25 | 9.2 | 2 | 97 ± 1 |
| Activated C | 10 | 10 | 2 | 98 ± 1 |
| Field Testing (Pasadena CA) | | | | |
| MgO-coated Al | 25 | 12 | 12 | 98 ± 2 |

^a HNO₃ = nitric acid; MgO = magnesium oxide.

^b % ± SD.

AT100 β Gauge Tests

By comparison with the other systems, the AT100 β gauge system offered by ATI had a strong β source and an integrated solid-state detection system (see Appendix A). The strong source provided excellent counting statistics and the solid-state detector provided increased long-term stability.

To test the long-term stability achievable with the AT100 system, we loaded a Fiberfilm filter into the final PPSS filter cassette and placed it in the β gauge. The gauge was placed inside the glove box. The gauge was run for 19 hours, and readings were logged at 1-minute intervals. Over that time the response of the detector drifted consistently to higher density readings owing to the slight but persistent effect of the decaying ¹⁴⁷Pm and unmonitored temperature drift. At the end of the run, the overall response had shifted by approximately 30 μg/cm²—less than 1%.

For an estimate of the precision of the gauge, the data were averaged into 10-minute intervals and the difference of consecutive pairings was taken. The variation of these numbers represented the precision of the β gauge measurements without external factors (eg, temperature or misalignments). The SD of these differences was 0.77 μg/cm². The theoretical Poisson uncertainty estimate, based on the 15.4 million counts per 10-minute interval observed, was 0.9 μg/cm². For the PPSS spot size, this measured density precision gives a theoretical minimum detection of $2 \times 0.77 \mu\text{g}/\text{cm}^2 \times 0.38 \text{ cm}^2 = 0.59 \mu\text{g}$, or for an 8-hour sample, 0.59 μg/m³.

Measurements were made to determine the effect of loading and unloading filter cassettes with the PPSS without sampling. The magnitude of this effect ranged from 0 to 40 μg/cm² and appeared to be strongly correlated with the amount of compression on the filter surface that was visible. Precompressing the filters, by first loading them into the

PPSS and unloading them, eliminated this bias as long as the filters were not loaded into the sampler with excessive force.

To reduce the chance of introducing unwanted loading errors, an additional step was taken. An extra retaining shim ring was inserted into the filter cassette to increase slightly the gap between the sealing faces of the support rings and thereby decrease the amount of compression. This effectively eliminated the variability of loading force used by the operator. Sharp deposit edges were observed in all cases except one in which the deposit area exhibited a slightly wavy border. Even in this case, however, the spread of the sample was negligible and should not have affected the β gauge measurement.

For 5 pairs of ambient samples collected in our laboratory, mass determinations by β gauging and gravimetry were compared (Figure 7A) and measurement precision was tested (Figure 7B). Sample duration varied from 1 to 10 hours to provide a wide range of total aerosol loads. The range of absolute deposited mass was 2 to 50 μg as measured by β gauging and 2 to 70 μg as measured by gravimetry. The range of aerosol concentrations was 14 to 70 $\mu\text{g}/\text{m}^3$. To allow direct comparisons of collected mass, each sample was normalized by the measured average flow rate for each channel. Both graphs show general well-correlated trends between the 2 PPSS units, but higher correlations in the β - β case (Figure 7B) than in the β -gravimetry case (Figure 7A).

The mean ratio of β mass to gravimetric mass for the entire set was 0.80, which increased to 0.93 when only those points (half) for which the gravimetric samples were within 12% agreement with each other were considered. Figure 7A shows good agreement between β -gauged mass and gravimetry mass when the collected mass was less than about 25 μg but revealed a bias toward low agreement for samples with mass greater than about 50 μg . This observation is consistent with the known effect that materials with smaller bulk densities (mass per unit volume instead of area) have an enhanced β attenuation factor. One can speculate that aerosol may deposit on the fibers of the Fiberfilm filter in such a way as to create a ramified structure that possesses a lower areal density than a comparable uniform deposit on the bulk of the filter. Moreover, because the calibration was based on Mylar films of varying thickness rather than particle deposits, one would expect increasing relative errors for larger deposits. Further ambient measurements are necessary to accurately determine this empirical correction factor.

Much of the above data were collected over very short sampling periods so as to assess precision at low levels of collected particles. To assess the corresponding precision for the planned use of the personal sampler (that is, for

8-hour monitoring), we examined the precision expressed in terms of the mass collected (Table 3), rather than mass concentration. The apparent outlier in Figure 7B, for which the relative difference between the paired β gauge measurements was 10 times the next-largest relative difference, was excluded from the precision analysis. With this exclusion, the measured precision for mass by β attenuation, as indicated by the pooled SDs, was within 0.8 μg , or 3% of the mean measured mass. For 8-hour collection the corresponding sample volume would be 1 m^3 , yielding an expected measurement precision of 0.8 $\mu\text{g}/\text{m}^3$ at 1 SD. Our gravimetric precision was much poorer (3.7 μg), which may have resulted from extra handling of the filters in obtaining both β attenuation and gravimetric measurements.

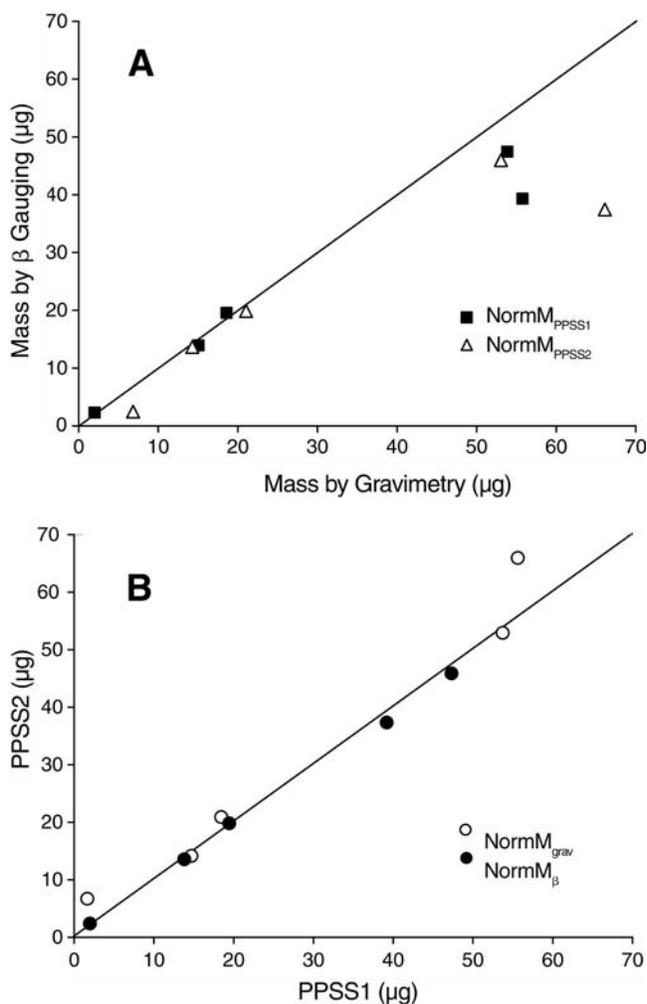


Figure 7. A: Comparison of PPSS filter mass determinations by gravimetry and by the AT100 β gauge system; **B:** Precision of sample mass determinations by gravimetry and β gauging. Samples were collected from 2 channels of a single PPSS prototype. Each sample was normalized by the measured average flow rate for each channel (normM).

Selection of β Gauge System

Of the 4 systems evaluated, satisfactory results were obtained only with the AT100 β gauge system. The long-term stability of the BAM-1020 system was poor, requiring a 2-spot assay system for accurate measurements. This was both cumbersome and time-consuming, requiring repeated measurements on the sample filters. The Aerosol Dynamics custom-built system provided the long-term stability desired but was subject to short-term drift that limited its sensitivity to 1 part in 1000. The UC Davis system showed the potential for providing accurate measurement, but most likely would have required temperature control that was not easily adapted to this system.

In contrast, the AT100 system provided stability of approximately 1 part in 4000. The uncertainty from the counting statistics reduced the required measurement time for a single sample to 10 minutes. Further, tests to compare measurement precision over a variety of sampling durations yielded a mass precision of 0.8 μg or 3% of the average measured mass of 23.6 μg . For 8-hour sampling the sample volume was 1 m^3 , giving an indicated measurement precision of 0.8 $\mu\text{g}/\text{m}^3$. For these reasons the AT100 β gauge system was deemed to be the best.

PROTOTYPE DESIGN

On the basis of the component testing described above, a prototype was constructed using (1) cyclone precut, (2) carbon honeycomb denuders, (3) Tissuequartz filter with 8-mm spot size, and (4) Fiberfilm filter with 7-mm spot size followed by a paper filter impregnated with sodium chloride.

In the prototype PPSS (Figure 8), the cyclone precut device is at the center of the sampler. The 2 filter channels are housed on either side, oriented vertically. Each channel is designed to hold one or two 25-mm-diameter filters and one denuder. Airflow enters at the side port, passes through the cyclone, exits into the upper plenum, splits between the 2 denuder-filter channels, and finally recombines and exits through the outflow plenum. A single personal sampling pump draws flow through the 2 channels. The design flow rate through each channel is 2 L/min with a combined flow of 4 L/min. The overall dimensions are 11 cm \times 5.4 cm \times 4.5 cm. This prototype was fabricated from aluminum (density 2.7 g/cm³) and weighed 550 g. Subsequent fabrication of selected parts from plastic has reduced this weight to 220 g.

The inlet is located on the front face of the PPSS body. The PPSS can be operated with the inlet face open if it is to be attached via a harness to the subject's torso. Alternatively, sampling can be conducted through low-particle-loss conducting tubing by means of an adapter inserted

Table 3. Precision of Mass Measurements by Gravimetry and AT100 β Gauge by Channel

| | Average Volume (m ³) | Gravimetric Mass (μg) | | β Gauge AT-100 Mass (μg) | |
|------------------------------|----------------------------------|------------------------------------|------|---|------|
| | | 1 | 2 | 1 | 2 |
| Run | | | | | |
| 1 | 1.11 | 55.5 | 65.8 | 39.0 | 37.2 |
| 2 | 0.77 | 53.6 | 52.7 | 47.2 | 45.7 |
| 4 | 0.26 | 14.7 | 14.0 | 13.6 | 13.4 |
| 5 | 0.89 | 18.3 | 20.7 | 19.3 | 19.6 |
| 6 | 0.12 | 1.7 | 6.5 | 2.0 | 2.2 |
| Mean mass (μg) | | | 30.3 | | 23.9 |
| Pooled SD (μg) | | | 3.7 | | 0.8 |
| Coefficient of variation (%) | | | 12.2 | | 3.2 |

^a Reported mass has been corrected to average sample volume for the 2 channels: mass reported = mass measured $(V_1 + V_2)/(2V_i)$, where V_1 and V_2 are sample volumes for channels 1 and 2, and i = channel reported.

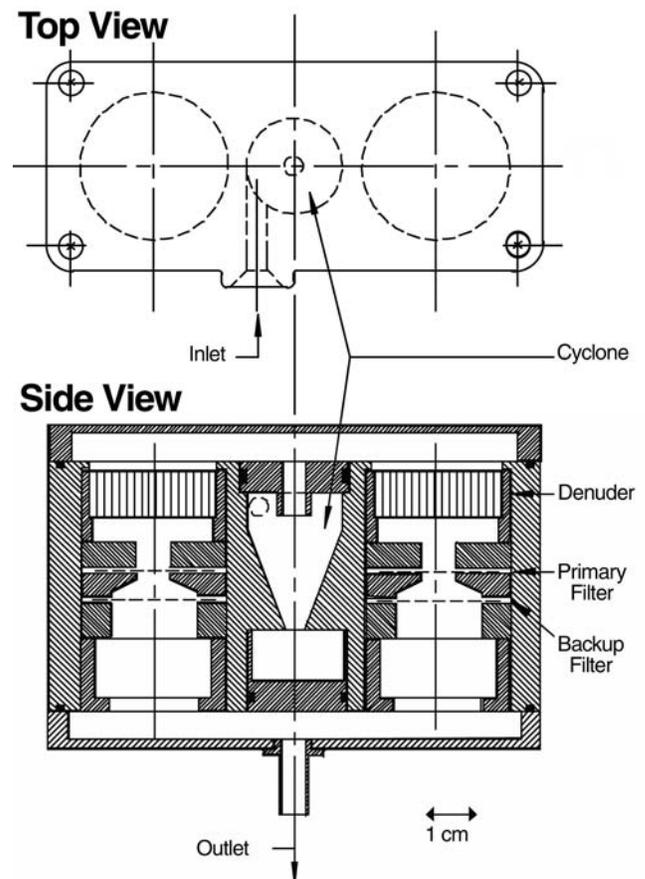


Figure 8. Prototype PPSS.

into the sampler's inlet. This option allows sampling in the breathing zone, which may be more representative of the subject's exposure.

During normal sampling operation, the exhaust of the PPSS is a single combined outlet from the 2 filter channels that are connected to a personal sampling pump. For flow checks the PPSS bottom may be removed and 2 plugs with tubes can be inserted into each filter channel to allow direct simultaneous measurement of the 2 flow rates.

The PPSS is designed for a single quartz filter (eg, Tissuequartz) for particulate carbon sampling and a denuded Teflon-impregnated glass fiber filter (eg, Fiberfilm) for mass and inorganic ion determinations. A backup cellulose filter impregnated with sodium chloride is placed downstream of the Teflon filter to capture the volatile nitrate that is lost from the Teflon filter during sampling. Nitrate-specific filter media such as those impregnated with sodium chloride often offer advantages over more generally adsorbing media such as nylon (Chow and Watson 1998). The impregnated filters have the additional advantage of a lower pressure drop at the same face velocity when compared with nylon filters. Each channel is sized to accommodate a 27-mm-diameter denuder as much as 25 mm in length. Each channel holds 25-mm filters of each type that are masked to increase sensitivity and improve detection limits.

With 2 L/min flow per channel, the sample volume within an 8-hour period is 1 m³. The 8-mm spot on the quartz filter is the sample size that Desert Research Institute currently uses for elemental and organic carbon analyses when these samples are analyzed. With analytic detection limits of 0.2 µg/cm² for elemental carbon and 0.8 µg/cm² for organic carbon, the PPSS limit of detection for these species is 0.1 and 0.4 µg, respectively. With the Teflon filter, the smaller filter deposit improves the detection limit for β attenuation determinations of particle mass. The small Teflon filter is easily extracted in 5 mL. At nominal ion chromatography detection limits of 0.05 µg/mL, the detection limit is 0.3 µg/m³.

The flow split between the 2 channels is handled passively, based on measured flow-dependent pressure drops across the filter media. The masked filter area is made larger on the quartz-filtered carbon side relative to the Teflon-filtered inorganic side to help equalize the pressure drops at 2 L/min flow. For particulate carbon sampling an 8-mm spot size is used, whereas for ion and mass sampling a 7-mm spot size is used. To provide the balance of the pressure drop equalization, an annular shim with 8 mm internal diameter is placed over the paper backup filter on the inorganic side. Tests with ambient particulate loadings

up to 100 µg per filter showed that the flow balance was maintained to within 5%.

Although not yet implemented, there is provision in the PPSS design to accommodate a denuder ahead of the quartz filter for organic carbon analysis. Unlike nitrate measurements, there is as yet no accepted means to accurately collect carbon particles. The baked quartz filters readily adsorb many organic vapor constituents, resulting in a positive artifact (McDow and Huntzicker 1990; Turpin et al 1994). Also, organic aerosols contain volatile constituents that may be lost during sampling (just as ammonium nitrate can be lost; Eatough et al 1993). Considerable debate can be found in the literature as to which of these effects dominates. Recently some investigators have been using denuders ahead of quartz filters for carbon analysis. The PPSS is designed to accommodate a carbon honeycomb denuder ahead of the quartz filter to remove organic vapors that might otherwise collect on the filter, as done by Kreiger and Hites (1992). However, this aspect has not yet been tested with the PPSS.

PROTOTYPE FIELD EVALUATION

Precision of Passive Flow Split

The prototype employs a passive flow split between the 2 channels. In other words, only the total flow is controlled, and the split between the 2 channels depends on the relative flow resistance of the 2 sets of filter media. This flow split can change if the filters load at different rates—in other words, if the relative pressure drop across one increases with loading faster than across the other. The question we address here is the precision with which the flows are known with this passive flow split.

In field testing the individual flows for each channel were measured at the beginning and end of each sample. Figure 9 shows the fractions of the total flow constituted by the initial and final flow through the Fiberfilm channel. Consistently we found that the relative fraction of the flow through the Fiberfilm filter decreased. This was because the pressure drop across the Fiberfilm filter increased with particle loading somewhat more quickly than the pressure drop across the Tissuequartz filter, leading to a higher proportion of the flow passing through the latter filter by the end of the sample period. With the exception of the 2 samples collected in the freeway tunnel, the total change in the pressure drop across the PPSS was less than 1 inch of water. Anomalously large pressure drops relative to the collected mass for the tunnel samples may be attributable to volatile organic species lost subsequent to sampling.

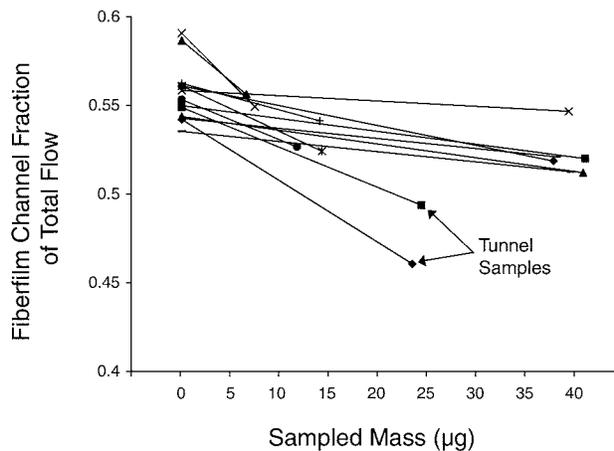


Figure 9. Dependence of flow split on collected sample mass. Lines show paired points for readings at the beginning and end of each sample.

For the 7 runs of the pair of prototype samplers for which accurate flow split measurements were made, including the tunnel samples shown in Figure 9, the fraction of flow through the Fiberfilm filter decreased by an average of $2.9\% \pm 0.9\%$. The corresponding 1 SD uncertainty in the sample volume from this passive flow split is estimated as the SD in the change in this flow split, or 0.9% .

Particle Chemistry Data

In field tests two PPSS prototypes and an AIHL cyclone sampler were operated as area samplers. The collocated PPSSs were used to assess precision. The AIHL cyclone

sampler provided a reference to which the PPSSs could be compared (Figure 10).

Regression statistics are shown in Table 4. For all 5 analytes, the square of the correlation coefficient, R^2 , was greater than or equal to 0.95, and out of the 10 possible correlations, 5 yielded an R^2 value greater than or equal to 0.99. According to paired Student t statistics shown in Table 4, the regression slopes for all analytes except sulfate were within the 95% confidence intervals for a slope of 1. Similarly, a 0 intercept fell within the 95% confidence intervals for all analytes except sulfate.

The different analytes measured provided different types of information with regard to sampler performance. The gravimetric mass values agreed, indicating equality in performance of the 2 inlets; that is, the PPSS did not yield any excess of $PM_{2.5}$ mass over that measured by the AIHL reference cyclone sampler. The agreement in sulfate values, which were consistently low, pointed to the precision with which chemistry measurements could be made for stable nonvolatile compounds predominantly found in the fine mode. The comparison for nitrate indicated that both samplers retained the volatile particulate nitrate. Because these measurements were made in the wintertime when nitric acid concentrations are low, however, the data set did not provide more than a preliminary evaluation for the nitric acid denuder.

There is not as yet an accepted procedure for accurate sampling of organic carbon. The agreement in organic carbon measurements seen here is in part attributable to the fact that care was taken to match the face velocity between

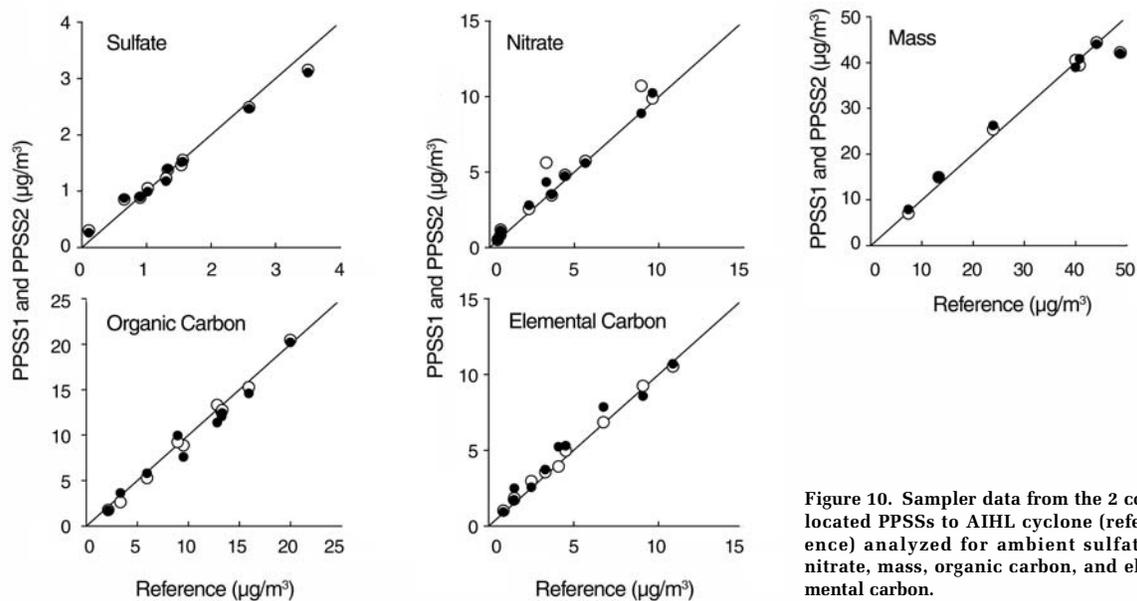


Figure 10. Sampler data from the 2 collocated PPSSs to AIHL cyclone (reference) analyzed for ambient sulfate, nitrate, mass, organic carbon, and elemental carbon.

Table 4. Regression Statistics for PPSS Versus AIHL Reference Cyclone Sampler

| | Sulfate | Nitrate | Organic Carbon | Elemental Carbon | Gravimetric Mass |
|---|-----------------|-----------------|------------------|------------------|------------------|
| No. of measurements | 10 | 10 | 10 | 10 | 8 |
| Mean reference concentration ($\mu\text{g}/\text{m}^3$) | 1.5 | 4.0 | 10.5 | 4.5 | 31.2 |
| R^2 for PPSS1 | 0.99 | 0.95 | 0.99 | 1.00 | 0.98 |
| R^2 for PPSS2 | 0.99 | 0.99 | 0.97 | 0.97 | 0.98 |
| Slope for PPSS1 | 0.85 ± 0.05 | 1.06 ± 0.19 | 1.04 ± 0.07 | 0.96 ± 0.05 | 1.08 ± 0.19 |
| Slope for PPSS2 | 0.84 ± 0.07 | 0.99 ± 0.09 | 0.96 ± 0.13 | 0.95 ± 0.13 | 1.11 ± 0.19 |
| Intercept for PPSS1 ($\mu\text{g}/\text{m}^3$) | 0.20 ± 0.09 | 0.27 ± 0.98 | -0.72 ± 0.81 | 0.33 ± 0.26 | -1.75 ± 6.26 |
| Intercept for PPSS2 ($\mu\text{g}/\text{m}^3$) | 0.19 ± 0.11 | 0.29 ± 0.45 | -0.18 ± 1.53 | 0.63 ± 0.71 | -2.75 ± 6.44 |
| Ratio of Means | | | | | |
| PPSS1 to reference | 0.98 | 1.13 | 0.97 | 1.03 | 0.98 |
| PPSS2 to reference | 0.97 | 1.07 | 0.94 | 1.09 | 0.98 |

the personal and reference samplers. If the face velocities are equal, then the organic vapor adsorption artifact, as well as any loss due to vaporization, will be approximately the same. To assess the magnitude of organic vapor artifact, the reference sampler was operated with a quartz backup filter, which collected organic material from the adsorption of vapors onto the quartz filter medium. Some of the organic vapor may have been in the gas phase initially, and some may have resulted from vaporization of particles collected on the primary filter. In our experiments the organic carbon

collected on the backup filter was $11\% \pm 4\%$ of that on the front filter. The 11% value we obtained is similar to that reported by McDow and Huntzicker (1990) for urban sampling in Portland, Oregon, and somewhat lower than the 16% value reported by Kirchstetter and colleagues (1999) for freeway tunnel measurements.

In the results from collocated PPSSs (Figure 11), precision was generally better for sulfate and elemental carbon than for nitrate or organic carbon. Pooled SDs were $0.03 \mu\text{g}/\text{m}^3$ for sulfate, $0.5 \mu\text{g}/\text{m}^3$ for nitrate, $0.6 \mu\text{g}/\text{m}^3$ for organic carbon,

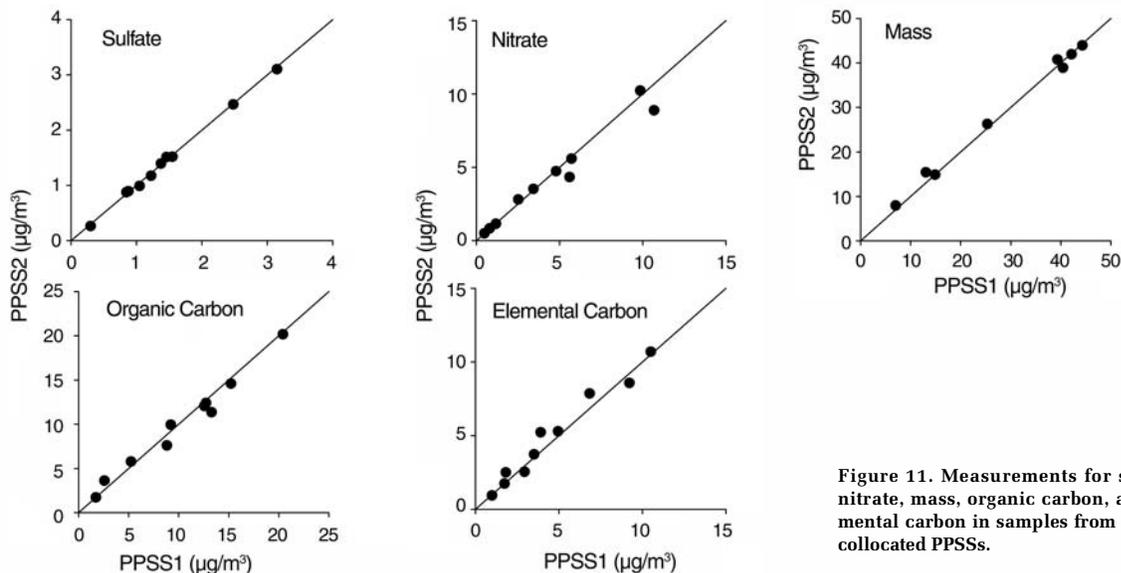


Figure 11. Measurements for sulfate, nitrate, mass, organic carbon, and elemental carbon in samples from the two collocated PPSSs.

Table 5. Measured Precision for Collocated PPSS Samples Compared with Target Detection Limits and Precision

| Measurement | Coefficient of Determination (R^2) | Pooled SD ^a ($\mu\text{g}/\text{m}^3$) | Target Detection Limit ($\mu\text{g}/\text{m}^3$) | Coefficient ^b of Variation (%) | Target Precision (%) |
|------------------|--|---|---|---|----------------------|
| Sulfate | 1.00 | 0.032 | 0.3 | 2 | 8 |
| Nitrate | 0.97 | 0.51 | 0.3 | 11 | 8 |
| Organic carbon | 0.98 | 0.64 | 0.5 | 6 | 8 |
| Elemental carbon | 0.97 | 0.44 | 0.5 | 9 | 8 |
| Mass | 0.99 | 0.85 | 1.0 | 3 | 8 |

^a Measured instrument detection limit.

^b Measured instrument precision.

0.4 $\mu\text{g}/\text{m}^3$ for elemental carbon, and 0.8 $\mu\text{g}/\text{m}^3$ for mass (Table 5). Sample durations varied from 4 to 16 hours with a mean sample volume of 1.1 m^3 per channel. Thus, on average, these precision values correspond to what could be expected for 8-hour sampling with a 1- m^3 collection per sampling channel. The measured precisions met the 8% precision level targeted at the outset of the study with the exception of nitrate, for which the measured precision was 11% (see Table 5). Absolute precision was better than target detection limits for sulfate and comparable to target levels for organic carbon, elemental carbon, and mass. Again, nitrate values were somewhat less precise.

DISCUSSION

A PPSS has been developed that meets the major design objectives set forth in the proposal for precise measurement of all primary constituents of ambient particles. Specifically, the PPSS possesses 2 channels to accommodate a Tissuequartz filter, compatible with organic carbon analysis, and a Fiberfilm filter, which is suitable for nitrate, other inorganic species, and total mass determinations by β gauging or gravimetry. The PPSS utilizes a compact cyclone to deliver a bounce-free, greaseless size fractionation that accurately matches the EPA FRM for $\text{PM}_{2.5}$ sampling while remaining compatible with organic carbon analysis, and it accommodates the use of carbon honeycomb or magnesium-oxide-coated aluminum denuders for accurate sampling of nitrate-containing species without interference from nitric acid. The unit can be operated with a passive flow split and a single pump to provide a total flow of 4 L/min, split nearly evenly between 2 filter chambers and is compatible with mass determination by β attenuation.

The specific performance goals for the PPSS were for the most part met by laboratory tests and the first field test.

The nitric acid exposure tests showed that the carbon honeycomb denuder reached 99% efficiency at removing nitric acid. The passive flow split was shown to be constant (on average to within a few percentage points with SD less than 1%). The AT100 β gauge in a small series of tests, excluding one outlier, possessed a pooled SD of 1 $\mu\text{g}/\text{m}^3$ that translates into a limit of detection of 2 $\mu\text{g}/\text{m}^3$ for mass. Initial estimates of the PPSS analyte-specific detection limits based on the pooled SDs of collocated field measurements were 0.058 $\mu\text{g}/\text{m}^3$ for sulfate, 1.0 $\mu\text{g}/\text{m}^3$ for nitrate, 1.3 $\mu\text{g}/\text{m}^3$ for organic carbon, 0.88 $\mu\text{g}/\text{m}^3$ for elemental carbon, and 1.7 $\mu\text{g}/\text{m}^3$ for mass (via gravimetry). These values are nearly uniformly double the original goals. Precision for side-by-side sampling during the initial study, as taken by the pooled SD divided by the mean concentration of a given analyte, ranged from 2% for sulfate to 11% for nitrate. The PPSS performance has been well characterized through laboratory and limited field testing; however, further testing should be undertaken to more rigorously define the range of applicability of this sampler for personal exposure or microenvironmental studies. Therefore, the following tests are recommended prior to routine use of the PPSS.

In a mode that uses gravimetric assay, we suggest field testing of denuder performance for nitric acid under conditions of high ambient nitric acid, with attention to capacity and efficiency; more extensive field testing in a variety of environmental conditions and locations to better establish detection limits and precision; testing on the lighter, plastic-body prototype; and testing as a personal sampler. Further work is needed to refine the β -mass measurement, specifically to resolve the mass discrepancy for the β gauging through empirical calibration of mass by β gauging with laboratory and atmospheric aerosols.

Future efforts that would further improve the sampler include testing of carbon denuders for organic vapor removal; testing with a conducting, flexible, inlet tube; and possible development of a 2-channel pump to avoid the ambiguities in passive split of the sample flow.

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APPENDIX A. OTHER β GAUGE SYSTEMS

Four different β attenuation systems were tested in the course of this study. Only the ATI AT100 system was found to be suitable for application to the small sample sizes expected for the PPSS. The test methods and results for the remaining systems are given here. Table A.1 outlines the main specifications of all of the β attenuation systems explored. They were (1) a commercial instrument called the BAM-1020, (2) a custom β gauge built by Aerosol Dynamics, (3) a custom system built by UC Davis, and (4) a commercial β gauge by ATI called the AT100.

TEST METHODS

Met One BAM-1020

Met One Instruments provided for use in this project a BAM-1020 designed for continuous ambient aerosol mass monitoring. This unit, which incorporates a scintillator and photomultiplier-tube-based detector with a 60- μ Ci ^{14}C source, was evaluated to determine its stability and the mass detection limits that could be expected for this application. Some effort was devoted to better understand the details of its operation. Met One also provided an independent detector with circuit board and mounting block that was more easily tailored to the needs of this project.

Precision tests were made on stationary filters placed within the instrument and monitored over long periods of

Table A.1. Specifications for β Gauge Systems

| System | β Source | Detector | Signal |
|--|------------------------------------|-----------------------------------|---------|
| BAM-1020 Met One Instruments, Grants Pass OR | 60 μCi ^{14}C | Scintillator/photomultiplier tube | Pulses |
| Aerosol Dynamics custom, IRD components | 60 μCi ^{14}C | Integrating silicon diode | Current |
| UC Davis custom, Ortec components | 100 μCi ^{14}C | Ion-implantation silicon diode | Pulses |
| AT100 ATI, Rockville MD | 3 mCi ^{147}Pm | Silicon diode | Pulses |

time. By comparing successive measurements and subdividing and averaging counts, we could explore the effect of sampling period on precision. To test for temperature and humidity correlations with β gauge readings, measurements with a Vaisala Humitter were recorded simultaneously with count readings from the β gauge. Tests on the reproducibility of readings were obtained by using a pair of filter-mounting carriages that rigidly hold a single filter in place while the operator slides them in and out of the gauge.

A more elaborate means of controlling the registration of filters with respect to the detector-source axis was used for an initial attempt at β gauging the collected aerosol mass. Filters were permanently mounted between stainless steel shims with a punched spot size of 1.3 cm (1.3-cm² area) that provided a rigid support for positive centering. A V-notch cut into the edge of this metal disk encapsulating the filter engaged a pin in the filter support plate. The carriage then slides in and out of the detector frame extracted from the BAM-1020 that holds the detector and source in place.

The indicated mass from the BAM-1020 was compared with gravimetric determinations made using a Sartorius MC-5 microbalance for several types of clean filter materials and for laboratory-generated aerosol collected on Fiberfilm filters.

Aerosol Dynamics β Gauge System

A custom β gauge was built in-house at Aerosol Dynamics around a device manufactured by International Radiation Detectors (IRD, Torrance CA) that produces silicon diode detectors with minimal surface barriers for high-sensitivity detection of charged particles. The incident β particles produce an integrated current, as opposed to discrete pulses that must be counted, which can be converted to analog output using a suitable electrometer. The Met One 60- μ Ci ¹⁴C source was used with this detector, and the resulting output voltage was read with a digital voltmeter.

The first set of tests of this detector was to connect directly to the input of an Analog Devices electrometer with integral Faraday cage taken from another instrument (TSI electrical aerosol analyzer). Although this approach provided sufficient electromagnetic (including ambient light) shielding, the electrometer was deemed too noisy to provide an adequate test of the detector. Since the prospect of direct analog output and multidiode sensors held the potential for long-term advantages, a second set of tests was conducted using a charge preamplifier manufactured by IRD with direct diode mounting. By reducing lead lengths and utilizing special printed-circuitboard shielding, this combination provided the best hope for eliminating external noise intrusion. A test was conducted to measure the inherent noise of the detection system minus the effects of the inherent noise of the sensor (or the random signal

produced by the β particle generation through radioactive decay). By attaching a stable picoamp current source built for this test to the input of the preamp, the noise level of the amplifier, cabling, and voltmeter can be measured. A cast aluminum instrumentation enclosure was used to provide shielding of radio frequency interference and visible light. Rigidly mounted inside this enclosure is a mount for the detector, preamplifier, and source, along with the filter mount used in the previous BAM-1020 β -gauge tests.

UC Davis β Gauge System

Professor Tom Cahill of the University of California at Davis provided us onsite access to a β detection system based on Ortec (formally EG&G) technology. This system includes an ion-implantation silicon detector (BU-13-150-300-5) combined with a charge preamplifier and pulse-counting electronics (amplifier, discriminator, and scalars). All of the components were selected for compatibility with low-energy electron detection and the counting rates encountered with a 100- μ Ci ¹⁴C source, which was also available for our use.

Two field tests were conducted with this system to measure ambient loadings on filters using β attenuation. Three samples were collected in parallel at a flow rate of 7 L/min for each channel. The combined flow of 21 L/min was drawn through an AIHL cyclone to provide a fine fraction. The 50% cutpoint resulting from this flow rate was 3 μ m. Two of the samples were collected on 25-mm Fiberfilm filters mounted inside a cylindrical canister with the same internal diameter as the PPSS, to allow for using the filter cassettes and support rings from the PPSS prototype. For a reference sample, another 25-mm Fiberfilm filter was used with a Gelman filter holder and a pair of stainless steel shims to mask the filter down to 7.9 mm, to better match the PPSS spot size.

Comparisons to gravimetric mass were made as measured by a Sartorius MC5 microbalance in our laboratory. After the gravimetric masses were measured, the filters were mounted in the PPSS prototype cassettes. Sufficient compression was achieved through the use of stainless steel shims to eliminate any rotation of the filter once mounted. To provide reproducible β gauging, a 2-piece mating jig was built to sandwich the filter cassettes between the Ortec detector and ¹⁴C source. To avoid rotations of the 2 basic parts, a pin and mating socket are employed. Similarly, a registration hole on the backside of the filter cassette mates with a fixed pin protruding from the base plate of the jig, thereby providing positive alignment during gauging. After β gauging the filters were removed from the cassettes and reweighed using the microbalance. Tests of loading and unloading filters without sampling demonstrated that the

mass of the Fiberfilm filter did not change as a result of this handling, to within the accuracy of the balance ($\pm 1 \mu\text{g}$).

For the first run 3 Fiberfilm filters were selected to provide a wide range of densities normally observed with this filter medium, with the intent of using them for narrow calibration of the detection system. These reference filters were mounted inside the PPSS filter cassettes to allow for repeated gauging. Besides providing a 3-point calibration of the detector, these reference standards were used to track drifts in the detection system during a filter-sample gauging session. The contribution by aerosol loads will always be small compared with the manufacturing variation of the filters themselves.

For the second run uniform Mylar (polyester) film was used to calibrate the response of the detector. Mylar is highly uniform and thus provides a better standard for calibration. Multiple layers of the film were mounted inside the PPSS filter cassettes to attain the desired density. By punching 1-inch circles of the Mylar film and weighing them in a Cahn microbalance (model C-33, Thermo Orion, Beverly MA) with a precision of $7 \mu\text{g}$, the areal density could be calculated. From individual weighing of 6 identically punched

circles, a density uniformity of 1.7% was determined. Using 6, 7, and 8 layers provided a range of densities (14.5 to 18.8 mg/cm^2) that spans the range of density observed with the Fiberfilm.

The procedure followed in both runs included pre-gauging the filters using counting intervals to provide sufficient counts to ensure adequate counting statistics. During the first test (run 1), eight 1-minute counts were taken so as to verify that Poisson statistics could account for observed variations. During the second test (run 2), single 8-minute counts were taken in which 10 to 14 million β particles were detected. Reproducibility of measurements between reloading of the same filter into the test jig indicated that precision within 1 to $2 \mu\text{g/cm}^2$ was achievable.

TEST RESULTS

Met One BAM-1020

During basic evaluations of the BAM-1020 system, measurements on different filter media were obtained and compared to gravimetric measurements. Results of these tests are contained in Table A.2, showing the mass per unit

Table A.2. Areal Density Measured with BAM-1020 β Gauge and Gravimetry

| Medium ^a | Pos ^b | I_0^c | I^d | $\mu\text{-BAM}^e$ (cm^2/mg) | Mass Density (mg/cm^2) | | |
|---------------------|------------------|------------|------------|---|-----------------------------------|-------------------------|-----------------------|
| | | | | | BAM-1020 ^f | Gravimetry ^g | BAM/Grav ^h |
| Fiberfilm | 0 | 12,844,400 | 5,017,256 | 0.259 | 3.631 ± 0.002 | 3.374 | 1.08 |
| Fiberfilm | 1 | 12,854,896 | 5,049,656 | 0.259 | 3.610 ± 0.002 | 3.374 | 1.07 |
| Fiberfilm | 2 | 12,867,664 | 5,079,680 | 0.259 | 3.591 ± 0.002 | 3.374 | 1.06 |
| Tissuequartz | 0 | 12,901,024 | 1,768,976 | 0.261 | 7.613 ± 0.003 | 7.130 | 1.07 |
| Tissuequartz | 1 | 12,917,824 | 1,790,768 | 0.261 | 7.572 ± 0.003 | 7.128 | 1.06 |
| Tissuequartz | 2 | 12,948,184 | 1,788,736 | 0.261 | 7.586 ± 0.003 | | |
| Nuclepore | 0 | 13,230,392 | 10,459,648 | 0.256 | 0.918 ± 0.002 | 0.857 | 1.07 |
| Nuclepore | 0 | 13,233,944 | 10,464,000 | 0.256 | 0.918 ± 0.002 | 0.857 | 1.07 |
| Nuclepore | 1 | 13,223,208 | 10,467,880 | 0.256 | 0.913 ± 0.002 | 0.857 | 1.07 |
| Nuclepore | 2 | 13,219,144 | 10,469,232 | 0.256 | 0.912 ± 0.002 | 0.857 | 1.06 |
| Teflo | 0 | 12,957,376 | 7,690,688 | 0.257 | 2.027 ± 0.002 | | |
| Teflo | 1 | 12,968,656 | 6,705,816 | 0.258 | 2.558 ± 0.002 | | |
| Saran | 0 | 13,457,560 | 7,768,632 | 0.257 | 2.138 ± 0.002 | | |

^a Fiberfilm is Teflon-coated glass fiber; Teflo, Teflon; Nuclepore, polycarbonate; Saran, polyvinyl chloride film.

^b Pos denotes position of a single filter for multiple gaugings.

^c I_0 is initial count in fixed 4-minute interval.

^d I is final count in fixed 4-minute interval.

^e $\mu\text{-BAM}$ is effective absorption coefficient from equation A.1 (see text).

^f BAM-1020 mass density is value as reported by instrument.

^g Gravimetric mass density is gravimetrically determined filter mass divided by total filter area = 17.35 cm^2 .

^h BAM/Grav is ratio of BAM-1020 density to microbalance gravimetric density.

area for several spots on each filter and the corresponding gravimetric density obtained by dividing the total mass by the filter’s area. The data are highly correlated over a range of values ($R^2 > 0.999$) although BAM-1020 values are 7% higher on average. Table A.2 also shows the raw β counts, both with (I_0) and without (I) the filter present. The corresponding statistical uncertainty, calculated from Poisson statistics, is 2 to 3 $\mu\text{g}/\text{cm}^2$, which is in accordance with manufacturer’s specifications.

In addition, the areal mass densities reported by the BAM-1020 were compared with those computed from the relation published by Macias and Husar (1976):

$$m = \mu^{-1} [\ln(I_0) - \ln(I)] \tag{A.1}$$

Here I_0 and I are the initial and final count rates, respectively; m is the indicated mass per unit area and μ is the mass attenuation coefficient. From this relation it was determined that the manufacturer’s algorithm uses a count-specific value for μ although all are close to the value of $0.26 \text{ cm}^2/\text{mg}$ used by Macias and Husar (1976).

Several measurements were made of the β instrument stability. These are relevant to the 2-spot method for β

mass determinations outlined in our proposal. Our approach is to β gauge 2 spots on the filter, prior to sampling, confine the particle deposit to 1 of these 2 spots, and then assay both spots again at the end of sampling. With this approach the hope is to minimize error due to variations in laboratory conditions and instrument response between the initial and final assays.

An example of repeated 4-minute counts of the β penetration through a blank Fiberfilm filter is shown in Figure A.1. These data were collected over 24 hours without removing the filter from the gauge. Essentially they correspond to variations in the blank value, which is a major component of the measurement precision. The right-hand axis shows the individual counts I for each 4-minute period referenced to the average count rate for the entire 24-hour period, I_0 , and expressed as a mass areal density using equation A.1 with $\mu = 0.26 \text{ cm}^2/\text{mg}$. The right-hand axis mass density values show the variation in indicated mass density of this filter if one were to use a fixed reference value. As anticipated, this variation is higher than is acceptable for this application. Evaluation of temperature

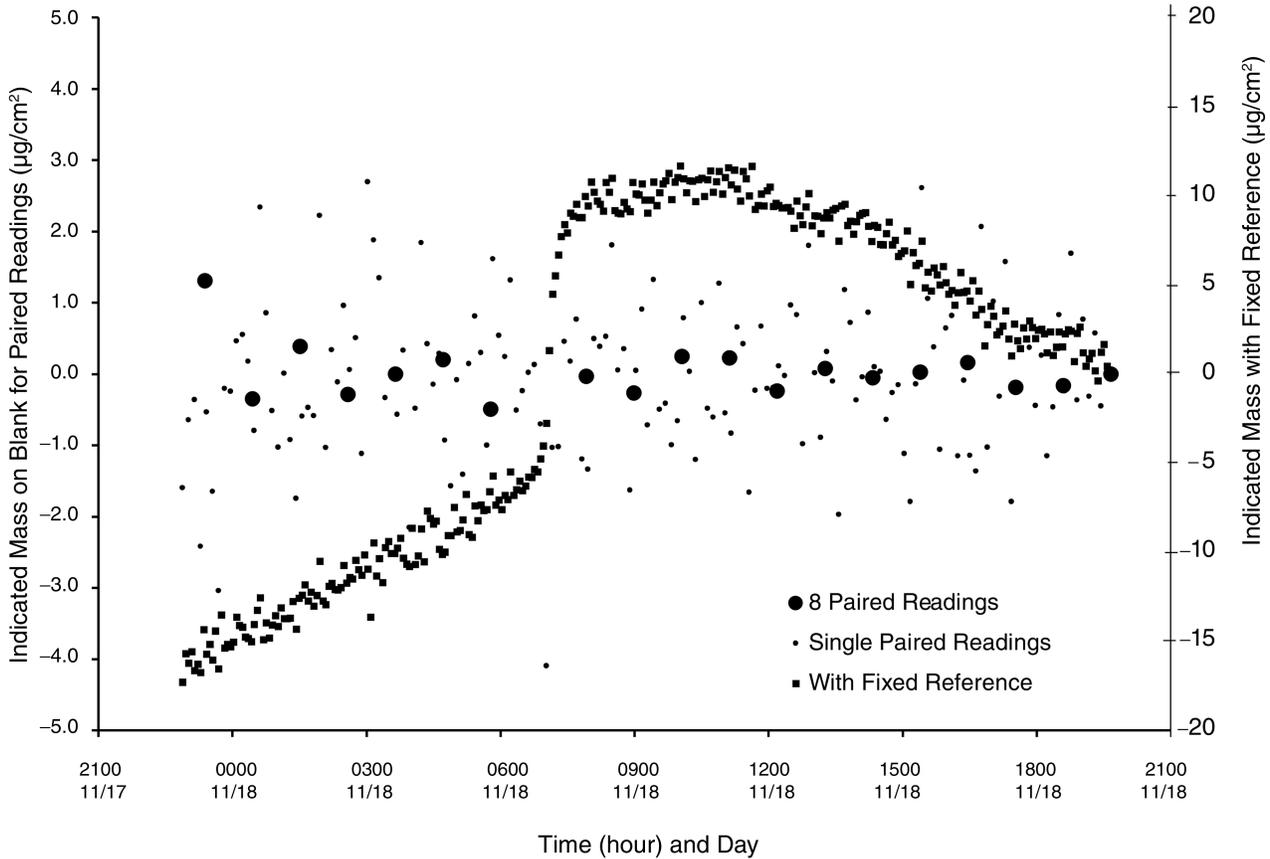


Figure A.1. Variation in β gauge readings for blank Fiberfilm filter over 24 hours. Counts are summed into groups to simulate longer sampling periods for improved statistics.

and humidity data collected simultaneously with the β gauge counts showed that the variability was not due to changes in the air density in the air gap but rather to electronic drift in the instrument.

Analogous to the reference spot technique, the left-hand axis of Figure A.1 shows the variability in indicated mass areal density obtained from paired readings. The small dots show data from 1 pair of consecutive 4-minute readings wherein the I_0 and I values used in Equation A.1 are from consecutive readings. The large dots show data from 8 pairs of readings wherein the value for I_0 is the sum of every other count, and the I is the sum from the other set of alternating counts. For 1 pair of counts, the measured SD was $1.1 \mu\text{g}/\text{cm}^2$; and for 8 pairs of counts, $0.4 \mu\text{g}/\text{cm}^2$. As shown below, the longer counting times give better counting statistics and hence more precise values.

The decay rate of the β source is not absolutely steady but rather is an unsteady statistical process governed by a Poisson distribution. Accordingly, the 1 SD fluctuation in a reading of I or I_0 is the square root of N , where N is the number of counts. By propagation of errors, the SD for the indicated mass density calculated from equation A.1 is $(1/\mu)(1/N_1 + 1/N_2)^{1/2} \cong (1/\mu)(2/N)^{1/2}$, where N_1 and N_2 are the 2 sets of counts for I and I_0 , both approximately equal to N . The actual count rates for this β gauge with the filter in place were 5.3×10^6 per 4-minute period, which corresponds to a 1-SD value of $1.2 \mu\text{g}/\text{cm}^2$ for 1 pair of counts, and $0.4 \mu\text{g}/\text{cm}^2$ for the 8 pairs of counts. These are essentially the same as that measured. Thus we see that the short-term fluctuations in the measurements are consistent with Poisson statistics.

Further experiments were done with repeated removal and replacement of the filter, and this showed no further increase in the standard deviation of the counts. With the current β gauge configuration with Teflon-coated glass-

fiber filters (Fiberfilm) and with a combined counting period of eight 4-minute pairs of data, the 1-SD precision for mass is $\pm 0.4 \mu\text{g}/\text{cm}^2$. We anticipate collecting 1 m^3 air on a single 1-cm^2 spot, and this translates to $\pm 0.4 \mu\text{g}/\text{m}^3$. The counting time required can be reduced with a stronger β source. The current source is $60 \mu\text{Ci}$, which is much smaller than the 3-mCi sources used by Macias and Husar (1976) in a β gauge. Because the source is easy to change, and because shorter measurement times would decidedly help, the possibility of a larger source was investigated, but no suppliers could be located.

The last experiment performed with the BAM-1020 β gauge was to measure filter densities with aerosol sample deposits. A pair of samples was exposed to nebulized oleic acid aerosol through a personal $\text{PM}_{2.5}$ spiral filter sampler (SKC). Gravimetric measurements were made with the Sartorius microbalance of the entire encapsulated filter. To reduce filter-handling effects on the microbalance measurements, the following measurement sequence was used: pre-gauge, preweigh, sample, postweigh, postgauge.

Results shown in Table A.3 indicate that for appreciable mass loading (approximately $0.12 \text{ mg}/\text{cm}^2$) agreement between mass density using the BAM-1020-derived μ factor and gravimetric mass density is consistent with filter media measurements (BAM/Grav = 5% for large loading in Table A.3 versus 7% in Table A.2). Light loading (approximately $40 \mu\text{g}/\text{cm}^2$) shows roughly twice the relative difference for β gauging relative to gravimetry (18%). Whether this difference stems from real differences in β attenuation response to light loadings or to measurement error cannot be determined from 2 data points. This experiment did serve to demonstrate that a reference Fiberfilm could be used to gauge changes in the system response and that to within the Poisson uncertainty, the measured density for

Table A.3. Density of Deposited Oleic Acid Aerosol onto Fiberfilm Filters Measured with BAM-1020 β Gauge and Gravimetry

| Media | I_0^a | I^b | Density (mg/cm^2) | | | |
|--------------------------------|-----------|-----------|-------------------------------------|------------------------|-------------|----------|
| | | | BAM-1020 | Corrected ^c | Gravimetric | BAM/Grav |
| Reference Fiberfilm | 5,613,268 | 5,614,812 | -0.0010 ± 0.0023 | | | |
| Fiberfilm + oleic acid aerosol | 5,608,347 | 5,430,444 | 0.1221 ± 0.0023 | 0.1231 ± 0.0033 | 0.1173 | 1.05 |
| Reference Fiberfilm | 5,616,692 | 5,614,812 | 0.0013 ± 0.0023 | | | |
| Fiberfilm + oleic acid aerosol | 5,608,981 | 5,549,729 | 0.0402 ± 0.0023 | 0.0390 ± 0.0033 | 0.0331 | 1.18 |

^a I_0 is initial count in fixed 4-minute interval.

^b I is final count in fixed 4-minute interval.

^c Uncertainties given are ± 1 SD based on Poisson statistics.

the fixed reference filter did not change between presampling and postsampling.

Although these experiments suggest a near attainment of the desired precision for the PPSS, certain aspects of this system are troublesome. Inherent instability of the electronics, as evidenced by systematic drifting (unrelated to air density effects) and occasionally abrupt changes in instrument response, requires frequent switching between the sample and the reference standard. Because filter registration is a significant source of error based on the relatively large density variation of the Fiberfilm media itself, this process of swapping in and out of the sample and reference increases the chance of operator-introduced error. Attempts at improving the system stability in conjunction with the manufacturer were not fruitful. Possibly, more elaborate temperature control measures could fix this drawback, but these were not undertaken given budgetary constraints. For these reasons, other approaches to β gauging were attempted.

Aerosol Dynamics β Gauge System

In key respects the IRD sensor used in the Aerosol Dynamics β gauge system was an improvement over the BAM-1020 detector. The increased short-term stability provided better precision through reduced handling of filters during gauging. Unlike the detector with scintillator and photomultiplier tube, the solid-state sensor enables a single measurement to be used for each gauged filter, rather than the previous method of switching back and forth between a sample and a reference filter to track drifting. Because each insertion of a filter into any type of mounting device introduces variation, a solid-state detector with its inherently greater stability is preferable (indeed, Macias and Husar arrived at this conclusion in the 1970s). For our goal of a detection limit on the order of 1 μg per spot, a precision of 1 part in 4000 or 0.25 parts per thousand is required. Because the required precision was never achieved with a

stationary filter, only static exposure tests were conducted with this system as summarized in Table A.4.

Initially, the output of the IRD sensor was measured by an electrometer. With a Fiberfilm filter placed between the detector and ^{14}C source, the output voltage from the electrometer was recorded every 10 seconds over night. The resulting data were then averaged down to 10-minute intervals to provide an equivalent sampling period of that duration. The average voltage (V_{avg}) and root mean squared (rms) deviation over a 12-hour period (V_{rms}) are given in Table A.4 with a resulting relative noise level of 1.9 parts per thousand, nearly an order of magnitude too high. When the data were smoothed to derive a slowly changing baseline that was then subtracted from the original data, the resulting rms noise was the same. This merely demonstrates the inherent stability of this detector.

To isolate potential sources of noise, measurements were made with no signal input (only the detector's dark current) and with 2 different-sized resistors replacing the detector. All 3 of these tests possessed comparable relative noise levels to that of the ^{14}C -Fiberfilm combination, suggesting that the electrometer was the major source of noise.

The final set of tests with the IRD sensor involved replacing the electrometer with a matched preamplifier and integrator built specifically for this sensor. The voltage output was measured with the voltage mode of a digital voltmeter (Fluke model 877), comparable to the previous measurements with the Analog Devices electrometer. The entire source, filter mount, detector, and amplifier ensemble was housed inside a shielded enclosure and placed inside a thermally isolating box.

Measurements were made with just an air gap and with a Fiberfilm filter in direct contact between the source and detector (ie, with a minimum air gap of less than 2 mm). Similar results to those with the electrometer tests (1.3 parts per thousand) were obtained for both of these cases. Finally, a stable picoampere current source was

Table A.4. Summary of Results with Aerosol Dynamics β Gauge System

| Signal | Amplifier | Media | V_{avg} (mV) | V_{rms} (mV) | $V_{\text{rms}}/V_{\text{avg}}$ ^a |
|-----------------|--------------|----------------------|-----------------------|-----------------------|--|
| ^{14}C | Electrometer | Fiberfilm | -7166 | 13.9 | 1.94 |
| Dark current | Electrometer | Steel | -3092 | 21.0 | 6.8 |
| Resistor | Electrometer | 100 M Ω | -314.9 | 0.92 | 2.9 |
| Resistor | Electrometer | 11.2 M Ω | -2747.2 | 4.3 | 1.6 |
| ^{14}C | IRD preamp | Air gap | 1210.4 | 1.6 | 1.3 |
| Test current | IRD preamp | ~ 93 pA | 929.3 | 0.23 | 0.25 |
| ^{14}C | IRD preamp | Fiberfilm in contact | 1313.1 | 1.7 | 1.3 |

^a Parts per thousand.

constructed and substituted for the IRD detector. Approximately 93 pA was driven into the preamplifier, and the output was again monitored over a period of 1 hour. The resulting relative noise was observed to decrease by nearly an order of magnitude, proving that the major contribution of noise was in the signal–detector combination.

In summary, the IRD-based system could not do better than 1 part in 1000 or, equivalently, roughly $4 \mu\text{g}/\text{cm}^2$ in precision. Attempts to further improve this system were deemed not warranted because the best approach would involve a much stronger radiation source that was not readily obtainable.

UC Davis β Gauge System

Long-term stability tests of this system were not possible in the short access periods we had arranged with UC Davis. Previous laboratory results with the Met One system indicated that at low loadings, there might be a systematic change in β gauge response. Taking measurements on filters with ambient samples was therefore a high priority.

Table A.5 shows the mass measurements based on β gauging and gravimetry of the 2 UC Davis field samples. Both were collected in an agricultural field near the campus for a period of 2½ hours each. Problems arose with both data sets that became apparent only after we returned to Berkeley to perform the postsampling weighing. The first run was hampered by a problem in the use of a Fiberfilm-based calibration of the detector. Two of the reference Fiberfilm standards exhibited a reverse trend in β gauge response to that indicated by gross density: that is, spatial variations in the Fiberfilm density were greater than the

differences in β attenuation. Nonuniformity in the radial dimension on the order of 5% was estimated by punching holes in the center of several filters and weighing the resulting inner disk and outer annulus. The data were reduced according to a linear fit of these calibration weights. Given the problem with using the Fiberfilm as a standard, the calibration for the second run was based on the more uniform Mylar film.

Results given in Table A.5 show systematic differences between mass measurements by gravimetry and β gauging. Both runs, using 2 different calibrations of the system, resulted in 25% to 30% lower mass from β gauging compared with gravimetry. The precision indicated by these 2 runs was on the order of 1 to 2 μg of absolute mass. Negative mass loading was indicated prior to applying a renormalization of the calibration based on changing response to one of the reference filters (ie, the 2-spot method).

The reference samples taken in a standard 25-mm Gelman holder were lower than the β -gauged samples by a factor of 2. A test run in the laboratory with the same sampling arrangement did not show this same disagreement. The 2 PPSS-type samples were in agreement to within 6%, and the reference sample was 20% higher. No reason for this discrepancy could be readily identified other than the 20% lower face velocity for the reference sample.

Although this system shows promise, system drift was too great, as indicated by calibration changes in the second run. Further tests and introduction of temperature control may have been sufficient to obtain the desired level of precision, but the acquisition of the AT100 β gauge made further efforts in this direction unnecessary.

Table A.5. UC Davis Field Test Comparison of Mass Determinations by β Gauging and Gravimetry^a

| | ΔM_{grav} (μg) | C_{grav} ($\mu\text{g}/\text{m}^3$) | ΔM_{β} (μg) ^b | C_{β} ($\mu\text{g}/\text{m}^3$) | $\Delta M_{\beta}/\Delta M_{\text{grav}}$ |
|--------------|---|---|--|---|---|
| Run 1 | | | | | |
| Filter 1 | 26.0 | 25.1 | 19.25 | 18.5 | 0.74 |
| Filter 2 | 26.3 | 25.7 | 20.37 | 20.0 | 0.77 |
| Reference | 14.37 | 13.6 | — ^c | — | |
| Run 2 | | | | | |
| Filter 1 | 7 | 7.9 | 4.2 (−2.5) | 4.8 | 0.6 |
| Filter 2 | 9 | 10.4 | 5.8 (−0.98) | 6.7 | 0.64 |
| Reference | 3.2 | 3.5 | — | — | |

^a Parenthetical β gauge masses are for nonnormalized calibrations. M indicates mass of deposit; C, concentration.

^b Change in mass of filter after loading.

^c — = not applicable. Reference filters could not be β gauged.

 ABOUT THE AUTHORS

Suzanne Hering is founder and president of Aerosol Dynamics Inc, a small research firm specializing in the development of measurement methods for fine, airborne particles. She holds an AB in physics from the University of California at Santa Cruz and a doctorate in physics in 1974 from the University of Washington, with an experimental thesis in the field of low-temperature physics. At Aerosol Dynamics Inc she codeveloped an automated system for high-time resolution measurement of fine particulate nitrate and sulfate (commercialized by Rupprecht and Patashnick) and a two-week integrated sampler for ambient fine particle mass and ionic species. She has directed numerous air quality field studies and is currently president of the American Association for Aerosol Research.

Nathan Kreisberg received an AB in physics from the University of California at Berkeley in 1983 and a PhD in physics from the University of Texas at Austin in 1991. His postdoctoral work was conducted at Los Alamos National Laboratory from 1991 to 1993 in numerical simulations of aerosol particle transport. Employed at Aerosol Dynamics Inc since 1994, he is involved with development of aerosol measurement techniques for atmospheric and laboratory sampling of airborne particles. His current research interests include the measurement of aerosol mass through β attenuation, personal sampling techniques, and air purification technology targeting airborne microorganisms.

Walter John has a BS in physics from California Institute of Technology and a PhD in physics from the University of California at Berkeley. He was an instructor at the University of Illinois and professor and chairman of the Physical Sciences Department, California State College at Stanislaus. His principal career appointments were at the Lawrence Livermore National Laboratory from 1958 to 1971, where he was Nuclear Reactor Research Group leader

and at the California Department of Health Services from 1974 to 1992, where he headed the aerosol and microscopy laboratories. He is presently retired and consults part time on the development of aerosol sampling instruments. His research interests include studies of the basic properties of aerosols in the laboratory and in the atmosphere as well as the technology of aerosol sampling and analysis. He has been a director of the American Association for Aerosol Research and on the editorial boards of several journals. He has over 100 publications in journals and books. He is a fellow of the American Physical Society.

 ABBREVIATIONS AND OTHER TERMS

| | |
|-------------------|--|
| AIHL | Air and Industrial Hygiene Laboratory (California State Health Department) |
| APS | aerodynamic particle sizer |
| ATI | Adaptive Technologies Inc |
| BAM | β attenuation monitor |
| CPC | condensation particle counter |
| EPA | Environmental Protection Agency (US) |
| FRM | federal reference method |
| GSD | geometric standard deviation |
| IRD | International Radiation Detectors |
| PM _{2.5} | particulate matter with an aerodynamic diameter below 2.5 μm |
| poly-PSL | polydisperse polystyrene latex |
| PPSS | personal particle speciation sampler |
| rms | root mean squared |
| UC Davis | University of California at Davis |

INTRODUCTION

Epidemiology studies have shown associations between short-term increases in particulate matter (PM*) air pollution and increases in adverse health effects (Katsouyanni et al 1990; Dockery and Pope 1994; Schwartz 1994; Pope and Dockery 1999; Samet et al 2000). Among these health effects are mortality and morbidity from cardiovascular and respiratory disease, and worsening symptoms in people with asthma (Dockery et al 1989; Pope et al 1991; Fosberg et al 1993; Yang and Yang 1994). Many studies conducted over the past decade have investigated mechanisms of PM toxicity and what particle constituents are associated with this toxicity (discussed in HEI 2002).

PM is a complex mixture of particles in the atmosphere. The size, chemical composition, and other physical and biological properties of these particles are highly variable because of differences in sources, geographic conditions, weather, and seasonal patterns (both in different regions and at different times in the same region). Although particles range in size up to an aerodynamic diameter of greater than 50 μm , attention has focused in recent years on the possible health effects of smaller particles with an aerodynamic diameter of 2.5 μm and smaller (PM_{2.5}). PM_{2.5} contains many chemical constituents, including organic carbon (which contains a large number of organic compounds), soot-like elemental carbon, absorbed and condensed hydrocarbons, water-soluble oxidants, sulfates, nitrates, and metals. Characterizing the composition of particles and linking it to toxicity may help reveal the underlying biological mechanisms of health effects, and in turn that information may point the regulatory community to the types of particles most likely associated with toxic effects. In addition, characterizing particles may help to trace particles back to their sources. For example, sulfate has few indoor sources (with the possible exception of kerosene heat sources) and thus can be used as a good tracer for outdoor sources. Examining combinations of constituents, like the proportion of organic carbon to elemental carbon, can also yield useful information.

Through its Request for Preliminary Applications process, HEI supports studies that are compatible with its overall research priorities but lie outside the areas defined

in its focused Requests for Applications. In January 1999, Dr Hering submitted a preliminary application proposing to design and validate a small, pump-driven, personal sampler that would concurrently measure several of the major constituents of PM_{2.5}. After evaluating Dr Hering's preliminary application, entitled "A Personal Particle-Speciation Sampler," the HEI Health Research Committee requested a full application and subsequently recommended funding the study. The Committee believed such a sampler could be beneficial to the research community, particularly those scientists who do not have the expertise to develop their own PM speciation sampler, and viewed the design ideas as promising. The study, which was designed as a 1-year study, began in July 1999.[†] (The authors were given a 4-month extension, and the final study lasted 16 months.)

This Critique is intended to aid HEI sponsors and the public by highlighting the strengths of the study, pointing out alternative interpretations, and placing the research in scientific perspective.

SCIENTIFIC BACKGROUND

Epidemiology studies often use area measures of exposure as surrogates for personal exposure measurements. Exposures to individuals reflect local exposures and time-activity patterns, however, and can vary greatly from exposures measured by centrally based monitors. Personal monitors better represent actual exposure for an individual and have been incorporated into some studies examining PM exposure (Brauer et al 1989; Clayton et al 1993; Demokritou et al 2001). Because it is not clear which components of PM are responsible for adverse health effects, personal monitors are needed that can collect information on different aspects of PM, including physical and chemical constituents—both organic and inorganic. This information is important both to complement epidemiology studies and to understand how different sources contribute to an individual's exposures. However, no single method allows determination of all characteristics of PM, and different sampling substrates are needed for assessing the presence and concentrations of the PM constituents of interest.

* A list of abbreviations and other terms appears at the end of the Investigators' Report.

This document has not been reviewed by public or private party institutions, including those that support the Health Effects Institute; therefore, it may not reflect the views of these parties, and no endorsements by them should be inferred.

[†] Dr Hering's study, *A Personal Particle Speciation Sampler*, began in July 1999. Total expenditures were \$156,480. The draft Investigators' Report from Dr Hering and colleagues was received for review in January 2001. A revised report, received in September 2001, was accepted for publication in January 2002. During the review process, the HEI Health Review Committee and the investigators had the opportunity to exchange comments and to clarify issues in both the Investigators' Report and in the Review Committee's Critique.

Ambient sampling systems generally involve large pumps and collect large volumes of air whereas a successful personal sampler must be small, lightweight, and nonintrusive. These requirements pose a challenge because PM sampling requires a pump to draw the air through the sampler. Personal pumps weigh 3 to 4 pounds and have a maximum volume of 5 L/min. Subjects will usually agree to wearing only one such pump. Therefore, traditional PM monitoring has focused on measuring a single characteristic of PM, usually integrated mass, limiting the exposure information that can be obtained from an individual at any one time.

Although it is a challenge to produce a small personal sampler for measuring exposure to PM_{2.5} and capturing its organic and inorganic constituents, some are already available. Several groups have modified the basic PM monitors in order to measure multiple pollutants and used them in field studies. One example is the Harvard personal sampler (Koutrakis et al 1988; Brauer et al 1989), which provides an accurate collection of particle nitrate and associated gases (including ammonia, nitric acid, and sulfur dioxide) as well as particle mass. Another example is the personal exposure monitor (PEM, MSP Corp, Minneapolis MN), which can be fitted with small inertial impactors to measure size-specific personal PM exposure (Clayton et al 1993; Thomas et al 1993). Turpin and colleagues used a PEM to measure particle mass concentration, 26 individual polycyclic aromatic hydrocarbon species, and 5 metal species using a combination of Fourier transform infrared spectroscopy, inductively coupled plasma mass spectrometry, and gas chromatography–mass spectrometry (Carlton et al 1999). Koutrakis and colleagues (Demokritou et al 2001) have recently modified the PEM to monitor multiple pollutants. This monitor, the multipollutant personal sampler (MPPS), splits airflow from a single pump either to a second impactor for simultaneous measurement of PM_{2.5} and PM₁₀ (PM less than or equal to 10 μm in aerodynamic diameter) or to a second filter that can be used to measure elemental and organic carbon. Passive filters that can simultaneously sample air for ozone, sulfur dioxide, and nitrogen dioxide can also be attached to the unit. These personal monitors are still bulky, however, and are limited in the range of constituents they can measure.

TECHNICAL EVALUATION

AIMS AND OBJECTIVES

The objective of this 16-month study was to design and validate a personal PM_{2.5} sampler suitable for subsequent

chemical speciation work. Specifically, the sampler was to meet the measurement needs for PM_{2.5} mass concentration and several major constituents of PM_{2.5} (including elemental carbon, organic carbon, sulfates, and nitrates). To allow personal monitoring, the device had to be portable and capable of battery operation for 8 continuous hours. The investigators specified 5 design requirements for this personal particle speciation sampler (PPSS):

- 2-channel sampling to allow use of both quartz and Teflon filters so that concentrations of both PM and its constituents can be determined;
- oilless, greaseless, size-selection inlet to allow precise measurement of organic carbon without the contamination problems that often occur when oil or grease is used;
- provision for a denuder (a device used to remove interfering vapors) and for recapture of semivolatile components of the particles, such as nitrate;
- compatibility with ββ gauge determination, a technique that measures PM mass by examining the scatter of β particles caused by the electron cloud associated with PM on a filter; and
- single-pump operation to keep weight and noise to a minimum.

The investigators set 5 objectives to assess the accuracy and precision of PPSS performance:

- penetration efficiency (an indication of penetration of particles larger than the 2.5-μm selection cutpoint) within 5% of the published PM_{2.5} federal reference method cutpoint for both liquid and solid particles;
- removal of more than 95% of nitric acid upstream of the filters used for nitrate anion;
- a detection limit capable of capturing 95% of the samples with a mass of 1 μg/m³ or greater;
- detection limits of 0.3 μg/m³ for sulfate and nitrate anions and 0.5 μg/m³ for organic and elemental carbon; and
- precision of 8% for side-by-side sampling using duplicate PPSSs when measured constituents are present at levels above the detection limit.

STUDY DESIGN AND RESULTS

In developing the PPSS, Dr Hering and her colleagues selected and tested individual components of the sampler and then performed limited field tests of a prototype that incorporated the selected components.

The overall design of the PPSS consists of a size-selective inlet to remove all particles larger than 2.5 μm in

diameter, 2 sampling channels, a flow controller, and a pump (seen in Figure 1 of the report). In this study, Dr Hering and her colleagues tested the following components of the sampler: inlet for efficiency in selecting PM_{2.5}; denuder for efficiency in capturing nitrate; filter selection for allowing measurement of a broad range of PM constituents; and filter sampling area to allow measurements on the small sample volumes obtained using personal samplers. In addition, they evaluated different methods for measuring PM mass.

Inlets

Three types of size-selective PM inlets were tested: microtrap, spiral, and compact cyclone—a modification of the cyclone impactor. Of these 3, the compact cyclone inlet performed closest to the federal reference method and therefore was selected for use. In addition, the compact cyclone inlet provided the best exclusion of larger particles. Figure 6 of the Investigators' Report shows the penetration of test particles, by size, using the compact cyclone inlet.

Sampling Channels

In order to measure both physical and chemical components of PM in their sampler, Dr Hering used 2 sampling channels. One sampling channel collected samples for measurement of mass and inorganic anions such as sulfate, nitrate, and ammonium, and the other channel collected samples for analysis of elemental and organic carbon.

Denuder

Many of the volatile compounds in the PM mixture can be present in either the vapor or particle phase. Use of a denuder coated with the appropriate material to eliminate selected components and placed upstream of the filter can aid in their accurate measurement. For example, detection of nitrate in the filter-collected mass sample requires stripping out vapor-phase nitrogen compounds, such as nitric acid, before they impact the filter. Collection of particle-phase nitric acid on the filters also requires stripping out ammonia prior to the filter.

In Dr Hering's study, 2 types of denuder were evaluated for their efficiency in removing nitric acid: an activated carbon honeycomb denuder, and an aluminum denuder coated with magnesium oxide. The investigators chose the carbon honeycomb denuder because it was more compact and more effective at removing nitric acid. The only disadvantage of this denuder was that it required regular regeneration (heating to 100°C for at least 1 hour) to prevent release of collected gas phase constituents.

Filters

Different filter media allow measurement of different components of PM. For example, Teflon-coated filters can be weighed for mass concentration and then extracted for analysis of inorganic ions such as sulfates or analyzed for metals using x-ray fluorescence or inductively coupled plasma mass spectrometry. Other particle constituents, such as elemental and organic carbon, cannot be measured from Teflon-coated filters but instead require a noncarbonaceous filter substrate such as quartz. These filters are first baked at 500°C to volatilize lower molecular weight species. They are then analyzed by thermal evolution of the deposited aerosols with nondispersive infrared detection of carbon dioxide or with flame ionization detection after conversion of evolved carbonaceous vapors to methane. Similarly, quartz filters cannot be used for the measurement of mass by gravimetric analysis.

Dr Hering selected quartz filters for one channel to measure elemental and organic carbon and Teflon-coated glass (Fiberfilm) filters for the other channel to measure particle mass and ions.

A backup filter coated or impregnated with appropriate chemicals, downstream of the primary Teflon-coated or quartz filter, can capture volatile material that might be stripped from the primary filter. For example, a backup filter impregnated with sodium chloride or carbonate can collect nitrate that might volatilize off a primary Teflon-coated filter. For the PPSS, Dr Hering and associates included a cellulose backup filter impregnated with sodium chloride downstream from the Teflon filter. Captured sulfate and nitrate were measured by ion chromatography; ammonium was measured by autocolorimetry; and sulfur was measured by x-ray fluorescence.

Filter Area

A sampling area with a diameter of 8 mm was used for the quartz filter. A sampling area with a diameter of 7 mm was used for the Teflon-coated filter. Sampling areas were isolated by use of a circular mask over the filter.

Assays for PM Mass Determination

There are many different methods for determining PM mass concentration. Among them are photometric techniques, gravimetric analysis, and methods based on use of a β gauge. Photometric determination measures the attenuation of a light beam transmitted through a filter while the aerosol is sampled; gravimetric analysis weighs a Teflon-coated filter using a microbalance; and the β gauge technique measures the scatter of β particles by the electron cloud in the PM on a filter. (This scattering is largely independent of the chemical composition of the PM.) The β

gauge technique is approximately 100-fold more sensitive to very low levels of PM than gravimetric techniques and can measure submicron amounts of carbon. Dr Hering and her colleagues therefore chose the β gauge technique to measure PM_{2.5} mass.

Four systems for using the β gauge technique were assessed for stability, precision, and the effects of loading and unloading filter cassettes. Investigators chose the AT100 β source and an integrated solid-state detection system because of its strong β source (providing good counting statistics) and long-term stability. Details of the AT100 system are described in the report; details of the other 3 systems are presented in Appendix A.

The Prototype PPSS

The selected components of the PPSS were incorporated into a complete prototype PPSS. In the second step of the study, this prototype PPSS was field-tested for ambient air in Berkeley, California; in addition, 2 samples were collected inside the Caldecott Tunnel, a freeway commuter tunnel east of Berkeley. The prototype was tested against reference samplers. The prototype PPSS, with dimensions of 11 cm \times 5.4 cm \times 4.5 cm, was made from aluminum and weighed 550 g. A personal sampling pump was used to draw flow through 2 filter channels, the flow split was passive, and the resulting flow rate was 2 L/min. A second-generation prototype, in which some metal parts were replaced with plastic, was developed at the end of the study and weighed 220 g. Further field tests on the second-generation prototype are being conducted in a follow-on study by Dr Alison Geyh at Johns Hopkins University.

DISCUSSION

Most of the specific performance goals for the PPSS were met as determined by both laboratory and field tests. The conflicts and problems associated with achieving such objectives are well described in the report.

Denuder

The denuder selection criteria and validation of performance were appropriate. The nitric acid exposure test showed that the carbon honeycomb denuder was 99% efficient at removing nitric acid. Other than the backup filter, however, there appears to have been no consideration of the potential for loss of filter-captured nitrate or sulfate during extended sampling periods or of potential influence by environmental conditions during sampling. The use of chemically impregnated reference filters as nitrate and sulfate sinks to prevent their volatilization could have been considered a separate issue.

Assays for PM Mass Determination

This study used β -attenuation techniques to overcome the problem of low sampling volumes required for personal sampling. The Adaptive Technologies Inc β gauge was selected based on a pooled standard deviation of 1 $\mu\text{g}/\text{m}^3$ for a series of tests that excluded one outlier value, resulting in a 2- $\mu\text{g}/\text{m}^3$ limit of detection for mass. These results were comparable to those obtained using the gold standard, gravimetric analysis. The average ratio of mass as determined by the 2 methods was 0.80. This ratio increased to 0.93 when only samples for which duplicate samplers agreed within 12% (as measured by gravimetric analysis) were considered.

Figure 7 of the report shows significant equivalent mass variation for a passive filter over 24 hours, particularly relative to the quoted limits of detection for the method. The use of reference filters to correct for drift is discussed, but it would have been useful not only to consider the median of paired samples but also to address the implications of the limit of detection for the range of drift observed. Figure 8A of the report suggests an underrecovery of mass by β attenuation relative to gravimetry at higher loadings, consistent with past observations for β attenuation.

The Prototype PPSS

Initial estimates of the PPSS species-specific detection limits were based on the pooled standard deviations of collocated field measurements. The values were 0.6 $\mu\text{g}/\text{m}^3$ for sulfate, 1.0 $\mu\text{g}/\text{m}^3$ for nitrate, 1.2 $\mu\text{g}/\text{m}^3$ for organic carbon, and 0.8 $\mu\text{g}/\text{m}^3$ for elemental carbon. As Dr Hering points out, these detection limits are nearly twice as high as the limits outlined in the goals set forth in her original proposal. Even within these detection levels, however, the data are quite useful.

Personal field experience with aluminum personal samplers has shown corrosion developing with prolonged use. It would be useful to know if there is any evidence of such wear on the aluminum portions of the prototype sampler and if so whether consideration has been given to using anodized aluminum or stainless steel.

The methods adopted for field testing the prototype PPSS were appropriate, and the results achieved versus reference methods indicate that the PPSS is fundamentally sound in design and performance.

CONCLUSION

This study was conducted in a systematic manner with appropriate results following from the methods and study design. The data collected and their analysis are presented logically in a clear and concise manner. The methods for

collecting and measuring specific components, such as carbon and anions, followed well-defined technical criteria in the choice of filters and denuders. This is reflected in good agreement recorded between the sampler and reference methods for sulfate, nitrate, organic carbon, and elemental carbon. In general, the results of comparisons with reference methods indicate that the PPSS is fundamentally sound. Because of its compact design, light weight, and ability to measure multiple constituents of PM, this personal sampler represents a large step forward in the use of personal monitors for PM. The potential for use by children is particularly exciting.

There are a few issues for which clarification would have been helpful, as listed below:

- statistical best fit and uncertainty of the cyclone inlet cutpoint;
- limit of detection for mass measurement by β attenuation, relative to the range of measured drift;
- implications of mass underrecovery by β attenuation versus gravimetry; and
- potential losses of sulfate and nitrate material from filters during extended sampling periods.

The Review Committee believes that this personal sampler has much promise, but some concerns remain. In laboratory and field experiments, the system underestimated particle concentration by about 25%. The Committee is also concerned about the impact of changes in ambient humidity during sampling, particularly in high-nitrate environments. The study included only 10 measurements in the controlled laboratory setting and only a few measurements in the field. The Committee therefore recommends further field testing in indoor and outdoor environments, including sites on both the east and west coasts (differing in ambient ammonia and nitric acid levels) and in both smoking and nonsmoking conditions (possible clogging of the filters and subsequent pressure drop). Dr Alison Geyh and colleagues at Johns Hopkins University are currently conducting these tests in the field and laboratory.

SUMMARY

For analysis of personal PM exposure, it is increasingly important to get speciation data from personal monitors. The careful attention to the weight and size elements, and the ability to measure PM_{2.5} mass concentration, elemental carbon, organic carbon, sulfates, and nitrates in the same instrument, make the personal sampler described by Dr Hering and colleagues a potentially valuable addition to personal monitoring tools. Once validated properly, this

sampler could allow measurement of personal exposures to fine PM over relatively short periods of time (ie, 8 hours) and could measure important PM characteristics such as size and chemical constituents. The lightweight, compact design of this sampler makes it suitable for widespread use, including personal monitoring for children and the elderly.

The study met the 5 design requirements that it set: 2-channel sampling; an oilless, greaseless inlet; provision for denuders; compatibility with β gauging; and single-pump operation. However, issues such as saturation still need to be addressed (as in environments high in tobacco smoke, ammonia, or nitric acid). Before being used widely, the sampler needs more comprehensive laboratory and controlled field testing, as is currently underway. This sampler therefore holds promise but is not yet ready for population studies.

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