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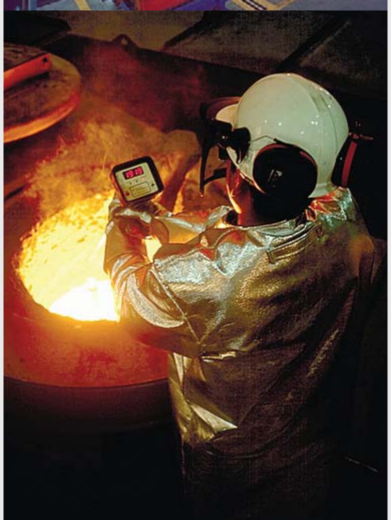

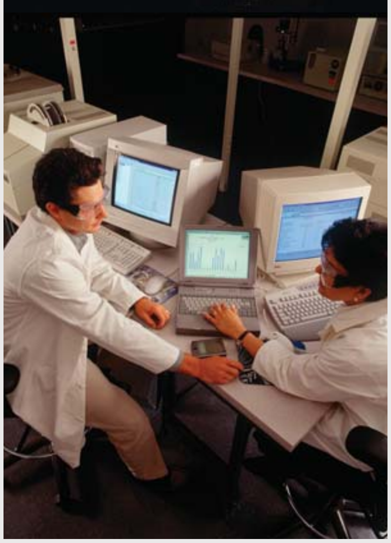

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Sampling and Measurement of Condensable Particulate Matter from Metal Foundry Emissions

1412-217 NA

March 2007
(Revised for public distribution - May 2007)

CASTING INDUSTRY SUPPLIERS ASSOCIATION
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1412-217 NA

This report has been reviewed for completeness and accuracy and approved for release by the following:

Director of Research Technologies	*//Original Signed//* Sue Anne Sheya, PhD	______________ Date
Vice President	*//Original Signed//* George Crandell	______________ Date

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EXECUTIVE SUMMARY

This report has been written to document the status of current and proposed methodologies for sampling and measurement of primary particulate matter emitted from point sources, and describes proposed protocols for conducting side-by-side comparison sampling of primary particulate from foundry emissions using a dilution tunnel and existing and proposed EPA methods.

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1.0 INTRODUCTION

1.1. Background

Technikon LLC is a privately held contract research organization located in McClellan, California, a suburb of Sacramento. Technikon offers emissions research services to industrial and government clients specializing in the metal casting and point source emissions areas. Technikon operates the Casting Emission Reduction Program (CERP). CERP is a cooperative initiative between the Department of Defense (US Army) and the United States Council for Automotive Research (USCAR). The parties to the CERP Cooperative Research and Development Agreement (CRADA) include The Environmental Leadership Council of USCAR, a Michigan partnership of DaimlerChrysler Corporation, Ford Motor Company, and General Motors Corporation; the U.S. Army Research, Development, and Engineering Command (RDECOM-ARDEC); the American Foundry Society (AFS); and the Casting Industry Suppliers Association (CISA). The US Environmental Protection Agency (US EPA) and the California Air Resources Board (CARB) also have been participants in the CERP program and rely on CERP published reports for regulatory compliance data. All published reports are available on the CERP web site at www.cerp-us.org.

1.2. CERP/Technikon Objectives

The primary objective of CERP is to evaluate materials, equipment, and processes used in the production of metal castings. Technikon's facility was designed to evaluate alternate materials and production processes designed to achieve significant air emission reductions. The facility's principal testing arena is designed to measure airborne emissions from individually poured molds. This testing facility enables the repeatable collection and evaluation of airborne emissions and associated process data.

1.3. Report Organization

This report has been written to document status of the current and proposed methodologies for sampling and measurement of primary particulate matter emitted from point sources, and describe proposed protocols for conducting side-by-side comparison sampling of primary particulate from foundry emissions using a dilution tunnel and existing and proposed EPA methods. Section 2.0 of this report includes an explanation of and background for understanding the problems associated with the release of particulate emissions. Section 3.0 summarizes current research in developing and modifying sampling protocols for source particulate. Section 4.0 discusses the proposed study to sample primary particulate from foundry pouring, cooling and shakeout processes.

2.0 Background

2.1. Particulate Matter Concerns

The definition of particulate matter (PM) has evolved as regulations associated with the Clean Air Act (CAA) have been updated. The actual definition of PM is provided in the National Ambient Air Quality Standard (NAAQS) and was originally identified as total suspended particulates (TSP). TSP was made up of all solid material in the air up to 100 microns (µm) in diameter. The NAAQS was subsequently revised and the component of PM used as the health indicator was redefined as material with a diameter less than 10 µm in diameter (PM_{10}). Currently, the definition includes material suspended in the air with a diameter less than 2.5 µm in diameter ($PM_{2.5}$) which includes condensable aerosols. The most recently proposed revision will, if promulgated, add the definition of "inhalable coarse particulate" as particles between 10 and 2.5 µm in diameter.

Particulate matter is identified as a criteria pollutant by the US Environmental Protection Agency (EPA) for which it has developed criteria standards, known as the National Ambient Air Quality Standards (NAAQS). The current NAAQS is based on a particle size of $PM_{2.5}$. Attainment status with the fine PM standard is to be submitted to the EPA for incorporation into State Implementation Plans (SIP). The due date for the new implementation plans for $PM_{2.5}$ is April 5, 2008.

There is a growing international body of epidemiological evidence showing adverse health effects related to exposure to particulate pollution. Large particles have little probability of being inhaled, and have an even lower probability of being deposited in the pulmonary tract. Fine particulates (defined as those equal to or smaller than 2.5 µm in diameter) have unique pulmonary dynamics. They selectively penetrate into lung alveoli, and are deposited deeper in the lungs than are larger particles.

As the definition of PM has evolved, so have the available test methods to determine the concentration of PM in exhaust gases from a source. As specified in the Code of Federal Regulations, 40 CFR Part 51, § 51.15 (a)(2), primary filterable and condensable PM are the components measured by a stack sampling train such as EPA Method 5 and have no upper particle size limit.

Primary particles are those that arise from bulk to particle conversion processes. These particles enter the atmosphere as a direct emission from a stack or an open source. They are comprised of both a filterable and condensable component. Particles that are directly emitted by a source as a solid or liquid at stack, release conditions, and captured on the filter of a stack test train are considered the filterable fraction. Material that is vapor phase at stack conditions, but which condenses and/or reacts upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack is considered the condensable component.

Particles that form through chemical reactions in the ambient air well after dilution and condensation have occurred are considered to be secondary PM. Secondary PM is usually formed at some distance downwind from the source. Secondary PM is not to be reported in the emission inventory and is not covered by the subpart defining particulate matter found in the Code of Federal Regulations.

2.2. Sampling Methods for PM

Particulate matter emissions can generally be classified as filterable or condensable, whether the emissions are PM, PM_{10}, $PM_{2.5}$, or any other size fraction. Typically, EPA's validated reference test methods for PM (EPA Methods 5 and 17) measure only that material that is collected on and ahead of the filter media of the sampling device. The type and size of material collected depends upon the temperature at which the filter media is maintained. These methods collect particulate at filter temperatures of the stack or higher. As a result, these test methods only capture the non-gaseous particulate material and do not capture the vaporous material that will condense in the atmosphere. This captured material is referred to as filterable particulate matter because it is the material that can be filtered out of the gas stream at the indicated temperature.

Other methods that are similar to Methods 5 and 17 are the PM_{10} methods, Methods 201 and 201A. These methods measure in-stack PM_{10} and the difference in these sampling trains and Methods 5 and 17 is that the probe nozzle is replaced by a cyclone, which has an aerodynamic cut size of 10 μm. The method requires only that the material collected behind the cyclone up to the filter be recovered and analyzed. Some source testers recover and weigh the larger than 10 μm material that is collected in and ahead of the cyclone. The summing of this material with the material following the cyclone up to the filter will result in a value similar to Method 17. However, as with Method 17, it may not give the same results as Method 5. With Methods 201 or 201A, the results should be reported as filterable PM_{10}. If the larger than 10-μm material is added to the PM_{10} material, the results should be reported as total filterable PM, with a note that describes the sampling train.

Primary emissions of the condensable PM (CPM) fraction from stationary sources are of increasing concern because studies indicate that these emissions could be significant contributors to ambient $PM_{2.5}$ in some areas. The US EPA has requested that stationary sources conduct CPM emission tests to compile the data necessary to evaluate future control strategies for the $PM_{2.5}$ NAAQS. Reporting of primary particulate matter emissions generated by stationary sources is also required for emission inventories for the National Emissions Inventory (NEI), SIPs, and the Consolidated Emissions Reporting Rule (CERR). The NEI, SIP emissions inventories, and the periodic emissions inventories required under the CERR measurements must contain accurate data for government agencies to effectively manage ambient air quality. These emission inventories are based on a combination of emission factors and site-specific test results, when test results are available.

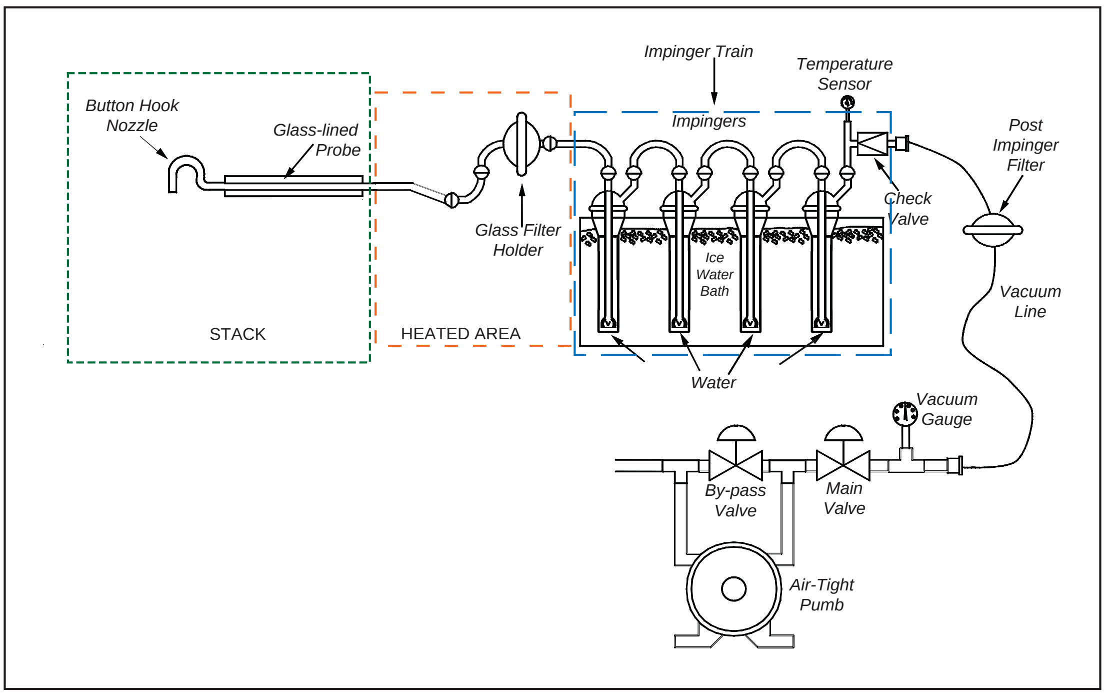
Site-specific test results provide a direct measurement of emissions and are conducted primarily to demonstrate compliance with an existing emission limitation. Emission factors are based on the averages of several site-specific tests. Emission factor development and emissions inventory reporting depend on site-specific tests. Results of site-specific compliance tests must be unbiased and have known uncertainty.

To date, promulgated emissions test methods have not provided reliable data to allow accurate correlation between source emissions and ambient air concentrations. Improved condensable PM emissions factors would enhance $PM_{2.5}$ emissions inventories used by state or local agencies and the US EPA in developing effective control strategies.

2.2.1. Method 202 for Condensable PM

The current EPA methods for sampling PM emissions from stationary sources utilize filters and impinger trains for catching both filterable and condensable particulates. At the present time, US EPA Method 202, Determination of Condensable Particulate Emissions from Stationary Sources, as published in Appendix M of 40 CFR part 51, is the only promulgated method available to measure and quantify CPM emissions. The method as it stands consists of a set of procedures performed on the water filled and chilled impingers used in standard stationary source sampling trains for PM (Figure 2-1). The method uses these water-filled impingers to cool, condense and collect materials that are vaporous at stack conditions and become solid or liquid PM at lower temperatures. It is usually conducted with US EPA Method 5 for the determination of the filterable PM emissions. An optional nitrogen purge is available in the method to minimize formation of artifact compounds by flushing absorbed sulfur dioxide (SO_2) in the impinger water before it can react.

Figure 2-1 Method 202 Sampling Train



Since the promulgation of Method 202 in 1991, air emission testing experience has shown that it is inappropriate to use water-filled impingers to cool the sample gas stream for condensable particulate matter (CPM) sources having SO_2, NO_2, and soluble organic compound emissions. These gaseous components can be partially absorbed in the impinger solutions and chemically react to form material counted as CPM in Method 202. These so-called "artifact" reaction products are not related to the emission of primary CPM from the source and can greatly overestimate actual PM emissions to the atmosphere.

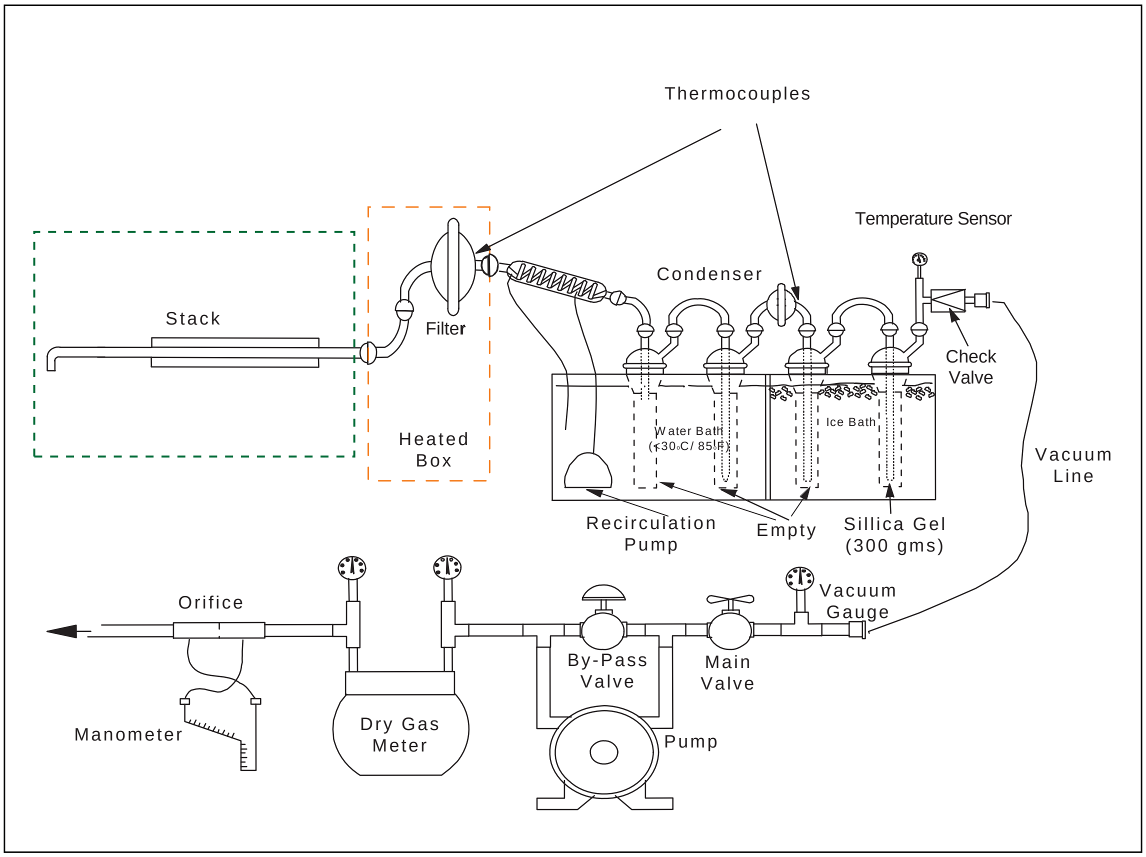
Recent studies have indicated that over 50% of the condensable PM mass can be formed from SO_2 absorbed in the impinger water and converting to sulfuric acid and sulfate artifact from a coal-fired boiler. In some tests, SO_2 related material was shown to be the major source of reportable condensable particulate. If emissions factors are developed using results from these tests, the biases result in biases in the emissions factors. This in turn produces biased national, regional, and facility-specific PM emissions inventories reported in the NEI, SIPs, and periodic reports required by the CERR.

2.2.2. Proposed Modification to Method 202

Discussions and public comments surrounding the rule establishing minimum requirements for the preparation, adoption, and submittal of acceptable SIPs for fine PM described problems with Method 202 in measuring the condensable fraction of PM emissions. The comments highlighted imprecision and biases in the condensable test method both with and without the optional nitrogen purge. Some commenters suggested that biases and variability of the method were due to the presence of ammonia in the emissions gas. Recommendations were made to subtract the ammonium collected in the test method to eliminate this bias.

To address the concerns associated with the existing Method 202, the EPA has proposed that modifications be made to improve the method and to reduce the formation of artifacts. One option for achieving this is to eliminate the water in the impingers. Figure 2-2 illustrates the Method 202 sampling train modifications for improving the method. This so-called "dry" Method 202 has been investigated by several researchers using simulated stack gas as well as using effluents from oil mist collectors on a machining line. The original purpose of the CPM study was "to establish a baseline for Method 202 performance under the ‘best’ EPA recommended conditions” and to compare the results of Method 202 with that of the “dry” train. The EPA does not expect to get zero artifacts using either the current Method 202 or the proposed “dry” impinger Method 202 modification.

Figure 2-2 Method 202 Sampling Train Modifications



2.2.3. Dilution Based Sampling Methods

In response to the positive bias associated with CPM in Method 202, the EPA has also been pursuing the development of a sampling method based on dilution of stack emissions with filtered ambient air. A dilution based method has the potential to be used on a wide range of stationary sources for measuring both filterable and condensable $PM_{2.5}$ and PM_{10} emissions, avoids the water chemistry issues associated with Method 202, and allows PM mass concentrations to approach those that are expected soon after an effluent exits a stack.

This alternative sampling method for stationary sources better reproduces the processes experienced by emissions as they exit a stack, thereby alleviating the discrepancies or artifacts introduced by a heated filter and cold water or "dry" impinger sampling train. Dilution tunnel sampling is internationally recognized as the standard methodology for mobile source sampling (e.g. ISO 8178).

Dilution tunnel sampling methods have the potential to more accurately represent particulate concentrations from stack emissions because they better simulate the natural physicochemical processes of particulate formation in the atmosphere. In these methods, after leaving the stack, hot emissions are rapidly cooled and mixed with ambient air allowing gases to nucleate both homogeneously and heterogeneously, and condense on pre-existing particles in processes analogous to those that occur naturally in the atmosphere. The sampling methodology of a dilution tunnel permits both condensable and filterable particulate to be collected simultaneously. A dilution tunnel provides a potentially continuous monitoring system that will enable measurement of $PM_{2.5}$, PM_{10}, and any other desirable size fractions at the stack.

To date, the EPA has two Conditional Test Methods (CTMs) for dilution tunnel sampling which are available for use but have not yet been certified. CTM-039 is a dilution sampling procedure that approximates the formation of particles that form in a plume downstream of a stack as the stack gases are cooled by mixing with ambient air. CTM-039 uses a PM_{10} cyclone followed by a $PM_{2.5}$ cyclone so both size cuts can be obtained. This method provides results directly in terms of total PM_{10} and total $PM_{2.5}$. Unfortunately, this method requires extremely large and bulky sampling equipment which is expensive to operate and which is vulnerable to wall losses of CPM. EPA has a second conditional test method, CTM-040, that also combines two cyclones in series, a PM_{10} cyclone followed by a $PM_{2.5}$ cyclone. The cyclones are located in the stack, as in a Method 201 or 201A train. The difference in the two methods is that CTM-039 does not have to be combined with Method 202 to obtain both filterable and condensable fractions whereas CTM-040 does.

ASTM International is also developing a dilution based sampling method, D2203 WK752, for particulate. This method will most likely be a performance rather than an instrument based method. It is currently undergoing committee revision and review, and is proposed to be submitted for approval in October 2007.

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3.0 CURRENT STUDIES

3.1. Modified Method 202 Tests

Limited research has been conducted on the proposed modification to Method 202. As briefly discussed in Section 2.2.2, both simulated stack gas and effluent from machine line oil mist collectors have been studied to evaluate artifact formation using impinger trains, which do not contain added water. Additional testing has been proposed to continue this effort using a wider range of conditions on simulated stack gas as well as on actual stack gases.

Limitations for the potential applicability of this method from the simulated stack gas tests, which are described below in more detail, include both the lack of the presence of ammonia and soluble or reactive organic gases to determine ammonium sulfate and organic artifact formation for CPM. The field study described in Section 3.1.3 included reactive organic gases, although results from that study are pending.

3.1.1. Energy Research Group (ERG) Test

Energy Research Group conducted a Round One study on simulated stack gas composed of water, nitrogen oxides, carbon dioxide, and oxygen along with two concentrations of SO_2 -- 25 ppm and 150 ppm. Paired tests were run using wet (existing Method 202) and dry (proposed modified Method 202) impingers. Standard Method 5 and Method 23 glassware was used, except for a short stem impinger insert for the modified dry Method 202. The condenser and impingers were kept at ice water temperature. All sampling trains were purged with Ultra High Purity (UHP) nitrogen for ~1 hour (1 cubic meter). The highest quality solvents available were also used. Samples were recovered following standard Method 202 procedures. Preliminary results indicate that the sulfate CPM residues from the dry impinger train are approximately 7% of those from the wet system. Residual sulfate averaged 13 mg for the low initial SO_2 concentration and 10 mg for the high SO_2 concentration for the wet system. Results for the low and high SO_2 concentrations for the dry train were 0.6 mg and 0.8 mg, respectively.

Round Two tests were the same as Round One with two exceptions; more replicate runs (4-paired trains), slightly more water in the gas, only the higher concentration of SO_2 was used for all runs, and the collection temperature was increased to reduce SO_2 gas solubility. One impinger was also removed to simplify the train. Results for CPM are pending at this time.

3.1.2. Electric Power Research Institute (EPRI) Test

EPRI is ready to conduct supplemental research on the formation of artifacts using the dry impinger train in parallel with the baseline Method 202 as part of EPA's Method 202 Test Plan. Their test plan will include one test replicating conditions from the ERG group. They are then proposing to expand test conditions to challenge the dry impinger method. These more extreme conditions include a greater range of simulated gas conditions, including 15% moisture and 500-ppmV SO_2/sulfuric acid. Testing will include more runs and a controlled condensation system correction alternate test method in an attempt to correct Method 202 inorganic CPM formation.

3.1.3. DaimlerChrysler Test

Parallel simultaneous sampling using the "wet" Method 202 and the "dry" Method 202 was conducted on an oil mist collector from gear cutting machines on a rooftop rectangular stack at a DaimlerChrysler facility. The results of these field tests will give a comparison of CPM from both methods and an estimate of artifact formed from stack gases, which contain organic constituents. Results for CPM are pending at this time.

4.0 PROPOSED STUDY

The great interest in solving the problem of sampling and measuring condensable particulate can best be accomplished by simultaneously sampling from a single source using the existing Method 202, the proposed "dry" Method 202, and a versatile and well characterized reliable dilution tunnel.

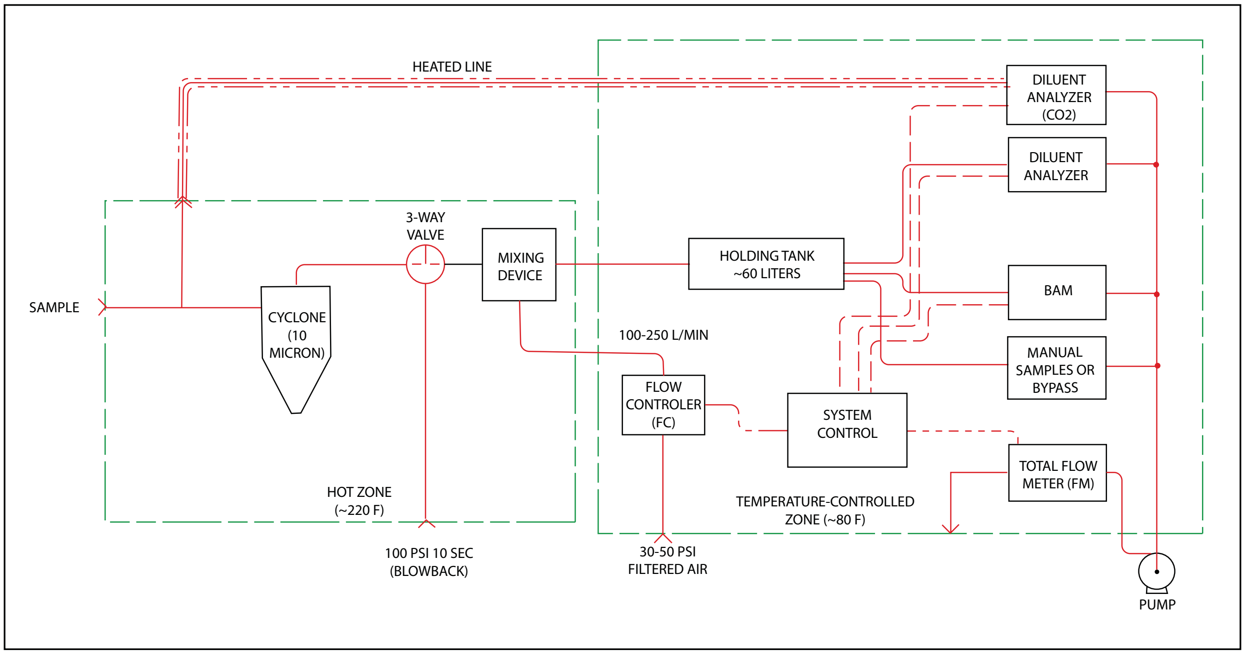
4.1. Dilution tunnel

Previous and current studies of PM measurement as well as most of the current dilution tunnel designs have been based on the so-called "Hildemann" design. This tunnel design has proven useful for many applications, but has never been well characterized in terms of flow characteristics, temperature and pressure profiles, wide ranges of dilution ratios, and the effects of these parameters on the character and mass of collected particulate. These tunnels have tended to be bulky and large, causing difficulties with using them for stack sampling.

To address these shortcomings, Baldwin Environmental, Inc. has successfully designed what they term a Fine and Coarse Particulate Monitoring Continuous Emissions Monitoring System (FCPM-CEMS). This system simultaneously measures and reports mass concentrations of fine and coarse particulate material using Atmospheric Dispersion Simulation (ADS) and Beta Attenuation Monitoring (BAM). This dilution tunnel potentially can provide a continuous monitoring system that will enable measurement of $PM_{2.5}$ and other size fractions at the source. At the present time, there is no commercially available system that performs these functions. The design is such that the tunnel will be fully controllable in terms of dilution ratios, temperature and humidity and can potentially meet dilution tunnel PM testing methods which are either performance based, such as that proposed by ASTM, or instrument based such as CTM-039.

The FCPM-CEMS is designed to maintain a stable and known mixing ratio, ensure thorough mixing of the sampled gas and diluent, equilibrate the mixture to nominal ambient temperature, and provide sufficient delay time before measurement for stable particle formation. The dispersed sample is then transported to a measurement system that will provide PM_{10} and $PM_{2.5}$ data. A supervisory computer control system is provided that manages and reports the results and sufficient system information to verify proper operation and alert the operator to needed maintenance or fault resolution. Figure 4-1 shows a schematic of the components and flow of the system.

Figure 4-1 Schematic of the Components and Flow of the System



The system is physically maneuverable and configurable, being on the order of 6' high and constructed with stainless steel tubing 6" in diameter. It can be positioned in numerous configurations to accommodate the most constrained testing location. Its packaging will allow placement of the system in the proper location at the source facility in order for representative samples to be taken and measured.

Initial testing of the unit will check key parameters to ensure agreement with manually collected samples and for sample losses through the system. Particle size distribution analyzers will be used to ensure that stable particle size formation is achieved. The long-term stability and accuracy of the dilution tunnel under a variety of operating temperature, sample pressure, and humidity conditions will be verified.

Laboratory tests will be conducted to fully characterize the dilution chamber for mixing and flow characteristics using laboratory-generated aerosols. Additional characterization will also be checked using a variety of sources. These sources could include fly ash samples, Arizona Road Dust, salt mist, diesel exhaust, and an oil fired boiler. Secondary filter samples will be collected manually for comparison.

4.2. Scope of Testing

The FCPM-CEMS will be installed at the Research Foundry at Technikon for a portion of the final phase of the verification testing during a pouring, cooling and shakeout test. This test will not only assist in determining the practicality and installation issues with the system and help evaluate the method's analytical accuracy, but provide an opportunity to compare the accuracy of PM measurement methodologies. Simultaneous side-by-side sampling will be conducted with the dilution tunnel, Method 202 and the modified Method 202.

EPA is very interested in comparison testing as CERP and Technikon have provided the means for a unique opportunity to generate data which can not only provide answers to many questions regarding PM method sampling, but also can provide data which will be publicly shared. Because of this, the EPA has offered to supply a CTM-039 sampling train so that PM_{10}, $PM_{2.5}$ and intermediate size fractions can be compared among all systems, thereby achieving the maximum amount of comparable information from the testing. The EPA has also offered to review the Quality Assurance Project Plan (QAPP) for this testing to ensure that the testing plan and generated data are of sufficiently high quality to be useful for both industrial and EPA purposes.

Testing is proposed to be conducted in the summer of 2007 with the assistance of personnel from BEI and the Desert Research Institute.

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APPENDIX A ACRONYMS AND ABBREVIATIONS

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ADS	Atmospheric Dispersion Simulation
AFS	American Foundry Society
ASTM	ASTM International, originally known as the American Society for Testing and Materials
BAM	Beta Attenuation Monitoring
CAA	Clean Air Act
CARB	California Air Resources Board
CERP	Casting Emission Reduction Program
CERR	Consolidated Emissions Reporting Rule
CFR	Cod of Federal Regulation
CISA	Casting Industry Suppliers Association
CPM	Condensable Particulate Matter
CRADA	Cooperative Research and Development Agreement
CTM	Conditional Test Method
DOD	Department of Defense
DRI	Desert Research Institute.
EPRI	Electric Power Research Institute
ERG	Easter Research Group
FCPM-CEMS	Fine and Coarse Particulate Monitoring Continuous Emissions Monitoring System
ISO	International Organization for Standardization
NAAQS	National Ambient Air Quality Standard
NEI	National Emissions Inventory
PM	particulate matter
QAPP	Quality Assurance Project Plan
RDECOM-ARDEC	U.S. Army Research, Development, and Engineering Command
SIP	State Implementation Plan
TSP	Total Suspended Particulates
UHP	Ultra High Purity
US EPA	The US Environmental Protection Agency
USCAR	United States Council for Automotive Research
WBS	Work Breakdown Structure
µm	Micron
mg	Milligram