INNOVATIVE INSTRUMENT FOR AN AMBIENT AIR PARTICULATE MASS MEASUREMENT STANDARD

FINAL REPORT 03-07

OCTOBER 2003

NEW YORK STATE
ENERGY RESEARCH AND
DEVELOPMENT AUTHORITY

NYSERDA

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Prepared for the

NEW YORK STATE
ENERGY RESEARCH AND
DEVELOPMENT AUTHORITY
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NYSERDA
Report 03-07

NYSERDA 6183

October 2003

PREFACE

The New York State Energy Research and Development Authority (NYSERDA) is pleased to publish this report on an "Innovative Instrument for an Ambient Air Particulate Mass Measurement Standard." The report was prepared by Rupprecht & Patashnick Co., Inc., with technical assistance from the University at Albany, Clarkson University, and the University of Duisburg - Germany. The product development effort presented here improves the accuracy and ease of monitoring fine particle mass in the atmosphere. The research represents a considerable advance in the measurement of fine particles and could serve as a new standard approach for mass measurements nationwide and internationally. It is our hope that public/private collaborative research such as this will lead to the next generation of technology for automated, real-time monitoring of environmental pollutants.

This project was funded as part of the New York State Energy $mart^{SM} Environmental Monitoring and Evaluation Program and represents one of several fine particle research and technology development efforts underway in New York State.

NOTICE

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ABSTRACT

Particulate matter (PM) in ambient air is composed of many chemical species of varying vapor pressures. A direct mass measurement of PM mass on filters is the basis of regulatory PM reference methods. The loss of semi-volatile PM mass collected on filters and filter sampling artifacts can produce non-quantifiable biases in reference method measurements depending on the thermodynamic history of the filter; therefore, a reference method cannot be considered a scientific reference standard. To address these issues Rupprecht & Patashnick Co., Inc., has developed a new measurement technique to overcome the difficulties inherent in PM mass measurement. The Differential TEOM® Mass Monitor is based on the highly reliable and accurate TEOM mass sensor, and provides an in-situ correction for sample artifacts caused by semi-volatile PM species. As part of this NYSERDA contract, prototype Differential TEOM Mass Monitors were developed and tested in laboratory studies and challenged with a wide range of aerosol and gaseous species, non-volatile, semi-volatile and highly volatile, and in field studies under a wide range of test conditions and ambient aerosol levels and compositions. Testing of the system illustrated that the Differential TEOM Mass Monitor is able to account for sample artifacts caused by sampling and semi-volatile species. Comparing the Differential TEOM Mass Monitor results to current reference method sample results indicate that under conditions where little volatile material is present, the two sampling approaches yield nearly identical results as expected. When semi-volatile species are present in the sampled environment, the Differential TEOM Mass Monitor will provide a more true representation of the PM concentration compared to the FRM samples and can correctly account for significant amounts of material lost by the reference method samples. The Differential TEOM Mass Monitor represents a significant advance in PM sampling methodology.

ACKNOWLEDGMENTS

Rupprecht & Patashnick Co., Inc., thanks NYSERDA for their support in this project; the Atmospheric Sciences Research Center at the University at Albany for their efforts in both laboratory testing and analyses, and in collecting and analyzing the field data for this project; Clarkson University for their efforts in analyzing the performance of the ESP in the laboratory and theor assistance in collecting field data for the project; the Particle Instrumentation Unit at the University of Southern California for providing assistance and support for the field work, the University of Duisburg for the efforts in analyzing components of the system in the laboratory, and the Environmental Monitoring, Evaluation and Protection (EMEP) Program Advisory Group and Science Advisors for their comments.. The success of this project would not have been possible without the assistance of these cooperators.

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Rupprecht & Patashnick Co., Inc., specializes in the development and manufacturing of technology-leading instrumentation to accurately measure particle mass and determine chemical speciation of samples collected from ambient air as well as selected source applications. These instruments are intended to aid in improving air quality at the sampling locations and to reduce the pollutants emitted from the designated source applications.

The TEOM® (Tapered Element Oscillating Micro-balance) Series 1400a Ambient Particulate Monitor is the world's best-selling USEPA-approved PM-10 continuous ambient particulate monitor. It is used by air monitoring organizations, industry and research organizations worldwide to measure ambient particulate concentration continuously. The time resolution of the Series 1400a Monitor allows users to identify high pollution episodes and determine trends in real time. When used in conjunction with meteorological data or information from gaseous criterial pollutant analyzers, the instrument can provide vital information in the study of human health effects. Other applications of time-sensitive data include source identification and control, short-term compliance monitoring, emergency response, forensic investigations and numerical modeling.

The TEOM monitor is well known for exacting near real-time (minute resolution) particle mass measurement with the unique characteristic of providing direct PM mass measurement without calibration uncertainty. By default, the instrument is usually operated using a 3 l/min sample airstream flow rate and a 50ºC filter and sample airstream conditioning temperature. The TEOM mass sensor is operated at a constant temperature and flow rate so that the net mass change is strictly due to material retained on the sample filter and not influenced by changes in operating or sampling parameters.

Specific attention has recently been focused regarding semi-volatile species retention using the TEOM method. Some studies have presented data and discussion concerning the retention of semi-volatile mass on the sample filter of the TEOM monitor relative to the FRM (Federal Reference Method). By operating the TEOM monitor at a fixed temperature of 50ºC the issue of retaining semi-volatile species on the TEOM sample filter becomes important. Studies have shown that under atmospheric conditions where there is a significant presence of semi-volatile particle mass component such as particulate nitrate or organic compounds from wood smoke the TEOM monitor does not provide a one-to-one correlation with the FRM. While this is not a problem from a sampling perspective, it is an issue when using the TEOM monitor as a continuous monitor for regulatory measurements.

The development of the Sample Equilibration System (SES) for the standard Series 1400a TEOM monitor

partially addressed this problem. The SES reduces the humidity level of the air being sampled and allowed the TEOM monitor to operate at lower temperatures, at 30ºC compared to 50ºC, of the standard operating TEOM monitor. By reducing the operating temperature of the TEOM monitor with the SES, the system collects more of the light molecular weight chemical components such as particulate nitrates and certain organic compounds. With the addition of the SES system to the TEOM monitor, the differences between the FRM results an 24-hour TEOM monitor results are reduced. In areas where there was little or no semi-volatile material in the atmosphere, the TEOM has always obtained 24-hour average values that were comparable with the FRM samples. The SES system resulted in better agreement when semi-volatile material was present in the atmosphere.

While testing showed that the SES equipped TEOM monitor correctly measures the amount of semi-volatile present in the atmosphere in short term testing, any "history" of the semi-volatile sampled by the system will result in the evaporation of the collected material over subsequent hours or days. This evaporation will then result in a negative bias or offset during the period when the material is evaporating. In addition to the collection and possible evaporation of semi-volatile material, filter artifacts such as gas adsorption/desorption and chemical reactions which can take place on the filter further complicate the measurement.

To measure ambient particulate matter (PM), the USEPA devised a reference method or procedure that samples the ambient PM on a filter over a 24-hour period. Under the FRM procedure, a filter is pre-conditioned under defined temperature and humidity, and then pre-weighed. Using well-defined hardware, a sample is collected on the filter for 24 hours at ambient temperature and humidity. The filter is then conditioned again under defined temperature and humidity, and post weighed. The difference between the mass of the post and preweights divided by the volume of sampled air yields the average 24-hour mass concentration. One of the major problems with the FRM procedure is that the sample filter and any collected material is constantly exposed to changing thermodynamic conditions and changing concentration of gaseous components at the filter during sampling. As a consequence, the FRM is only an indicator of PM in the air. It does not represent precisely the mass of PM as it exists and is breathed under ambient conditions. Furthermore, the method can only agree with itself under all conditions. No other instrument will always agree with the FRM unless the filter history precisely matches the FRM. When the method defines the measurement, it is unclear exactly what is being measured.

The development of a reference standard instead of a reference method for PM mass in ambient air would represent a major advance in the field. Consideration of these issues and additional desirable features led to the conceptualization and development of a new instrument called the Differential TEOM system.

The Differential TEOM monitor concept is based on the direct mass reading and real-time capability of the TEOM mass monitor. Instead of sampling the ambient PM continuously, upstream of the TEOM mass sensor is an electrostatic precipitator (ESP). The ESP is alternately switched on and off for a known period of time. During the period when the ESP is switched off, the TEOM mass senor samples the PM similar to a conventional TEOM monitor. During the periods when the ESP is switched on, or energized, the PM is removed from the sample stream and retrained by the ESP. During this ESP on period, any evaporation of collected PM or filter artifacts, such as gas adsorption or chemical reactions, are able to occur. These artifacts or evaporation also occur during the normal sampling periods when the ESP is off, and occur at the same rates as during the periods when the ESP is switched on. Subtracting the reported mass concentrations from the two periods and determining the resultant mass concentration, the system determines the actual PM present in the atmosphere at the time of collection. The system becomes self referencing, or self correcting, and removes the artifacts from the final reported value that are problematic with the FRM.

The Differential TEOM monitor was evaluated over many months, under many different environmental conditions, including laboratory testing. Testing was performed over multiple seasons, and at different geographical locations. The sampled atmosphere consisted of areas where there was little semi-volatile PM and in areas where the level of semi-volatile material was quite high.

During testing as part of an USEPA sponsored intensive study with the Atmospheric Sciences Research Center (ASRC) at the University at Albany, two co-located Differential TEOM monitors were compared to standard TEOM monitor, SES equipped TEOM monitor, and FRM results over a one month period. The testing showed that during this test period, very little semi-volatile material existed in the atmosphere in the area and time of sampling. Comparing the results showed that under these conditions, the different methods reported similar results as expected for the PM collected.

Laboratory testing at the ASRC facilities showed that when sampling sodium chloride aerosol, a non-volatile aerosol, the Differential TEOM monitor and the SES equipped TEOM monitor collected similar amounts of material and thus reported similar mass concentrations. When sampling ammonium nitrate aerosol, a semi-volatile aerosol at room temperature that evaporates at 30ºC, the SES equipped TEOM monitor reported lower mass concentration levels of ammonium nitrate compared to the Differential TEOM monitor as expected. When the ESP was turned off on the Differential TEOM monitor, the reported mass concentration was similar to the mass concentration reported by the SES equipped monitor during the entire test period. During the periods when the ESP was turned on, the Differential TEOM monitor showed that the ammonium nitrate was evaporating from the sample filter of the instrument. The mass concentration measured during these ESP on periods indicated the evaporation rate of the ammonium nitrate, and was used to correct the final reported mass concentration yielding a final overall reported mass concentration that was significantly greater than that reported by the SES equipped TEOM monitor.

The Differential TEOM monitor was also evaluated in Rubidoux, CA, an area of high ambient ammonium nitrate levels. The value of the system was shown in the field in the same fashion as illustrated in the laboratory. Comparing the Differential TEOM monitor to the SES equipped TEOM monitor, it was clear that the SES equipped TEOM monitor results were highly affected by the levels of ambient ammonium nitrate present to the extent that the SES equipped TEOM monitor reported significant negative levels of ambient PM. The two co-located Differential TEOM monitors did not exhibit such behavior. The results of the two co-located Differential TEOM monitors were well within the expected accuracy of the instruments.

INTRODUCTION

Problems in the measurement of particulate matter (PM) mass in ambient air are well known. Both direct and indirect measurement techniques have been employed in an effort to determine PM mass. Each method developed to date, however, has limitations in obtaining the actual mass of PM as it exists in its suspended form. Indirect methods are inherently inaccurate as there is no consistent physical connection between other particle properties and particle mass. To measure particulate matter mass directly, particles need to be collected (typically on a filter) and weighed. Particulate matter, as defined by condensed phase matter suspended in ambient air, is composed of chemical species exhibiting widely varying vapor pressures. As a consequence, the post weighing of a filter after particle collection can represent a questionable measure of the particulate matter mass as it existed in its undisturbed state in the atmosphere. This is largely due to the changes in thermodynamic conditions that the mass "sees" on the filter during sampling and subsequent weighing. This problem is exacerbated with fine particle mass measurements as the greater surface area to mass ratio as well as the composition of fine particulate matter results in significantly greater volatile fraction of the mass compared to coarse particulate matter. In addition, filter artifacts such as gas adsorption/desorption and chemical reactions, which can take place on the filter further complicate the measurement.

The United States Environmental Protection Agency faced with these seemingly intractable measurement difficulties, has adopted for regulatory monitoring purposes a combination of standardized hardware and procedures for particulate matter mass measurements that it defines as the Federal Reference Method (FRM). The terminology "reference method" as opposed to "reference standard" is important to note as the difference is critical to the understanding of the meaning of the measurement and is far more than a semantic distinction. The FRM is a filter-based 24-hour sampling period technique with pre and post conditioning of the filter under standardized laboratory conditions. After each conditioning period, the filter is weighed to determine the current mass of the filter. The collected mass is the difference between the two filter weights. Cut point issues aside, it is one of many conceivable potential methods all of which would produce different measurements depending upon the thermodynamic treatment of the filter specified in the method. In essence there is an unfortunate dichotomy between regulatory measurements and scientific measurements as the regulatory reference method cannot be considered a reference standard in the scientific sense.

The development of a reference standard for PM mass in ambient air would represent a major advance in the field. To accomplish this task with a practical, field applicable instrument as the final product is an additional challenge.

FEDERAL REFERENCE METHOD

Under the FRM procedure, a filter is pre-conditioned under defined temperature and humidity, and then pre-weighed. Using well-defined hardware, a sample is collected on the filter for 24 hours at ambient temperature and humidity. The filter is then conditioned again under defined temperature and humidity, and post-weighed. The difference between the mass of the post- and pre-weights divided, by the volume of sampled air yields the average 24-hour mass concentration. There are both good and poor scientific attributes of the FRM. The good attributes include:

1. Well-defined cut point.
2. Precise volumetric flow.
3. Direct, NIST traceable mass measurement.

Unfortunately there are also poor scientific attributes including:

1. Ill-defined, non-quantifiable volatilization of semi-volatile material.
2. Ill-defined, non-quantifiable adsorption/desorption of gaseous matter.
3. Ill-defined, non-quantifiable gas to particle conversion and chemical reactions on the filter.

Most of the problems result from both constantly changing thermodynamic conditions and changing concentration of gaseous components at the filter during sampling. As a consequence, the FRM is only an indicator of PM in the air. It does not represent precisely the mass of PM as it exists and is breathed under ambient conditions. Furthermore, the method can only agree with itself under all conditions. No other instrument will always agree with the FRM unless the filter history precisely matches the FRM. When the method defines the measurement, it is unclear exactly what is being measured.

THE IDEAL SYSTEM

With the FRM discussion in mind, an ideal system, i.e. one that measures the actual mass of PM in the air, would be one that also maintains the good scientific attributes of the FRM while preventing the poor attributes from compromising the measurement. A list of essential and desirable features of such a system would include:

1. Filter based (essentially 100% collection efficiency for PM of any appreciable mass).
2. True NIST traceable mass calibration.
3. Well-defined particle size cutpoint maintained through precise volumetric flow with minimal flow calibration uncertainty.

4. No measurement uncertainty from PM volatile component loss.
5. No measurement uncertainty from filter artifacts (gas adsorption/desorption, chemical reactions, etc.)
6. Measurements represent the PM mass as it exists at ambient temperature.
7. Real time measurements.

Consideration of these required and desirable features has led to the conceptualization and development of a new instrument called the Differential TEOM® (Tapered Element Oscillating Microbalance) system.

THE DIFFERENTIAL TEOM MONITOR

The Differential TEOM monitor concept is based on the direct mass reading and real-time capability of the well established TEOM mass monitor. Consider a matched pair of TEOM sensors that are run at ambient temperature represented by sides 'A' and 'B' in Figure 1. Downstream from a common size selective inlet and ahead of each TEOM sensor is an electrostatic precipitator (ESP). The ESPs are alternately switched on and off and out of phase with each other. Each ESP is on or off for a time period, Δt. Frequency data are collected for both TEOM sensors on a continuous basis. (The measured frequency can be converted to a measured mass through a simple spring mass approach and is described in detail by Patashnick and Rupprecht.[1])

It is possible to write a somewhat simplified expression for the "effective" amount of mass, M_{eff}, measured by each sensor during the time period, Δt_n. The effective mass is the mass that is calculated from the frequency of the TEOM sensor including all sources that affect the frequency during the given time period. At given time interval, Δt_n, assume ESP A is off and ESP B is on.

In that case for side A:

$$M_{Aeff} = M_{pnv} + M_{pv} - \alpha M_{pv} \pm M_{filt\ art.} \pm M_{eff\ \Delta T,\ etc.} \qquad (1)$$

Where:
M_{Aeff} = Effective mass reported for side A
M_{pnv} = non-volatile component of particle mass collected during the time interval

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[1] Patashnick, H., and Rupprecht, E., "Continuous PM-10 Measurements Using the Tapered Element Oscillating Microbalance", J. Air Waste Manage. Assoc., Vol. 41, No. 8, August 1991

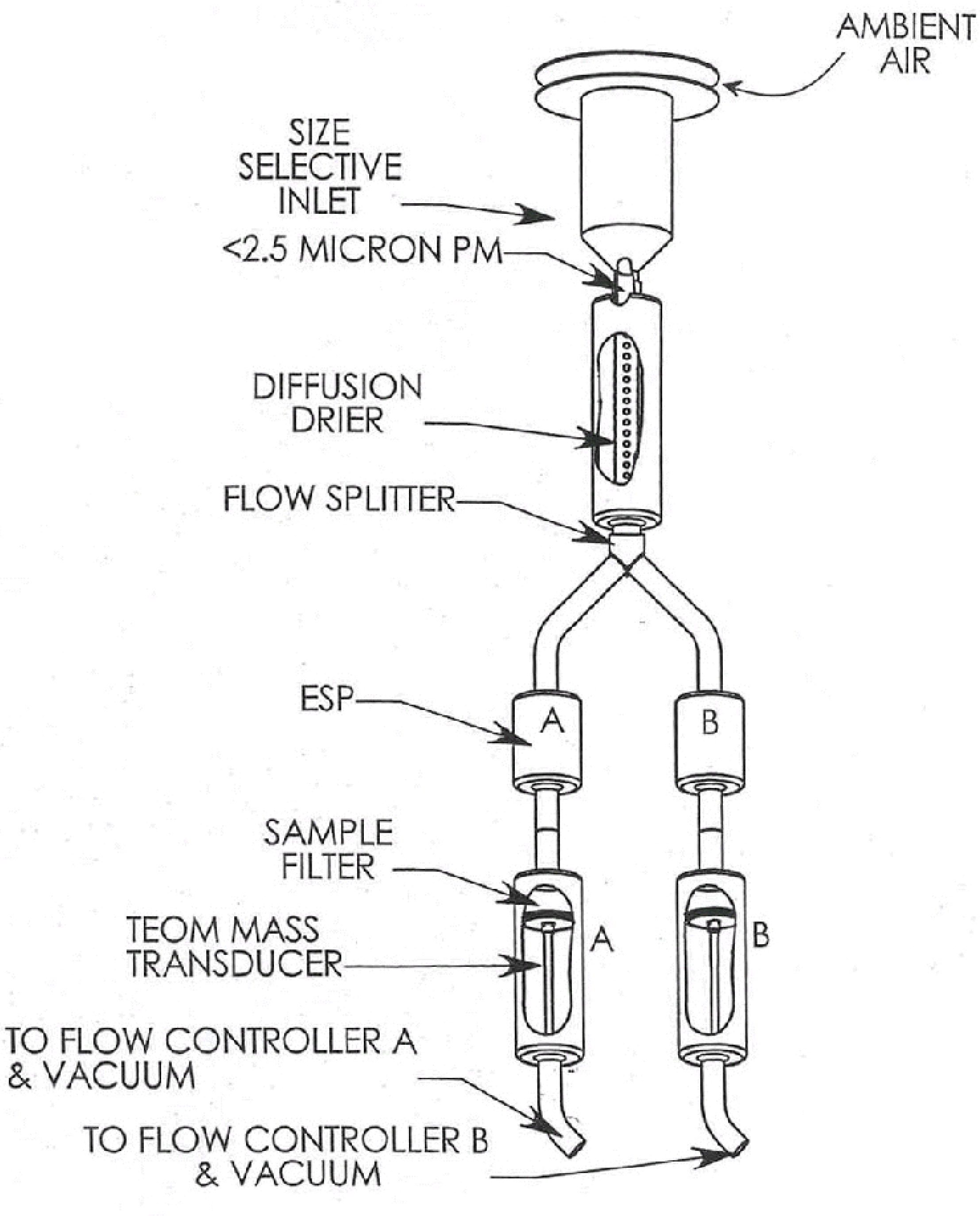

Figure 1. Schematic of the Differential TEOM system concept.

M_{pv} = volatile component of particle mass collected during the time interval

αM_{pv} = fraction of volatile mass that vaporizes during the time interval

$M_{filt\ art}$= mass gain or loss due to filter artifacts during the time interval

$M_{eff\ \Delta T}$, etc.= effective mass equivalent of frequency change due to temperature and/or other sensor sensitivities during the time interval

For side B at this time since ESP B is on, particles are not collected on the filter but the volatilization of previously collected particles continues:

$M_{Beff} = - \alpha M_{pv} \pm M_{filt\ art} \pm M_{eff\ \Delta T,\ etc.}$ (2)

Therefore:

$M_{eff} = M_{Aeff} - M_{Beff} = M_{pnv} + M_{pv}$ (3)

The technique works due to the referencing aspect of the TEOM sensors in combination with the strict equivalency of both sides maintained by the switching. The switching time must be chosen to be less than the time for changes to occur in the ambient particle concentration. In addition, the chosen time interval must be less than the time it takes for a volatile species of interest on the particles to vaporize. Clearly, the system approaches the most accurate representation of particle mass as it exists in its undisturbed state in the atmosphere as Δt approaches zero. This also raises the theoretical possibility that a sufficiently short switching time would allow the use of a single channel TEOM system that self-references. There are practical limits here that need exploration. In most situations, the differential TEOM system would be operated with a diffusion dryer before the ESPs. This would produce a measurement of particulate mass with unbound water removed. A quantification of water associated with the particles in the atmosphere might be possible by comparing results from two differential TEOM systems, one with and the other without a diffusion dryer.

An important point to note is that the differential TEOM system eliminates the problems associated with other particle measurement techniques (including manual filter systems) especially in its handling of volatile material, as a result of the strongest feature of TEOM instrumentation: direct mass measurement in real time.

As an example of the measurements made using the Differential TEOM approach, consider the results presented in Figure 2. During this example, the two mass sensors represented in Figure 1 were operated with a switching period of 15 minutes. That is the ESP on side A was energized for 15 minutes and the ESP on side B was turned off. After the 15 minutes, ESP A was turned off and ESP B was energized. Figure 2 shows raw frequency data obtained over a six-hour period from the matched pair of TEOM sensors operating at frequencies of approximately 287 and 280 Hz for sides A and B respectively. As can be seen in the figure, the slope of the frequency changes sign every 15 minutes and out of phase between the channels as would be expected from the switching of the ESPs.

During normal collection, the measured frequency decreases with a mass gain on the TEOM sample filter, and would have a zero slope during period with no mass change. Referring back to Figure 2, it is clear that both side A and side B exhibit mass gains when their respective ESPs are turned off, and exhibit a noticeable increase in frequency when the two ESPs are energized. This frequency increase represents a mass loss from the TEOM sample filter, presumably caused by the evaporation of material previously collected on the TEOM sample filter.

The mass concentrations during each switch segment were calculated by obtaining the least squares fit of the frequency data during each 15 minute interval and converting the computed slope, df/dt, to mass change, dm/dt, through the calibrated TEOM detectors. Dividing by the flow rate yields the effective mass concentration for each detector at each 15 minute interval. A plot of these results are shown in Figure 3 for the two units tested. The solid circles represent the mass concentration during the periods where ESPs was off and the open circles the periods when the ESPs were energized. Subtracting the results from the ESP "on" side from the ESP "off" side at each interval yields the average mass concentration of the particulate matter during each interval. These final mass concentration calculations are compared with the standard Series 1400 AB TEOM monitor results in Figure 4 for a 24 hour period rather than the six hour period presented in the previous two figures. This figure shows the promise of the Differential TEOM monitor technique to measure greater PM levels compared to conventional techniques.

Differential TEOM Monitor Benefits

The Differential TEOM monitor would not be necessary if the ambient aerosol only consisted of solid non-volatile particles. Instead, ambient aerosols are composed of a multitude of organic, inorganic, and mineral species, including solid carbon, silica and other minerals, ammonium nitrate, oxalic acid, and other organic materials. Some of these are non-volatile under normal sampling conditions, silica, for example. Others are highly volatile, including some alcohols present in various locations. Still others, such as ammonium nitrate, are classified as semi-volatile. That is they can be colleted at low temperatures and then evaporate as the sample temperature increases.

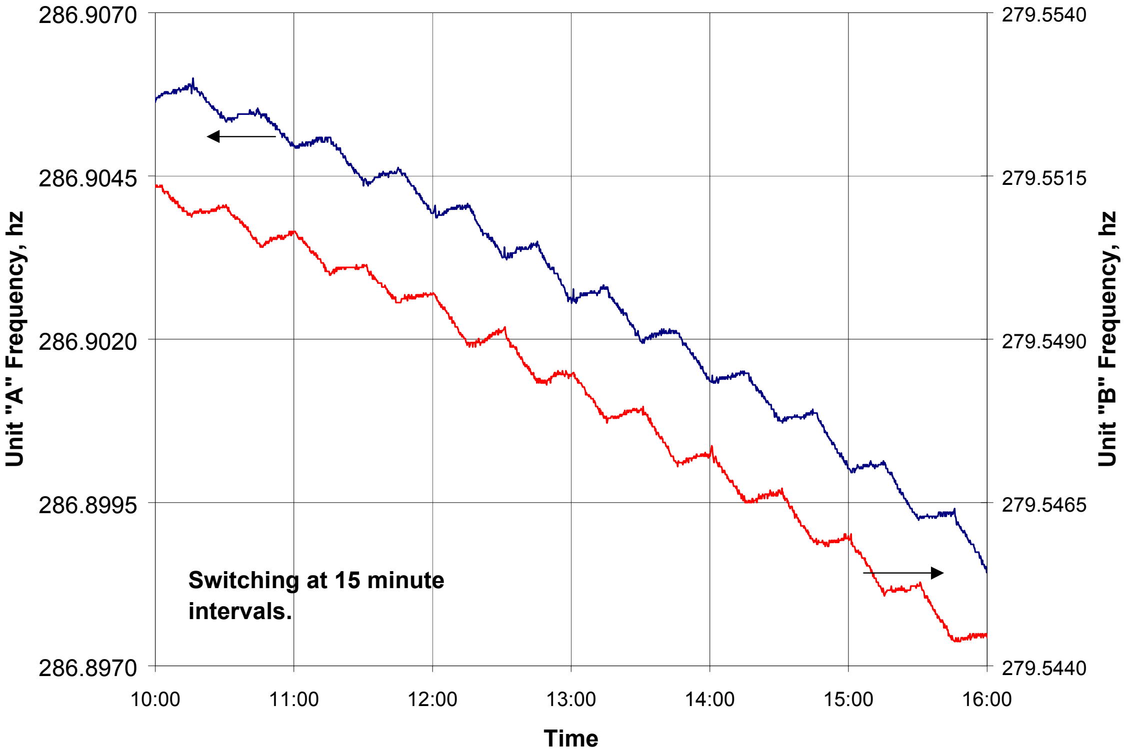

Figure 2. Raw Frequency output from a switched pair of Series 1400AB TEOM monitors with ESPs. (Differential TEOM monitor approach.)

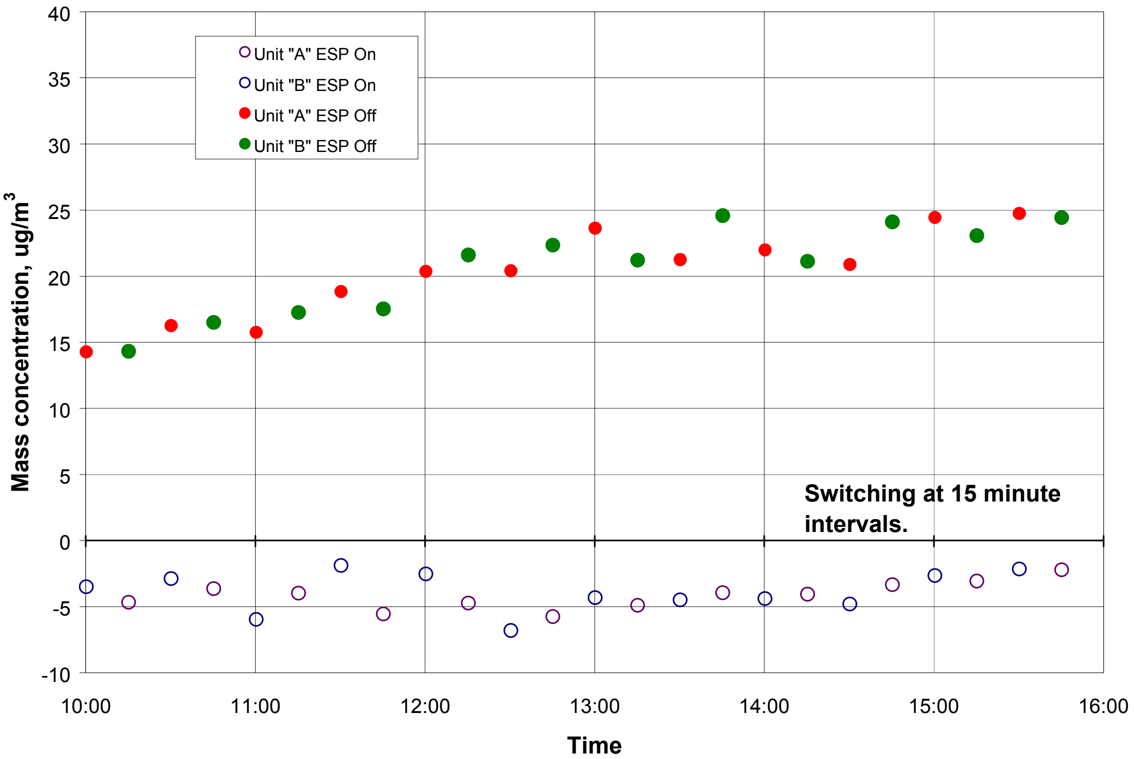

Figure 3. Mass concentrations obtained from a matched pair of Series 1400AB TEOM monitors operating as Differential TEOM monitors with ESPs.

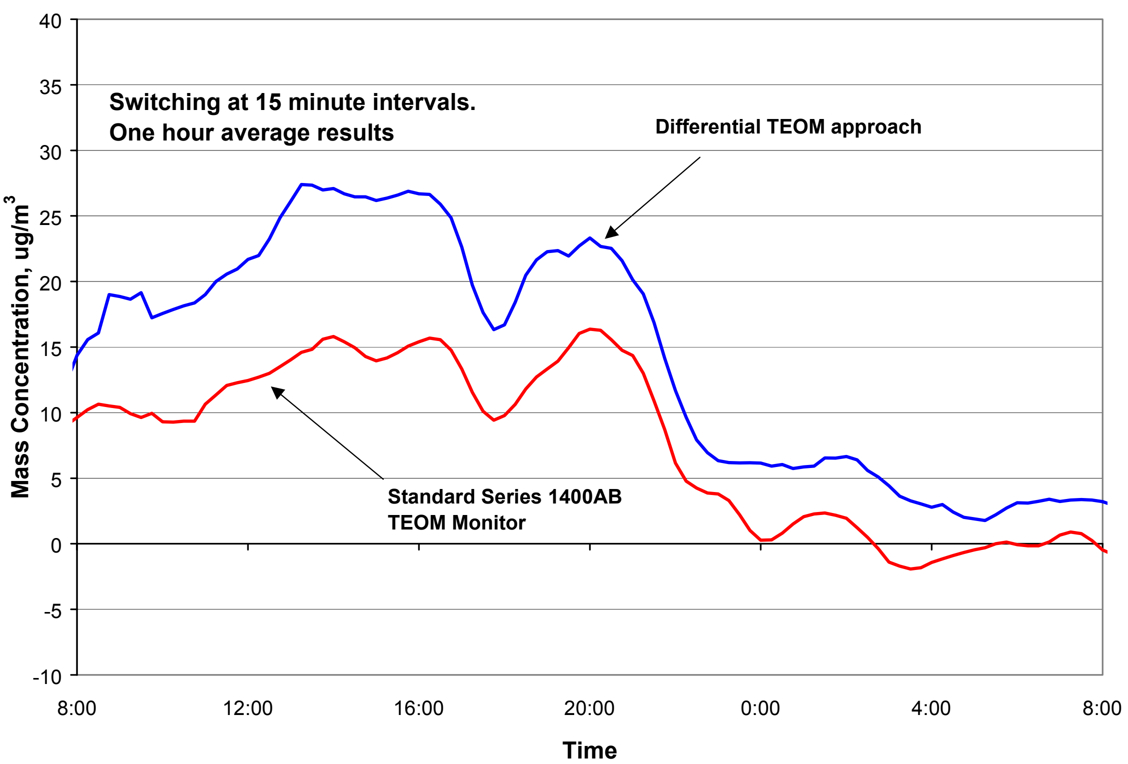

Figure 4. 24-hour comparison of hourly average mass concentration data collected using a standard Series 1400AB TEOM monitor and a Series 1400AB TEOM monitor with ESP switching at 15 minute intervals. Both units operating at 50ºC.

The standard Series 1400 TEOM monitor operates at a fixed control temperature of 50ºC. Under certain circumstances, there will be loss or evaporation of material from the sample filter because of the elevated sample temperature relative to the ambient temperature. In addition, there are chemical species that are not collected properly by the standard Series 1400 TEOM monitor because they are highly volatile an evaporate prior to being collected on the sample filter.

In recent years scientific discussion has included the influence of thermodynamic conditions (e.g., temperature, relative humidity and filter face velocity) on particulate matter (PM) retention efficiency of filter-based samplers and monitors. Method-associated thermodynamic conditions can, in some instances, dramatically influence the presence of particle-bound water and other light molecular weight chemical components such as particulate nitrates and certain organic compounds. The measurement of fine particle mass (e.g., $PM_{2.5}$) presents a new challenge for all PM measurement methods since a relatively greater fraction of the mass is semi-volatile. [2]

Specific attention has been focused regarding semi-volatile species retention using the standard TEOM method. [3] Some studies have presented data and discussion concerning the retention of semi-volatile mass on the sample filter of the TEOM monitor relative to the FRM. By operating the TEOM monitor at a fixed temperature of 50ºC the issue of retaining semi-volatile species on the TEOM sample filter becomes important. Studies have shown that under atmospheric conditions where there is a significant presence of semi-volatile particle mass component such as particulate nitrate or organic compounds from wood smoke the TEOM method does not provide a one-to-one correlation with the FRM. Since the standard TEOM sampling specifications are well defined, this is not a problem from a sampling perspective, but it is an issue when using the TEOM monitor as a continuous monitor for regulatory measurements.

The obvious solution is to reduce the operating temperature of the TEOM monitor to retain more of the light molecular weight chemical components such as particulate nitrates and certain organic compounds. However, simply lowering the operating temperature of the TEOM monitor was not a practical solution as this raises other sample issues. By lowering the temperature, the influence of small changes in particle bound water and water vapor becomes significant. Figure 5 shows the behavior of a standard TEOM monitor operating at 30ºC when exposed to normal temperature fluctuations as observed in many sampling

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[2] Meyer, M. B., and R. N. Olson, “A Field Assessment of the Effect of Volatile Constituents on the Measurement of Ambient Particulate Matter Mass Concentration”, Presented at “Measurements of Toxic and Related Air Pollutants”, Research Triangle Park, NC, 7-9 May 1996.

[3] Wirtz, K. And M. Martin-Reviejo, “Direct Measurement of Aerosol Concentration by Using a TEOM Analyzer in the Atmospheric Simulation Chamber EUPHORE, Spain”,

trailers. These wide swings in mass concentration are not acceptable when trying to observe changes in ambient mass concentration over short term observations. If the ambient conditions are 20ºC and 50% relative humidity (%RH), typical summer conditions, the %RH at 50ºC is approximately 12%, while at 30ºC the %RH is over 35%. As the temperature cycles inside the sample environment (the sampling trailer or outdoor enclosure), this influences the amount of water bound to the particles as they pass through the sample tubes. (This temperature cycling is typical of the temperature changes caused by the air conditioning systems present in a standard environmental sampling trailer.) At a low %RH, the amount of water present is small, so these small fluctuations in temperature do not affect the sample results. As the humidity increases, as what happens when the temperature is reduced, the effect of small changes in temperature become problematic, as can be seen in the figure.

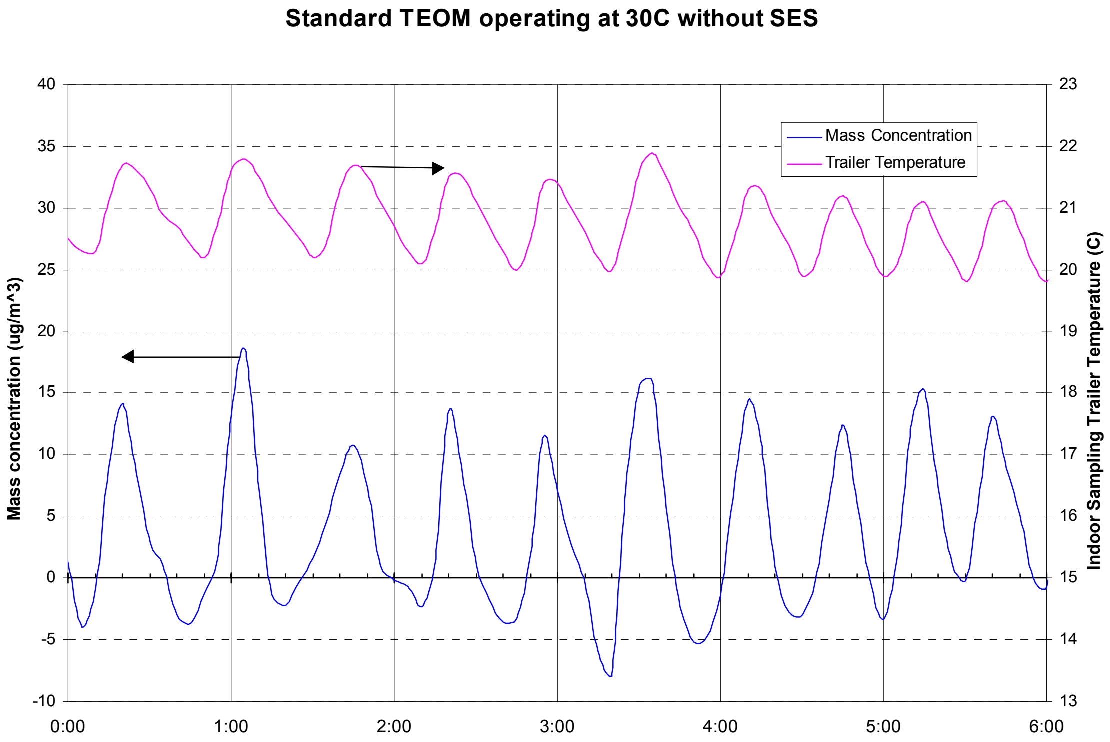


Figure 5. Effect of changing sampling environment temperature on mass concentration in a standard TEOM monitor operating at 30°C without an SES system.

ELECTROSTATIC PRECIPITATOR DEVELOPMENT & COMPONENT EVALUATION

An electrostatic precipitator (ESP) is used for the efficient removal of particles from gas streams without imparting a pressure drop or otherwise influencing the gas through the device. The gas is passed through a section containing high voltage rods or wires. The high voltage produces a corona which generates ions in the gas stream and can be either positive or negative. It is the effectiveness of the corona that primarily determines the effectiveness of the ESP. These ions impart a charge on any incoming particles in the gas stream. The charged particles then pass though an electric field of opposite polarity. This field causes the charged particles to collect on the surface of the ESP and are thus removed from the gas stream. If designed properly, the collection efficiency of the ESP can approach 100%.

The ESP designed by R&P is a two stage device with the charging section separate from the collection section. This allows the system to be more efficient in particle removal, while reducing exposed high voltage areas of the ESP, for operational safety of the system. The ESP uses positive high voltage to generate the corona and negative voltage in the collection section of the ESP. One of the concerns about using an ESP is the generation of unwanted interference gases inside of th ESP, such as ozone and NO_x. By using a positive high voltage to generate the corona, the production of these gases can be greatly reduced. The issue of interference gas generation is discussed in a later section of this report.

Figure 6 is a photograph of the prototype design of the ESP used during this project. The actual ESP is the silver metal and white plastic device in the center near the bottom of the enclosure. The gas enters at the top of the ESP and passes through the longer red tube into the corona charging section. To generate the corona, the ESP uses a 1/4 inch diameter rod with a sharply ground tip made of nickel. In order to reduce the voltage required to generate the corona, the field density is increased significantly by grinding the corona electrode tip to a sharp point. With this design the voltage required to generate the corona begins at approximately 2800 volts. The incoming particles are charged in the corona section, obtaining a positive charge due to the positive high voltage. They pass into the collector section, where the voltage field is set at approximately -5000 volts. Even though the absolute voltage level is greater in the collector section, no corona is generated because the collector electrode has a smooth rounded end exposed to the gas stream, this causes the field density to be low. The positively charged particles are then exposed to the negative electric field and are collected on the surface of the electrode.

The simple design for an ESP is to apply a constant high voltage and allow the generated current to vary depending on the performance of the ESP. However, the ESP performance and charging of the incoming particles is more dependent on the corona current rather than the high voltage. The ESP developed for this project was designed such that the corona voltage and current levels could be monitored to control the corona current at a constant level rather than the corona voltage.

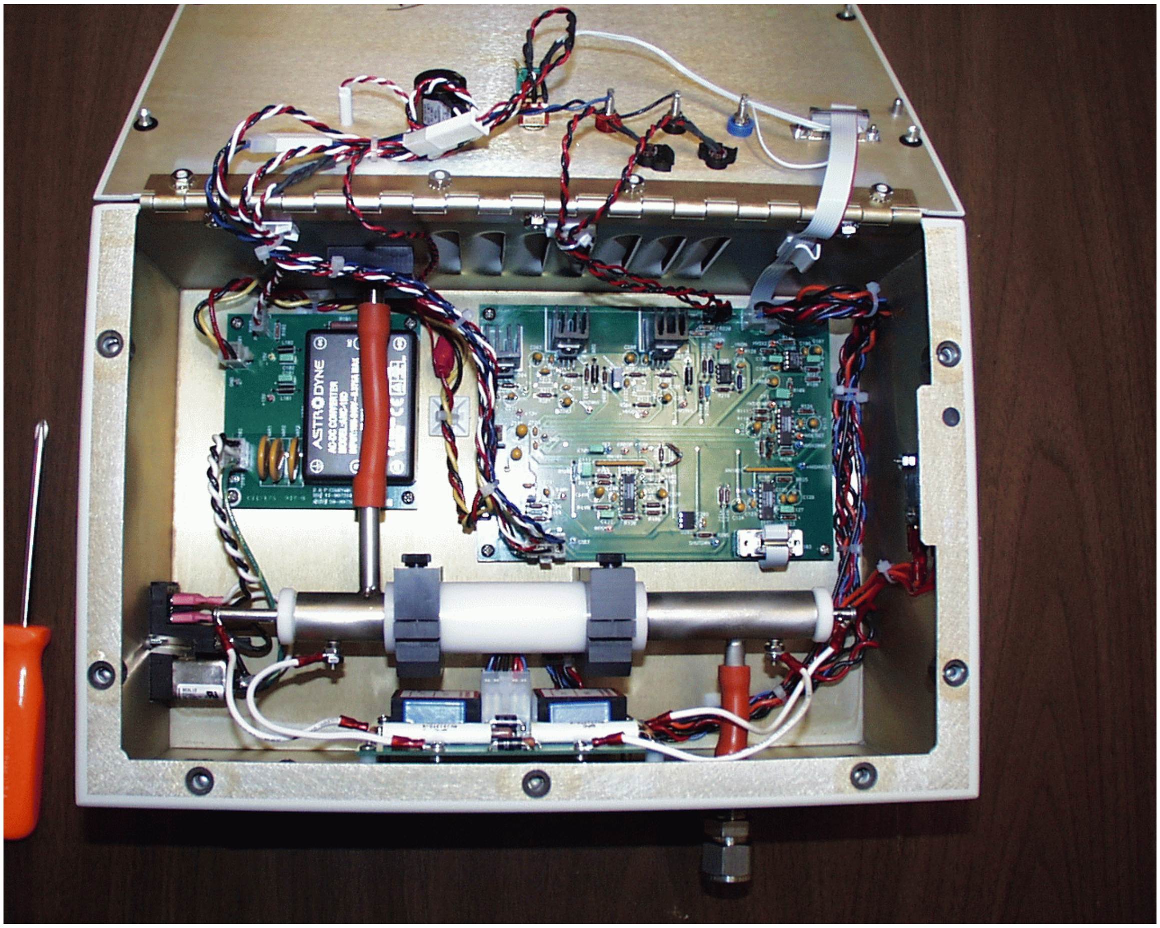


Figure 6. Photograph showing the prototype ESP developed for the Differential TEOM Monitor.

EVALUATION OF DIFFERENTIAL TEOM COMPONENTS

One aspect of making a new reference standard, or any instrument, is that all of the separate components of the system much be properly characterized for sample loss and other factors. Of the many components of the Differential TEOM monitor, some of these have been previously characterized and others are new for this product. Each component is discussed below.

Sample Inlet

All PM samplers use some sort of sample inlet to classify or segregate the desired materials being collected from those not desired. For ambient PM analysis, these usually include inlets that allow sampling of particles up to 2.5 or 10 µm, depending on the specific requirements of the test. In all cases with the Differential TEOM monitor, standard sampling inlets will be used eliminating the need to develop and test a new inlet for the system.

Sample Equilibration System

As mentioned above, the system uses a Sample Equilibration System (SES) to remove water vapor from the incoming sample to minimize the effect of changes in humidity on the apparent mass measurements. This system has been fully described and tested in a NYSERDA Contract, (Contract No. 5060-ERTER-ER-99). In effort described in the NYSERDA contract, the SES system and TEOM monitor was tested as a total system and compared to standard TEOM monitors and against FRM samples. This testing only looked at the SES as part of an overall monitoring instrument that provides a mass measurement reading and did not investigate the size selective measurements that would be required for a new mass measurement standard.

R&P cooperators at the University of Duisburg evaluated the SES to determine the penetration efficiency of different sized particles through the sample dryer in the SES. NaCl aerosol was generated as the challenge aerosol to investigate the sample losses in the SES dryer.

The system used to evaluate sample losses in the SES dryers consisted of four main components. An atomizer was used to generate the NaCl aerosol, a neutralizer, the Nafion® dryer used in the SES and a straight sample tube in parallel, and a scanning mobility particle sizer (SMPS). The SMPS was used to record the particle size distribution (PSD) first with the dryer in-line, and then with the straight sample tube. From the ratio of the two PSDs the penetration rate is determined, which also provides the relationship between particle size and sample loss. The experiments were performed for sample flow rates of 0.3 l/min, 1 l/min and 3 l/min.

Results for the testing of the sub-micron generated aerosol are illustrated in Figure 7. This plot shows the results of the experiments for penetration versus particle size for the three different flow rates. From the results obtained, when sampling the sub-micrometer particles, it is apparent that there is no appreciable loss in measured PM mass due to sample losses in the dryer when sampling the aerosol from dry air.

ESP Collection Efficiency Testing

The dryers used in the Differential TEOM monitor are used to condition the sample to reduce the effect of changing environmental conditions and so testing these for impact (losses) on the incoming sample, the ESP is used to remove particles from the sample stream during a portion of the sample period in order to determine the volatile effects of the previously collected sample on the overall results. As such, instead of determining sample losses, it is necessary to evaluate the collection efficiency and unwanted sample penetration through the ESP during the periods when the ESP is energized. Sample losses in the dryer could be accounted for through statistical reporting, but, loss of efficiency in the ESP would result in incorrect values being reported from the instrument. In the Differential TEOM monitor, if the ESP collection efficiency is not effectively 100% the particles that are not captured by the ESP, or "leak" through, would be reported as mass during the period when the ESP is energized, misrepresenting the mass concentration during that period of the instrument operation.

Clarkson University performed laboratory studies to determine the performance of ESP in capturing different sized particles. Ideally, the ESP will collect 100% of all particles from 10 µm down to nanometer sized particles during the periods when it is energized. The complete Clarkson University report is presented in Appendix B.

The ESP was evaluated using the fine (< 100 nm) and coarse particles (> 90 nm) generated using an aerosol atomizer. The fine particles were generated using a solution of NaCl, while the coarse aerosol was generated from a suspension containing three different sizes of polymer microspheres (PSL), 100 nm, 500 nm, and 1 µm. The fine and coarse particles were measured with a SMPS and LAS-X, a laser based particle measuring system, respectively.

Coarse Particle Measurements.

The LAS-X measured size distributions for the number concentrations of the coarse particles are presented in Figures 8 and 9. From the number concentration plot, it is clear that the collection efficiency approaches 100% for all particle sizes sampled. There are a number of different curves on each graph in the figures, each corresponding to a different numerical setting on the ESP control panel. The settings represent a range in corona current levels from approximately 20 nA (a setting of 100) up to 140 nA (a setting of 700).

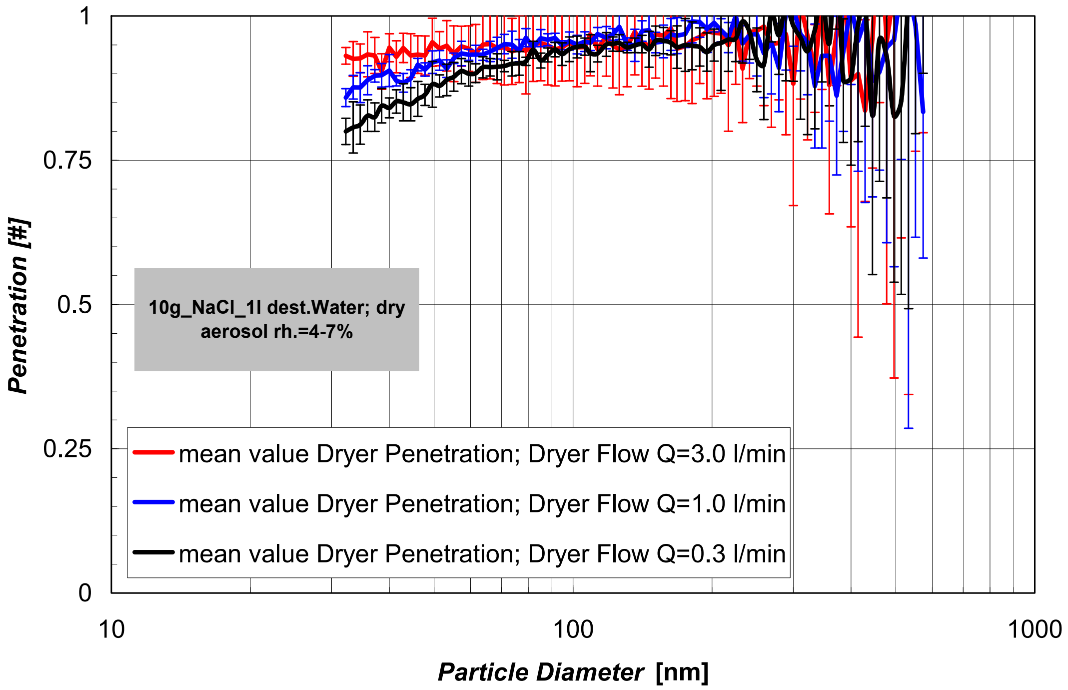


Figure 7. Penetration efficiency of submicron particles through the sample dryer of the SES.

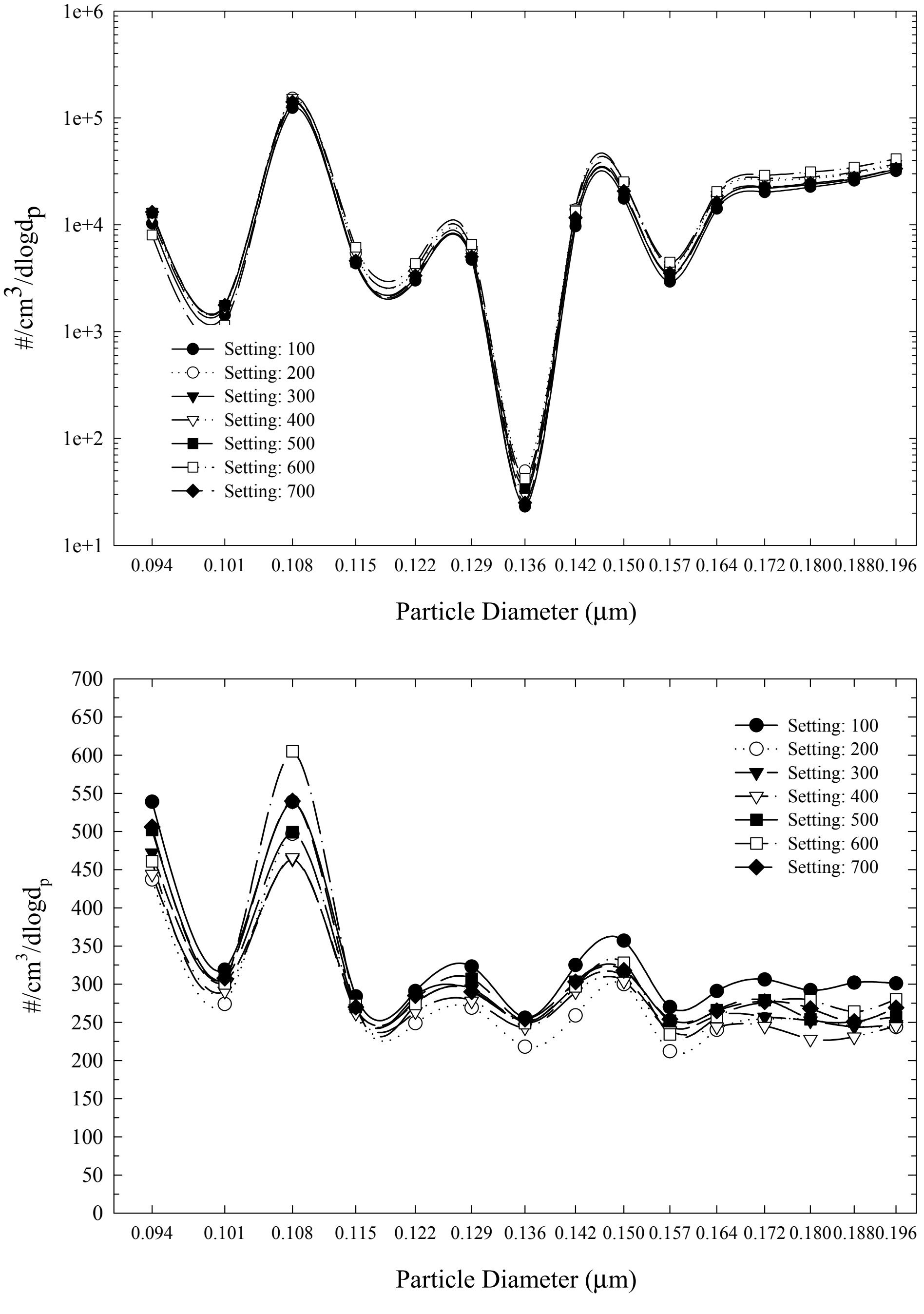
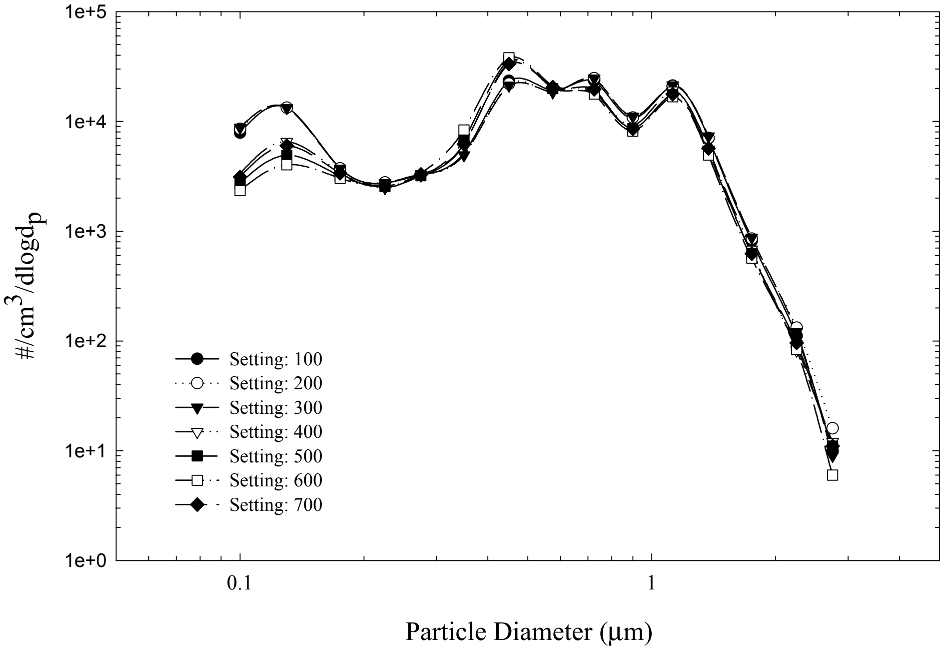


Figure 8. Size distributions measured with and without the ESP energized for 100 nm PSL spheres. Upper figure ESP off and lower figure for ESP energized.



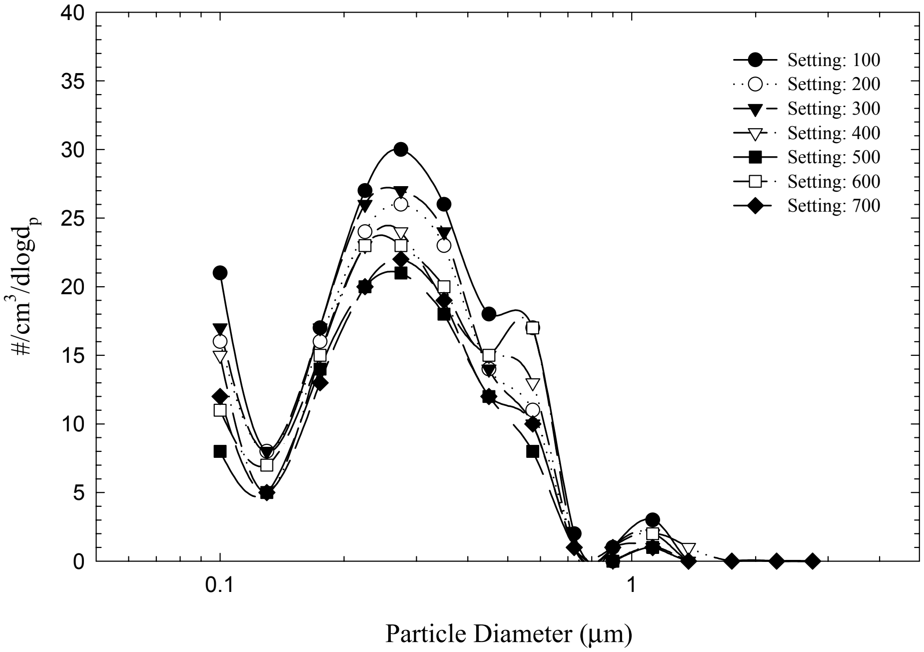


Figure 9. Size distributions sampled downstream of the ESP with the ESP energized (lower figure) and with the ESP turned off (upper figure) for PSL spheres of 500 nm and 1 μm.

In addition to the number concentration measurements, the mass concentrations with ESP off and on were calculated for the range in ESP settings. These mass concentrations were calculated using the measured size distributions assuming a particle density of 1.05 g/cm^3 and spherical particles. Finally, the overall collection efficiency of the ESP was calculated from the mass size distributions with the different nominal diameters of 100 nm, 500 nm, and 1 µm. Table 1 shows that the calculated mass based collection efficiencies of the ESP were near 100% over the entire range of operation for the ESP.

Potentiometer Setting	**Nominal Diameter**	
	100 nm	500 nm, 1 µm
100	**98.390**	**99.977**
200	**98.906**	**99.986**
300	**98.700**	**99.989**
400	**98.925**	**99.983**
500	**98.652**	**99.989**
600	**98.868**	**99.981**
700	**98.666**	**99.988**

Table 1. The overall collection efficiencies of the ESP calculated from the mass size distributions with the different nominal diameters

Fine Particle Measurements.

The ESP collection efficiency was evaluated for the fine particles using the SMPS. The size distributions for the number concentrations with the different ESP current settings were tested. The results indicate, Figure 10, that at a corona current of approximately 80 nA or greater, all of the particles less than 100 nm are collected by the ESP.

These ESP collection efficiency tests illustrate that over a wide range of particle sizes the ESP is nearly 100% effective at removing the sample aerosols. The difficulty in maintaining high ESP performance with small sized particles is they are less likely to retain a charge from the corona than the larger particles. Particles greater than 1 µm were not evaluated because of the difficulty in generating these sized particles and because there should be no difficulty charging particles larger than 1 µm sized particles.

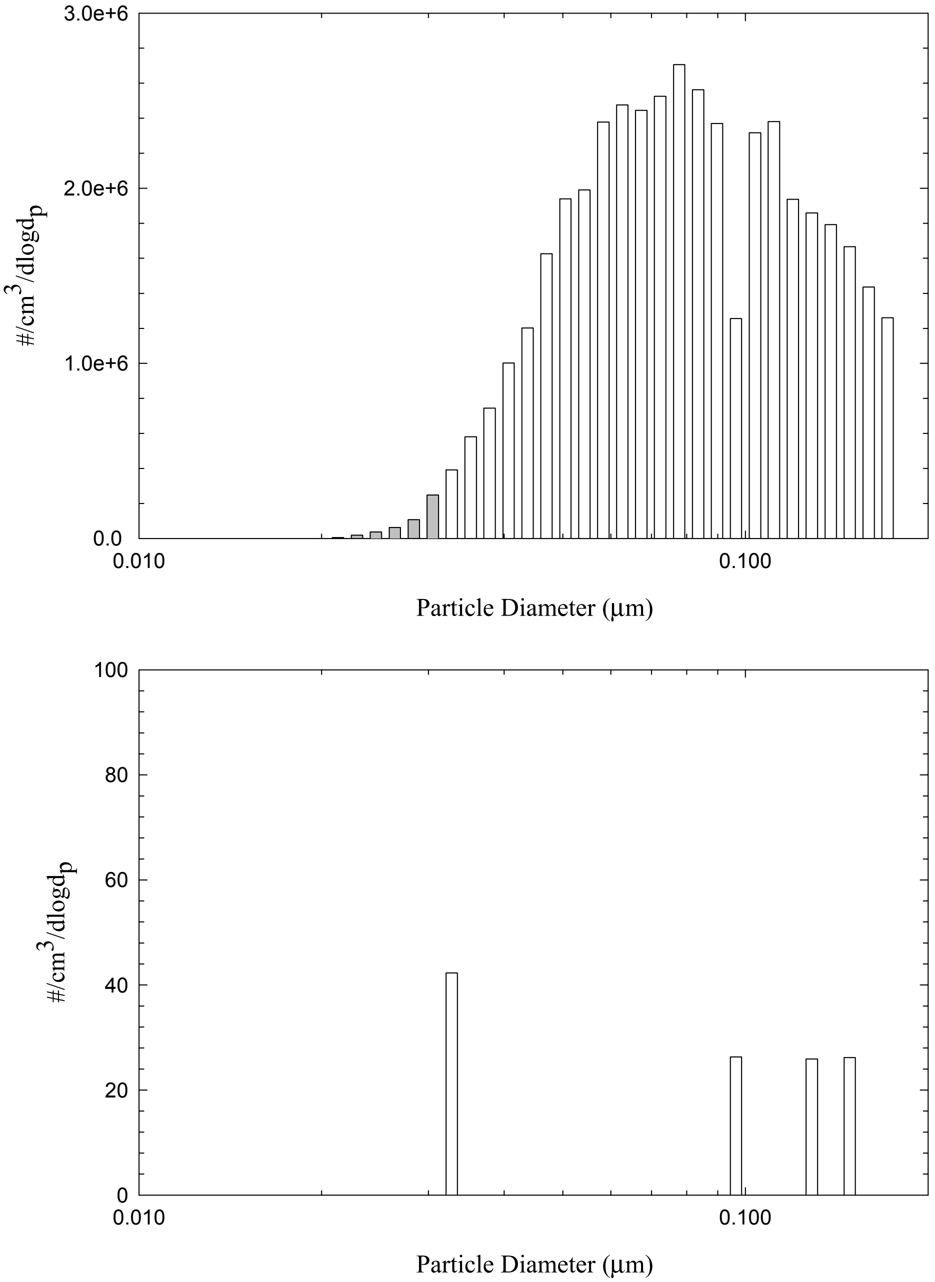


Figure 10. Representative size distribution measurements for polydisperse NaCl particles sampled downstream of the ESP with the ESP energized (lower figure) and with the ESP turned off (upper figure).

ESP Ozone and NO_x Gas Generation

ESPs are primarily designed to remove aerosol particles from the sample gas stream. In addition to the particle removal, they can also contribute to high levels of unwanted gases if not properly designed. The possibility that the ESP operation will generate interfering gases, including ozone and NO_x, through the energy released by the charging corona was investigated during the development of the ESP. Like ozone, NO_x is a highly reactive gas and may react with the sampled gases and particles creating interfering artifacts in the Differential TEOM monitor measurements. It is known that ESPs can generate significant amounts of ozone due to the high voltage levels and subsequent current levels used in many commercially available ESPs. Less well known is the ability of ESPs to generate NO_x gases in the corona sections. Since the main goal of most ESPs in commercial use is for the control of particle emission levels and not for use in sampling instrumentation, most of the published information is not relevant to our application as the current levels used in commercial ESPs are well above the 1 µA maximum current level used in the Differential TEOM monitor. Most commercial ESPs operate by setting the voltage level in the corona section to a constant level and allowing the current to fluctuate to maintain the constant voltage. As the generation of ozone and NO_x are related to the corona current and not voltage, the fluctuating current levels will result in variable ozone and NO_x gas levels. Figure 11 shows a plot of ozone generated inside the ESP as a function of ESP corona current up to 500 nA. Even at 500 nA, the measured ozone levels are not significantly greater than the background ambient levels. The ESP being used in the Differential TEOM is designed to operate only up to current levels of 150 nA, where the ozone levels are statistically similar to the background levels measured when the ESP was not energized.

Similar results were observed when measuring NO_x gases generated by the ESP. Figure 12 shows the measured NOx levels over an ESP operating current range of over 2000 nA. At this current level the NOx readings are only slightly greater than the background levels. In fact, at the expected operational level of no greater than 200 nA, there was no difference in the measured NOx levels.

ESP Corona Electrode Contamination

After testing the ESP for some time, we discovered an unexpected phenomena, the build-up of material on the tip of the corona electrode. Figure 13 illustrates this problem and can be seen as a build-up of crystalline material on the tip. The University of Albany Institute of Materials (UAIM) has been working with R&P to resolve this issue. Different tip deposits have been analyzed under a scanning electron microscope as well as with the optical microscope. Analysis of the material collected on the ESP corona electrodes operated at the R&P facilities in Albany, NY, show that the material on the tip of the electrode is primarily silica, while the analysis of material collected at a test location in Claremont, CA, indicated that the material from that location was composed primarily of carbon. The build-up on the ESP electrode is easily removed by wiping the tip with alcohol.

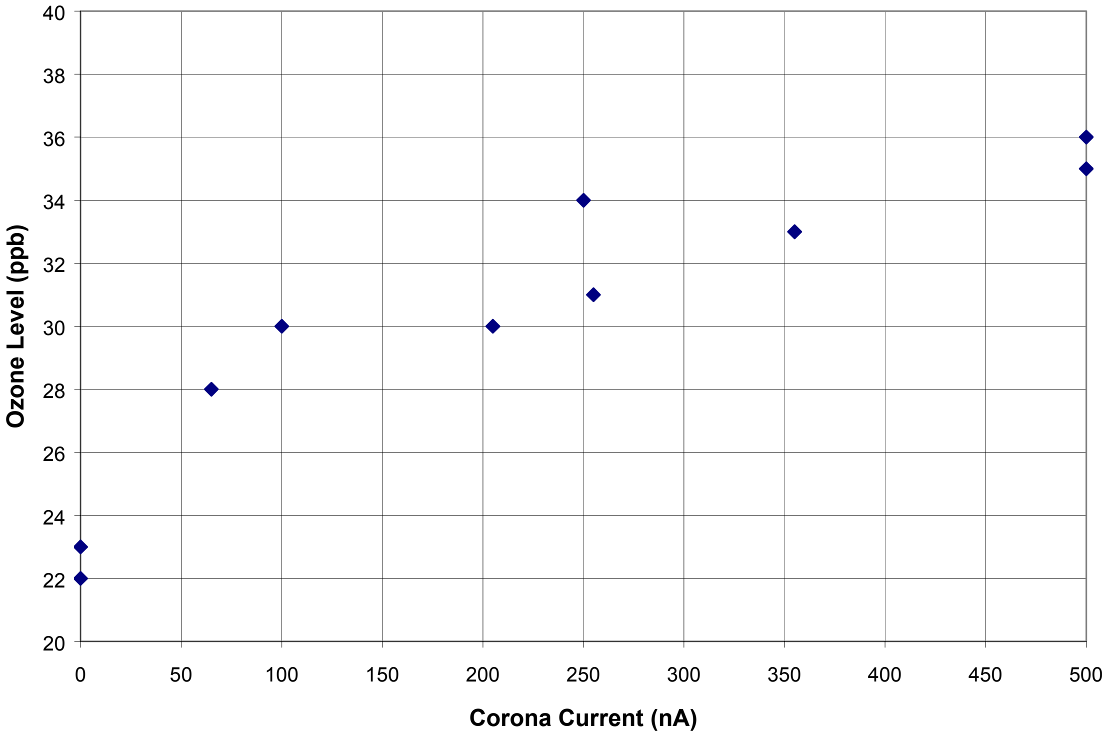


Figure 11. Ozone production levels measured downstream of an energized ESP.

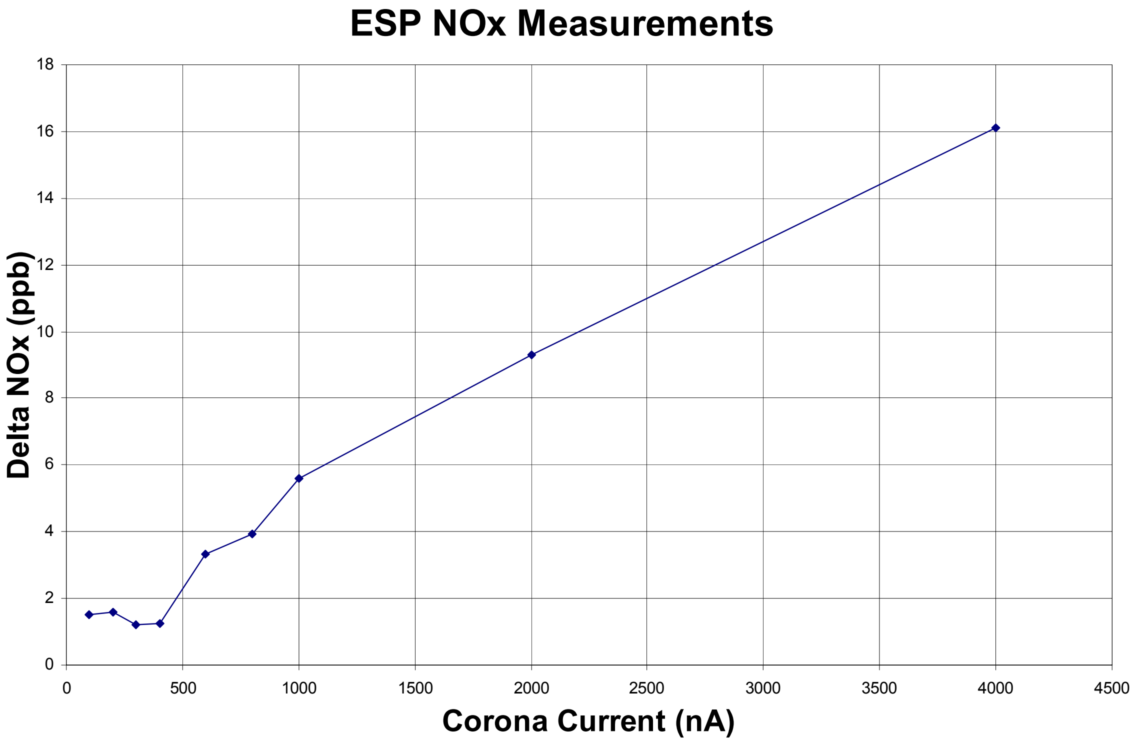


Figure 12. NO_x generation from energized ESP.

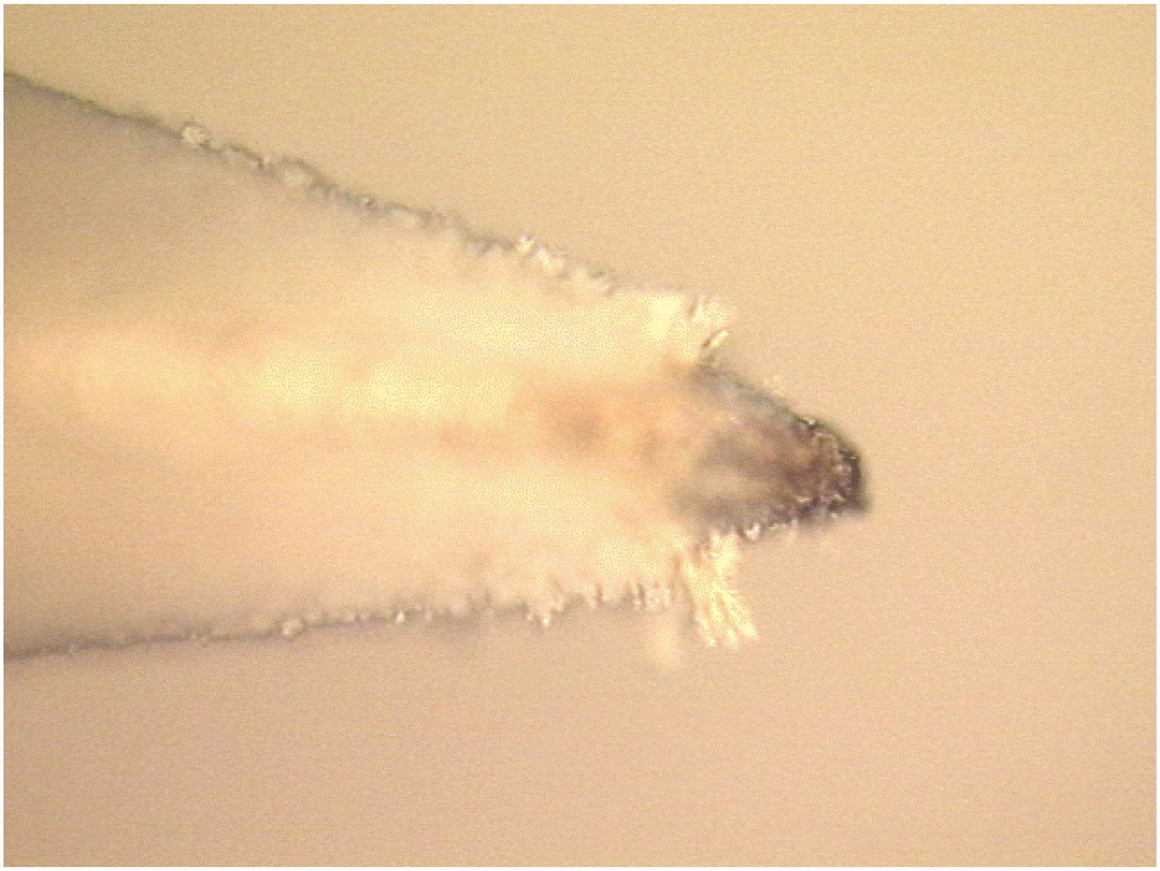


Figure 13. Photomicrograph showing the contamination build-up on the tip of the corona charging electrode.

The build-up of material on the tip of the corona electrode in the ESP has the potential to effect the operation of the ESP and thus the performance of the Differential TEOM monitor. One method used to check the ESP performance was to monitor the corona current and corona voltage during the period when the ESP was energized. As the build-up of material on the corona electrode increases the possibility that the corona becomes unstable increases. As the corona becomes unstable, not all of the particles in the sample gas will become charged and thus will pass through the ESP and be collected on the TEOM filter resulting in incorrect high mass concentration readings during the periods when all of the particulate mass should be collected in the ESP.

The problem of the tip contamination and corona instability are shown in the Figures 14 and 15 Figure 14 illustrates the corona current and voltage behavior of and ESP that is not maintaining constant corona current levels as designed. During this particular test period, the corona current was set to 40 nA, and overall, the current level is slightly higher than this setting, and the current varies by less than ± 10%. Contrast this behavior with the current and voltage levels presented in Figure 15 In comparing these two figures it is obvious that the ESP corona in the Figure 14 is unstable as the current levels in figure 15 vary by perhaps 1% during this period. The unstable corona current levels shown in Figure 14 are presumably caused by the contamination of the ESP tip, as simply wiping clean the corona electrode resulted in the stable behavior shown in Figure 15.

In addition to the unstable corona current, the voltage required to maintain the corona is also higher with the dirty electrode. The clean electrode required no more than 3500 volts to maintain the corona while the dirty electrode required nearly 5000 volts. The issue of corona voltage increasing can be seen in Figure 15. The data presented in this Figure was collected beginning just after the ESP tip was cleaned, and the corona voltage was initially only 3300 volts. After only 24 hours, the voltage required to establish and maintain the corona increased to 3500 volts before leveling off. This is likely caused by an initial build-up of material or a coating on the tip and stays that way until the build-up reaches a threshold where the performance begins to degrade more rapidly. The time until unsatisfactory performance of the ESP is highly variable and is a function of ambient PM levels, the composition of the ambient PM, the ESP tip material, and the ESP tip geometry. The time intervals before cleaning is required can vary from 5 days to many months, depending on the variables listed.

While the build-up does not pose a problem for the operation of the ESP or Differential TEOM in a general sense, it does present a commercialization hurdle. UAIM has been investigating two different techniques to automate the cleaning of the material from the tip of the corona electrode, reversing the polarity of the voltage on the electrodes in the ESP, and the introduction of ozone into the flow stream prior to the ESP inlet.

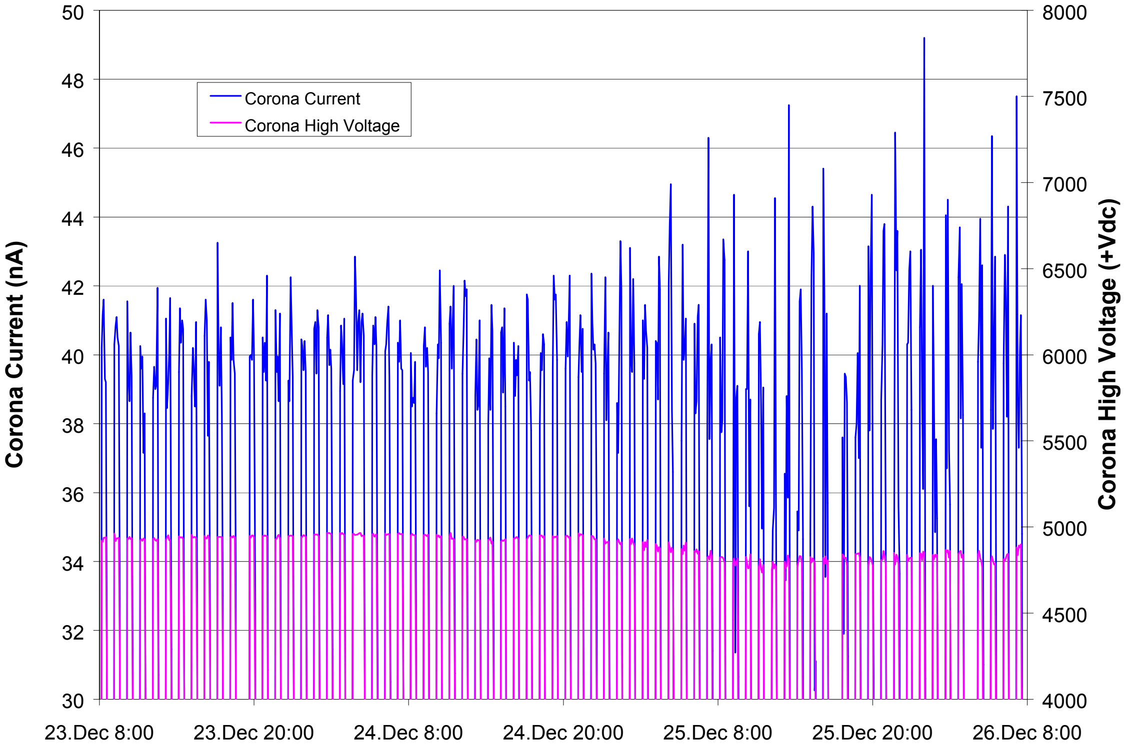


Figure 14. Corona current and corona high voltage levels representative of a contaminated corona electrode.

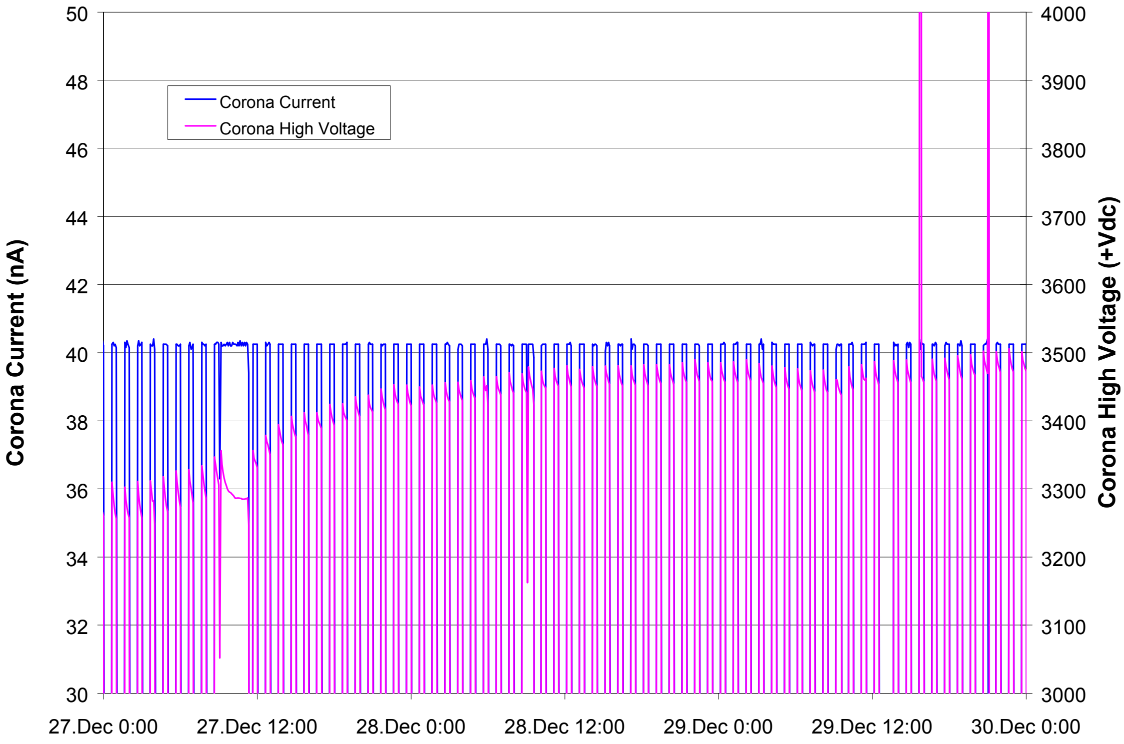


Figure 15. Stable corona current indicating a clean corona electrode tip.

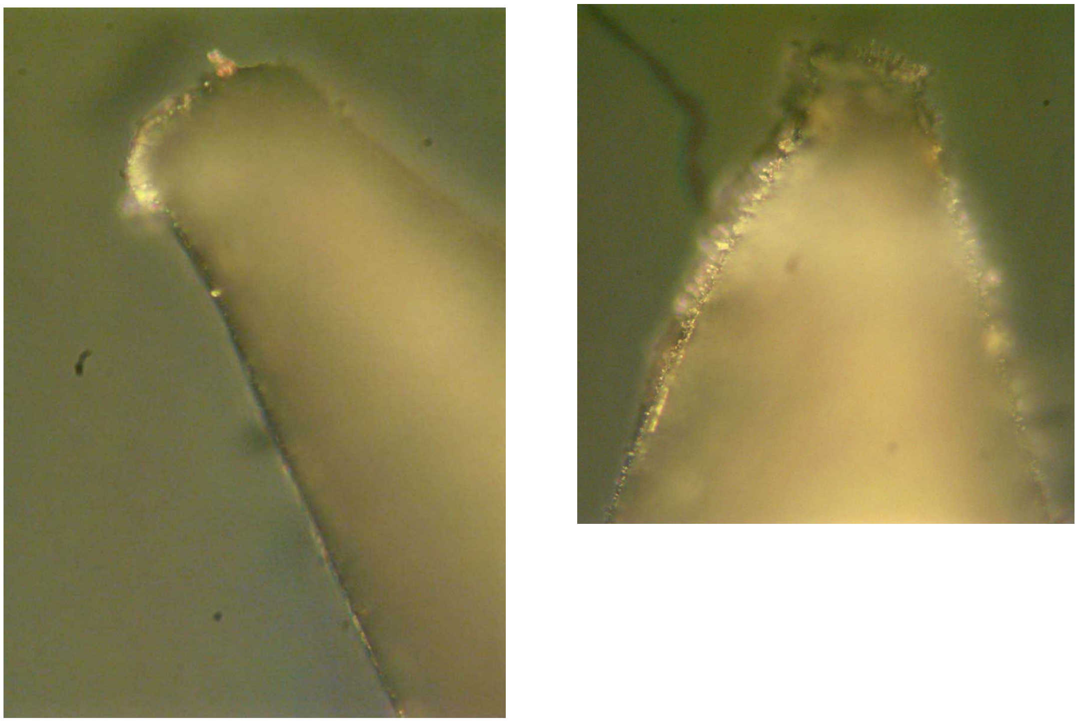
Presumably the material that deposits on the corona electrode is due to the presence of particles with a native negative charge. These negatively charged particles are attracted to the electrode due to the positive electric field surrounding the electrode. One possible automatic means of cleaning the electrode is to briefly reverse the field on the corona electrode and “drive off” the collected material. This could easily be accomplished in a production ESP by switching off the positive high voltage from the corona electrode and switching the negative voltage used on the collector electrode to the corona electrode.

UAIM has performed a series of tests to investigate this possibility. They operated two ESPs in parallel, both sampling ambient air to generate a build-up of material on the tips. One unit (ESP A) was operated upstream of a TEOM sensor in order to monitor the performance of the ESP and the second unit (ESP B) was operated without a mass sensor as the reference unit for the cleaning process. During this testing, ESP A was run through a cleaning cycle and ESP B was operated continuously, allowing comparisons of the two ESPs to determine the effect of the cleaning cycle on the behavior of the cleaned ESP. Both ESPs were operated continuously during the collection/contamination phase of the testing with a corona current of approximately 180 nA.

Since the ESPs were not designed to automatically switch the positive and negative voltages between the two electrodes, to apply a negative voltage to the corona electrode required a manual operation with an external power supply. Initial testing of the cleaning procedure involved supplying a negative high voltage (approximately -7500 volts) to the corona electrode for a period of 45-60 minutes to investigate the efficacy of the approach. These initial tests showed that amount of material on the corona electrode was reduced by this procedure, such that further testing was warranted.

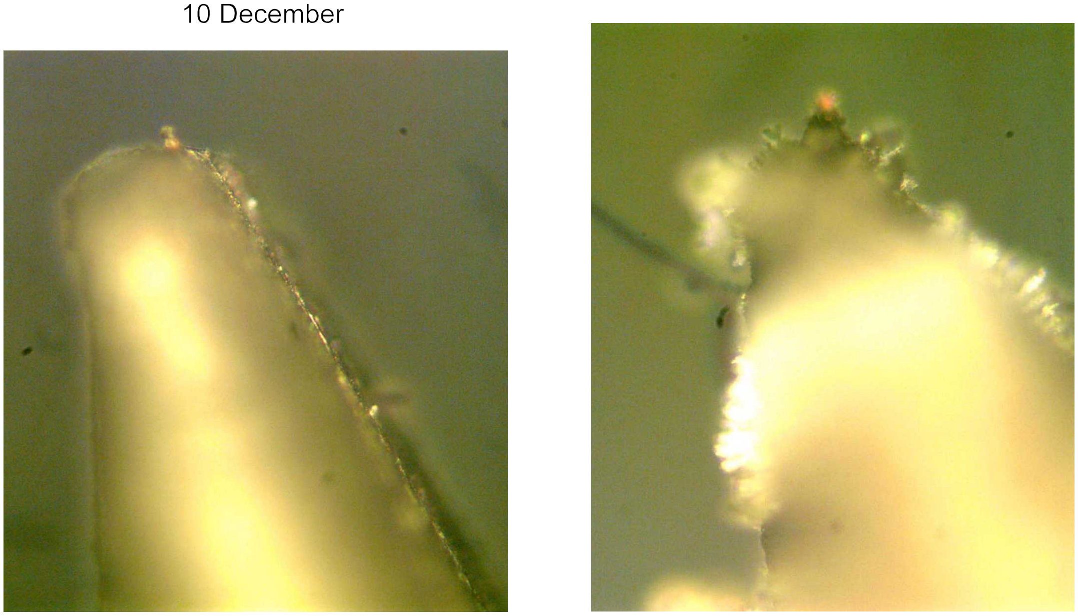
Because an interruption in the operation of the Differential TEOM monitor of 45 minutes or longer would not be acceptable during the normal operation of the monitor, the process was revised to allow for multiple cleaning periods every 24 hours. During the next phase, the two units were operated for 4 weeks with two 10 minute cleaning periods every 24 hours. Once per week the two systems were shut-off and the corona electrodes were removed from the ESPs and photographed under the microscope. Photographs of the two electrodes are presented in Figures 16 and 17 covering the duration of the testing. During this testing, it is visually obvious that the build-up on the cleaned electrode is reduced through the application of the negative high voltage to the corona electrode.

These initial results were promising, but upon further review and further testing , it was not clear the consistency of the results. Subsequent tests of this procedure suggested that the revers polarity cleaning procedure did not result in any cleaning of the ESP electrode. One of the aspects of applying a high voltage to the electrode is the generation of ozone by the ESP. Further, applying a negative high voltage will result



Clean ESP Electrode
3 December

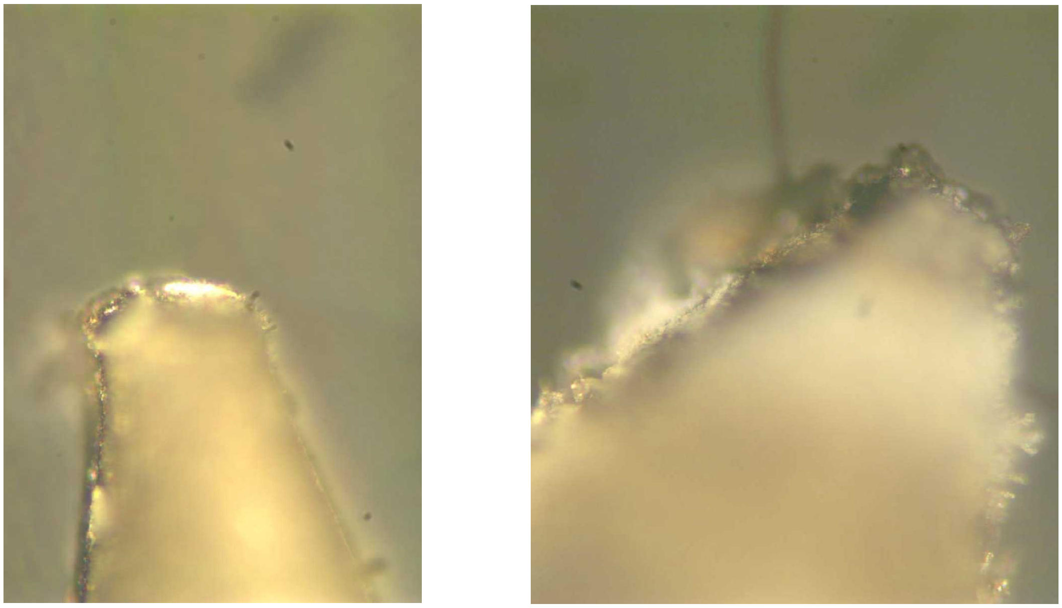
Dirty ESP Electrode
3 December



Clean ESP Electrode
10 December

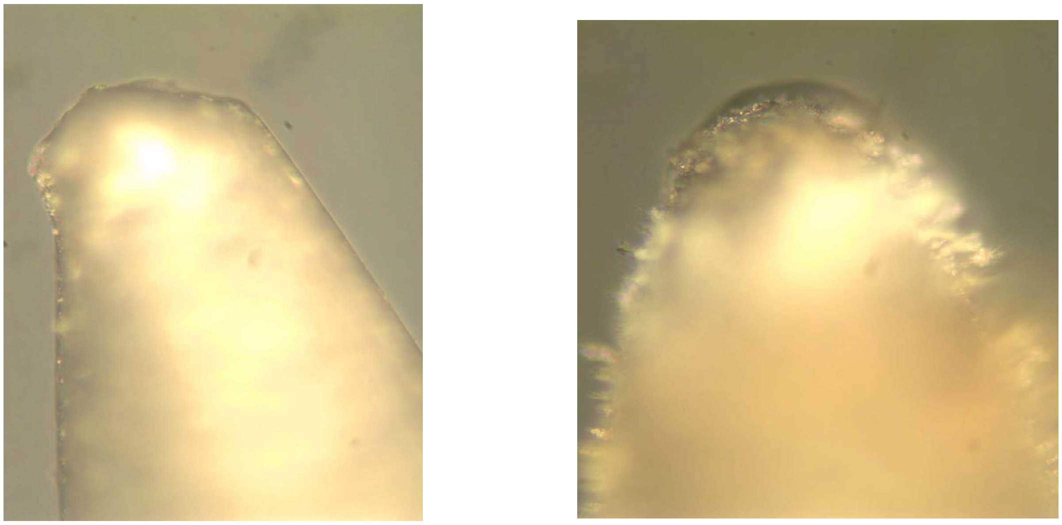
Dirty ESP Electrode
10 December

Figure 16. Photographs showing the cleaned electrode and non-cleaned electrodes after the first two weeks of the cleaning procedure.



Clean ESP Electrode
18 December

Dirty ESP Electrode
18 December



Clean ESP Electrode
31 December

Dirty ESP Electrode
31 December

Figure 17. Photographs comparing the results of the cleaning procedure with the non-cleaned electrode through the end of the test sequence.

in significantly greater ozone production than positive high voltage.[4] Because of the likelihood of ozone generation in the ESP with the high negative voltage, it is also likely that the removal of the contamination from the ESP electrode during the reverse polarity tests was the result of ozone production inside the ESP rather than the forced removal of the material from the electrode. Ozone as the active agent in removing the contamination from the ESP tip could also explain the variable cleaning results with the reversed polarity to the ESP. Since the reversed polarity was voltage controlled and not current controlled, the production of ozone in the ESP could highly variable.

There are two primary methods used to produce ozone for scientific or other applications. The first method is through the use of high voltage, similar to the ESP. The second method is through the use of an ultraviolet (UV) lamp. The UV method to produce ozone is more common for commercial applications.

During the evaluations of the UV ozone cleaning, the test system was operated as described above to allow deposit to form on the corona tip of the ESP. After the deposit was formed on the corona electrode, the ESP was removed from the test system and connected to the UV lamp to evaluate the cleaning process. The UV lamp was installed in a tee fitting just upstream of the inlet of the ESP for the cleaning process. The deposit was allowed to form on the corona electrode for a period of 5 days. After the deposit was formed on the electrode, cleaning of the electrode was attempted using the ozone generated from the UV lamp. During the cleaning process, the UV lamp was energized for 30 minutes. The results obtained using the UV lamp were similar to the successful results during the reverse polarity testing on the electrodes, all of the deposit on the corona electrode was removed by the ozone present in the system during the cleaning tests. These tests were performed over multiple weeks of testing and unlike the reverse polarity tests, the use of the UV lamp to clean the corona electrode were successful for 100% of the tests.

Specific ozone levels required to clean the corona electrode were not determined during these tests. For the commercial system, the actual ozone threshold required for electrode cleaning was not required. As long as the ozone level was sufficient to remove the deposited material from the corona electrode, determining the minimum level was not required. The ozone levels were evaluated during this testing and found to be approximately 15 ppm. This is compared to the background ozone levels measured of less than 20 ppb when the UV lamp was not energized.

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[4] Boelter, K. J., and J. H. Davidson, “Ozone Generation by Indoor, Electrostatic Air Cleaners”, Aerosol Science and Technology, 27:689-708 (1997).

Differential TEOM Thermal Testing

One goal for the project was to develop the Differential TEOM to operate at uncontrolled ambient conditions. By operating at ambient temperature, the system will provide direct PM measurements of the ambient particulate at the conditions as they exist at the time of collection without being be influenced by instrument or method temperature constraints. It is well understood that the TEOM mass sensor is highly sensitive to changes in sensor temperature, such that the changing signal caused by the changing temperature overwhelms the mass concentration signal from the transducer. For example, during startup, the standard model 1400 TEOM monitor heaters are activated to reach the desired setpoint temperature of 50ºC. The change in frequency during this period is such that until the system has been at setpoint temperature for a period of approximately 30 minutes, no usable mass concentration readings are available. In the Differential TEOM monitor, it is important to understand how these changes in ambient conditions affect the frequency response of the system.

Extensive thermal effects studies were performed on different configurations of the Differential TEOM during this project. Initial testing earlier in this project identified the problem of operating the initial proposed low mass TEOM mass sensor system in the Differential TEOM monitor. This testing showed that small changes in sample temperature can significantly skew the reported mass concentration. (This testing also showed that these temperature fluctuations can also affect the reported mass concentration when using a standard 1400 TEOM mass sensor.) The long term (normal diurnal) temperature changes are easily handled using the differential approach, as these changes take place over tens of minutes and hours rather than seconds or a couple of minutes.

The testing in this program showed that ambient or instrument temperature changes occur not just in a typical diurnal pattern, but also on a time scale as short as a few seconds, for example when a cloud passes in between the sun and the instrument, or when there is a wind gust. Figure 18 illustrates ambient temperature variability on a short time scale. While the average temperature changes gradually, the short term excursions occur within 5 minute segments. Since the changes in measured TEOM frequency are strictly related to changes in temperature in this case, any apparent mass change results in measurement noise.

The original project plan was to use a new small light weight TEOM mass sensor, so that the system would be able to respond quickly to changes in temperature. However, due to the effect described above, it became clear that having greater thermal mass was important to minimize the effects of these short term temperature fluctuations. Thus the decision was made to use the standard TEOM mass sensor with the much greater thermal mass and slower reaction to changing temperatures

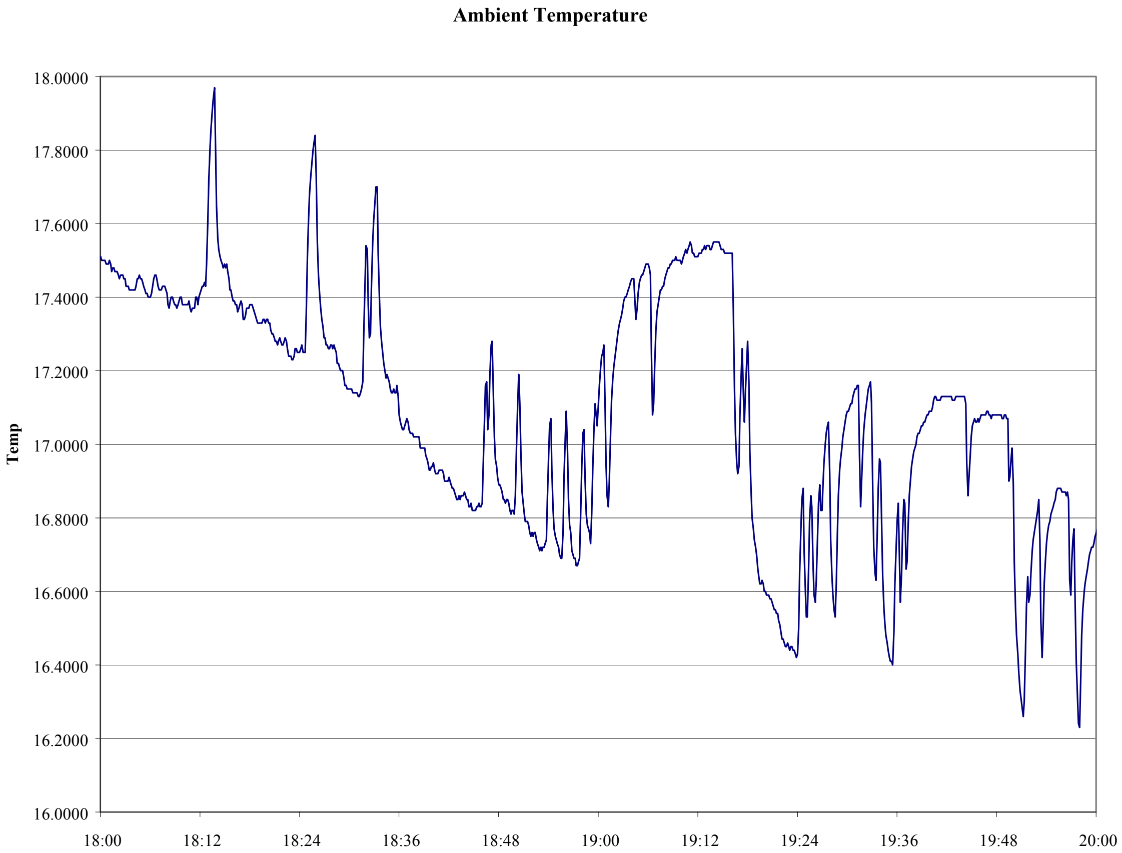


Figure 18. Measurement of ambient temperature fluctuation at the inlet of a Differential TEOM monitor, Albany, NY.

To evaluate different instrument variables to minimize the effect of short term temperature fluctuations, five different monitor hardware configurations were evaluated, along with three different software or heater settings. Three different instruments were used during this phase of the test program. One was a standard Series 1400 AB TEOM monitor and the other two were the prototype ambient Differential TEOM monitors constructed for this project. The two prototype ambient units were located outdoors next to the R&P sampling trailer. The Series 1400 AB TEOM unit was installed in two different locations with different ambient exposures. Because the unit was not designed for ambient exposure, the system had to be evaluated either inside the R&P sampling trailer or in an outdoor enclosure. The 1400 AB monitor was initially located in an isolated corner inside of the R&P sampling trailer. This corner was insulated from the rest of the trailer with the windows open. This allowed the monitor to be near ambient temperature without direct ambient exposure. For subsequent testing the unit was installed inside of an outdoor enclosure.

The purpose of this testing was to identify the configuration that yielded the lowest sample noise due to changes in ambient temperature. In all cases the systems were operated without the ESPs operating and with a prefilter installed to prevent ambient PM from reaching the mass sensor. All data was collected using standard Differential TEOM monitor software, including the ESP cycling routines. By using the system in this way, the operating software would calculate the mass concentrations as if the system was configured and operating as a Differential Monitor, however, since no PM should be reaching the mass sensor, the units should report a zero mass concentration at all times if there was no deviation in measured TEOM frequency influence due to temperature fluctuations. If the temperature fluctuations did affect the measured frequency, these frequency changes would be calculated and would be reported as non-zero mass concentrations and interpreted as measurement noise in this test configuration.

The test matrix included frequency gate time, ESP switching time, case temperature, and cap temperature. The gate time is the averaging time used by the TEOM monitors in calculating each frequency value and thus the mass concentration. TEOM hardware counts the number of sweeps of the tapered element (TE) during each gate period and calculates the average frequency of the TE during that period. Shorter gate times use fewer counts in determining the frequency, resulting in less certainty in the frequency calculation. Longer gate times use greater numbers of counts and results in a more stable frequency reading. If too long of a gate time is used however, frequency change could be real, caused by mass change, which would result in measurement error than reported as a mass change by the TEOM sensor. To minimize the measurement error issue, gate times of 5 and 10 seconds were tested.

ESP switching time is the most significant of these parameters for determining noise of the system. Short switching times use fewer frequency values to calculate the mass concentration, and longer switching times use more values. Like the gate time, fewer values result in greater uncertainty, and with longer switching times, there can be real mass changes that would show up as noise in the mass calculations. Switching times of 1, 2, 5, and 10 minutes were tested.

The standard TEOM monitors control the case temperature, cap temperature and air or sample temperature. The case and cap are parts of the actual mass sensor in the instrument, while the air temperature is equivalent to the temperature of the sample as it is collected on the sample filter. By controlling the case or cap temperatures it may be possible to minimize the effect of temperature fluctuations on the reported mass concentrations.

The three systems were initially configured using the same settings to obtain baseline readings. Thus, any changes in the future could be referenced to these initial baseline values to identify optimum settings. The initial settings for all three instruments were, all heat zones off, gate time at 5 seconds, and switching time at 5 minutes. A representative plot is shown in Figure 19. The one hour average mass concentrations for all three systems are shown. Any excessive deviation in the mass concentration readings from a zero baseline is due to the thermal noise of the system. Comparing the averages and standard deviations of the data, it is clear that the 1400 monitor is significantly more stable than the other two instruments. The 24 hour averages of the three systems were zero, but the standard deviation of the Series 1400AB TEOM monitor was 2.6 and for the two ambient monitors instruments the standard deviations were approximately 14. There are a number of possible explanations for these differences. The instruments were constructed using the same mass sensor and electronics, but the assembly and instrument locations were different. The Series 1400 AB monitor was protected from direct ambient exposure, while the other instruments were located outside next to the sampling trailer. The other possibility, is that the Series 1400 AB contains more thermal mass to potentially dampen the effects of the temperature changes on the mass concentration. The standard Series 1400 AB air or sample tube was approximately 24 inches long and consisted of an insulated center stainless steel sample tube (½ inch in diameter) surrounded by a rigid support tube and insulated on the outside. This air tube was then mounted directly to the top of the mass sensor. For the ambient units the air tube consisted only of the ½ inch diameter stainless steel tube without the insulation and not close mounted to the mass sensor.

After comparing the baseline levels of the three instruments, the units were operated at the different settings of the test matrix. Comparing the results from the different test settings, the settings used during the baseline testing appeared to yield the lowest noise levels on the mass concentrations. The detailed results for each setting follow. In addition to the 5 second gate time, and 5 minute switching time, it was clear that the increased thermal mass of the 1400 monitor does reduce the noise produced by fluctuations in the ambient temperature.

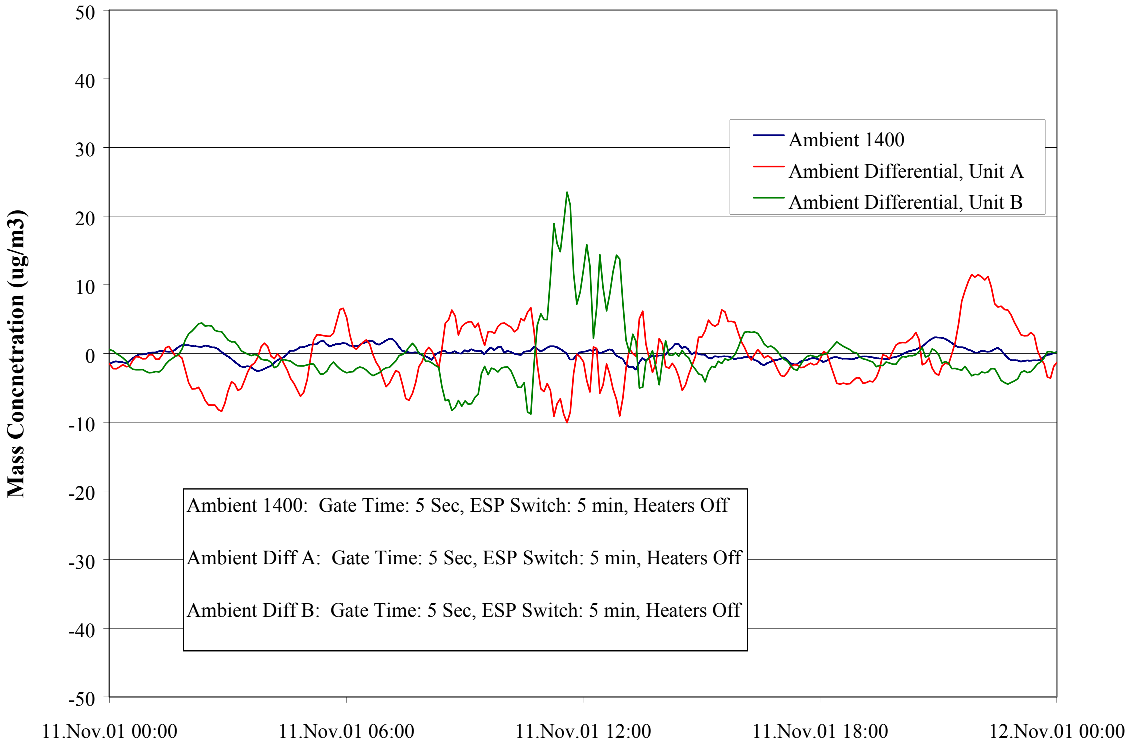


Figure 19. Baseline comparison between three ambient test units. One unit a standard Series 1400AB TEOM monitor and two ambient Differential TEOM monitor test units. All heat zones off and all units prefiltered.

TEOM Mass Sensor Gate Time.

There was no appreciable difference in noise levels introduced by using the two different gate time settings. 5 seconds was ultimately chosen as it provides double the data points for the mass concentration calculations versus the 10 second gate time.

ESP Switching Time.

Figure 20 illustrates the results for the three systems using the three different switching times. The three systems were operated simultaneously, each with a different switching time. Based on these observations, a 1-minute switching times were unacceptable as the noise levels inherent with that switching time are significantly greater than for the other two settings. The two minute switching time is somewhat noisier than the 5 minute switching time, but as shown in Figure 20, the difference in noise levels were similar to the variation in noise between the Series 1400 AB monitor operated in the trailer and the ambient Differential Monitor operating under identical settings.

TEOM Mass Sensor Temperature Control.

The standard TEOM monitor was designed with three regions to precisely control the temperature of the TE and sample gas in the TEOM (the case, cap and air temperatures, using the nomenclature from the TEOM manual). While the goal of designing the Differential TEOM monitor to float at ambient temperature requires the sample temperature to remain uncontrolled, it may be possible to control the operating temperature of other regions on the instrument and still maintain the requisite floating temperature parameters. The active element in the TEOM is the TE, and is housed in the case section of the mass sensor. The TE extends through the case to the point where the sample filter is located, approximately ½ inch above the case. During operation, the mass sensor cap is fitted over the sample filter and allow for the direct attachment of the sample or air tube. Under normal operation of the TEOM monitor these three regions are operated at a controlled 30ºC or 50ºC. This maintains the sample filter at the desired operating temperature. If the sample air tube temperature control was turned off, the sample filter temperature would be much less than the control temperature of the surrounding mass sensor, and did approach ambient conditions. The intent of testing under these conditions was to determine if by controlling either the case or cap temperatures only, would the frequency response be more thermally stable than if they were allowed to float at ambient temperature. Both the case temperature and cap temperature were controlled at 30ºC and 50ºC. The results showed that this temperature control acted as delta T control for the system and had no statistical effect of the thermal noise of the systems. Figure 21 is representative of the results at the different settings and temperature control points. The 24 hour average values for the three units are all approximately zero, with the standard deviations similar to the results obtained during the baseline tests shown in Figure 19.

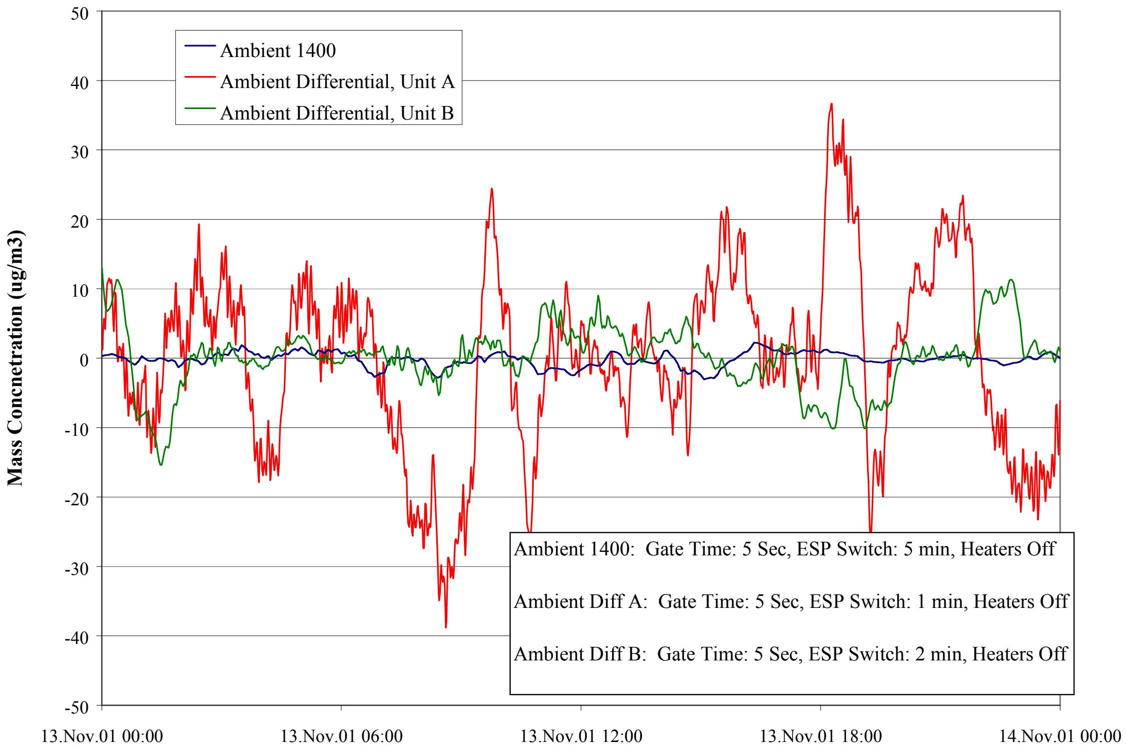


Figure 20. Comparison of signal noise levels from three TEOM monitors operating with different ESP switching times. All heaters off and units prefiltered.

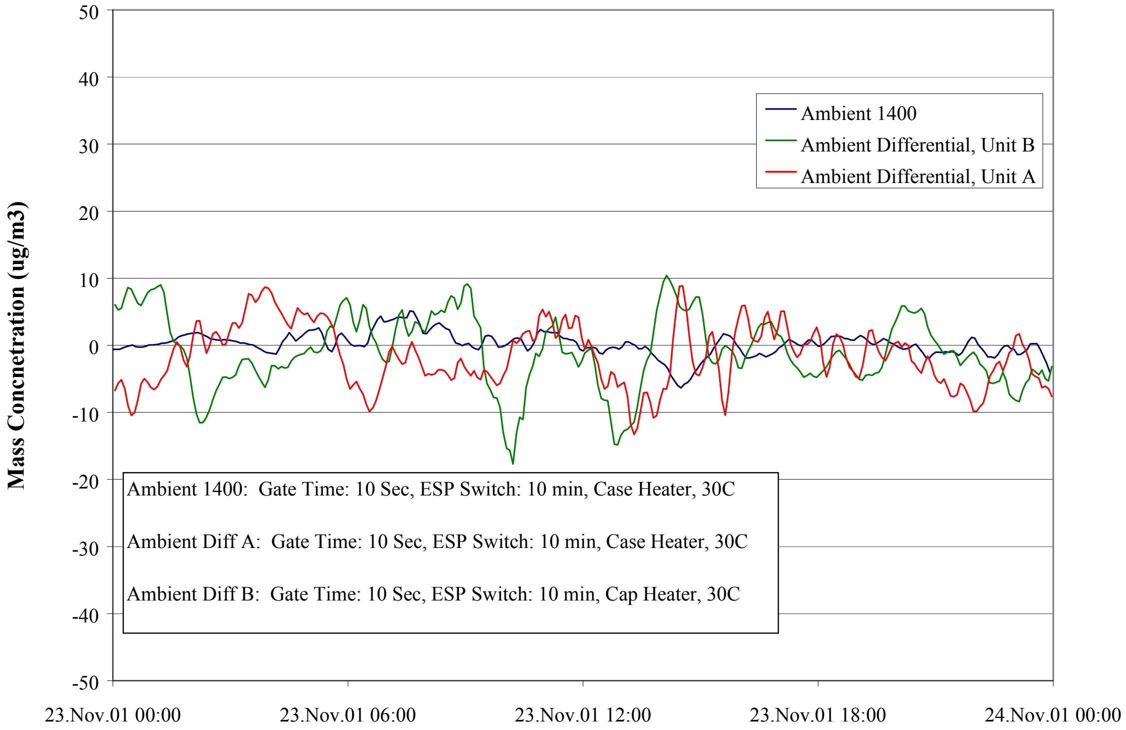


Figure 21. Representative graph showing results obtained with TEOM monitor heater control active on all three units. Case temperature control on all three units set to 30ºC. All units prefiltered.

The final segment of testing was designed to resolve the issue of the location of the Series 1400 AB monitor during the testing and how that may have affected the response of the system to fluctuating temperatures. Since the Series 1400 AB was operated inside of the trailer, albeit at or near ambient temperature, the temperature exposure was likely moderated by the thermal mass of the sampling trailer. The system was next installed in an outside enclosure for final comparisons. The enclose was equipped with an air conditioning fan to blow outside air into and circulate air within the enclosure. The system was operated with the fan on and off. The outdoor enclosure acted as a shelter and no TEOM or enclosure temperature control was operating during this testing.

This testing showed that the trailer did have a moderating effect on the thermal noise of the mass sensor. Figure 22 illustrates the results the three systems operating with 10 minute switching times and the Series 1400 AB in the outdoor enclosure with the enclosure fan turned on. By having the fan on, the 1400 was exposed to changing ambient conditions similarly to the two ambient Differential units. The 24 hour average and standard deviations are not significantly different from those obtained with the system inside the trailer, however, it is clear from the figure that the signal has more noise when compared to the other cases.

The overall results of the thermal analysis of the different systems illustrate that the greater thermal mass and thermal protection provided by the standard Series 1400AB TEOM monitor hardware. Since the actual mass sensors and electronics were identical for the three systems tested, any deviation in the noise levels was caused by other factors including the sample air tube and any insulation around the hardware. The ambient Differential monitors intentionally had little thermal insulation around the sample air tube and entire sensor unit. The main conclusion from these results was that the final system must have sufficient thermal mass and insulation to moderate the temperature deviations and yet still allow the system to float with the normal diurnal temperature patterns.

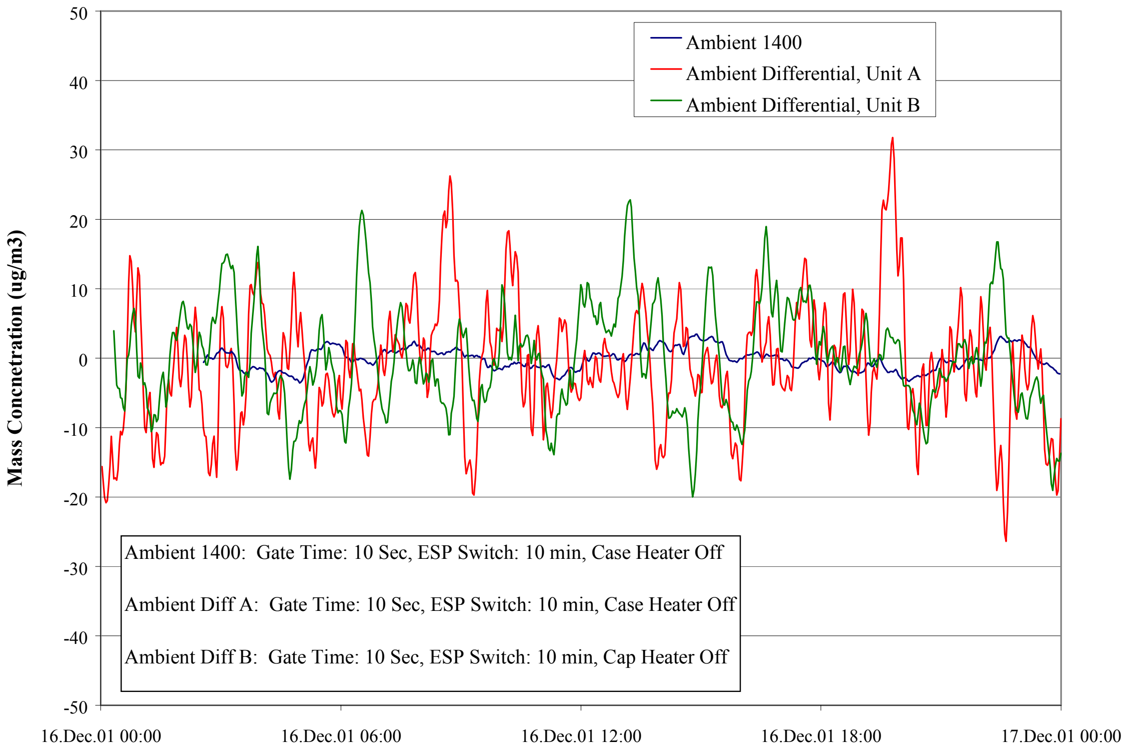


Figure 22. Comparison of two ambient Differential TEOM monitors test units and a Series 1400AB TEOM monitor. The Series 1400AB TEOM monitor installed inside of outdoor enclosure with enclosure fan turned on.

DIFFERENTIAL TEOM MONITOR LABORATORY PERFORMANCE TESTING

Laboratory performance testing of the ESP and Differential TEOM monitor as a system was performed by the Atmospheric Sciences Research Center (ASRC) at the University at Albany. The work involved generating various challenge aerosols and sampling the aerosols with different instruments to determine the behavior and effectiveness of instruments under test to the different challenging components. The work involved a number of different challenge aerosols including sodium chloride, ammonium nitrate, ammonium sulfate and different organic aerosols, including glutaric acid and oxalic acid. The sodium chloride and ammonium sulfate are both non-volatile and stable aerosols under normal laboratory and ambient conditions. The ammonium nitrate and organic aerosols are semi-volatile over the normal sampling range. The tests compared the results of the Differential TEOM and the SES TEOM, both systems operating at an instrument temperature of 30°C. The complete ASRC report is included in Appendix C.

The Differential TEOM monitor used for the laboratory evaluations was constructed of a standard Series 1400AB TEOM monitor with a SES dryer and ESP attached to the inlet of the sampling air tube of the TEOM monitor. The sample was extracted from the aerosol chamber in the laboratory, dried in the SES dryer and passed through the ESP before being collected by the sample filter in the TEOM mass sensor.

As expected, the Differential TEOM and the SES TEOM monitors agreed closely when sampling the sodium chloride aerosol as shown in Figure 23. As the aerosol is non-volatile, no sample loss from the TEOM monitors was expected. During the initial segment of the testing the ESP was not energized as indicated in the figure. Since the software does not recognize that the ESP is not energized during the initial test segment, the standard subtraction yields zero values for the reported mass concentration.

In sampling the ammonium nitrate aerosol, there was significant differences in the behavior of the two instruments as expected. Ammonium nitrate is a volatile aerosol and the amount of material collected is dependent on the temperature of the aerosol and of the sampling system. Figure 24 shows the reported mass concentrations from the two instruments as reported in final mass concentration values. The SES TEOM monitor reports lower values than the Differential TEOM monitor. However, comparing the SES reported mass concentration with the mass concentrations reported during the different periods when the ESP was on and off on the Differential TEOM monitor, it is clear what mechanism caused the differences in reported overall mass concentration. Figure 25 plots the reported mass concentration from the SES TEOM monitor and the mass concentration during the periods when the ESP is on and when the ESP is off on the Differential TEOM monitor as separate curves on the figure. (Remember that the final mass concentration levels reported by the Differential TEOM monitor is the mass concentration reported during the periods when the ESP is off, minus the mass concentration reported when the ESP is energized.) The mass

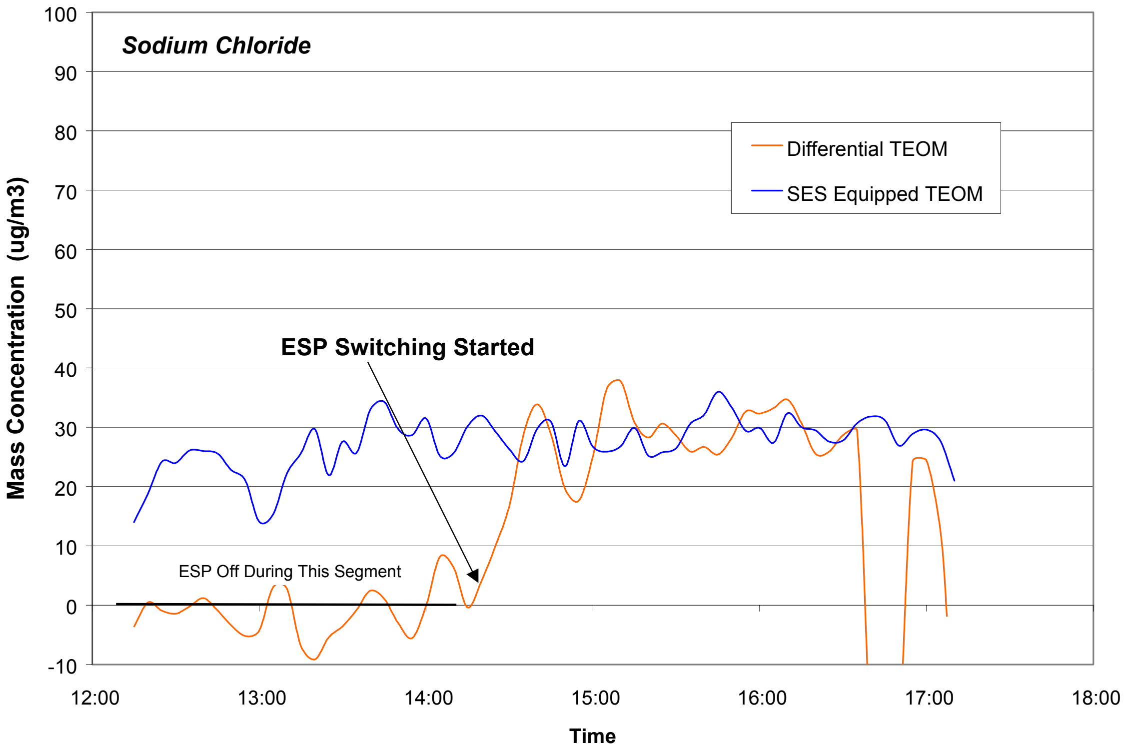


Figure 23. Comparison between SES equipped TEOM monitor and Differential TEOM monitor sampling sodium chloride from aerosol chamber. Both units operating at 30°C. Five minute ESP switching times.

concentration reported by the SES TEOM monitor and the mass concentration reported by the Differential

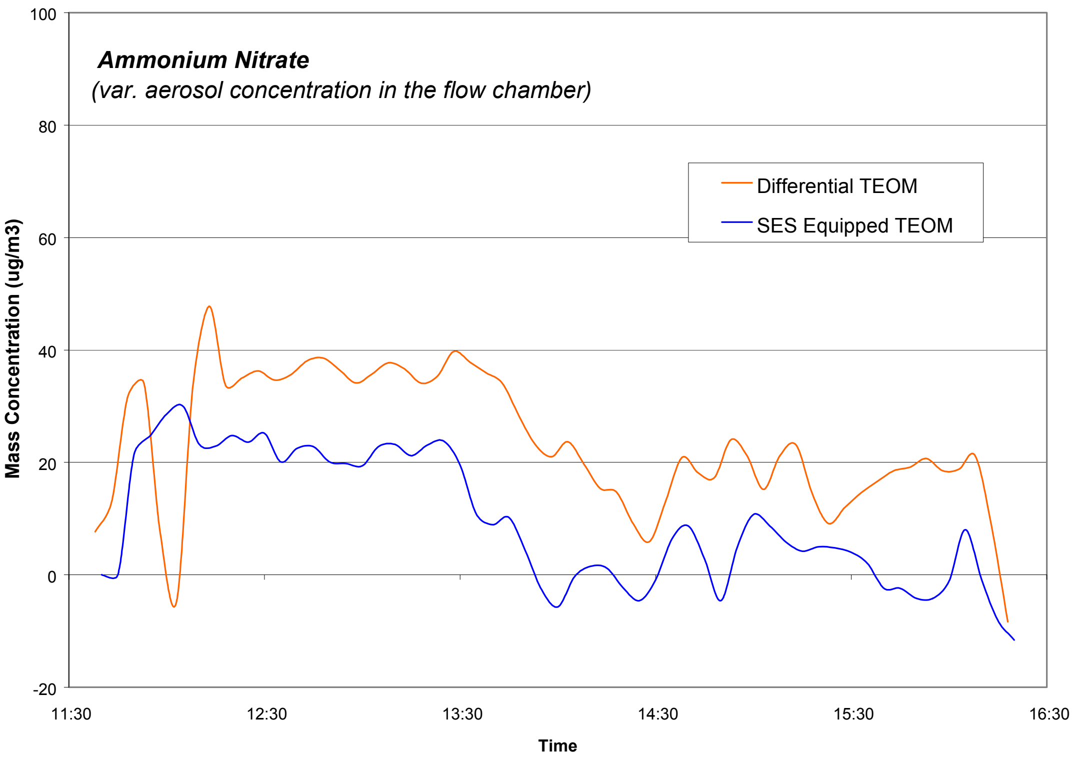


Figure 24. Comparison of mass concentrations sampled using a SES equipped TEOM monitor and a Differential TEOM monitor when sampling ammonium nitrate aerosol from an aerosol chamber. Both monitors operating at 30ºC. Five minute ESP switching times.

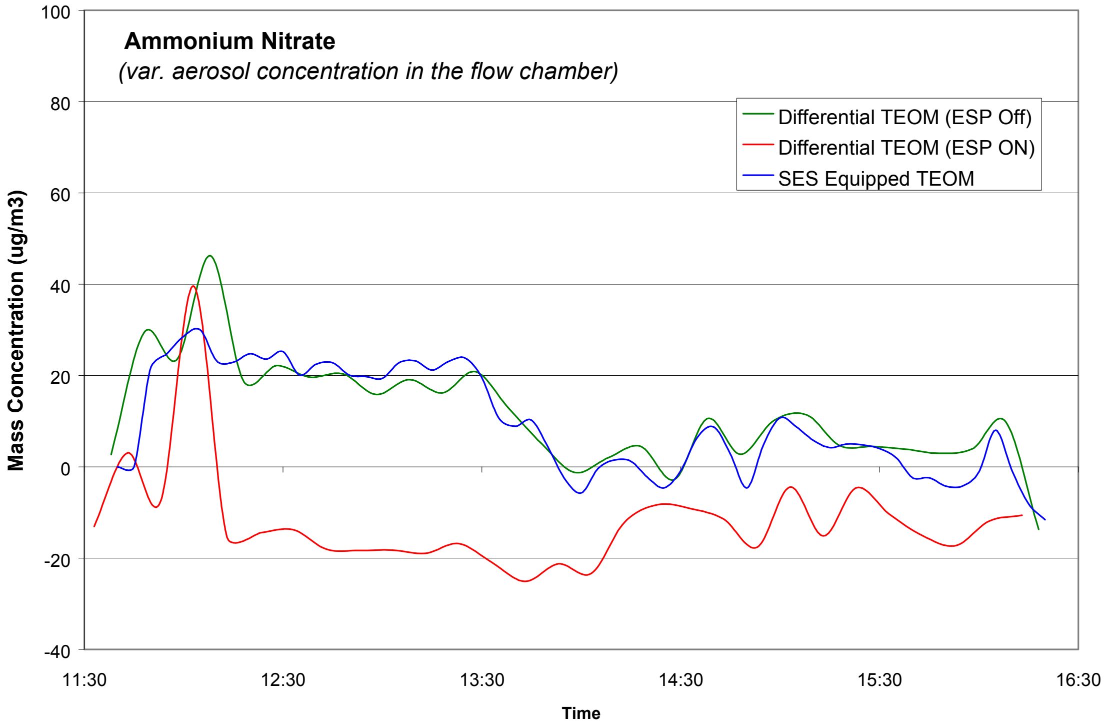


Figure 25. Reported mass concentrations from a Differential TEOM monitor during ESP energized and de-energized collection periods compared to SES equipped TEOM monitor results. Both monitors operated at 30°C. Five minute ESP switching time.

TEOM monitor during the periods when the ESP was off closely agree over the duration of the test. This was expected as the two systems functioned nearly identically during these periods. The mass concentration shown in the figure during the periods when the ESP was energized was reported as a sample loss from the Differential TEOM monitor. Clearly the two instruments are collecting the same amount of ammonium nitrate, and a fraction of that material is evaporating from the sample filter. In the Differential TEOM monitor, this sample loss is identified when the ESP was energized and thus corrected for in the final reported mass concentration (Figure 24). This sample loss was not identified by the SES TEOM monitor, which thus under reports the value of mass concentration.

The final test during this period involved challenging the two instruments with a combination of ammonium sulfate and glutaric acid. Glutaric acid, a semi-volatile organic aerosol, was used as a component in the challenge aerosol because it is a common constituent of ambient aerosols. Since ammonium sulfate is non-volatile under the conditions in the laboratory and at the TEOM monitor operating temperatures, any variation in the results from the two instruments is due to the glutaric acid. Figure 26 compares the final reported results from the two instruments showing the SES TEOM monitor reporting values higher than the Differential TEOM monitor. This would happen only under the condition where there is an increase in mass caused by volatile material that is not an aerosol under the operating conditions of the TEOM monitors. And as seen in figure 27, the mass concentration reported by the Differential TEOM when the ESP is on, clearly indicates that there is an addition of mass on the sample filter caused by the adsorption of a volatile component (glutaric acid). This mass is accounted for by the Differential TEOM monitor and not by the SES TEOM monitor.

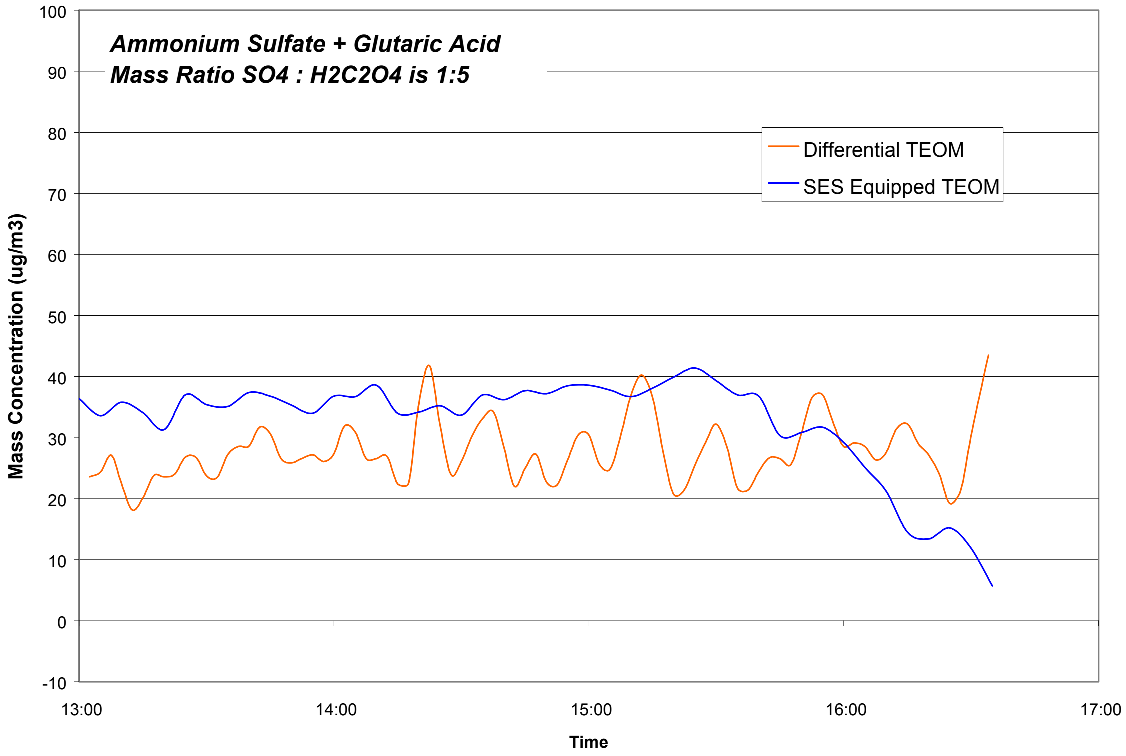


Figure 26. Ammonium sulfate and glutaric acid aerosol mass concentrations reported by a SES equipped TEOM monitor and a Differential TEOM monitor when sampling from an aerosol chamber. Both units operated at 30ºC. Five minute ESP switching periods.

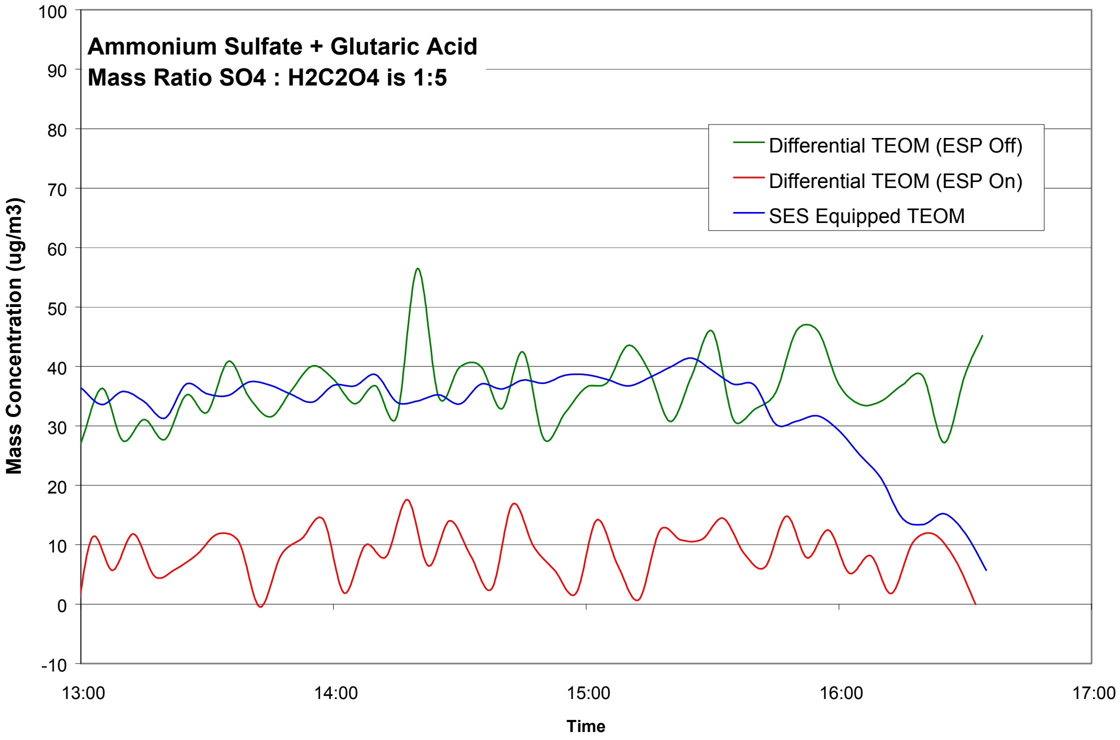


Figure 27. Reported Differential TEOM monitor mass concentrations during segments when ESP is energized and de-energized compared to the mass concentrations reported by a SES equipped TEOM monitor when sampling ammonium sulfate and glutaric acid aerosol from an aerosol chamber. Both units operated at 30ºC. Five minute ESP switching periods.

PROTOTYPE DIFFERENTIAL TEOM MONITOR

Because of the problems resolving the response of the Differential units to short term changes in ambient temperature conditions, Series 1400AB TEOM monitors were modified and used as part of the prototype instruments used during the initial field demonstrations. Instead of the self contained units designed to operate exposed to ambient conditions, these systems were configured similar to standard Series 1400 TEOM monitors including the temperature control. Each unit was configured with standard PM-10 and PM-2.5 inlets and SES Nafion dryers. Downstream of the dryers, the ESP was mounted onto the inlet tube of the TEOM monitor. Figure 28 illustrates the configuration used for the field testing. This figure shows the relationship of the ESP mounted on top of the TEOM monitor and does not illustrate the SES dryer in the figure. In the field test units, the dryer was mounted upstream of the ESP inlet. This configuration for the field work was chosen in order to eliminate the effect of temperature changes on the collected results, allowing the researchers to investigate the performance of the ESP and differential approach to sampling and provide good comparisons between the Differential TEOM monitors and other standard equipment.

As part of the field test configuration, computer software was developed to monitor and control the performance of the ESP during testing. This software, written in the LabView programming language, allowed two Differential TEOM monitors to be controlled from a single computer. While all of the work performed alternated the switching of the two ESPs, the software permitted the two units to be controlled independently.

The systems were operating similar to standard TEOM monitors with attached ESPs and dryers, with the ESP turning on and off the particle flow through the system. All control of the ESP switching and logging of necessary data was performed using the computer hardware and software previously developed for the system. These units were configured for installation either inside of a sampling trailer or in a temperature controlled outdoor enclosure. The temperature control setpoint was either 30ºC or 35ºC, depending on the conditions present at the sampling location.

FIELD TESTING OF PROTOTYPE DIFFERENTIAL TEOM MONITOR

Field testing was performed at three different locations during this project to date. As the field evaluations will take many months, only the initial field work performed during 2001 is discussed here. The three sampling locations, in addition to the testing performed at the R&P facilities in Albany, NY, were in Queens, NY, Rubidoux, CA, and Claremont, CA. The work in the three locations was performed and coordinated by different researchers.

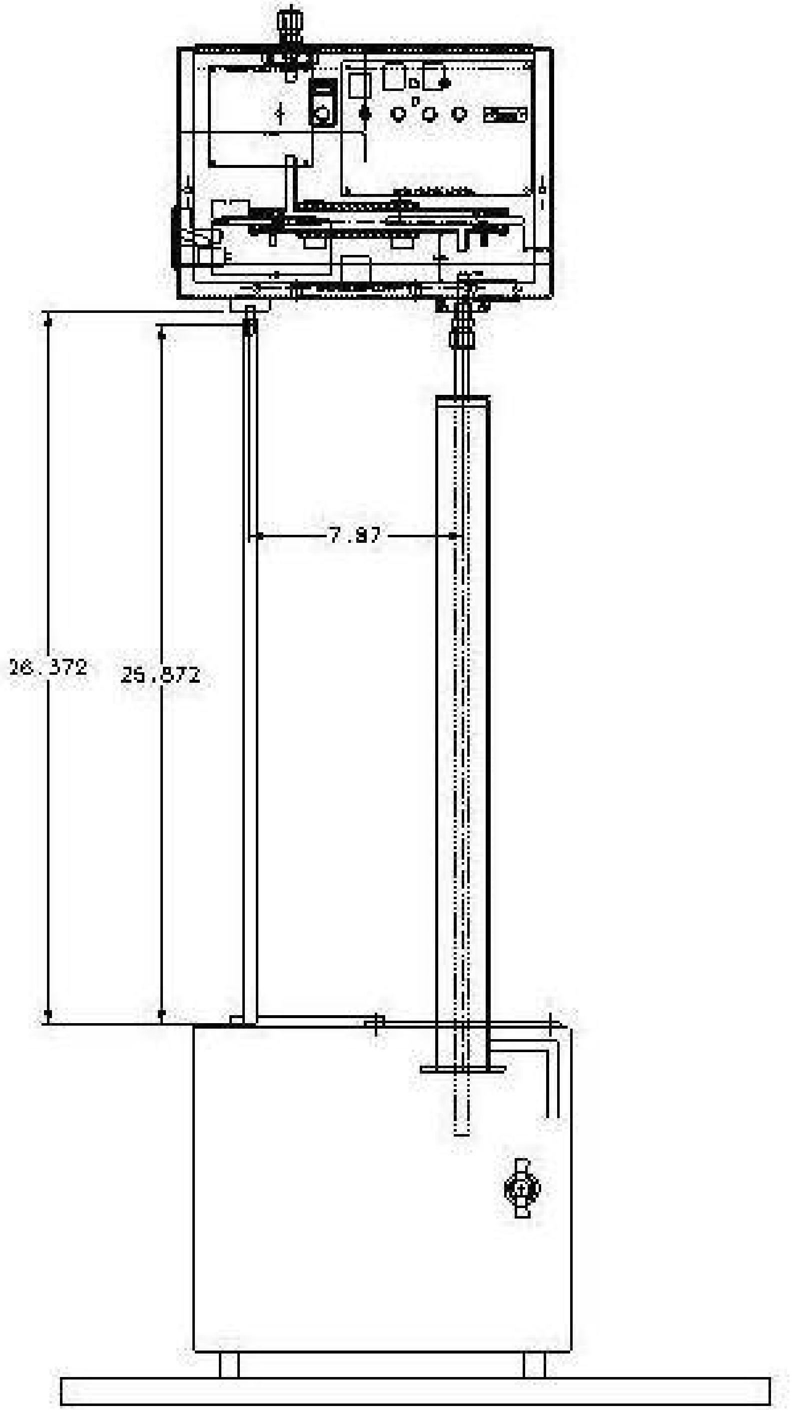


Figure 28. Schematic of Differential TEOM monitor used during the initial field studies. ESP sits on top of standard Series 1400AB TEOM monitor sensor unit. SES (not pictured) dryer would be up stream of the inlet of the ESP.

Queens, NY Field Test

The Atmospheric Sciences Research Center was responsible to coordinate, setup, and operate, an EPA Supersite intensive study during the month of July, 2001. At this study, two Differential TEOM monitors and a SES TEOM monitor were installed and operated at the site during the intensive study. The two Differential TEOM monitors were installed in two outdoor enclosures with the sample inlets approximately 1.5 meters apart. The SES TEOM monitor was installed inside of one of the sampling trailers on the site. All three monitors were configured to operate a controlled temperature of 30ºC during the entire month long intensive study. FRM data was also being collected for comparison to the continuous monitor results.

The first comparison of the data was to examine the precision between the two Differential TEOM monitors. If the two instruments did not agree, then either there was a problem with one of the instruments, or a problem with the measurement technique. Figure 29 shows that the two Differential TEOM monitors agree quite well over the entire month of the study. Based on these results, it is clear that the Differential technique does provide good repeatability over long term sampling.

In addition to comparing the two Differential TEOM monitors with each other, it was important to examine how these instruments compared with other commercial and regulatory samplers. The results presented in Figure 30 illustrate the correlation between the two Differential TEOM monitors, the SES TEOM monitor and the FRM samples. This correlation shows that the FRM samples under report the ambient particulate mass compared to the two Differential TEOM monitors by approximately 10%. Similar results are obtained when comparing the SES TEOM monitor results to the Differential TEOM samples over the study, with the Differential TEOM monitors measuring about 10% more ambient PM mass.

Comparing the SES TEOM monitor results with the FRM samples, these two sets of samples yield nearly identical results, also with good correlation. The fact that the SES TEOM monitor and the FRM monitor report consistently lower values for the ambient PM mass, suggests that there was some semi-volatile material being sampled during the test period. As the SES TEOM monitor and the two Differential TEOM monitors were all operating at nominally the same operating conditions, they would measure identical PM levels unless there were volatile materials present during the test period. And as the SES and FRM samples were nearly identical, this also implies that the FRM samples under reported the actual PM levels as well.

In addition to correlation between the different instruments, examining the results on a daily basis is also useful. Examining the results in this way can provide information on instrument bias or identify instrument problems. Figure 31 is a plot of the daily results from the two Differential TEOM monitors, the SES TEOM monitor and the FRM samples. The data early in the test program highlights problems that may be identified. The scatter in the data early in the program is due to the variations in the installation times of the

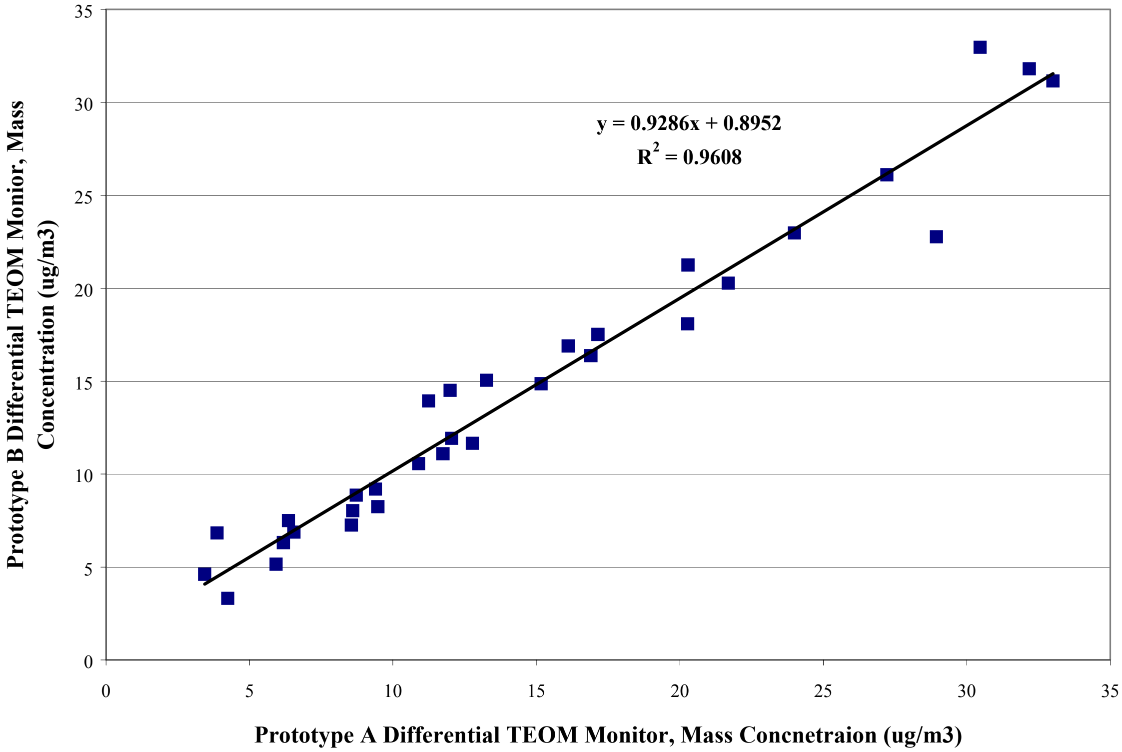


Figure 29. Correlation between two co-located prototype Differential TEOM monitors during Queens, NY, summer intensive study. July 2001.

different instruments and this data was not used for the regression analysis. For the purposes of this study,

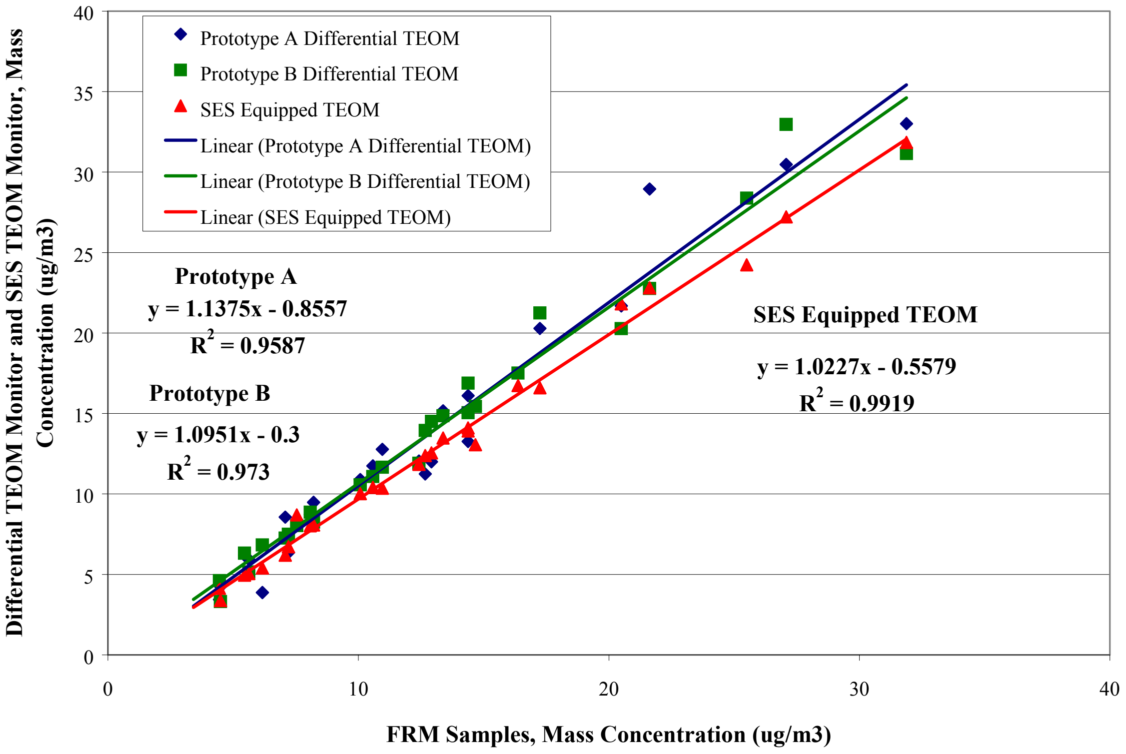


Figure 30. Comparison between 24-hour average mass concentrations obtained using two prototype Differential TEOM monitors and a SES equipped TEOM monitor versus collected FRM samples. Queens, NY. July 2001.

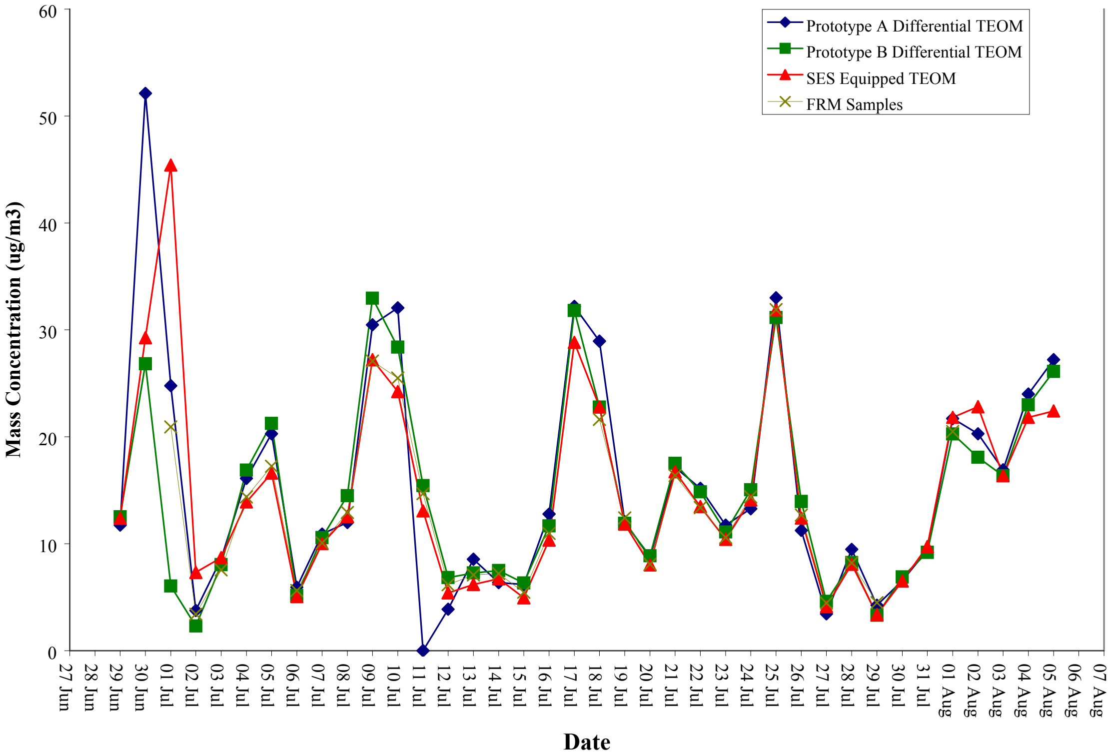


Figure 31. Comparison of daily 24-hour average values. Differential TEOM monitor, SES equipped TEOM monitor, and FRM samples. Queens, NY. July 2001.

all comparisons were performed starting with the results obtained on 3 July. The one major discrepancy occurred with the prototype A Differential TEOM on 11 July. The ESP corona tips were cleaned that day and the control cable for that ESP was accidentally dislodged for approximately 24 hours.

While providing good 24 hour data is important with the Differential TEOM, it is more important to analyze the short term or hourly data from the instrument. An hourly comparison between the two Differential TEOM monitors and the SES TEOM monitor is presented in Figure 32 for 25 July 2001. As the three instruments track quite well over the entire 24 hour period, it is clear that the Differential TEOM monitors are capable of providing the precision required of a continuous ambient PM monitor. The data presented in this figure also illustrates two additional points. Since the three instruments track closely over the sample period presented here, it is obvious that the amount of volatile material in the atmosphere during this sample period is quite low. If there were significant amounts of volatile material present, the SES TEOM monitor would measure different PM levels than the two Differential TEOM monitors. The main feature of the data from this day is the sharp drop in PM levels just before 6 PM in the evening. This drop was the result of localized thunderstorms that removed the PM from the atmosphere in the area around the sampling location. After the storms moved out of the area, the ambient PM levels returned to their original levels. It is important to note, that while the ambient PM levels changed rapidly on a relatively short time frame, perhaps 15-30 minutes, the Differential TEOM monitors, operating with a switching time of 5 minutes, were clearly able to track these rapid changes in PM levels.

Rubidoux, CA, Field Test

While the field work in Queens, NY, provide much useful information on the operation and behavior of the Differential TEOM, because of the observed levels of volatile materials present during the test period, the results did not provide much insight into the operation under challenging environmental conditions. As part of this program two Differential TEOM monitors were installed in the sampling trailer at a cooperative sampling location in Rubidoux, CA, and operated by Clarkson University over the period from 18 August through 8 September 2001. The sampling trailer is part of a mobile EPA Supersite being operated by the University of Southern California (USC). During this period, Clarkson University was scheduled to operate a number of different instruments at the site for comparisons between different sampling methods and to collect samples for chemical speciation and other purposes. For the purposes of this study, we are comparing the Differential TEOM, the SES TEOM, and FRM data. During the study, there were two Differential TEOM monitors operating and one SES equipped TEOM monitor. Because of the ambient temperature conditions during the study and the high ambient temperatures and the conditions inside of the sampling trailer, all three TEOM monitors were operated at a controlled temperature of 35°C instead of 30°C as during the Queens Supersite work.

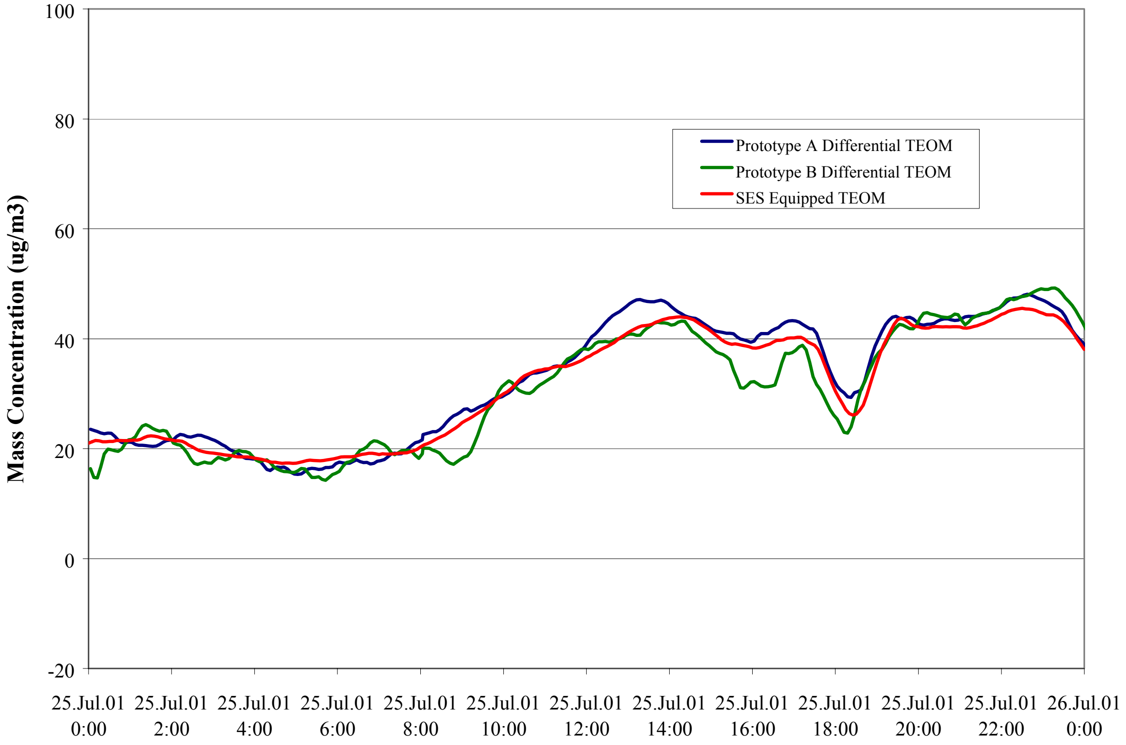


Figure 32. 24-hour average comparison of samples collected with two prototype Differential TEOM monitors and a single SES equipped TEOM monitor at the EPA Supersite in Queens, NY. 25 July 2001.

Figures 33 and 34 are representative of the hourly average data collected using the two prototype Differential TEOM monitors and the one SES equipped TEOM monitor collected on two different days. Figure 33 illustrates that there is very little correlation between SES TEOM monitor results and the Differential TEOM samplers during the entire 24 hour period, however the two Differential units show good agreement. The results from prototype B Differential TEOM monitor results are compared to the SES monitor results in Figure 34 In this case, there is very good agreement between the Differential TEOM monitor and SES TEOM monitor during the initial part of the day, until about 10:00. At that time there is a significant and sharp increase in the reported mass concentration from the SES TEOM monitor followed by a sharp decease in concentration one hour later. There was little apparent change in the mass concentration reported by the Differential TEOM monitor during this short period. After about 12:00, the two monitors again trend closely with a difference in magnitude, until about 21:00 when they once again report similar values. This data is quite representative of the samples collected during the duration of the study and suggests that there are extreme compositional changes to the concentration of volatile material in the atmosphere over a typical daily cycle.

The collection and calculation methods of the Differential TEOM monitor provide two different mass concentration measurements every 10 minutes. These are readings for when the ESP is off and another when the ESP is energized. When the ESP is off, the reported mass concentrations should be similar to those reported by the SES TEOM monitor as the sampling configurations of the two instruments are essentially identical. It is when the ESP is energized that there should be significant differences between the mass concentration readings of the two instruments. Figure 35 presents the raw data for prototype unit A with the ESP on and off along with the 1 hour average data collected from the SES TEOM monitor. This is the same 24-hour period presented in Figure 33 comparing only the hourly data from the SES TEOM monitor and the two prototype Differential TEOM monitors. (Note that the data from the Differential TEOM monitors in these two figures are raw 5 minute data where as the data from the SES monitor is 1 hour average data. This difference in reporting of the results can lead to a shift in the events between the two data sets by one hour or so.) Comparing the data from prototype A when the ESP is off with the SES TEOM monitor data shows that these two data sets agree reasonably well over the 24 hours reported. Examining the data from when the ESP is on suggests the cause of the results obtained with the SES TEOM monitor. At approximately 10:00 am, there is a sharp drop in the mass concentration reported by the SES monitor. There is a similar drop in the mass concentration for the Differential monitor results only when the ESP was energized, suggesting that a weather or air change occurred that caused a reduction in the volatile content of the sampled aerosol. A similar event seems to occur at 5:00 pm as well. One of the dominant pollutants present at the Rubidoux, CA, sampling location was ammonium nitrate, a compound that is certainly a semi-volatile at the collection temperature of 35ºC. Most of the ammonium nitrate will be collected on the TEOM monitor sample filters at 35ºC, and will then evaporate at a rate depending on the

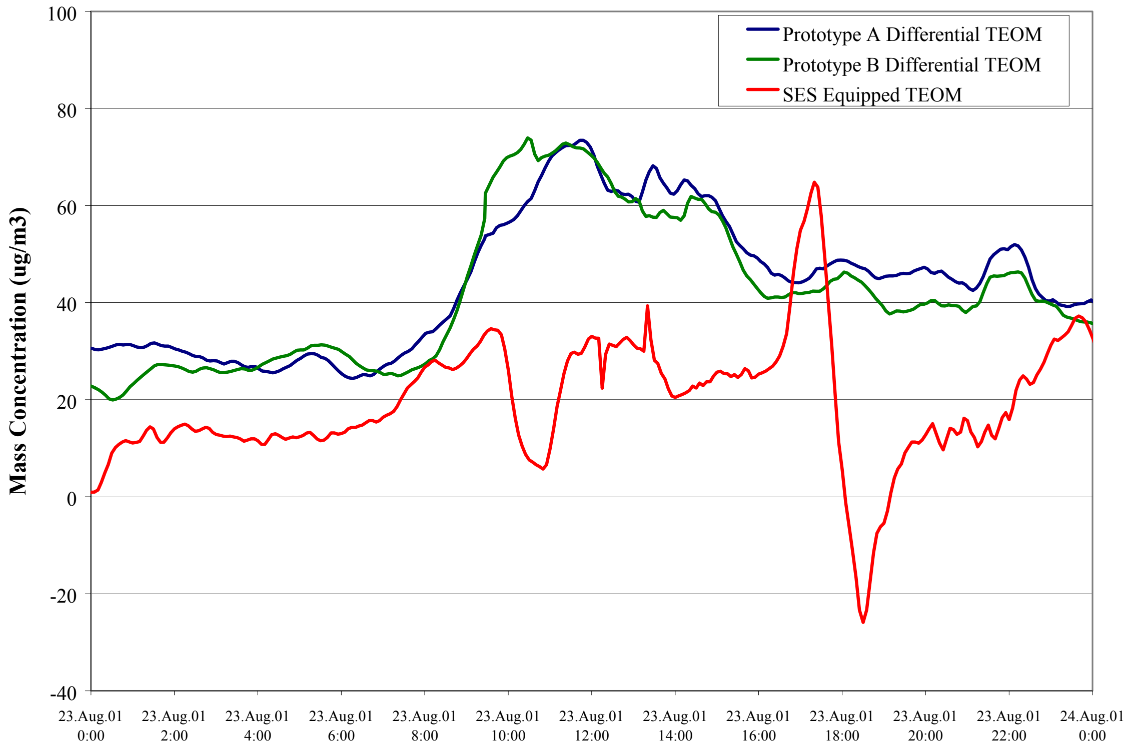


Figure 33. Hourly average mass concentration data collected using two prototype Differential TEOM monitors and a SES equipped TEOM monitor. Note good agreement between the two Differential TEOM monitors. Rubidoux, CA. 23 August 2001.

amount of material collected. It is also important to note that the sample filter in the Differential TEOM

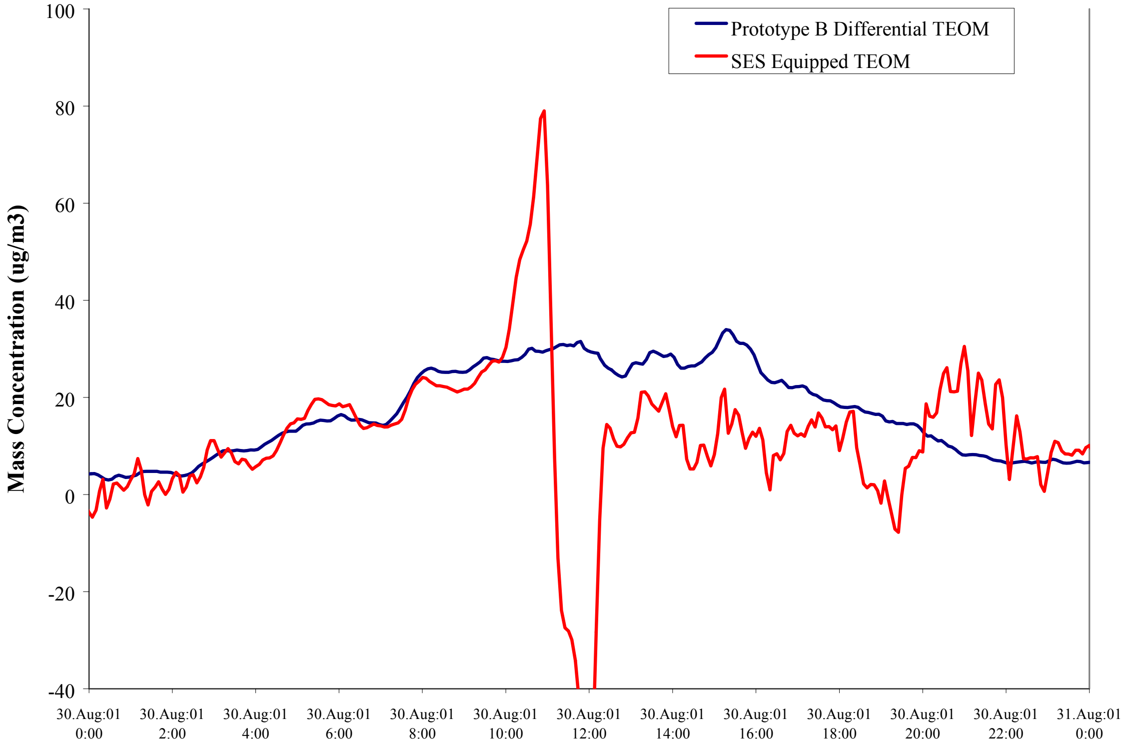


Figure 34. Hourly average comparison between a prototype Differential TEOM monitor and a SES equipped TEOM monitor. Rubidoux, CA. 30 August 2001.

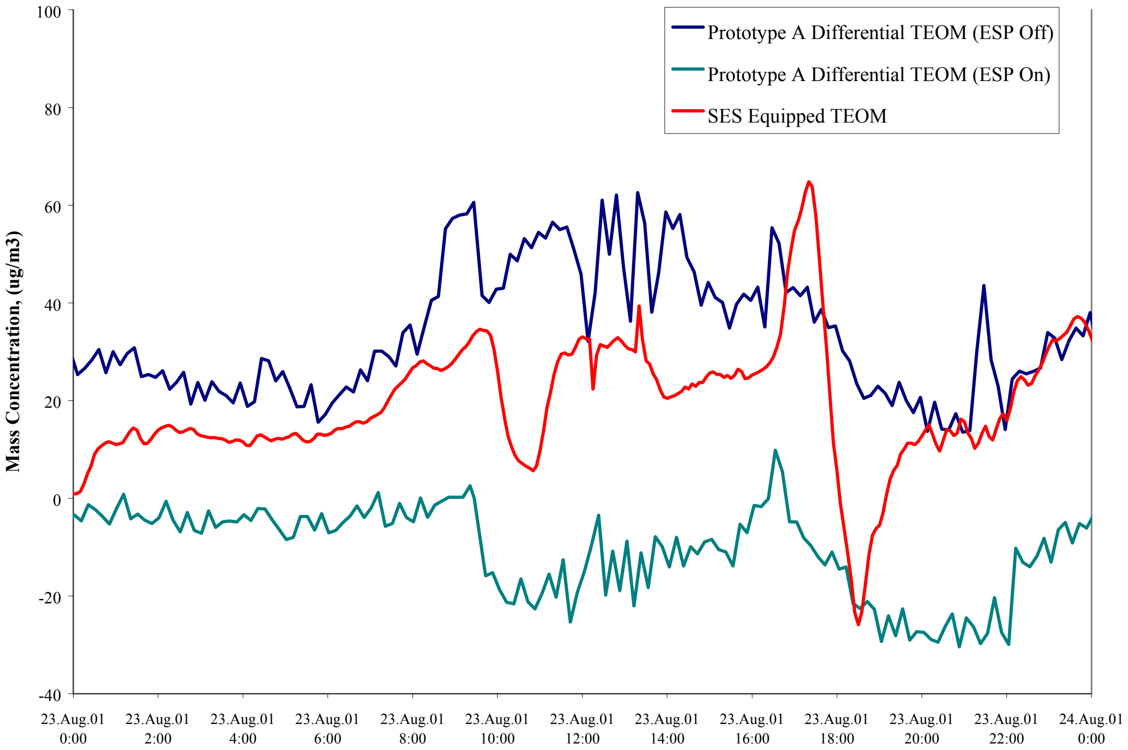


Figure 35. Comparison between SES equipped TEOM monitor and prototype Differential TEOM mass concentration data. Data for Differential TEOM monitor presented for periods when ESP was on and off. Rubidoux, CA. 23 August 2001.

monitors collect only half of the particulate material collected by the SES monitor, the other half is captured by the ESP. This difference is one possible reason that the SES monitor results are still lower in magnitude than the reported mass concentrations when the ESP is off on the Differential TEOM monitor, there should be twice as much material to evaporate.

The results presented in Figure 36 show the idea of evaporation and air change more clearly. Throughout most of the day, the reported mass concentrations of the two instruments agree quite closely (Figure 34), however at approximately 10:00 am, there is a definite change in the collected material and was reported in all of the data sets presented except for the final reported mass concentration from the Differential TEOM monitor. The mass concentration presented by the Differential TEOM monitor does not show any sharp changes in concentration during the entire 24-hour period. Examining the raw data obtained from prototype monitor when the ESP was on and off, it is clear that the signal observed by the SES monitor was caused by gas phase artifacts and not by a change in ambient particulate mass concentration. There is a sharp increase in reported mass concentration by the SES monitor, and a sharp increase in raw mass concentrations for when the ESP is on and off for the Differential TEOM monitor. As the reported SES monitor concentration sharply declines, the same behavior is happening to the concentrations on the Differential TEOM monitor both when the ESP is on and when the ESP is off. These signals cancel one another resulting in the smooth curve presented in Figure 34. This implies that the event is purely a gas phase or an evaporation phenomena, because if it was a function of changing particle mass being sampled, the sharp drop would only have occurred during the periods when the ESP was not energized.

Performing a comparison between the two Differential TEOM monitors for precision yields good agreement between the two instruments. Because of a problem with side A during a portion of the test program, the amount of comparison data is not as extensive as that obtained during the Queens field work. However, the comparison of the two monitors, Figure 37, indicates a difference between the two of approximately 5%.

Comparing the 24 hour average values from the Differential monitors with the values from the SES monitor illustrates the value of the Differential TEOM monitor approach, especially in areas with high levels of volatile material present in the atmosphere. While the two Differential monitors compare favorably, the SES unit does not correlate at all with the other two units. Figure 38 is a plot of the 24 hour average values for the two Differential monitors versus the SES monitor. As seen in the figure, the results are almost random across the plot showing almost no correlation.

During this field study, FRM sample were only collected every three days by the researchers at USC.

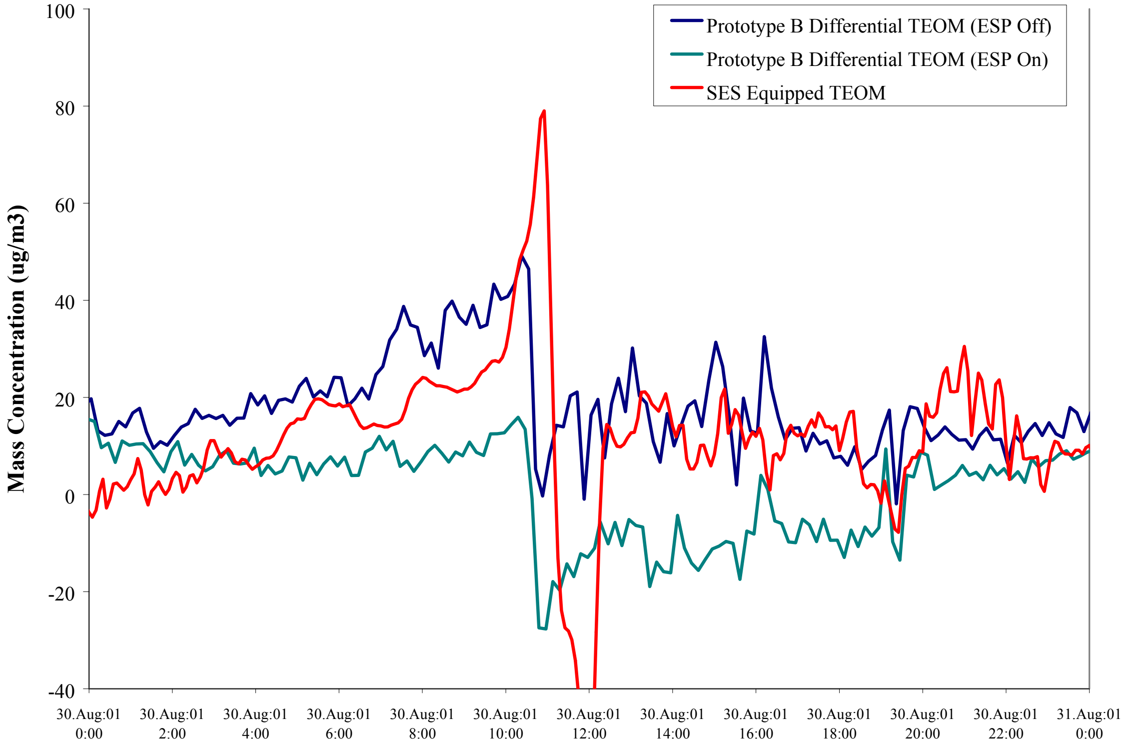


Figure 36. ESP on and off mass concentration data from a prototype Differential TEOM monitor compared to results from a SES equipped TEOM monitor. Rubidoux, CA. 30 August 2001.

Because of the limited numbers of FRM data, performing a direct correlation between the Differential

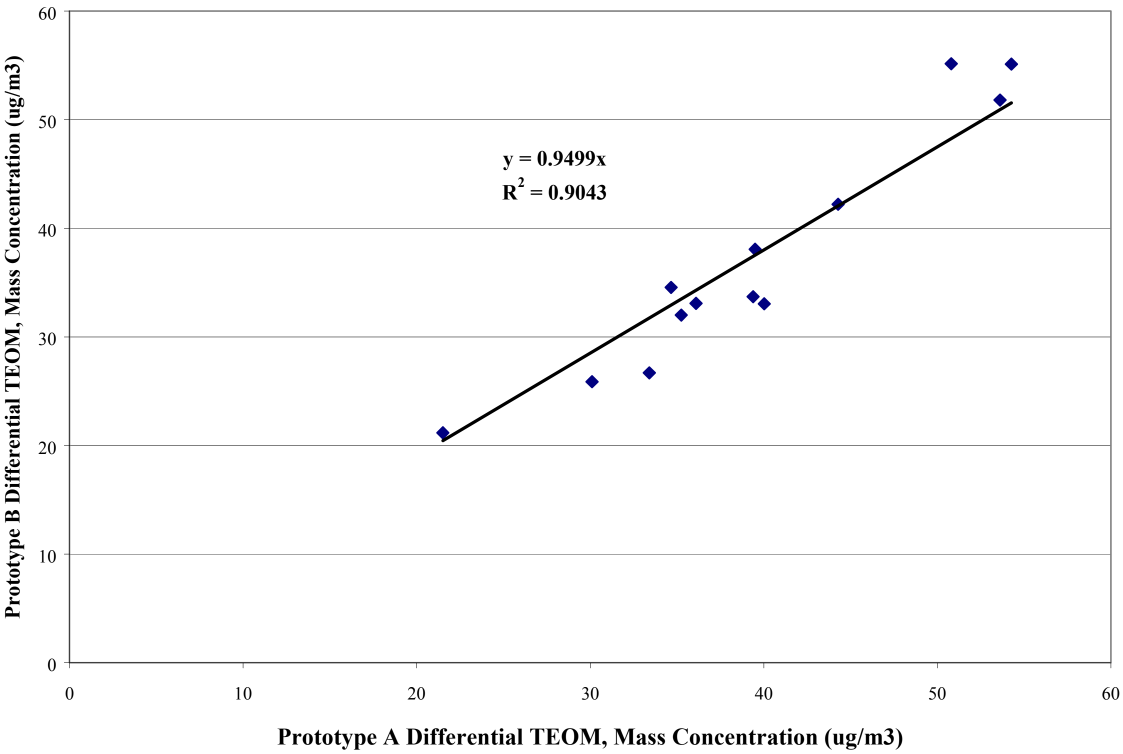


Figure 37. Correlation between 24-hour average results of two Prototype Differential TEOM monitors operated at Rubidoux, CA. August/September 2001.

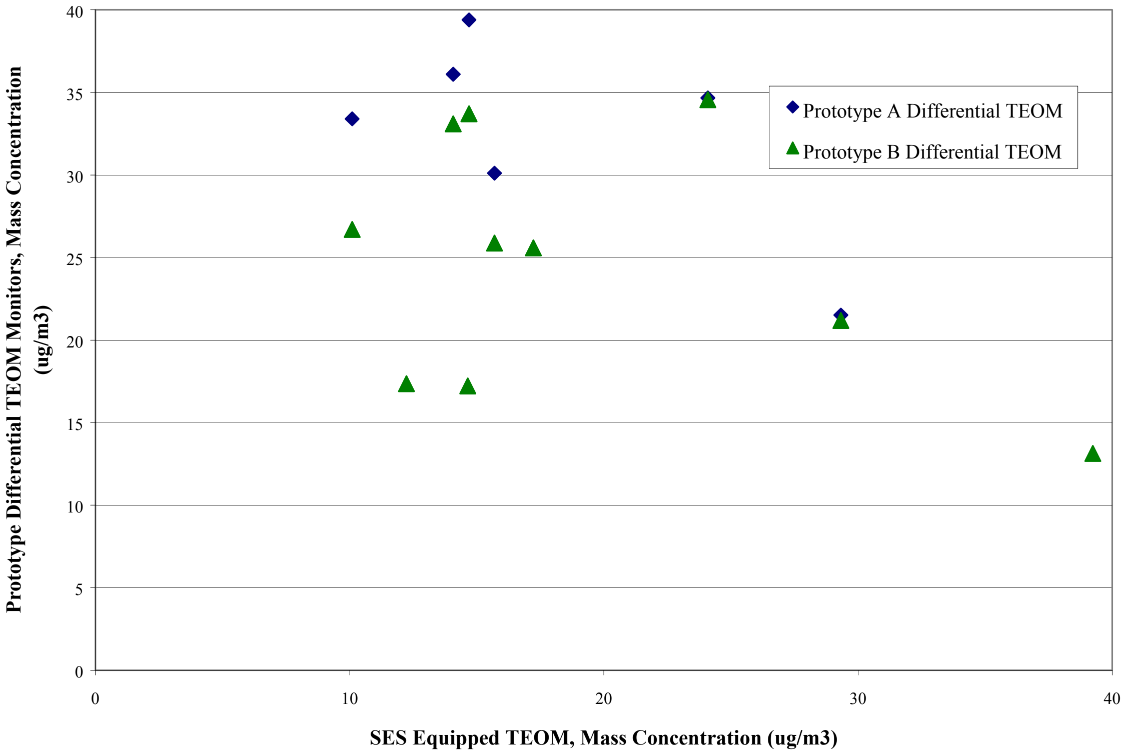


Figure 38. Plot illustrating lack of correlation between two prototype Differential TEOM monitors and a SES equipped TEOM monitor operated at Rubidoux, CA. August/September 2001.

TEOM monitor results and the FRM results is not valid, instead comparing the data on a daily basis is the only viable means of performing a comparison. As seen in Figure 39, the daily FRM results appear to trend with the Differential TEOM results over the duration of the study, but as the number of correlation data points is limited, it is not valid to make a definite comparison.

PROTOTYPE AMBIENT MONITOR OPERATION

During the final phase of this project R&P has been comparing two prototype Differential TEOM monitors, one operating at a fixed temperature of 30ºC and a second unit where there was no temperature control and the monitor temperature was freely floating along with the changes in ambient temperature conditions. The temperature controlled monitor (Unit A) was installed inside the R&P sampling trailer and operated in a similar mode as the instruments tested during the field studies. The second unit (Unit B) was installed inside of the isolated corner of the R&P trailer as in the installation described in the section on thermal behavior above.

Figures 40 and 41 are two representative comparison plots showing one hour average mass concentrations for the two instruments. Since Unit B is located inside of an isolated corner of the trailer, it is not at ambient temperature, but rather the measured sample temperature is approximately 10ºC higher than the actual ambient temperature and also shows a slight tempering or averaging effect on the exposed temperature. While this situation is not ideal, it should not cause any discrepancies in the results collected during this series of tests. The final goal is for the system to be closer to the actual ambient temperature, but the system will still need to smooth out the short term temperature spikes seen by the instrument, similar to that observed during this testing. Regardless of the actual temperature exposure during these tests, Unit B was still exposed to significant temperature swings during the testing. Comparing the results in the two figures shows that the two systems respond closely to changes in ambient PM mass concentration. The results for Unit B in Figure 40 exhibit significantly greater noise levels than the temperature controlled system, but overall the two units show similar results. In Figure 41, Unit B does not show the same noise levels as in the previous figure, and matches the Unit A results extremely well. Of particular note is the sharp drop in mass concentration at about 3:00 AM, presumably as a weather front passed through the area. The two units respond nearly identically to this sharp change in PM mass concentration.

As seen in the two figures, the noise levels are almost entirely caused by small ambient temperature fluctuations. Whenever the noise levels are greatest, is appears that these occur at the same times as the temperature fluctuations.

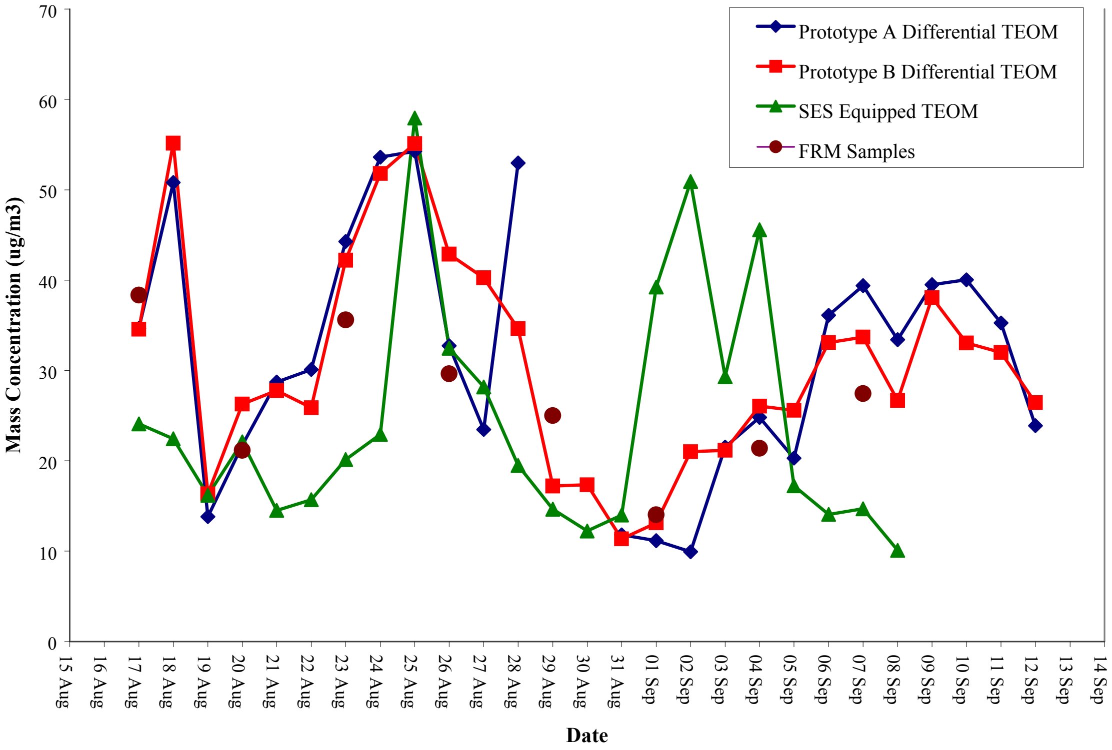


Figure 39. Daily 24-hour average mass concentration comparison between prototype Differential TEOM monitors, a SES equipped TEOM monitor, and FRM samples. Rubidoux, CA. August/September 2001.

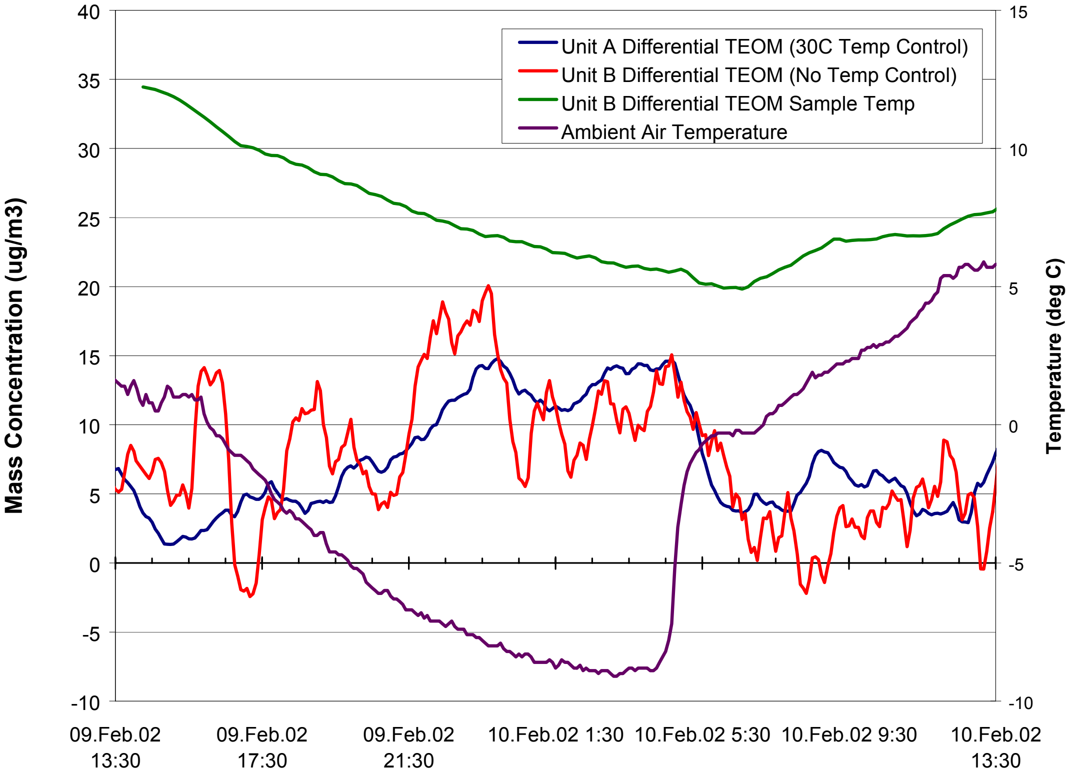


Figure 40. Representative hourly average comparison between two prototype Differential TEOM monitors. Unit A operating at controlled (30ºC) temperature and one floating at ambient temperature. Albany, NY.

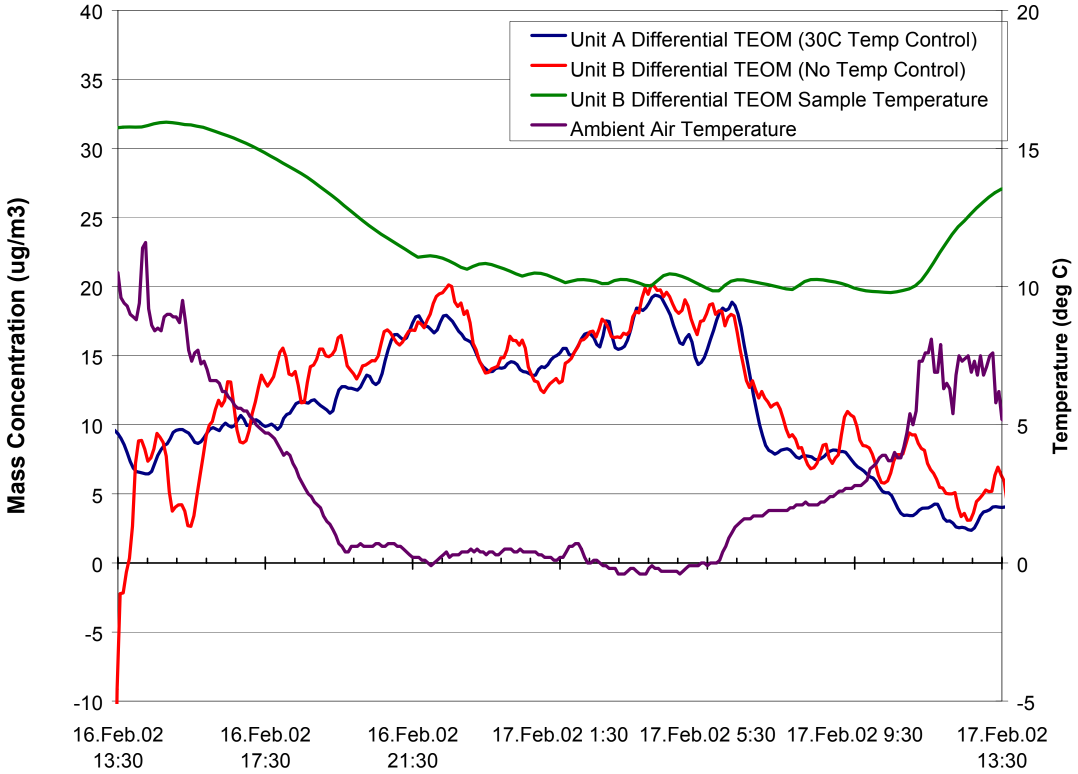


Figure 41. Comparison between 30ºC temperature controlled prototype Differential TEOM monitor and a prototype differential TEOM monitor floating at ambient temperature. Albany, NY.

DIFFERENTIAL TEOM MONITOR OPERATIONAL ISSUES AND FUTURE WORK

The results of the testing clearly indicate that the Differential TEOM design provides significant information and performs well, both in the laboratory and during field testing in locations with vastly different ambient PM level, compositions, and atmospheric chemistries. However, there are a number of issues that need to be resolved prior to commercialization of the system. These include PM-10 operation, ESP tip longevity and cleaning, ambient operation, and overall system configuration

PM-10 OPERATION

All testing on the Differential TEOM was performed under PM-2.5 sampling conditions. While there is no fundamental difference in the operation of the monitor, there are a number of items that would need to be modified in order to operate the system under PM-10 sampling conditions. One reason for this development path was due to the nature of PM-10 versus PM-2.5. The beauty of the Differential technique is its ability to resolve the volatile aspects of the sampled PM. Since the larger particles present in PM-10 are generated primarily through mechanical means, they consist primarily of non-volatile crustal materials, while the smaller particles are composed of significant fractions generated in automobile exhaust and other combustion sources. Thus the fraction of volatile and semi-volatile materials in the PM-2.5 aerosol can be significantly higher than the PM-10 aerosol. The Nafion dryers and the ESP are the only components of the system that may need to be revised for PM-10 operation.

As shown in the work performed at the University of Duisburg, the Nafion dryer may have high sample losses when sampling particles larger than PM-2.5. While the testing at the University of Duisburg illustrated losses when sampling these larger particles, other testing and normal sampling by monitors in various locations around the world do not show that there is a problem in sampling these larger particles through the nafion dryers. The inlet design of the tubes inside of the dryer needs to be investigated to reduce sample losses.

The ESP designed for the prototype Differential TEOM monitors was not configured with PM-10 in mind. The ESP design used for the prototype development was chosen to allow easy access to the ESP electrodes and thus easy cleaning when the electrodes became contaminated. Sampling of PM-10 was not a specific issue during prototype development. The prototype ESP design has two 90º bends, one at the inlet, and one at the outlet of the ESP. While these bends do not affect the measurement of PM-2.5, they can present a problem for sampling PM-10 aerosol. Calculations of the potential losses in the bends of the ESP for PM-10 aerosol indicate that these losses could be as high as 10-15% for 10 µm sized particles. By straightening the flow path in the ESP, these losses can be significantly reduced if no eliminated altogether.

ESP LONGEVITY AND CLEANING

As shown in the UAIM work, the ESP corona electrode can be contaminated by a build-up of deposits on the tip of this electrode. This work also showed that it an automatic cleaning of the ESP tip is possible by introducing ozone into the system upstream of the ESP. The commercialization work will further investigate and refine the automation of this process.

Regardless of the success of the electrode cleaning process, the ESP was not designed with easy replacement of the two ESP electrodes by field operators. While they are easy to remove and clean, there are steps that are required that make it unpractical for a monitoring instrument. The current design requires that the ESP be opened and completely removed from the enclosure. While this process may only take a few minutes when inside the laboratory, it can be a difficult process when the device is installed inside of an outdoor enclose.

AMBIENT OPERATION

Data collected by R&P in Albany, NY, shows that the Differential TEOM monitor is capable of operating at near ambient temperatures even when allowed to float as the ambient conditions change during a daily cycle. The final design needs to take into account the issue of delayed or smoothed response to changes in ambient thermal conditions. While the prototype system was able to respond to these changing ambient condition, converting this over to the new commercialized product will require additional effort.

OVERALL SYSTEM CONFIGURATION

Currently, the prototype Differential TEOM monitor consists of components which were designed independently from their usage in this project. As part of the commercialization of the Differential TEOM monitor, all of these components will undergo a redesign, if not in function, at least in form. In order for the Differential TEOM monitor to be a successful product all components must be redesigned to function as a single system. Of the major components of the system, the sample inlet, sample equilibration system, the ESP, and the TEOM monitor, only the sample inlet will likely remain unchanged. As mentioned above, the ESP will need to be redesigned to handle PM-10 sampling, as may the SES. Since the system will be configured to operate at ambient temperature, but these temperature swings will need to moderated, the system will be designed around an enclosure to provide some thermal buffering to stabilize the mass concentration measurements.

Appendix A

University of Duisburg

Determination of Sample Losses in Nafion Dryer used in the Differential TEOM Mass Monitor

Internal Report No. 8

NYSERDA Project

Date:	13.08.2001
Author:	U. Drosten, T.A.J. Kuhlbusch, H. Fissan
Attach File:	
Title:	Determination of Particle Losses in the Nafion® Dryer of the SES

Experiment No. 8:

Task:

Determination of particle losses in the Nafion® dryer used in front of a TEOM® sensor. First NaCl (sodium chloride) as an inertial particle substance is used for the investigations. The experiments are done for sample flow rates in the dryer of 0.3 l/min, 1 l/min and 3 l/min.

Testing procedure:

First of all we concentrate on the devices for particle mass concentration measurements we are using. Therefore we separate the SES from the existing complex Test set-up (described in the Reports No.2-7) and analyze the behaviour of the Nafion® dryer in a more simple stand alone Test set-up without the use of a TEOM®. After testing other particle material like $(NH_4)_2SO_4$ (ammonium sulfate) and NH_4NO_3 (ammonium nitrate) we will determine the particle losses under working conditions.

We build up a Test set-up with four main components (see fig.1; details of the set-up see fig.7):

1. Aerosol Generation (TSI Atomizer)
2. Neutralizer
3. Measurement Object Nafion® Dryer in parallel a Bypass line
4. Measuring Analyzer: Scanning Mobility Particle Sizer (SMPS)

With the SMPS we recorded the Particle Size Distribution (PSD) first with the Dryer-line and then for the Bypass-line. From the ratio of this two PSDs we got a penetration rate, which gives an idea about particle losses depending on particle size. For each experiment this procedure rerun for six times due to statistic safety. For this 6 measurements we calculated a mean PSD for the Dryer, the Bypass and mean data of the Penetration rate (ratio from Dryer/Bypass). In the diagram we also plotted the standard deviation. To verify the results we rerun the complete measurement series for 5 times (in this report only the representative results are shown).

With the diffusion theory from standard literature (Hinds, Aerosol Technology, 2nd Edition, John Wiley& Sons, 1999) the experimental results are compared with particle losses of a tube.

Test Set-up:

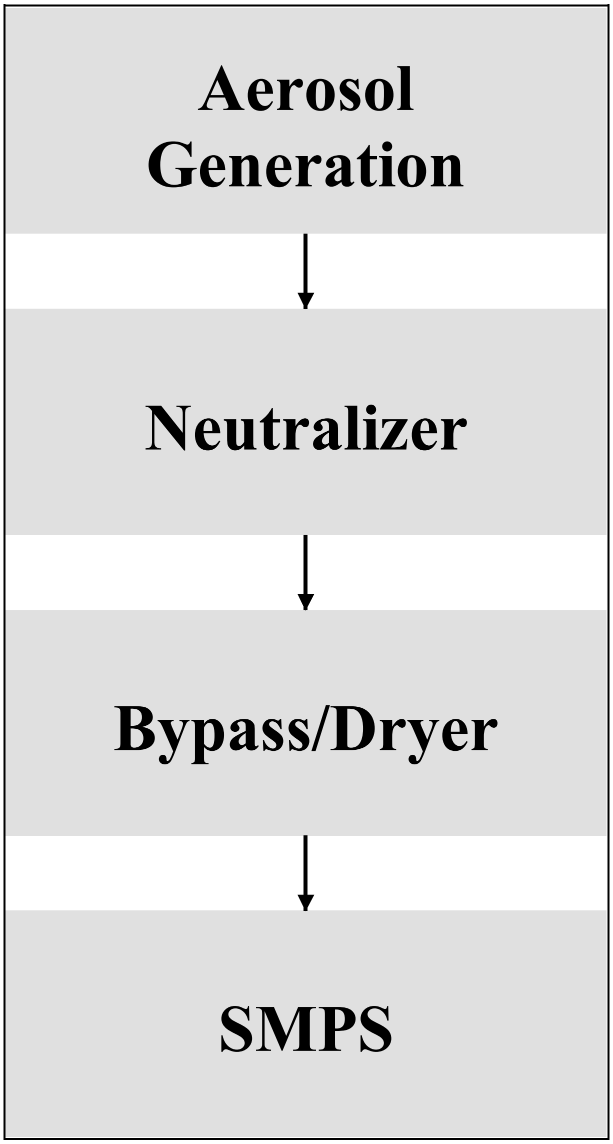


Fig.1: Schematic Test set-up for investigations of particle losses in a Nafion® dryer

Fig. 1 shows the principle of the set-up used for the determination of particle losses in the Nafion® dryer. In the measurements we take a TSI atomizer for aerosol generation. A liquid with the species (here: NaCl (sodium chloride)) are nebulized and the aerosol flows through a conventional silica gel dryer. Before the aerosol flows into the test track of the Dryer/Bypass line, the dry aerosol (rH<10%) are neutralized by a radioactive source. Behind the Dryer/Bypass a SMPS measure the PSD. For the investigations of practical interest with flow rates of 1 l/min and 3 l/min in the Dryer/Bypass line, a flow adaption is needed, because the UCPC works with a flow rates of 0.3 l/min. The reason that we make also experiments with flow rates of 0.3 l/min is to get more operational experience with the measuring system. Details of the Test set-up are shown in the appendix (fig.8).

Test parameters:

Air Temperature: 23˚C

Relative Humidity: rH < 10 % before Dryer/Bypass Strand

Mixture of the liquid: 10 g NaCl/ 1 l aqua dest

Aerosol Parameter: D_{pmean}=72 [nm]; σ=1.72, concentration c: 2.4 E+06 [#/cm3]

Dryer Flow: 0.3 l/min, 1 l/min and 3 l/min

Volume Flow UCPC: 0.3 l/min

Time of Measuring with the SMPS:

- 90 seconds scanning time
- 10 seconds turning off the voltage of DMA in the SMPS
- 20 seconds standby

number of iteration Dryer/Bypass: 6 times (first Dryer then Bypass again Dryer etc.)

Results:

Fig.2 shows the experiments for a flow rate of 0.3 l /min in the Dryer and Bypass line. The good accuracy is shown by the low standard deviation.

In fig.2 the number concentration of the Dryer (red curve) and the Bypass (blue curve) is plotted versus the particle diameter. On the second vertical axis the ratio (here called penetration) of Dryer/Bypass (black curve) are plotted. For Particle Diameter d_p>250 nm we get a higher standard deviation which depends on the lower particle concentration of this particle sizes.

In fig. 3 the penetration for different flow rates are shown. For increasing flow rate, this is contributed with a lower period of stay in the Dryer/Bypass, the penetration rate of particles with diameter d_p<200 nm also increases. This is in good agreement with diffusion losses theory, if you keep in mind that:

$$\boxed{P = 1 - A}$$

P: Penetration; A: Precipitation

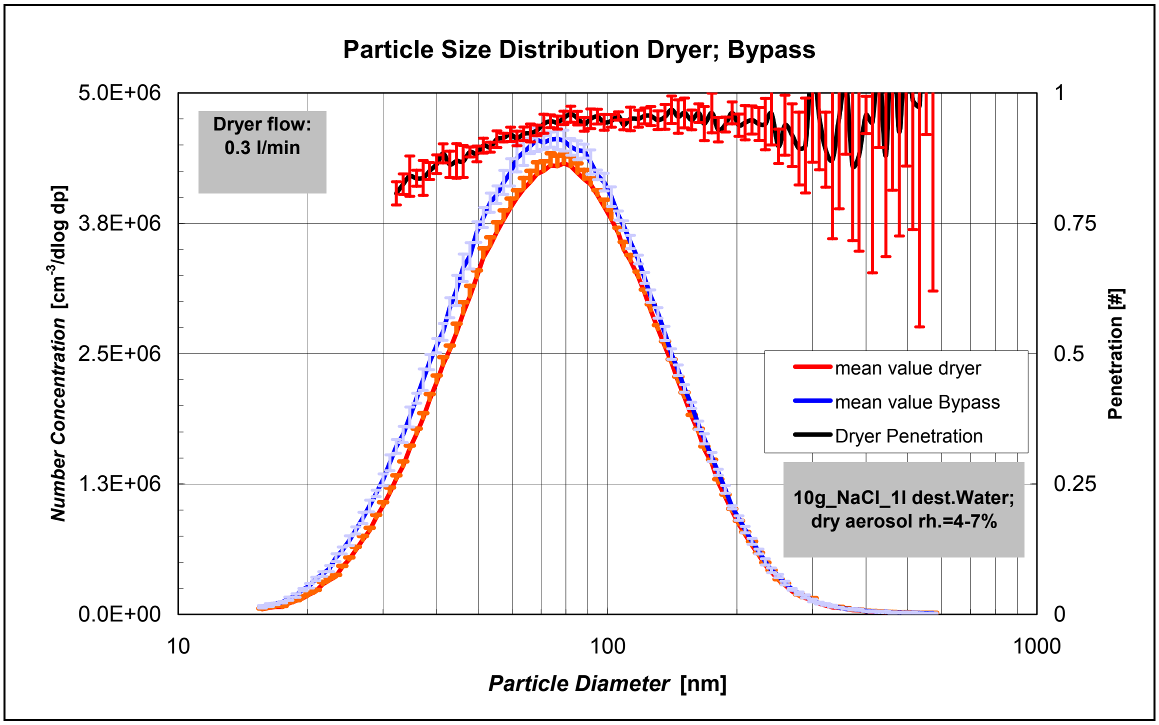


Fig.2: Relative humidity level behind SES for high initial data of relative humidity

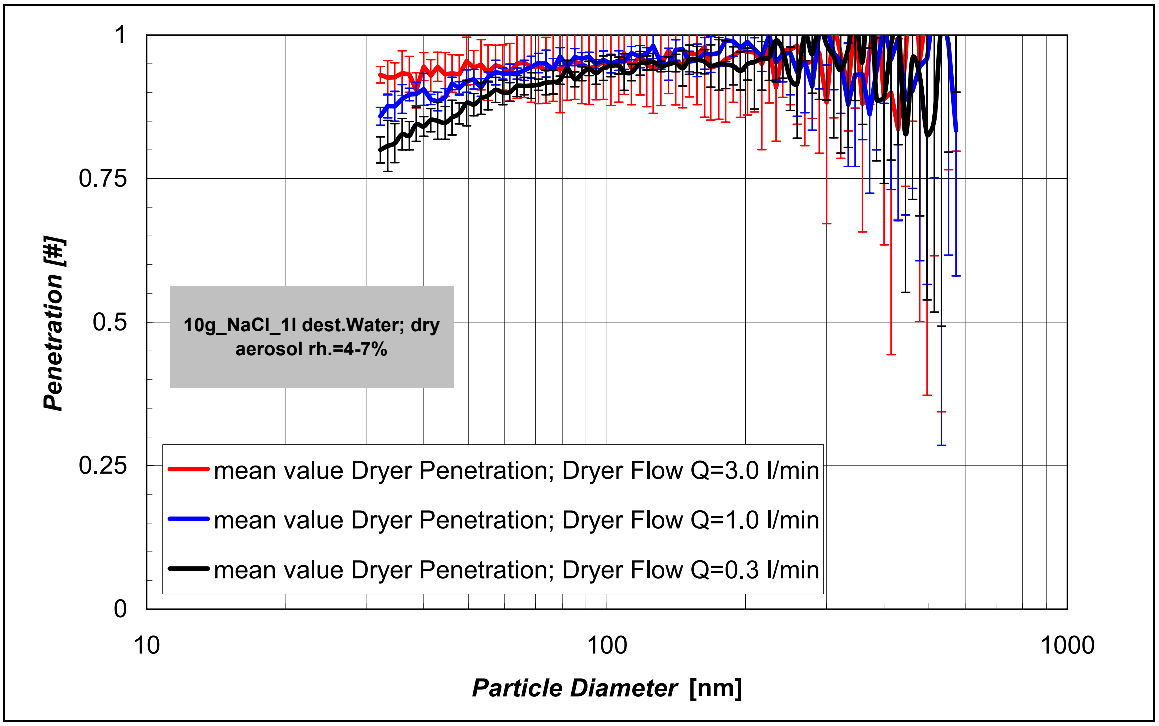


Fig.3: Relative humidity level behind SES for low initial data of relative humidity

Comparison experimental data with calculations of diffusion theory:

If we want to interpret the measured penetration rates of the Dryer we had to compare it with the diffusion theory from standard literature. Therefore we compare the experimental results with a tube the same flow rate and the same geometric size. The equations from diffusion theory are taken from *Hinds, Aerosol Technology*. If we compare the penetration rate we got from the experimental with the penetration from conventional tube with the geometric size of the Dryer, we must take into consideration a correction factor. This factor caused by the different fittings in the Dryer and Bypass line and can also be calculated with diffusion theory. We want to mention that the correction factor (see fig.4) have no great influence on the experimental data for particle dp> 100 nm for the interesting flow rates of 1 l/min and 3 l/min .

Equations from diffusion theory:

$$\boxed{\mu = \frac{DL}{\dot{Q}}}$$

$$\boxed{P = 1 - 5.5\mu^{\frac{2}{3}} + 3.77\mu}; \qquad \boxed{\mu < 0.009}$$

$$\boxed{P = 0.819 \cdot \exp(-11.5\mu) + 0.0975 \cdot \exp(-70.1\mu)}; \qquad \boxed{\mu \ge 0.009}$$

μ: Dimensionless deposition parameter for tubes

D: Particle Diameter

L: Tube Length

$\boxed{\dot{Q}}$: Volume Flow

P: Penetration

Fig.5-7 show especially good agreement between the calculated and measured penetration rates of flow rates of 0.3 l/min and 1 l/min.

Conclusion:

- ***No evident particles losses in the Nafion Dryer are expected for inertial particles (NaCl) in the Submicrometer Size range***

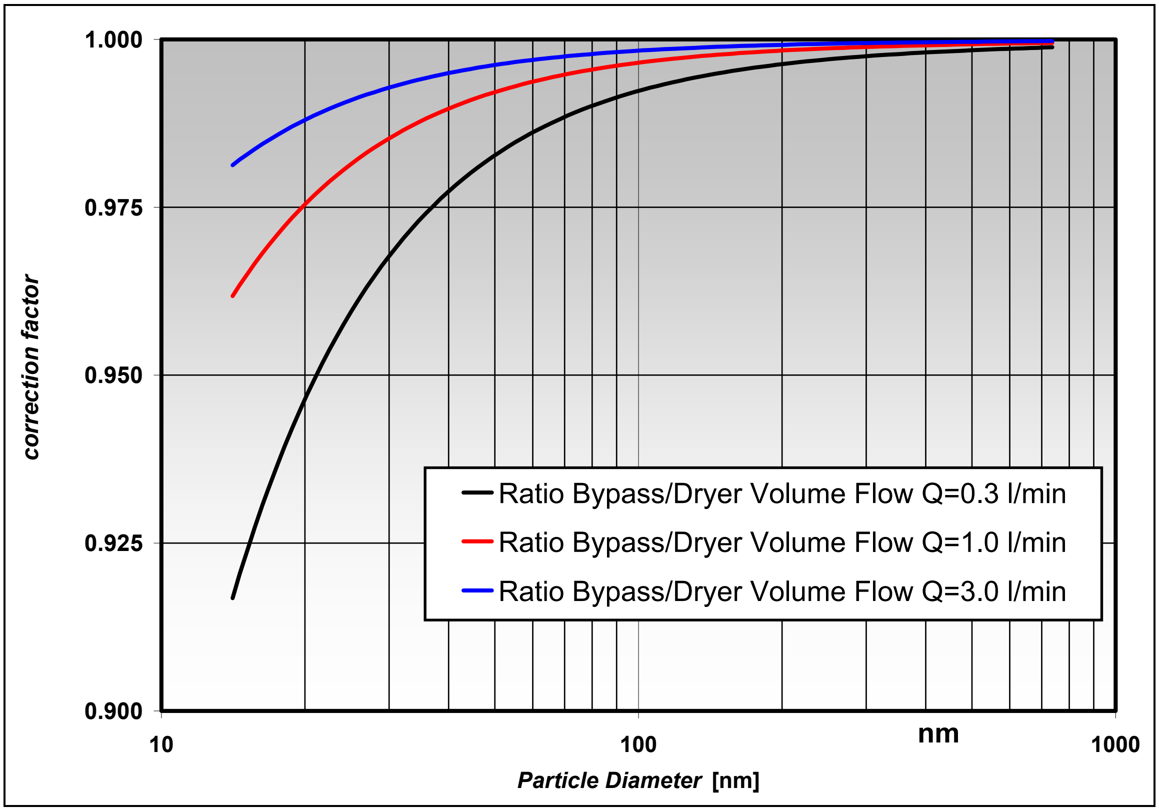


Fig.4: Correction factor versus Particle Diameter

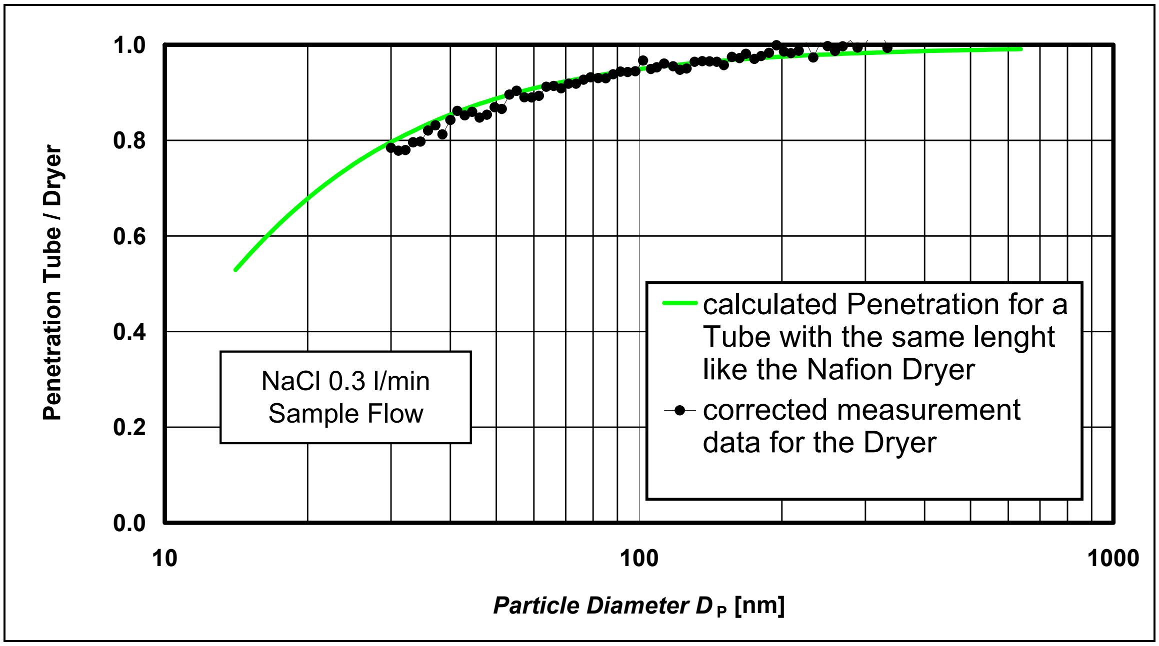


Fig.5: Comparison of experimental Penetration rate with theory for Q=0.3 l/min.

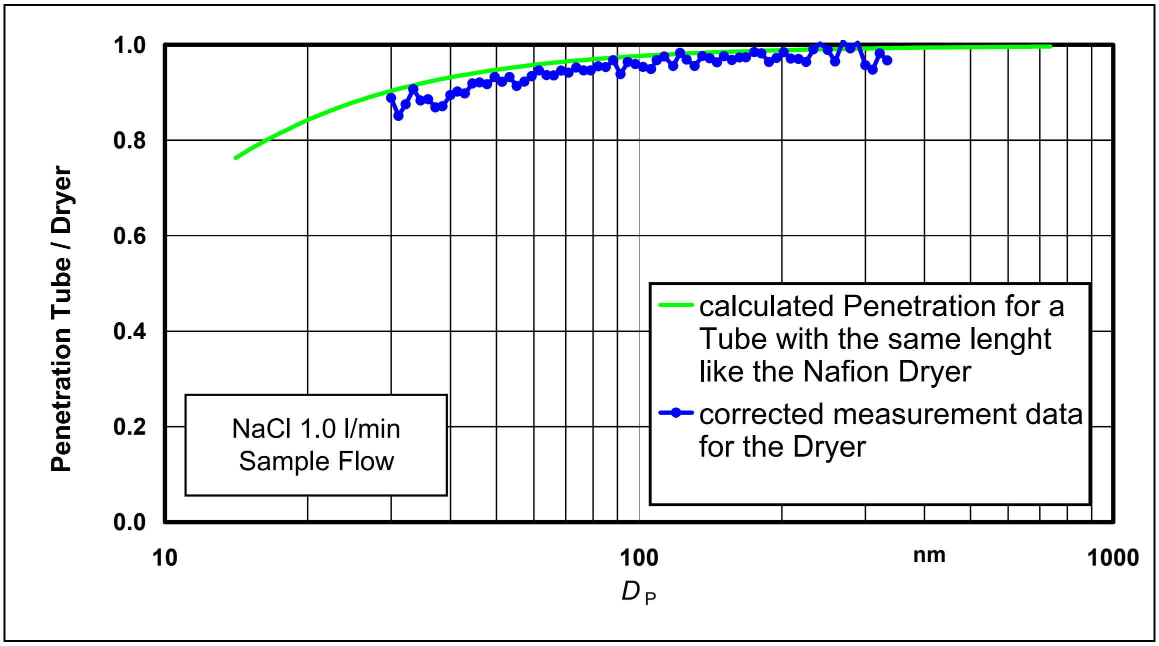


Fig.6: Comparison of experimental Penetration rate with theory for $\boxed{\dot{Q}}$*=1.0 l/min*

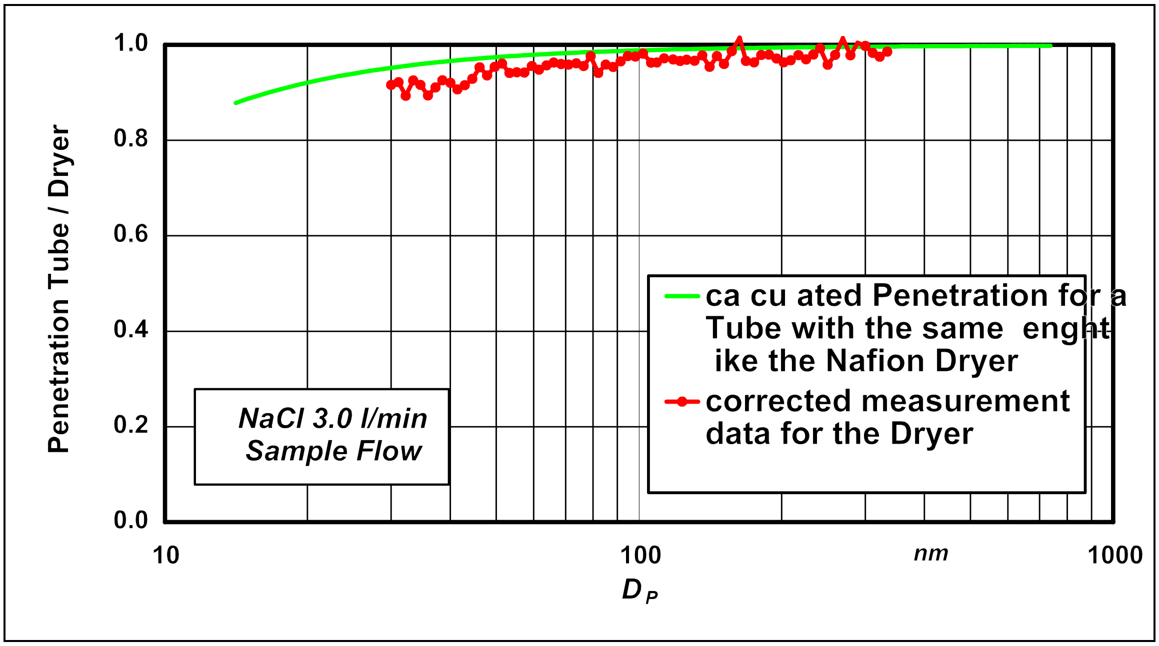


Fig.7: Comparison of experimental Penetration rate with theory for $\boxed{\dot{Q}}$*=3.0 l/min*

Appendix:

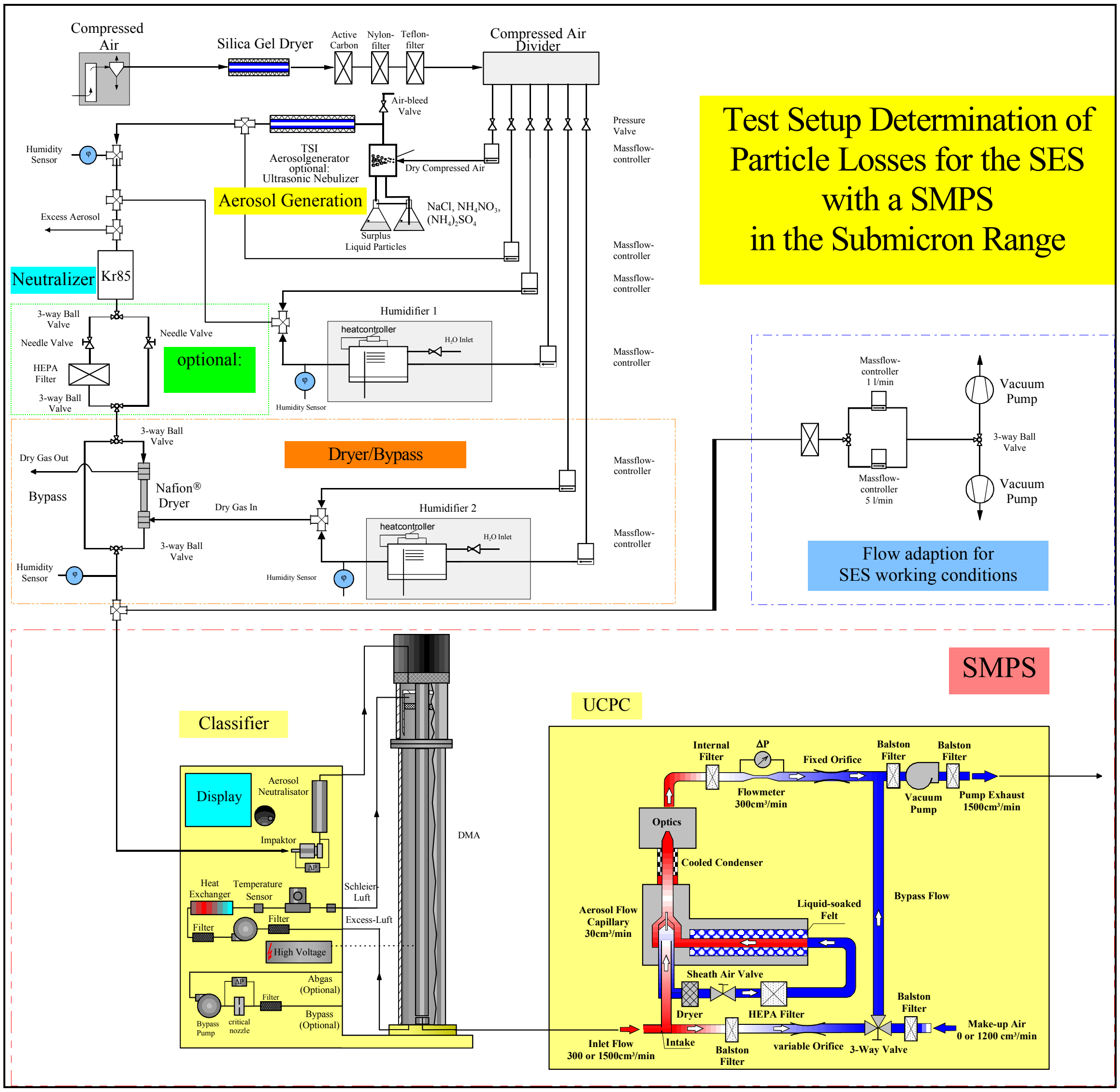


Fig.8: Detailed Set-up for the Determination Particle Losses in the Nafion® dryer

Appendix B

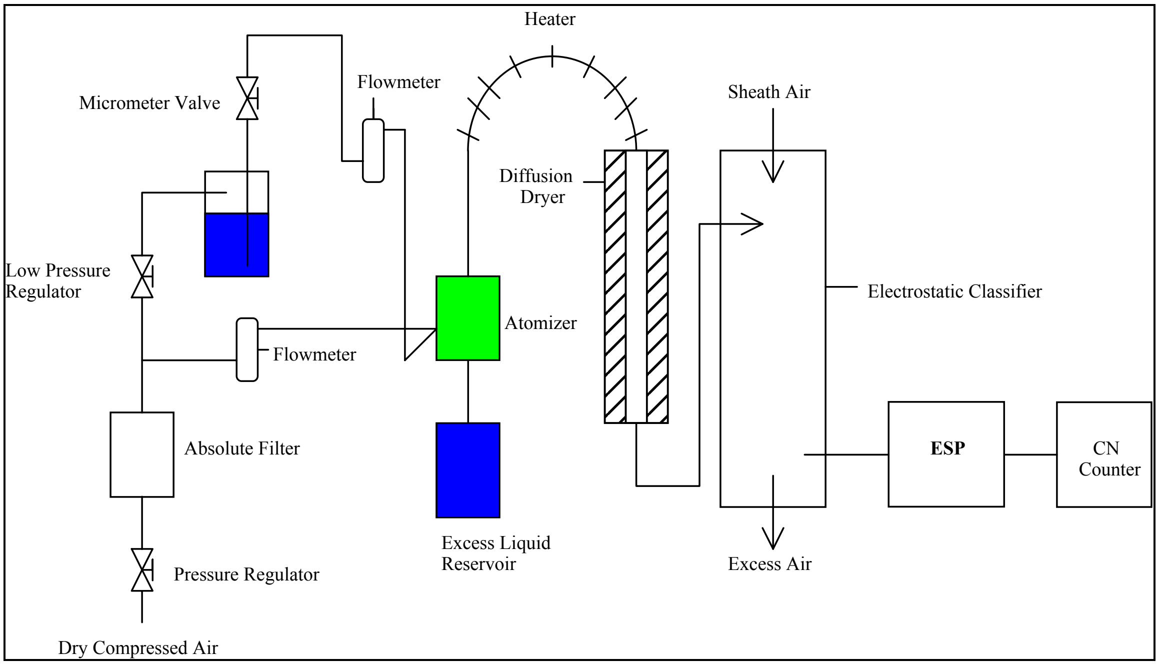
Clarkson University

Evaluation of the Collection Efficiency of the Electrostatic Precipitator used in the Differential TEOM Mass Monitor

1. Experimental Section

The prototype ESP was evaluated generating the fine (< 100 nm) and coarse particles (> 90 nm) using improved atomizer system developed by Leong et al. (1982). The fine particles were generated using a 5% solution of sodium chloride while the coarse particles were generated with the different sizes of polymer microspheres. Suspensions (100 nm, 500 nm, and 1 µm). The fine and coarse particles were measured with a SMPS and LAS-X, respectively (Figure 1 and 2). The number concentration normalized with the different particle size ranges were measured when an ESP was off and on.

Figure 1. The experimental apparatus for the fine particles generator.



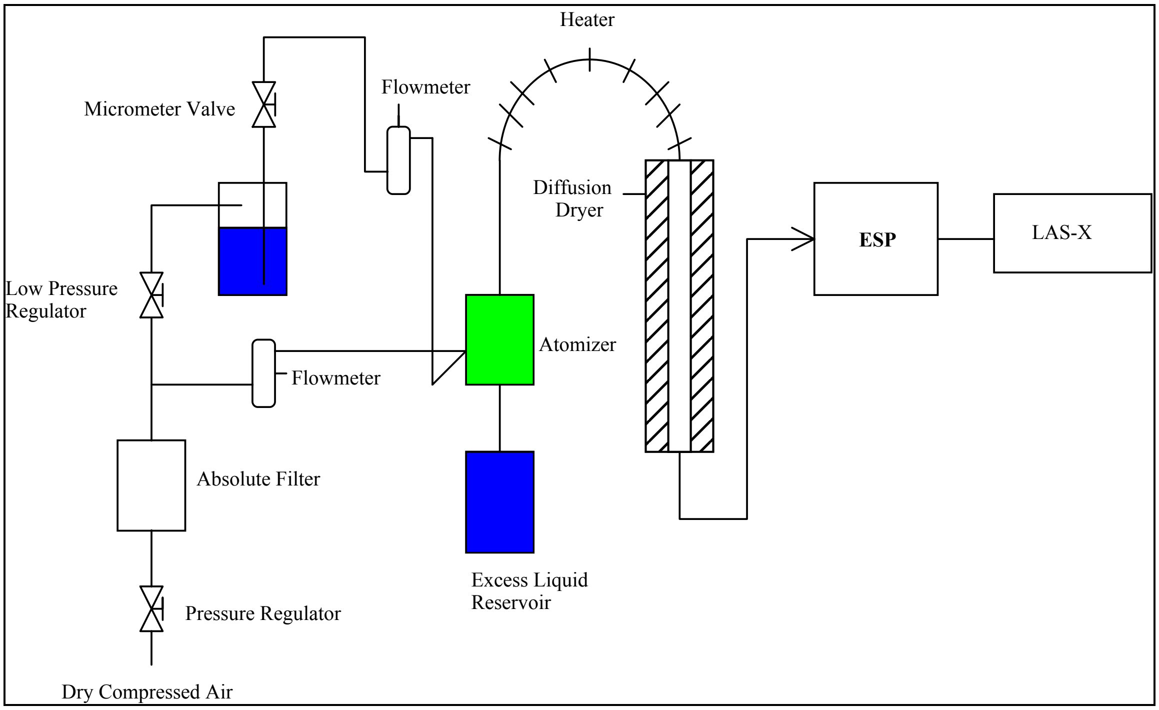


Figure 2. The experimental apparatus for the coarse particles generation.

The potentiometer on the front panel of the ESP box was used to adjust the corona current for the charging section of the ESP.

2. Results

Tables 1 and 2 show the results of the corresponding current and positive high voltage reading with the different potentiometer setting. The potentiometer settings for the coarse particles ranged from 100 to 700 because ozone might possibly be generated with the corona current above 140 nA. As for the fine particles measurement, the potentiometer was set from 300 since the current reading was not stable with the potentiometer setting below 300 (Table 2). Since the positive high voltage reading changed during operation with ESP on, the value at the end of the run was taken as the result while the current reading was steady.

Table 1 The corona current and the corona high voltage readings for the fine particles

Potentiometer Setting	Corona Current (nA)	Corona High Voltage Reading (V)
300	59.2	5301
400	78.8	5284
500	98.4	5301
600	118.0	5368
700	137.5	5374

Table 2 The corona current and the corona high voltage readings for the coarse particles (upper table: 500 nm and 1 µm, lower table: 100 nm)

Potentiometer Setting	Corona Current (nA)	Corona High Voltage Reading (V)
100	19.7	4765
200	39.6	4819
300	59.2	4858
400	79.0	4888
500	98.5	4925
600	118.0	4947
700	137.5	4979

Potentiometer Setting	Corona Current (nA)	Corona High Voltage Reading (V)
100	19.6	4879
200	39.6	4892
300	59.2	4910
400	78.8	4939
500	98.4	4951
600	118.0	4973
700	137.4	4999

Coarse Particles

The probe ranges in LAS-x system were selected as 2 and 3 to measure the 100 nm and the one greater than 100 nm in the nominal particle diameter, respectively. The measured size distributions for the number concentration with ESP off and on were showed in Figures 3 and 4. The results showed that the collection efficiency of the ESP increased as the particle size in diameter increased.

The mass concentrations with ESP off and on as the potentiometer setting ranged from 100 to 700 were calculated from the measured size distributions for the number concentration assuming the particle density, 1.05 g/cm^3, and the spherical particles. Then, the overall collection efficiency of the ESP was calculated from the mass size distribution with the different nominal diameters, 100 nm, 500 nm, and 1 μm and the different potentiometer settings (Table 3). Table 3 shows that the collection efficiencies of the ESP were almost in the same range for the different potentiometer settings.

Table 3 The overall collection efficiencies of the ESP calculated from the mass size distributions with the different nominal diameters

Potentiometer Setting	**Nominal Diameter**	
	100 nm	500 nm, 1 μm
100	**98.390**	**99.977**
200	**98.906**	**99.986**
300	**98.700**	**99.989**
400	**98.925**	**99.983**
500	**98.652**	**99.989**
600	**98.868**	**99.981**
700	**98.666**	**99.988**

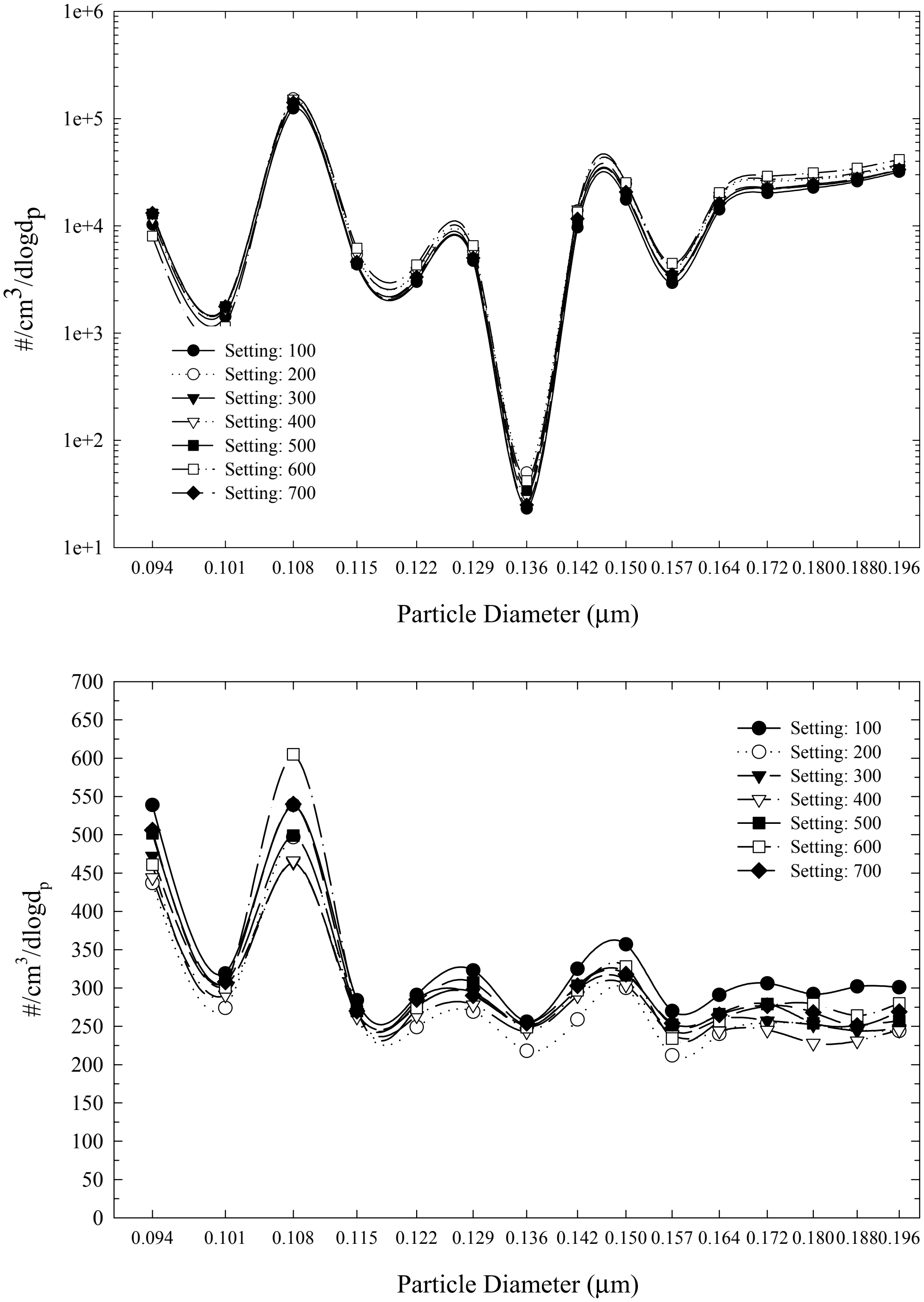
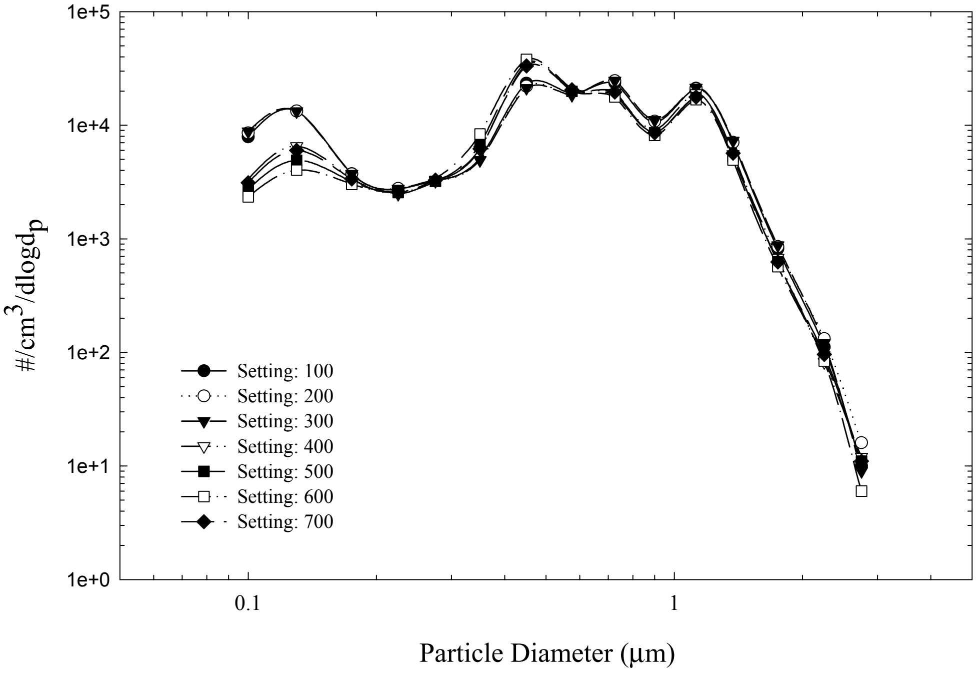


Figure 3. Size distributions for the number concentration with a nominal particle diameter, 100 nm (upper figure: ESP off, lower figure: ESP on).



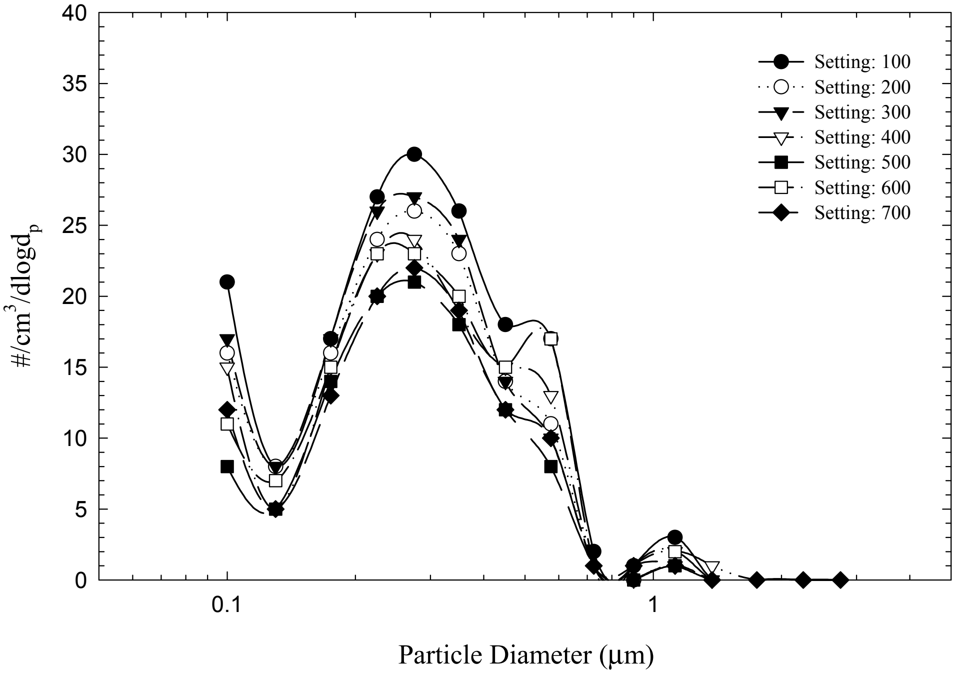


Figure 4. Size distributions for the number concentration with the nominal particle diameters, 500 nm, and 1 µm (upper figure: ESP off, lower figure: ESP on).

Fine Particles

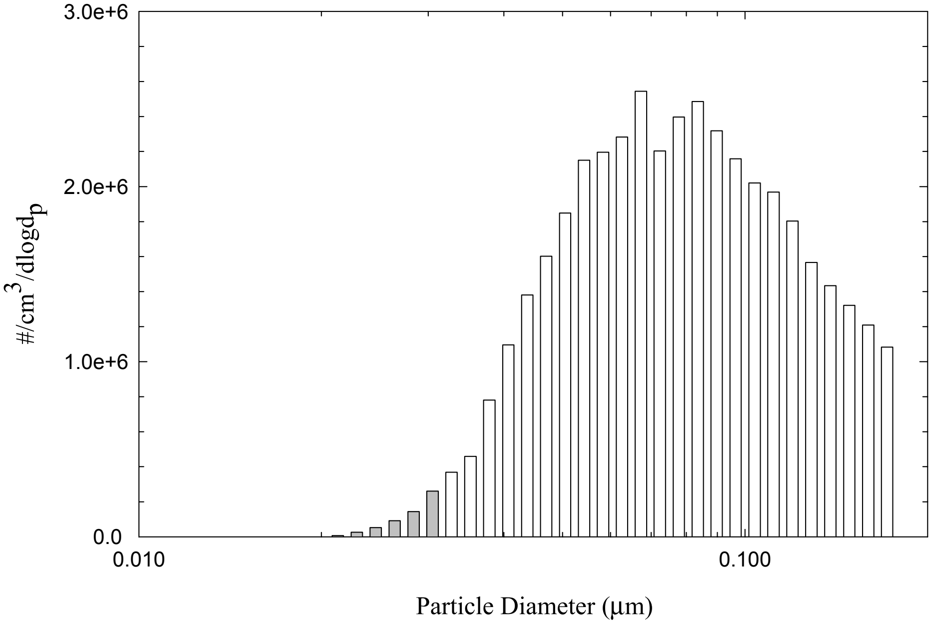
The ESP was evaluated for the fine particles using SMPS system. The size distributions for the number concentrations with the different potentiometer settings ranged from 300 to 700 were shown in Figures 5, 6, 7, 8, and 9. Especially, it took about two minutes to stabilize the corona current with the potentiometer setting, 300. The results indicated that the potentiometer setting, 400, corresponding corona current, 79 nA, could eliminate the most of fine particles less than 100 nm. Table 4 shows the individual collection efficiencies of the ESP with the different potentiometer settings calculated from the size distributions for the number concentrations.

In summary, the potentiometer setting for prototype ESP is recommended to be set at values over 400, equals to 79 nA, corona current. This conclusion is based on the facts that the collection efficiencies of the ESP were almost in the same range for the coarse particles greater than 100 nm in diameter and the majority of the ambient mass concentration of PM 2.5 was from the large particles.

At the higher potentiometer settings, there is an increase in the concentration of the smallest sized "particles" as seen in Figures 7-9. We suspect that these may be small ions coming from the ESP that are inducing ion nucleation of butanol in the CPC. Studies are in progress to test this hypothesis.

Table 5 The individual collection efficiencies of the ESP with the different potentiometer settings calculated from the size distributions for the number concentrations.

Collection Efficiency				
Potentiometer Setting				
300	**400**	**500**	**600**	**700**
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	0	0	0	0
0	1	0	0.823608	0
0.990993	1	0	1	0
0	1	0	0	0
1	1	1	0	1
1	1	1	1	1
1	1	0.999593	1	1
1	1	0.999749	1	0.9998
1	0.999892	1	1	0.999971
1	1	1	1	0.999942
1	1	1	1	0.999945
1	1	0.999966	1	0.999967
1	1	1	1	0.999975
1	1	1	1	1
1	1	0.999981	0.99998	1
1	1	1	1	1
0.999986	1	1	0.999998	1
1	1	1	0.999989	1
1	1	1	1	1
1	**1**	**1**	**1**	**0.999976**
1	**1**	**1**	**1**	**1**
1	**1**	**0.999987**	**1**	**1**
1	1	1	1	0.999989
1	0.999979	1	1	1
1	1	0.999967	1	1
1	1	1	1	1
0.999986	1	0.999985	1	1
0.99995	0.999986	1	1	1
0.999982	1	0.999981	0.999983	1
1	0.999984	1	1	1
1	1	1	1	0.999979
0.999918	1	0.999971	1	0.999902



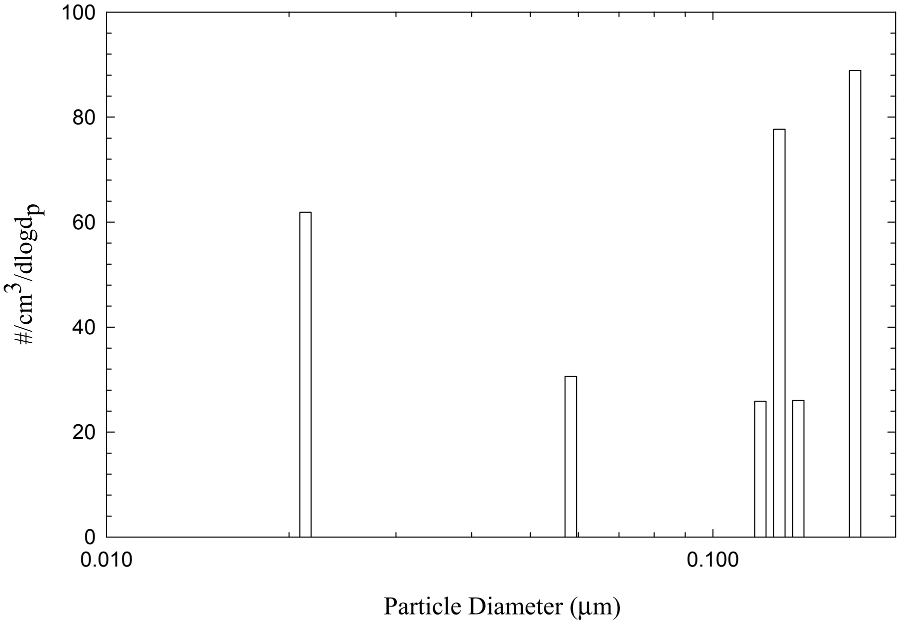
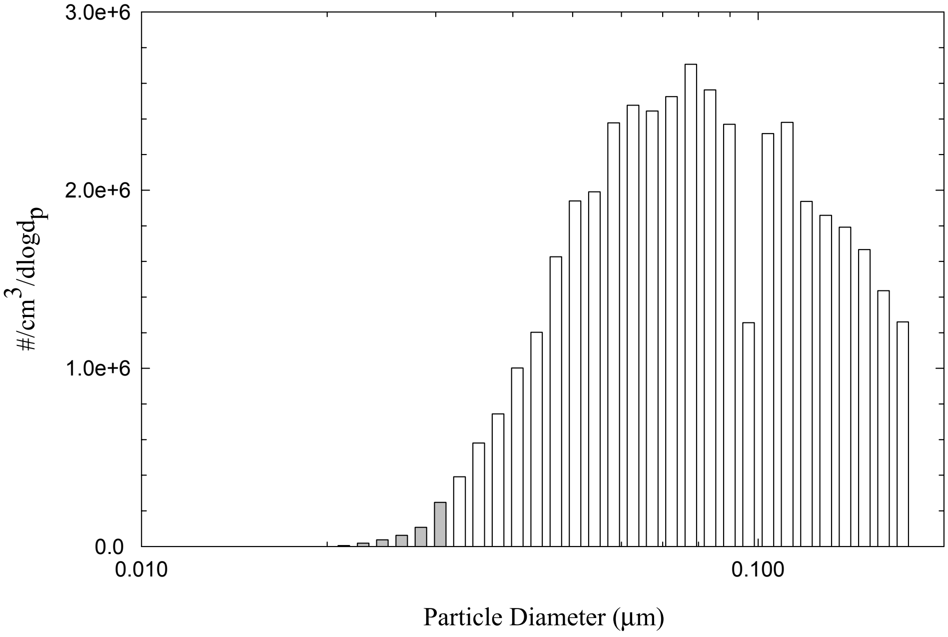


Figure 5. The size distributions of the number concentrations for the fine particles less than 100 nm in diameter with the potentiometer setting, 300 (upper figure: ESP off, lower figure: ESP on).



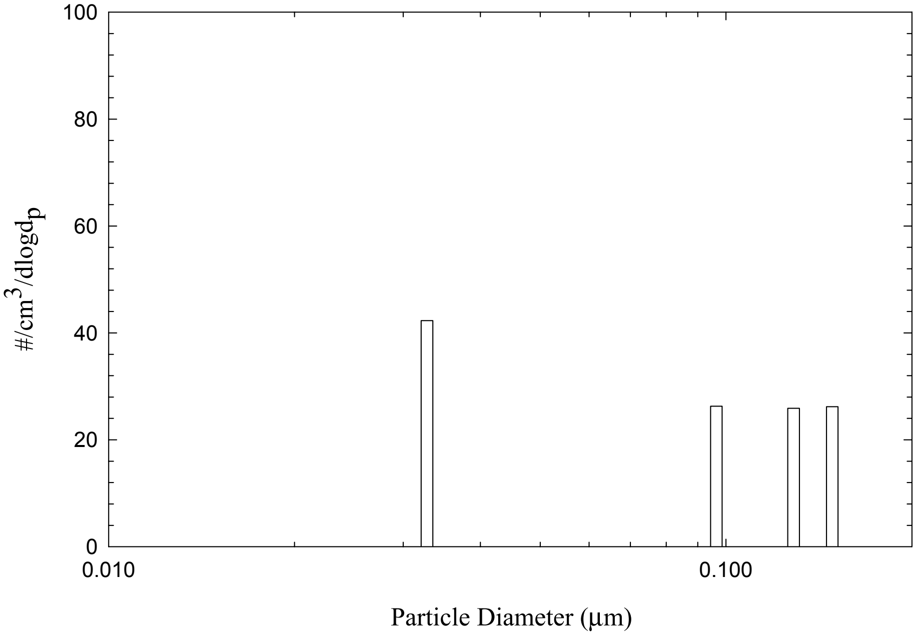
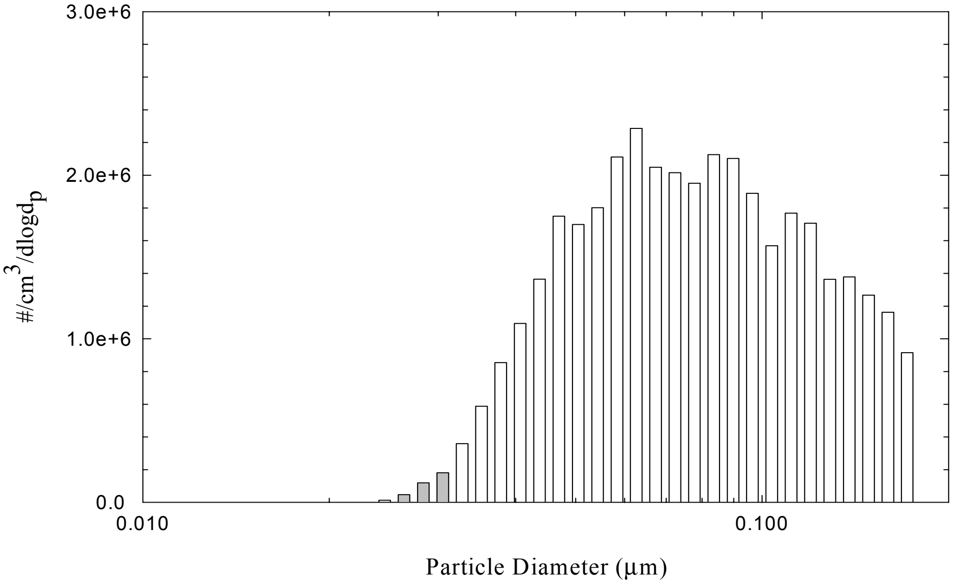


Figure 6. The size distributions of the number concentrations for the fine particles less than 100 nm in diameter with the potentiometer setting, 400 (upper figure: ESP off, lower figure: ESP on).



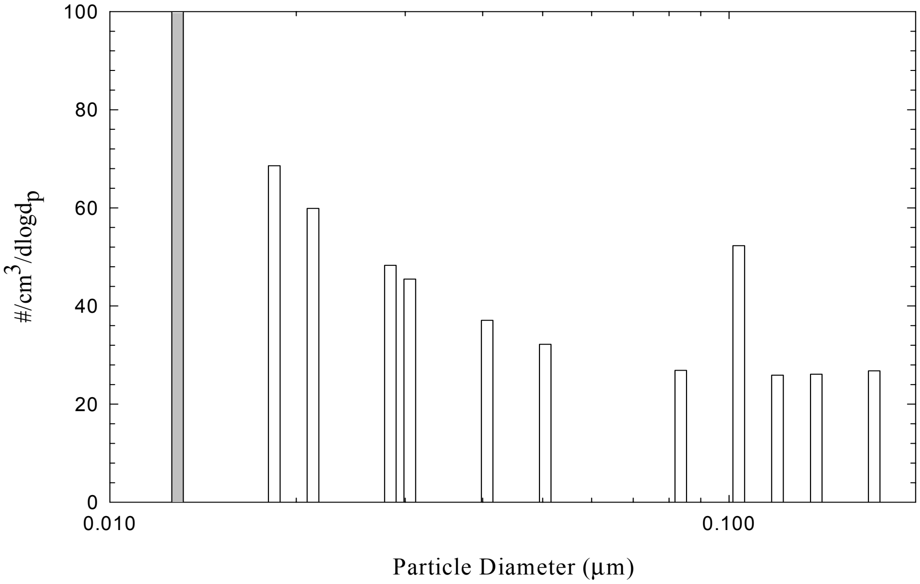


Figure 7. The size distributions of the number concentrations for the fine particles less than 100 nm in diameter with the potentiometer setting, 500 (upper figure: ESP off, lower figure: ESP on).

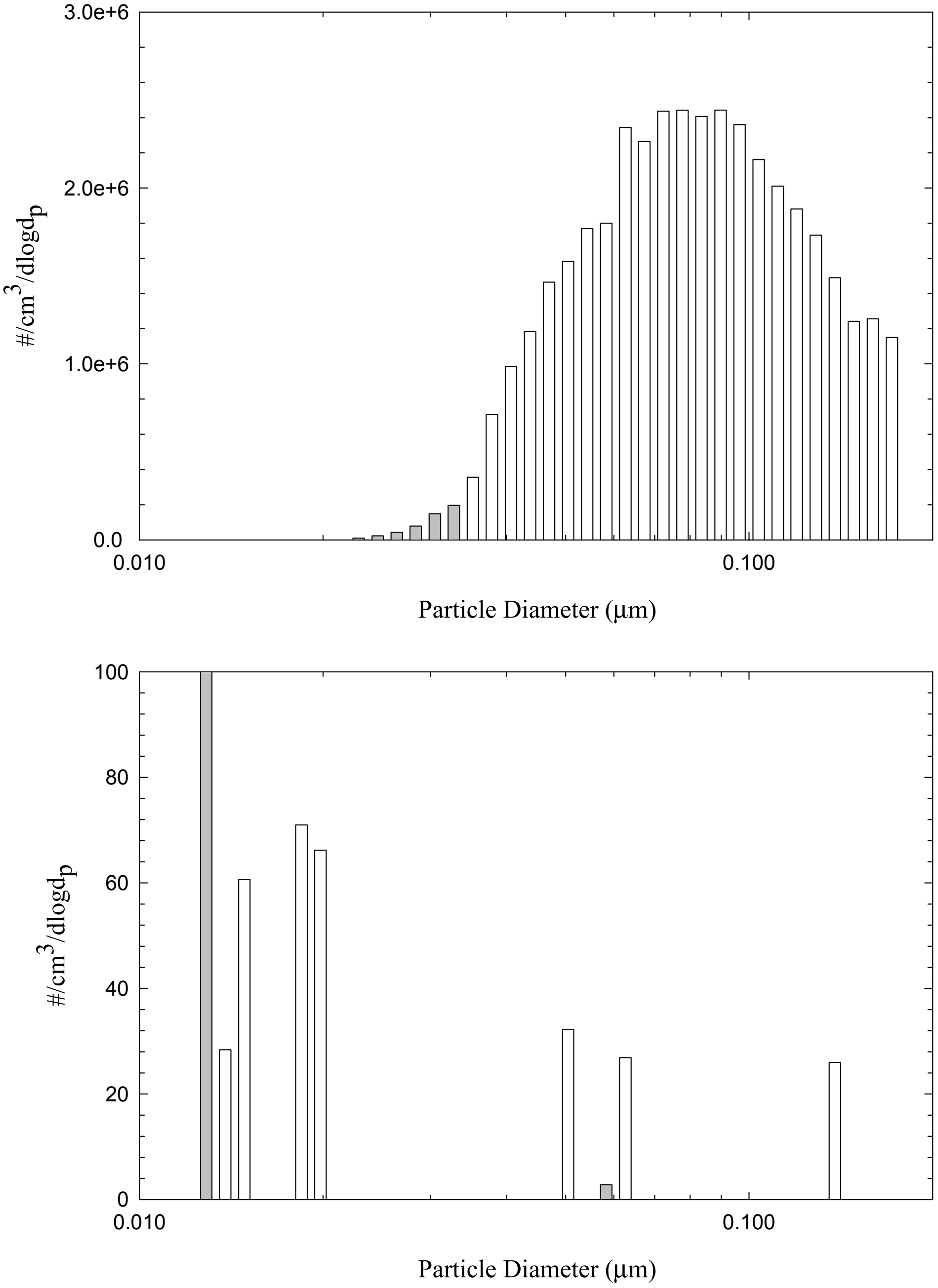


Figure 8. The size distributions of the number concentrations for the fine particles less than 100 nm in diameter with the potentiometer setting, 600 (upper figure: ESP off, lower figure: ESP on).

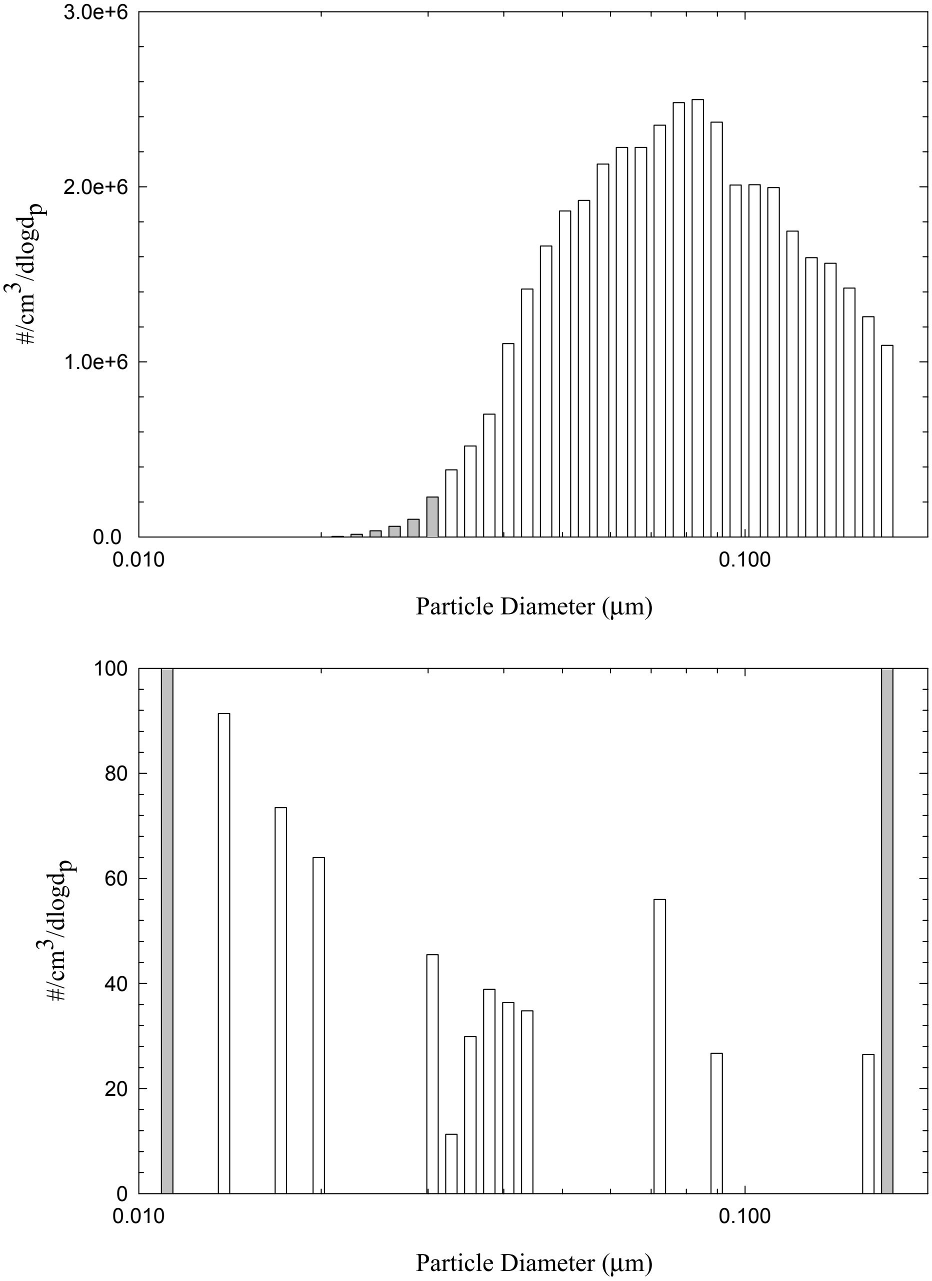


Figure 9. The size distributions of the number concentrations for the fine particles less than 100 nm in diameter with the potentiometer setting, 700 (upper figure: ESP off, lower figure: ESP on).

Appendix C

Atmospheric Sciences Research Center
The University at Albany

Laboratory Evaluation of the Differential TEOM Mass Monitor When Challenged with Volatile and Non-Volatile Aerosol

ESP TEOM Laboratory Tests (ASRC PMlab)

Laboratory evaluations of ESP equipped TEOM were performed in the Aerosol Generation and Characterization Facility of the Atmospheric Sciences Research Center of SUNY-Albany. During these tests stable mass concentrations of aerosol were generated. Aerosol was sampled from a flow chamber using the ESP TEOM, SES equipped TEOM (R&P Model 1400) and a Partisol-FRM Air Sampler (R&P Model 2000). In several tests concentration of aerosol particles in the flow leaving the ESP, was measured using an Ultrafine Condensation Particle Counter (TSI Model 3025), and a Scanning Mobility Particle Sizer (TSI Model 3936).

Aqueous solutions of the following chemical compounds were used to generate polydisperse test aerosol: sodium chloride, sodium nitrate, ammonium nitrate, ammonium sulfate, ammonium sulfate/oxalic acid, ammonium sulfate/glutaric acid. Test aerosols were generated using a Constant Output Atomizer (TSI Model 3076), operating in a recirculation mode. Droplets larger than 3 ?m were removed by a flat-plate impactor, which was installed at the generator outlet. For generation of ammonium nitrate aerosol (semi-volatile compound), the impactor was removed from the generator outlet. The aerosol, after pre-dilution with dry particle-free air and passing through an Aerosol Neutralizer (TSI Model 3054), was directed into a dilution tube, where it underwent main dilution with particle-free air with controlled relative humidity, and then was introduced into the slow flow 480 L chamber. Rate of the air flow used for main dilution varied from 20 to 55 l/min. Size of aerosol particles sampled from the middle of the chamber was less than 1 ?m. The ESP TEOM was also equipped with the SES, the ESP corona current was set to 200, and switching time varied from 2.5 to 6 min. The averaging time for the SES TEOM was 5 minutes. Both TEOMs were operated at 30ºC, and for the most experiments, sampled air at 3 l/min rate. Typical mass concentrations for the experiments ranged from 1 to about 60 ?g/m^3. The tests were conducted with the flow chamber RH below 5%, with the exception of ammonium nitrate experiments, for most of which RH was maintained around 50-60%.

First group of tests included intercomparison of aerosol mass concentrations, or MCs, measured by the ESP TEOM and the SES TEOM. In addition, the SES TEOM MC was compared to the one measured by the ESP TEOM during a period when the ESP was off. In most cases, the ESP TEOM (with ESP off) and the SES TEOM tracked each other very closely (see Fig. 1, 2, 3). The mass concentrations, measured by the ESP TEOM during the priod when the ESP was
on, were looked at as well.

For involatile inorganic aerosols (sodium chloride, ammoium sulfate, sodium nitrate), the ESP TEOM MC fluctuates around zero, when the ESP is on (see Fig. 1). As a result, the ESP TEOM/SES TEOM MC ratio for those aerosols was very close to unity.

For a semi-volatile inorganic aerosol (ammonium nitrate), during the “ESP on” period, the mass concentration, measured by the ESP TEOM was below zero, which indicated that there was an evaporation of particulate matter from a TEOM filter (see Fig. 2). ESP TEOM MC is therefore higher than SES TEOM MC ratio. These results may lead to a conclusion, that the ESP TEOM provides more reliable measurements of ammonium nitrate aerosol concentrations than the SES TEOM. This was further confirmed by a comparison of the aerosol mass concentrations measured by the ESP TEOM with those inferred from the Partisol-FRM Air Sampler (R&P Model 2000) measurements. The Partisol was run twice, sampling ammonium nitrate aerosol in dry and humid conditions (flow chamber RH 0% and 40%, correspondingly). For ESP TEOM vs. Partisol tests, average aerosol mass concentration in the chamber was increased from typical values to 120-220 ?g/m^3. Partisol sampling time was 4 hours, and sample flow was 16.7 L/min. The ESP TEOM/Partisol MC ratio was 0.9 (at 0% RH) and 1.06 (at 40% RH), which translates into ESP TEOM MC errors (relative to Partisol): -9.5% and +5.6%, correspondingly.

Mixed aerosol consisting of an involatile inorganic compound (ammonium sulfate, sodium sulfate) and a volatile dicarboxylic acid (oxalic, glutaric), exhibited behavior, which was different, depending on a type inorganic salt/organic acid used. For sodium sulfate/oxalic acid aerosol, the ESP TEOM MC measured during the “ESP on” period, was above zero, which indicated that there was either a re-adsorption of particulate matter (from the sampling inlet/ESP/TEOM tubing) or a re-deposition of organic vapors on a TEOM filter (see Fig. 3). The ESP TEOM MC is therefore lower than SES TEOM MC ratio.

For aerosol consisting of a “less involatile” inorganic salt (ammonium sulfate) and a volatile dicarboxylic acid (oxalic, glutaric) the ESP TEOM MC measured during the “ESP on” period, was above and below zero, depending on the day of the experiment. This may indicate, that two (or more) competing processes were taking place: irreversible evaporation of inorganic aerosol component from and a re-deposition of organic vapor/re-adsorption of aerosol on the ESP TEOM filter.

In order to check if a significant number of small aerosol particles was generated as a result of the ESP corona discharge, thus leading to an apparent mass concentration increase during the “ESP on” period, an Ultrafine Condensation Particle Counter, or CPC, was connected (through a T-connector) to an ESP outlet, and ran continuously, measuring particles leaving the ESP. The CPC was operated in a high flow mode (1.5 l/min) to minimize potential small particle losses. The size distribution of aerosol, leaving the ESP, was measured using the Scanning Mobility Particle Sizer, or SMPS. The SMPS consisted of an Electrostatic Classifier (TSI Model 3080) with a Long DMA (TSI Model 3081) and the CPC. The SMPS was connected to the ESP outlet, after CPC measurements were completed. The SMPS was operated in a high flow mode as well (1.1 l/min sample flow). During the “ESP on” period, number concentration of aerosol at the ESP outlet was on the order of 20,000 particles/ cm^3, as measured by the CPC. The median number diameter was around 25-30 nm (see Fig.4). Presence of these particles is more likely to result from an incomplete removal of small particles, rather than from particle generation in the ESP corona discharge. Also, the results of the aerosol number concentration and the size distribution measurements at the ESP outlet, may suggest that increased aerosol MC during the "ESP on" is not a result of the presence of the small particles in the aerosol flow.

Second group of tests was conducted to study the effect of NO_2 and SO_2 gases in the flow chamber, on ESP performance. In those experiments, controlled amounts of NO_2 and SO_2 gases were added to the aerosol flow, using a Dynamic Gas Calibrator (Thermo Environmental Instruments Inc., Model 146C). Aerosol mass concentration was monitored continuously with the ESP TEOM and SES TEOM. Gas concentrations in the chamber were measured using a Trace Level Pulsed Fluorescence SO_2 Analyzer (Thermo Environmental Instruments Inc., Model 43C) and a Trace Level Chemiluminescence NO-NO_2-NO_x Analyzer (Thermo Environmental Instruments Inc., Model 42C). Averaging time for the gas instruments was 1 minute. The CPC and the SMPS were used to measure the number concentration and the size distribution of aerosols at the ESP outlet as well (similarly to the experiments described in the previous paragraph). The tests were conducted for ammonium sulfate aerosol (with about 50 and 100 ppb of gaseous SO_2 and 100 ppb of gaseous NO_2), and for ammonium nitrate (with about 50 and 100 ppb of gaseous NO_2 and 50 ppb of gaseous SO_2) sulfate. Results of those tests are shown in Fig. 5 and 6. Addition of the gases did not seem to affect the ESP performance. Aerosol size distributions and number concentrations, measured at the ESP outlet, were similar to those, measured in the absence of the gases.

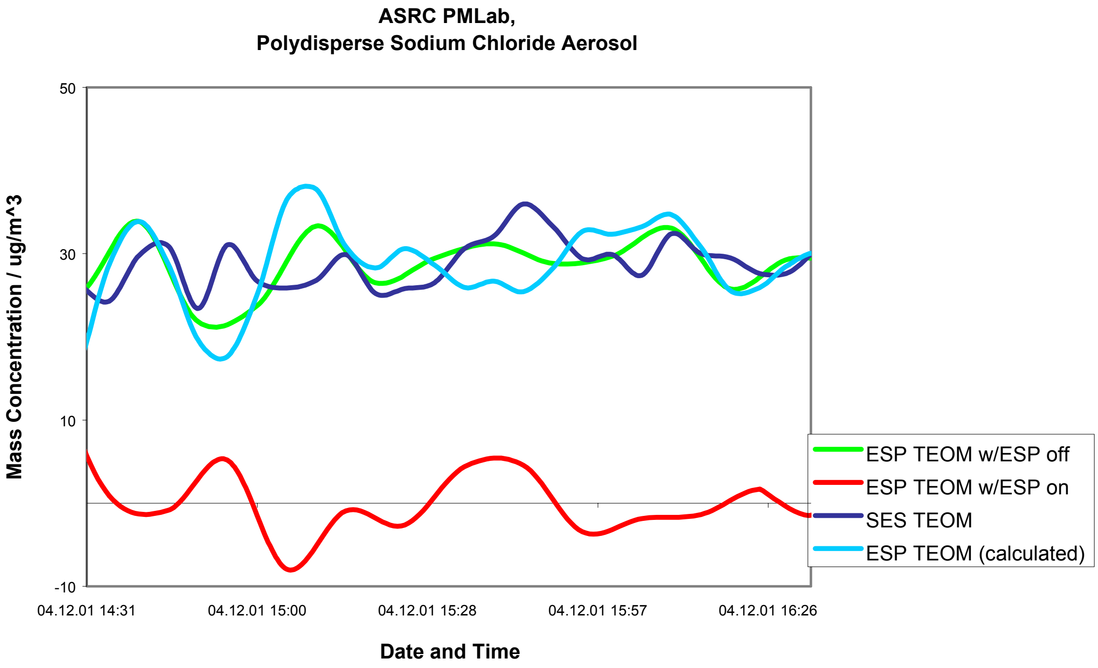


Figure 1. ESP TEOM - SES TEOM comparison for the involatile aerosol.

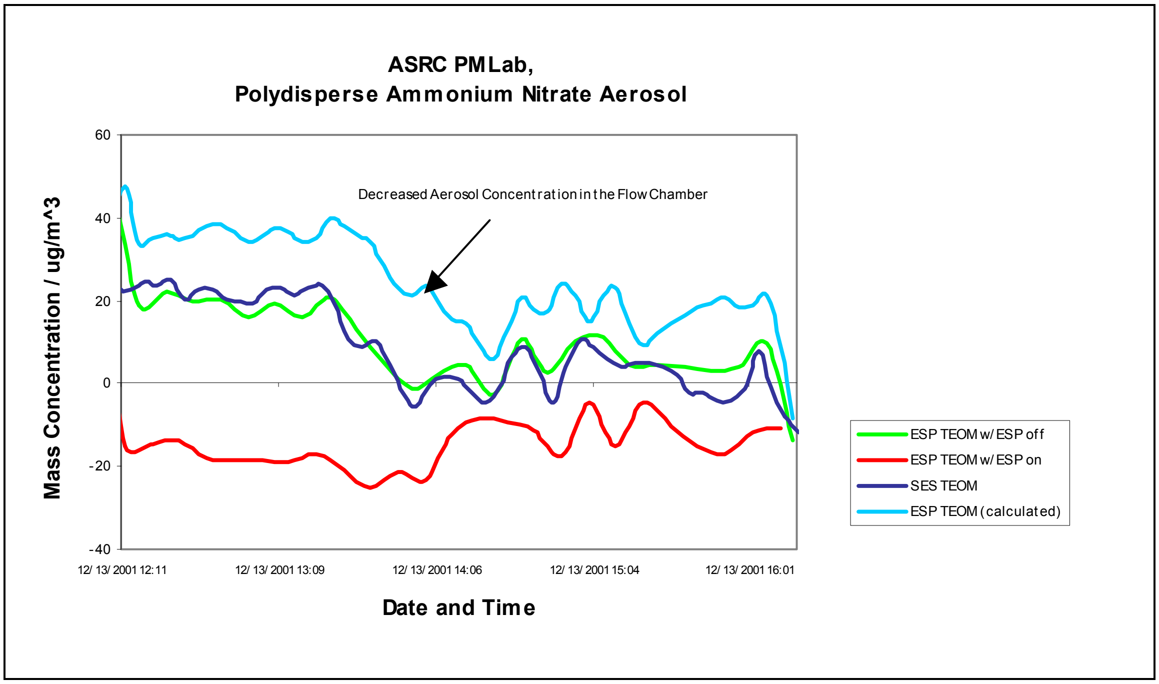


Figure 2. ESP TEOM - SES TEOM comparison for the semi-volatile aerosol.

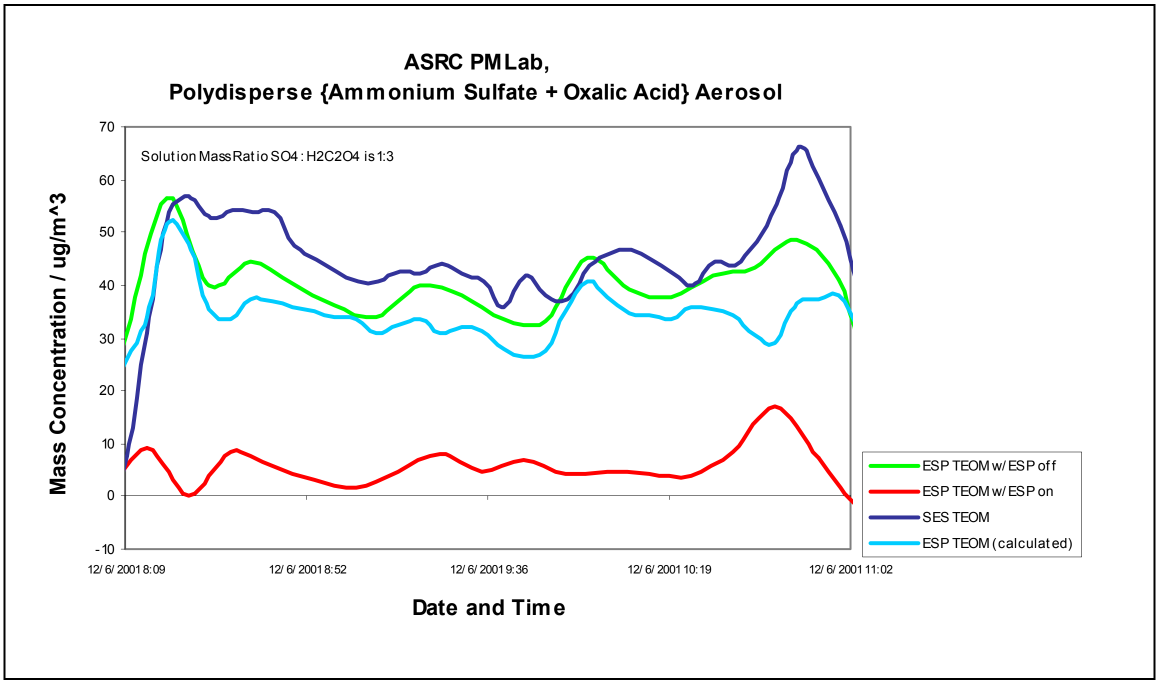


Figure 3. ESP TEOM - SES TEOM comparison for the mixed aerosol.

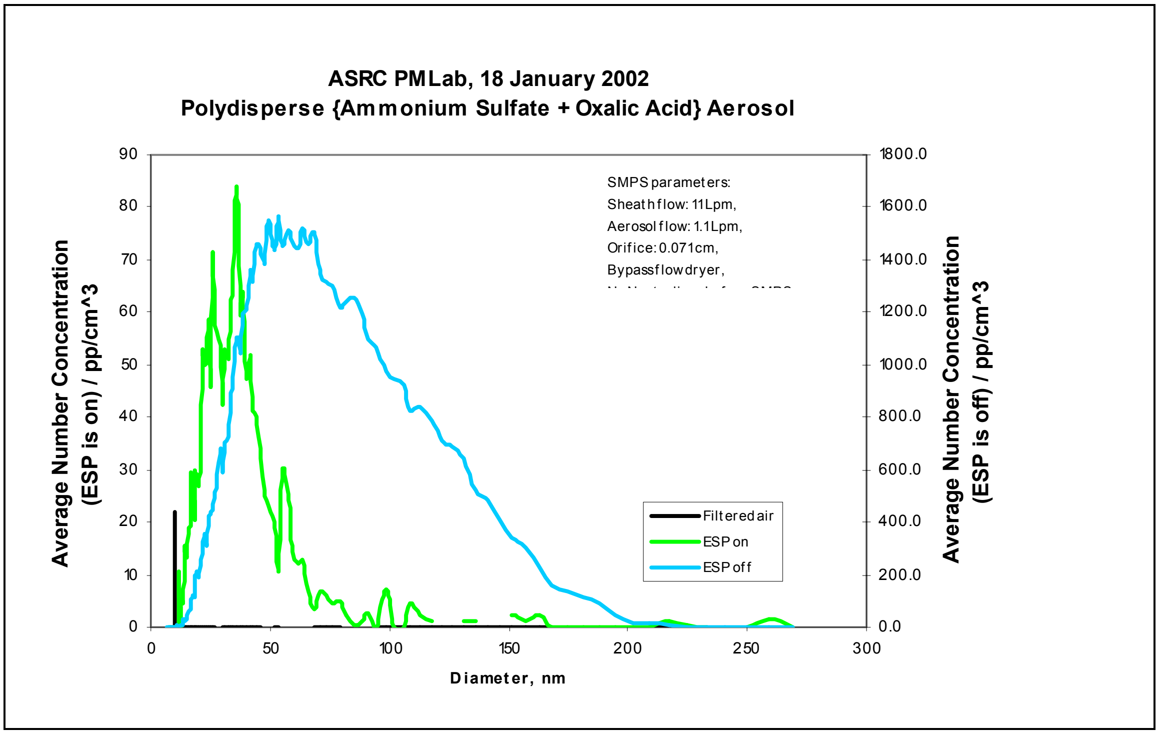


Figure 4. Aerosol size distributions, measured by the SMPS at the ESP outlet.

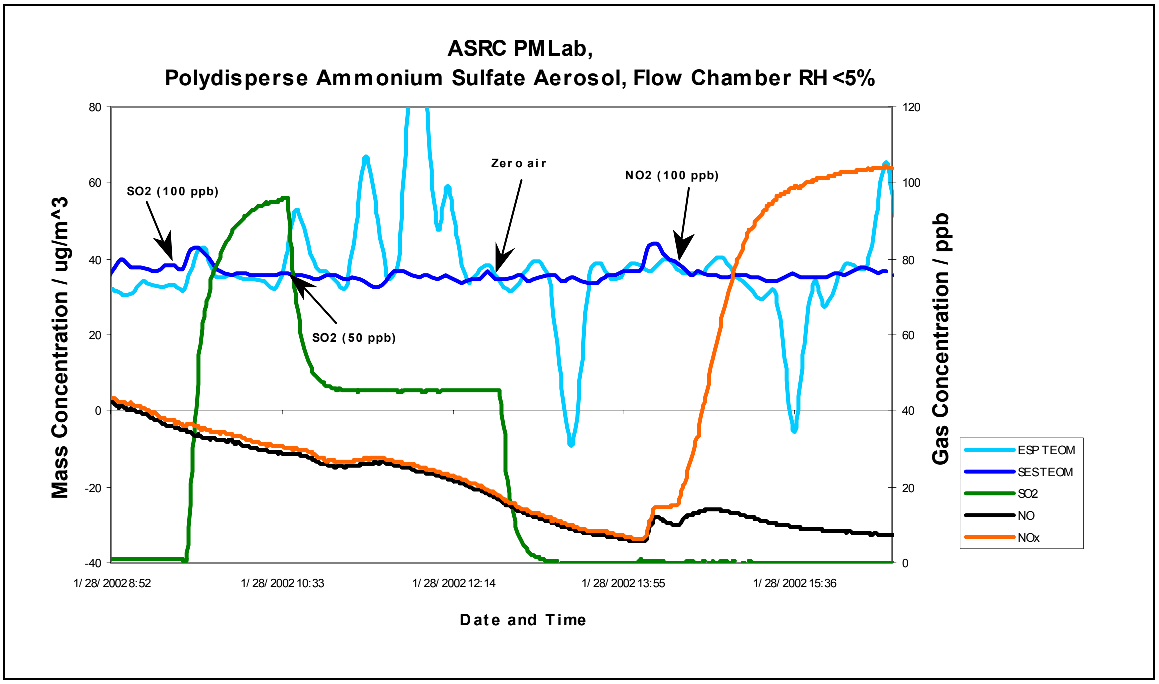


Fig. 5. ESP TEOM - SES TEOM comparison for ammonium sulfate aerosol in the presence of gaseous NO_2 and SO_2 (ESP TEOM peaks result from connecting and disconnecting CPC).

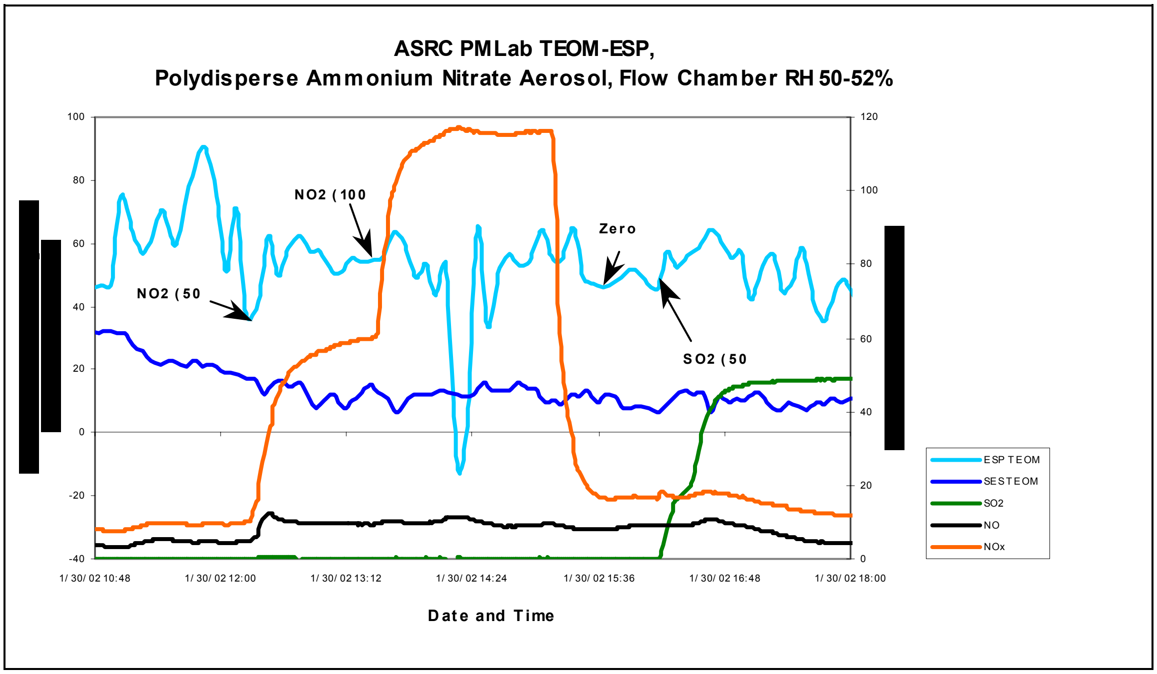


Figure 6. ESP TEOM - SES TEOM comparison for ammonium nitrate aerosol in the presence of gaseous NO_2 and SO_2 (ESP TEOM peaks result from connecting and disconnecting CPC).

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