

DEVELOPMENT OF FINE PARTICULATE EMISSION FACTORS AND SPECIATION PROFILES FOR OIL- AND GAS-FIRED COMBUSTION SYSTEMS

TECHNICAL MEMORANDUM: CONCEPTUAL MODEL OF SOURCES OF VARIABILITY IN COMBUSTION TURBINE PM10 EMISSIONS DATA



When citing this document, please use the following citation:
Lanier, W.S. and G.C. England, “Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Technical Memorandum: Conceptual Model Of Sources Of Variability In Combustion Turbine PM10 Emissions Data” (March, 2004).

DEVELOPMENT OF FINE PARTICULATE EMISSION FACTORS AND SPECIATION PROFILES FOR OIL- AND GAS-FIRED COMBUSTION SYSTEMS

TECHNICAL MEMORANDUM: CONCEPTUAL MODEL OF SOURCES OF VARIABILITY IN COMBUSTION TURBINE PM10 EMISSIONS DATA

Prepared by:

W. Steven Lanier and Glenn C. England
GE Energy and Environmental Research Corporation
18 Mason
Irvine, CA 92618

Prepared for:

Natural Petroleum Technology Office
National Energy Technology Laboratory
United States Department of Energy
(DOE Contract No. DE-FC26-00BC15327)

Gas Research Institute

California Energy Commission – Public Interest Energy Research (PIER)
New York State Energy Research and Development Authority
(GRI contract No. 8362)

American Petroleum Institute
(API Contract No. 00-0000-4303)

Draft (Revision 0): March 11, 2004
Final (Revision 1.2): April 30, 2004
Final (Revision 1.3): November 5, 2004

LEGAL NOTICES

GE Energy and Environmental Research Corporation

This report was prepared by GE Energy & Environmental Research Corporation (as part of GE Power Systems and GE, collectively hereinafter “EER”) as an account of sponsored work. EER, nor any of their employees, makes any warranty, express or implied or otherwise, or assumes any legal liability or responsibility of the accuracy, completeness, or usefulness of any information, apparatus, processes, systems, products, methodology or the like disclosed herein, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply an endorsement, recommendation, or favoring by EER. The views and opinions of the authors expressed herein do not necessarily state or reflect those of EER. This report has not been approved or disapproved, endorsed or otherwise certified by EER nor has EER passed upon the accuracy or adequacy of the information in this report.

United States Department of Energy:

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Gas Research Institute:

This report was prepared by GE Energy and Environmental Research Corporation (GE EER) as an account of contracted-work sponsored by the Gas Research Institute (GRI). Neither GE EER, GRI, members of these companies, nor any person acting on their behalf: a. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any apparatus, methods, or process disclosed in this report may not infringe upon privately owned rights; or b. Assumes any liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

California Energy Commission:

This report was prepared as a result of work sponsored by the California Energy Commission (Commission). It does not necessarily represent the views of the Commission, its employees, or the State of California. The Commission, the State of California, its employees, contractors, and subcontractors make no warranty, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the use of this information will not infringe upon privately owned rights. This report has not been approved or disapproved by the

Commission nor has the Commission passed upon the accuracy or adequacy of the information in this report.

New York State Energy Research and Development Authority:

This report was prepared by GE EER in the course of performing work contracted for and sponsored by the New York State Energy Research and Development Authority, the California Energy Commission, the Gas Research Institute, the American Petroleum Institute, and the U.S. Department of Energy National Petroleum Technology Office (hereafter the “Sponsors”). The opinions expressed in this report do not necessarily reflect those of the Sponsors or the State of New York, and reference to any specific product, service, process, or method does not constitute an implied or expressed recommendation or endorsement of it. Further, the Sponsors and the State of New York make no warranties or representations, expressed or implied, as to the fitness for particular purpose or merchantability of any product, apparatus, or service, or the usefulness, completeness, or accuracy of any processes, methods, or other information contained, described, disclosed, or referred to in this report. The Sponsors, the State of New York, and the contractor make no representation that the use of any product, apparatus, process, method, or other information will not infringe privately owned rights and will assume no liability for any loss, injury, or damage resulting from, or occurring in connection with, the use of information contained, described, disclosed, or referred to in this report.

American Petroleum Institute:

API publications necessarily address problems of a general nature. With respect to particular circumstances, local, state and federal laws and regulations should be reviewed. API is not undertaking to meet the duties of employers, manufacturers, or suppliers to warn and properly train and equip their employees, and others exposed, concerning health and safety risks and precautions, nor undertaking their obligations under local, state, or federal laws. Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

ACKNOWLEDGEMENTS

The following people are recognized for their contributions of time and expertise during this study and in the preparation of this report:

GE ENERGY AND ENVIRONMENTAL RESEARCH CORPORATION

PROJECT TEAM MEMBERS

Glenn England, Project Manager

Stephanie Wien, Project Engineer

Dr. W. Steven Lanier, Project Engineer

Dr. Oliver M.C. Chang, Project Engineer

Prof. Barbara Zielinska, Desert Research Institute

Prof. John Watson, Desert Research Institute

Prof. Judith Chow, Desert Research Institute

Prof. Glen Cass, Georgia Institute of Technology

Prof. Philip Hopke, Clarkson University

AD HOC COMMITTEE MEMBERS

Dr. Karl Loos, Shell Global Solutions

Prof. Jaime Schauer, University of Wisconsin

Dr. Praveen Amar, NESCAUM

Thomas Logan, U.S. EPA

Ron Myers, U.S. EPA

Karen Magliano, California Air Resources Board

PROJECT SPONSORS

Kathy Stirling, U.S. Department of Energy National Petroleum Technology Office

Marla Mueller, California Energy Commission

Dr. Paul Drayton, Gas Research Institute

Karin Ritter, American Petroleum Institute

Barry Liebowitz, New York State Energy Research and Development Authority

Janet Joseph, New York State Energy Research and Development Authority

FOREWORD

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (PM_{2.5}). PM_{2.5} in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and/or incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. These deficiencies in the current methods can have significant impacts on regulatory decision-making. The current program was jointly funded by the U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL), California Energy Commission CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the American Petroleum Institute (API) to provide improved measurement methods and reliable source emissions data for use in assessing the contribution of oil, gas and power generation industry combustion sources to ambient PM_{2.5} concentrations. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source apportionment and source receptor analysis for PM_{2.5} NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities.

The goals of this program were to:

- Develop improved dilution sampling technology and test methods for PM_{2.5} mass emissions and speciation measurements, and compare results obtained with dilution and traditional stationary source sampling methods.
- Develop emission factors and speciation profiles for emissions of fine particulate matter, especially organic aerosols, for use in source-receptor and source apportionment analysis;
- Identify and characterize PM_{2.5} precursor compound emissions that can be used in source-receptor and source apportionment analysis.

This report is part of a series of progress, topical and final reports presenting the findings of the program.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
LEGAL NOTICES.....	IV
ACKNOWLEDGEMENTS.....	VI
FOREWORD.....	VII
LIST OF FIGURES.....	IX
LIST OF TABLES.....	X
ABSTRACT.....	1
1. INTRODUCTION.....	3
Potential Sources of PM Data Variability.....	4
Measurement Methods and Applications.....	5
Design And Operating Conditions.....	6
External Factors.....	6
2. TECHNICAL APPROACH.....	8
3. VARIABILITY OF SOURCE EMISSIONS.....	9
4. POTENTIAL SOURCES OF VARIABILITY IN GAS TURBINE PM EMISSIONS DATA.....	13
Process Design and Operation.....	13
Process Design.....	13
Process Operation.....	22
Measurements.....	24
Measurement Methods.....	24
Sample Collection (Field Procedures).....	34
Sample Analysis (Laboratory Procedures).....	42
Quality Assurance/Quality Control.....	44
Data Reduction and Reporting.....	45
External Factors.....	47
Alternate Measurement Approaches.....	47
5. DISCUSSION.....	50
6. FINDINGS.....	52
REFERENCES.....	53

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 3-1. Cumulative Probability Distribution of Filterable and Condensable Particulate Matter Concentration from Gas-Fired NGCC, Cogeneration Plants and Gas Turbines.....	10
Figure 4-1. Potential Sources of Gas Turbine PM Emissions Data Variation.....	14
Figure 4-2. Schematic Diagram of a Utility Gas Turbine.....	15
Figure 4-3. EPA Method 5 – Particulate Matter Sampling Train.....	26
Figure 4-4. EPA Method PRE-004/202 Sampling Train.....	28
Figure 4-5. Modified Method 8 Sampling Train	30
Figure 4-6. Dilution Sampling System Design (Hildemann <i>et al.</i> , 1989).....	32
Figure 4-7. California ARB Dilution Sampling System (Wall, 1996).	33
Figure 4-8a. Comparison of dilution tunnel and traditional method results (boiler).	39
Figure 4-8b. Comparison of dilution tunnel and traditional method results (process heater).	39
Figure 4-8c. Comparison of dilution tunnel and traditional method results (steam generator)...	40
Figure 4-9. Method 202 Bias Test Results (Wien et al., 2003).	41
Figure 4-10. Cumulative Probability Distribution of PM Emissions Data from 4 Large Combined Cycle Plants Using Modified Method 8.....	49

LIST OF TABLES

<u>Table</u>	<u>Page</u>
Table 4-1. Summary of Critical Fuel Parameters	23
Table 5-1a PM Variability Drivers – Equipment Considerations.....	50
Table 5-1b. PM Variability Drivers – Measurement Considerations.....	51

ABSTRACT

Consistent, accurate measurement of particulate matter emissions from gas-fired turbines is difficult due to the high amount of run-to-run variability that is typically seen when using traditional EPA stack test methods, such as Methods 5 or 17. This high variability is observed in an examination of 92 source tests on 36 different combustion turbines in California. Results of tests using different methods for filterable and condensable PM measurement were examined to determine possible causes for the sources of variability. Large Particles (debris), sample collection time, and artifact sulfate formation were all identified as possible causes of variability by the study.

Artifact sulfate formation impacts the condensable catch, which is not always required by regulatory agencies as part of PM_{2.5}. The problem with the sulfate artifact is the inability to distinguish between sulfates formed in the stack or sulfates formed within the sample collection system, which in traditional condensable sampling is an iced impinger train. Comparisons of condensable PM results obtained using other methods, such as EPA Method 202, and EPA Method 8 indicate that isopropyl alcohol (IPA) in the Method 8 train is less susceptible to absorption of sulfur dioxide gas than the water used in Method 202. A modification to the analytical steps in Method 8 involves drying down the IPA catch and weighing the residue in the same manner as set forth in Method 202. Purging with nitrogen post-test also reduces the sulfate artifact.

A further improvement on measurements from low-emission sources is the use of dilution sampling, where the stack gas is mixed with cleaned ambient air to better simulate the atmospheric processes that emissions undergo as they exit the stack. The cooling and diluting process allows aerosol nucleation and condensation to occur under conditions similar to the stack plume. The mass sample obtained on the filter downstream of the dilution tunnel is subsequently comprised of both filterable and condensable particulate matter free of the sulfate artifact that occurs in the liquid impinger methods. A larger variety of sample media may be used due to the low temperature of the sample stream allowing for broader chemical speciation of fine particulate matter.

Recent tests of emissions from combustion turbines using improved traditional stack testing techniques (e.g., addition of in-stack cyclone to eliminate spurious large particles, gravimetric analysis using a higher resolution balance, greater attention to potential contamination) show more consistent mass emissions from the traditional methods. Chemical speciation of samples from traditional stack test methods indicates a predominance of sulfate particulate matter while dilution test methods show much lower mass emission rate and the predominance of carbon.

1. INTRODUCTION

In 1997, the United States Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles with aerodynamic diameter smaller than 2.5 micrometers (PM_{2.5}). PM_{2.5} in the atmosphere also contributes to reduced atmospheric visibility, which is the subject of existing rules for siting emission sources near Class 1 areas and new Regional Haze rules. There are few existing data regarding emissions and characteristics of fine aerosols from oil, gas and power generation industry combustion sources, and the information that is available is generally outdated and incomplete. Traditional stationary source air emission sampling methods tend to underestimate or overestimate the contribution of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack. Primary aerosol includes both filterable particles that are solid or liquid aerosols at stack temperature plus those that form as the stack gases cool through mixing and dilution processes in the plume downwind of the source. These deficiencies in the current methods can have significant impacts on regulatory decision-making. PM_{2.5} measurement issues were extensively reviewed by the American Petroleum Institute (API) (England et al., 1997), and it was concluded that dilution sampling techniques are more appropriate for obtaining a representative stack gas sample from combustion systems for determining PM_{2.5} emission rate and chemical speciation. These techniques have been widely used in recent research studies. For example, Hildemann et al. (1994) and McDonald et al. (1998) used filtered ambient air to dilute the stack gas sample followed by 80-90 seconds residence time to allow aerosol formation and growth to stabilize prior to side stream collection and analysis. More accurate and complete emissions data generated using the methods developed in this program will enable more accurate source-receptor and source apportionment analysis for PM_{2.5} NAAQS implementation and streamline the environmental assessment of oil, gas and power production facilities. The U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL), California Energy Commission (CEC), Gas Research Institute (GRI), New York State Energy Research and Development Authority (NYSERDA) and the American Petroleum Institute (API) jointly funded this project.

Ambient particulate matter data is collected using measurement methods developed based on particulate loadings, size distributions, and chemical speciation characteristic of ambient conditions. A very different situation exists relative to PM₁₀ and PM_{2.5} (PM_{10/2.5}) source emissions data. Even though environmental regulations limited particulate emissions from stationary combustion sources before the creation of EPA, the methods used to measure particulate emissions were designed for relatively high mass loadings (>0.08 grains/dscf) in stack gases dominated by relatively large diameter particles (>10 μm). The most common approaches for source-level particulate sampling employ an in-stack filter or an external filter heated to a constant temperature (e.g., EPA Method 17 or Method 5). Heating the filter avoids condensation of moisture and/or acid aerosols, depending on the temperature selected. Particles that are aerosols at stack conditions are referred to as “primary” particulate matter. 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 also are referred to as primary particulate matter. Ambient PM_{2.5} data typically indicate that the majority of PM_{2.5} particles in the atmosphere are formed from species that exit source stacks while still in the gas phase. These gases react in the atmosphere to form PM_{2.5} far downstream of the stack discharge, typically over timescales on the order of hours to days. Such particulate matter is generally referred to as “secondary” particulate matter.

POTENTIAL SOURCES OF PM DATA VARIABILITY

A variety of approaches have been used to estimate or measure PM_{10/2.5} emissions. Procedures range from simply assuming that PM_{10/2.5} is a given fraction of the primary particulate matter measured with EPA Methods 5 or 17, to use of in-stack particle sizing methods (cyclones, cascade impactors) and attempts to determine the condensable material in a stack gas stream. Section 4 of this report provides a brief review of many of the measurement methods being employed. Available measurement data indicates that PM_{10/2.5} emissions can be highly variable for many types of sources. To help support scientifically sound strategies for achieving air quality objectives, it is critical to obtain a better understanding of the sources of this data variability. Potential sources of variability fall into three major categories:

- Measurement methods and their application,

- Design and operating conditions of the source, and
- External factors.

Measurement Methods and Applications

As noted earlier, the standard source level particulate measurement methods (Methods 5 and 17) were initially designed to determine compliance with stack particulate emission limits typically on the order of 0.08 grains/dscf (175 mg/dscm). Emission sources that generated stack particulate emissions on this order included combustion systems fired on fuels such as coal, heavy oil, or waste or any of a variety of industrial process such as metal processing. For coal, oil, and waste-fired combustion systems, the majority of the filterable particulate matter in the stack comes from inorganic material (ash) that is an inherent part of the fuel. Natural gas-fired systems, which contain no inorganic material in the fuel, were typically exempted from stack particulate matter regulations.

Since the 1970s, there have been major strides in the ability of control devices to limit particulate emissions. Coincident with those technology developments, new particulate matter emission limits have become increasingly stringent. Because control devices typically are most efficient for larger particles, the fraction of the remaining PM emissions after the control device accounted for by PM₁₀/PM_{2.5} is greater since the removal efficiency is typically lower for these smaller particles. There was general concern among environmental regulators and the regulated community that the low emissions limits were below the level that could be reliably measured. As part of the US EPA's effort to develop emissions standards for hazardous waste fired combustors, the precision of EPA Methods 5 and 5i were examined. Based on comparison of dual train data (two sampling trains simultaneously applied to the same stack) the EPA concluded (EPA, 1999) that the precision of filterable particulate measurements (expressed as the relative standard deviation (RSD) of triplicate dual train measurements) was approximately 10 percent for stacks with PM loadings in excess of 10 mg/dscm. Measurement variability increased exponentially as PM loading dropped toward 1 mg/dscm. (>25 percent RSD at loadings below 1 mg/dscm). A similar result was found in an ASME sponsored study of measurement precision (Lanier and Hendrix, 2001).

Methods to measure condensable aerosols in stack emissions often pass the filtered gases through iced impingers. The mass of condensed material in the impinger catch is subsequently analyzed and the results added to the initial filter catch to determine PM_{10/2.5}. Several studies (discussed in Section 4) have found that artifact sulfate formation from conversion of gaseous SO₂ in the impingers can represent a major bias in measurement of condensed material. Depending on a variety of conditions, this artifact can increase the indicated level of condensable PM_{10/2.5} and increase variability since the determining factors are neither well known nor controlled. Considering the precision issues associated with measuring both filterable and condensable particulate matter, the measurement methods themselves must be considered as a major source of the observed data variability.

Design And Operating Conditions

In addition to the measurement methods, it is also possible that source design configuration and operational parameters can contribute to the observed PM_{10/2.5} data variability. For example, sulfates, nitrates, amines and carbonaceous compounds are significant constituents in secondary particulate matter. Combustion systems, including gas-fired systems can vary greatly in the exhaust concentrations of NO_x as well as the fraction of the NO_x that is NO₂. Natural gas contains trace amounts of sulfur compounds originating from the source gas and mercaptans (sulfur compounds) added as an odorant, leading to trace concentrations (typically less than 1 ppm) of SO₂ in the combustion exhaust gas. Variation in the mercaptan dosing level can impact SO₂ emission levels from a source. Units equipped with selective catalytic reduction NO_x control use ammonia as a reagent and some of that reagent slips into the exhaust. Each of these factors is an example of how system design and operation can affect parameters that might in turn lead to variability in PM_{10/2.5} emission data.

External Factors

Finally, the potential importance of external factors cannot be ignored. Combustion sources such as gas turbines suck in and exhaust large quantities of ambient air. Ambient temperature has a slight impact on peak temperature in most gas turbine combustors that directly impacts NO_x emission concentrations. Shifting wind patterns can cause changes in the level of suspended PM_{10/2.5} concentrations in the air. Ambient PM_{10/2.5} particles may be drawn into the

combustion system and then released as filterable particulate matter. Thus, external factors as simple as shifting wind patterns may contribute to observed variability in PM10/2.5 data.

In considering the overall issue of PM10/2.5 emissions and the variability of the available data, it is also important to keep the significance of data in perspective. Combustion systems such as natural gas fired turbines have inherently low concentrations of key pollutants in their stack exhausts. Since the fuel contains essentially no inorganic material, the majority of the filterable particulate matter will be generated by external sources. (There may be trace levels of filterable carbonaceous particulate matter from inefficiently operated units.) Precursors to secondary PM2.5 such as NO_x, SO_x and ammonia are typically present at single digit part per million (ppm) concentration levels in current state-of-the-art systems. However, the low stack concentrations are at least partially off set by the high volume of gas being exhausted from the stack. In California, PM10 offsets must be acquired to build a new power plant emitting greater than 1 ton per year of PM10. Based on the prevailing PM10 emission factors and test data, a typical 500 MW combined cycle plant employing 2 heavy-duty frame gas turbines have PM10 emissions that may exceed this 1-ton per year threshold. However, if the database is biased high by factors such as those mentioned above, there may not be a need for such a new facility to seek PM10 offsets.

In consideration of the above-described issues, the purpose of this report is to explore the potential sources of PM emissions variability to identify possible avenues for future research programs.

2. TECHNICAL APPROACH

As outlined in the introduction section, available PM10/2.5 source emissions data indicate a high degree of variability, causing uncertainty about the quality of the data and even greater concern about the potential consequences from relying on those data to make regulatory and permitting decisions. Of particular concern are the data from gas turbines. It is clear that a significant effort is required to understand the sources of the observed data variability, to establish appropriate measurement protocols, and to plan and execute test programs to augment the current database. There are, however, many potential parameters that may contribute to the observed data variability. Considering the time and cost of developing a validated database, it is necessary to first compile a list of potential sources of data variability and then to screen that list to identify those parameters with the highest risk impact on PM2.5 emissions from gas turbines. The result of that effort will be a set of recommendations for laboratory and field studies to quantify potentially critical parameter effects. The approach selected for achieving these goals consisted of the following steps:

- **Identify Potential Causes of Variability.** First, an internal project team meeting was held to develop a matrix of potential causes for PM2.5 emissions variation. Results were captured in a “fishbone” chart that served as an initial platform for detailed discussions with selected gas turbine manufacturers and source testing companies.
- **Initial Impact Assessment.** Each of the identified parameters was further assessed to identify whether each parameter was expected to have a high, medium, or low impact on PM measurement results.
- **Key Parameter Analysis and Recommendations.** In this task the parameters deemed to have the highest probability for impacting PM measurement accuracy and precision were further evaluated to determine what insights might be gleaned from the existing database. This analysis helped to develop recommendations for further parameter assessments in laboratory analysis or in additional field tests.

3. VARIABILITY OF SOURCE EMISSIONS

At initiation of this program the California Energy Commission (CEC) had archived a large database of test data on the PM emissions from natural gas-fired power and cogeneration plants employing gas turbine engines. Included were data from 92 source tests on 36 different units of varying size in California. All of the units tested were fired with gaseous fuels. This included units fired on natural gas as well as units fired with various process gases such as might be generated at a refinery. The units tested included combined cycle and simple cycle units, some with supplementary firing and others not, and most with post-combustion emission control equipment such as oxidation catalysts and selective NO_x (SCR) reduction systems. Data were collected using various test methods and measurement protocols. Included in the database is information on the reported levels of filterable and condensable particulate matter for each test.

Examination of the data indicates extremely wide variation in both the filterable and condensable PM mass concentrations from the various facilities. The concentration of filterable particulate matter varied from essentially zero to nearly 9 mg/dscm. Similarly, the condensable particulate matter concentrations ranged from essentially zero to about 7.5 mg/dscm. To further examine trends, data were rank ordered and plotted on a normal cumulative probability plot (Figure 3-1). Also included on the plot are results from regression analysis (solid lines) for the means and 95 percent confidence intervals (dotted lines) assuming that the data are normally distributed.

The filterable particulate matter data shows potentially explainable trends. As seen in the probability plot, the first 25 percent of the data is from tests where filterable PM is reported to be less than about 0.2 lb/hr and appear as an almost vertical line segment on the probability plot. Next, there is a large segment of data covering 25 percent to 90 percent that are ordered in a very linear fashion. Finally, there is a third group of filterable particulate matter data (the last 10 percent) that appear to follow a different slope on the probability curve.

The next section of this report addresses measurement methods in some detail but the more basic concepts can be used here to place the filterable particulate matter data into context.

Measurement of filterable particulate matter involves extracting a sample of the flue gas and passing that sample through a filter. The weight of the filter is determined pre-and post-test after

drying in a dessicator and/or oven with the difference (net weight) defined as the mass of filterable particulate matter collected. The volume of sample extracted depends on many testing variables including the length of the sample process – usually one hour but occasionally extending to as much as 4 to 6 hours per run. For a typical 1-hour sampling run the volume of sample extracted will be on the order of 1 cubic meter. On this basis it is reasonable to assume that, for the first 25 percent of the filterable particulate matter data, the reported mass of filterable particulate matter was on the order of 0.2 milligrams or less. The filter weighing process typically uses a balance with a resolution of 0.1 milligrams. The methods require that the initial and final filter weights be determined to within an accuracy of ± 0.5 mg. Thus, the weight of particulate matter on the filter is known to accuracy no better than ± 0.5 mg. The weight may be reported to a tenth of a milligram but uncertainty of those data far exceeds actual reported results.

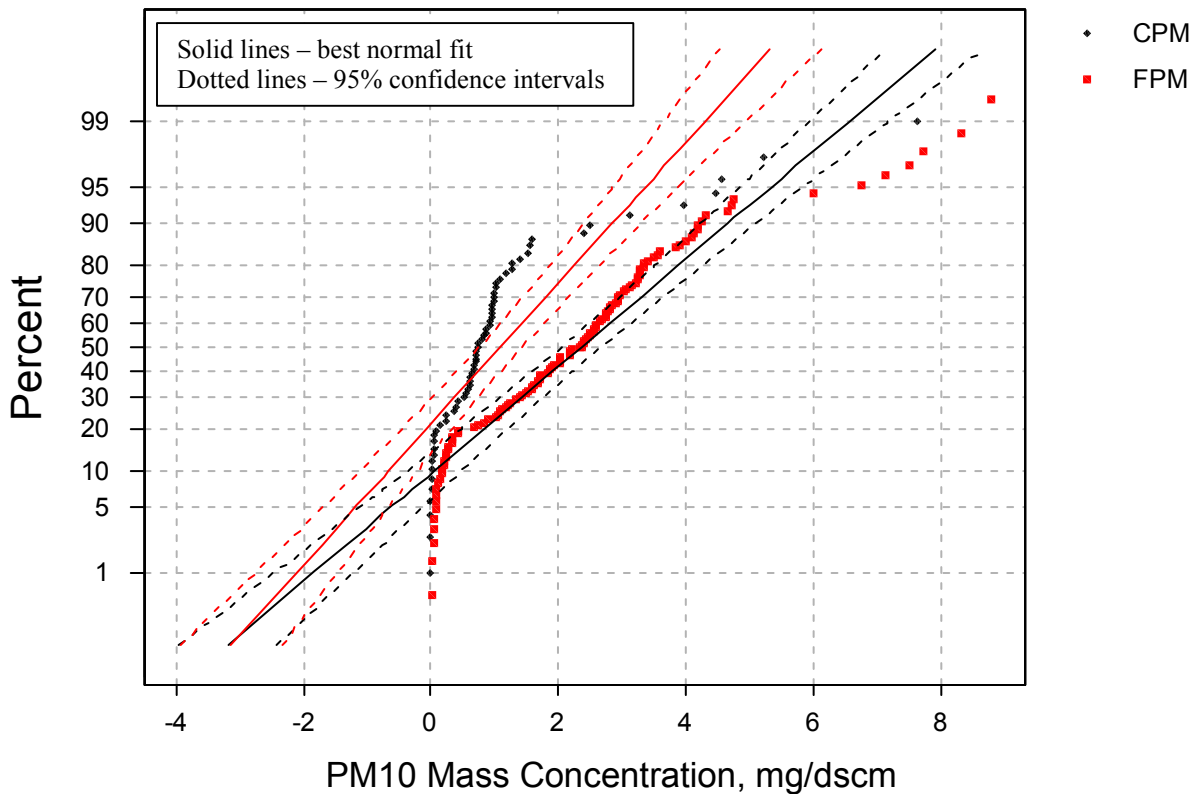


Figure 3-1. Cumulative Probability Distribution of Filterable and Condensable Particulate Matter Concentration from Gas-Fired NGCC, Cogeneration Plants and Gas Turbines.

A further consideration on the first section of the filterable particulate matter data involves a classical problem associated with PM measurement. Following a test, the filter must be removed from its holder for shipment back to the lab for analysis. It is not unusual for the filter to stick to the holder during the sampling process and for small fibers of the filter to be torn away as the filter is lifted from the holder. For sampling events with extremely low actual particulate loadings, the weight of the torn fibers can equal or exceed the mass of collected particulate matter. Assuming perfectly accurate gravimetric analysis in the laboratory, the measured quantity of particulate matter collected can be negative. Since a negative mass makes no sense physically, most firms count and report the negative mass as zero. Some firms may report the negative filter mass, provided care is taken to recover any lost filter fragments in the other sample fractions (e.g., in the acetone rinse of the front half of the filter housing and the filter support), although this is not common.

Considering the accuracy limitations for gravimetric analysis and the existence of negative weight gain, it is not surprising that the first portion of the probability plot does not conform to the remainder of the data set. As noted earlier the vast majority of the filterable particulate matter data (data representing 25 percent to 90 percent of the data) follows a classical normal probability distribution. The final segment of the filterable particulate matter data set (the last 10 percent of the data) appears to have a different characteristic from the remainder of the data. For this segment, it is likely that some key factor or factors were occurring which biases these data from the remainder of the data set. Those factors might have to do with external conditions during the test, a different type of fuel being burned, a problem with sampling process or a problem in the laboratory. The range of potential factors will be discussed in the next section of the report.

Condensable particulate measurements were made for some but not all of the tests shown in Figure 3-1. There appears to be less variability in the total emissions than in the filterable emissions, however this is somewhat misleading because of no all of the filterable particulate measurements have corresponding condensable particulate results and in a small number of tests in the middle range condensable particulate matter was reported together with filterable particulate matter. There are no easy explanations for the trends. From a probability perspective, there appear to be as many as five different segments to the curve. This may be due

to several factors affecting known artifacts (e.g., conversion of SO₂ to solid residue in the impingers, ammonia effects, etc.) that are neither well known nor controlled during the tests and analysis. Clearly the data does not follow a normal distribution and is being significantly influenced by factors other than random variation. Consideration of potential data drivers is provided in the next section.

4. POTENTIAL SOURCES OF VARIABILITY IN GAS TURBINE PM EMISSIONS DATA

An internal meeting was held to brainstorm ideas on potential sources of the observed data variability discussed in the previous chapter. The objective of this meeting was to capture as many potential root causes as possible without regard to the likelihood of a specific potential cause being a major contributor. To provide structure to the process, potential sources of data variability were divided into three major categories:

- Process Design and Operation,
- Measurements, and
- External causes.

An overall summary of the brainstorming session is presented in Figure 4-1. The following subsections discuss the results for each of the three areas.

PROCESS DESIGN AND OPERATION

There are a wide variety of gas turbine systems in operation today and it is certainly possible that differences in the design, fuels, overall system configuration, operating mode, and installed emissions control equipment could contribute to variation in the actual PM emissions.

Process Design

Figure 4-2 illustrates a simple cycle gas turbine that might be installed at an electric utility facility. Although different turbines may have major differences in process design details, there are a number of basic gas turbine process steps. There are three major components to all gas turbines: a compressor, a combustor, and a turbine. The compressor draws in ambient air and compresses it to high pressure. The combustor provides constant pressure heating of the gases while the turbine expands the gases and extracts power.

Gas Turbine PM Emissions

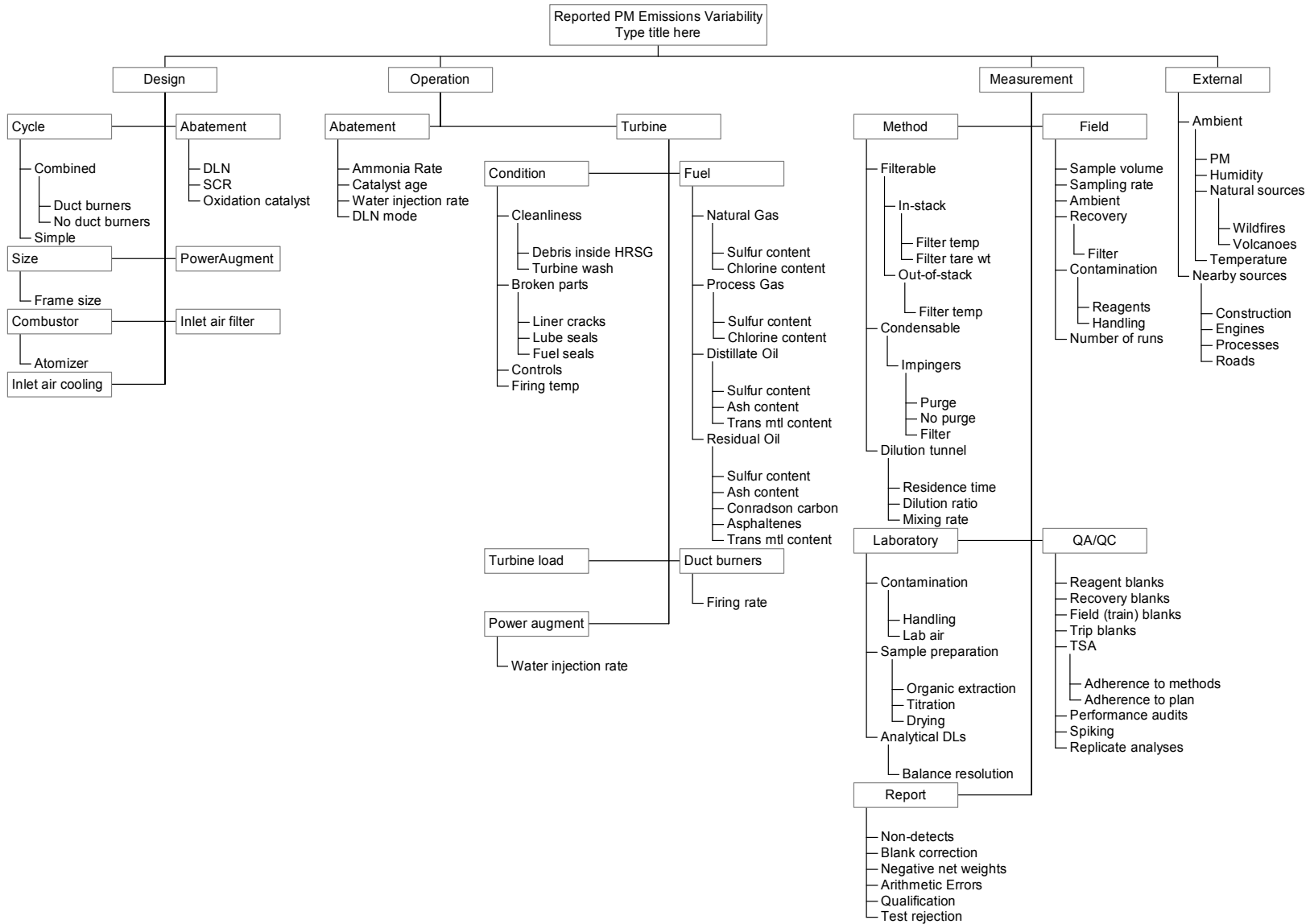


Figure 4-1. Potential Sources of Gas Turbine PM Emissions Data Variation

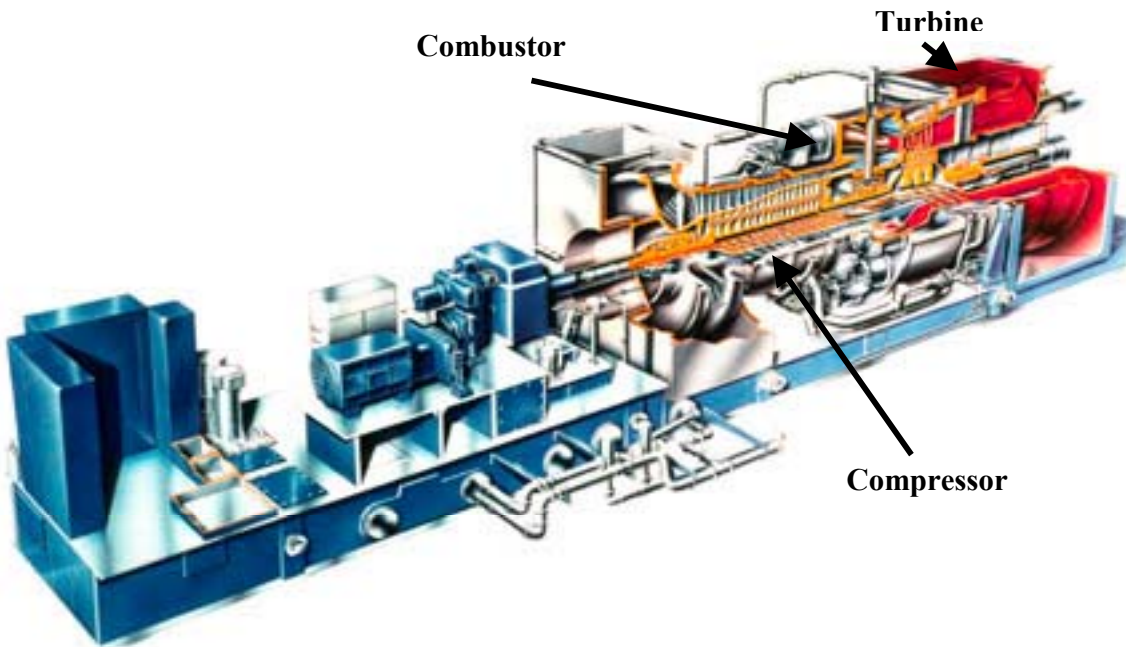


Figure 4-2. Schematic Diagram of a Utility Gas Turbine

Operating the generator at near constant rotational speed facilitates maintaining constant frequency for the output electricity. Constant generator speed is easier to maintain by operating the turbine (and interconnected compressor) at constant speed. This results in nearly constant inlet gas flow rate and compressor outlet pressure ratio (at all power settings). The compressor airflow will vary considerably with ambient temperature, humidity and ambient pressure variations. In modern stationary gas turbines, the use of inlet guide vanes will cause airflow to vary with load changes. For electric utility applications, the compressor will be a multi-stage, axial flow device generating outlet pressure typically in the range of 10 to 20 atmospheres (depending on design).

The most basic design features of gas turbine combustors are actually dictated by the turbine. To extract work, the rotating turbine blades must directly contact the hot gases. For relatively simple turbine designs, metallurgical considerations can limit the combustor outlet temperature to values as low as 1200 to 1500 °F. More modern designs, with advanced materials and sophisticated blade cooling schemes allow turbine inlet temperature to increase to levels well

above 2000 °F, typically on the order of 2500 °F in the current generation of large stationary gas turbines and up to 2600 °F in the latest, state-of-the-art high efficiency stationary gas turbine designs. This temperature limitation applies to all turbine power levels. Since the maximum temperature occurs at maximum power setting, reduced power or idle conditions will necessarily have much lower turbine inlet temperature.

There are several combustor design implications to the turbine inlet temperature limitations. A natural gas flame with a near stoichiometric fuel-to-air ratio will produce a peak temperature of nearly 3500 °F – well above the upper inlet temperature limit for even the most modern commercial turbines. To control the combustor exit temperature, combustors are operated at high overall excess air levels. The full load operating condition will vary between designs but a typical turbine will have about 12 to 15 percent oxygen in its exhaust at maximum power, depending on the size and vintage of the unit. This is achieved by supplying air at about 3 times the stoichiometric requirement. For reduced power settings, even higher excess air levels are required. Inlet guide vanes installed on many units reduce the inlet airflow as load to maintain higher turbine inlet temperatures and hence higher efficiency at reduced power settings.

The flame in the combustor must be stable over the entire operating envelope. Unless the fuel and air mixing process is carefully controlled, attempting to burn fuel with high levels of excess air can result in unstable operation. To maintain flame stability, gas turbine combustors are designed to mix only a portion of the total system flow with the fuel at the beginning of the combustion process. The remainder of the air is sequentially added down the length of the combustor. This allows the combustion air to provide cooling for the combustor walls while maintaining a stable combustion process. The final portion of air addition serves primarily as a dilution process, to achieve the desired overall mean combustor exit temperature level and to tailor the temperature profile of the gases entering the turbine.

When the hot, high-pressure gases from the combustor enter the turbine, power is extracted by expansion. The pressure level drops from levels commensurate with the compressor exit to near ambient conditions. The gas temperature also drops. The turbine exit temperature will vary depending on the power setting or turbine inlet temperature. For a modern, large frame machine the turbine exit temperature will be on the order of 1000 to 1200 °F at maximum power. These

exhaust gases contain a relatively high level of sensible heat. To enhance the overall cycle efficiency, many electric utility gas turbines are equipped with exhaust gas heat recovery components. Such systems are essentially boilers or heat exchangers that cool the gases while generating steam. The major components may be as simple as a steam/air heat exchanger or the unit may burn additional fuel to generate larger quantities of steam. The produced steam can then be used to turn a steam turbine powering a separate electrical power generator.

Within the context of providing the above basic system components, there are many design and configurational differences among different gas turbines. The major process design features identifies as potentially impacting gas turbine PM emissions included:

- Unit Size.
- Operating Cycle
- Power Augmentation
- Combustor Design Type
- Post-combustion air pollution control equipment installed

Unit Size. Gas turbines are manufactured and installed in a wide size range. Units are installed with ratings as small as few hundred kilowatts for emergency power generation while large combined cycle gas turbines for utility application can produce nearly 300 MW. Power output from a gas turbine is directly proportional to the mass flow rate of gases passing through the turbine. Holding other factors constant, variations of gas flow rate between different turbines should have little direct impact on a turbine's PM emission quantity or the speciation of trace constituents that contribute to the condensable portion of the PM emissions. One possible impact of changing mass flow of gases processed by the turbine is the potential for change in the quantity of debris drawn in by the turbine. However, as long as the facility's inlet system is appropriately adjusted to account for the increased airflow rate, the relative concentration of injected debris should be relatively constant.

A second impact of unit size is that the total quantity of fuel burned in the turbine increases with power output. Thus, the mass emission rate of particulate matter directly associated with a fuel

constituent (such as the ash content of a liquid fuel) should be expected to increase with increasing unit size. If the overall power generating efficiency (heat rate) of different turbine sizes is approximately constant, the concentration of particulate matter should also remain roughly constant even though the mass emission rate increases. Finally, there is a general trend toward larger gas turbine systems having higher overall efficiency. Accordingly, large turbines with high efficiency might potentially have lower particulate matter exhaust concentration than small units with lower efficiency.

Operating Cycle. The above discussion of unit size, noted that the efficiency of an installation might have a direct effect on PM emissions since the relative quantity of fuel consumed decreases with increasing efficiency. Significant increases in overall efficiency can be realized by changing a turbine from a simple cycle design to a combine cycle design. Moreover, the heat recovery equipment may be either an air-to-water heat exchanger or the system may be equipped with a duct burner to further increase the quantity of power generated in the steam cycle. To the extent that the relative quantity of fuel consumed might directly impact gas turbine PM emissions, such a trend might be discernable through examination of emissions results for similar size facilities but with different operating cycle.

It is also possible that there could be an impact of the facility's power cycle on the quantity of condensable particulate matter released. Such an impact might occur through complex chemical processes such as an impact on the concentration of nitrates and sulfates in the stack. At temperatures commensurate with levels that occur in gas turbine combustors and turbine sections (at full load), species such as NO_x and SO_x are almost exclusively in the form of NO and SO_2 . As temperature drop toward ambient conditions, there is a shift in thermodynamic equilibrium toward NO_2 and SO_3 . However, chemical kinetic barriers only allow that conversion to occur at a slow rate (relative to the residence time of the gases in the turbine or the heat recovery steam generator (HRSG)). The oxidation reactions can occur rapidly in the presence of certain catalysts. Stainless steel is one of the classic catalysts for oxidizing NO to NO_2 . Thus it is possible that passing the turbine exhausts through a HRSG might impact the relative quantity of NO_2 or SO_3 in the facility exhaust. This could, in turn impact the quantity of condensable particulate matter released. Though possible, this potentiality must be considered remote. Available NO_x

emissions data do not indicate a significant trend of higher NO₂ emissions from combined cycle turbines than from simple cycle systems.

Inlet Air Filtration. Many large turbine facilities are equipped with filters in the inlet air system to limit the quantity of entrained debris entering the turbine. These devices are installed primarily to protect the turbine internal parts from erosion and corrosion. Presence or absence of an inlet air filter could also impact the quantity of filterable particulate matter in the stack. Accordingly, it is possible that presence of an air filter as well as the maintenance state of that filter could impact the variability of turbine exhaust PM emissions data. Filters could be particularly important in preventing large diameter particle ingestion.

Power Augmentation. A number of approaches can be used to augment the overall power output from a turbine installation. One approach is to inject water into the process either at a mid point in the compressor or into the combustor. The added water increases mass flow through the turbine, which increases power output. A second approach is to add an inner cooler at a mid point in the compressor. The use of inner cooling will increase the efficiency of a gas turbine but should have little impact on PM emissions outside those considerations discussed above for unit size and efficiency. Use of water injection may have an additional impact since the mineral and organic impurities in the water may increase the level of filterable particulate matter.

Combustor Design. General issues associated with gas turbine combustor design, including excess air levels, flame stability, and turbine inlet temperature were discussed earlier. Prior to the advent of NO_x emissions requirements, gas turbine combustors were typically designed to provide near stoichiometric fuel/air ratio at the dome section of the combustor and then to sequentially add additional air through slots in the combustor wall. The initial fuel/air mixing process was designed to occur as rapidly as possible, typically with a diffusion flame. This configuration provided maximum flame stability and allowed for very compact combustor hardware. Unfortunately, that general design also tended to provide relatively high NO_x emissions. The advent of environmental regulations (beginning in the mid 1970s) drove major advances in gas turbine combustor design.

Since gas turbines are generally fired with fuels such as natural gas or distillate oil that contain essentially no chemically bound nitrogen, the primary route for NO_x formation is oxidation of

molecular nitrogen in air. The controlling chemistry for this process is relative well understood and is driven by local temperature in the burning process. In fact, for any give pressure and fuel air ratio, the rate of NO_x formation increases exponentially with local temperature. Two basic approaches were used to limit local peak flame temperature and to control NO_x formation. The first approach was to inject water into the head end of the combustor. Vaporization of the water consumed a portion of the heat release and resulted in a decrease in local, peak flame temperature. This is an effective approach that is still widely applied for stationary turbines firing oil. There are certainly adverse impacts of water injection but there is at least one positive side benefit. Since power output is directly proportional to the mass flow of gases passing through the turbine, water addition generates a small positive increment in power generation.

The second basic combustor design approach used controlling peak flame temperature (and NO_x emissions) is to premix (or rapidly mix) the inlet fuel and air and to increase the stoichiometric ratio of gases in the inlet region (more fuel lean). If a combustor generates a classical diffusion flame, there will be a fuel-rich core and an air-rich outer zone with the flame front itself located at the interface where the mixture is at near stoichiometric conditions. That condition provides maximum local temperature and maximum local NO_x production. If the fuel and air can be premixed, the local flame temperature will be consistent with the local stoichiometry. By going to more fuel-lean mixtures, it is possible to suppress the local peak temperature and to achieve a commensurate decrease in NO_x production. The critical issue is accomplishing this change while maintaining combustion stability over the complete envelope of system operation – including full- power, low-load, idle, and start-up as well as transitioning between the various power conditions.

As discussed above, gas turbine combustors may be of the conventional design, may be with or without water injection, or may be of the more modern design broadly referred to as dry low NO_x combustion. These variations in combustor design may have a slight impact on the measured level of condensable particulate matter and thus may impact the observed variability in PM emissions data. One of the clear potential impacts is through the variation in NO_2 emissions – a water-soluble species that may react to form a nitrate that would contribute to the condensable fraction of PM. Note that NO is the predominant constituent in NO_x from turbines and variations in NO should not impact PM emissions. However, since NO_2 is typically formed in the lower

temperature regions, including in the HSRG, variations in total NO_x could indirectly contribute to variations in condensable PM emissions. A second avenue for potential PM impact is through variation in the level of carbonaceous particulate matter produced. Gas turbines generally achieve high combustion efficiency levels and create only trace levels of unburned carbon or higher organic compounds that might contribute to condensable PM. However, the total PM loading from gas turbines is extremely small and variations in carbonaceous particulate matter could contribute to the observed variability in PM emissions.

Post-combustion air pollution control equipment. Many gas turbines comply with federal, state, and local air pollution requirements without use of add on air pollution control equipment. However, in key areas such as California, more stringent state and local regulations have led to broad application of selective catalytic reduction (SCR) for enhanced NO_x control. Some units are also being equipped with oxidation catalysts. Presence of these add-on devices could have an impact on the level of both filterable and condensable particulate matter. Filterable particulate matter could be impacted through processes such as erosion of the catalysts material in either an SCR or an oxidation catalyst.

For an SCR there are at least two avenues by which PM emissions could be impacted. SCRs destroy NO_x through reactions with ammonia (or urea) forming molecular nitrogen and water as by products. Reagent suppliers blend anhydrous ammonia with either distilled/deionized (DI) water or with water processed through a reverse osmosis (RO) process. Typically, aqueous ammonia is procured with about 20 to 30 percent ammonia in the water. Any impurities in the water used to generate the reagent (usually calcium based compounds) will eventually contribute to the level of filterable particulate matter in the turbine exhaust. An additional contribution to PM could come from ammonia that slips through the SCR. In a typical SCR application, ammonia slip concentration will be on the order of 1 to 10 ppm. Ammonia is highly soluble in water and thus will be captured in the condensable portion of most PM sampling systems. Free NH₃ in the samples can increase the amount of dissolved SO₂, and thereby increase artifact sulfate formation, since it instantly reacts in aqueous solution forming ammonium sulfite/bisulfite ions and additional SO₂ must dissolve to maintain equilibrium (Seinfeld and Pandis, 2000).

For an oxidation catalyst, at least two potential processes can lead to variability in PM emissions results. First the catalyst is provided to reduce the level of CO and other organics emitted from the turbine. Presence of an oxidation catalyst could clearly result in reduced levels of carbonaceous material in a facility's stack. The oxidation step is not limited to organics, however. These catalysts can also be effective at oxidizing NO to NO₂. The potential impact of increased NO₂ on condensable PM emissions was discussed above.

Overall, the presences of add on air pollution control devices to the exhaust of a gas turbine installation could certainly impact PM emissions and/or the measurement of PM emissions, positively or negatively. Moreover, variation in the design and operation of those add-on devices could have a variable impact on PM emissions and contribute to the variability seen in the existing database.

Process Operation

The previous section discussed how basic system configuration could potentially impact PM emissions from gas turbine installations. This section discusses how system operations could impact PM emissions.

There are several key parameters in the turbine, HRSG, and emission abatement system operation that could influence PM emissions. These key parameters can be grouped into the following categories:

- Fuels,
- Equipment Condition, and
- Operating Rate.

Additionally there are key operating parameters associated with the emission abatement systems included at a facility.

Fuels. Turbines and fired HSRGs may burn any of a variety of fuels including natural gas, process gas, distillate oil and some units can be operated on residual fuel oil. Table 4-1 summarizes the key characteristics for each fuel type that might have an impact on a turbine's

PM emission rate. The parameters considered potentially important include the fuel’s sulfur, bound nitrogen and chlorine content. The sulfur and bound nitrogen will directly impact the SO_x and NO_x concentrations generated in the turbine. The chlorine content is critical since it will react to form salts that directly contribute to particulate emissions. The level of ash and transition metals in the fuels are also obvious contributors to PM emissions. Finally, fuels such as residual oils can contain high levels of asphaltenes and the Conradson carbon content may be high. These two parameters serve as an indicator for ease of achieving complete combustion. Fuels with high asphaltenes and/or high Conradson carbon will have a propensity to generate carbonaceous particulate matter in the exhaust.

Equipment Condition. The overall condition of a turbine system can have an influence on the PM emissions and thus contribute to the observed variability in the available data. The first consideration is the general cleanliness of the system. Turbines are often washed to remove deposits from various sections of the system. A recently washed turbine could have different PM emissions from the same unit in a dirty state. It is also possible for debris to accumulate inside the HSRG and to variably contribute to PM emissions.

Table 4-1. Summary of Critical Fuel Parameters

	Natural Gas	Process Gas	Distillate Oil	Residual Oil
Sulfur Content	X	X	X	X
Chlorine Content	X	X		
Bound Nitrogen Content		X		X
Ash Content			X	X
Transitional Metals Content			X	X
Asphaltene Content				X
Conradson Carbon Number				X

A second general area where equipment condition could influence PM emissions is existence of broken parts. If there were conditions such as a crack in a combustor liner, or a leak in a lubrication seal or a fuel seal, there could be a direct impact on either the filterable or condensable PM emissions. Clearly such conditions do not represent the norm in gas turbine operation and PM emissions data from units with those problems should be segregated from data used to characterize typical turbine emissions. Failure to segregate the data or to note the general condition of the turbine can contribute to the observed variability in the data.

Finally, the general condition of the emission abatement system can be an important variable in determining the PM emissions from a turbine installation. As noted previously, erosion of catalysts can directly contribute to filterable PM emissions.

Operating Rates. The previous discussion on gas turbine design noted several areas where operating rates could directly impact PM emissions. These include the turbine load, the firing rate of the duct burner (if present) and the rate of water injection for power augmentation or for NO_x abatement. Clearly, variations in any of these parameters could have a direct or indirect impact on PM emissions.

An additional operating parameter of importance is the ammonia injection rate to the SCR system. Many SCR control systems adjust the ammonia injection rate to achieve a desired NO_x emission rate. As the catalyst ages or becomes poisoned, achieving the set point requires increasing the ammonia injection rate. This can directly impact the ammonia slip level, which can have a direct impact on the measured level of condensable emissions.

MEASUREMENTS

The previous portion of this chapter addressed how the design and operation of a gas turbine installation might impact the PM emissions from the facility. Variations in those parameters might contribute to variability in the actual PM emissions. An equally important consideration is the system used to measure PM emissions. There are many different methods used to make PM measurements and various factors can influence the precision and accuracy of the results. This portion of the report briefly describes the various test procedures being used and then examines various factors that could impact the results achieved through their use.

Measurement Methods

The Introduction section of this report provided broad background information of methods used to measure PM emissions from turbines. There are four basic types of systems used to make the measurements, including:

- In-stack filter methods,
- Out-of-stack filter methods,

- Impinger methods, and
- Dilution methods.

Each of the basic approaches is discussed in the following sections. It should be noted, however, that the vast majority of the data on gas turbine PM emissions has been gathered using impinger methods.

In-Stack Filter Methods. The primary example of an in-stack filter method is the US EPA's Method 17. Use of this method is strictly limited to measurement of filterable particulate matter and is normally applied to stack containing gases that may condense at temperature below the stack temperature but above 250 °F. In this method a pre-weighed filter is inserted into the stack and sample is pulled through the filter at a rate to achieve isokinetic conditions. External to the stack a series of iced impingers is provided to cool the sample and to dry the gases to a dew point near 32 °F. Following the impingers are a dry gas meter and a sample pump. The dry gas meter is used to determine the volume of dry sample extracted. The location of the sampling probe and in-stack filter is moved to different positions in the stack to obtain a spatially representative sample. At the end of the sampling period, the probe is removed and weight gain of the filter determined. The ratio of the filter weight gain and the measured sample volume are used to calculate the concentration of filterable particulate matter in the stack.

Out-Of-Stack Filter Methods. The majority of PM emissions data gathered in the US from stationary emission sources use one of several variations on US EPA Method 5. Hardware for Method 5 is illustrated in Figure 4-3. As shown, a nozzle and heated probe are inserted into the stack where a sample is withdrawn isokinetically. The probe is directly connected to a heated box containing a pre-weighed filter. Equipment downstream of the heated filter box is identical to the out-of-stack portion of Method 17 discussed above. In Method 5, the temperature of the probe and the filter box is maintained at approximately 250 °F. About the only difference between Methods 17 and 5 are the physical location of the filter and the temperature of the filter. Any condensed material in the impingers is not considered in determination of PM emissions using this method.

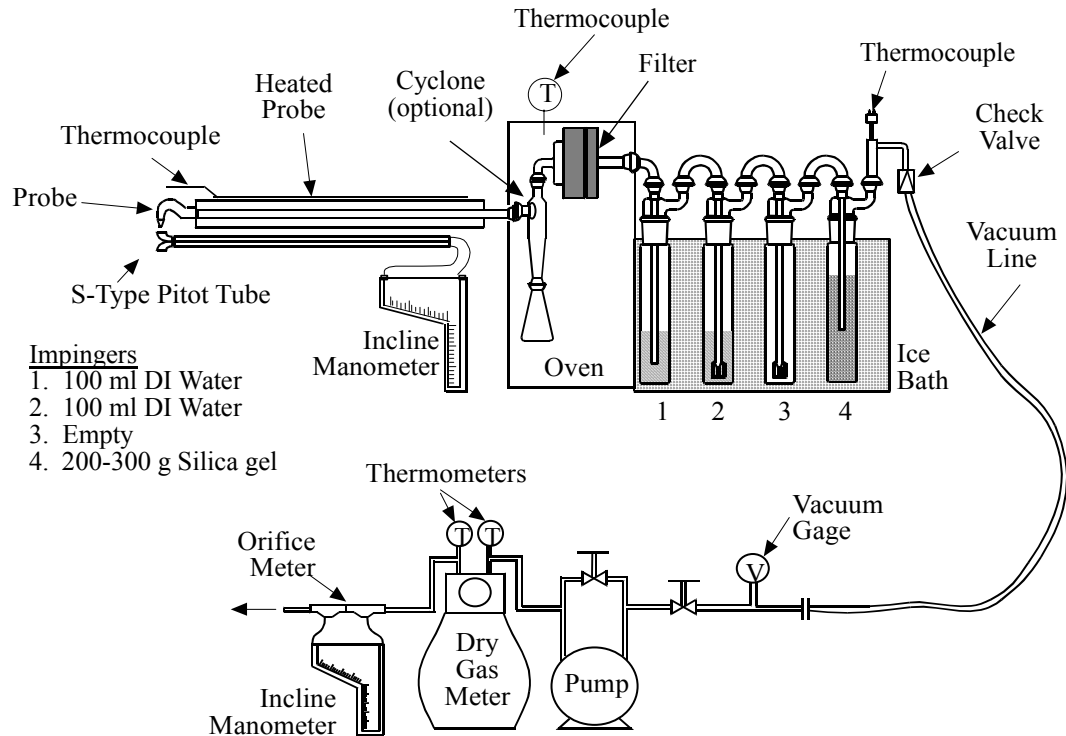


Figure 4-3. EPA Method 5 – Particulate Matter Sampling Train.

As discussed in an earlier section, Method 5 was developed for measurement of stacks with relatively high PM emissions. There was general concern among both regulators and the regulated community that application of this method to stack with PM concentrations below about 0.01 grains/cubic foot could lead to excessive measurement imprecision. One of the perceived sources of data variability dealt with the process of determining the weight gain of the Method 5 filter. In the Method, a 4-inch diameter filter is carefully pre-weighed and placed in a glass filter holder. At the completion of a test run, the filter is carefully removed from the holder and analyzed to determine the tare weight. One observed problem was that the final weight of the “dirty” filter could be lower than the initial filter weight. The usual cause for this obvious problem is that a small portion of the filter gets stuck to the filter housing and is torn away and lost when removed for weighing. In PM sampling situations such as gas turbines, the mass of the torn portion of the filter can be greater than the mass of particulate matter collected in a sample run – thus a negative weight gain and meaningless PM emissions data.

To circumvent the filter problem, the US EPA adapted a procedure pioneered in Europe and developed Method 5i. In Method 5i, the filter and filter holder hardware are different than in Method 5. A 52 mm diameter filter, frit, and filter holder are assembled as a composite unit and pre-weighed. At the completion of a test, the composite assembly is recovered and weighed. This eliminates the possibility of tearing off a portion of the filter during the recovery process. The drawback to this method is that the combined mass of the filter, frit, and holder assembly is high relative to the mass of particulate matter collected. Thus, the net sample weight is a small difference between two large numbers (the weights of the assembly before and after the test) – a classic contributor to measurement imprecision.

Impinger Methods. Several methods have been developed that attempt to determine the emission rate of condensable material. These methods are generally an adaptation of procedures such as Method 5 but providing for analysis of the material collected in the impingers downstream of the filter. In its simplest form, some states require that the impinger water plus condensed sample gas constituents be analyzed for condensed phase material and those results reported as condensable particulate matter. It is common convention to refer this as an EPA 5 “back half” procedure.

To standardize the analytical procedures used for the back half analysis, EPA published Method 202. This procedure has been further refined into a procedure now designated as PRE-004 as illustrated in Figure 4-4. As shown, the hardware incorporates an in-stack 10 μ m and a 2.5 μ m cyclone upstream of an in-stack filter. This is followed by an iced impinger train using water as the impinger solution. Method 202 uses the same hardware except that it does not include the cyclone separators. Two known problems with the

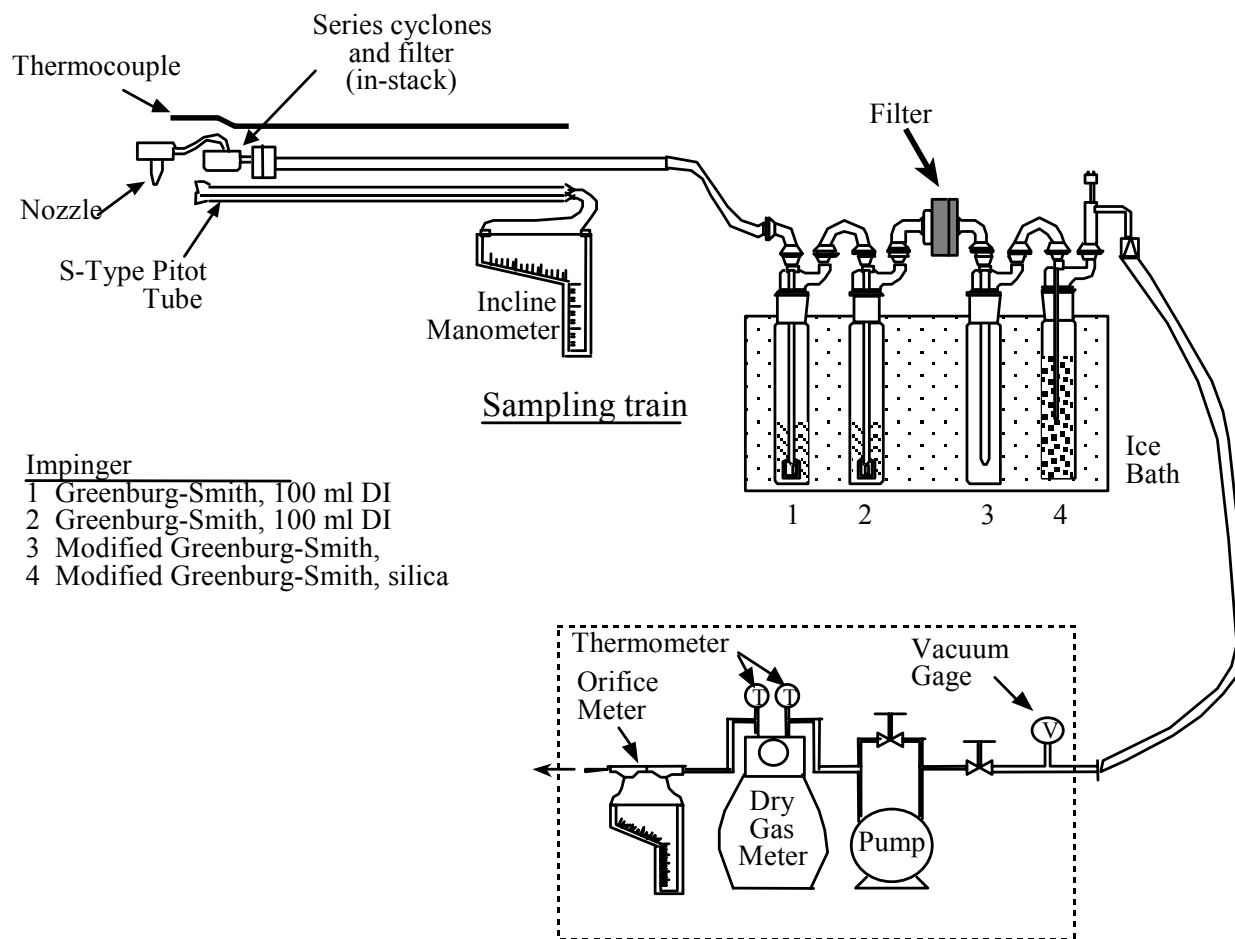


Figure 4-4. EPA Method PRE-004/202 Sampling Train

EPA back half method led to development of these methods. Including the cyclones in Method PRE-004 allow for measurement of only the filterable particulate matter that is smaller than 2.5 microns. Use of the in-stack cyclone significantly impacts the quality of resultant data by removing spurious nonfuel- and noncombustion related particles before they enter a portion of the train that will subsequently be analyzed and reported as part of the facility's PM emissions. In the back half (known as the Method 202 portion of the train), a second filter is added between the second and third impinger. This component is included to address the issue of fine organic fumes that tend to pass through the initial hot filter as well as through the water impingers. The final key feature of Method 202, as compared to a Method 5 back half, is in the manner in which the sampling train is recovered and the potential impact of absorbed SO₂ on the measured level

of sulfates in the condensable fraction. Specifically, Method 202 requires that if the pH of the impinger catch is less than 4.5, the impinger train should be post-test purged with nitrogen. This procedure is an attempt to drive the absorbed SO₂ from the impingers before it has an opportunity to oxidize SO₂ to SO₃ and form sulfate.

There are many variations on the above-described EPA Method 202. Some of the major variants concern initial filtration of the sample. The form of EPA Method 202 illustrated in Figure 4-4 included cyclones to separate particles larger than 2.5 microns from the remainder of the train. A sampling system can be configured with only a 10µm cyclone or with no cyclone at all. Finally, there are measurement methods such as EPA Modified EPA Method 8 that are specifically designed to capture key constituents of PM such as the sulfate fraction. This method is illustrated in Figure 4-5. The key differences between Modified Method 8 and Method 202 are the impinger arrangement, the absorbents used in the impingers, and the analytical procedures used to analyze the material collected in the impingers. Another example variation on Method 202 is South Coast Air Quality Management District Method 5.2 (SCAQMD, 2002_[GCE1]), which includes a different analytical finish on the impinger solutions to determine total acid and total sulfates in addition to gravimetric analysis for mass. A subtraction allowed for the difference between total acid and total sulfates, which is presumed to be sulfuric acid potentially, formed as an artifact of gaseous SO₂ oxidation to H₂SO₄ in the impingers during sampling/storage, and for ammonia if present. EPA recently identified at least 7 significant variations in impinger methods among 22 states surveyed (Riley and Myers, 2002). These variations can have significant impact on the measured result, and are seldom taken into account in emission databases.

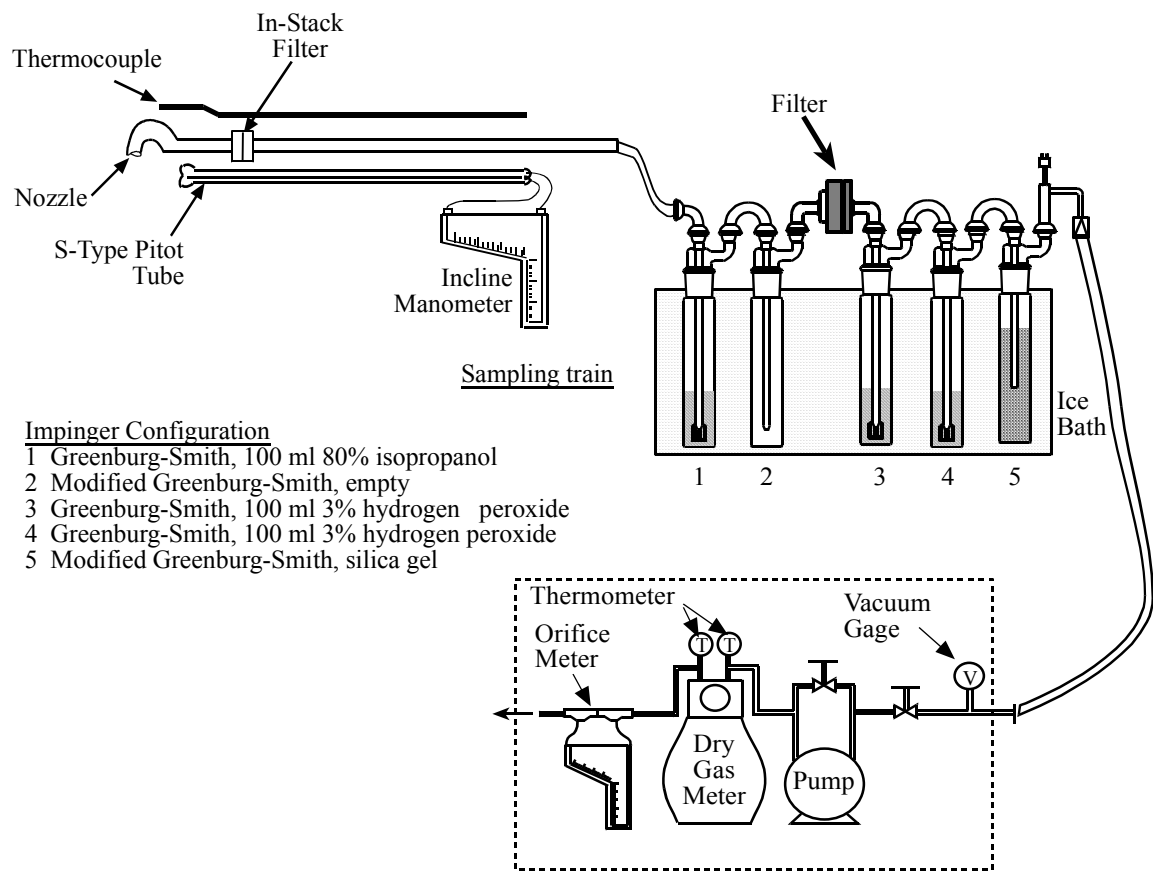


Figure 4-5. Modified Method 8 Sampling Train

Dilution Methods. None of the above measurement processes do a particularly good job of simulating the thermal, mixing, and oxidation conditions that exist as exhaust gases exit the stack. Clearly stack exhaust gases are not immediately quenched to the ice point nor are the absorbed constituents allowed to react in a liquid bath of either water or some other reagent. A different approach that more closely simulates conditions in the plume from a combustion source stack involves first diluting an extracted sample and then sampling and analyzing the diluted gases with ambient air measurement methods. A key component of most modern dilution sampling system is provision of a long residence time section to allow some of the key plume processes such as condensation of low concentration aerosols and diffusion of condensing organic vapors to particle surfaces.

Figure 4-6 illustrates a dilution sampling system developed by Hildemann et al. (1989) designed specifically for analyzing organic aerosols at very low concentration. The system is constructed entirely of stainless steel and Teflon[®] to prevent contamination artifacts and to facilitate solvent

rinsing between sample runs. Stack gas is extracted through an isokinetic nozzle and 10- μ m cyclone. Sample then flows at a high sample flow rate through a heated probe to a dilution chamber, where it is injected in a cross-flow pattern to a high efficiency particulate arresting (HEPA)- and activated carbon-filtered dilution air stream. Hildemann recommended a minimum dilution ratio of 40:1 with this system, and showed that at dilution ratios below 20:1 mixing began to degrade immediately prior to the residence time chamber extraction point. Initial mixing is turbulent, with a Reynolds number (Re) of approximately 10,000. After following the dilution tunnel for 10 tunnel diameters, 20 percent of the diluted stream is withdrawn into a residence time chamber, where the sample is aged prior to extraction of analytical samples. Residence time is approximately 40-60 seconds, to allow condensation processes to go to completion prior to sample collection. Twelve sampling ports at the bottom of the residence time chamber allow parallel sample extraction. Sampling the diluted exhaust directly can capture PM₁₀ samples, while fine aerosol is sampled by equipping each of the 12 ports with cyclone separators of different sizes and sampling downstream from the separators. Flow through each of the sampling filters is measured using a ± 1 percent-calibrated rotometer before and after each experiment. During sampling events, the flow of sample gas is measured using a venturi meter, and flows of dilution air and total exhaust are measured using calibrated orifice plates and Magnahelic differential pressure gauges.

The basic dilution sampling system concept developed by Hildemann has been further developed by a number of groups including Desert Research Institute, Energy and Environmental Research Corporation, Natural Resources Canada, U.S. EPA, and the Pulp and Paper Research Institute of Canada (PAPRICAN).

A number of other groups have used slightly different dilution sampling approaches with varying degrees of success. The US EPA is now actively involved in development of a dilution sampling system. The initial EPA system experienced significant particulate matter loss in the vicinity of a static mixer used to mix the sample gas with the dilution airflow. They are currently designing a new system that will hopefully overcome that limitation.

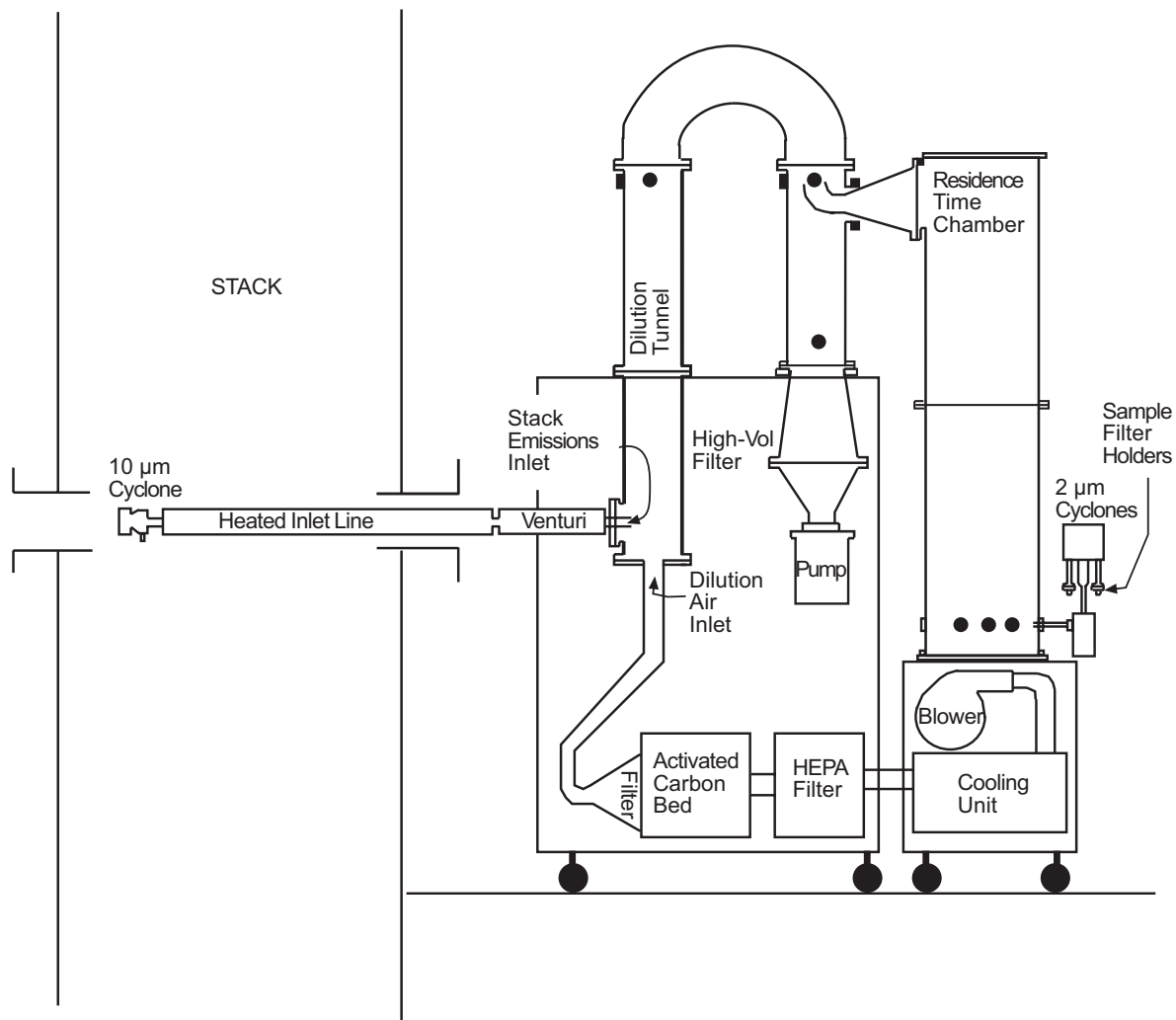


Figure 4-6. Dilution Sampling System Design (Hildemann *et al.*, 1989).

The California Air Resources Board (CARB) has also developed a dilution sampling system designed to characterize condensable species. The CARB system, referred to as the reduced artifact dilution sampler (RADS) is illustrated in Figure 4-7. The system has been applied by the California Department of Health Services (DHS) laboratory to characterize gaseous and aerosol PAH emissions from diesel engines (Lindner and Wall, 1995; Wall, 1996).

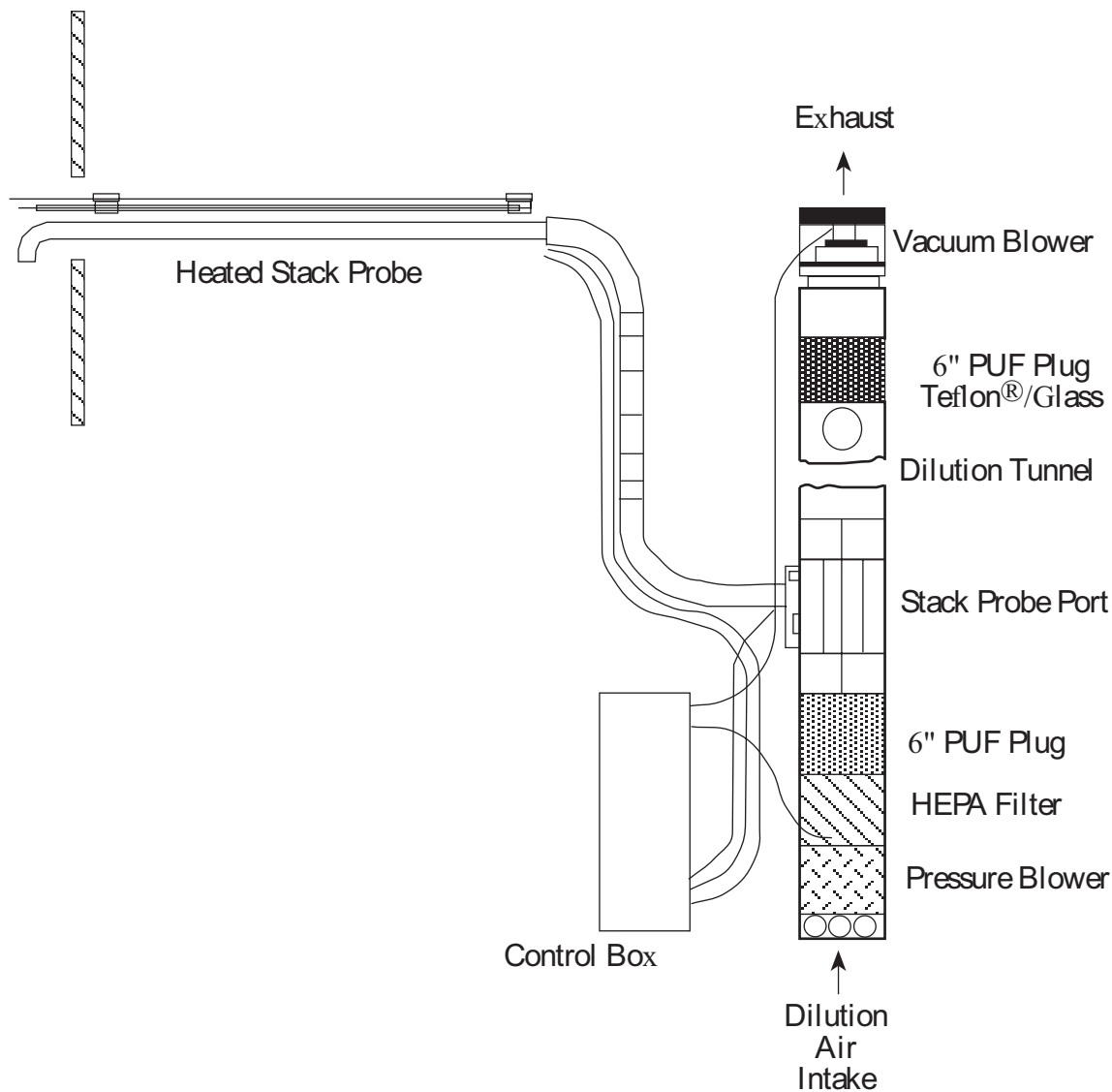


Figure 4-7. California ARB Dilution Sampling System (Wall, 1996).

The sample is extracted from the stack isokinetically without primary particle removal, passes through a heated inlet line and is injected in cross-flow into a flowing stream of purified dilution air. The diluted stream flows through 10 diameters to develop flow before entering the sampling section. The dilution ratio is adjustable from 10:1 to 50:1; at 35:1 dilution, the dilution chamber residence time is 1.5 seconds, while at 10:1 dilution, the residence time is 5 seconds.

Dilution and sample flow rates in the RADS are controlled by microprocessor using mass flow controllers. Several “reduced artifact sampling trains” may be installed in parallel downstream of the dilution chamber; each is equipped with a variable cut size cyclone to remove large

particles upstream of the sample media, followed by a denuder, a 5-inch Teflon[®] filter to capture particulate matter, and a 6-inch diameter PUF cartridge for absorption of gaseous PAH.

Sample Collection (Field Procedures)

The preceding section described the basic methods used to collect PM emissions data from a wide variety of source types. The majority of the available data from gas turbines has been developed using methods similar to that described as EPA Method PRE-004 involving cyclone filters to remove any large diameter particles, a heated filter to catch particles followed by a series of iced impingers to collect condensable particulate matter. The current section discusses how this type of sampling system is applied in the field along with discussion of various ways that the field procedures may influence data variability.

The formal EPA measurement method recognize that the concentration of pollutants may not be constant across a stack, that sources do not always operate in exactly the same manner over an extended time period, and that there can be data variability introduced by the field testing technicians. Accordingly, the EPA specifies that sample gas must be extracted from a sufficient number of stack locations to obtain a composite sample representative of the total stack. To account for temporal variations, the reported emissions data are to be the average of at least three sequential test runs with each run providing approximately one hour of actual sample extraction. The rate of sample extraction should be between about 0.5 and 1.0 scfm. Thus the total volume of sample extracted during a 1-hour run will be between 30 and 60 cubic feet. A typical sample volume will be on the lower end of that range (e.g., about 40 cubic feet is typical). Note that the Methods do not limit the sampling time to 1-hour.

Before the start of a test run several critical steps must be taken. First, the weight of each filter to be used in the tests must be accurately determined (to within ± 0.5 mg) and recorded. When the train is being assembled, the technician must carefully determine the volume of reagent (usually water) added to each impinger and weigh each impinger. Great care must be taken to prevent contamination of the train during assembly.

During the run, the field technician will regularly record the volume of sample collected, adjust the sample extraction rate (based on velocity data from the pitot probe) to assure an isokinetic sampling rate, and note the temperature of the gases leaving the impinger train. The ambient

pressure should also be determined. At the end of the run, a post-test leak check of the equipment must be performed to assure that the sample was not being diluted.

After each run is complete, the assembled train (including probe, filter, and the entire impinger train) is taken from the stack to an on-site clean area for recovery. There are multiple steps in the recovery process. The initial portion of the sample probe (either the entire nozzle and connecting section leading to the filter or just the connector between the cyclones and the filter) must be triple rinsed and brushed to recover any particles that may have deposited on the probe walls. Acetone and a Teflon® brush are used for this rinsing step. The rinsate is collected in a beaker that is either 125 or 250 mL volume. Traditionally the beaker was made of glass but for low PM loading measurements, most test firms now use a thin Teflon® liner inside a support beaker. Those liners are referred to as “baggies”. Next, the filter is carefully removed from the holder and substrate and transferred to a petri dish that is sealed for shipping to an off-site laboratory. The filter holder is also rinsed with acetone and the rinsate added to the probe rinse. This completes the recovery for the front half of the train.

For a traditional EPA Method 5 test, the only remaining recovery step is to weigh the impinger. The difference between initial and final weight indicates the amount of moisture collected from the sample. For determining condensable particulate matter, the impinger water is transferred to a Teflon® jar for shipment to the laboratory. The impingers and connecting glassware are first triple rinsed with ultra-pure water and the rinsate added to the impinger jar. This is to collect any inorganic condensables that may remain on the impinger walls. Next the impingers are triple rinsed with methylene chloride to recover organic condensable residue. This is also added to the same jar of impinger liquid.

It is important to note that EPA Method 202 contains a provision to account for the potential of bias due to absorption of SO₂ in the impinger water and with subsequent liquid phase oxidation to sulfate. Specifically, if the pH of the impinger catch is < 4.5, then the impingers should (or may) be post-test purged with nitrogen for approximately 30 minutes to strip absorbed SO₂ from the impingers. Such a low pH typically occurs when a sampling a source with high SO_x level. Generally, the impinger catch for natural gas fired devices will be closer to neutral.

Opportunities For Introducing Data Variability. Within the sample collection and recovery process there are numerous opportunities for contamination of the sample and for introducing bias in the results. Some of the more classical opportunities include scraping the probe nozzle tip on the wall of the sampling port when the probe is being inserted into the stack. It is also very easy to break a quartz nozzle, allowing a portion of the nozzle debris to be sucked onto the filter.

Sampling Time. When sampling PM emissions from sources burning clean fuels such as natural gas, the total quantity of particulate matter collected will be inherently low. Often, the mass of collected material will be at or below the detection limit for the analytical analysis equipment. For example, the pre- and post-test weights of filters are determined to an accuracy of ± 0.5 mg. If the mass particulate matter deposited on the filter is less than 1 mg, it is likely that this critical analytical result will be lost in the precision and accuracy of the analytical process. To at least partially overcome this data limitation, the sampling time can be increased above the minimum 1-hour limit set by the EPA method. It is suggested that the PM sampling time for measuring gas turbine combustor exhaust be increased from 1 to as much as 6 hours.

Contamination. As noted earlier, great care must be used to prevent contamination of the hardware and recovered sample. One precaution is that the technicians assembling the hardware and recovering the sample must wear latex gloves. This prevents body salts and oils from contaminating the glassware or sample. However, the gloves must be of the non-powdered variety. Many people prefer to wear powdered gloves but the powder can easily contaminate the measurements.

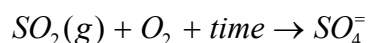
Another potential source of data bias is contamination in the acetone, water and methylene chloride used for sample recovery. Use of reagents that are not ultra-pure can add bias to the sample. This bias is at least partially controlled through use of reagent blanks that are sent to the lab for analysis and then blank correcting the analytical results.

Filter recovery. Another key opportunity for data bias occurs when the filter is removed from the holder and substrate. This process was addressed earlier in the discussion of EPA Method 5i. The concern is that small fibers of the filter will stick to the holder and be torn away during recovery. The prevalence of this problem is documented by the fact that a large portion of the

filterable particulate matter data from tests of gas fired combustion devices show negative weight gain. That is, the small mass of the fibers remaining on the edge of the holder exceeds the mass of true particulate matter deposited on the filter during the test run.

Operator training and experience. A further potential source of data variability relates to the training and experience of the field-testing crew. Most field-test technicians learn the trade performing measurements on sources with relatively high PM emission levels. Often they simply do not know about all the precautions that must be taken to obtain high quality data from sources with extremely low PM exhaust concentrations. Moreover, there is seldom any feedback to help them understand the criticality of the small details. The early history for field application of EPA Method 5i, serves to illustrate these considerations. In addition to the modified filter holder and recovery steps, Method 5i also requires that data be collected using dual sampling trains and that the difference between the simultaneous measurements be less than 10 percent. Two different testing firms, Energy and Environmental Research Corp. and Air Techniques were retained to perform extensive test series using this new method. Both groups report that, using seasoned test crews, results from approximately the first twenty test runs had to be discarded because of data precision shortcomings. After the crews learned of the precautions necessary for low-level measurements, subsequent results easily met the Method precision requirements. The filterable PM concentration levels being measured by these two test teams (on different sources) were on the order of 10 to 40 mg/dscm. Emissions from gas-fired gas turbines are typically lower by an order of magnitude (or more). It is likely that for measurements in this range, there are many other details that must be tended to if high precision data is to be gathered.

Artifacts. Perhaps the most significant single source of variation in measurement of PM from gas fired combustion systems is the potential for forming sulfate artifacts. The existence of this bias is well documented in previous studies including papers by the US EPA (1990), by Filadelfia and McDannel (1996), and by Corio and Sherwell (2000). The bias is caused by absorption of SO₂ in the impinger water and subsequent conversion to sulfate via the following mechanism:



The overall importance of this bias in gas turbine PM measurements is illustrated by the work of Wien, et al. (2003). Wien reports results from tests conducted on a refinery gas-fired boiler, a refinery gas-fired refinery process heater, and a natural gas-fired steam generator in an oil field. Simultaneous tests were conducted using an EPA PRE-004 sampling train (see figure 4-4) and a dilution sampling train similar to the system illustrated earlier in Figure 4-6. Results from those tests, shown in Figure 4-8, found major differences between the dilution tunnel tests and the Method PRE-004 tests. In all cases the PRE-004 results found that filterable particulate matter was at or below the method detection limit while substantial levels of condensable PM was detected. Tests at the boiler and the process heater did not include the post-test nitrogen purge since the impinger pH was above 4.5. However, the purge was performed in steam generator tests. Note that the indicated levels of condensable particulate matter were substantially lower at the steam generator site. The PM_{2.5} results from the dilution tunnel were more than an order of magnitude lower than the PRE-004 results for all three test programs.

Based on the large reduction in condensable particulate matter results at the steam generator site, Wien et al. suspected that the impinger results may have been biased high due to dissolved SO₂. To better quantify the bias, a series of controlled laboratory experiments were conducted. Simulated stack gas (O₂, CO₂, NO, N₂, and SO₂) was passed through Method 202 trains, varying the sample time at 1 and 6 hours and the SO₂ concentration

at 0, 1, and 10 ppm; no condensable substances were added. (Note that the stack SO₂ concentration at the three sites varied between 0.3 and 8 ppm.) The lab tests were performed with and without a post-test nitrogen purge. The trains were then analyzed according to Method 202 for inorganic and organic condensable mass and sulfate concentration. Results from the tests are presented in Figure 4-9. Data from the field tests are also shown for comparison on the 6-hour run graph and are seen to agree relatively well with the lab scale data. In examining these data it is important to reiterate that there was no condensable material added to the lab scale test and thus any indicated sulfate from the tests represents a measurement bias. The post-test purge did significantly reduce the sulfate concentration but did not entirely eliminate the bias.

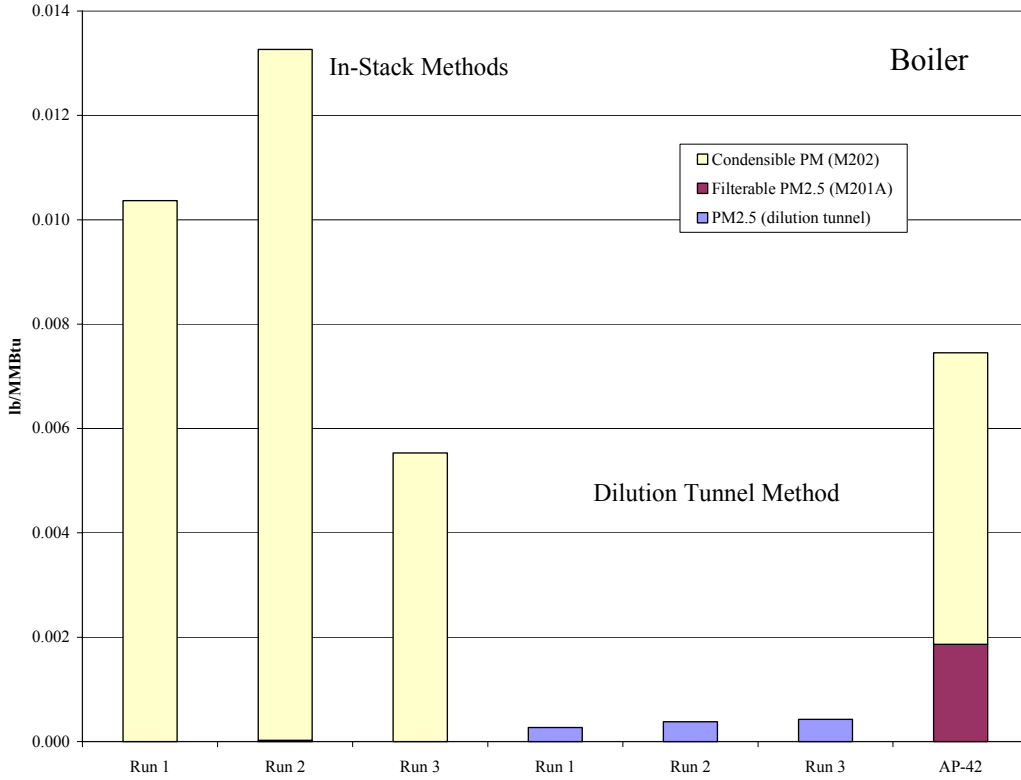


Figure 4-8a. Comparison of dilution tunnel and traditional method results (boiler).

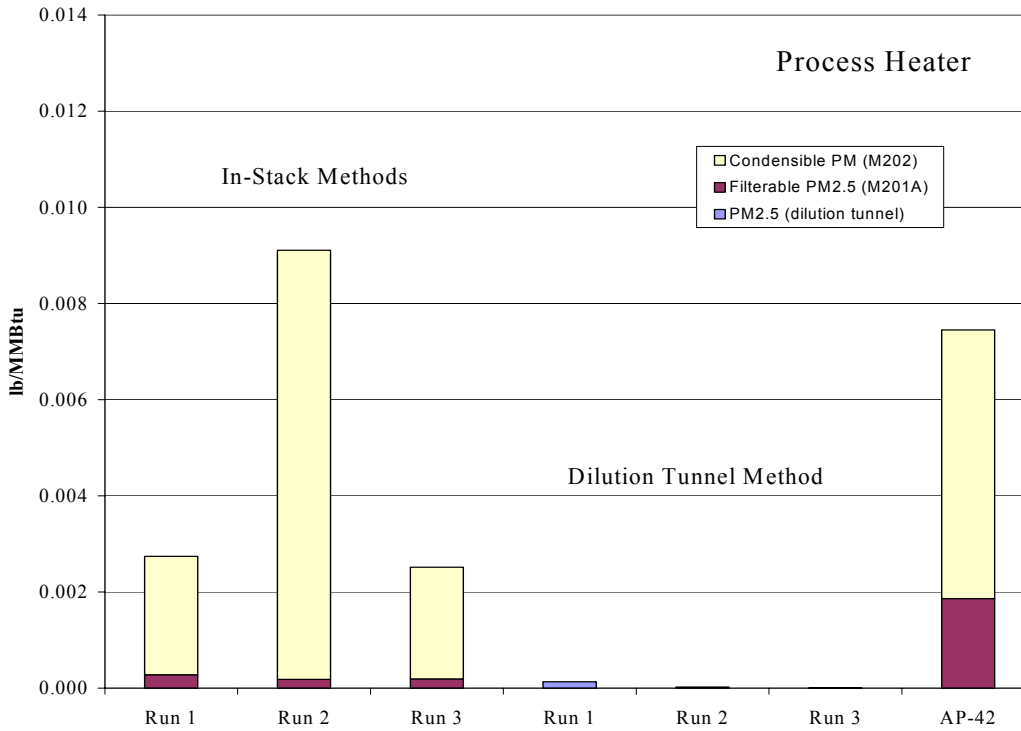


Figure 4-8b. Comparison of dilution tunnel and traditional method results (process heater).

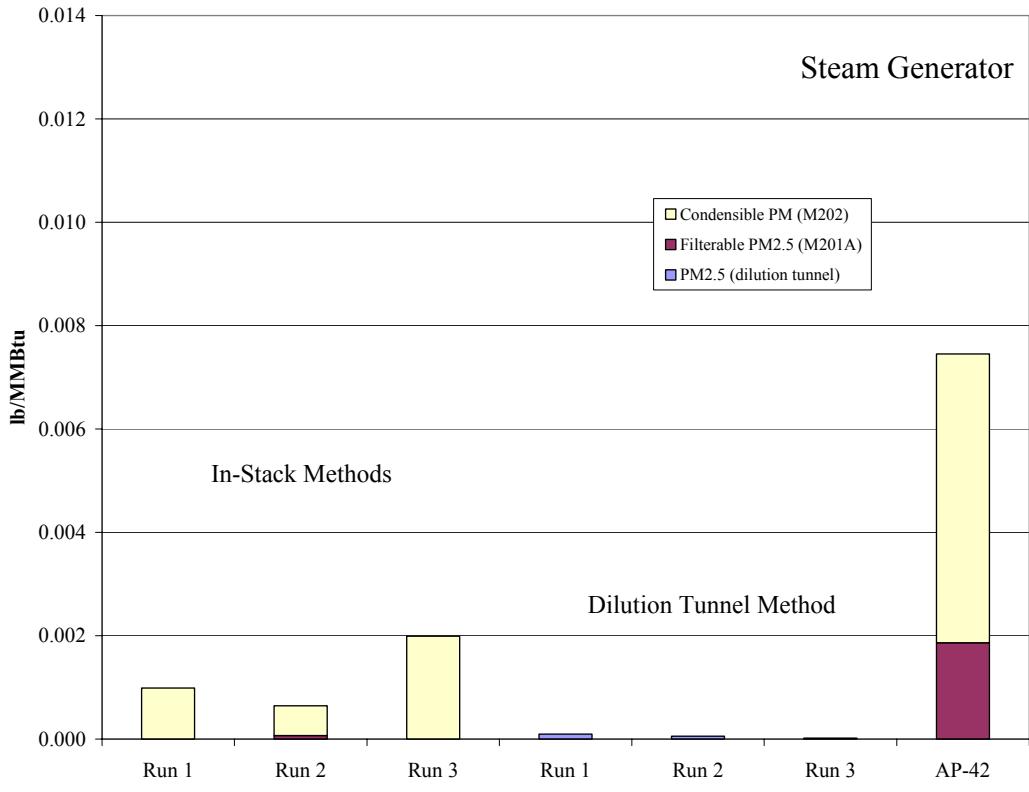


Figure 4-8c. Comparison of dilution tunnel and traditional method results (steam generator).

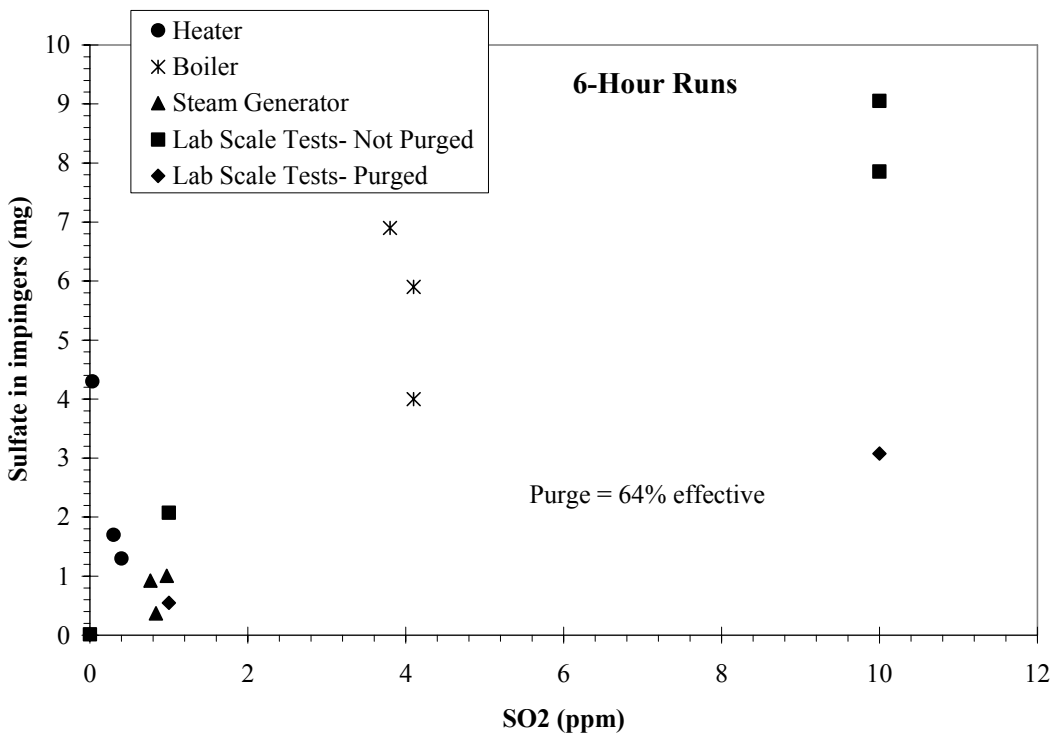
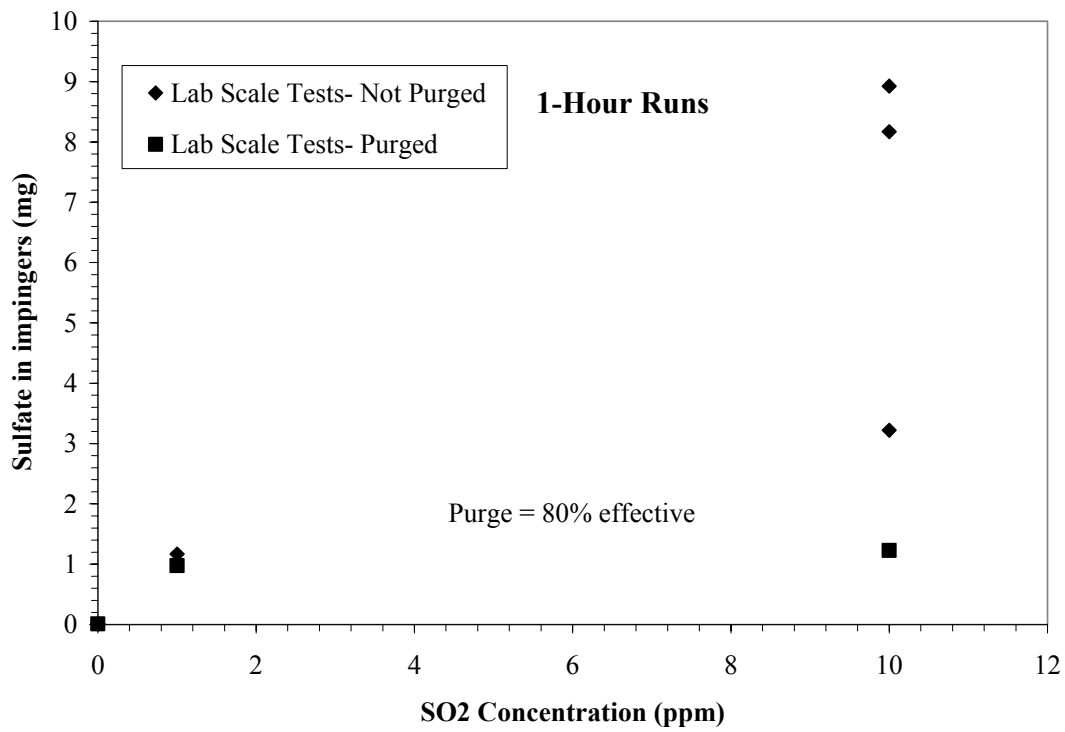


Figure 4-9. Method 202 Bias Test Results (Wien et al., 2003).

The purge was considerably less efficient for the 6-hour runs than for the 1-hour runs, indicating that significant SO₂ oxidation occurs in that time frame. Even though the amount of SO₂ absorbed into the impingers may be small, the resulting bias is significant due to the already low particulate emissions coming from gas-fired sources. Based on the above-described data, Wien et al., suggest that condensable PM emissions data collected with EPA Method 202 may be significantly biased.

Sample Analysis (Laboratory Procedures)

When the various sample fractions arrive at the analytical laboratory they must first be logged in to maintain a chain of custody. The analytical procedures for the various fractions are described below:

Probe Rinse. The acetone based probe rinse is contained in either a glass beaker or a Teflon® baggie. The acetone is evaporated to dryness and then weighed. The mass of the residue (determined as the tare weight) is considered part of the filterable particulate matter.

Particulate Filter. The filter must first be desiccated to remove any moisture absorbed by the filter during sampling, recovery or in transit. The filter is then weighed to an accuracy of ± 0.5 mg.

Impinger Catch. The impinger catch is transferred to a distillation flash. Then methylene chloride is added to the liquid and the mixture shaken. The water and methylene chloride will separate into two layers, allowing the methylene chloride layer to be drained from the bottom of the flask. This process is repeated three times to assure complete separation of the catch into two fractions. The methylene chloride fraction will contain any condensable organic PM while the water fraction will contain condensable inorganics including sulfates.

Organic Fraction. The organic fraction is evaporated to dryness and the mass of residue determined gravimetrically.

Inorganic Fraction. There are two options for analysis of the inorganic fraction. The first option is to simply evaporate the fraction to dryness and to weigh the residue. That residue can then be reconstituted in water and analyzed for sulfates and other ions using ion chromatography. The

second option is to evaporate the inorganic fraction to a volume of about 1 to 3 mL rather than to complete dryness. This avoids potential loss of HCl or H₂SO₄ from the residue. The partially dried liquid is then diluted with water and titrated with NH₄OH to stabilize the H₂SO₄. The stabilized mixture is then dried and weighed.

Reagent Blanks. Blanks for the acetone, water and methylene chloride used in the field are driven to dryness and the residue weighed. These data are then used to blank correct the measurement results.

Though involved, the major laboratory equipment needs for determining the mass of filterable and condensable particulate matter are a highly accurate balance to weigh the various fractions and an environmentally controlled laboratory space. Additional equipment is needed to determine the sulfate content and to analyze the catch for metal content and speciation. The balance should have measurement resolution of at least 0.1 milligram. Note that a 250 mL beaker weighs approximately 100 grams and the weight of the beaker plus residue must be determined to within ± 0.5 mg. Several other factors must be addressed to accurately and precisely make this type gravimetric analysis. Small particles can easily pick up a static charge causing the particles to lift from the filter. To solve this problem, most labs place a small radioactive source in the immediate vicinity of the balance. This eliminates (or at least minimizes) the static charge. A further precaution is to electrically ground both the balance beam and the technician operating the balance.

The laboratory area itself must be appropriately configured. The area should have an isolated ventilation system, provide a high level of dust control and provide control of both temperature and humidity. The samples, particularly the filter will absorb moisture from the ambient air influencing the accuracy of the gravimetric operations. Of particular concern is that the humidity be approximately the same during the initial and final filter weighing.

Before leaving the laboratory analysis area, it is important to further address the sulfate issue. Wien's data strongly suggests that SO₂ is being absorbed into the impinger catch where it is oxidized to sulfate. If the sampling event was for an extended period (e.g., 6 hours per run), significant levels of sulfate might be expected even if a post-test nitrogen purge is performed. When the impinger catch samples are analyzed at the laboratory, how the water fraction is

processed will likely impact the final data. If that fraction is simply driven to dryness, a portion of the H₂SO₄ will likely be lost. Conversely, including the stabilization step will conserve the acid as part of the reported inorganic condensable particulate matter. Thus, it is expected that the detailed steps used in the laboratory analysis will contribute significantly to the observed data variability.

Quality Assurance/Quality Control

All of the above described measurement methods have accompanying quality Assurance/Quality Control requirements. These procedures generally include provisions for periodic calibration of the sampling and analytical hardware, for gathering and analysis of blanks, and for periodic audits of the laboratories.

The major periodic calibration requirement for PM measurements includes calibration of the meter boxes used in the sampling trains and calibration of the scales used for gravimetric analysis. At least every 6 months, the dry gas meter and meter box on a sampling train must be five point calibrated against known standards. In essence this QA/QC procedure is to assure the accuracy of the measured volume of gas passing through the train during a sampling event. The allowable deviation in this parameter is ± 5 percent. For the gravimetric analysis there are two basic requirements. First the manufacturer must check the operation of the balance at once every year. Additionally, accuracy of the balance must be assured as part of each analysis session using class S weights. Here the balance is challenged with a calibrated standard in the general range of the weight being determined. For example, if a 250 mL glass beaker is used for analysis of the acetone rinse, the balance output should be using a 100-gram calibration standard. Conversely, if a Teflon® beaker liner is used for the analysis, a 1 or 2 gram standard would be used.

In addition to calibration procedures, the PM measurement methods such as PRE-004 and Method 202 require several blanks to be gathered and sent to the laboratory for analysis. These include blanks for acetone, water, and methylene chloride. These are the materials used for charging the impingers and for rinsing the glassware during sample recovery. The objective is to assure that trace contaminants in the reagents do not unduly contribute to the reported data. Some groups may also require collecting a filter blank, but how data from analysis of that blank

is used is seldom, if ever defined. Accordingly, most testing groups do not include filter blanks as part of their QA/QC program.

Finally, certified analytical laboratories are required to participate in routine audits of laboratory procedures. Moreover, for most EPA Methods, EPA has developed audit samples containing known concentrations of some key analyte. These audit samples are periodically sent to the lab to determine the overall accuracy of results relative to the known standard. For PM measurements, audit samples are not a routine portion of the QA/QC procedures although it is possible to challenge the lab relative to sulfate, condensable organic, or condensable inorganic measurement.

Data Reduction and Reporting

The preceding sections have described the processes involved with generating data on the filterable and condensable PM loading from emission sources. As discussed, the raw data includes several components. The various elements include:

- Volume of sample gas collected along with data on the sample temperature and ambient pressure.
- Data on the basic composition of the stack gases including sufficient information to determine the oxygen content of the sampled gas.
- Information from the impingers on the total mass of moisture contained in the sampled gas volume.
- Initial and final weight of the filter
- Weight of the residue in the acetone rinse.
- Weight of condensable organic material in the methylene chloride portion of the impinger catch
- Weight of condensable inorganic material in the water portion of the impinger catch
- Weight of residue in the water, acetone, and methylene chloride blanks.

The Methods define exactly how these data are to be used in determining the PM emissions from a source. EPA Method PRE-004 and most other extractive methods allow the data to be blank corrected. Thus, the mass of residue in the acetone blank can be subtracted from the measured

mass of the residue in the probe rinse. Similar corrections are allowed for the two fractions of the impinger catch.

The basic information on sample volume, flue gas major constituents, sample temperature, and ambient pressure are used to correct the sample volume to standard temperature and pressure and then to correct the data to a reference oxygen content in the stack. This is a straightforward calculation process but is often a source of considerable data variability. Different industries in the US have adopted their own definition for reference temperature and pressure. It is unusual to assemble a large database, compiled using results reported in the literature and to have consistent data reduction procedures used for the entire database.

Earlier discussion addressed the fact that loss of small filter fibers during the recovery process can result in measurement of negative filter weight gain. Although this situation occurs frequently in PM sampling for low PM emission sources, there are no defined procedures for how such results should be treated during data reduction. Since a negative filter weight gain has no physical significance, such results are conventionally reported as zero rather than as a negative emission when summing results from different fractions of the sampling train. However, this convention lends false credibility to the accuracy of the measurement method and is probably at least part of the explanation for the non-normal characteristic of the available database.

Two final data reduction issues might also contribute to the observed data variability. First is the issue of how data outliers are handled. In most instances, the reported emissions are the average of triplicate runs without regard for the possibility that one or more of the runs may represent an outlier. Good field-test practice should include annotation of any problems encountered during a sampling run but that practice is not universally followed. Moreover, notations of field issues are often ignored when data are reported or transcribed from reports into large electronic databases. Absent a valid reason to exclude experimental results, it is better statistical practice to err on the side of including all results. The second issue that could potentially contribute to data variability is existence of mathematical errors during data reduction. Historically, this has been a significant issue with field test data but widespread use of computers has dramatically reduced the frequency of such problems.

EXTERNAL FACTORS

Uncontrolled factors external to both the process and measurement systems might also have an impact on measured emissions and the variability of results in the database. Several factors that might influence the data include:

- Ambient air particulate matter concentration
- Ambient humidity
- Ambient air temperature
- Nearby sources and activities.

From this list, the external factors most likely to influence PM measurement results are the ambient air particulate matter concentration and nearby sources and activities. Humidity and temperature have a direct impact on NO_x emissions from gas turbines but that parameter should have only a small impact on measured PM emissions. Ambient temperature and humidity also effects humans and thus might impact the attention given to important details of field-testing. Such an impact is considered a low probability as a source for large variability observed in the database.

Gas turbines consume large quantities of ambient air. As such, factors such as high ambient PM loading or high ambient loading of condensable organic or inorganic compounds might influence measurement results. Such factors are a likely contributor to high concentration tail on the filterable particulate matter in the database (see discussion in Section 3.)

ALTERNATE MEASUREMENT APPROACHES

In recognition of SO₂ absorption and sulfate sampling issue, some recent tests were performed that attempted to remove the bias. PM emissions data was gathered from four F-class gas turbines using the modified EPA Method 8 sampling train illustrated earlier in Figure 4-5. The intended use for Method 8 sampling is to determine the concentration of SO₂ and SO₃ in flue gas. It is an alternative to use of continuous emissions monitoring for measuring SO_x emissions. The SO₂ is absorbed in the 80 percent isopropanol impinger and its concentration can be accounted

for in the analysis. Other condensable materials, including sulfates in the stack are absorbed in the 3 percent hydroxide impingers.

Results from these tests exhibited several of the aspects discussed earlier including the fact that several of the filterable particulate matter gravimetric analyses showed negative weight gain. For current use those negative values were retained in the overall data analysis rather than being reported a zero. Results from those tests are presented as a normal probability distribution plot in Figure 4-10. By including the negative data points, the filterable particulate matter data clearly follow a normal distribution pattern. If they had been reduced to zero or near zero, the data would have had the same pattern seen earlier in figure 2-1. The condensable particulate fraction also exhibits a pattern that conforms to a normal distribution but the data do have more scatter than the filterable portion.

The use of modified measurement procedures such as Method 8 may allow the sulfate artifact bias to be removed. However, a thorough assessment of this modified measurement procedure for determining condensable PM has not been performed. Results of a test comparing Method 202 to Method 8 showed that the sulfate content of the impinger residues was comparable and dominated the total condensable particulate mass, but Method 202 showed a slight amount of other substances that Method 8 did not capture (Wien et al., 2004). The potential for the same SO₂ artifact potential in Method 202 and in Method 8 is acknowledged by the requirement for a post-test purge of the impingers in Method 8. Thus, while a modified Method 8 procedure for reducing the variation in condensable particulate emissions shows potential, there remain a number of unresolved questions regarding its use. At this time, EPA does not accept Method 8 as an approved alternate method for demonstrating compliance with PM₁₀ emission standards and limits.

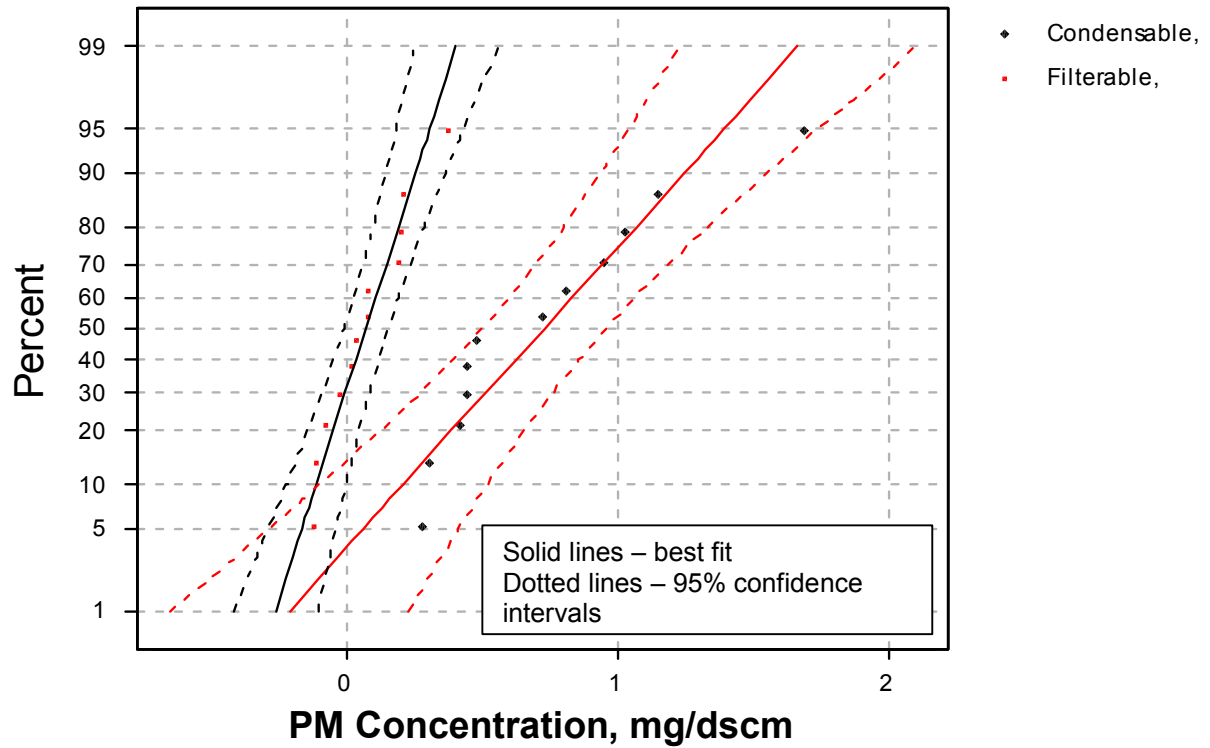


Figure 4-10. Cumulative Probability Distribution of PM Emissions Data from 4 Large Combined Cycle Plants Using Modified Method 8.

5. DISCUSSION

Available data describing PM emissions from gas turbine installations indicate wide variation in the overall level of reported emissions. Analysis of the data shows that the variation does not follow a normal distribution indicating that factors other than random variation contribute to the observed data trends. Information presented in Section 4 examined a wide range of factors that might contribute to data variability including gas turbine design features, system operating factors, and the methods used to make source PM emission measurements. The current section recaps the array of data variability drivers and provides a coarse ranking of the likely importance of various factors. Within the scope of this effort, the factors considered are ranked on an arbitrary scale of 1 to 5 (low to high importance).

It is noted that others may certainly have provided different relative rankings.

Results are summarized in Tables 5-1a and 5-1b addressing combustion equipment and measurement considerations respectively.

Table 5-1a PM Variability Drivers – Equipment Considerations

Factor	Relative Importance*	Considerations
Turbine Size	2	Data should be segregated to separate very small units
Fuel burned	3	Ash to filterable particulate matter and sulfur drives sulfate artifact issue. Segregate data by gross fuel type
Operating Cycle	2	Low temperature fired HRSG might increase carbonaceous PM emissions
Unit efficiency	1	Most emissions not directly related to relative quantity of fuel consumed
Inlet Air Filtration	3	Typical ambient air PM loading small relative to measured PM exhaust emissions. Filters would likely remove large debris for filterable PM data.
Power Augmentation	2	Contaminants in water could be a large contributor to filterable and condensable inorganic PM
Combustor type	3	Carbonaceous PM emission impact
SCR or Oxidation Catalyst Erosion	1	Age, maintenance condition
NH ₃ reagent water	1	Trace constituent in a low flow rate stream
NH ₃ Slip	3	Collects in impingers and impacts artifact formation
NO ₂ from oxidation catalyst	2	Nitrate artifact formation in impingers?
Equipment failure	1	

*1=low importance, 5=high importance

Table 5-1b. PM Variability Drivers – Measurement Considerations

Factor	Relative Importance*	Considerations
Method employed	5	Impinger vs. dilution sampling. Also pre-filter cyclones to remove large diameter particles
Sampling time	4	Affects mass of material being analyzed relative to analytical detection limits
Contamination in train assembly	1	Should be a random factor – normal distribution
Reagent Quality	1	Blank correction of data
Scraping Probe on port.	2	Impact on filterable particulate matter which is usually small portion of total PM
Filter Recovery	3	Negative filter weight issue
Field tester experience	4	Pushing measurements into new concentration regime.
Sulfate Artifact	5	Likely the most important factor driving data variability
Post-test Nitrogen Purge	5	Major impact on magnitude of sulfate artifact
Analytical lab contamination	2	Important but unquantifiable variable in database
H ₂ SO ₄ stabilization	5	Loss driver for sulfate artifact
Meter Box calibration	1	Impact less than a few percent on any given data point
Data Handling	3	Defined procedures and computerization. Inconsistent handling of negative tare weights.
Outlier treatment	2	Clear protocols not established.
Ambient conditions	1	Unlikely major contributor

*1=low importance, 5=high importance

As indicated in the tables, the most important drivers for gas turbine PM emission variability are measurement related issues. Within that group, 6 factors were given a ranking of 4 or 5. Those factors include, (1) the measurement method used, (2) the length of each sampling run, (3) the experience level of the field-testing team, (4) sulfate artifact in impinger method sampling, (5) post-test nitrogen purge, and (6) H₂SO₄ stabilization during analysis of the inorganic condensable particulate fraction.

None of the combustion equipment parameters were given a ranking higher than 3. This is largely driven by a belief that the existing database is compromised by significant but variable measurement biases. If those biases could be removed, the data would likely exhibit different trends that should be reexamined in defining the relative importance of equipment issues.

6. FINDINGS

The key findings from this evaluation are summarized below:

- Mass emission measurements from gas-fired combustion turbines are highly measurement method dependent. Dilution tunnel methods report significantly lower emissions than traditional impinger train based methods.
- Traditional measurement methods probably overestimate the contribution of condensable particulate emissions due to the way in which condensation is driven in the train and existence of sulfate artifacts.
- Variation of filterable PM₁₀ and PM_{2.5} emission measurements can be reduced by adding an in-stack cyclone on the probe inlet to remove spurious nonfuel and noncombustion related particles.
- Variation of condensable PM₁₀ and PM_{2.5} emission measurements can be reduced by increasing the sampling time/volume and by modifying the impinger method to minimize SO₄ artifacts by implementing a 30-minute post-test purge with nitrogen gas immediately following sample collection. Further investigation is needed to identify alternate impinger solutions for collecting condensable particulate matter that do not facilitate the sulfate (and possibly nitrate) artifacts.
- Dilution tunnel methods are feasible for gas turbine emission characterization; provide broader chemical speciation, better sensitivity, and direct comparability to ambient particulate matter measurement methods. Further investigation is needed to formally validate the measurement technique.

REFERENCES

- Corio, L.A.; Sherwell, J. In-Stack Condensable Particulate Matter Measurements and Issues. *J. Air & Waste Management Assoc.* 2000, 50, 207-218.
- DeWees, W.G.; Steinsberger, K.C.; *Method Development and Evaluation of Draft Protocol for Measurement of Condensable Particulate Emissions*; U.S. Environmental Protection Agency. U.S. Government Printing Office: Washington, D.C. 1990; EPA-450/4-90-012.
- Filadelfia, E.J.; McDannel, M.D. *Evaluation of False Positive Interferences Associated with the Use of EPA Method 202*. Air and Waste Management Association 89th Annual Meeting and Exhibition, Nashville, Tennessee, June 1996.
- Hildemann, L.M.; Cass, G.R.; Markowski, G.R. (1989) A Dilution Stack Sampler for Organic Aerosol Emissions: Design, Characterization and Field Tests. *Aerosol Sci. Technol.* 1989, 10, 193-204.
- Lanier, W.S. and Hendrix, C.D. (2001), *Reference Method Accuracy and Precision (ReMAP), Phase 1, Precision of Manual Stack Emission Measurements*, American Society of Mechanical Engineers, Research Committee on Industrial and Municipal Waste. (February, 2001.)
- Linder, G. and S. Wall (1995). "Comparison of PAH emissions determined by ARB Method 429 and a dilution sampling (DS) method." Unpublished presentation to Engineering Foundation Conference on Stationary Source Sampling and Analysis for Air Pollutants XIX, San Diego, CA (March, 1995).
- Riley, G.R. and R. Myers, *Comments From States That Require Method 202*, International Conference on Stationary Source Sampling and Analysis for Air Pollutants XXVI, Destin, Florida, 2002.
- SCAQMD, 2002. *Method 5.2: Determination of Particulate Matter Emissions from Stationary Sources Using Heated Probe and Filter*, District Source Test Manual, Monitoring & Source Test Engineering Branch, South Coast Air Quality Management District, Diamond Bar, California (2002).
- U.S. Environmental Protection Agency. Federal Register, Volume 64. No. 189/Thursday, September 30, 1999/Rules and Regulations.
- Wall, S.M. (1996) "Improved methods for PAH combustion source sampling." Final Report, California Air Resources Board Contract A932-098, NTIS PB97148746.
- Wien, S.E.; England, G.C.; Loos, K.R.; Ritter, K. *Investigation of Artifacts in Condensable Particulate Measurements for Stationary Combustion Sources*. Paper No. 536, 2003.

Wien, S.E., England, G.C., and Chang, M.C. 2004. "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil and Gas-fired Combustion Systems, Topical Report: Test Results for A Combined Cycle Power Plant with Supplementary Firing, Oxidation Catalyst and SCR at Site Bravo," GE Energy and Environmental Research Corporation, Irvine, CA.

Page: 29

[GCE1]Need reference for SCAQMD method, check that 5.2 is the right one.